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A Study of Reverse Osmosis Separations Involving Nonaqueous Solutions

by

Brian A. Farnand

Thesis presented to the School of Graduate Studies
of the
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for the degree of
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UNIVERSITÉ D'OTTAWA
UNIVERSITY OF OTTAWA

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Abstract

The general validity of the physicochemical approach to the description of reverse osmosis performance with regard to solvent is studied in this work. Reverse osmosis experiments were performed with cellulose acetate membranes and with both inorganic electrolyte and organic nonelectrolyte solutes in their methanol and ethanol solutions. Liquid chromatography experiments with the same solutions and a column filled with cellulose acetate powder were used to model the reverse osmosis systems. These data were used to determine the physicochemical parameters of the Kimura-Sourirajan model and the surface potential-pore flow model. Their success in describing and predicting reverse osmosis experiments in nonaqueous solutions confirms the validity of the physicochemical description of reverse osmosis. A cellulose membrane (precipitated from a formaldehyde/dimethylsulfoxide solution) was developed to exploit the interesting properties of cellulose in aqueous solutions as well as its resistance to solvent degradation in nonaqueous solutions. The physicochemical parameters which describe the aqueous reverse osmosis experiments with cellulose membranes were compared for the same solutions with the parameters which describe reverse osmosis performance with cellulose acetate and polyamidohydrazide membranes. Reverse osmosis fractionations of the ethanol-heptane binary mixtures were

also performed with cellulose, cellulose acetate, and polyamidohydrazide membranes to demonstrate the suitability of these membranes for use in nonaqueous mixtures.

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Chapter 1

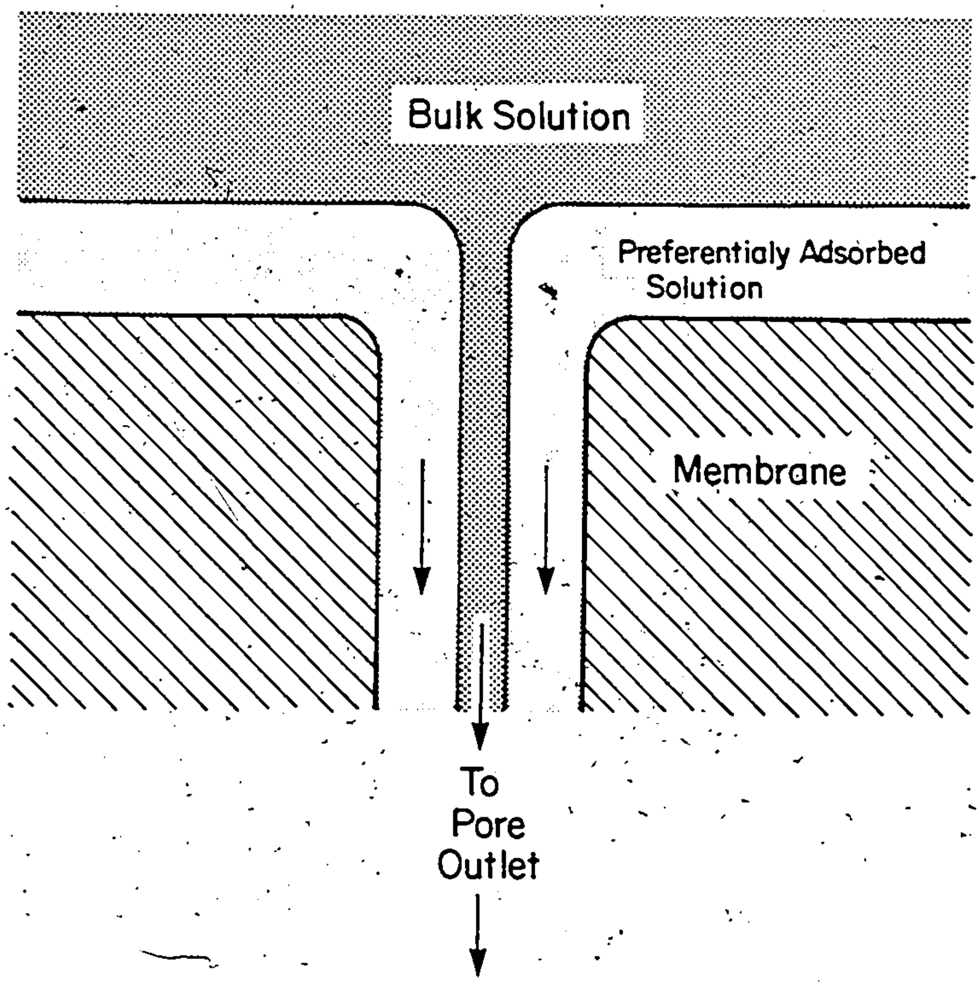
Introduction

Reverse osmosis is a general separation technique for fluid phases. It consists of letting a solution flow under pressure across the surface of an appropriate porous membrane and collecting the membrane's permeate. The permeate product is enriched in one or more of the components of the mixture and leaves an enrichment of the remaining components of the high pressure side of the membrane. Throughout this process, there is no heating of the membrane nor is there a vapour-liquid phase change. Reverse osmosis is applicable to the separation, concentration and fractionation of inorganic and organic substances in aqueous and nonaqueous solutions of liquids and gases.

Reverse osmosis separations are controlled by the nature of the membrane surface and interactions with the solvent and solutes with which it is in contact. For example, if the surface of a porous membrane in contact with a solution is of such a chemical nature that it preferentially adsorbs the solvent, then a steep concentration gradient exists at the membrane-solution interface which corresponds to the layer of solvent as shown schematically in Fig 1-1. This interfacial solvent can be removed by flow under pressure through the pores in the membrane (Sourirajan, 1981a, 1981b).

Figure 1-1

Schematic Representation of Preferential Adsorption at a Membrane Surface


Bulk Solution
Preferentialy Adsorbed Solution
Membrane
To Pore Outlet

Historically, the preferential adsorption effect has been observed in the study of osmotic phenomena and flow through osmotic barriers. Early studies of osmotic barriers showed that flow through these barriers followed the Hagen-Poiseuille model of viscous flow in capillaries. Mathieu (1902) observed what he referred to as negative adsorption with solutions in capillaries and noted that solute concentration in capillaries decreased with capillary radius. Other workers (Bigelow, 1907; Bartell, 1911) reported that clogging osmotic barriers with precipitate increased the osmotic effects (i.e. reduced the amount of solute diffusion from the concentrated phase and increased the osmotic pressure to account for the difference in concentration).

Subsequent work with precipitated membranes was performed by Tinker (1916; 1917) with copper-ferrocyanide membranes. He caused a membrane to precipitate under microscopic observation and was able to observe small particles closely packed together with (calculated) interstitial gaps of 150 to 200 x 10^{-10}m. These distances were too large to cause osmotic effects by mechanical blocking, yet the membrane was capable of exhibiting osmotic phenomena. He suggested that osmotic effects were caused by selective adsorption of solvent at the surface of the membrane caused by the interstitial pores' ability to "control" their interiors by means of radially decreasing surface adsorption forces.

Weiser (1930) also studied this case and reported that solute diffusion across the copper-ferrocyanide membrane would not occur for negatively adsorbed solutes, and that positively adsorbed solutes would diffuse at a rate proportional to their strength of adsorption. Weiser also related adsorption to the Gibbs' surface adsorption equation.

However, this evidence of preferential adsorption at a solid-solution interface was not used directly in the initial development of reverse osmosis, but air-solution interface preferential adsorption was. Based upon the well-known surface skimming experiments of McBain and Dubois (1929) for the determination of surface excess concentration at the air-solution interface, Yuster et al. (1958; Sourirajan, 1963) used a porous membrane to exploit the difference of concentration at a solution-solid interface. The existence of this surface excess concentration was predicted by the Gibbs' adsorption equation, and a porous membrane was chosen as the solid. Based upon the description given by the schematic diagram of Fig 1-1, if the membrane pores were of appropriate size, there would be a difference in solute concentration of the liquid inside the pores compared to the bulk phase. The work of Yuster et al. has been the starting point for the practical use of the solution-solid preferential adsorption phenomena for separation with small pore membranes.

Developments since that time have included the

Kimura-Sourirajan analysis (Kimura and Sourirajan, 1967) for reverse osmosis performance and its prediction, the surface potential-pore flow model (Matsuura and Sourirajan, 1981) and several other models that were not related to these (discussed later). As well, membrane development has proceeded to include more materials and greater control over the membranes' properties which has resulted in more reliable data. Commercial applications for desalination and water pollution control have increased the interest in membrane development as well as demanded more reliable methods for the prediction of performance. To achieve these goals of superior performance and predictability, a greater understanding of the role of membrane-solute-solvent interactions and membrane structure is required.

Literature Survey. Several methods of analysis are available for describing reverse osmosis transport through membranes. The solution-diffusion approach is based on treating the membrane as a single solid phase through which solvent passes by Fickian diffusion (Lonsdale et al., 1965; Lonsdale, 1966; Merten, 1966). Thus for the solvent

$$J_A = -\frac{D_{AM}\ c_{AM}\ \bar{V}_A}{\Delta x\ \underset{\sim}{R}T}\,(P - \Delta\Pi)$$
$$= A(P - \Delta\Pi) \qquad (1\text{-}1)$$

and for the solute

$$J_B = -\,D_{BM}\left(\frac{\Delta c_{BM}}{\Delta x}\right) \qquad (1\text{-}2)$$

where Δx is the membrane thickness, and P and $\Delta\Pi$ are the differences in hydrostatic and osmotic pressures across the membrane, respectively. The concentration of salt inside the membrane, c_{BM}, is determined by equilibrium with bulk phase solution, so that eq 1-2 becomes

$$J_B = -\frac{D_{BM}\ K\ \Delta c_B}{\Delta x} = B\ \Delta c_B \qquad (1\text{-}3)$$

This derivation is based upon the assumptions of uncoupled solute-solvent transfer and a nonporous membrane. To determine J_A and J_B, data for A and B are required, which also requires the distribution of salt between membrane polymer material and solution. This model does not account for concentration polarization at the interface, and has only been applied to simple salts in aqueous solutions. As well, the presence of pores in the membrane are considered to be defects through which feed solution will pass without change in concentration. This does not agree with surface interactions for surface excess concentration and does not admit the Gibbs' adsorption effect. For these reasons, the analysis presented in eqs 1-1 to 1-3 was not used in this work. As well, similar versions proposed by Banks and Sharples (1966) and Merten (1966) which allowed for concentration polarization at the membrane surface and the presence of surface defects including pores were not used in this work, since it assumed that pore flow was a leak permitting the passage of unaltered feed solution. This still does not accommodate the Gibbs' adsorption effect.

The Kedem and Katchalsky (1958) analysis for biological membranes has also been applied to the description of reverse osmosis. It was originally developed to describe biochemical active transport in complex biological membranes and is based upon irreversible thermodynamics. It takes the form

$$J_B = L_p\ (\Delta P - \sigma\ \Delta\Pi) \qquad (1\text{-}4)$$

$$J_B = \omega\ \Delta\Pi + (1 - \sigma)(J_A + J_B)\bar{c} \qquad (1\text{-}5)$$

where

$$\sigma = \left(\frac{\Delta P}{\Delta \Pi}\right)_{(J_A+J_B) = 0} \qquad (1\text{-}6)$$

The physical significance of the reflection coefficient, σ, has been interpreted as the ratio of "perfect" membrane sections which do not permit the passage of salt to "imperfect" sections that do. Again, this does not specifically accommodate surface effects, and is not considered for the analysis of the reverse osmosis data in this work.

Sherwood et al. (1967) proposed a model to describe reverse osmosis based upon the assumption that solvent and solute cross the membrane by the parallel processes of diffusion and pore flow. They postulated that the solvent and solute were dissolved into the solvent swollen polymer matrix at the upstream membrane surface, followed by their diffusion through the membrane as a result of chemical potential gradients, and desorbed. As well, they assumed feed solution passes through open channels and pores in the membrane with negligible change in solute concentration caused by diffusion in the liquid, at a rate proportional to the hydrostatic pressure difference. Their model was represented as

$$N_A = k''' N_B (c_{A2} - c_{A3}) + k'' M_B \, \Delta P \, c_{A2} \qquad (1\text{-}7)$$

and

$$N_B = k' \, (\Delta P - \Delta \Pi) + k'' M_B \, \Delta P \, c_{B2} \qquad (1\text{-}8)$$

where k', k'', and k''' are the membrane coefficients for the diffusion of solvent, pore flow, and diffusion of solute respectively, at the upstream surface of the membrane. Equation 1-8 rearranges to

$$N_B = k'/(k'' M_B c_{B2})(\Delta P - \Delta \Pi/(k'' M_B c_{B2})) \qquad (1\text{-}9)$$

which is similar to eq 1-4. Because of the treament of pores as imperfections without the ability to cause a change in solute concentration and without osmotic pressure considerations across them, this model was not used in this work.

Glueckauf (1965) presented a model for the analysis of reverse osmosis results for salt solutions based upon the determination of the work to move an ion from bulk solution to an interface with different dielectric properties. This model takes the form

$$\Delta W = \left(\frac{e_o^2 Z_i^2}{2\varepsilon}\right) \cdot \frac{(1 - \alpha_g) Y}{R + \alpha_g b_i Y} \qquad (1\text{-}10)$$

where ΔW represents the excess energy of the ion inside the pore. Y is defined as

$$\varepsilon = \frac{\varepsilon - \varepsilon'}{\varepsilon'} \qquad (1\text{-}11)$$

α_g is defined as

$$\alpha_g = 1 - (1 + \kappa^2 R^2)^{-\frac{1}{2}} \qquad (1\text{-}12)$$

where κ is the inverse of the Debye-Huckel ionic cloud distance, which can be simplified to (Glasstone, 1951)

$$\kappa = \frac{4\Pi e_o^2 \sum(n_i Z_i)^2}{\varepsilon \underset{\sim}{k} T} \qquad (1\text{-}13)$$

Boltzman's distribution law is applied to the work term of eq 1-10 to give

$$\ln(c_{A3}/c_{A2}) = \Delta \bar{W}/\underset{\sim}{k}T$$

$$= \frac{e_o^2\ Z_i^2}{2\varepsilon \underset{\sim}{k} T} \cdot \frac{(1 - \alpha_g)\ Y}{R + \alpha g\ b_i\ Y} \qquad (1\text{-}14)$$

where c_{A3} is the concentration of the pore's permeate, and c_{A2} the membrane boundary concentration, and is determined by mass transfer considerations. The means of determining R that was outlined by Glueckauf (1965) was based upon a correlation of the relation c_{A3}/c_{A2} with c_{A3} and its relation to the pure water permeation rate (PWP) to give

$$(\mathrm{PWP}) \propto R^{1.5} \qquad (1\text{-}15)$$

for cellulose acetate in water. This analysis accounts for negative adsorption of the solute but requires physicochemical parameters that are difficult to evaluate such as the dielectric constant of the liquid inside a membrane pore. While this analysis contains all of the essential elements, the difficulty of determining some of the physicochemical parameters requires assumptions of these properties. As well, the model is insensitive to the nature of the salt being considered since it is based solely on the mean of the crystallographic radii for the salt's size, as represented by eq 1-10.

According to the concepts outlined previously, reverse osmosis should be governed by two distinct effects: a) the preferential adsorption effect that occurs near the membrane surface caused by surface forces; and b) a kinetic effect which describes the mobilities of the solute and solvent through the membrane pores as governed by steric effects as well as surface forces. This work is a study of these concepts and is a demonstration of their validity for the description of reverse osmosis performance in nonaqueous solutions. This includes an experimental and analytical study of nonaqueous reverse osmosis for both the cases of dilute organic and inorganic solutes in methanol and ethanol solutions as well as the reverse osmosis fractionation of ethanol-heptane binary liquid mixtures. As well, suitable membranes were developed for use with some of the nonaqueous solutions to resist solvent-polymer effects. To provide the necessary physico-chemical data to describe reverse osmosis systems, appropriate gas and liquid chromatography experiments were conducted to model the membrane material-solution interface.

The analysis of reverse osmosis performance that was used for this work is that of Kimura and Sourirajan (1967) and the surface potential-pore flow model (Matsuura and Sourirajan, 1981) which were slightly extended to include the nonaqueous solutions that were studied in this work. Their developments are based upon the Gibbs' preferential adsorption effect and the porous nature of the membrane and for these reasons they were felt to best represent the reverse osmosis process.

This work is of general significance from several points of view. It extends the scope of reverse osmosis to include the area of nonaqueous solution systems, and demonstrates the viability of reverse osmosis for cases other than aqueous solutions. The generality of the physicochemical basis of reverse osmosis separation is confirmed for nonaqueous systems. The description and prediction of reverse osmosis performance has been extended from the aqueous case to the nonaqueous case, and several schemes to predict behaviour in an unknown solvent based on results in a given solvent are suggested. It establishes a means of obtaining precise physicochemical parameters which distinguish the different membrane-solution interfaces. It offers a new physicochemical basis for reverse osmosis process design in terms of equilibrium and kinetic factors governed by interfacial forces and transport through pores. A new small pore reverse osmosis membrane (cellulose) has been developed and evaluated with both aqueous and nonaqueous solvents with dilute solutions as well as for the fractionation of binary mixtures of liquids. Details for the experimental study of nonaqueous reverse osmosis are outlined and experimental data have been tabulated for future reference.

Chapter 2

Experimental Details

Reverse Osmosis Experiments. The apparatus used for the reverse osmosis experiments studied in this work was the same as was used in aqueous experiments (Matsuura and Sourirajan, 1971b) with modifications for the nonaqueous liquids. An outline of this apparatus is shown by the schematic diagram of Fig 2-1. The tubing throughout the pressurized section of the apparatus was of stainless steel with pressure fittings as were the reverse osmosis cells. The low pressure section of the system was also made of stainless steel with the exception of two short lengths of polyethylene tubing. To accommodate the anhydrous and high vapour pressure components, the solution circulation system was completely enclosed and without contact with the atmosphere. The temperature of the solution was maintained at 25.0°C for all of the experiments reported in this work. The pressure drop across the six reverse osmosis cells was measured to be less than 14 kPa for methanol at 5.0×10^{-4} m^3/min. This flowrate was used for all of the reverse osmosis experiments, based on the observations of Sourirajan and Agrawal (1969) and Matsuura and Sourirajan (1971a) for the variation of solute separation with liquid flowrate. They observed an increase in solute separation up to a flowrate of 3.0×10^{-4} m^3/min, with a constant value of solute separations at higher flowrates.

Figure 2-1

Reverse Osmosis Flow Diagram for the

System Used in This Work

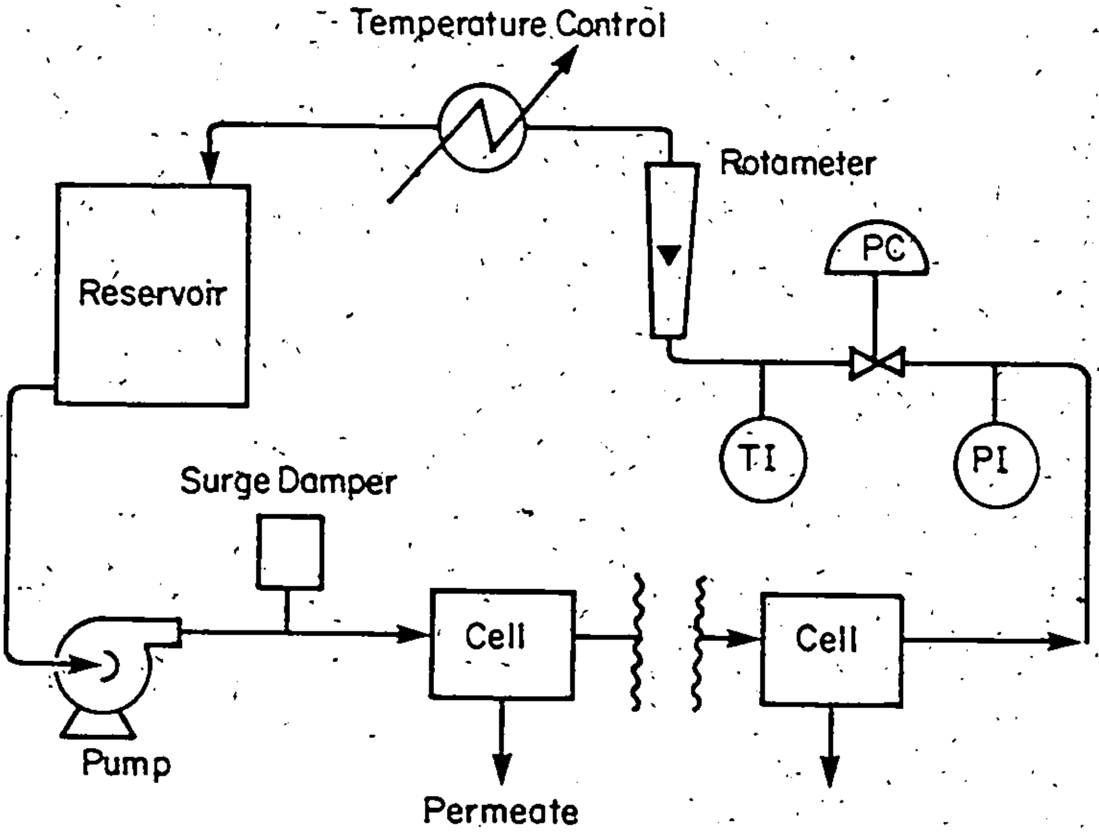
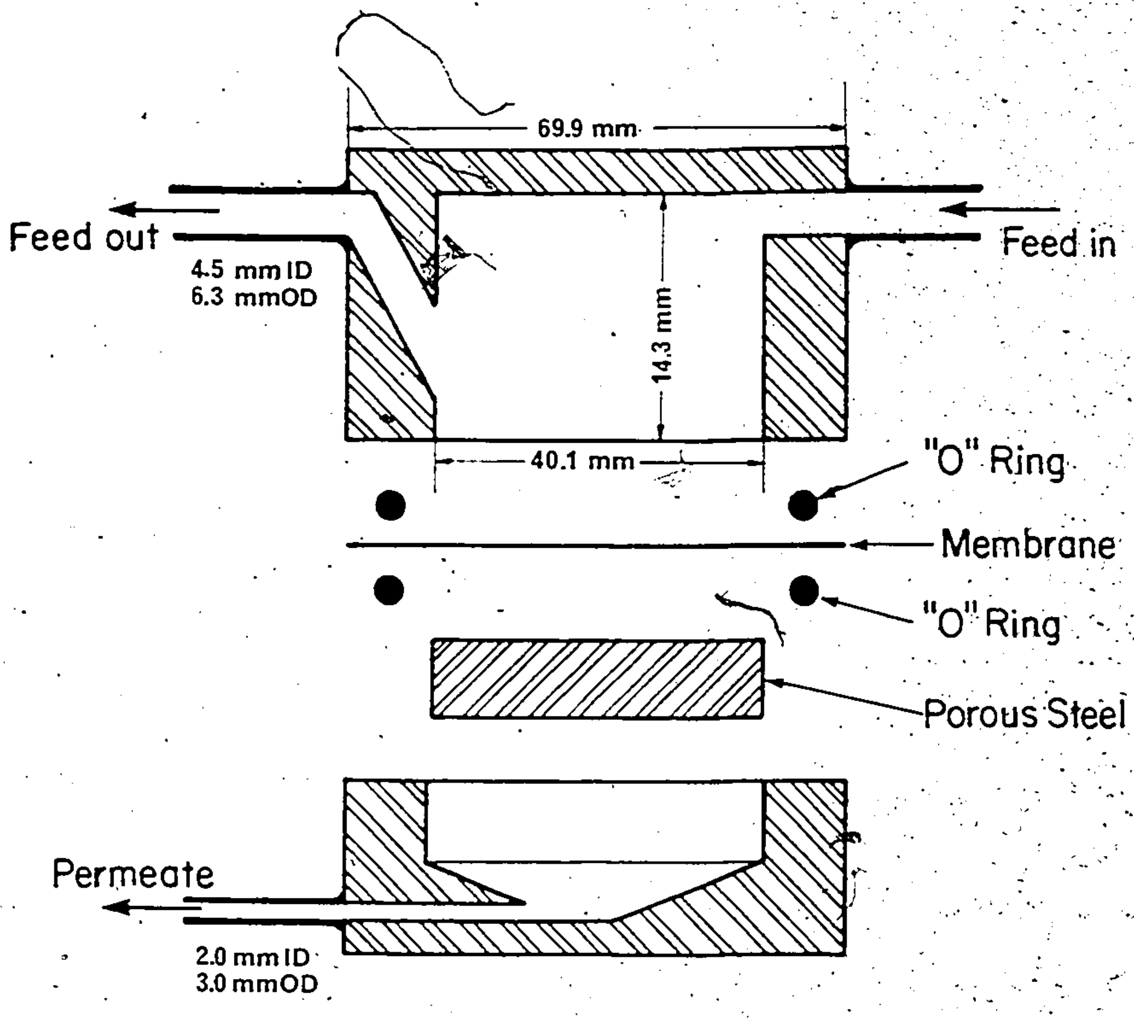

Temperature Control
Rotameter
PC
Reservoir
TI
PI
Surge Damper
Cell
Cell
Pump
Permeate

Figure 2-2

Sectioned View of a Reverse Osmosis Cell

of the Type Used in This Work



NOTE: NOT TO SCALE

A detailed schematic diagram of the reverse osmosis cells used in this work are shown in Fig 2-2. The permeate was collected at atmospheric pressure so that the solution circulation system's gauge pressure could be assumed equivalent to the hydraulic pressure across the reverse osmosis membrane. The characteristic dimensions of the cells used are summarized as follows. The upper part of the cell consisted of an inlet and an outlet for the feed solution, connected to a chamber on top of the membrane. This chamber had an inside height of 1.43 cm and an inside diameter of 4.10 cm. This gave 13.2 cm^2 of membrane surface that was presented to the feed solution. Six cells with these dimensions were placed in series as shown in Fig 2-1.

For dilute solutions, the reverse osmosis experiments were conducted as follows. First, the membranes were pressurized at 120% of their operating pressure for one hour with pure solvent to offset the effects of membrane compaction. At operating pressure, a sample of the pure liquid's permeate was collected for a given time and the weight was determined. This was recorded as the pure solvent permeation rate (PSP) and was reported in units of g/h for 13.2 cm^2 effective surface area. At this point, the solution to be studied was placed in the reservoir and the pure solvent was flushed from the circulation system. The volume of liquid needed to rinse out the low pressure side of the reverse osmosis cells was determined to be

6 mL, and 8 mL of permeate were collected at operating conditions from the membrane with the lowest permeation rate before the rinsing was considered completed. A sample of feed solution was taken from the circulating side of the lowest permeation rate before the rinsing was considered completed. A sample of feed solution was then taken from the circulating side of the system and permeate was collected for a given time and reported as the product rate (PR) in units of g/h for 13.2 cm^2 of effective surface area. A second sample of the feed solution was taken at the end of the experiment. The circulation system was then flushed with pure solvent to prevent osmosis generated back flow when the operating pressure was relieved which could alter the membrane porosity. The two samples of the feed solution were analyzed for concentration as were the product samples and the separation, f, was determined for each membrane by

$$f = \frac{\text{feed concentration-permeate concentration}}{\text{feed concentration}} \qquad (2-1)$$

where the feed concentration was determined as the mean of the two samples. A more detailed description of a typical experiment is given in Appendix B. In order to determine the permeate concentration from data for f, eq 2-1 can be rearranged to

$$\text{permeate concentration} = (1-f) \times \text{feed concentration} \qquad (2-2)$$

The apparatus and operational procedure described above is for a quasi-steady state process. However, the small amount of permeate (50 mL) with respect to the feed solution (3 L), does not affect the feed solutions concentration, as shown in the following examples.

On the basis of a sampling time of 45 minutes and 6 membranes that have 100% separations for a hypothetical solute and 30 mL/h permeation rates, the change in concentration, c, would be

$$3{,}000\ \text{mL} \cdot c/(3{,}000\ \text{mL} - 6 \times 30\ \frac{\text{mL}}{\text{h}} \times 0.75\ \text{h}) = 1.047\ c$$

or an approximate 5% increase in solute concentration. For the same case with another hypothetical solute which is concentrated by the membranes (negative separation) by 30% ($f = -0.30$) the change in concentration would be

$$\frac{3{,}000\ \text{mL} \cdot c - 6 \times 30\ \frac{\text{mL}}{\text{h}} \times 0.75\text{h} \times (1-(-0.3))c}{3{,}000\ \text{mL} - 6 \times 30\ \frac{\text{mL}}{\text{h}} \times 0.75\text{h}} = 0.9859\ c$$

or an approximate 1.5% decrease in concentration. These conditions exceed the performance obtained by the membranes used in this study, and the concentration of the feed solution was assumed to be constant. The effect of the dead volume of the permeate side of the membrane cell on concentration was ignored.

As well, the circulation rate of the feed solution through the reverse osmosis cells far exceeded the permeation through the membranes, and the concentration throughout the serially connected cells was assumed to be constant. This is demonstrated by assuming the same-membrane conditions above with 100% separation of a hypothetical solute and the 500 mL/minute circulation rate. Thus for a concentration c of feed solution entering the first cell the outlet concentration would be

$$(60 \times 500)\ \frac{mL}{h} \cdot c/[(60 \times 500)\ \frac{mL}{h} - 30\ \frac{mL}{h}]$$
$$= 1.0010\ c$$

or a 0.1% increase in concentration.

By means of a geometric series, the concentration at the outlet of the sixth cell would be approximately 0.7% greater than the first cell's inlet. Similarly, for a solute concentrated by 30% (f = -0.30), the outlet concentration of the first cell would be

$$\frac{(60 \times 500)\ \frac{mL}{h} \cdot c - 30(1 - (-0.3))\ c}{(60 \times 500)\ \frac{mL}{h} - 30\ \frac{mL}{h}}$$
$$= 0.9996\ c$$

or a 0.03% decrease in concentration. By accounting for the other cells, the sixth cell's outlet concentration would be approximately 0.2% less than the feed concentration at the first cell's inlet. This change in concentration was ignored for the purposes of this study, since the assumed performance far exceeds the actual conditions. Results of these experiments are shown in Appendix A-1 in Table A-1-5 for methanol, Table A-1-6 for ethanol, and Table A-1-7 for water.

For the ethanol-heptane binary liquid reverse osmosis experiments the preceeding experimental procedure was modified. Since the reverse osmosis membranes would not tolerate sudden changes in concentration without a catastrophic failure, the pure solvent permeation test was not included. Thus the solution to be studied was made in the reservoir by dilution and circulated under operating pressure. When 8 mL of solution were collected from the lowest permeation rate membrane, a sample of the feed was taken and the membrane permeate was collected for each membrane for a known time period. At the end of this time period, a second feed sample was taken and the pump was turned off. The solution was left standing in the apparatus until the next solution was introduced. As before, the mass of the circulation system was large enough to preclude changes in concentration when the feed samples were analyzed. These experimental results are also shown in the Appendix A-1, Table A-1-8 and A-1-9, with dilute solution data in Table A-1-10.

Analysis for concentration varied according to the solution in question. Salt solutions in alcohols were analyzed by electrical conductance and atomic absorption spectroscopy with the exception of NH_4Cl which was analyzed by a nitrogen analyser. Aqueous salt solutions were analyzed by electrical conductance. Dilute organic solutes in alcohol solutions were analyzed by nitrogen analysis or ultraviolet absorption spectroscopy while dilute organic solutes in aqueous solutions were analyzed by a total organic carbon analyser. The high concentration ethanol solutions were analyzed by refractometry as were the ethanol-heptane solutions.

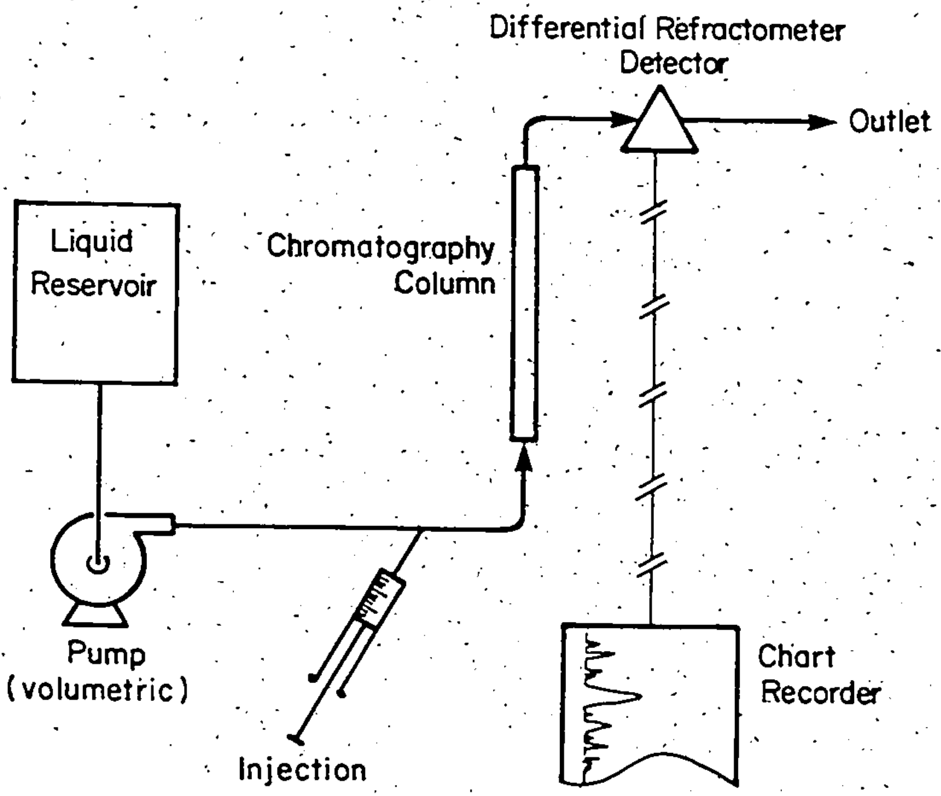
Several types of reverse osmosis membranes were used in this work. The cellulose acetate reverse osmosis membranes were made according to the batch 316 (10/30) outline (Pageau and Sourirajan, 1972) and were heat treated to vary their porosity. The aromatic polyamide membranes were made by the method described by Matsuura et al. (1974). The cellulose membranes were fabricated by a new method which is described in a later section.

The reverse osmosis membranes that were used in alcohol solutions were solvent exchanged from water to the alcohol by three hour soakings in each of 50%, 75%, and 100% alcohol-water solutions. No visible changes in the colour or texture of the membranes were observed with the exception of the tendency of the membranes to dry out quickly when removed from the alcohol solutions. When they were loaded into the reverse osmosis cells the membranes were continuously moistened with alcohol to prevent drying. A piece of filter paper was placed over the porous stainless steel plug of the bottom part of the reverse osmosis cell to prevent damage to the underside of the membrane.

Liquid Chromatography Experiments. Liquid chromatography experiments were used to simulate the reverse osmosis membrane polymer-solution interfacial region. The apparatus used for these experiments was a Waters Associates Model ALC 202 liquid chromatograph fitted with a Waters Associates Model R401 differential refractometer and the apparatus is outlined schematically in Fig 2-3. The columns that were used were made of stainless steel tubing 60 cm in length and 3.2 mm inner diameter. These were filled with polymer powder that had been crushed and sieved to obtain a size range of 38 to 53 μm (Tyler Screen sizes of 400 to 270 mesh). The procedure for filling the tubes was as follows. The tubing was cut to the required length and care was taken to avoid crimping the ends. The tubing was washed with water, methanol, acetone, and again with water to remove any dirt or oil from the steel. This was followed by a 4 hour oven drying at 260°C. A glass wool plug was placed in one end of the tubing and a known mass of polymer powder was poured in while the tubing was vibrated. The polymer powder was enclosed with a second glass wool plug and pressure fittings were installed. The column was then attached to the chromatograph and pure solvent was passed through for 4 to 5 hours. The solvents that were used were degassed by vacuum and in the case of ethanol, contact with humidity in the atmosphere was avoided by the use of an air inlet packed with a dessicant.

Figure 2-3

The Basic Elements of the Liquid Chromatography Apparatus Used in This Work


Differential Refractometer Detector
Outlet
Liquid Reservoir
Chromatography Column
Pump (volumetric)
Injection
Chart Recorder

In general, 10 μL samples of 1% by weight or saturated solutions were injected into the column. Saturated solutions were used in the case where the solutes were insufficiently soluble. Retention times for the solutes were defined as the time between injection and the detectors maximum response (peak). As well as the solutes, deuterated analogues of the solvent were injected without dilution and were assumed to define the solvent's front. The results obtained from these experiments are shown in Appendix A-1, Table A-1-1 and Table A-1-2.

Surface Area Determinations. In order to obtain the interfacial properties of the polymer used in reverse osmosis by liquid chromatography, the total surface area of the polymer powder in the chromatography column was necessary. The method chosen was a vapour-liquid saturation method as outlined by Huber and Gerritse (1971), Mohlin and Gray (1974) and Matsuura et al. (1981). Polymer powder in the size range that was used for the liquid chromatography experiments (38 to 53 μm) was placed in a 10 cm length of 3.2 mm inner diameter stainless steel tubing. The column was loaded into a Tracor Model 160 gas chromatograph with helium as the carrier gas at a flowrate of approximately 24 cm^3/minute. Solvent was injected into the column in amounts that were varied from 2.5 μL to volumes that caused saturation (in excess of 100 μL). For each of these injections, the retention time and the peak heights as determined by a thermal conductivity detector were reported. These results for the methanol-cellulose acetate and the ethanol-cellulose acetate cases are shown in Appendix A-1 in Table A-1-3 and Table A-1-4.

Chemical Quality.- Many different types of chemicals of varying purities were used in this work. The methanol and heptane solvents were both of A.C.S. reagent grade. All of the salts and most of the organic solutes were of A.C.S. reagent grades or superior, while some of the organic solutes were of technical grade. The ethanol solvent was 99.96% pure as supplied by Commercial Alcohols Ltd. The water used was from a distilled source in the laboratory. The cellulose acetate polymer was Eastman 398 ASTM-3 and was reported to be 39.8% acetylated and passed the ASTM Viscosity 3 test. The cellulose powder used was supplied by J.T. Baker Co. It was of "Chromatographic Quality" and was acid free and ashless. In the cases where a salt was bound to waters of crystallization, they were heated overnight in a drying oven at 250°C and used immediately. It should be noted that $MgCl_2 \cdot 6H_2O$ was heated to drive off the waters of crystallization, which does not give $MgCl_2$ as a product. However, this product was used in methanol solution experiments, and was treated as pure $MgCl_2$.

Chapter 3

Free Energy Parameters for Ions and Ion Pairs For the Reverse Osmosis Separation of Inorganic Solutes in Methanol and Ethanol Solutions With Cellulose Acetate Membranes

Introduction

The use of free energy parameters for the description of reverse osmosis performance in aqueous salt solutions has been well developed (Matsuura et al., 1975). They have been used to describe the reverse osmosis separation of completely dissociated ions as well as the cases of incompletely dissociated ions (Rangarajan et al., 1976). It is the objective of this chapter to demonstrate that the concept and use of free energy parameters can be directly applied to the case of non-aqueous reverse osmosis. This required the generation of data for the reverse osmosis separation of alcohol-salt solutions for both completely dissociated ions as well as incompletely dissociated ions. These data were analyzed by the same method of analysis as used in aqueous systems.

The successful demonstration of the validity of the reverse osmosis analysis in the nonaqueous cases as well as the aqueous case will be a confirmation of the generality of the physicochemical basis used to describe reverse osmosis. The success of this demonstration for several solvents would also increase the confidence of using the free energy parameter model for all three solvents considered in this work (i.e. water, methanol, and ethanol). Speculation as to the universality of the reverse osmosis mechanism with regard to solvent would also be enhanced by this work.

Transport Equations. The reverse osmosis experiments with salts in alcohol solutions were analyzed by the Kimura-Sourirajan preferential adsorption-capillary flow model (Kimura and Sourirajan, 1967; Sourirajan, 1970b; Matsuura et al., 1975). This analysis is based upon the assumptions that the surface pores are not excessively larger than the solution molecules, the interfacial forces are of sufficient magnitude to cause preferential adsorption of the solvent, the solvent flux is proportional to the difference between hydraulic and osmotic pressures across the membrane, and the solute flux is due to the porous nature of the membrane and is proportional to the concentration difference across the membrane. The following basic transport equations are developed by the Kimura-Sourirajan analysis.

$$A = \frac{(PSP)}{M_B \cdot S \cdot 3600 \cdot P} \tag{3-1}$$

$$N_B = A\left[P - \Pi(X_{A2}) + \Pi(X_{A3})\right] \tag{3-2}$$

$$= \left(\frac{D_{AM}}{K\delta}\right)\left(\frac{1-X_{A3}}{X_{A3}}\right)\left(c_2 X_{A2} - c_3 X_{A3}\right) \tag{3-3}$$

$$= k\, c_1\, (1 - X_{A3})\, \ln\left[\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}\right] \tag{3-4}$$

In the range of solution concentrations used in this work, the molar density of the solution, c, is essentially constant so that $c_1=c_2=c_3=c$. Equations 3-3 and 3-4 become

$$N_B = \left(\frac{D_{AM}}{K\delta}\right) \frac{1-X_{A3}}{X_{A3}} \; c \left(X_{A2}-X_{A3}\right) \tag{3-5}$$

$$= k\ c\ (1-X_{A3})\ \ln\left[\frac{X_{A2}-X_{A3}}{X_{A1}-X_{A3}}\right] \tag{3-6}$$

By using eqs 3-1,-2,-5 and -6, one can calculate the values of the pure solvent transport parameter, A, the solute transport parameter, $(D_{AM}/K\delta)$ and the mass transfer coefficient, k.

A further assumption can be made for very dilute solutions that do not exert a significant osmotic pressure. The above equations can be simplified to (Sourirajan and Matsuura, 1977)

$$\left(\frac{D_{AM}}{K\delta}\right) = \frac{(PSP)}{3600\cdot S\cdot d} \cdot \frac{1-f}{f}\left[\exp\left(\frac{(PSP)}{3600\cdot S\cdot d\cdot k}\right)\right]^{-1} \tag{3-7}$$

This requires that (PSP) be equivalent to (PR).

Ionic Contributions to the Solute Transport Parameter. The Born equation for the free energy of solvation is (Bockris and Reddy, 1970b)

$$\Delta G_{B,i} = \frac{-N_o(Z_i e_o)^2}{2r_i} \left(1 - \frac{1}{\varepsilon}\right) \qquad (3\text{-}8)$$

where r_i is the crystallographic radius of the ion, i, e_o is the electronic charge, and ε is the solvent's dielectric constant. Equation 3-8 may be rewritten as

$$\Delta G_{B,i} = \frac{-E}{r_i} \qquad (3\text{-}9)$$

A modification of the Born equation is a correction applied to the crystallographic radius term to give (Bockris and Reddy, 1970a)

$$\Delta G_{B,i} = \frac{-E}{r_i+\Delta} \qquad (3\text{-}10)$$

which is used in the form

$$\frac{1}{\Delta G_{B,i}} = \frac{-r_i}{E} - \frac{\Delta}{E} \qquad (3\text{-}11)$$

At an interface, despite the different dielectric fields in effect, eq 3-11 is assumed to be valid, and by analogy is written in the form (Matsuura et al., 1975)

$$\frac{1}{\Delta G_{I,i}} = \frac{-r_i}{E_I} - \frac{\Delta_I}{E_I} \qquad (3\text{-}12)$$

where the subscript I is used to describe the interfacial values. The surface excess free energy is then defined as

$$\Delta\Delta G_i = \Delta G_{I,i} - \Delta G_{B,i} \tag{3-13}$$

$$= \left(\frac{-E_I}{r_i+\Delta_I}\right) - \left(\frac{-E_B}{r_i+\Delta_B}\right) \tag{3-14}$$

The term $\Delta\Delta G_i$ represents the energy required to move an ion from the bulk of the solution to the interfacial region.

The solute transport parameter has been related to the surface excess free energy by (Matsuura et al., 1975)

$$\ln\left(\frac{D_{AM}}{K\delta}\right) = \ln C^*_{ref} + \sum_i n_i \, (-\Delta\Delta G/RT)_i \tag{3-15}$$

where C* is a proportionality factor related to the membrane porosity and the summation term includes contributions from all of the ions in solution.

With eq 3-15, reverse osmosis performance for various salt solutions can be predicted given the appropriate free energy parameters that describe $(-\Delta\Delta G/RT)_i$.

Effects of Incomplete Ionic Dissociation on the Solute Transport Parameter. There is a possibility that ions of opposite charge in an electrolyte solution will have sufficient energy for mutual attraction to form an uncharged ion pair. The mass action for the dissociation of ion pair AB to ions A^+ and B^- can be written as (Robinson and Stokes, 1959d; Bockris and Reddy, 1970b)

$$AB \overset{K_D}{\rightleftharpoons} A^+ + B^- \tag{3-16}$$

$$K_D = \frac{\alpha^2 \gamma_\pm^2 X}{(1-\alpha)} \tag{3-17}$$

where K_D is the dissociation constant, $\gamma_\pm$ is the mean ionic activity coefficient of the charged species, and α represents the degree of dissociation. The degree of dissociation is determined by solving eq 3-17 for α

$$\alpha = \frac{1}{2}\left[\frac{-K_D}{X\gamma_\pm^2} + \sqrt{\left(\frac{K_D}{X\gamma_\pm^2}\right)^2 + \frac{4K_D}{X\gamma_\pm^2}}\right] \tag{3-18}$$

which can be written as

$$\alpha = \frac{1}{2}\left[-\beta + \sqrt{\beta^2 + 4\beta}\right] \tag{3-19}$$

where

$$\beta = \frac{K_D}{X\gamma_\pm^2} \tag{3-20}$$

For the case of incomplete dissociation, the solute transport parameter can be described by a modified form of eq 3-15 that includes the contribution of the ion pair's free energy (Rangarajan et al., 1976)

$$\ln\left(\frac{D_{AM}}{K\delta}\right) = \ln C^* + \alpha \sum_i (-\Delta\Delta G/RT)_i + (1-\alpha)(-\Delta\Delta G/RT)_{IP} \qquad (3\text{-}21)$$

where $(-\Delta\Delta G/RT)_{IP}$ is the surface excess free energy of solvation of the ion pair.

The effect of pressure on ionic dissociation has been studied (Strauss, 1957; Cussler and Fuoss, 1966; 1967; Hamann, 1982). It was found that ionic dissociation decreased for large excursions of pressure from atmospheric conditions but found that pressure ranges similar to those employed in this work had little effect. Thus, the effect of pressure on ionic dissociation was ignored.

Correlation of Mass Transfer Coefficient. Sourirajan and Kimura (1967) observed that the mass transfer coefficient varied with feed solution circulation rate, feed solution concentration, and the permeation rate through the membrane. They demonstrated that for a given Reynold's number, N_{Re}, Schmidt and Sherwood numbers (N_{Sc} and N_{Sh}, respectively) were related as

$$N_{Sh}/(N_{Sc})^{1/3} = \text{constant} \tag{3-22}$$

where

$$N_{Re} = Q/h\nu \tag{3-23}$$

$$N_{Sh} = k\, d_m/D_{AB} \tag{3-24}$$

$$N_{Sc} = \nu/D_{AB} \tag{3-25}$$

where Q is the feed solution's circulation rate through the high pressure side of the cell, h is the height of the chamber above the membrane, d_m is the membrane's diameter, and D_{AB} is the solute's diffusion coefficient. If the mass transfer coefficient is determined for a reference case then eq 3-22 can be applied to calculate the mass transfer coefficients for other cases provided that the Reynold's number was the same for both cases. The use of eq 3-22 can be simplified by assuming that the changes of kinematic viscosity for dilute solutions and a fixed solvent are negligible. Thus a more useful form of the above can be written as

$$k_A = k_{ref} \, (D_{AB}/(D_{AB})_{ref})^{2/3} \qquad (3\text{-}26)$$

As well, the assumptions of negligible changes of kinematic viscosity and a fixed solvent can be used to reduce the Reynold's number requirement to that of the same feed solution flowrate, Q, for the two cases.

It should be noted that the conditions for determining the reference mass transfer coefficient should be chosen in order to avoid having the ratio $(X_{A2}-X_{A3})/(X_{A1}-X_{A3})$ close to unity when it is used in the logarithmic term of eq 3-6. This condition can usually be avoided by choosing experimental conditions where osmotic pressure is significant. As well, D^{o}_{AB} was used in eq 3-26 for cases where the solute was of such a dilute concentration that osmotic pressure could be ignored.

Physical Properties of Salts in Alcohol Solutions. In general, the data required by the Kimura-Sourirajan analysis consisted of solution activities, diffusion coefficients, ionic dissociation constants, viscosity and density data. Osmotic pressure calculations were made with

$$\Pi = \frac{-RT}{\bar{V}s} \ln a_s \tag{3-27}$$

$$\cong \frac{-RT}{\tilde{V}s} \ln a_s \tag{3-28}$$

where the partial molar volume of the solvent was assumed equivalent to the pure solvent's molar volume. The difference of the two was found to be negligible for the concentrations considered in this work. Since most of the literature sources gave the activity of the ions in solution, these had to be converted to solvent activities. They were obtained by integration of the Gibb's-Duhem equation (Lewis et al., 1961).

$$\sum_i n_i \, d\mu_i = 0 \tag{3-29}$$

where n_i is the number of mols of species i and μ_i is the chemical potential of i. Equation 3-29 was transformed to

$$d\mu_1 = \frac{-X_2}{X_1} d\mu_2 \tag{3-30}$$

and

$$d \ln a_1 = \frac{-X_2}{X_1} d \ln a_2 \tag{3-31}$$

The binary solution identity

$$X_1 d \ln X_1 = -X_2 d \ln X_2 \tag{3-32}$$

was algebraically subtracted from eq 3-31 to give

$$d \ln \gamma_1 = \frac{-X_2}{X_1} d \ln \gamma_2 \tag{3-33}$$

and when integrated, eq 3-33 becomes

$$\ln \gamma_1 - 0 = -\int_0^{X_2} \frac{X_2}{X_1} d \ln \gamma_2 \tag{3-34}$$

Equation 3-34 is valid providing that the reference state is chosen as

$$\lim_{X_1 \to 1} \gamma_1 = 1 \tag{3-35}$$

Equation 3-34 was integrated numerically with data obtained from the literature to transform mean ionic activity coefficients, $\gamma_\pm$, to pure solvent activity coefficients.

Diffusion coefficients were determined by the Nernst-Haskell equation (Reid et al., 1977b)

$$D^\circ_{AB} = \frac{RT}{F^2} \left[\frac{1/n_+ + 1/n_-}{1/\lambda_{o+} + 1/\lambda_{o-}} \right] \tag{3-36}$$

combined with

$$D_{AB} = D^\circ_{AB} \left[1 + \frac{d \ln \gamma}{dm} \right] \tag{3-37}$$

where F is Faraday's constant, n_+ and n_- represent the mols of cations and anions per mol of salt, D°_{AB} is the diffusion coefficient for infinite dilution, λ_{oi} is the limiting conductivity of ion i, and m is the molal concentration of the salt. Values of λ_{oi} are shown in Table 3-1 for ions that were considered in this work. The fluoride ion was assigned an approximate value on the assumed basis that λ_{oi} varied linearly with crystallographic radius as demonstrated in Fig 3-1. Calculated values of D°_{AB} are shown in Table 3-2.

From eq 3-18, it is apparent that the degree of dissociation is inversely proportional to salt concentration. In order to determine the reverse osmosis properties of ions it is essential that the salt concentrations are low enough to give complete dissociation. Several experimental values of ionic dissociation constants for alkali metal halides in alcohol solutions are available in the literature and are shown in Table 3-3. In the case of the methanol solutions, the reverse osmosis experiments were performed at 0.005 molal. As an example of the ionic dissociations usually obtained, the case of NaBr was chosen since it has a low K_D value as shown in Table 3-3. For 0.005 molal of salt, $X = 1.6 \times 10^{-4}$ and $\gamma_{\pm} \cong 1.0$ so that β of eq 3-24 is 24.9 which corresponds to $\alpha = 0.96$ or 96% ionic dissociation.

For ethanol solutions, the dissociation constants for alkali metal halides are smaller which leads to less dissociation than the methanol solutions. For this reason, the salt concentrations were reduced to 0.001 molal. Thus for LiCl at 0.001 molal in ethanol, $X = 4.6 \times 10^{-5}$ and $\gamma_{\pm} \cong 1.0$. This

Table 3-1

Limiting Conductivities and Crystallographic Radii for Ions in Alcohol Solutions

Ion	Crystallographic Radius, m x 10^{10} [a]	λ_{0i}, $\frac{S}{\text{equiv.}}$ x 10^4	
		Methanol	Ethanol
Li^+	0.60	39.82[b]	14.9[f]
Na^+	0.95	45.22[b]	18.7[f,g]
K^+	1.33	52.40[b]	22.0[h]
Rb^+	1.43	56.27[c]	23.6[h]
Cs^+	1.69	62.6[d]	25.5[h]
F^-	1.36	38.9[e]	19.1[e]
Cl^-	1.81	52.38[b]	24.3[f,g]
Br^-	1.95	56.55[b]	25.8[f,g]
I^-	2.16	62.75[b]	28.7[f]
NH_4^+	1.48	57.8[c]	19.2[i]
Mg^{++}	0.65	56.7[c]	--
Ca^{++}	0.99	58.7[c]	--
Sr^{++}	1.13	58.7[c]	--
Ba^{++}	1.35	59.2[c]	--
NO_2^-	2.60[j]	--	25.9[h]
NO_3^-	2.66[j]	62.0[c]	27.9[h]
ClO_3^-	2.75[j]	63.5[c]	29.3[h]
ClO_4^-	2.90[j]	71.1[c]	33.8[h]
BrO_3^-	3.14[j]	57.3[c]	--

[a] Robinson and Stokes (1965b).
[b] Robinson and Stokes (1965c).
[c] Landolt-Bornstein (1961).
[d] Sadovnichaya (1975).
[e] Assumed, see Fig 3-1
[f] Lange (1941).
[g] Graham et al. (1957).
[h] El-Aggan et al. (1958).
[i] Barak et al. (1933).
[j] Podolsky (1958).

Figure 3-1

Extrapolation of the Limiting Ionic Conductivity
of Fluoride in Methanol and Ethanol Solutions

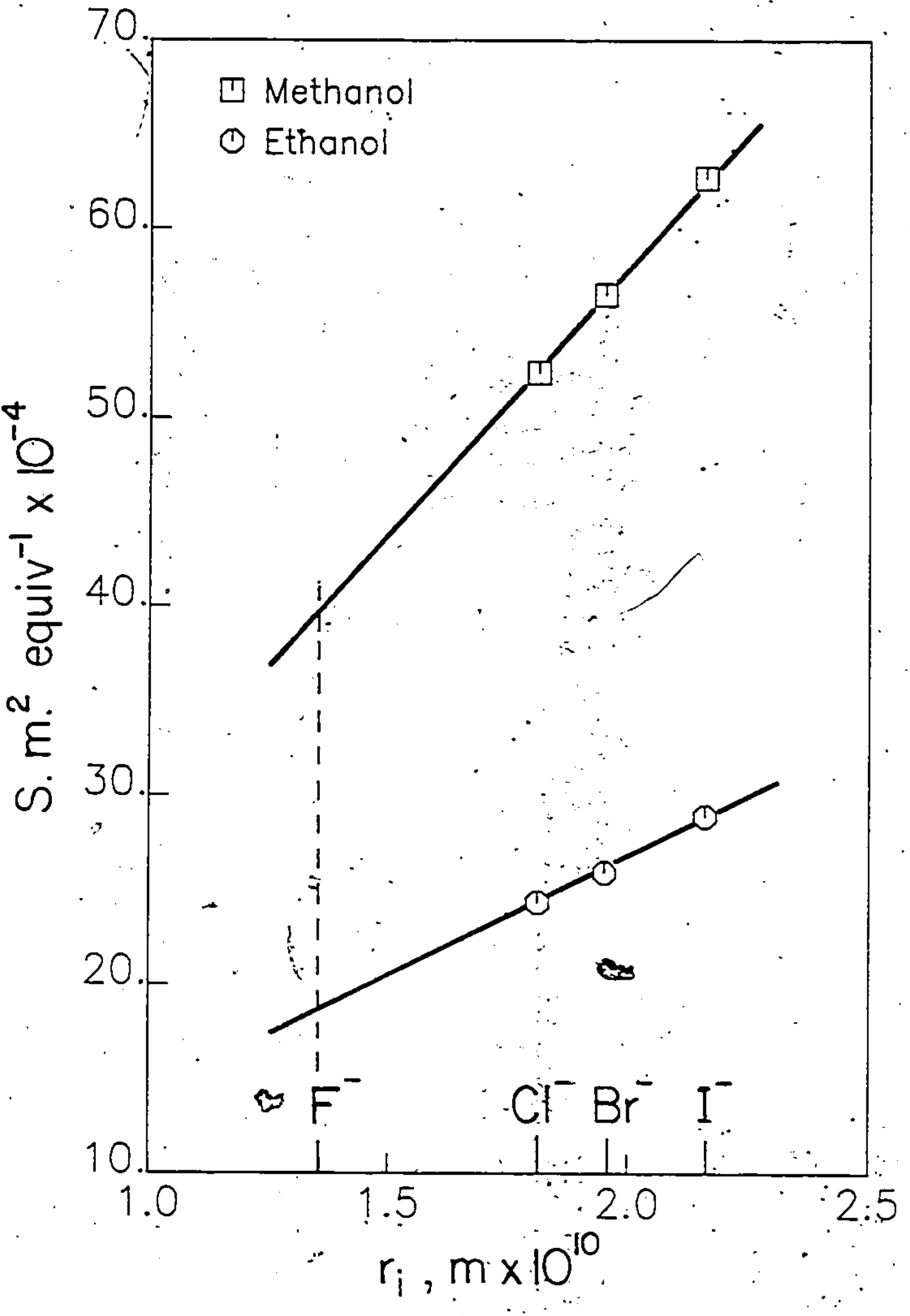

70.
60.
50.
40.
30.
20.
10.
1.0
1.5
2.0
2.5
Methanol
Ethanol
S. m^2 equiv^{-1} x 10^{-4}
r_i , m x 10^{-10}
F$^-$
Cl$^-$
Br$^-$
I$^-$

Table 3-2

Diffusion Coefficients at Infinite Dilution as Calculated by the Nernst-Haskell Equation for Salts in Alcohols

Salt	D°_{AB}, $m^2 \cdot s^{-1} \times 10^{10}$	
	Methanol	Ethanol
LiCl	12.07	4.92
LiBr	12.56	5.03
NaCl	13.17	5.62
NaBr	13.37	5.77
NaI	14.03	6.03
KF	11.88	5.44
KCl	14.24	6.15
KBr	14.41	6.32
KI	15.20	6.63
RbCl	14.33	--
RbBr	--	6.56
RbI	--	6.89
CsCl	14.98	6.62
CsBr	15.16	6.80
CsI	--	7.19
NH_4Cl	14.62	5.71
$MgCl_2$	10.87	--
$CaCl_2$	11.05	--
$SrCl_2$	11.05	--
$BaCl_2$	11.09	--
$NaNO_2$	--	5.78
$NaNO_3$	13.80	--
$NaClO_3$	14.60	6.08
$NaClO_4$	14.71	6.41
$NaBrO_3$	14.21	--
$Sr(NO_3)_2$	11.05	--

Table 3-3

Ionic Dissociation Constants in Methanol and Ethanol Solutions

Salt	$K_D \times 10^3$, mol fraction basis	
	Methanol	Ethanol
LiCl	10.55[a]	1.032[e]
LiBr	10.58[a]	0.911[f]
NaCl	4.123[b]	0.719[e]
NaBr	3.996[c]	--
NaI	--	0.433[g]
KCl	--	0.457[e]
KI	4.058[c]	0.943[g]
RbI	--	0.580[g]
CsCl	4.539[d]	--
CsI	--	0.372[g]

[a] Skabichevskii (1975).
[b] Evers and Knox (1951).
[c] Cussler and Fuoss (1967).
[d] Kay and Hawes (1965).
[e] Graham et al. (1957).
[f] Shkodin et al. (1972).
[g] Beronius et al. (1970).

gives $\beta = 22.4$ which corresponds to 95.9% dissociation. The smallest dissociation constant was for CsI and for the same conditions as for LiCl, β is calculated as 8.09 and there is a 90% ionic dissociation. For both of the solvents at the appropriate concentrations it was assumed that dissociation was complete for the alkali metal halides and other univalent-univalent (1:1) salts.

The case of the divalent ions is slightly different from the monovalent salts. Because of the possibility of the formation of 2:1 and 2:2 ion pairs from the divalent cations-monovalent anions in solution, there are two dissociation constants which can be written for the salt MX_2 as

$$K_{D1} = \frac{[M^{2+}][X^-] \cdot \gamma_{M^{2+}} \cdot \gamma_{X^-}}{[MX^+]\ \gamma_{MX^+}} \qquad (3\text{-}38)$$

and

$$K_{D2} = \frac{[MX^+][X^-]\ \gamma_{MX^+} \cdot \gamma_{X^-}}{[MX_2]\ \gamma_{MX_2}} \qquad (3\text{-}39)$$

where γ_A is the activity of the ionic species A. Lee and Wheaton (1978) show that for alkaline earth halides, K_{D2} is very small and can be ignored with respect to K_{D1}. In terms of concentration, eq 3-38 can be written as

$$K_{D1} = \frac{2\alpha^2 c_{A2}}{1-\alpha} \qquad (3\text{-}40)$$

where all γ's were assumed to be unity and α is the dissociation constant for

$$X^- + MX^+ \overset{K_{D1}}{\rightleftarrows} M^{2+} + 2X^- \qquad (3-41)$$

In terms of α, eq 3-40 becomes

$$\alpha = \frac{-K_{D1} \pm \sqrt{K_{D1}{}^2 + 4(2c_{A2}K_{D1})}}{2(2c_{A2})} \qquad (3-42)$$

Several values of dissociation constants were available for alkaline earth halides in methanol solutions as shown in Table 3-4. As an example of the estimated ionic dissociation of these salts, the calculation of $BaCl_2$ at 0.005 molal is considered. In eq 3-42,

$$\alpha = \frac{-0.001861 + \sqrt{(0.001861)^2 + 4(2)(0.005)(0.001861)}}{2(2(0.005))}$$
$$\cong 0.348 \qquad (3-43)$$

which corresponds to 34.8% dissociation. The same calculation for $MgCl_2$ at 0.005 molal gives 42% ionic dissociation.

Because of these calculations the alkaline earth halides cannot be assumed to be completely dissociated in methanol solutions. Thus, the reverse osmosis experiments for these salts in methanol solutions cannot represent the completely dissociated ions. Though dissociation constants

Table 3-4

Dissociation Constants for Divalent Salts in Methanol Solutions

Salts	Ion Pair	K_D, kg/mol[a]
$MgCl_2$	$MgCl^-$	0.003077
$CaCl_2$	$CaCl^-$	0.001951
$SrCl_2$	$SrCl^-$	0.001882
$BaCl_2$	$BaCl^-$	0.001861

[a] Lee and Wheaton, (1978).

were not available for the ethanol solutions, it is expected that the same conditions prevail.

Bulk solution values of the free energies of solvation are required for use in the modified Born equation. Data are available in the literature for both solvent cases and are shown in Table 3-5. To obtain the values of E and Δ for the alkali metal cations and the halide anions, the inverse of the free energies were plotted with the ions' crystallographic radii. As shown in eq 3-11, the slope would be the inverse of E, and the intercept would be the ratio, Δ/E. This is shown in Fig 3-2 and the parameters obtained are shown in Table 3-6 for both methanol and ethanol solutions. Other relevant physicochemical data from the literature are given in Table 3-7 for several salts in methanol solutions and for LiCl in ethanol solutions.

Table 3-5

Bulk Solution Free Energies of Solvation for Alkali Metal Cations and Halide Ions in Methanol and Ethanol Solutions

Ion	ΔG_B, kJ·mol^{-1}		
	Methanol[a]	Methanol[b]	Ethanol[a]
F^-	--	--	--
Cl^-	305.9	--	303.3
Br^-	282.8	--	280.3
I^-	253.5	---	244.7
Li^+	481.9	481.9	472.8
Na^+	385.5	385.5	374.5
K^+	314.3	314.3	303.3
Rb^+	289.1	289.0	278.2
Cs^+	249.3	247.2	244.8

[a] Izmailov (1963).

[b] Allen et al. (1967).

Figure 3-2

Modified Born Equation for Bulk Solutions

in Methanol and Ethanol Solvent

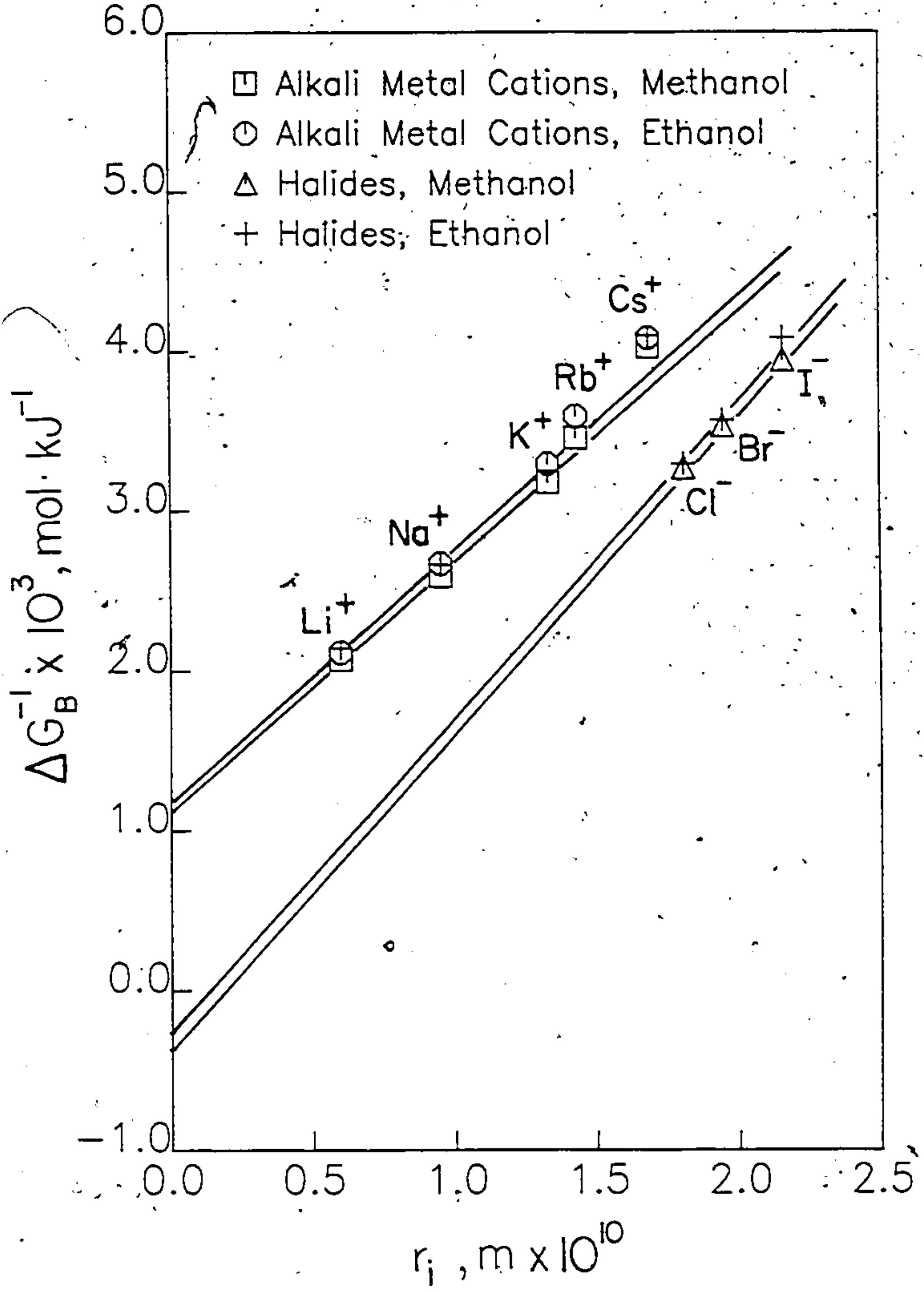

□ Alkali Metal Cations, Methanol
○ Alkali Metal Cations, Ethanol
△ Halides, Methanol
+ Halides, Ethanol
Li+
Na+
K+
Rb+
Cs+
Cl−
Br−
I−
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1.0
0.0
0.5
1.0
1.5
2.0
2.5
$\Delta G_B^{-1} \times 10^3$, mol·kJ^{-1}
r_i, m x 10^{10}

Table 3-6

Modified Born Equation Parameters for Alkali Metal Halides in Bulk Methanol and Ethanol Solutions

Ion	Solution	E_B, $kJ \cdot mol^{-1} \times m \times 10^{10}$	Δ_B, $m \times 10^{10}$
Alkali Metal Cation	Methanol	656.5	0.753
	Ethanol	564.4	0.661
Halide	Methanol	499.5	-0.180
	Ethanol	510.0	-0.129

Table 3-7

Alkali Metal Halide Properties in Methanol and Ethanol Solutions at 25°C and Atmospheric Pressure

LiCl - Methanol

X, x 10^3	Π,[a] kPa	ν,[b] $\frac{m^2}{s}$ x 10^7	D_{AB}, $\frac{m^2}{s}$ x 10^{10}
0	0	6.912	12.07
0.640	42.6	6.934	8.267
1.278	85.1	6.952	7.602
1.916	137.8	6.969	7.631
2.553	194.5	6.987	7.840
3.190	255.3	7.005	8.110
3.825	304.0	7.022	8.400
5.094	413.4	7.057	8.985
5.727	472.2	7.075	9.270
6.359	529.9	7.092	9.549
6.991	584.6	7.110	9.815
7.261	638.3	7.127	10.08
8.251	693.1	7.145	10.33
8.859	725.5	7.157	10.57
9.515	778.2	7.174	10.81
10.14	829.9	7.197	11.04
10.77	883.6	7.208	11.26
11.40	935.2	7.225	11.47
12.02	993.0	7.242	11.68
12.65	1035.8	7.259	11.89
13.27	1104	7.276	12.09
13.89	1164	7.293	12.28
14.52	1223	7.310	12.47
15.14	1280	7.327	12.66
15.76	1342	7.344	12.84
16.38	1408	7.361	13.06
17.00	1469	7.378	13.18
17.62	1533	7.395	13.35
18.23	1600	7.412	13.52
18.85	1672	7.429	13.67
19.45	1745	7.446	--
2.007	1833	7.463	--
2.068	1899	7.480	--
2.130	1986	7.497	--
2.191	2077	7.514	--
2.252	2179	7.531	--
2.312	2289	7.548	--
2.374	2432	--	--

[a] Shkodin and Shapovalova (1966).

[b] Einfeldt and Gerdes (1971).

Table 3-7 (cont'd)

LiBr - Methanol

X, x 10^3	Π,[a,b] kPa	ν $\frac{m^2}{s}$ x 10^7	D_{AB}, $\frac{m^2}{s}$ x 10^{10}
0	0	6.912	12.56
0.640	42.56	7.005	8.603
1.278	85.11	7.083	7.911
1.916	137.8	7.165	7.941
2.553	194.5	7.239	8.158
3.190	255.3	7.313	8.439
3.825	304.0	7.385	8.741
4.460	390.1	7.454	9.047
5.094	413.4	7.523	9.350
5.727	472.2	7.592	9.646
6.359	529.9	7.660	9.934
6.991	584.6	7.776	10.21
7.621	638.3	7.786	10.48
8.251	693.1	7.862	10.75

[a] Skabečhevskii (1969).

[b] Experimentally determined.

Table 3-7 (cont'd)

NaCl - Methanol

$X, \times 10^3$	$\Pi,^{a,b}$ kPa	$\nu,^{c,d}$ $\frac{m^2}{s} \times 10^7$	D_{AB}, $\frac{m^2}{s} \times 10^{10}$
0	0	6.912	12.73
0.468	27.6	6.955	9.40
0.810	58.6	7.000	8.65
1.21	90.3	7.500	8.19
1.63	123.4	7.102	7.90
2.03	155.1	7.165	7.83
2.43	187.5	7.228	7.85
2.83	220.6	7.295	7.93
3.24	261.9	7.363	8.10
3.64	289.5	7.432	8.25
4.05	327.4	7.506	8.40
4.45	358.4	7.580	8.55
4.85	392.2	7.655	8.71
5.25	423.9	7.732	8.85
5.65	454.9	7.810	9.05
6.06	488.0	7.890	9.18
6.46	520.4	7.970	9.34
6.86	546.6	8.050	9.50
7.26	583.8	8.150	9.65
7.66	616.9	8.250	9.81
8.07	648.0	8.289	9.96
8.45	679.0	8.360	10.13
8.83	710.0	8.445	10.27
9.23	741.0	8.525	10.43
9.63	772.0	8.605	10.57
10.06	803.0	8.685	10.74

[a] Vlasov and Antonov (1973).
[b] Izmailov and Ivanova (1955).
[c] Werblan et al. (1971).
[d] Einfeldt and Gerdes (1971).

Table 3-7 (cont'd)

NaBr - Methanol

X, x 10^3	Π,[a] kPa	ν,[b] $\frac{m^2}{s}$ x 10^7	D_{AB}, $\frac{m^2}{s}$ x 10^{10}
0	0	6.912	13.39
0.640	55.7	7.01	12.45
1.278	110.5	7.10	11.78
1.916	172.3	7.17	11.37
2.553	234.1	7.25	10.93
3.190	297.0	7.32	10.77
3.825	358.8	7.39	10.63
4.460	427.7	7.46	10.52
5.094	496.6	7.53	10.42
5.727	558.4	7.59	10.33
6.359	627.4	7.65	10.26
6.991	690.2	7.71	10.20
7.621	756.1	7.82	10.15
8.251	817.9	7.89	10.10
8.880	882.8	7.95	10.06
9.509	950.7	8.00	10.02
10.14	1010	--	--
10.77	1074	--	--
11.40	1139	--	--
12.02	1203	--	--
12.65	1267	--	--
13.67	1331	--	--
13.89	1395	--	--
14.52	1458	--	--
15.14	1522	--	--
15.76	1586	--	--
16.38	1650	--	--
17.00	1714	--	--
17.62	1778	--	--
18.23	1842	--	--
18.85	1906	--	--

[a] Izmailov and Ivanova (1955).

[b] Ewart and Raikes (1926).

Table 3-7 (cont'd)

KI - Methanol

X, x 10^3	Π,[a] kPa	ν,[b] $\frac{m^2}{s}$ x 10^7	D_{AB}, $\frac{m^2}{s}$ x 10^{10}
0	0	6.920	15.20
0.640	48.6	6.930	12.89
1.278	94.4	6.939	12.48
1.916	149.4	6.946	12.25
2.553	195.2	6.955	12.08
3.190	245.8	6.961	11.95
3.825	292.9	6.967	11.85
4.460	343.1	6.973	11.77
5.094	394.0	6.978	11.70
5.727	442.0	6.983	11.63
6.359	490.4	6.988	11.57
6.991	537.5	6.993	11.52
7.621	585.7	6.998	11.48
8.251	633.7	7.003	11.44
8.880	681.8	7.008	11.40
9.509	729.9	7.012	11.36
10.14	780.0	7.017	11.33
10.76	826.1	7.021	11.30
11.39	874.2	7.025	11.27

[a] Skhodin and Shapovalova (1966).

[b] Jones and Fornwalt (1935).

7

Table 3-7 (cont'd)

CsCl - Methanol

$X, \times 10^3$	Π,[a] kPa	ν,[b] $\frac{m^2}{s} \times 10^7$	D_{AB}, $\frac{m^2}{s} \times 10^{10}$
0	0	6.916	13.86
0.640	59.8	6.918	9.43
1.597	161.1	6.922	8.53
2.235	228.0	6.924	8.64
3.190	327.3	6.928	9.16
3.825	392.1	6.930	9.49

[a] Minc and Jastrzebska (1968).
[b] Einfeldt and Gerdes (1971).

Table 3-7 (cont'd)

LiCl - Ethanol

m, mol/kg	ϕ,[a] (mol/kg)$^{-1}$	Π,[b] kPa	X, molfr. LiCl	$\gamma_{\pm}$[a]	D_{AB}, m^2/s x 10^{10}
0	--	0	0	---	4.916
0.3	0.6756	793	0.0136	0.192	3.893
0.5	0.7284	1425	0.0225	0.1735	4.15
1.0	0.8461	3310	0.0440	0.1719	5.46
1.5	1.0075	5913	0.0645	0.1888	--
2.0	1.2108	9473	0.0842	0.2378	--
2.5	1.4715	14400	0.1031	--	--
3.0	1.7527	20580	0.1213	--	--

[a] Osmotic Pressure Coefficient from Vlasov and Antonov (1974).

[b]
$$\Pi = \frac{(n_{anion} + n_{cation})\, RT\, M_A}{1000\, \bar{V}_A}\, \phi m$$

$$= 3912.\ (\phi m),\ \text{kPa (for LiCl)}.$$

Results.

Mass Transfer Coefficients. Several 0.15 molal NaCl in methanol solutions were used in reverse osmosis experiments at 1725 kPag operating pressure and 25°C (Table A-1-5, Run No's 519, 520, 521, 531). The data obtained from these experiments was used to solve for the parameters in eq 3-1, -2, -5 and -6 for each membrane. The values for the mass transfer coefficient, k, were adjusted to 0.1500 molal by eq 3-26 and are plotted in Fig 3-3 with the pure solvent permeability for each membrane. A first order linear equation was fitted to these data to give

$$k = 0.1000\,A + 1.271 \times 10^{-6} \qquad (3\text{-}44)$$

with a correlation coefficient of 0.513.
This correlation was used for all subsequent calculations that required mass transfer coefficients in methanol solutions.

The mass transfer coefficient in ethanol solutions was generated in the same manner as the methanol solutions. Reverse osmosis experiments with 0.15 molal LiCl in ethanol solutions at 1725 kPag and 25°C were performed (Table A-1-6, Run No.'s 73, 74) and the mass transfer coefficients were calculated, set to their values for 0.001 molal by eq 3-26, and plotted in Fig 3-4 with the pure solvent permeabilities for each membrane. The first order linear correlation was determined to be

$$k = 0.04951\,A + 5.962 \times 10^{-6} \qquad (3\text{-}45)$$

with a correlation coefficient of 0.508.

Figure 3-3

Mass Transfer Coefficient With Solvent Permeability for Cellulose Acetate Membranes and 0.1500 Molal NaCl-Methanol Solutions

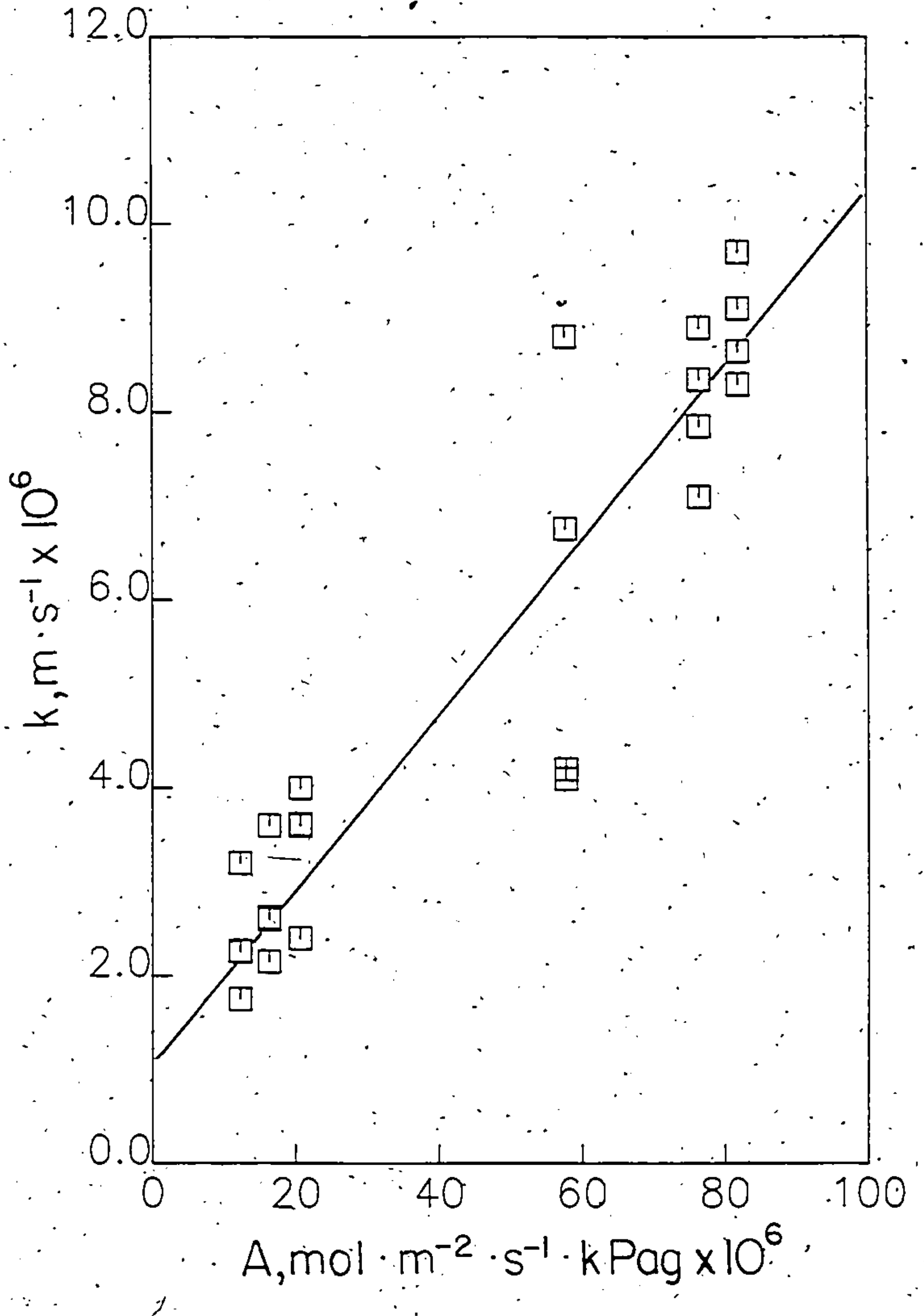
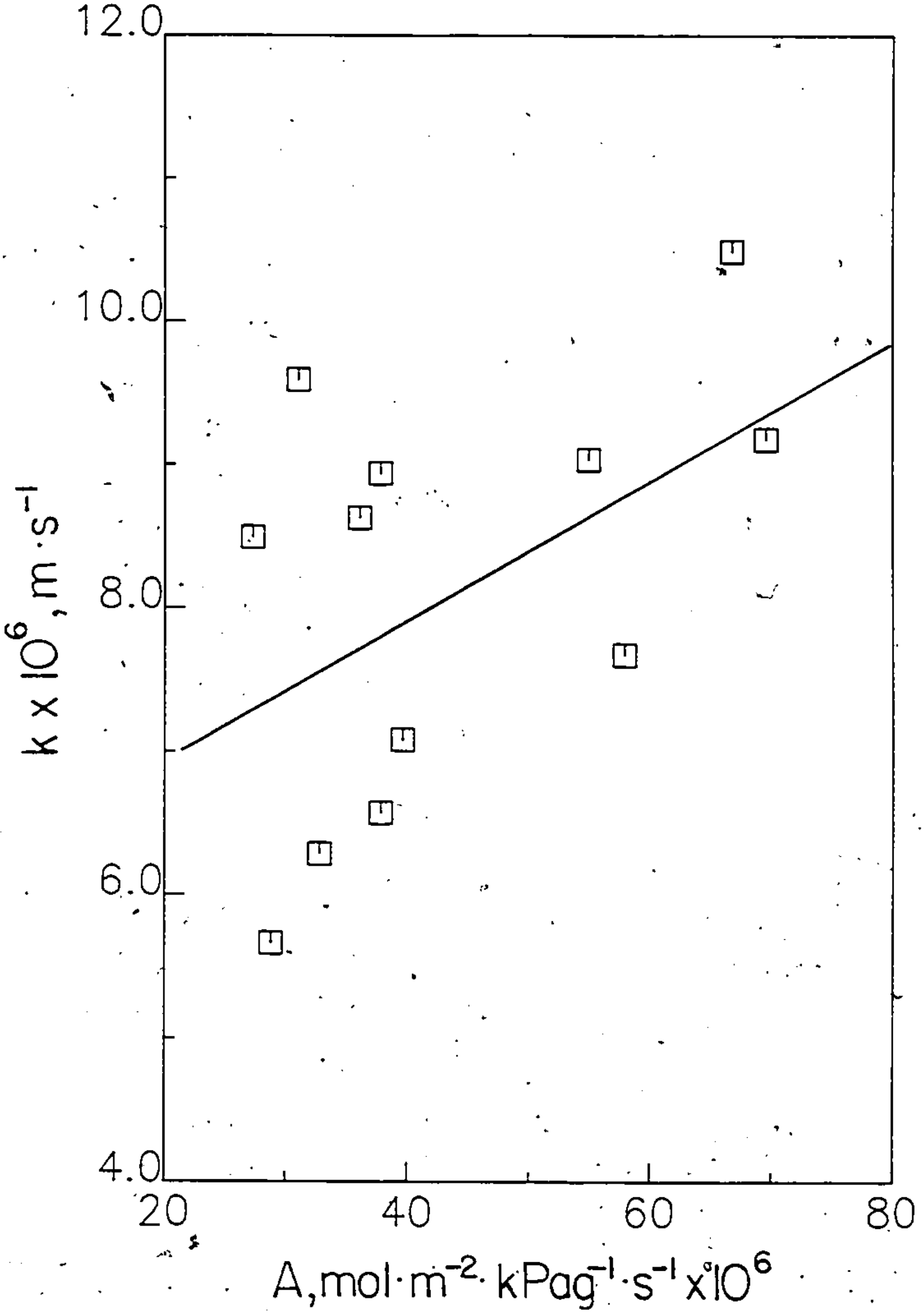

12.0
10.0
8.0
6.0
4.0
2.0
0.0
0
20
40
60
80
100
k, m · s^{-1} x 10^6
A, mol · m^{-2} · s^{-1} · kPag x 10^6

Figure 3-4

Mass Transfer Coefficient With Solvent Permeability for Cellulose Acetate Membranes and LiCl-Ethanol Solutions


12.0
10.0
8.0
6.0
4.0
20
40
60
80
k x 10^6, m·s^-1
A, mol·m^-2·kPag^-1·s^-1 x 10^6

Experimental Determination of Surface Excess Free Energies of Solvation for Alkali Metal and Halide Ions. In the case of the methanol solutions, reverse osmosis experiments were performed at 1725 kPag operating pressure with 12 alkali metal halide salts. For the alkali metal halides, eq 3-7 was used to calculate the $\left(\frac{D_{AM}}{K\delta}\right)$ values of Table 3-8. These values of $\left(\frac{D_{AM}}{K\delta}\right)$ were used to calculate the interfacial phase parameters of the Modified Born equation with a non-linear regression applied to eq 3-14 and 3-15. The means of these parameters for all the membranes are shown in Table 3-9 and values of $(-\Delta\Delta G/RT)_i$ for the alkali metal and halide ions were calculated with eq 3-14 and are shown in Table 3-10 and the membrane porosities, $\ln C^*_{NaCl}$, are shown in Table 3-11.

For the alkali metal and halide ions in ethanol solutions, reverse osmosis experiments with 14 salts comprised of these ions were used. As with the methanol case, the data for the alkali metal halides were used in eq 3-7 to calculate the values of $\left(\frac{D_{AM}}{K\delta}\right)$ in Table 3-12. The Modified Born equation parameters are shown in Table 3-9 and the values of $(-\Delta\Delta G/RT)_i$ calculated by eq 3-14 are listed in Table 3-10 and the membrane porosities are shown in Table 3-13.

Table 3-8

$(D_{AM}/K\delta)$ for Alkali Metal Halide Salts in Methanol Solutions at 1725 kPag and 0.005 Molal

Salt	$(D_{AM}/K\delta)$, m/s x 10^7, for Membrane No.					
	1	2	3	4	5	6
LiCl	8.901	2.045	1.320	5.329	8.138	0.9184
LiBr	10.11	1.915	1.326	5.884	9.058	0.8125
NaCl	24.03	4.218	--	14.42	22.97	--
NaCl	25.01	3.867	2.714	13.51	20.39	1.669
NaCl	23.47	4.048	2.864	13.79	21.13	1.944
NaBr	28.58	5.302	4.067	17.31	25.82	2.809
NaI	31.63	5.130	3.635	19.12	28.51	2.149
KF	23.91	4.204	2.875	13.12	21.34	1.915
KCl	44.41	6.716	4.878	26.76	40.09	3.146
KBr	49.68	7.590	5.454	29.99	44.97	3.701
KI	50.64	8.001	5.919	32.85	49.82	4.881
KI	55.49	8.542	5.911	33.39	48.44	4.076
RbCl	45.31	6.395	4.731	26.73	41.11	2.486
CsCl	49.58	6.795	5.461	30.56	43.05	3.392
CsBr	54.41	7.911	6.419	32.90	50.65	4.017

Table 3-9

Born Equation Parameters for Alkali Metal Halides with Cellulose Acetate Membranes

Ion	Solution	E_B, kJm/mol × 10^{10}	Δ_B, m × 10^{10}	E_I, kJm/mol×10^{10}	Δ_I, m × 10^{10}
Alkali Metal Cations	Ethanol	564.4	0.661	543.5	0.652
	Methanol	656.5	0.753	665.6	0.781
	Aqueous[a]	761.5	0.890	824.7	0.976
Halides	Ethanol	510.0	−0.129	515.1	−0.104
	Methanol	499.5	−0.179	492.9	−0.180
	Aqueous[a]	504.2	−0.200	477.4	−0.230

[a] Matsuura et al. (1975).

Table 3-10

$(-\Delta\Delta G/RT)_i$ for Alkali Metal and Halide Ions in Ethanol, Methanol, and Aqueous Solutions

Ion	$(-\Delta\Delta G/RT)_i$		
	Ethanol	Methanol	Aqueous
Li^+	-5.40	-1.36	5.77
Na^+	-4.45	-0.43	5.79
K^+	-3.72	0.03	5.91
Rb^+	-3.49	0.14	5.86
Cs^+	-3.22	0.24	5.72
F^-	-1.72	-2.34	-4.91
Cl^-	-0.61	-1.71	-4.42
Br^-	-0.43	-1.58	-4.25
I^-	-0.25	-1.41	-3.98

Table 3-11

Parameter $\ln C^*_{NaCl}$ Representing the Porosity of Cellulose Acetate Membranes as Determined by 0.005 Molal NaCl Methanol Solutions, 25°C and 1725 kPag

Membrane No.	$\ln C^*_{NaCl}$	Average (PSP),[a] g/h	A, $\frac{mol}{m^2 s kPag} \times 10^6$
1	-10.78	21.76	82.88
2	-12.58	5.37	20.45
3	-12.94	4.20	16.00
4	-11.25	15.22	57.97
5	-10.94	20.36	77.55
6	-13.43	3.26	12.42
7	-12.23	6.10	23.24
8	-12.58	4.44	16.91
9	-12.84	3.50	13.33
10	--	1.03	3.92
11	-12.97	3.51	13.37
12	-12.75	3.40	12.95
13	-12.32	16.14	61.48
14	-11.01	50.38	190.6
15	-11.06	45.53	173.4
16	-11.89	30.75	117.2
17	-11.65	36.30	138.3
18	-11.93	31.79	121.1

[a] 13.2 cm² surface area, 1725 kPag operating pressure

Table 3-12

Calculated Values of ($D_{AM}/K\delta$) for Alkali Metal Halide Salts in Ethanol Solution at 1725 kPag and 0.001 Molal

Salt	$D_{AM}/K\delta$ for Membrane No., x 10^7, m/s					
	1	2	3	4	5	6
LiCl	5.534	3.987	1.721	1.250	2.866	1.262
LiCl	5.306	4.149	1.213	0.8294	3.074	1.327
LiCl	2.895	3.264	1.120	0.7210	1.940	1.080
LiCl	8.182	6.001	1.721	0.9733	2.809	2.232
LiCl	2.542	3.330	1.654	1.023	2.145	1.177
LiBr	5.680	4.362	2.040	0.8719	3.264	1.395
NaCl	5.853	9.904	5.623	3.947	7.606	3.466
NaBr	13.64	10.58	12.44	4.768	6.652	5.033
NaI	7.374	11.63	7.063	5.657	14.47	4.918
KF	3.607	5.523	4.319	2.210	4.641	2.781
KCl	10.06	13.01	10.00	7.621	10.60	5.518
KBr	11.81	15.67	13.21	8.239	12.77	6.951
KI	14.07	19.71	14.83	11.76	17.58	86.70
RbBr	16.83	28.27	18.39	13.06	20.25	10.47
RbI	19.32	33.05	22.83	17.57	27.08	12.37
CsCl	20.14	37.67	18.95	18.86	22.51	15.72
CsBr	19.98	24.68	19.07	17.48	21.71	11.32
CsI	28.78	43.77	32.85	28.87	34.88	21.01

Table 3-13

Parameter $\ln C^*_{LiCl}$ Representing the Porosity of Cellulose Acetate Membranes as Determined by 0.001 Molal LiCl in Ethanol Solutions at 25° and 1725 kPag

Membrane	$\ln C^*_{LiCl}$	Average (PSP),[a] g/h	A, $\frac{\text{mol}}{\text{m}^2\text{skPag}} \times 10^6$
1	-9.26	17.50	46.46
2	-8.81	28.58	75.90
3	-9.38	22.49	59.72
4	-9.62	16.76	44.50
5	-9.19	23.29	61.85
6	-9.84	13.61	36.14

[a] for 13.2 cm^2 surface area.

$(-\Delta\Delta G/RT)_i$ for Other Ions. For both methanol and ethanol solutions, other ions were considered in reverse osmosis experiments. As with the alkali metal halide salts, values of $\left(\frac{D_{AM}}{K\delta}\right)$ were calculated for each case as shown in Tables 3-14 and 3-15. Data for these salts were not available in the literature for the determination of bulk solution parameters for the modified Born Equation. However, since the membrane porosities were already available, their values of $(-\Delta\Delta G/RT)_i$ could be calculated directly from eq 3-14. These are shown in Table 3-16 for the methanol and ethanol solvents. It should be noted that the oven dried $MgCl_2$ salt used in this work was not a true sample. However, it was treated throughout this work as $MgCl_2$.

To compare the data of $(-\Delta\Delta G/RT)_i$ for ethanol, methanol, and aqueous solutions of a given ion it was necessary to describe a reference. This was obtained by letting the $(-\Delta\Delta G/RT)_i$ values for a given solution be compared with Na^+ ion for the cations and Cl^- ion for the anions according to

$$\Delta(-\Delta\Delta G/RT)_i = (-\Delta\Delta G/RT)_i - n_i(-\Delta\Delta G/RT)_{ref} \quad (3\text{-}46)$$

where n_i is the charge of ion i. This basis permits the comparison of $\Delta(-\Delta\Delta G/RT)_i$ shown in Fig 3-5 for the cations and Fig 3-6 for the anions.

Table 3-14

Calculated Values of $(D_{AM}/K\delta)$ for Several Salts in Methanol Solutions at 1725 kPag and 0.005 Molal

Salt	$(D_{AM}/K\delta)$ for Membrane No., x 10^8, m/s					
	13	14	15	16	17	18
$MgCl_2$	0.7015	0.2740	0.2505	1.470	1.357	1.515
$CaCl_2$	0.7086	6.083	8.985	1.796	3.144	2.761
$SrCl_2$	0.7086	4.644	3.802	2.087	1.385	1.851
$BaCl_2$	0.7086	4.202	5.560	1.796	2.087	1.546
NH_4Cl	65.79	248.6	265.7	105.1	128.7	97.17
$NaNO_2$	44.95	121.6	116.0	57.54	84.99	55.84
$NaNO_3$	63.84	228.0	207.6	97.56	120.2	100.5
$NaClO_3$	135.6	208.4	493.5	—	169.6	83.22
$NaClO_4$	69.79	231.0	173.4	86.53	88.81	68.27
$NaBrO_3$	97.76	202.9	263.9	99.83	355.8	120.8

Table 3-15

Calculated Values of $(D_{AM}/K\delta)$ for Several Salts in Ethanol Solutions at 1725 kPag and 0.001 Molal

Salt	$(D_{AM}/K\delta)$ for Membrane No., x 10^7, m/s					
	1	2	3	4	5	6
$CaCl_2$	2.188	3.231	0.4551	0.3338	1.044	0.6459
$SrCl_2$	1.687	3.818	0.7967	0.5449	1.201	0.5729
NH_4Cl	2.699	6.043	2.542	1.589	3.680	0.8130
$NaNO_2$	10.12	18.45	11.59	9.650	13.89	6.705
$NaClO_3$	14.07	35.02	18.26	11.62	29.99	11.67
$NaClO_4$	43.77	25.97	17.85	20.76	30.23	11.46

Table 3-16

Values of $(-\Delta\Delta G/RT)_i$ for Some Ions in Ethanol, Methanol, and Aqueous Solutions

Ion	$(-\Delta\Delta G/RT)_i$		
	Ethanol	Methanol	Aqueous[a]
Mg^{++}	--	-2.92	8.72
Ca^{++}	-6.06	-2.30	8.88
Sr^{++}	-6.07	-2.59	8.76
Ba^{++}	--	-2.60	8.50
NH_4^+	-5.28	-0.19	5.97
NO_2^-	-0.01	-2.04	-3.85
NO_3^-	--	-1.54	-3.66
ClO_3^-	0.58	-1.20	-4.10
ClO_4^-	0.70	-1.69	-3.60
BrO_3^-	--	-1.38	-4.89

[a] Sourirajan and Matsuura (1979).

Figure 3-5

Comparison of $\Delta(-\Delta\Delta G/RT)_i$ for Cations and Cellulose Acetate Membranes for Aqueous, Methanol, and Ethanol Solutions

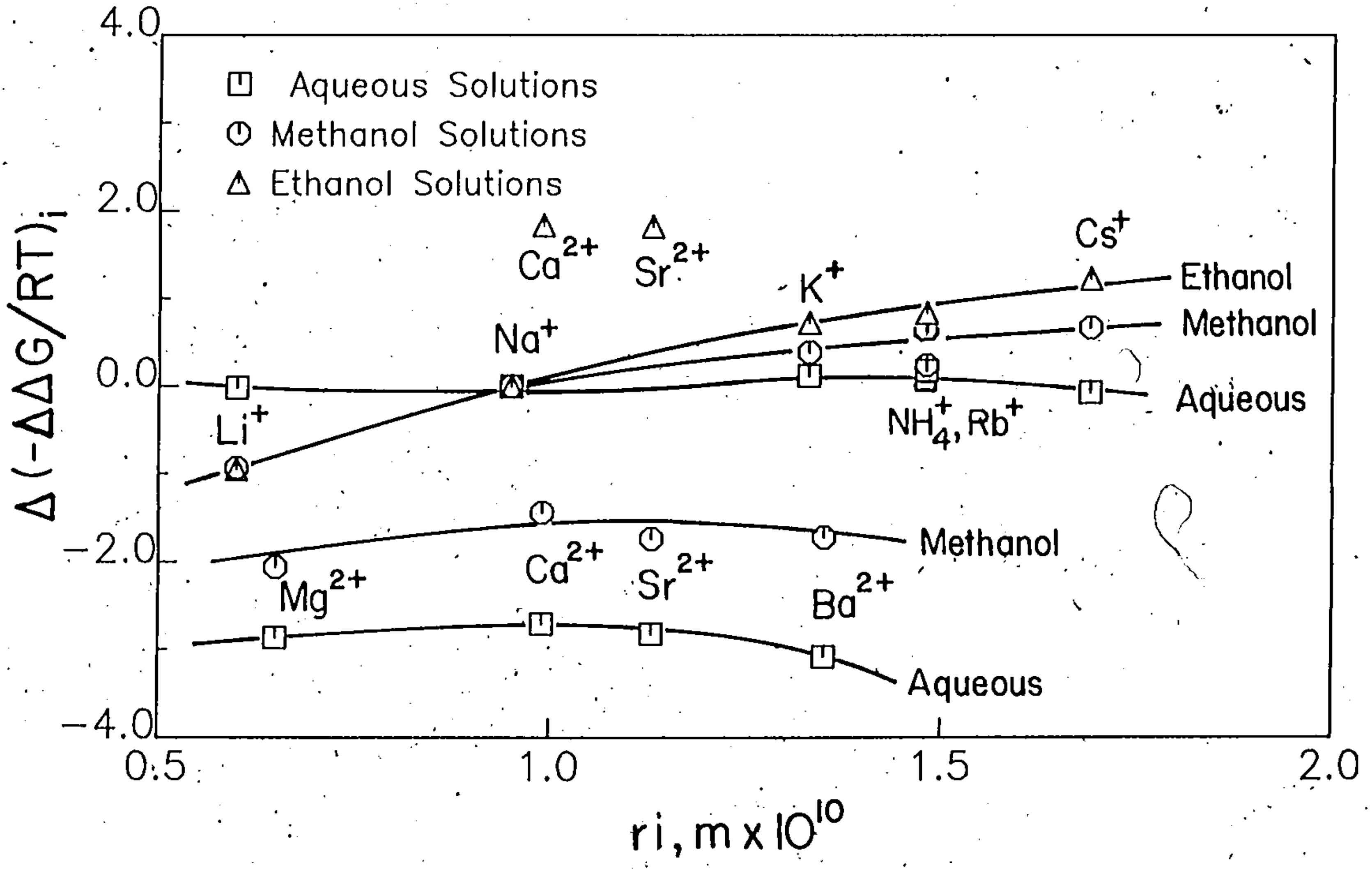
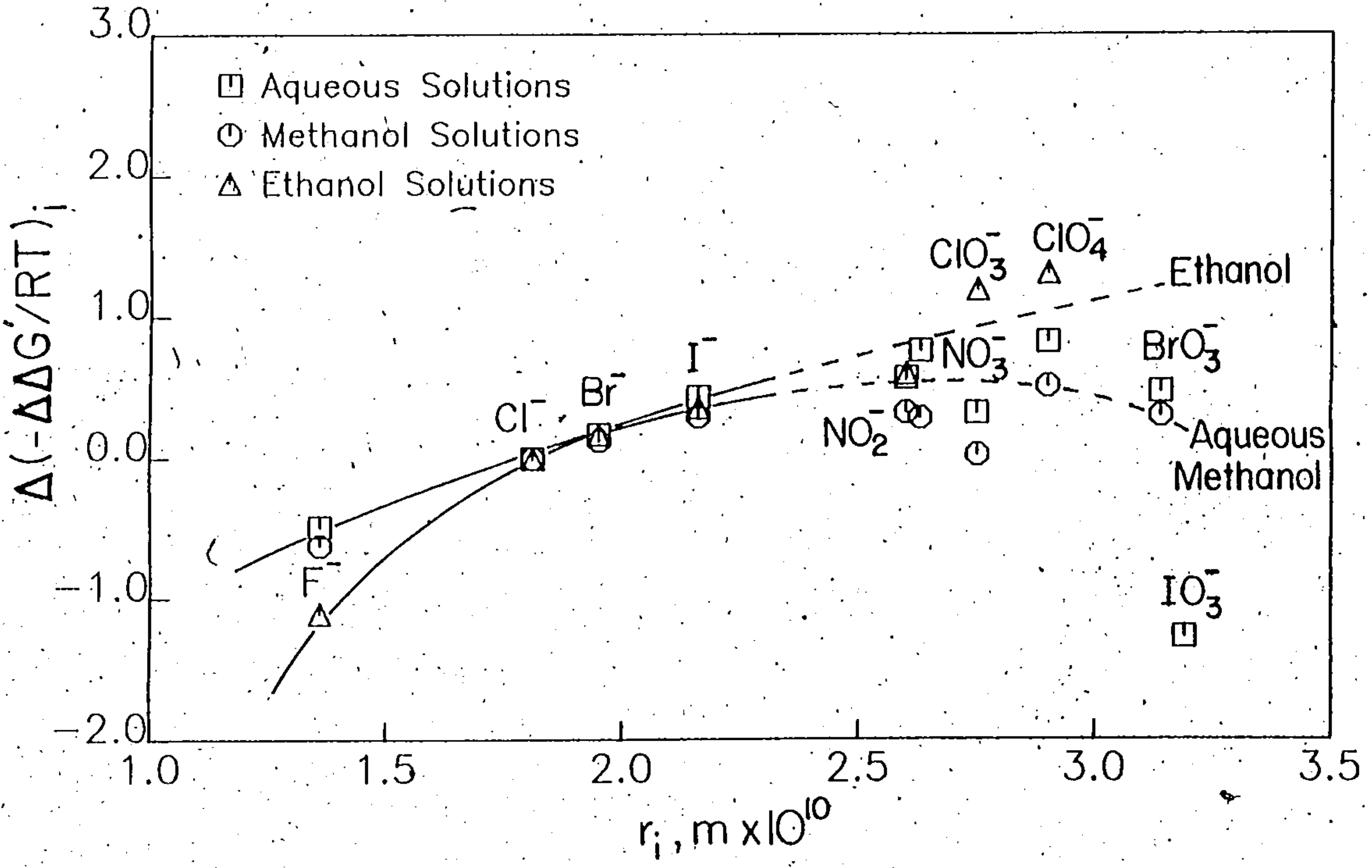

Aqueous Solutions
Methanol Solutions
Ethanol Solutions
Ca2+
Sr2+
Cs+
K+
Na+
Li+
NH4+, Rb+
Ethanol
Methanol
Aqueous
Methanol
Aqueous
Mg2+
Ca2+
Sr2+
Ba2+
4.0
2.0
0.0
−2.0
−4.0
0.5
1.0
1.5
2.0
Δ(-ΔΔG/RT)i
ri, m x 10^10

Figure 3-6

Comparison of $\Delta(-\Delta\Delta G/RT)_i$ for Anions and Cellulose Acetate Membranes for Aqueous, Methanol, and Ethanol Solutions


Aqueous Solutions
Methanol Solutions
Ethanol Solutions
$\Delta(-\Delta\Delta G'/RT)_i$
r_i, m x10^{10}
3.0
2.0
1.0
0.0
−1.0
−2.0
1.0
1.5
2.0
2.5
3.0
3.5
F^-
Cl^-
Br^-
I^-
NO_2^-
NO_3^-
ClO_3^-
ClO_4^-
BrO_3^-
IO_3^-
Ethanol
Aqueous
Methanol

Determination of $(-\Delta\Delta G/RT)_{IP}$. Reverse osmosis experiments were performed with 4 alkali metal halide salts at 0.15 molal in methanol solutions at 1725 kPag and 25 °C. With the use of the membrane porosities of Table 3-11, $(-\Delta\Delta G/RT)_{IP}$ was calculated with eq 3-21 and the results are shown in Table 3-17. Both LiCl and LiBr solutions were included in this study but at 0.15 molal in methanol, they were 98% dissociated as calculated by eq 3-18.

Table 3-17

Surface Excess Solvation Energies for Ion Pairs in Methanol Solutions

Ion Pair	$(-\Delta\Delta G/RT)_{IP}$	α^a
NaCl	-1.30	0.73
NaBr	-0.34	0.80
KI	5.18	0.85
CsCl	1.71	0.82

[a] average calculated degree of dissociation at 0.15 molal.

Prediction of Reverse Osmosis Performance for Completely Dissociated Salt Solutions. The reverse osmosis performance of any of the salt solutions reported above can be calculated for a characterized cellulose acetate membrane. This characterization consists of determining the membrane porosity, $\ln C^*$, and the pure solvent permeability, A. For the case of very dilute salts, eq 3-7 can be rearranged to calculate the solute separation, f (Sourirajan and Matsuura, 1977)

$$f = \left[1 + \left(\frac{D_{AM}}{K\delta}\right) \cdot \frac{3600 \cdot S \cdot d}{(PSP)} \exp\left[\frac{(PSP)}{3600 \cdot S \cdot d \cdot k}\right]\right]^{-1} \quad (3\text{-}47)$$

Membranes were characterized by a reverse osmosis experiment with a single reference salt, either NaCl in the methanol case or LiCl in the ethanol case. $\left(\frac{D_{AM}}{K\delta}\right)$ for the reference solute was then calculated with eq 3-7 and with the known values of $\sum_i (-\Delta\Delta G/RT)_i$ for the salt, $\ln C^*_{ref}$ was calculated by eq 3-15.

For the methanol case, the membrane porosities that were calculated are shown in Table 3-11. The values of $(-\Delta\Delta G/RT)_i$ for the ions of the salts were taken from Tables 3-10 and 3-16 as required. Then eq 3-15 was used to determine the solute transport parameters and eq 3-47 was used to calculate the solute separation as shown in Table 3-18. It should be noted that the product rates, (PR), were assumed to be the same as the pure solvent permeability, (PSP).

For the ethanol solutions, eq 3-47 was used to calculate reverse osmosis separations for dilute solutions. This calculation required the membrane porosities of Table 3-13 and the values of $(-\Delta\Delta G/RT)_i$ of Tables 3-10 and 3-16. A comparison of experimental and calculated values for separation is shown in Table 3-19 for the salts studied.

Table 3-18

Comparison of Experimental and Calculated Reverse Osmosis Separations for Dilute Salt Solutions in Methanol at 1725 kPag and 0.005 Molal

Salt	Separation for Membrane No., %							
	7		8		9		11	
	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd
LiCl	83.6	85.9	83.2	87.1	83.2	87.6	86.6	89.2
LiBr	84.4	84.1	87.3	85.3	85.6	85.9	87.6	87.6
NaCl[a]	70.2	70.2	72.2	72.2	72.9	72.9	75.6	75.6
NaBr	71.6	67.7	75.5	70.0	73.8	70.7	76.5	73.9
KI	56.7	53.1	61.0	55.6	59.8	56.3	61.0	59.9
RbCl	59.4	57.5	62.5	59.8	62.5	60.2	65.6	64.1
CsCl	58.1	55.3	60.0	57.7	60.0	58.5	63.8	62.2
CsBr	39.6	52.3	52.1	54.8	54.2	55.5	54.2	59.0

[a] $\ln C^*_{NaCl}$ for these membranes was determined by this experiment.

Table 3-18 (cont'd)

Salt	Separation for Membrane No., %											
	1		2		3		4		5		6	
	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd
$MgCl_2$	99.6	99.5	99.4	99.3	99.5	99.6	99.6	99.5	99.6	99.5	99.5	99.6
$CaCl_2$	99.6	99.1	98.7	98.8	97.9	98.8	99.4	99.2	99.1	99.2	99.1	99.3
$SrCl_2$	99.6	99.3	99.0	99.1	99.1	99.1	99.3	99.4	99.6	99.4	99.4	99.5
$BaCl_2$	99.6	99.3	99.1	99.1	98.7	99.1	99.4	99.4	99.4	99.4	99.5	99.5
NH_4Cl	76.9	75.5	70.6	70.5	67.0	69.7	78.3	78.5	77.4	77.0	80.1	79.7
$LiNO_3$	86.3	87.0	81.6	83.7	80.0	83.2	86.3	88.8	88.3	87.8	88.3	89.5
$Sr(NO_3)_2$	96.8	95.2	91.1	93.8	89.4	93.6	93.4	95.9	94.8	95.5	95.2	96.2
$NaNO_2$	82.4	83.9	82.4	80.1	81.7	79.5	86.3	86.1	83.2	84.9	87.0	86.9
$NaNO_3$	76.7	73.7	71.4	68.4	71.4	67.6	78.8	76.9	77.8	75.2	78.8	78.1
$NaClO_3$	61.1	59.8	73.5	53.4	51.6	52.6	27.0	63.8	71.6	61.7	82.0	65.4
$NaClO_4$	75.9	79.5	72.2	74.9	75.9	74.3	81.5	82.1	83.3	80.7	85.2	83.1
$NaBrO_3$	68.7	73.4	74.2	68.7	66.8	68.0	78.8	77.1	54.8	75.5	76.0	78.3

Table 3-19

Comparison of Experimental and Calculated Reverse Osmosis Separations for Dilute Salt Solutions in Ethanol at 1725 kPag and 0.001 Molal

Salt	Separations for Reverse Osmosis Separations for Membrane No., %											
	1		2		3		4		5		6	
	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd
LiCl	90.2	91.9	91.5	90.6	96.5	93.7	97.3	94.1	94.2	92.6	96.1	94.6
LiBr	82.6	90.6	89.1	89.0	93.9	92.6	96.8	93.0	90.1	91.4	94.3	93.6
NaCl	82.7	82.2	79.1	79.7	85.3	85.7	87.3	86.4	81.4	83.6	87.3	87.4
NaBr	67.4	79.7	78.2	77.1	72.6	83.7	85.2	84.4	83.5	81.3	82.6	85.5
NaI	79.5	76.7	76.9	73.9	82.6	81.1	83.1	82.0	70.3	78.5	83.1	83.1
KF	88.4	87.2	87.2	85.7	88.3	89.9	92.5	90.4	87.8	88.3	89.5	91.1
KCl	74.1	69.8	75.0	66.6	77.1	75.2	79.4	76.1	76.5	72.0	81.5	77.6
KBr	71.1	66.0	71.6	62.8	72.1	71.9	77.4	72.9	73.2	68.4	77.9	74.4
KI	67.7	62.3	67.2	59.0	70.1	68.5	70.9	69.5	66.9	64.8	74.1	71.1
RbBr	63.6	61.2	58.7	57.9	65.3	67.5	68.6	68.6	63.6	63.8	70.2	70.2
RbI	60.7	57.0	55.4	53.8	60.7	63.6	62.5	64.7	57.1	59.8	66.1	66.4
CsCl	59.4	58.9	51.7	55.6	64.7	65.4	60.3	66.4	61.2	61.6	61.2	68.1
CsBr	59.8	54.7	62.3	51.4	64.8	61.4	62.3	62.5	62.3	57.5	68.8	64.3
CsI	51.2	50.6	48.8	47.4	52.1	57.5	50.4	58.6	51.2	53.5	54.5	60.4
$CaCl_2$	92.2	95.6	91.3	94.7	98.5	96.5	98.7	96.8	96.7	95.9	97.2	97.1
$SrCl_2$	93.9	95.6	92.8	94.8	97.4	96.6	97.9	96.8	96.2	96.0	97.5	97.1
$NaNO_2$	73.6	71.8	67.3	68.6	74.0	76.9	74.0	77.9	70.8	73.8	78.1	79.3
$NaClO_3$	67.1	59.2	52.6	55.6	64.8	65.5	70.6	66.7	53.4	61.7	67.5	68.5
$NaClO_4$	40.0	56.7	60.5	53.2	65.8	63.3	58.2	64.4	53.7	59.4	68.2	66.2
NH_4Cl	91.2	91.5	86.2	90.2	92.8	93.3	94.5	93.7	90.1	92.2	96.7	94.2

Prediction of Reverse Osmosis Performance for Incompletely Dissociated Salt Solutions. Several reverse osmosis experiments were performed in methanol solutions at concentrations where the salts were not completely dissociated. Osmotic pressure effects were significant which precluded the use of eq 3-51 to calculate the solute separation. The calculation procedure consisted of the simultaneous solution of eqs 3-1, -2, -5, -6, and -21 along with the membrane porosities of Table 3-11 and $(-\Delta\Delta G/RT)_i$ values from Tables 3-10 and 3-17. Comparison of the experimental and calculated results are shown in Table 3-20 for 1725 kPag operating pressure and Table 3-21 for 3450 kPag operating pressure.

Table 3-20

Comparison of Experimental and Calculated Reverse Osmosis Performance with Incompletely Dissociated Salt-Methanol Solutions at 1725 kPag

Salt[a]	Measured	Membrane No.							
		7		8		9		11	
		exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd
LiCl 0.1444	(PR), g/h	5.65	5.52	4.08	4.06	3.22	3.22	3.20	3.24
	f, %	81.7	81.3	84.8	83.1	83.6	83.5	85.0	85.3
	α[b]		1.0		1.0		1.0		1.0
LiBr 0.1498	(PR), g/h	5.75	5.50	4.17	4.05	3.30	3.21	3.31	3.22
	f, %	78.0	79.2	81.7	81.2	80.5	81.6	82.2	83.5
	α		1.0		1.0		1.0		1.0
NaCl 0.1587	(PR), g/h	6.32	5.90	4.61	4.31	3.65	3.41	3.60	3.40
	f, %	60.5	60.6	65.8	63.6	63.9	64.1	65.5	67.3
	α		0.74		0.74		0.74		0.74
NaBr 0.1530	(PR), g/h	6.04	5.90	4.37	4.22	3.47	3.33	3.47	3.32
	f, %	59.6	59.0	63.9	61.9	62.5	62.3	64.9	65.5
	α		0.80		0.80		0.80		0.80
KI 0.1524	(PR), g/h	5.94	6.89	4.39	5.02	3.43	3.95	3.48	3.95
	f, %	32.3	30.4	36.1	33.0	34.9	33.5	38.1	36.7
	α		0.865		0.865		0.865		0.865
CsCl 0.07222	(PR), g/h	6.87	6.90	4.99	5.03	3.94	3.95	3.97	3.98
	f, %	35.1	36.1	41.7	39.2	41.7	40.7	43.0	43.4
	α		0.83		0.83		0.83		0.83

[a] molal concentration.
[b] degree of ionic dissociation.

Table 3-21

Comparison of Experimental and Calculated Reverse Osmosis Performance With Incompletely Dissociated Salt-Methanol Solutions at 3450 kPag

Salt[a]	Measured	Membrane No.									
		7		8		9		11		12	
		exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd
LiCl 0.4586	(PR), g/h	9.17	7.61	6.71	5.64	5.38	4.57	5.51	4.73	4.54	3.95
	f, %	80.1	81.6	83.5	85.2	82.0	83.9	83.9	85.4	74.8	79.2
	α[b]		1.0		1.0		1.0		1.0		1.0
LiCl 0.4930	(PR), g/h	8.25	7.34	6.10	5.40	4.86	4.40	5.05	4.49	4.16	3.85
	f, %	79.0	79.6	82.8	83.8	81.5	81.9	83.5	83.2	73.7	76.6
	α		1.0		1.0		1.0		1.0		1.0
LiBr 0.4093	(PR), g/h	9.88	8.49	7.29	6.30	5.79	5.01	5.99	5.24	4.84	3.78
	f, %	76.8	80.2	81.4	84.1	80.0	83.6	81.6	84.6	72.9	88.7
	α		1.0		1.0		1.0		1.0		1.0
LiBr 0.2617	(PR), g/h	11.10	10.20	8.21	7.59	6.53	6.07	6.71	6.27	5.47	5.11
	f, %	82.1	81.6	85.6	85.3	84.0	84.2	86.1	85.3	77.1	79.0
	α		1.0		1.0		1.0		1.0		1.0
NaBr 0.3853	(PR), g/h	11.48	12.12	8.50	8.65	6.73	7.04	6.91	7.18	5.42	6.10
	f, %	55.4	55.1	61.6	61.5	60.0	59.1	61.7	62.1	51.5	51.7
	α		0.73		0.73		0.73		0.73		0.73
NaBr 0.2686	(PR), g/h	11.04	10.90	8.15	7.95	6.45	6.17	6.72	6.51	5.34	5.51
	f, %	58.3	55.2	67.6	61.3	66.1	59.0	68.4	61.9	57.1	51.7
	α		0.75		0.75		0.75		0.75		0.75

[a] molal concentration

[b] degree of ionic dissociation.

Discussion.

A requirement for the validity of the Kimura-Sourirajan analysis is the assumption that the surface porosity of the membranes does not change. A change in membrane porosity would be perceived as a variation of $\ln C^*_{ref}$ for various solutes. A demonstration of the validity of this assumption is the comparison of $\ln C^*_A$ for the alkali metal halides as calculated with eq 3-15 and experimental $(D_{AM}/K\delta)$ data (Matsuura et al., 1975). It should be noted that for these salts, their values of $(-\Delta\Delta G/RT)$ were determined by the modified Born equation while for other salts, values of $(-\Delta\Delta G/RT)$ were calculated using $\ln C^*_{ref}$ and eq 3-15 with experimental data for $(D_{AM}/K\delta)$. The comparison of $\ln C^*_A$'s is shown in Table 3-22 for the methanol case and Table 3-23 for the ethanol case. Despite the scatter of these values, they demonstrate the relative constancy of the membrane's surface porosities with regard to salt.

Based upon the work of Matsuura et al. (1981b), a method of comparing $\Delta(-\Delta\Delta G/RT)_i$ with the ionic Jones-Dole viscosity "B_i" terms for water and methanol solutions was developed (Farnand et al., 1981). The difficulty of determining the viscosity B_i terms of ethanol-salt solutions because of solubility limits precluded the extension of this correlation. For this reason, the approach of Farnand et al. was modified to use physicochemical parameters available in

Table 3-22

Comparison of $\ln C_A^*$'s for Methanol Solutions and Cellulose Acetate Membranes at 1725 kPag and 0.005 Molal

Salt	Membrane Number					
	1	2	3	4	5	6
LiCl	-10.86	-12.33	-12.77	-11.37	-10.95	-13.13
LiBr	-10.86	-12.53	-12.90	-11.41	-10.97	-13.39
NaCl	-10.80	-12.54	--	-11.31	-10.84	--
NaCl	-10.76	-12.63	-12.98	-11.37	-10.96	-13.47
NaCl	-10.82	-12.58	-12.93	-11.35	-10.93	-13.31
NaBr	-10.63	-12.31	-12.58	-11.13	-10.73	-12.95
NaI	-10.82	-12.64	-12.99	-11.33	-10.93	-13.51
KF	-10.63	-12.37	-12.75	-11.23	-10.75	-13.16
KCl	-10.64	-12.53	-12.85	-11.15	-10.75	-13.29
KBr	-10.66	-12.54	-12.87	-11.17	-10.76	-13.26
KI	-10.81	-12.66	-12.96	-11.25	-10.83	-13.15
KI	-10.72	-12.59	-12.96	-11.23	-10.86	-13.33
RbCl	-10.73	-12.69	-12.99	-11.26	-11.26	-13.64
CsCl	-10.74	-12.73	-12.95	-11.23	-10.89	-13.43
CsBr	-10.78	-12.71	-12.92	-11.28	-10.85	-13.39

Table 3-23

Calculation of $\ln C_A^*$'s for Ethanol Solutions and Cellulose Acetate Membranes at 1725 kPag and 0.001 Molal

Salt	Membrane Number					
	1	2	3	4	5	6
LiCl	-8.99	-8.83	-9.07	-9.38	-9.06	-9.88
LiCl	-8.94	-8.69	-9.51	-9.80	-8.99	-9.83
LiCl	-9.55	-8.93	-9.39	-9.54	-9.45	-10.03
LiCl	-8.96	-8.62	-9.54	-8.64	-9.08	-9.31
LiCl	-9.48	-8.94	-9.40	-9.69	-9.34	-9.95
LiBr	-8.95	-8.82	-9.58	-10.43	-9.11	-9.96
NaCl	-9.29	-8.77	-9.33	-9.69	-9.03	-9.82
NaBr	-8.63	-8.88	-8.72	-9.68	-9.34	-9.62
NaI	-9.42	-8.96	-9.46	-9.69	-8.75	-9.83
KF	-9.40	-8.97	-9.22	-9.89	-9.14	-9.66
KCl	-9.48	-9.22	-9.49	-9.76	-9.43	-10.08
KBr	-9.50	-11.52	-9.25	-9.86	-9.42	-10.03
KI	-9.50	-9.17	-9.45	-9.68	-9.28	-7.69
RbBr	-9.37	-8.86	-9.29	-9.63	-9.19	-9.85
RbI	-9.42	-8.88	-9.25	-9.51	-9.08	-9.86
CsCl	-9.38	-8.75	-9.44	-9.44	-9.26	-9.62
CsBr	-9.47	-9.26	-9.52	-9.61	-9.39	-10.04
CsI	-9.29	-8.87	-9.16	-9.29	-9.10	-9.60

in the literature. This was done by first considering the Jones-Dole equation for a salt (Gurney, 1953; Robinson and Stokes, 1965e; Podolsky, 1958)

$$\eta/\eta_0 = 1 + A_1 \sqrt{c_A} + B_1 c_A \qquad (3\text{-}48)$$

where A_1 is an electrostatic contribution and B_1 is considered to be a salt-solvent interaction term. Gurney (1953) and Podolsky (1958) developed a scheme to relate the ionic contributions as

$$B_1 = (B_i)_{\text{cation}} + (B_i)_{\text{anion}} \qquad (3\text{-}49)$$

where they assumed the K^+ and Cl^- contributions were related as

$$\frac{(B_i)_{K^+}}{(B_i)_{Cl^-}} = \frac{(v_E)_{K^+}}{(v_E)_{Cl^-}} = \frac{(r_E)^3_{K^+}}{(r_E)^3_{Cl^-}} \doteq \frac{(\lambda_0)^{-3}_{K^+}}{(\lambda_0)^{-3}_{Cl^-}} \qquad (3\text{-}50)$$

where r_E and v_E are the solvated ion's size and volume as used in Einstein's viscosity relation

$$\eta/\eta_0 = 1 + 2.5\, v_E \qquad (3\text{-}51)$$

Gurney and Podolsky related the terms of eq 3-50 by arguing that B_i is an ionic mobility term, and that it was related to the solvated ion's size because of the mobility of the solvation sphere. On this basis, they invoked the Nernst relation

$$r_{A,i} \propto (\lambda_0)_i^{-1} \qquad (3\text{-}52)$$

to relate the ionic conductivity to B_i. The limiting ionic conductivity was used because of the dilute solutions considered, and the inverse of $(\lambda_0)_i$ is often referred to as ionic mobility.

Limiting ionic conductivities in different solvents have been related by the Walden rule

$$\lambda_0 \eta_0 = \text{constant} \qquad (3\text{-}53)$$

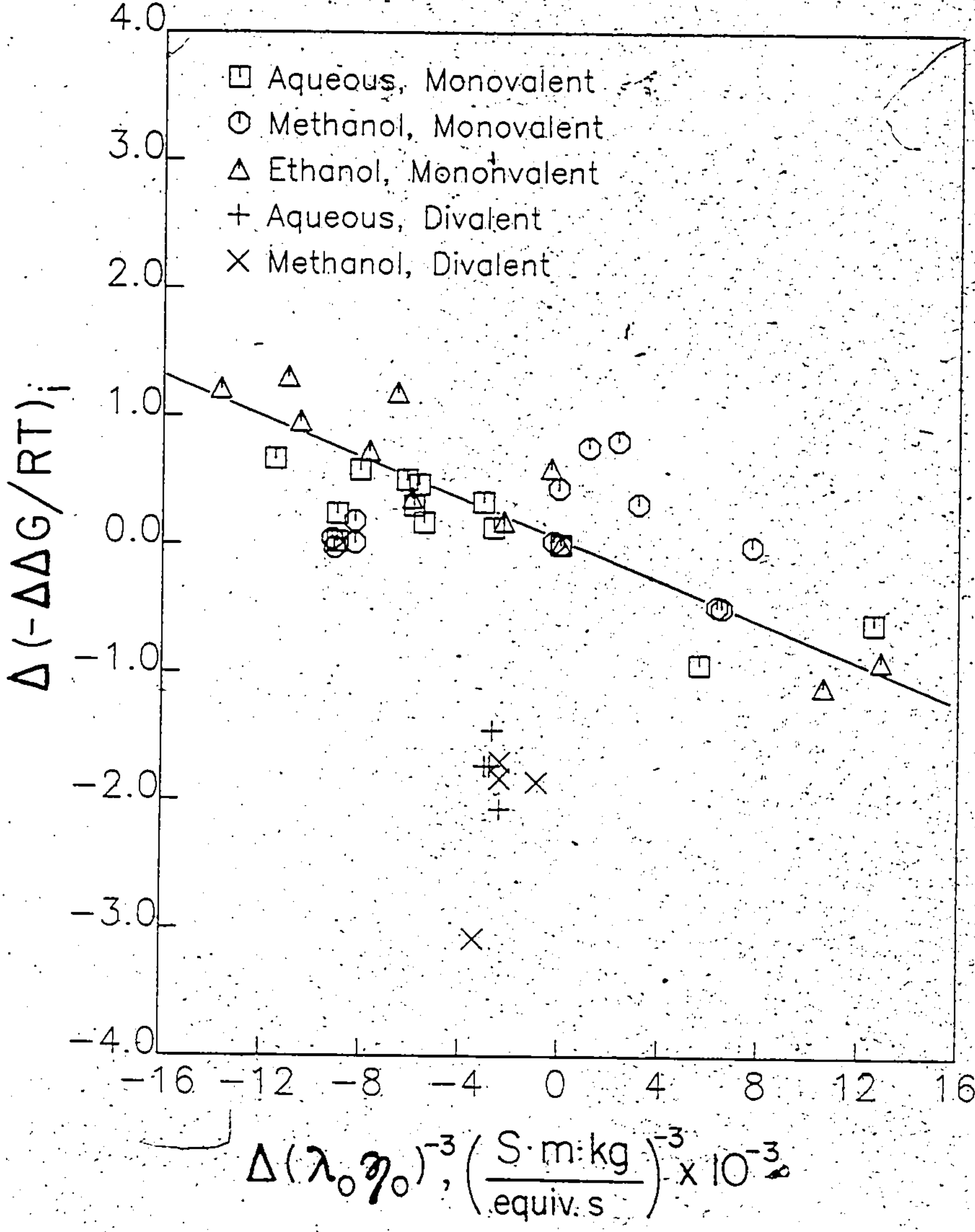
To account for the solvent's mobility, as well as incorporating the well studied limiting ionic conductance, and its relation to ionic mobility, the B_i term as used by Farnand et al. (1981) was replaced by

$$\Delta(\lambda_0\eta_0)_i^{-3} = (\lambda_0\eta_0)_i^{-3} - (\lambda_0\eta_0)_{Na^+ \text{ or } Cl^-}^{-3} \qquad (3\text{-}54)$$

where Na^+ is used as the reference for the cations and Cl^- is used as the reference for the anions. This correlation is shown in Fig 3-7, and it can be used as a guide for determining $(-\Delta\Delta G/RT)_i$ for cases where the conductivity of the ion and the viscosity of the solvent is known.

Figure 3-7

Variation of $\Delta(-\Delta\Delta G/RT)_i$ for Both Anions and Cations, in Aqueous, Methanol, and Ethanol Solutions, and Cellulose Acetate Membranes With Modified Walden Product


Aqueous, Monovalent
Methanol, Monovalent
Ethanol, Mononvalent
Aqueous, Divalent
Methanol, Divalent
4.0
3.0
2.0
1.0
0.0
−1.0
−2.0
−3.0
−4.0
−16
−12
−8
−4
0
4
8
12
16
Δ(−ΔΔG/RT)i
Δ(λ0η0)−3, (S·m·kg / equiv. s)−3 x 10−3

For the cases of the alkali metal cations in Fig 3-5, there is a greater difference of $\Delta(-\Delta\Delta G/RT)_i$ with respect to the reference ion (Na^+) in the order of ethanol > methanol > water. This appears to be related to the Born equation (eq 3-8) when the dielectric constant of these three solvents is considered. The dielectric constant varies as ethanol(25.8) < methanol (31.2) < water(81.1), which would cause a decrease of ΔG_B values and increase the relative importance of ΔG_I, all other factors being equal. This suggests that the selectivity of a given membrane in terms of different separations of different ions will increase as the dielectric constant of the solvent decreases. A similar effect is observed for the other groups of ions, although the conclusions for the alkali earth cations are complicated by their low degrees of dissociation. This same effect is predicted by the model described by Glueckauf (1965) where the work to move an ion from solution to the liquid in the membrane's pores was inversely proportional to their differences in dielectric constant.

In order to demonstrate the adequacy of the Kimura-Sourirajan analysis, the residuals of the experimental and calculated reverse osmosis separations ($f_{exptl} - f_{calcd}$) were plotted with the calculated separation for the methanol solutions in Fig 3-8 and for the ethanol solutions in Fig 3-9. As well, the residuals have been plotted with $\sum_i(-\Delta\Delta G/RT)_i$ for the salts in Fig 3-10 for the methanol solutions and Fig 3-11 for the ethanol solutions. The random nature of these residuals is a demonstration of the unbiased nature of the Kimura-Sourirajan model.

Figure 3-8

Residuals for Separation Plotted with Calculated Separation for Salt in Methanol Solutions

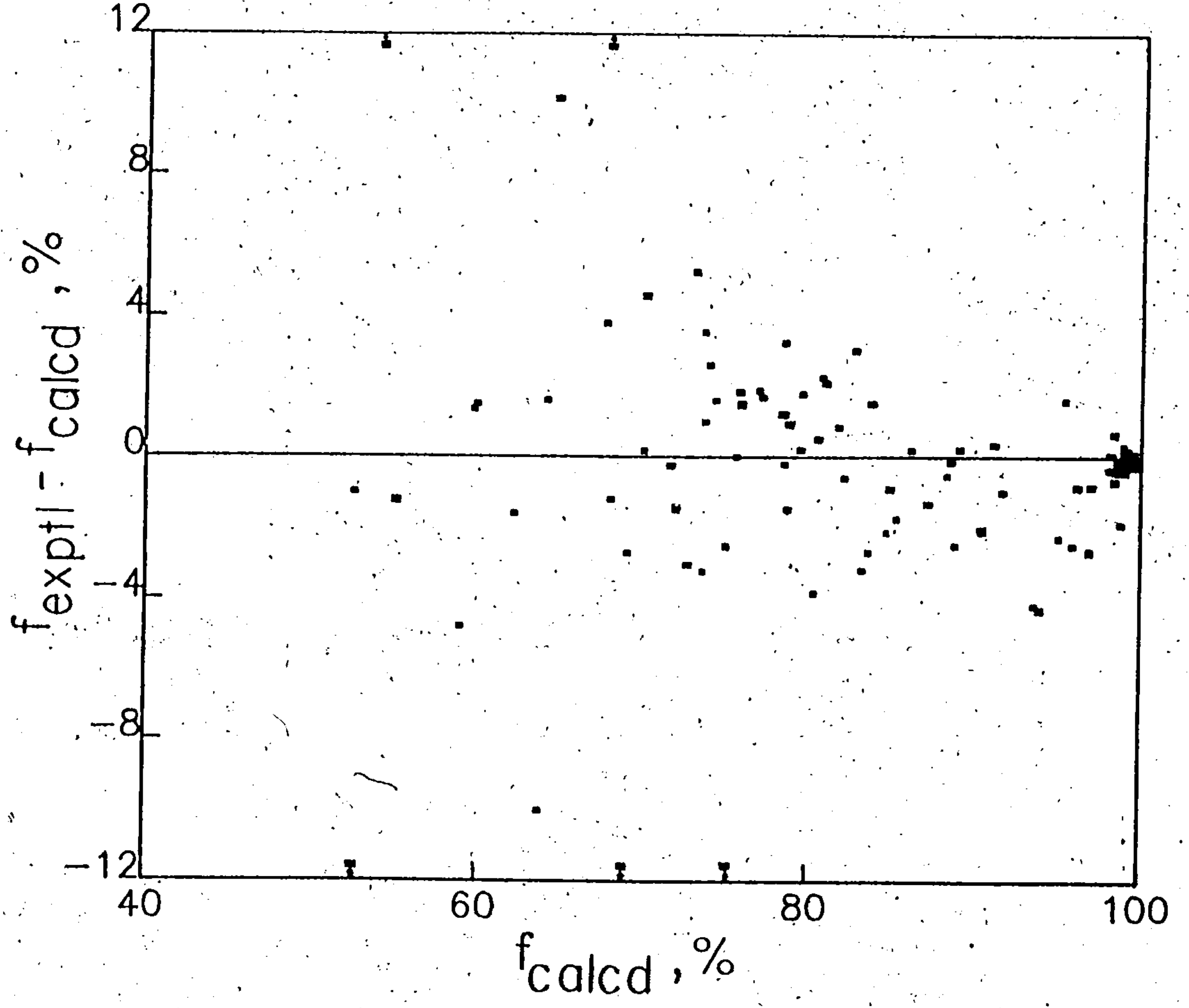

12
8
4
0
−4
−8
−12
40
60
80
100
$f_{exptl} - f_{calcd}$, %
f_{calcd} , %

Figure 3-9

Residuals for Separation plotted with Calculated Separation for Salt in Ethanol Solutions

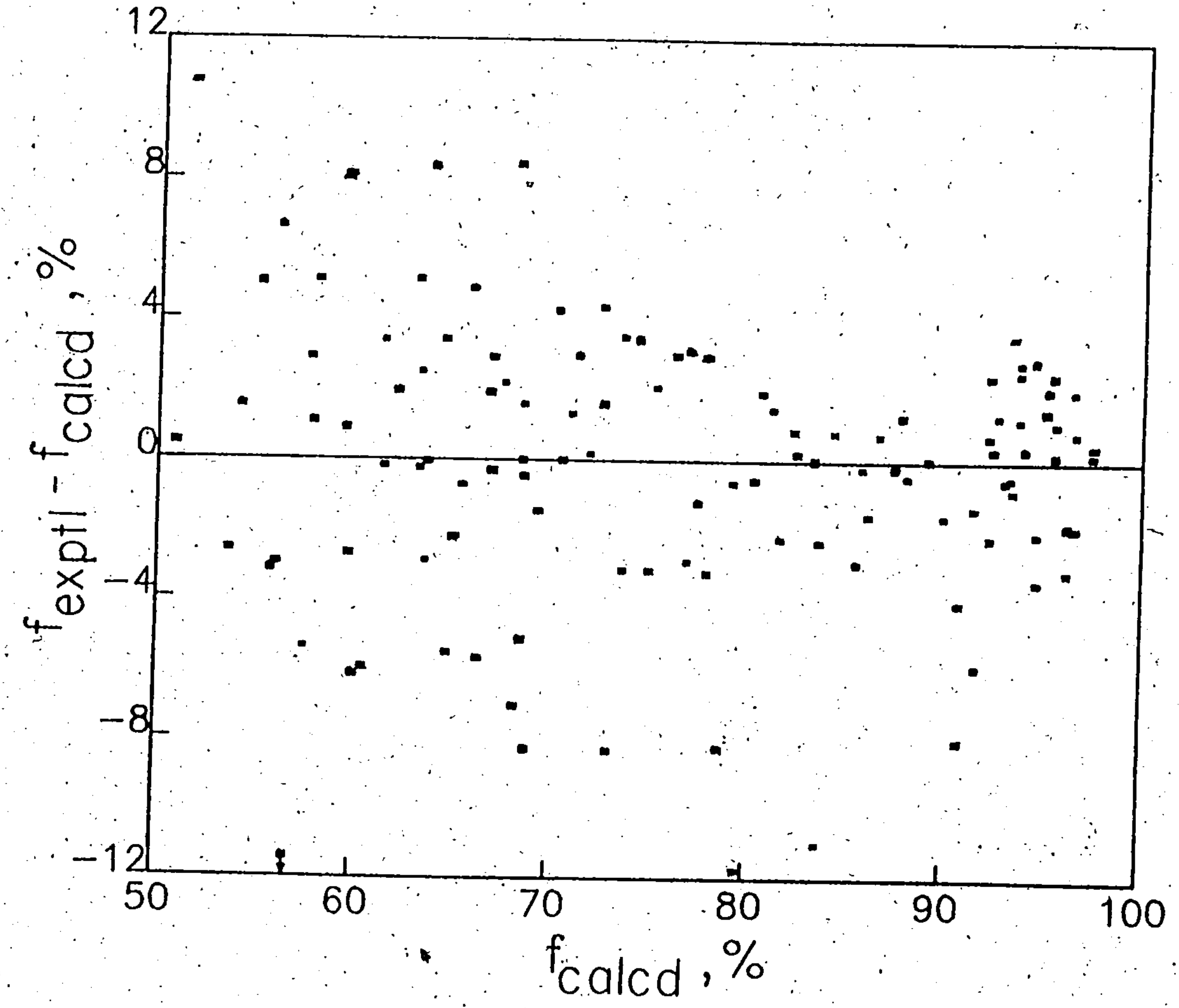
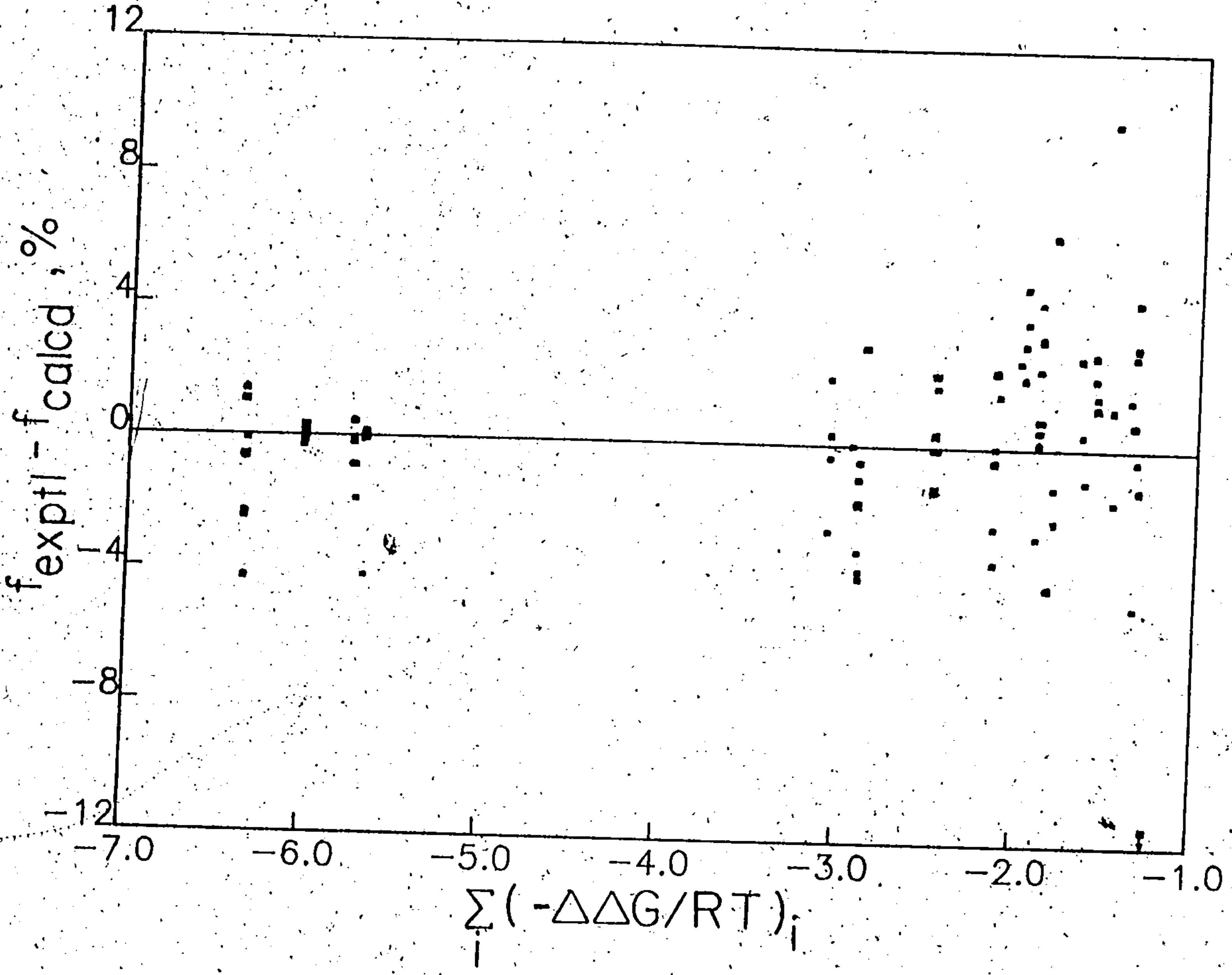

12
8
4
0
−4
−8
−12
50
60
70
80
90
100
$f_{expt1} - f_{calcd}$, %
f_{calcd} , %

Figure 3-10

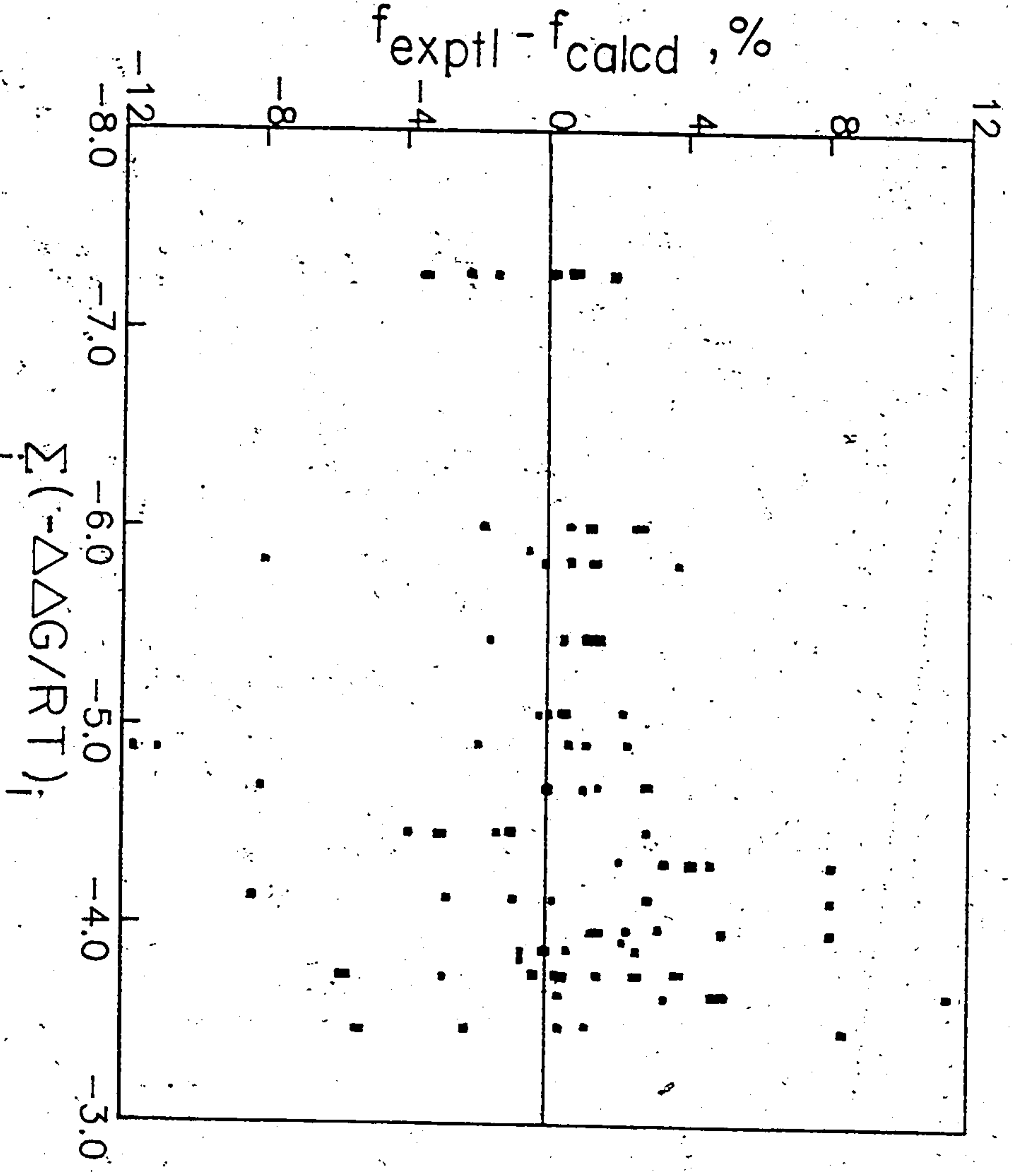
Residuals for Separation Plotted with Free Energy Parameters for the Salts in Methanol Solutions



$f_{exptl} - f_{calcd}$, %
12
8
4
0
-4
-8
-12
-7.0
-6.0
-5.0
-4.0
-3.0
-2.0
-1.0
$\sum_i(-\Delta\Delta G/RT)_i$

Figure 3-11

Residuals for Separation Plotted with Free Energy Parameters for the Salts in Ethanol Solutions



$f_{exptl} - f_{calcd}$, %
−12
−8
−4
0
4
8
12
−8.0
−7.0
−6.0
−5.0
−4.0
−3.0
$\sum_i (-\Delta\Delta G/RT)_i$

Another means of testing the adequacy of a model is to apply a significance test for the comparison of the inadequacy of the model with the experimental error. The experimental error is estimated by using replicated experiments (Draper and Smith, 1966a)

$$s_p{}^2 = \frac{1}{m_i - 1} \sum_i (f_i - \bar{f})^2 \qquad (3\text{-}55)$$

where s_p is the estimated pure error variance, m_i is the number of replicated experiments, $\bar{f}$ is the mean of all the replicates, and f_i is the individual experimental separation. This estimate of pure error variance was calculated for each membrane, and the weighted mean of these were used as an overall estimate of the pure error variance. The model's inadequacy was determined as (Draper and Smith, 1966b)

$$\frac{SSR}{n - p} \qquad (3\text{-}56)$$

where SSR is the sum of the squares of the residuals, n is the number of residuals, and p is the number of parameters in the model. Since an external estimate of s_p was used for this work, eq 3-56 was simply divided by s_p^2 to give

$$\left(\frac{SSR}{n - p}\right) / s_p{}^2 \qquad (3\text{-}57)$$

The test then compares this ratio with the $F_{(n-p),\ \gamma_p}$ distribution where γ_p is the number of degrees of freedom associated with the pure error variance. A successful test for the lack of fit would have the ratio of eq 3-57 less than the corresponding F-distribution.

It should be noted that the above test was developed for linear models and does not apply to the nonlinear case of the Kimura-Sourirajan model. However, Draper and Smith (1966c) maintain that the test does provide a measure of comparison, and as such serves as an qualitative indication of nonlinear model adequacy.

The case of the methanol solutions is now considered. The pure error variance is estimated with the data for run numbers 513 and 527 for NaCl in Table A-1-6. The value of s_p^2 calculated was 1.48 with γ_p as 6. For the alkali metal halides only, in Table 3-18, SSR is 225.8. The number of parameters in the model was taken as 5(C^*_{NaCl}, E^+_I, E^-_I, Δ^+_I, Δ^-_I). Thus eq 3-57 was calculated as

$$\left(\frac{SSR}{n - p}\right)/s_p^2 = \frac{225.8}{(31-5)}/1.48 = 5.86$$

This is compared with $F_{(31-5),6,.01}$ which is estimated as 7.27 (Beyer, 1966).

For the balance of the salts in methanol solutions, the model consisted of 3 parameters (C^*_{NaCl}, $(-\Delta\Delta G/RT)_i$ for both the cations and the anions). The value of SSR was calculated as 233.9 with 67 residuals. Equation 3-57 was then calculated as

$$\left(\frac{233.9}{67-3}\right)/1.48 = 2.47$$

and $F_{64,6,.01}$ was estimated as 7.04.

For the ethanol solutions, the same equations were used. The replicates were taken from run numbers 5, 9, and 27 of Table A-1-7 and the pure error variance was estimated as 4.08 with γ_p as 12. For the alkali metal halides in Table 3-19, SSR was calculated as 1048.3 from 103 residuals, and the number of parameters was 5. Equation 3-57 was calculated as

$$\frac{1048.3}{103-5}/4.08 = 2.62$$

and $F_{98,12,.01}$ was estimated as 3.47.

For the balance of the salts in Table 3-19, the SSR was 425 for 35 residuals and 3 model parameters. Equation 3-57 gives

$$\left(\frac{425}{35-3}\right)/4.08 = 3.25$$

and $F_{32,12,.01}$ was estimated as 3.68.

Despite the limited applicability of the F-test to the nonlinear Kimura-Sourirajan model, it is considered that its success in this evaluation is an indication of its adequacy.

A further evaluation of the data by the Kimura-Sourirajan model based upon predicting separation directly was made. Instead of using experimental $(D_{AM}/K\delta)$ values as the response variable for regression purposes, a scheme using eq 3-47 where $(D_{AM}/K\delta)$ was replaced by eq 3-14 and eq 3-15 was studied. As well, relevant reverse osmosis data for all the membranes concerned were pooled together as opposed to separate regressions for each membrane. For this calculation, a package computer program of the Statistical Analysis System (SAS) Institute (1982) based upon a derivative-free nonlinear regression with a multivariate secant method was used (NLIN DUD). This was applied to both the methanol and ethanol cases as shown in Table 3-24 for the alkali metal and halide ions. As well as these parameters, their approximate standard deviations were determined as shown in Table 3-24. These are approximate because of the extension of linear model theories to the nonlinear model considered in this work. The values reported in Table 3-24 are similar to those previously reported in Table 3-9 and lie well within the 95% confidence range.

As part of the same computation, ln C^* was calculated directly for each membrane and these were compared with the previously calculated ln C^*_{ref}'s in Table 3-25. It should be noted that the difference between the two sets of ln C^*'s is caused by the difference of the free energy parameters. Because of a lack of a standard reference for the surface excess free energy for the ions, the previously calculated and the recalculated values of ln C^* cannot be directly compared in terms of their absolute values since this only reflects its definition as a proportionality constant. However, the influence of membrane porosity can be seen in the similar variation of ln C^* in the two sets.

Table 3-24

Recalculated Interfacial Born Equation Parameters for Alkali Metal Halides with Cellulose Acetate Membranes

Ion	Solution	E_I^- kJm/mol $\times 10^{10}$	Approximate Standard Error kJm/mol $\times 10^{10}$	Δ_I^- m $\times 10^{10}$	Approximate Standard Error m $\times 10^{10}$
Alkali Metal Cations	Ethanol[a]	539.6	7.9	0.644	0.014
	Methanol[b]	673.2	16.3	0.794	0.043
Halides	Ethanol[a]	513.2	12.3	−0.107	0.020
	Methanol[b]	478.7	36.8	−0.163	0.079

[a] 90 data points.

[b] 78 data points.

Table 3-25

Comparison of ln C^*_{NaCl} and ln C^*_{LiCl} with Recalculated ln C^*

Membrane No.	Methanol		Ethanol	
	ln C^*_{NaCl}	ln C^* recalcd	ln C^*_{LiCl}	ln C^* recalcd
1	-10.78	-7.56	-9.26	-8.84
2	-12.58	-9.20	-8.81	-8.74
3	-12.94	-9.53	-9.38	-8.98
4	-11.25	-8.98	-9.62	-9.17
5	-10.94	-7.59	-9.19	-8.91
6	-13.43	-9.85	-9.84	-9.31

Conclusion.

For both the methanol and ethanol experiments, it can be seen that significant salt separations can be obtained by the use of reverse osmosis. As well, the reverse osmosis performance was successfully predicted in both alcohol cases, which demonstrates the validity of the Kimura-Sourirajan analysis. The relation of free energy parameters for the different solutions can be seen in Fig 3-7 where a mobility term was chosen as the common parameter. The importance of the membrane-solute interactions in reverse osmosis is demonstrated by the relative similarity of the free energy parameters in the various solvents. Further, it should be noted that the model was successful for completely and incompletely dissociated salts, at several concentrations and operating pressures, and for cellulose acetate membranes of varied porosity (although limited).

These results show that reverse osmosis is not limited to the aqueous case, but can be considered in other solvents. Also, the use of the Kimura-Sourirajan analysis is not limited by solvent and can successfully describe reverse osmosis performance in other solvents.

Chapter 4

Interfacial Surface Force Parameters for the Reverse Osmosis Separation of Inorganic and Organic Solutes from Methanol and Ethanol Solutions with Cellulose Acetate Membranes

Introduction

For the case of organic solutes in aqueous solutions, there is a preferential adsorption of certain organic solutes on to the surface of the membrane (Matsuura and Sourirajan, 1981). One of the requirements of the Kimura-Sourirajan analysis is preferential adsorption of the solvent, which limits its application to such systems. For this reason, the surface potential-pore flow model was developed (Matsuura and Sourirajan, 1981) and because of its ability to account for preferential adsorption of solutes and the prediction of negative separations as well as preferential adsorption of the solvent, it was considered for the analysis of the alcohol systems studied in this work. Both inorganic and organic solutes in alcohol solutions were used in reverse osmosis experiments with cellulose acetate membranes. These experimental results were analyzed using the surface potential-pore flow model to determine the surface potential parameters for the solutes, as well as the average pore sizes of the membranes. These data were then used to predict reverse osmosis performance for the various solutes studied in this work.

As with the Kimura-Sourirajan analysis, the successful application of the surface potential-pore flow model for the nonaqueous cases will be a further demonstration of the validity of the preferential adsorption and pore flow concept of reverse osmosis. As well, the success of this model in the alcohol solutions will make it a candidate for the analysis of reverse osmosis performance in other nonaqueous systems.

Surface Interaction Potentials. As an ion approaches an uncharged dielectric discontinuity, it is repelled from the surface as if there was an identically charged "image" ion on the opposite side of the interface. The potential energy of this interaction is described as (Israelachvili and Tabor, 1973)

$$\phi = \frac{\underset{\sim}{A}_i}{x} \underset{\sim}{R} T \qquad (4\text{-}1)$$

where $\underset{\sim}{A}_i$ consists of terms describing the dielectric constant of the two media and the ion charge. In order to account for steric hindrance, it was assumed that the ion behaves as a hard sphere with an infinitely strong repulsion from the polymer surface at the limiting approach distance $\underset{\sim}{D}$. Equation 4-1 was also modified to combine the ions' contribution to $\underset{\sim}{A}$ for the salt (Matsuura and Sourirajan, 1981)

$$\phi = \begin{cases} \infty & ; \; x < \underset{\sim}{D} \\ \dfrac{\underset{\sim}{A}\,\underset{\sim}{R}T}{x} & ; \; x > \underset{\sim}{D} \end{cases} \qquad (4\text{-}2)$$

where x is considered to be the surface to sphere-center distance.

Israelachvili and Tabor (1973) also described the interaction of an organic molecule with an infinite planar surface by modifying Sutherland's intermolecular interaction potential. They also assumed that the organic molecule behaved as a hard sphere, so that the potential took the form

$$\phi = \begin{cases} \infty & ; x \leq \underset{\sim}{D} \\ \dfrac{-\underset{\sim}{B}\, \underset{\sim}{R}T}{x^3} & ; x > \underset{\sim}{D} \end{cases} \qquad (4\text{-}3)$$

where $\underset{\sim}{D}$ represents the hard sphere version of steric hindrance and $\underset{\sim}{B}$ represents the induction forces between the molecule and the solid surface. Both eq 4-2 and 4-3 can be applied to the solution-membrane interactions present in reverse osmosis (Matsuura and Sourirajan, 1981).

Surface Excess Concentration and Liquid Chromatography. The concentration gradient from a surface to the bulk of the solution was assumed to be described in terms of surface potentials by the Maxwell-Boltzmann distribution law (Matsuura and Sourirajan, 1981)

$$c_A(x) = c_{A,bulk} \cdot \exp\left(-\phi(x)/\underset{\sim}{R}T\right) \tag{4-4}$$

where c_A is the solute concentration.

Surface excess concentration is defined as

$$\Gamma_A = \int_0^\infty \left(c_A(x) - c_{A,bulk}\right)d(x) \tag{4-5}$$

With eq 4-4 and with the hard sphere assumption ($\phi = \infty$, $x < \underset{\sim}{D}$) it becomes

$$\Gamma_A = \int_0^{\underset{\sim}{D}} \left(0-c_{A,bulk}\right)d(x) + \int_{\underset{\sim}{D}}^\infty \left[c_{A,bulk}\exp(-\phi/\underset{\sim}{R}T)-c_{A,bulk}\right]d(x) \tag{4-6}$$

The solvent is also assumed to behave as a hard sphere with the limiting distance of $\underset{\sim}{D}_{solvent}$.

When $\underset{\sim}{D}_{solvent}$ is introduced, eq 4-6 becomes

$$\Gamma_A/c_{A,bulk} = \underset{\sim}{D}-\underset{\sim}{D}_{solvent} + \int_{\underset{\sim}{D}}^\infty \left[\exp(-\phi/\underset{\sim}{R}T)-1\right]d(x) \tag{4-7}$$

Thus with eq 4-7, the surface excess concentration can be used to determine the surface potential, ϕ.

Chuduk et al. (1981) and Huber and Gerritse (1971) related the surface excess concentration to chromatography retention volumes by

$$\Gamma_A = \frac{1}{A_p} \int_0^{c_A} \left([V'_R]_A - [V_R']_{solvent} \right) dc_A \qquad (4\text{-}8)$$

where A_p is the surface area of the solid phase in the chromatography experiments and c_A is the solute concentration in the mobile phase. Chuduk et al. (1981) simplified eq 4-8 by demonstrating that Γ_A/c_A was constant at low concentrations so that

$$\frac{\Gamma_A}{c_A} = \frac{[V_R']_A - [V_R']_{solvent}}{A_p} \qquad (4\text{-}9)$$

When eq 4-9 and eq 4-7 are combined, they give a relation for the surface potential and the liquid chromatography results

$$\left(\underset{\sim}{D}-\underset{\sim}{D}_{solvent}\right) + \int_0^{\infty} \left[\exp(-\phi/\underset{\sim}{R}\ T)-1\right] d(x)$$

$$- \frac{[V_R']_A - [V_R']_{solvent}}{A_p} = 0 \qquad (4\text{-}10)$$

where $c_{A,bulk}$ (the bulk solution concentration in reverse osmosis as modified by mass transfer considerations) was assumed equivalent to the c_A (chromatographic mobile phase concentration of eq 4-9.

Transport Equations. In order to describe the flow of liquid in the membrane under the influences of the surface potentials described above, it was assumed that membrane pores are cylindrical in shape with average radius R. For computational convenience a set of dimensionless parameters were developed to describe the conditions of the pore region (Matsuura and Sourirajan, 1981):

$$\rho = r/R \tag{4-11}$$

where r is the radial distance from the center of the pore and ρ is the dimensionless version of r;

$$c_A(\rho) = c_{A_3}(r)/c_{A_2} \tag{4-12}$$

where $c_{A_3}(r)$ is the radial solute concentration at the pore outlet;

$$\alpha(\rho) = \frac{u_B\ (r)\cdot\delta\cdot\chi_{AB}}{\underset{\sim}{RT}} \tag{4-13}$$

where $u_B(r)$ is the radial velocity, δ is the pore length, and χ_{AB} is a solute-solvent interaction term;

$$\beta_1 = \frac{\eta}{\chi_{AB}\ R^2 c_{A_2}} \tag{4-14}$$

where η is the solution viscosity;

$$\beta_2 \fallingdotseq \frac{(P_1 - P_0)}{\underset{\sim}{RT}\ c_{A_2}} \tag{4-15}$$

where P_1 is the hydraulic pressure on top of the pore and P_0 is the hydraulic pressure on the underside of the membrane;

$$\phi(\rho) = \phi(r)/\underset{\sim}{RT} \tag{4-16}$$

where $\phi(r)$ is the radial surface potential.

The radial velocity profile inside a pore is then described by the differential equation (Matsuura and Sourirajan, 1981)

$$\frac{d_2\alpha(\rho)}{d\rho^2} + \frac{1}{\rho}\,\frac{d\alpha(\rho)}{d\rho} + \frac{\beta_2}{\beta_1} + \frac{1}{\beta_1}\left(1-\exp[-\phi(\rho)]\right)\cdot\left(C_A(\rho)-1\right) - \frac{\left(b(\rho)-1\right)\cdot\alpha(\rho)C_A(\rho)}{\beta_1} = 0 \tag{4-17}$$

The boundary conditions for the differential equation are: a) no flow at the pore wall so

$$\alpha(\rho) = 0 \text{ at } \rho = 1 \tag{4-18}$$

and; b) the pore centerline has the maximum flow rate so that

$$\frac{d\alpha(\rho)}{d\rho} = 0 \text{ at } \rho = 0 \tag{4-19}$$

The reverse osmosis separation based on the solute concentration at the boundary is calculated as

$$f' = \frac{c_{A_2} - c_{A_3}}{c_{A_2}} \qquad (4\text{-}20)$$

and in terms of the radial velocity profile

$$f' = 1 - \int_0^1 [\exp(\alpha(\rho))/(1 + \frac{b(\rho)}{\exp(-\Phi(\rho))} \cdot [\exp(\alpha(\rho)-1)]\alpha(\rho)\rho d\rho \, / \int_0^1 \alpha(\rho)\rho \, d\rho \qquad (4\text{-}21)$$

where $b(\rho)$ represents the radial solute friction in the pore. The ratio of pure solvent permeation and product permeation, (PR)/(PSP), can be calculated as the ratio of Poiseuille flow to the radial velocity profile integrated radially over the pore to the Poiseuille flow

$$(PR)/(PSP) = \frac{2\int_0^1 \alpha(\rho)\rho \, d\rho}{-\beta_2/8\beta_1} \qquad (4\text{-}22)$$

In order to correct f' to f, the mass transfer considerations of the Kimura-Sourirajan analysis were used to describe c_{A_2} as a function of c_{A_1}

$$c_{A_2} = c_{A_3} + (c_{A_1} - c_{A_3})\exp\left(\frac{\frac{(PSP)}{3600.S.d}}{k}\right) \qquad (4\text{-}23)$$

Based upon the definition of solute separation f,

$$f = \frac{c_{A_1} - c_{A_3}}{c_{A_1}} \qquad (4\text{-}24)$$

f' and f are related as

$$f = f'/\left[f' + \left\{(1-f')\exp\left(\frac{\frac{(PSP)}{3600.S.d}}{k}\right)\right\}\right] \qquad (4\text{-}25)$$

The solute friction in the pore, b(ρ), is expressed as a function of the molecular radius and pore radius, R, by

$$\lambda = D/R \qquad (4\text{-}26)$$

On the basis of work by Faxen (1959) and Satterfield et al. (1973), Matsuura et al. (1981) described b as

$$1/b = \begin{cases} 1-2.104\lambda + 2.09\lambda^3 - 0.95\lambda^5 & ;\ \lambda \le 0.22 \\ 1/(44.57 - 416.2\lambda + 934.9\lambda^2 + 302.4\lambda^3) & ;\ \lambda > 0.22 \end{cases} \qquad (4\text{-}27)$$

which changes b(ρ) from a radial function to a constant for a given pore size and solute size.

The "hard wall" radius, R_b, of the pore is related to the laminar flow region by

$$R_b = \underset{\sim}{D}_{solvent} + R_a \tag{4-28}$$

While the interaction forces inside the pore act from the hard wall, the laminar flow of solvent in the pore occurs inside the radius R_a. Thus the dimensionless equation for pore radius, eq 4-11, should use R_a for the pore radius, while R_b is used in eq 4-26.

In terms of the dimensionless parameters, the surface potentials of the salts and organic solutes become

$$\phi = \begin{cases} \infty & ; \left(\dfrac{R_b}{R_a} - \rho\right) \le \lambda \\ \left(\dfrac{\underset{\sim}{A}}{R_a}\right) \Big/ \left(\dfrac{R_b}{R_a} - \rho\right) & ; \left(\dfrac{R_b}{R_a} - \rho\right) > \lambda \end{cases} \tag{4-29}$$

and

$$\phi = \begin{cases} \infty & ; \left(\dfrac{R_b}{R_a} - \rho\right) \le \lambda \\ \dfrac{\left(-\underset{\sim}{B}/R^3{}_a\right)}{\left(\dfrac{R_b}{R_a} - \rho\right)^3} & ; \left(\dfrac{R_b}{R_a} - \rho\right) > \lambda \end{cases} \tag{4-30}$$

Computation of Surface Potential Parameters. The surface potential parameters for solute-membrane material interactions can be calculated with the above equations. The first part is the determination of an average pore radius on the membrane surface. A reference solute is chosen and with data for retention volumes from liquid chromatography and reverse osmosis performance, the calculation routine proceeds as follows.

Step 1. Calculate the Stokes' radius, r_A, from the reference solute's diffusion coefficient

$$r_A = \frac{\underset{\sim}{k}\ T}{6\pi\eta\ D^{\circ}_{AB}} \qquad (4\text{-}31)$$

This calculated value is used as an initial guess of $\underset{\sim}{D}$.

Step 2. With the liquid chromatography retention volume, the total surface area of the chromatography column, and $\underset{\sim}{D}_{solvent}$ from the literature, calculate $\underset{\sim}{B}$ by eq 4-10 with eq 4-3.

Step 3. Assume a value of R_b and calculate R_a by eq 4-28. Calculate λ (eq 4-26) and then b (eq 4-27).

Step 4. With the reverse osmosis data for (PSP) and $\underset{\sim}{f}$, and the appropriate mass transfer coefficient, calculate c_{A_2} by eq 4-23.

Step 5. Calculate β_1 and β_2 by eq 4-14 and 4-15 where

$$\chi_{AB} = \frac{\underset{\sim}{R}T}{D_{AB}} \qquad (4\text{-}32)$$

Step 6. Solve eq 4-17 numerically for $\alpha(\rho)$. This was by a Romberg integration method (see Appendix 3, program QATR.FTN.).

Step 7. Calculate f' with eq 4-21.

Step 8. Calculate f with eq. 4-25. If f calculated by this step and the experimental separation agree, then R_b assumed in Step 3 is regarded as the average pore radius for the membrane. If they do not agree then return to Step 3 and repeat the calculation.

To determine the interfacial parameters $\underset{\sim}{B}$ and $\underset{\sim}{D}$ for other solutes, reverse osmosis data for membranes of known R_b are required as well as the liquid chromatography data for the solute-membrane material system in question. The procedure is outlined as follows.

Step 9. Assume a value of $\underset{\sim}{D}$ for the solute to determine steric hindrance. Usually the Stokes' radius is a good estimate.

Step 10. Calculate the value of $\underset{\sim}{B}$ (or $\underset{\sim}{A}$) by the method of Step 2.

Step 11. Calculate b according to Step 3.

Step 12. Calculate c_{A_2} according to Step 4.

Step 13. Calculate β_1 and β_2 by Step 5.

Step 14. Calculate $\alpha(\rho)$ as a function of ρ according to Step 6.

Step 15. Calculate f' by Step 7.

Step 16. Calculate f by Step 8 and compare it with the experimental value of separation. If they agree, then $\underset{\sim}{D}$ and $\underset{\sim}{B}$ (or $\underset{\sim}{A}$) from Steps 9 and 10 are the final values. If they do not agree return to Step 9 and alter the value of $\underset{\sim}{D}$.

To calculate the reverse osmosis separation of a solute in a solution-membrane system for which R_b, $\underset{\sim}{D}$ and $\underset{\sim}{B}$ (or $\underset{\sim}{A}$) are known, follow the calculation of Steps 3 through 8 where the known values replace the assumed values. Then calculate the (PR)/(PSP) ratio by eq. 4-22.

Surface Area Determination. The total area of the solid in the chromatography column, A_p, is necessary to evaluate eq 4-9. The data for the adsorption of methanol and ethanol by cellulose acetate powder in gas chromatography experiments was used in this calculation. The computational analysis of these data are outlined by Huber and Gerritse (1971), Mohlin and Gray (1974), John and Bohra (1967) and Matsuura et al. (1981b). By using the peak height, peak areas, and locus of the peak maxima, the adsorption isotherm of the solvent can be generated. Then a form of the Kelvin radius equation is used

$$r_K = \frac{2\,\sigma\,\tilde{V}}{\underset{\sim}{R}T}\,\ln(P_o/P_1) \qquad (4\text{-}33)$$

where r_K is the critical pore radius for condensation for vapour pressure P_1, P_0 is the saturated vapour pressure, $\tilde{V}$ is molar volume of the condensate, and σ is the condensate's surface tension. By assuming cylindrical pore shapes and calculating the P_0/P_1 ratio for the different solvent volumes injected, it is possible to calculate the total volume of the pores and their pore wall surface areas. These areas are shown in Table 4-1. As well, the number of mols of solvent adsorbed on the polymer surface are plotted with solvent vapour pressure in Fig 4-1.

Table 4-1

Surface Area Presented by Cellulose Acetate Powder of 38 to 53 μm Size to Water, Methanol and Ethanol

	Water[a]	Methanol	Ethanol
Temperature, °C	55	58	67
Density, g/mL, at Temperature	--	0.7886	0.7477
Monolayer Thickness, m x 10^{10}	1.91	4.5[b]	4.78[c]
Mean Area per Molecule, m^2 x 10^{20}	9.82	18.06[d]	20.7[e]
γ, dyne/cm^2, at Temperature	--	22.07[f]	18.48[f]
Surface Area (dry powder basis), m^2/g	106.8	153.4	107.0

[a] from Matsuura et al. (1981b).

[b] from Silverman (1930).

[c] Calculated as the average of methanol and propanol (5.0×10^{-10} m) from Harkins and Jura (1944).

[d] Calculated as Area/Molecule = $1.091 \left(\frac{M}{\rho \cdot N_o}\right)^{2/3} \times 10^{16}$ (Mohlin and Gray, 1974).

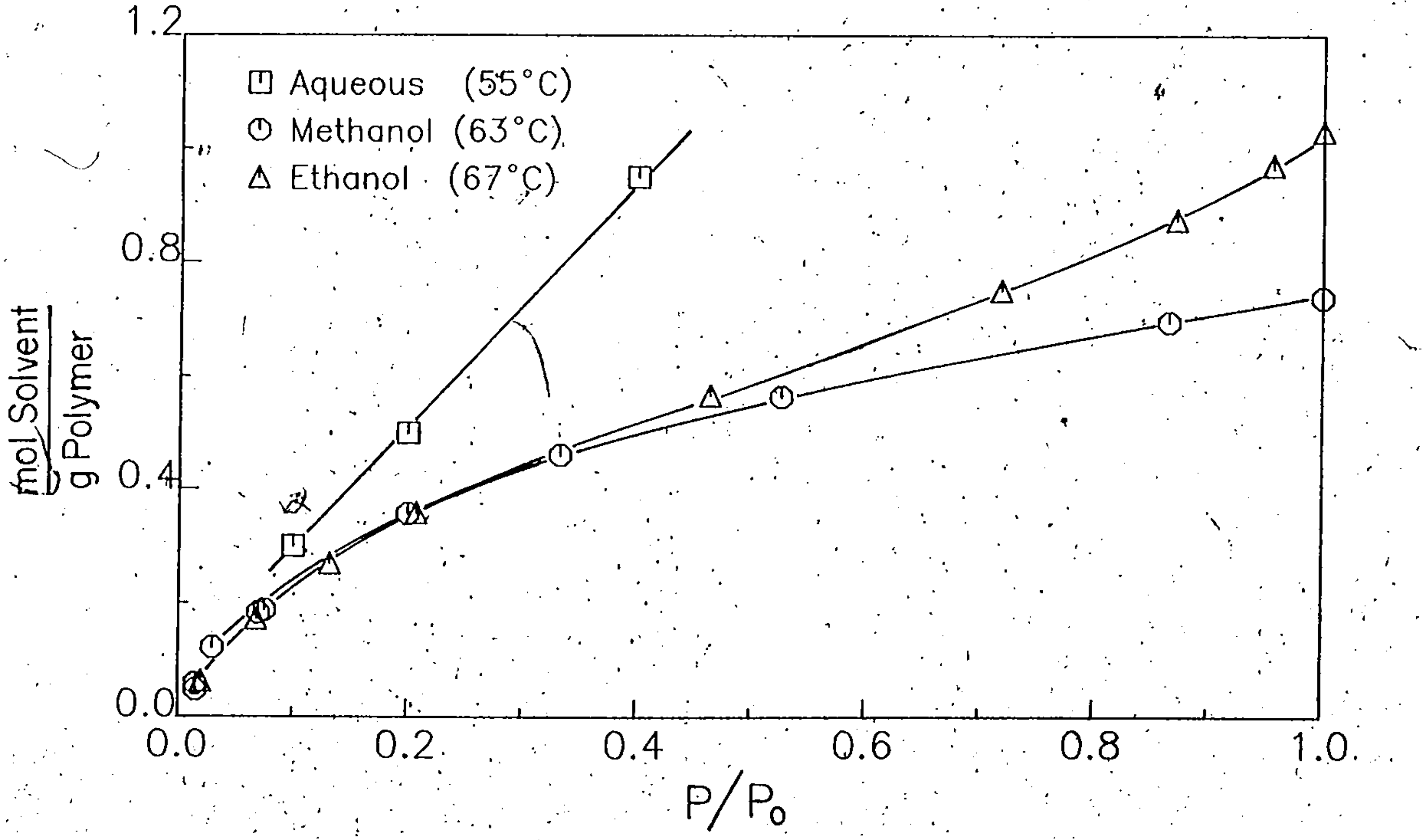
[e] from Bahtia (1970).

[f] from Jasper (1972).

Figure 4-1

Solvent Adsorbed on Cellulose Acetate Powder

With Relative Vapour Pressure


Aqueous (55°C)
Methanol (63°C)
Ethanol (67°C)
mol Solvent / g Polymer
0.0
0.4
0.8
1.2
0.0
0.2
0.4
0.6
0.8
1.0
P/Po

Results

Surface Potential Parameters. From the data for liquid chromatography retention volumes and the surface areas of the cellulose acetate powder used in the chromatography, surface excess concentrations for dilute solutions were calculated by eq 4-9. These results are shown with dilute solution diffusivities and Stokes' radii in Tables 4-2 and 4-3 for the methanol solutions and Tables 4-4 and 4-5 for the ethanol solutions. The membrane pore radii were then calculated for both solvent systems by the method of Steps 2 to 8 as outlined previously with the Stoke's radii of the reference solutes. This calculation required the use of $\underset{\sim}{D}_{solvent}$, which was assumed to be the Stoke's radius of the solvent as determined by self diffusion studies. For methanol, the value of $\underset{\sim}{D}_{solvent}$ used was 1.69 x 10^{-10} m (Dullien, 1972) and for ethanol, 2.08 x 10^{-10} m (Rossi and Bianchi, 1958). The membrane pore radii are shown in Table 4-6 for the methanol solvent case and in Table 4-7 for the ethanol solvent case.

It should be noted for the methanol case, Table 4-6 shows two solutes were used for classification. In this case, the N,N-dimethyl-benzylamine was used to characterize membranes 1 to 6. However, data for the reverse osmosis separation of N,N-dimethyl-benzylamine were not available for membranes 7 to 12. Because of this, a common solute (NaCl) for which $\underset{\sim}{D}$ and $\underset{\sim}{A}$ were known was used to characterize the pore sizes of the second set of membranes. For both the methanol and ethanol cases, the pore

Table 4-2

Surface Potential Parameters and Other Physicochemical Quantities Pertinent to Organic Solutes in Methanol Solutions

Solute	$D^{\circ}_{AB}\times10^{9}$, m^2/s^a at 25°C	Γ_A/c_{A_0} $m\times10^{10}$	Stokes' law^b radius, $m\times10^{10}$	$\underset{\sim}{B}$ $m^3\times10^{30}$	$\underset{\sim}{D}$ $m\times10^{10}$
<u>Polar organic compounds</u>					
Acetonitrile	2.73	54.06	1.44	79.76	2.54
Propionitrile	2.16	45.14	1.82	50.04	3.31
Valeronitrile	1.97	35.22	2.00	70.43	2.54
Benzonitrile	1.68	34.22	2.34	70.01	2.55
Nitromethane	2.58	81.77	1.53	–	–
1-Nitropropane	1.88	47.05	2.10	–	–
2-Nitropropane	1.88	37.20	2.10	–	–
Propionamide	2.08	3.54	1.89	26.57	2.55
n-Butyramide	1.82	–0.50	2.16	0	2.66
i-Butyramide	1.76	–2.48	2.23	–8.03	2.69
Aniline	1.95	52.01	2.02	76.41	2.51
Triethylamine	1.55	–7.72	2.54	–105.4	2.69
N,N-Dimethyl-benzylamine	1.39	6.16	2.83	43.95	2.83
N,N-Dimethylaniline	1.48	32.24	2.66	61.21	2.44
<u>Hydrocarbons</u>					
Benzene	2.20	16.37	1.78	46.59	2.41
Toluene	1.77	10.42	2.23	37.29	2.38
Ethylbenzene	1.59	4.46	2.48	26.84	2.45
o-Xylene	1.60	12.40	2.46	47.72	2.54
p-Xylene	1.58	7.44	2.50	36.67	2.51
Cumene	1.46	0.50	2.67	13.31	2.58
n-Propylbenzene	1.44	0.50	2.75	11.09	2.47
Mesitylene	1.45	2.48	2.72	25.07	2.64
n-Butylbenzene	1.38	–2.48	2.86	–10.37	2.44
s-Butlybenzene	1.36	–5.46	2.90	–50.40	2.48
i-Butylbenzene	1.31	–5.46	3.01	–50.37	2.50
t-Butylbenzene	1.28	–4.39	3.08	–32.30	2.66

[a] Diffusion Coefficients were calculated by the Wilke-Chang equation (Reid et al., 1979a)

[b] Stokes' law radius was calculated by Stokes' equation. (Reid et al., 1979a).

Table 4-3

Surface Potential Parameters and Other Physicochemical Quantities Pertinent to Inorganic Solutes in Methanol Solutions

Solute	$D^{\circ}_{AB}\times10^{9}$, m^2/s[a] at 25°C	Γ_A/c_A, m×10^{10}	Stokes' radius,[b] m×10^{10}	A, m×10^{10}	D, m×10^{10}
$MgCl_2$	1.087	-21.54	3.62	3.243	6.34
$CaCl_2$	1.105	-19.77	3.57	2.944	5.79
$SrCl_2$	1.105	-19.77	3.57	2.660	6.84
$BaCl_2$	1.109	-18.07	3.55	2.385	6.34
LiCl	1.207	-21.54	3.26	3.826	3.55
LiBr	1.256	-19.77	3.14	3.413	3.54
$LiNO_3$	1.105	-18.92	3.57	3.109	3.55
NaCl	1.317	-19.77	2.99	3.465	3.18
NaBr	1.337	-19.84	2.95	3.495	3.12
NaI	1.403	- 5.95	2.81	0.602	3.29
KF	1.188	1.77	3.32	-0.810	3.46
KCl	1.424	- 4.25	2.77	0.313	3.18
KBr	1.441	- 3.40	2.73	0.172	3.15
KI	1.520	4.39	2.59	-1.188	3.23
RbCl	1.433	2.55	2.75	-0.878	3.27
CsCl	1.498	2.69	2.63	-0.881	3.24
CsBr	1.516	6.09	2.60	-1.420	3.25

[a] Diffusion coefficients were calculated by the Nernst-Haskell equation (Reid et al., 1979b).

[b] Stokes' law radius was calculated by Stokes' equation (Reid et al., 1979a).

Table 4-4

Surface Potential Parameters and Other Physicochemical Quantities Pertinent to Organic Solutes in Ethanol Solutions and Cellulose Acetate Membranes.

Solute	D^o_{AB} [a], $m_2/s \times 10^{-10}$	Γ_A/c_A, $m \times 10^{10}$	Stoke's Radius [b] $m \times 10^{10}$	B, $m^3 \times 10^{30}$	D, $m \times 10^{10}$
Polar Organic Compounds					
Acetonitrile	13.73	31.2	1.43	81.79	2.59
Propionitrile	11.47	112	1.72	—	—
Valeronitrile	10.44	63.7	1.89	—	—
Benzonitrile	8.93	87.9	2.20	74.36	2.29
Nitromethane	13.73	28.2	1.43	74.83	2.54
1-Nitropropane	9.97	96.1	1.97	75.39	2.28
2-Nitropropane	9.97	104	1.97	76.67	2.29
Propionamide	11.07	27.5	1.78	67.54	2.45
n-Butyramide	9.69	26.9	2.03	87.44	2.70
i-Butramide	9.34	18.2	2.11	72.02	2.63
Phenol	7.80	35.3	2.52	—	—
Aniline	10.38	164	1.90	117.0	2.57
Triethylamine	8.23	37.4	2.39	—	—
N,N-Dimethyl-benzyl-amine	7.36	31.5	2.67	97.35	2.76
N,N-Dimethylaniline	7.36	76.2	2.50	—	—
Hydrocarbons					
Benzene	10.64	35.8	1.85	81.73	2.55
Toluene	9.40	33.1	2.09	58.76	2.28
Ethylbenzene	8.45	21.2	2.33	68.21	2.53
o-Xylene	8.52	26.5	2.31	77.11	2.58
p-Xylene	8.31	20.1	2.37	62.16	2.46
Cumene	7.76	10.3	2.54	57.58	2.63
n-Propylbenzene	7.63	8.16	2.58	47.54	2.54
Mesitylene	7.71	12.0	2.55	59.50	2.75
n-Butylbenzene	7.32	−1.64	2.69	−18.27	2.42
s-Butylbenzene	6.96	−3.01	2.83	−49.23	2.53
i-Butylbenzene	7.22	−7.31	2.73	−16.62	2.67
t-Butylbenzene	6.82	−0.82	2.89	− 3.13	2.66

[a] Diffusion coefficients were calculated by the Wilke-Chang equation (Reid et al., 1979a).

[b] Stokes' law radius was calculated by Stokes' equation (Reid et al., 1979a).

Table 4-5

Surface Potential Parameters and Other Physicochemical Quantities for Inorganic Solutes in Ethanol Solutions and Cellulose Acetate Membranes.

Solute	D°_{AB}[a], $m^2/s \times 10^{10}$	Γ_A/c_A, $m \times 10^{10}$	Stokes'[c] Radius, $m \times 10^{10}$	$\underset{\sim}{A}$, $m \times 10^{10}$	$\underset{\sim}{D}$, $m \times 10^{10}$
$CaCl_2$	5.00[b]	−24.1	3.97[b]	8.39	4.75
$SrCl_2$	5.00[b]	−24.7	3.97[b]	8.71	4.18
LiCl	4.92	−36.3	4.04	15.58	3.17
LiBr	5.03	−35.3	3.95	14.87	3.21
NaCl	5.62	−29.3	3.53	11.25	2.85
NaBr	5.77	−11.4	3.44	3.18	3.43
NaI	6.03	+ 0.4	3.29	−0.64	3.86
KCl	6.15	−35.3	3.23	14.99	2.43
KBr	6.32	−28.5	3.14	10.80	2.66
KI	6.63	−30.9	2.99	12.30	2.45
RbBr	6.56	−28.5	3.03	10.81	2.51
RbI	6.89	−12.0	2.88	3.46	2.91
CsCl	6.62	−26.6	3.00	9.82	2.44
CsBr	6.80	−22.5	2.92	7.80	2.62
NH_4Cl	5.71	−26.6	3.48	9.77	3.38
$NaNO_2$	5.78	+24.2	3.43	−6.21	4.31
$NaClO_3$	6.08	−29.6	3.27	11.43	2.49
$NaClO_4$	6.41	+30.7	3.10	−6.87	3.82

[a] Calculated by the Nernst-Haskell equation. (Reid et al. 1979b).

[b] Estimate

[c] Stokes' law radius was calculated by Stokes' equation (Reid et al. 1979a)

Table 4-6

Cellulose Acetate Membrane Pore Radii for Methanol Solutions[a]

Film No.	1	2	3	4[b]	5	6	7[b]	8	9	10	11	12
Pore Radius, R_b, m × 10^{10}	11.62	11.94	11.56	11.57	13.01	12.01	12.66	12.95	12.41	12.33	12.29	11.86

[a] Film Nos. 1-4: pore sizes calculated on the basis of data on N,N-Dimethyl-benzylamine. Film Nos. 5-12: pore sizes calculated on the basis of data on sodium chloride.

[b] Reference membranes used for the calculation of $\underset{\sim}{A}$, $\underset{\sim}{B}$ and $\underset{\sim}{D}$.

Table 4-7

Cellulose Acetate Membrane

Pore Radii for Ethanol Solutions

Film No.	1	2	3	4[b]	5	6
Pore Radius,[a] m × 10^{10}	11.48	11.73	11.65	11.42	12.67	11.86

a) Pore sizes determined on the basis of data for N,N-Dimethyl-benzylamine, Cumene, and t-Butylbenzene.

b) Used as the reference membrane to calculate A, B and D.

sizes reported were the averages of calculations based upon several reverse osmosis experiments.

Once the membranes were characterized by their pore radii, the surface potential parameters were calculated for all the solutes for which data were available, according to the method outlined in Steps 4-9 to 4-16. These are shown in Tables 4-2 to 4-5 for both inorganic and organic solutes in methanol and ethanol solutions.

It should be noted that the oven dried $MgCl_2$ salt used in this work was not a pure sample. However, it was treated throughout this work as $MgCl_2$.

<u>Calculation of Reverse Osmosis Performance</u>. As outlined above, the parameters in Tables 4-2 to 4-5 along with the membrane pore radii of Tables 4-6 and 4-7 can be used to calculate and predict reverse osmosis separations and product rates. A set of calculated product rates and separations are compared with experimental data for both methanol and ethanol solution in Tables 4-8 and 4-9 respectively.

Table 4-8

Comparison of Experimental and Calculated Reverse Osmosis Performance in Methanol Solutions

Solute	Concn, molal × 10^3	P, kPag	Membrane No.	(PR)^a exptl g/h	(PR)^a calcd g/h	f,% exptl	f,% calcd
Acetonitrile	0.824	1725	1	15.81	15.88	3.4	2.5
			2	48.21	48.82	3.3	1.0
			3	29.22	29.45	2.0	2.8
			4	34.98	34.69	2.8	2.8
Propionitrile	1.045	1725	1	15.46	16.03	0.1	−2.2
			2	48.08	49.29	−1.2	−2.2
			3	29.62	29.73	−0.3	−0.3
			4	34.61	35.57	−0.9	−0.9
Valeronitrile	0.820	1725	1	15.38	15.87	0.3	3.0
			2	47.67	49.04	0.6	1.0
			3	29.32	30.33	1.6	3.5
			4	34.58	35.30	3.5	3.5
Benzonitrile	0.911	1725	1	15.30	15.75	−1.3	3.2
			2	48.06	48.13	0.7	0.9
			3	28.92	29.53	4.8	3.8
			4	34.74	34.18	3.8	3.7
Propionamide	0.916	1725	1	14.96	15.68	7.4	6.6
			2	46.39	48.87	5.8	4.4
			3	28.28	29.22	7.4	7.2
			4	33.37	34.22	7.2	7.1
n-Butyramide	0.954	1725	1	15.53	15.65	16.7	17.9
			2	47.98	47.96	13.0	13.9
			3	29.22	29.21	19.1	18.8
			4	34.37	34.43	18.7	18.7
Aniline	0.910	1725	1	14.98	15.75	0.9	1.5
			2	48.53	48.63	0.1	0.1
			3	29.70	29.66	2.4	1.9
			4	34.90	35.11	2.0	1.9
Triethylamine	1.539	1725	1	15.16	15.35	40.7	43.0
			2	42.26	43.36	36.7	37.4
			3	27.03	27.41	39.3	44.2
			4	33.68	33.97	38.8	44.1

Table 4-8 - (cont'd)

Solute	Concn, molal × 10^3	P, kPag	Membrane No.	$(PR)^a$		f, %	
				exptl g/h	calcd g/h	exptl	calcd
Triethylamine	2.670	1725	1	15.21	15.78	42.5	43.0
			2	43.59	44.41	36.5	37.4
			3	27.72	28.02	42.9	44.2
			4	34.74	35.36	43.2	44.1
Triethylamine	11.72	1725	1	15.23	15.34	47.8	42.9
			2	43.10	43.56	43.0	37.3
			3	27.33	27.06	52.4	44.1
			4	33.75	34.16	44.6	43.9
Triethylamine	5.730	1208	1	10.69	10.65	36.8	36.8
			2	30.49	30.86	32.9	31.7
			3	19.22	19.58	38.9	37.9
			4	24.40	24.61	35.0	37.8
Triethylamine	5.118	690	1	6.52	6.60	27.3	27.6
			2	18.83	18.97	23.3	23.8
			3	11.58	12.05	28.8	28.7
			4	14.95	15.46	26.0	28.7
N,N-Dimethylbenzylamine	1.128	1725	1	15.38	15.46	–	28.4
			2	41.98	43.06	22.0	23.9
			3	27.39	27.43	25.9	29.4
			4	33.87	34.29	25.9	29.3
N,N-Dimethylbenzylamine	5.021	1725	1	15.10	15.03	28.5	28.4
			2	42.28	42.56	23.9	23.8
			3	26.94	27.18	29.4	29.3
			4	33.50	33.82	29.3	29.2
N,N-Dimethylbenzylamine	10.34	1725	1	15.13	15.26	28.1	28.3
			2	41.07	42.53	23.3	23.8
			3	26.93	27.19	28.0	29.3
			4	33.31	33.64	27.8	29.2
N,N-Dimethylbenzylamine	5.159	1208	1	11.12	10.88	25.2	23.9
			2	31.40	30.55	18.9	20.1
			3	15.70	18.72	25.6	24.7
			4	24.94	24.31	23.0	24.7

Table 4-8 - (cont'd)

Solute	Concn, molal × 10^3	P, kPag	Membrane No.	(PR)[a]		f, %	
				exptl g/h	calcd g/h	exptl	calcd
N,N-Dimethyl-benzylamine	5.192	690	1	6.12	6.60	16.1	17.8
			2	18.05	19.00	13.1	15.1
			3	11.46	12.08	17.9	18.4
			4	14.51	15.46	16.5	18.3
N,N-Dimethyl-benzylamine	0.999	1725	1	16.02	15.74	-0.1	0.0
			2	49.02	48.84	-0.3	-0.8
			3	29.37	29.54	0.2	0.3
			4	34.92	34.96	0.3	0.3
Glycerol	1.096%[b]	1725	1	14.28	14.12	26.4	26.2
			2	41.58	44.26	23.2	21.7
			3	26.55	26.88	27.2	27.3
			4	33.15	31.00	27.1	27.0
Benzene	4.977	1725	1	14.88	15.01	2.6	1.2
			2	45.69	46.65	0.4	1.0
			3	28.14	28.54	0.9	1.4
			4	32.49	32.98	1.4	1.4
Toluene	5.067	1725	1	14.88	14.89	1.1	0.4
			2	45.78	46.45	0.4	-2.1
			3	28.23	27.97	1.1	1.5
			4	32.67	32.28	0.9	1.4
Ethylbenzene	4.846	1725	1	15.00	14.90	4.8	3.6
			2	45.66	46.05	3.4	2.5
			3	28.53	28.54	4.2	4.0
			4	32.73	32.99	4.0	3.9
Ethylbenzene	4.721	1035	1	8.87	8.72	2.6	3.2
			2	26.96	26.96	1.6	2.5
			3	16.64	16.66	2.6	3.5
			4	19.67	19.62	2.4	3.4
o-Xylene	4.938	1725	1	14.88	14.89	5.7	4.9
			2	45.81	45.87	4.0	2.4
			3	28.35	27.94	5.4	5.5
			4	32.88	32.26	5.4	5.4

Table 4-8 - (cont'd)

Solute	Concn, molal × 10^3	P, kPag	Membrane No.	$(PR)^a$		f,%	
				exptl g/h	calcd g/h	exptl	calcd
p-Xylene	4.798	1725	1	14.85	15.01	2.8	4.7
			2	45.66	46.26	3.4	2.6
			3	28.17	28.61	5.2	5.2
			4	32.67	32.63	5.2	5.2
Cumene	4.832	1725	1	14.97	15.01	13.7	11.5
			2	45.72	46.29	9.9	7.7
			3	28.32	28.51	13.0	13.6
			4	32.97	32.91	13.2	13.5
n-Propylbenzene	4.723	1725	1	14.91	15.10	6.5	6.0
			2	45.57	46.29	4.6	4.5
			3	28.32	28.85	6.5	6.5
			4	33.00	33.02	6.5	6.5
n-Propylbenzene	4.784	1035	1	8.82	8.93	6.5	4.8
			2	26.91	27.14	4.4	3.8
			3	16.58	16.69	6.0	5.1
			4	19.55	19.64	5.7	5.1
Mesitylene	4.522	1725	1	14.20	15.01	16.1	15.6
			2	43.31	46.30	12.3	11.5
			3	26.86	28.44	16.2	16.5
			4	31.26	32.92	16.4	16.4
n-Butylbenzene	4.821	1725	1	14.94	15.23	8.8	8.4
			2	45.66	46.42	5.8	7.3
			3	28.23	28.42	7.3	8.8
			4	32.83	33.24	8.8	8.7
n-Butylbenzene	4.839	1035	1	8.79	8.81	6.5	6.3
			2	26.73	26.77	6.0	5.6
			3	16.35	16.46	7.7	6.6
			4	19.43	19.73	7.8	6.6
s-Butylbenzene	4.890	1725	1	14.91	14.97	20.3	20.0
			2	45.30	45.72	16.2	16.9
			3	28.20	28.10	20.6	20.9
			4	32.55	32.79	20.8	20.8
i-Butylbenzene	4.903	1725	1	14.91	14.94	18.8	18.5
			2	45.69	46.32	14.0	16.0
			3	28.29	28.58	18.6	19.3
			4	32.66	32.97	19.2	19.2

Table 4-8 - (cont'd)

Solute	Concn, molal × 10^3	P, kPag	Membrane No.	$(PR)^a$		f,%	
				exptl g/h	calcd g/h	exptl	calcd
t-Butylbenzene	4.787	1725	1	15.24	15.52	26.9	28.7
			2	43.38	44.09	24.0	23.3
			3	27.36	27.72	29.9	29.9
			4	33.81	34.68	29.9	29.9
$MgCl_2$	4.319	1725	1	16.23	16.61	99.6	99.4
			2	48.41	49.83	99.1	99.4
			3	29.54	30.25	99.4	99.4
			4	35.15	35.99	99.4	99.4
$CaCl_2$	4.865	1725	1	17.12	17.18	99.6	99.0
			2	51.36	51.67	98.7	98.9
			3	31.68	31.51	99.4	99.0
			4	37.56	37.16	99.1	99.0
$SrCl_2$	5.257	1725	1	15.60	15.93	99.6	99.6
			2	48.03	49.20	99.0	99.5
			3	29.34	29.95	99.3	99.6
			4	34.83	35.18	99.6	99.3
$BaCl_2$	7.051	1725	1	15.90	15.28	99.6	99.3
			2	48.41	49.52	99.1	99.3
			3	29.54	30.05	99.4	99.4
			4	35.15	34.52	99.4	99.3
LiCl	4.315	1725	9	7.56	7.65	83.6	85.4
			10	5.48	5.63	83.2	85.8
			11	4.38	4.46	83.2	86.0
			12	4.47	4.59	86.6	87.9
LiCl	4.611	1725	5	21.50	21.68	80.2	80.5
			6	4.10	4.10	86.0	86.7
			7	14.86	14.94	82.8	82.8
			8	20.05	20.16	80.6	80.9
LiCl	5.431	1725	1	15.79	15.89	87.9	88.2
			2	48.58	49.61	84.1	86.9
			3	29.64	29.84	88.5	88.4
			4	35.06	35.47	88.1	88.4
LiCl	144.4	1725	9	5.65	5.55	81.7	81.7
			10	4.08	3.99	84.8	82.1
			11	3.22	3.10	83.6	82.2
			12	3.20	3.07	85.0	84.3

Table 4-8 – (cont'd)

Solute	Concn, molal × 10^3	Operating Pressure, kPag	Membrane No.	$(PR)^a$		Solute Separation	
				exptl g/h	calcd g/h	exptl %	calcd %
LiCl	458.6	3450	9	9.17	8.29	80.1	85.6
			10	6.71	5.89	83.5	85.7
			11	5.38	4.41	82.0	85.6
			12	5.51	4.37	83.9	87.0
LiBr	5.710	1725	5	21.27	21.54	78.2	78.9
			6	4.03	4.09	85.9	85.9
			7	14.66	14.82	81.4	81.3
			8	19.68	20.17	78.9	79.3
LiBr	149.8	1725	9	5.75	4.34	78.0	80.1
			10	4.17	3.97	81.7	80.6
			11	3.30	3.12	80.5	80.7
			12	3.31	3.10	82.2	82.8
LiBr	409.3	3450	9	9.88	9.08	76.8	85.1
			10	7.29	6.50	81.4	85.3
			11	5.79	4.88	80.0	85.2
			12	5.99	4.93	81.6	86.8
$LiNO_3$	5.710	1725	1	16.74	17.37	86.3	88.0
			2	51.00	52.52	81.6	86.7
			3	31.14	31.90	86.3	88.2
			4	37.14	37.69	88.3	88.2
NaCl	4.864	1725	9	7.43	7.33	70.2	68.4
			10	5.41	5.36	72.2	69.3
			11	4.27	4.14	72.9	69.8
			12	4.29	4.17	75.6	74.2
NaCl	4.989	1725	5	21.67	21.68	61.3	60.6
			6	4.15	4.11	74.4	72.7
			7	14.98	14.98	65.7	65.3
			8	20.12	20.15	62.2	61.4
NaCl	6.216	1725	1	16.65	16.91	77.8	76.7
			2	50.38	51.85	72.1	73.2
			3	30.70	31.93	79.7	77.2
			4	36.43	37.47	78.3	77.1
NaBr	5.003	1725	5	21.92	21.88	56.8	55.0
			6	4.14	4.16	67.2	70.4
			7	15.18	15.06	60.7	60.3
			8	20.43	20.37	57.7	55.9

Table 4-8 - (cont'd)

Solute	Concn, molal × 10^3	P, kPag	Membrane No.	(PR)[a] exptl g/h	(PR)[a] calcd g/h	f,% exptl	f,% calcd
NaI	5.037	1725	5	21.39	21.86	54.3	54.1
			6	4.19	4.28	70.0	67.0
			7	15.37	15.20	58.8	58.7
			8	20.13	20.36	55.4	54.9
KF	5.947	1725	5	22.01	21.81	60.3	62.2
			6	4.14	4.16	73.9	73.3
			7	14.79	14.10	66.0	65.8
			8	20.39	20.48	61.4	62.4
KCl	5.247	1725	5	21.62	21.64	46.1	44.7
			6	4.08	4.03	63.1	59.7
			7	14.87	14.63	50.1	50.0
			8	20.11	19.73	47.0	45.6
KBr	4.770	1725	5	21.76	22.10	43.5	40.4
			6	4.10	4.12	60.6	56.0
			7	14.94	14.94	47.4	47.1
			8	20.21	20.42	44.3	41.3
KI	5.309	1725	5	21.49	21.37	43.2	39.9
			6	4.02	4.03	58.5	55.7
			7	14.68	14.77	45.2	45.0
			8	19.89	19.84	41.9	40.8
RbCl	4.916	1725	5	21.41	21.30	45.5	45.6
			6	4.17	4.29	64.2	60.6
			7	15.30	15.07	50.6	50.5
			8	20.09	20.06	46.4	46.4
CsCl	4.928	1725	5	21.59	21.48	43.7	42.9
			6	4.21	4.29	61.2	57.3
			7	15.35	15.43	47.6	47.9
			8	20.15	20.47	45.6	43.8
CsBr	4.940	1725	5	21.59	21.79	41.5	40.1
			6	4.04	4.07	56.6	55.7
			7	14.73	14.86	45.2	45.1
			8	19.94	20.23	41.5	41.0

[a] for 13.2 cm^2 surface area.

[b] weight %

Table 4-9

Comparison of Experimental and Calculated Reverse Osmosis Performance in Ethanol Solutions

Solute	Concn, molal × 10^3	P, kPag	Membrane No.	(PR)^a		f, %	
				exptl	calcd	exptl	calcd
Acetonitrile	0.831	1725	1	16.19	16.57	3.6	2.5
			2	26.55	26.59	3.1	1.6
			3	21.75	21.76	−0.1	2.3
			4	16.19	16.06	4.2	4.2
			5	21.94	22.01	0.2	−2.5
			6	12.92	13.08	0.1	0.7
Benzonitrile	1.196	1725	1	17.20	16.99	−11.0	−14.4
			2	28.20	27.23	−3.0	−14.5
			3	22.68	22.25	12.1	−14.4
			4	16.90	16.61	−5.5	−3.6
			5	23.14	22.02	8.0	−15.9
			6	13.60	13.17	11.7	−14.9
Nitromethane	0.938	1725	1	16.73	17.00	8.2	0.7
			2	27.35	27.22	7.3	0.0
			3	22.02	22.26	5.3	0.5
			4	16.34	16.62	1.9	2.2
			5	23.31	22.01	−13.0	−2.1
			6	13.07	13.17	−12.1	−0.7
1-Nitropropane	0.827	1725	1	17.16	17.00	−4.9	−13.1
			2	27.99	27.99	−2.9	−13.2
			3	22.54	22.26	−10.7	−13.1
			4	16.81	16.62	−8.1	−3.3
			5	23.08	22.94	−14.9	−14.5
			6	13.59	13.17	−16.5	−13.5
2-Nitropropane	0.774	1725	1	16.70	17.00	0	−13.5
			2	27.33	27.23	−7.6	−13.2
			3	21.97	21.78	−9.9	−13.1
			4	16.36	16.61	−6.5	−3.4
			5	22.21	22.02	−8.8	−14.6
			6	13.04	13.17	−14.7	−13.5

Table 4-9 – (cont'd)

Solute	Concn, molal × 10^3	P, kPag	Membrane No.	(PR)^a		f, %	
				exptl	calcd	exptl	calcd
n-Propionamide	0.974	1725	1	16.25	16.17	0.5	-1.5
			2	26.57	26.58	8.8	-1.9
			3	21.77	21.78	0.5	-1.6
			4	16.22	16.05	-0.4	-0.4
			5	21.90	22.02	-2.3	-13.5
			6	12.90	12.94	7.4	-2.3
n-Butyramide	0.884	1725	1	16.27	16.38	6.4	9.0
			2	26.57	26.56	8.0	7.7
			3	21.73	21.76	10.0	8.7
			4	16.18	16.04	11.6	11.6
			5	21.89	22.01	9.5	-1.6
			6	12.89	12.94	0.3	6.2
i-Butyramide	1.093	1725	1	15.93	16.15	4.7	6.4
			2	26.15	26.56	2.7	5.1
			3	21.37	21.76	3.5	6.0
			4	15.90	16.05	8.9	8.9
			5	21.51	22.01	8.9	-2.4
			6	12.65	12.94	12.3	3.7
Phenol	3.779	1725	1	–	14.09	2.5	2.8
			2	–	25.84	3.1	1.8
			3	–	14.12	4.8	2.5
			4	–	10.76	3.4	4.9
			5	20.86	21.59	3.4	-3.1
			6	–	12.19	5.9	0.6
Aniline	1.068	1725	1	17.35	17.12	-18.3	-0.2
			2	28.11	28.00	0	-1.1
			3	22.57	22.15	-4.7	-0.5
			4	16.83	16.54	1.7	1.6
			5	23.08	22.85	-20.2	-5.4
			6	13.55	13.11	-0.5	-2.2
N,N-Dimethyl-benzylamine	1.003	1725	1	16.63	16.69	16.1	14.1
			2	27.00	27.95	15.6	12.5
			3	21.56	22.21	6.8	13.6
			4	15.92	16.59	17.0	17.0
			5	21.80	22.90	-1.5	-0.1
			6	12.70	13.14	16.1	10.7

Table 4-9 - (cont'd)

Solute	Concn, molal × 10^3	P, kPag	Membrane No.	(PR)^a		f,%	
				exptl	calcd	exptl	calcd
Benzene	4.013	1725	1	14.76	14.46	-1.3	1.1
			2	-	26.14	17.0	0.2
			3	14.13	14.05	2.3	0.9
			4	10.78	10.76	3.0	3.0
			5	-	21.68	23.6	-3.2
			6	12.47	12.23	0	-0.7
Toluene	4.428	1725	1	14.60	14.40	-8.9	-13.1
			2	19.18	26.17	-7.8	-13.2
			3	14.04	14.28	-4.9	-13.1
			4	10.68	10.92	-8.9	-2.4
			5	18.26	22.00	-8.4	-14.4
			6	12.34	12.52	-3.4	-13.4
Ethylbenzene	4.725	1725	1	15.04	14.10	3.3	1.3
			2	26.64	25.22	-3.9	0.3
			3	14.61	14.40	5.0	1.0
			4	11.15	10.63	3.4	3.4
			5	22.15	21.35	1.8	0.0
			6	27.63	11.45	2.2	-0.8
o-Xylene	4.399	1725	1	17.86	14.09	3.8	3.1
			2	25.83	25.22	4.3	1.9
			3	17.41	14.04	5.6	2.8
			4	13.31	10.63	5.6	5.5
			5	21.62	21.34	3.6	-3.6
			6	15.42	11.44	3.2	0.6
p-Xylene	4.650	1725	1	14.29	14.10	0.9	-1.1
			2	25.24	25.23	0.9	-1.7
			3	13.92	14.05	1.7	-1.3
			4	10.62	10.63	0.4	0.4
			5	21.06	21.35	1.1	0.0
			6	12.28	11.45	-0.2	-2.3
Cumene	4.338	1725	1	14.84	14.39	6.4	8.1
			2	26.07	26.15	11.0	6.6
			3	14.22	14.28	13.4	7.7
			4	10.89	10.91	11.0	11.0
			5	21.63	21.69	5.8	-1.7
			6	12.62	12.51	5.2	5.0

Table 4-9 - (cont'd)

Solute	Concn, molal × 10^3	P, kPag	Membrane No.	$(PR)^a$		f,%	
				exptl	calcd	exptl	calcd
n-Propylbenzene	4.671	1725	1	14.32	14.06	-11.4	3.7
			2	25.40	25.49	5.9	2.6
			3	13.95	13.93	6.7	3.4
			4	10.60	10.49	6.1	6.1
			5	21.14	21.27	2.7	-1.2
			6	12.24	11.97	3.3	1.4
Mesitylene	4.110	1725	1	14.55	14.24	–	16.5
			2	25.62	25.57	12.3	14.8
			3	14.07	14.04	18.7	16.0
			4	10.79	10.63	19.5	19.5
			5	21.36	21.25	15.5	2.1
			6	12.47	11.62	15.7	11.6
n-Butylbenzene	4.399	1725	1	14.22	13.92	2.3	7.1
			2	25.25	25.32	6.0	6.7
			3	13.98	13.99	7.0	7.0
			4	10.54	10.56	8.4	8.4
			5	21.34	21.29	6.5	-12.1
			6	12.11	12.07	10.9	6.5
s-Butylbenzene	4.399	1725	1	–	13.92	16.5	19.4
			2	–	25.31	17.2	17.8
			3	–	14.00	15.0	19.0
			4	–	10.55	22.7	22.7
			5	–	21.29	16.0	-9.0
			6	–	12.07	18.7	16.4
i-Butylbenzene	2.086	1725	1	14.14	13.83	7.9	23.3
			2	26.05	25.55	23.2	21.3
			3	–	13.99	19.6	22.8
			4	10.88	10.55	27.1	27.1
			5	20.49	21.27	21.1	8.6
			6	–	12.06	6.1	19.2
t-Butylbenzene	4.429	1725	1	13.87	13.83	19.1	20.5
			2	25.51	25.54	11.2	18.5
			3	13.85	13.99	16.6	19.9
			4	–	10.55	24.1	24.2
			5	21.86	21.27	14.6	6.4
			6	13.67	12.06	10.8	16.4

Table 4-9 – (cont'd)

Solute	Concn, molal × 10^3	P, kPag	Membrane No.	$(PR)^a$		f, %	
				exptl	calcd	exptl	calcd
$CaCl_2$	0.858	1725	1	17.20	17.08	92.2	98.6
			2	28.47	28.94	91.3	98.6
			3	22.36	22.29	98.5	98.6
			4	16.56	16.56	98.7	98.7
			5	23.04	22.95	96.7	98.1
			6	13.43	13.22	97.2	98.5
$SrCl_2$	1.110	1725	1	16.84	16.50	93.9	97.8
			2	27.74	28.28	92.8	97.7
			3	22.39	28.28	97.4	97.7
			4	16.72	16.82	97.9	97.9
			5	22.97	22.93	96.2	96.8
			6	13.49	13.53	97.5	97.6
LiCl	0.897	1725	1	16.74	16.40	91.3	96.5
			2	27.52	29.48	91.3	96.3
			3	22.17	22.93	94.9	96.5
			4	16.52	16.78	96.2	96.9
			5	23.65	23.47	93.6	93.7
			6	13.29	13.26	95.1	96.0
LiBr	0.955	1725	1	18.47	18.40	82.6	96.4
			2	29.55	29.49	89.1	96.2
			3	23.39	22.94	93.9	96.4
			4	17.18	16.79	96.8	96.8
			5	23.94	23.48	90.7	93.6
			6	14.00	13.27	94.3	95.9
NaCl	1.116	1725	1	17.09	16.11	82.7	85.8
			2	28.00	28.06	79.1	84.8
			3	22.44	22.60	85.3	85.5
			4	16.72	16.79	87.3	87.3
			5	22.98	22.90	81.4	75.7
			6	13.54	13.28	87.3	83.8
NaBr	1.272	1725	1	18.11	17.25	67.4	84.1
			2	29.63	29.32	78.2	83.5
			3	23.84	22.97	72.6	83.9
			4	17.55	17.02	85.2	85.1
			5	24.33	23.59	83.5	77.1
			6	14.30	13.59	82.6	82.8

Table 4-9 - (cont'd)

Solute	Concn, molal × 10^3	P, kPag	Membrane No.	$(PR)^a$		f,%	
				exptl	calcd	exptl	calcd
NaI	1.066	1725	1	17.73	16.96	79.5	82.4
			2	29.15	28.65	76.9	81.9
			3	23.48	22.70	82.6	82.2
			4	17.30	16.59	83.1	83.1
			5	23.99	23.36	70.3	77.6
			6	14.13	13.23	83.1	81.5
KCl	1.108	1725	1	17.13	17.06	74.1	78.4
			2	28.07	28.54	75.0	77.9
			3	22.65	23.00	77.1	78.2
			4	16.63	16.90	79.4	79.3
			5	22.87	23.63	76.5	62.8
			6	13.42	13.27	81.5	77.8
KBr	1.238	1725	1	17.47	17.05	71.1	75.0
			2	28.65	28.54	71.6	73.6
			3	23.15	23.00	72.1	74.6
			4	17.06	16.90	77.4	77.4
			5	23.59	23.63	73.2	64.3
			6	13.89	13.27	77.9	72.2
KI	1.319	1725	1	17.15	17.05	67.7	69.3
			2	28.00	28.19	67.2	68.6
			3	22.54	22.60	70.1	69.1
			4	16.58	16.49	70.9	70.8
			5	22.87	22.97	66.9	49.4
			6	13.40	13.28	74.1	68.3
RbBr	0.902	1725	1	17.84	17.48	63.6	66.3
			2	29.81	29.93	58.7	65.1
			3	22.93	22.60	65.3	65.9
			4	17.03	16.78	68.6	68.5
			5	23.97	23.76	63.6	41.3
			6	13.96	13.05	70.2	64.3
RbI	0.835	1725	1	17.75	17.48	60.7	69.5
			2	29.66	29.64	55.4	57.8
			3	22.62	22.60	60.7	59.0
			4	16.82	16.75	62.5	62.5
			5	23.61	23.75	57.1	42.0
			6	13.68	13.05	66.1	56.0

Table 4-9 (cont'd)

Solute	Concn, molal × 10^3	P, kPag	Membrane No.	$(PR)^a$		f, %	
				exptl	calcd	exptl	calcd
CsCl	1.112	1725	1	18.34	18.19	59.4	58.6
			2	30.86	30.89	51.7	57.9
			3	23.15	23.02	64.7	58.3
			4	17.22	17.18	60.3	60.2
			5	24.31	24.38	61.2	36.3
			6	14.11	13.62	61.2	57.6
CsBr	1.169	1725	1	17.28	17.06	59.8	59.1
			2	28.20	28.56	62.3	57.4
			3	22.76	22.51	64.8	58.6
			4	16.61	16.40	62.3	62.3
			5	22.96	22.81	62.3	47.9
			6	13.49	13.29	68.8	55.7
NH_4Cl	0.9601	1725	1	17.04	17.04	91.2	93.9
			2	27.67	28.24	86.2	93.6
			3	22.33	22.49	92.8	93.9
			4	16.35	16.53	94.5	94.5
			5	22.37	22.77	90.1	90.3
			6	13.12	13.26	96.7	93.3
$NaNO_2$	1.042	1725	1	16.96	16.95	73.6	73.4
			2	27.82	28.03	67.3	73.0
			3	22.30	22.26	74.0	73.2
			4	16.61	16.54	74.0	73.9
			5	22.81	22.92	70.8	69.7
			6	13.37	13.03	78.1	72.7
$NaClO_3$	1.116	1725	1	17.09	17.05	67.1	68.7
			2	28.28	28.26	52.6	67.7
			3	22.45	22.50	64.8	68.4
			4	16.75	16.54	70.6	70.6
			5	24.31	23.15	53.4	46.1
			6	13.57	13.28	67.5	67.1
$NaClO_4$	1.888	1725	1	16.81	16.92	40.0	57.1
			2	27.67	28.05	60.5	56.4
			3	22.00	22.22	65.8	56.9
			4	16.49	16.51	58.2	58.2
			5	22.58	22.88	53.7	50.2
			6	13.15	13.00	68.2	55.8

[a] for 13.2 cm^2 surface area.

Discussion.

According to this model, reverse osmosis separation is the combined effect of two factors, an equilibrium effect which is concerned with preferential sorption in the vicinity of the membrane surface, and a kinetic effect which is concerned with the mobility of the solute relative to that of the solvent through the membrane pore. These are represented by Γ_A/c_A and λ which are the physicochemical parameters that apply to these two effects. When Γ_A/c_A is positive, the solute is preferentially adsorbed on the polymer surface and when Γ_A/c_A is negative, the solute is rejected from the polymer surface. As the value of λ increases, the friction of transporting the solute through the membrane pore increases, which tends to increase the solute separation in reverse osmosis. The similar effect of decreasing solute separation as Γ_A/c_A increases may be assumed but the mobility of the solute in the membrane pores must be considered.

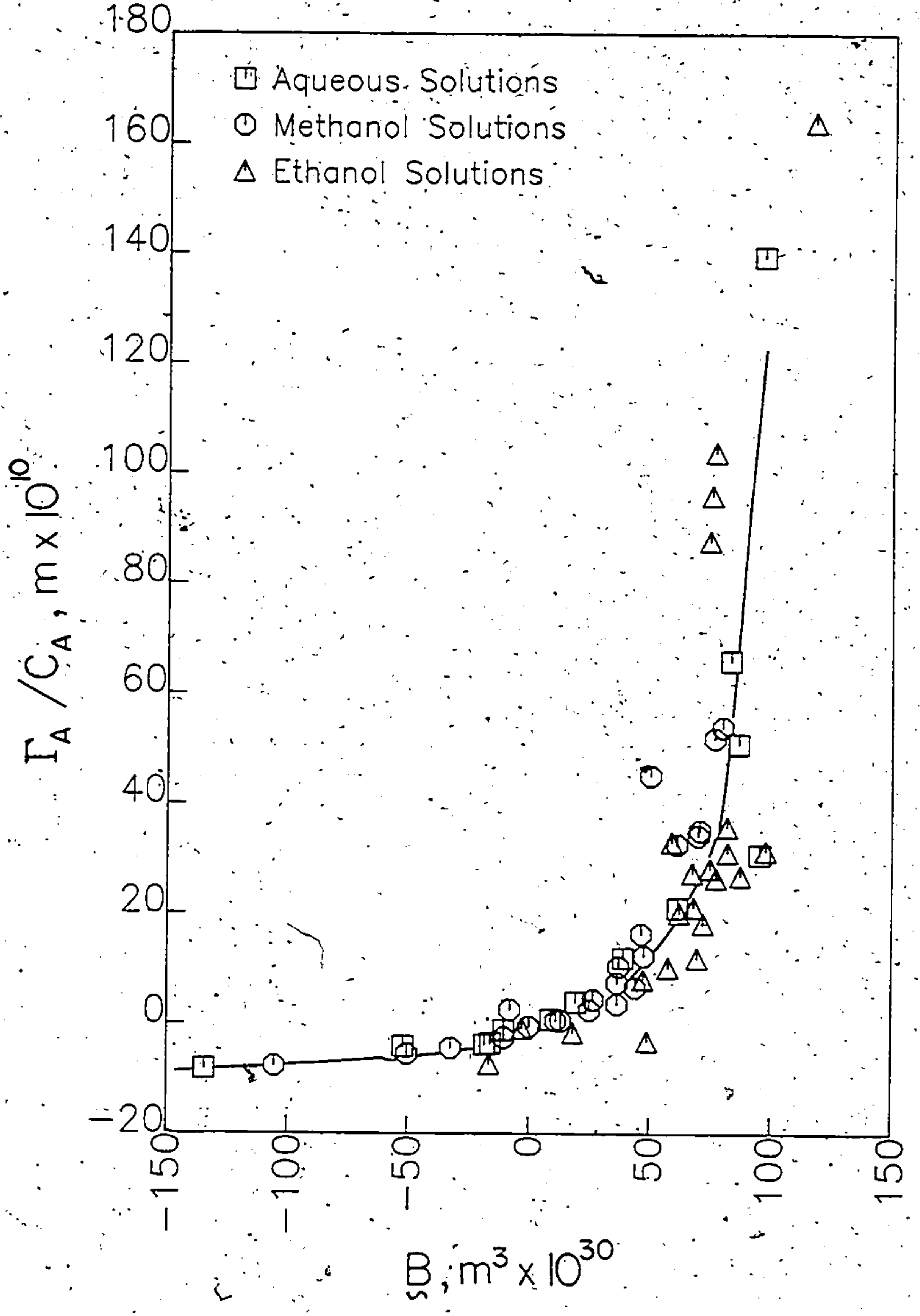
When Γ_A/c_A and $\underset{\sim}{B}$ were compared in Fig 4-2 for aqueous, methanol and ethanol solutions and cellulose acetate membranes, a remarkable correlation of surface excess concentration and the surface potential is obtained. This relation includes all three of the solvents and shows the same relation of $\underset{\sim}{B}$ and Γ_A/c_A. While the same equations were used in the calculation of $\underset{\sim}{B}$ for all three cases, several physicochemical parameters were significantly different and there is no indication of the effects of the different solvents. This is further evidence that the surface

Figure 4-2

Surface Potential Parameter, $\underset{\sim}{B}$, with Γ_A/c_A for Aqueous,[a] Methanol, and Ethanol Solutions and Cellulose Acetate Membranes

[a] Polar organic solutes only. Data of Matsuura et al. (1981a).

7



□ Aqueous Solutions
○ Methanol Solutions
△ Ethanol Solutions
180
160
140
120
100
80
60
40
20
0
−20
Γ_A / C_A, m x 10^{10}
−150
−100
−50
0
50
100
150
B, m^3 x 10^{30}

excess concentration as measured by liquid chromatography is a controlling factor for reverse osmosis performance as well as demonstrating the applicability of these physicochemical parameters to various solvent cases.

In Fig 4-3, a similar comparison to Fig 4-2 is shown for Γ_A/c_A and the $\underset{\sim}{A}\cdot\varepsilon$ product of monovalvent salts, where ε is the dielectric of the solvent. This latter term was chosen on the basis of image rejection forces on an ion at a dielectric discontinuity (Israelachvili and Tabor, 1973)

$$\text{Rejection Force} = \frac{-Z^2 e_0^2}{16\pi\varepsilon x^2} \cdot \frac{\varepsilon-\varepsilon'}{\varepsilon+\varepsilon'} \qquad (4\text{-}34)$$

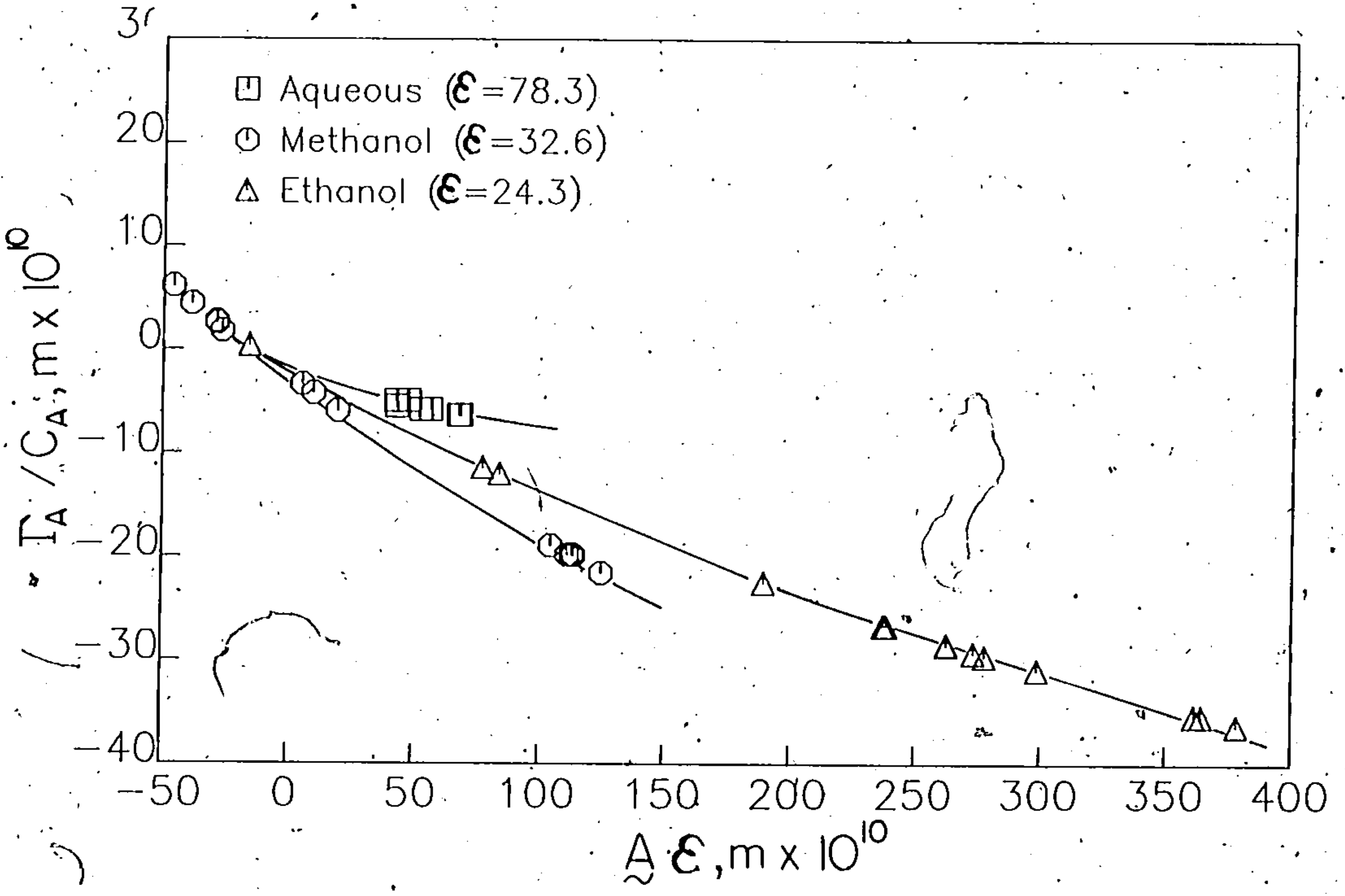
where ε is the dielectric constant of the solvent and ε' is the dielectric constant of the other side of the dielectric discontinuity, which in this case is the membrane polymer. Since ε' is undetermined, the extreme right hand term of eq 4-34 was not included in Fig 4-3. It is evident from Fig 4-3 that the $\underset{\sim}{A}$ term includes factors other than the simple dielectric image repulsion. This may be the result of treating salts as if they were ionic species. However the variation of Γ_A/c_A with $\underset{\sim}{A}\cdot\varepsilon$ in Fig 4-3 indicates a relation between the two terms which seems to apply to all three solvent cases.

When the surface potential $\underset{\sim}{B}$ parameters are compared for the same solutes in ethanol and methanol solutions (Tables 4-2 and

Figure 4-3

$\underset{\sim}{A} \cdot \varepsilon$ with Γ_A/c_A for Monovalent Salts in Aqueous,[a] Methanol, and Ethanol Solutions and Cellulose Acetate Membranes

[a] Matsuura et al. (1981b).


Aqueous (ε=78.3)
Methanol (ε=32.6)
Ethanol (ε=24.3)
Γ_A / C_A, m x 10^{10}
30
20
10
0
−10
−20
−30
−40
−50
0
50
100
150
200
250
300
350
400
$\underset{\sim}{A}\,\varepsilon$, m x 10^{10}

4-4), the ethanol values are larger and both solutions have similar values of $\underset{\sim}{D}$. This does not extend the trend observed by Taketani et al. (1982) based on water and methanol, where it was expected that the increase of R' for alcohols in R'OH would increase solute rejection from the membrane surface and decrease $\underset{\sim}{B}$. However, the suggestion of Taketani et al. (1982) with regard to the use of alcohols and other nonaqueous solvents to remove strongly adsorbed organic foulants from reverse osmosis and ultrafiltration membranes in aqueous media are still valid since the large difference of aqueous and methanol Γ_A/c_A values is not offset by the ethanol results, and ethanol solvent could also be used.

The agreement of experimental and calculated reverse osmosis performance as shown in Tables 4-8 and 4-9 for methanol and ethanol solutions demonstrates the validity of the numerical parameters generated by this work. When these results are combined with the calculations of aqueous reverse osmosis performance by Matsuura et al. (1982; 1981a; 1981b), they demonstrate the generality of the surface force-pore flow model of reverse osmosis with regard to the solvent as well as inorganic and organic solutes.

As in Chapter 3, an evaluation of the residuals can be considered. The residuals of separation ($f_{exptl} - f_{calcd}$) were plotted with calculated separation for the surface potential-pore flow model in Fig 4-4 for the methanol solutions, and Fig 4-5

Figure 4-4

Residuals for Separation Plotted with the Calculated Separation for Methanol Solutions

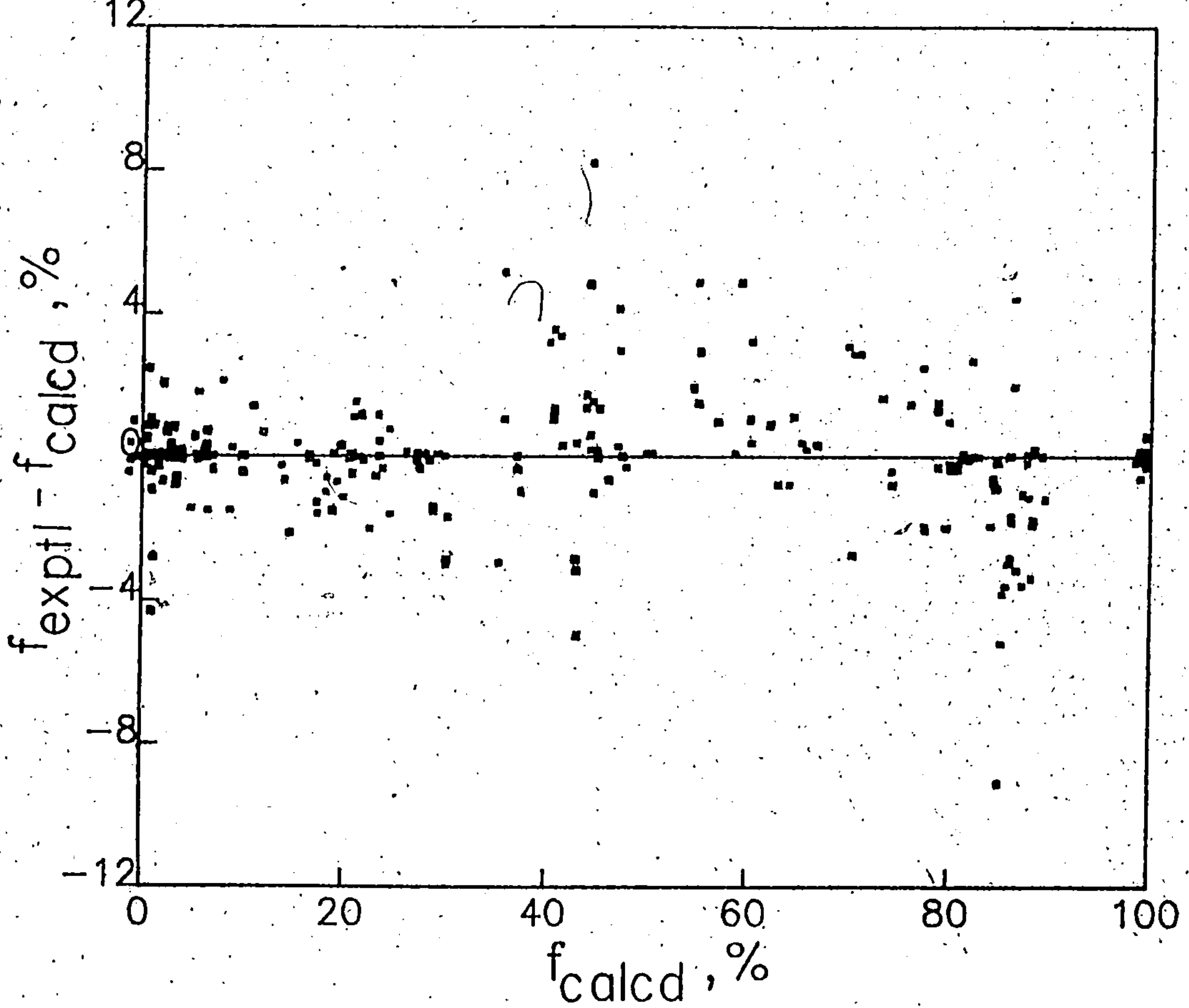
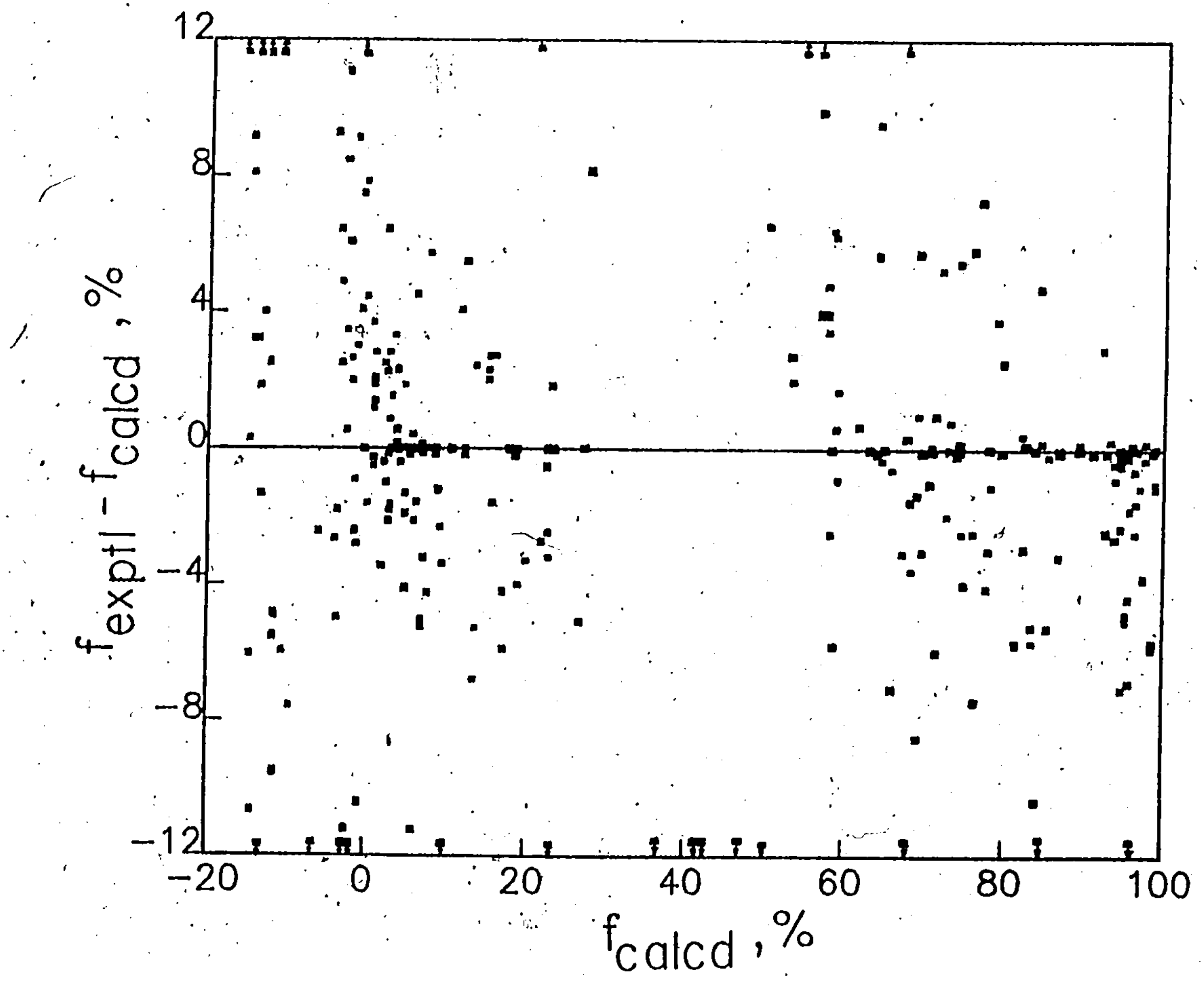

12
8
4
0
−4
−8
−12
0
20
40
60
80
100
$f_{exptl} - f_{calcd}$, %
f_{calcd}, %

Figure 4-5

Residuals for Separation Plotted with the Calculated
Separation for Ethanol Solutions


12
8
4
0
-4
-8
-12
$f_{exptl} - f_{calcd}$, %
-20
0
20
40
60
80
100
f_{calcd} , %

for the ethanol solutions. As well, the residuals of the organic solutes were plotted with $\underset{\sim}{B}$ in Fig 4-6 for the methanol solutions and Fig 4-7 for the ethanol solutions. The residuals of the salts were plotted with $\underset{\sim}{A}$ for the methanol solutions in Fig 4-8 and for the ethanol solutions in Fig 4-9. As in Chapter 3, the lack of trends for these plots is an indication of the unbiased responses of the surface potential-pore flow model.

The F-test outlined in Chapter 3 was also studied for the surface potential-pore flow model. For the organic solutes in methanol solutions as shown in Table 4-8, the SSR was calculated as 365.0 with 127 residuals and with a 3 parameter model (R, $\underset{\sim}{B}$, $\underset{\sim}{D}$). The value of s_p^2 used here is the same as used in Chapter 3: 1.48 with 6 degrees of freedom. Thus eq 3-57 is calculated as

$$\left(\frac{SSR}{n - p}\right)/s_p^2 = \left(\frac{365.0}{127-3}\right)/1.48 = 1.99$$

and $F_{124,6,.01}$ was estimated as 6.96. For the inorganic solutes in methanol solutions, SSR was 51.84 for 28 residuals and 3 model parameters (R, $\underset{\sim}{A}$, $\underset{\sim}{D}$). Equation 3-57 is calculated as

$$\left(\frac{51.84}{28-3}\right)/1.48 = 1.40$$

and $F_{25,6,.01}$ is estimated as 7.30.

Figure 4-6

Residuals for Separation Plotted with the Parameter $\underset{\sim}{B}$ for Organic Solutes in Methanol Solutions

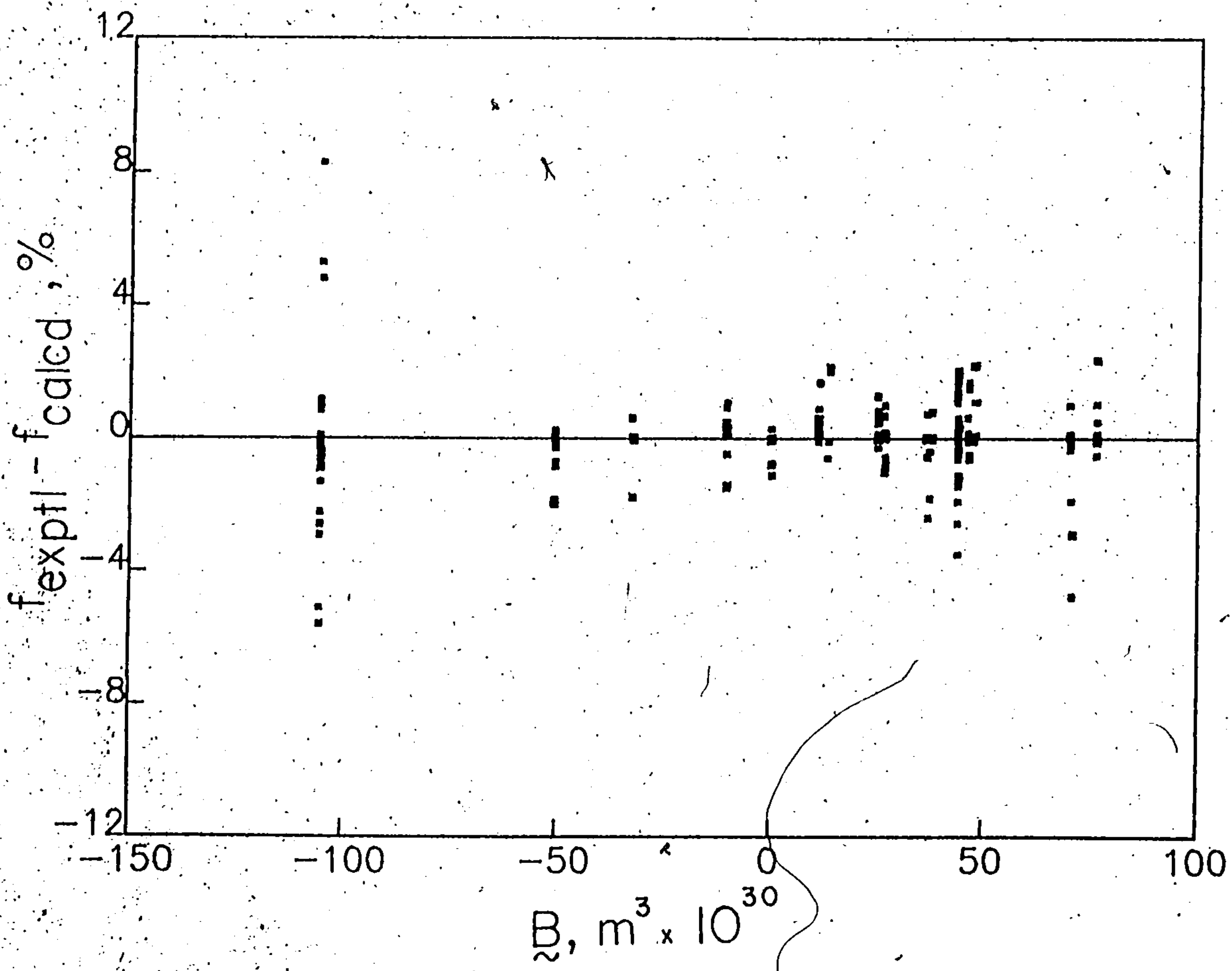

12
8
4
0
−4
−8
−12
−150
−100
−50
0
50
100
$f_{exptl} - f_{calcd}$, %
$\underset{\sim}{B}$, m^3 x 10^{30}

Figure 4-7

Residuals for Separation Plotted with the Parameter $\underset{\sim}{B}$

for Organic Solutes in Ethanol solutions

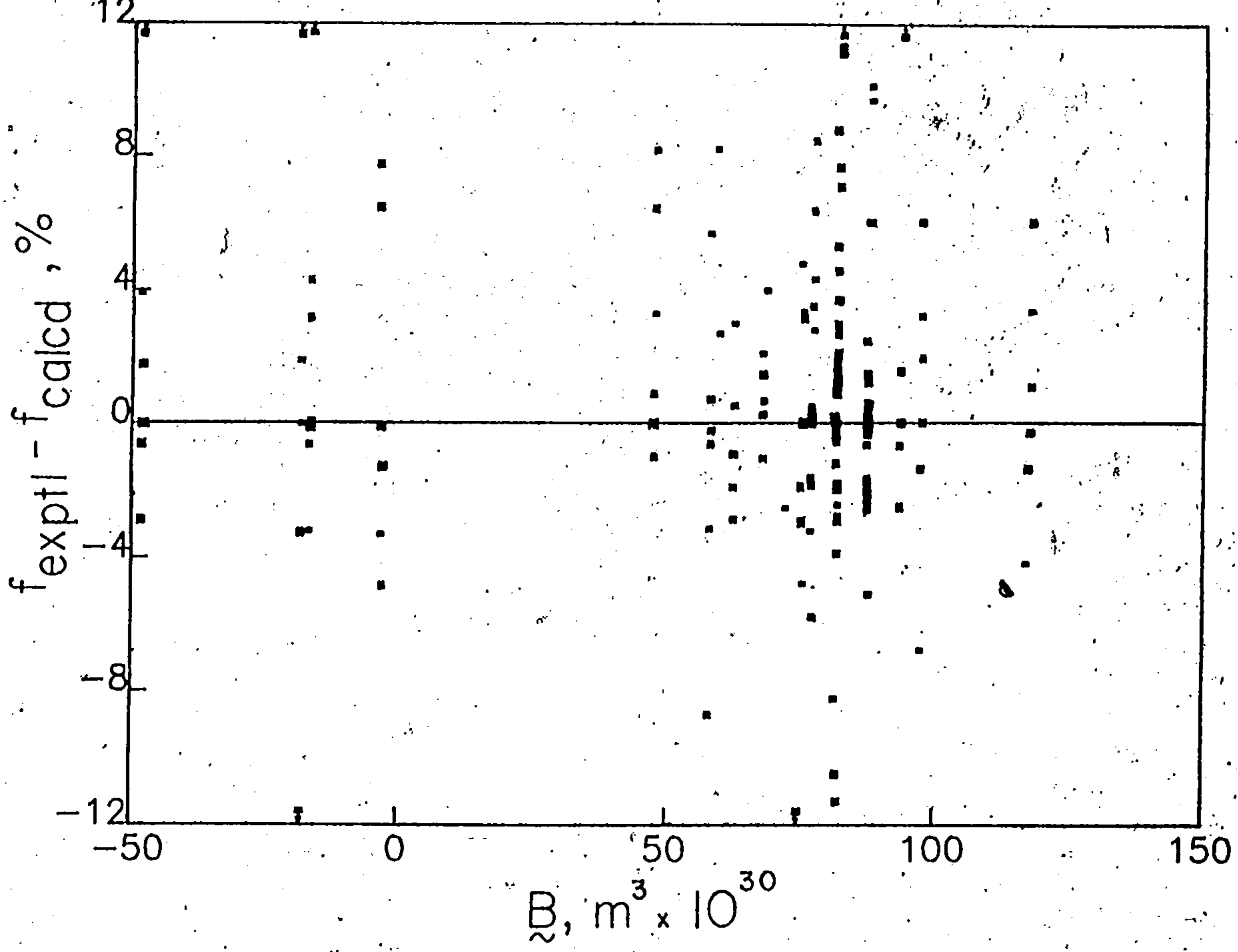

12
8
4
0
−4
−8
−12
−50
0
50
100
150
$f_{exptl} - f_{calcd}$, %
$\underset{\sim}{B}$, $m^3 \times 10^{30}$

Figure 4-8

Residuals for Separation Plotted with the Parameter $\underset{\sim}{A}$ for Inorganic Salts in Methanol Solutions

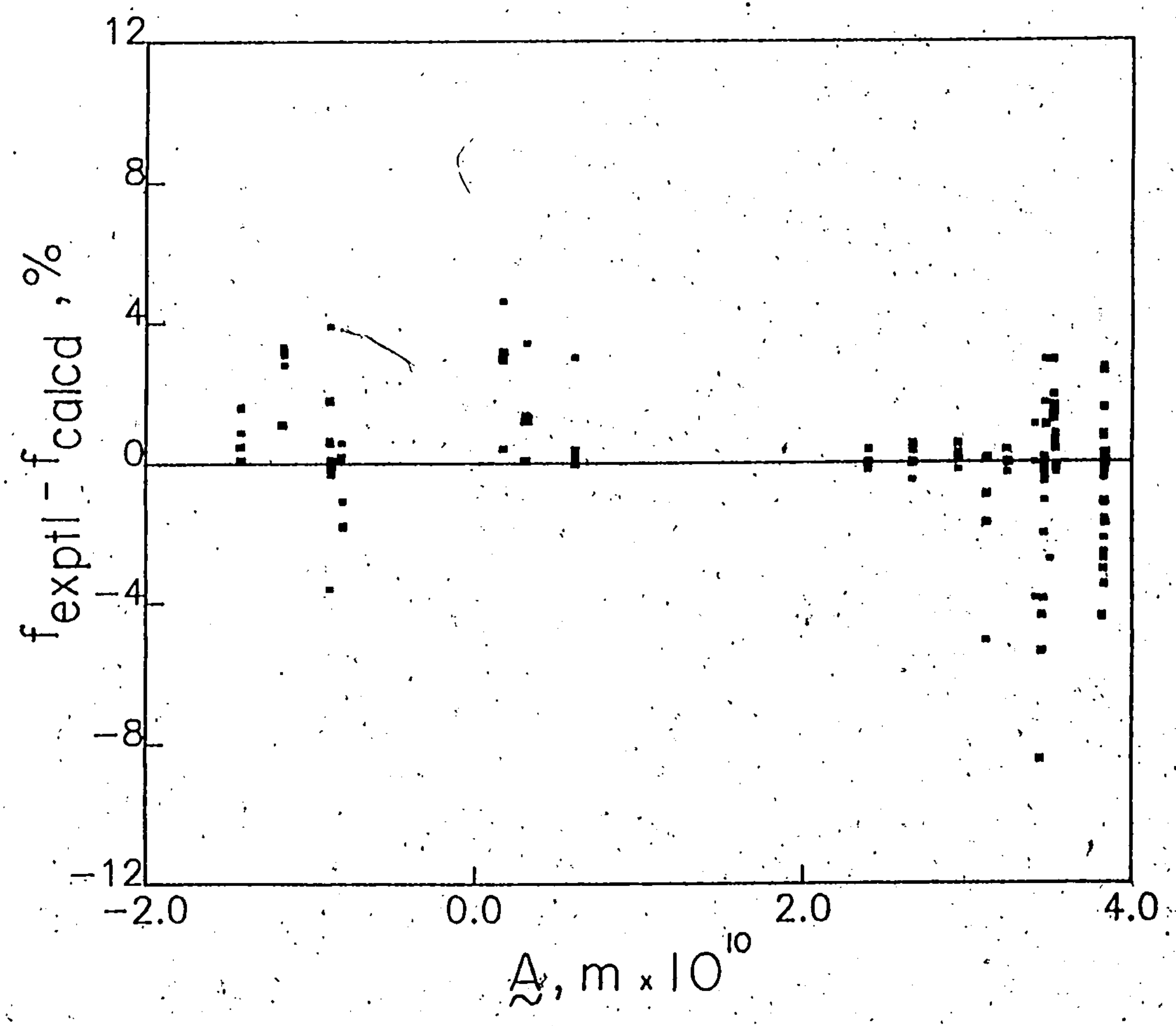
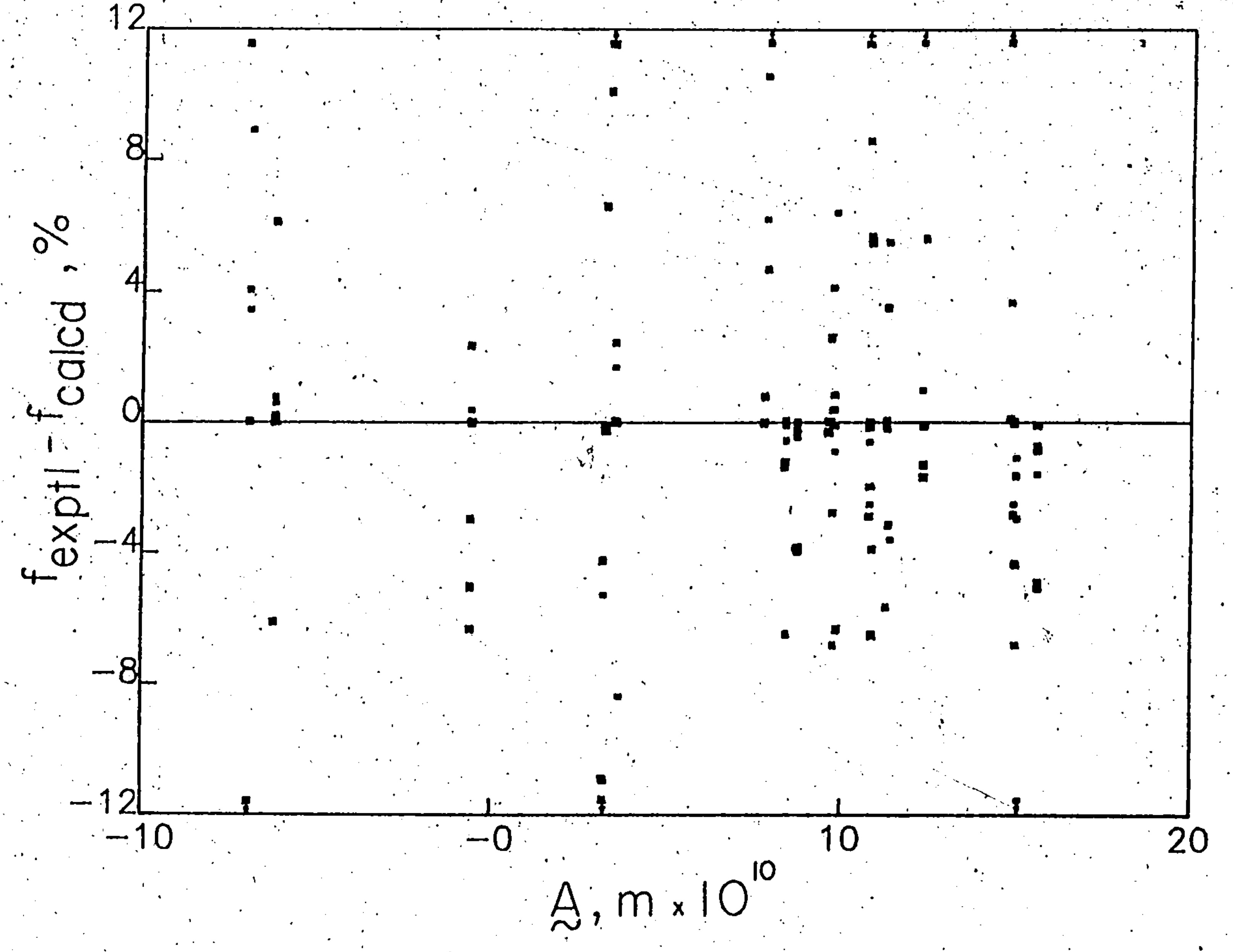

12
8
4
0
−4
−8
−12
−2.0
0.0
2.0
4.0
$f_{exptl} - f_{calcd}$, %
$\underset{\sim}{A}$, m × 10^{10}

Figure 4-9

Residuals for Separation Plotted with the Parameter $\underset{\sim}{A}$
for Inorganic Salts in Ethanol Solutions


12
8
4
0
−4
−8
−12
−10
−0
10
20
$f_{exptl} - f_{calcd}$, %
$\underset{\sim}{A}$, m × 10^{10}

For the organic solutes in methanol solutions, the SSR was 1479.8 for 107 residuals and 3 model parameters. The estimated of s_p^2 was 4.08 and γ_p was 12 as in Chapter 3. Equation 3-57 is calculated as

$$(\frac{1479.8}{107-3})/4.08 = 3.45$$

and $F_{105,12,.01}$ is estimated as 3.45. For the inorganic solutes, SSR is 1285 for 93 residuals and 3 model parameters. Equation 3-57 is calculated as

$$(\frac{1285}{93-3})/4.08 = 3.50$$

and $F_{90,12,.01}$ is estimated as 3.45.

The methanol results easily pass the test, but the ethanol results are just on the verge of passing this test. Since the test is only a coarse indication of the success of nonlinear models, it is considered that the ethanol results are sufficient.

In order to determine the precision of the parameters used in the surface potential - pore flow model, several replicate experiments for each solute would have had to be performed. In the absence of these replicate experiments, an indication of the sensitivity of the response with respect to the parameters was determined by altering their values and observing the changes in the model's response. In the case of dilute solutions, the response of interest is the solute separation. To demonstrate the sensitivity of the model to the surface potential parameters, upper and lower limits for $\underset{\sim}{D}$, $\underset{\sim}{B}$, and $\underset{\sim}{A}$ were determined for an approximate ±0.03 variation of the calculated separation (f_{calcd}). This is an arbitrarily selected range which was chosen to demonstrate the corresponding ranges of the parameters. They are shown in Table 4-10 for the methanol case and in Table 4-11 for the ethanol case.

From these calculations, the range of $\underset{\sim}{B}$'s and $\underset{\sim}{A}$'s which can be tolerated for a ±0.03 range of f_{calcd} are large enough to suggest that they can be confidently used to model reverse osmosis performance. However, for the case of $\underset{\sim}{D}$, a greater sensitivity was observed, which suggests that it is a more influential parameter than $\underset{\sim}{B}$ or $\underset{\sim}{A}$.

Table 4-10

Parameter Ranges for Solutes in Dilute Methanol Solutions That Calculate an Approximate ±0.03 Range of f_{calcd}

Solute	Parameter	Parameter's[a] Values	f_{calcd}[b]	f_{exptl}[b]
n-Butyramide	$+\underset{\sim}{B}$	-20	0.147	0.167
	$\underset{\sim}{B}^c$	0.0	0.179	
	$-\underset{\sim}{B}$	25	0.204	
	$+\underset{\sim}{D}$	2.79	0.204	
	$\underset{\sim}{D}^c$	2.66	0.179	
	$-\underset{\sim}{D}$	2.41	0.143	
s-Butylbenzene	$+\underset{\sim}{B}$	-30.0	0.170	0.203
	$\underset{\sim}{B}^c$	-50.40	0.200	
	$-\underset{\sim}{B}$	-70.0	0.233	
	$+\underset{\sim}{D}$	2.63	0.170	
	$\underset{\sim}{D}^c$	2.48	0.200	
	$-\underset{\sim}{D}$	2.05	0.231	
NaI	$+\underset{\sim}{A}$	1.2	0.511	0.543
	$\underset{\sim}{A}^c$	0.602	0.541	
	$-\underset{\sim}{A}$	0.0	0.572	
	$+\underset{\sim}{D}$	3.33	0.577	
	$\underset{\sim}{D}^c$	3.29	0.541	
	$-\underset{\sim}{D}$	3.25	0.510	

[a] $\underset{\sim}{B}$ has units of $m^3 \times 10^{-30}$, $\underset{\sim}{D}$ in $m \times 10^{-10}$, and $\underset{\sim}{A}$ in $m \times 10^{-10}$.

[b] For methanol solutions and membrane number 7.

[c] As reported previously.

Table 4-11

Parameter Ranges for Solutes in Dilute Ethanol Solutions That Calculate an Approximate ±0.03 Range of f_{calcd}

Solute	Parameter	Parameter's[a] Values	f_{calcd}[b]	f_{exptl}[b]
s-Butylbenzene	$+\underset{\sim}{B}$	-36.0	0.170	0.165
	$\underset{\sim}{B}$[c]	-49.23	0.190	
	$-\underset{\sim}{B}$	-63.0	0.219	
	$+\underset{\sim}{D}$	2.57	0.227	
	$\underset{\sim}{D}$[c]	2.53	0.190	
	$-\underset{\sim}{D}$	2.48	0.159	
t-Butylbenzene	$+\underset{\sim}{B}$	-21.0	0.168	0.191
	$\underset{\sim}{B}$[c]	-3.13	0.205	
	$-\underset{\sim}{B}$	15.0	0.234	
	$+\underset{\sim}{D}$	2.69	0.237	
	$\underset{\sim}{D}$[c]	2.66	0.205	
	$-\underset{\sim}{D}$	2.61	0.163	
NaI	$+\underset{\sim}{A}$	0.64	0.858	0.795
	$\underset{\sim}{A}$[c]	-0.64	0.824	
	$-\underset{\sim}{A}$	-1.50	0.797	
	$+\underset{\sim}{D}$	4.00	0.799	
	$\underset{\sim}{D}$[c]	3.86	0.824	
	$-\underset{\sim}{D}$	3.75	0.850	
CsBr	$+\underset{\sim}{A}$	8.50	0.624	0.598
	$\underset{\sim}{A}$[c]	7.80	0.591	
	$-\underset{\sim}{A}$	7.20	0.572	
	$+\underset{\sim}{D}$	2.66	0.623	
	$\underset{\sim}{D}$[c]	2.62	0.591	
	$-\underset{\sim}{D}$	2.58	0.562	
$NaClO_4$	$+\underset{\sim}{A}$	-6.10	0.601	0.400
	$\underset{\sim}{A}$[c]	-6.87	0.571	
	$-\underset{\sim}{A}$	-7.50	0.543	
	$+\underset{\sim}{D}$	3.92	0.602	
	$\underset{\sim}{D}$[c]	3.82	0.571	
	$-\underset{\sim}{D}$	3.73	0.541	

[a] $\underset{\sim}{B}$ has units of $m^3 \times 10^{-30}$, $\underset{\sim}{D}$ in $m \times 10^{-10}$, and $\underset{\sim}{A}$ in $m \times 10^{-10}$.

[b] For ethanol solutions and membrane number 1.

[c] As reported previously.

Conclusion

The reverse osmosis separation of organic solutes in alcohol solutions has been demonstrated by this work. Again, this is evidence that reverse osmosis can be extended to nonaqueous cases, and can be used for the upgrading and purification of nonaqueous systems. As well, the validity of using a single reverse osmosis model to describe performance in various solvent systems has been demonstrated, both for the surface potential-pore flow model discussed here and the Kimura-Sourirajan model discussed previously.

The comparison of $\underset{\sim}{B}$ and Γ_A/c_A for all three solvents may represent a method of predicting surface potential parameters in other solvents given data for Γ_A/c_A on cellulose acetate. This is of interest in cases where if given values of $\underset{\sim}{B}$ and Γ_A/c_A for a solvent system and Γ_A/c_A for a new solvent system, an estimate of $\underset{\sim}{B}$ in the new solvent can be made. Thus, the effort of developing membranes suitable for use in a new solvent can be directed toward the most promising cases. The attempt to obtain a similar relation for Γ_A/c_A and $\underset{\sim}{A}\cdot\varepsilon$ was not as successful, which may be a demonstration of a simplification of the surface potential-pore flow model in eq 4-2. The model treats salts as single entities and does not have the capacity to deal with ionic contributions. While this may be resolved by the modification of eq 4-2, the same treatment of Γ_A/c_A does not appear to be as amenable to this.

Chapter 5

Reverse Osmosis Separation of Inorganic and Organic Solutes in Aqueous Solutions by Cellulose Membranes

Introduction.

Almost all of the polymer membranes that are used for reverse osmosis processes are made from polymer solutions by a casting process. This requires a solvent or a solvent system that is capable of dissolving the polymer and can be removed to leave a solid polymer matrix. As an example, the cellulose acetate membranes used previously were made from the cellulose acetate-acetone polymer solution. The acetone was removed by evaporation and water gelation. However, there has been little success in the preparation of small pore reverse osmosis membranes of cellulose material which can be explained by the lack of a suitable nondegrading solvent.

Cellulose itself has interesting properties for membrane uses as shown by the work of Matsuura et al. (1976; 1981; 1982). These include a strong adsorption of water and solvent resistance which would be necessary for nonaqueous reverse osmosis. For these reasons, small pore reverse osmosis membranes have been prepared with a new method to test their behaviour in aqueous and nonaqueous solutions.

Cellulose Dissolution. Several methods are available to dissolve cellulose but the major disadvantages of these are the irreversible modification of the cellulose and low solubility limits. Most methods that are used for dissolution involve a regeneration step to obtain the precipitated polymer where regeneration is defined as a precipitation of cellulose caused by the removal of one of the substituents of the solutions (Nissan and Hunger, 1965; Turbak et al., 1980). The dissolution method that was finally chosen for the cellulose membranes used here is based on the work of Johnson et al. (1976). It consists of using dimethyl sulphoxide (DMSO) as a solvent for methylol cellulose. Methylol cellulose is formed by the reaction of formaldehyde and cellulose in an aprotic solvent (DMSO in this case). The methylol cellulose reverts to cellulose in water or aprotic solvent. The reaction scheme occurs as

$$\text{Cellulose+formaldehyde} \xrightarrow{\text{DMSO}} \text{Methylol Cellulose} \xrightarrow{H_2O} \text{Cellulose} \qquad (5\text{-}1)$$

Johnson et al. (1976) studied the regenerated product by X-ray diffraction, infrared and Raman spectroscopy and found the solid was amorphous in nature and of a high degree of polymerization.

Recent work by Uragami et al. (1982a; b) describe the use of similar solutions but at lower cellulose concentrations to make hemodialysis membranes. The solutes and operating conditions studied by them do not overlap with the results of this work and a direct comparison cannot be made. However, the membranes used in this work appear to have smaller pores than those of Uragami et al. (1982 a;b) as based upon the separation of polyethylene glycol solutions. They obtained no separation of polyethylene glycol of 200 molecular weight (PEG 200) and 50-60% separation of PEG 1000 while the membranes produced in this work were capable of 40-60% separation of PEG 200 and 65 to 90% separation of PEG 1000. As well, solutions of upwards of 15% by weight of cellulose in DMSO were prepared, which appears to exceed the concentrations reported by Uragami et al. (1982 b).

Asymetric Membrane Fabrication. Known weights of Cellulose (CE) powder, PF powder and DMSO were slurried at room temperature in a flask that was closed off from the atmosphere except for an atmospherically cooled condenser tube to prevent the loss of solvent. The flask was placed in an oil bath which was heated up to 125° ± 2°C in combination with vigorous stirring. As the temperature of the bath exceeded 105°C, gas bubbles were observed in the agitated slurry, presumably caused by the decomposition of the PF to form formaldehyde gas. As well, the slurry's viscosity increased as observed by the labouring of the stirring motor. At the outset of bubble formation, the mixture was opaque but after a 30 minute period the solution became clearer. The solution was held at this temperature for 1½ hours in combination with continual stirring. The flask was then sealed off from the atmosphere. At this point the solution was transparent with gas bubbles and residual PF solids. This solution was pressure filtered to remove the solids and was left to stand overnight to let the bubbles rise.

Because of the repolymerization of the formaldehyde when it cooled, there was a crust deposited on the cold surfaces. To counter this, the flask was equipped with a female ground glass joint into which the atmospherically cooled condenser tube was inserted. The flask was then immersed as fully as possible into the oil bath , with the oil level approximately halfway up the ground glass joint. When the reaction was completed, the flask was left in the oil to cool, so that a crust would not be formed except in the tube. The flask was taken from the cooled oil bath and the tube was gently removed from the mouth of the flask and replaced by a ground glass stopper. This procedure reduced the amount of solid PF particles in the polymer solution, and facilitated its filtration.

The membranes were cast on a smooth glass plate edged with poly vinyl chloride electrical tape to control the casting thickness. The solution was poured on the plate and spread in one continuous drawing motion with a glass rod. The plate was immediately placed in a preheated oven at a controlled temperature to evaporate DMSO solvent. At the high oven temperatures there was no evidence of gas bubbles that could have been caused by the PF. When the evaporation time was complete the glass plate was immediately placed in the gelation solution. In the cases of aprotic gelation solvents which do not cause cellulose regeneration, the glass plates were left for $1^3/_4$ hours and were then solvent exchanged to a protic solvent to regenerate the cellulose. The membranes produced were transluscent and were 0.17 mm in thickness. They were cut into discs and their orientation was conserved despite their resistance to marker pen inks while they were stored in 20% ethanol-water solutions. For the reverse osmosis experiments, the membranes were used in this "as-cast" condition. Membrane compositions and fabrication details are shown in Table 5-1 for the aqueous reverse osmosis experiments considered in this chapter. It should be noted that the presence of water in the slurry will prevent the dissolution from occurring. For these experiments, the cellulose powder was stored in a dessicator after removal from the original container.

Table 5-1

Cellulose Reverse Osmosis Membrane Compositions and Casting Details

Membrane No.	1	2	3	4	5	6
Cellulose, g	17.53	17.53	17.96	17.96	8.33	8.33
DMSO, g	108.15	108.15	113.75	113.75	53.78	53.78
Paraformaldehyde, g	17.25	17.25	17.65	17.65	8.15	8.15
Evaporation Temp, °C	175	175	152	152	122	140
Evaporation Time, min	10	10	10	10	10	10
Gelation Solvent[a]	EtOH	EtOH	i-PrOH	i-PrOH	--	--
Gelation Time, min.	105	105	105	--	--	--
Regeneration Solvent[a]	H_2O	H_2O	H_2O	H_2O	H_2O	H_2O

[a] H_2O = Water, EtOH = Ethanol, i-PrOH = i-propanol. Room Temperature gelation solutions in all cases.

Reverse Osmosis Evaluation with Kimura-Sourirajan Analysis. The reverse osmosis membranes described above were tested by reverse osmosis experiments in aqueous solutions and in ethanol-heptane mixtures as discussed later. For the case of aqueous salt solutions, the mass transfer coefficient was determined by performing several reverse osmosis experiments with 0.050 molal NaCl solutions (Table A-1-7, Run No.'s 5, 28, 48, 69). The data obtained from these experiments was analyzed with the Kimura-Sourirajan method of analysis as before to obtain the mass transfer coefficients which were plotted in Fig 5-1. A first order linear equation was fitted to the data to give

$$k = 1.592\ A - 8.057 \times 10^{-6} \qquad (5\text{-}2)$$

with a correlation coefficient of 0.578.

Data from reverse osmosis experiments at 25°C and 6900 kPag operating pressure with 10 alkali metal halide salts in the concentration range of 0.0045 ± 0.0007 molal were used to calculate $(D_{AM}/K\delta)$'s as shown in Table 5-2 by using data from Table 5-3 to modify the mass transfer coefficient by the Schmidt-Sherwood equation. These were used to determine the modified Born equation parameters of Table 5-4 and the appropriate $(-\Delta\Delta G/RT)_i$ values in Table 5-5. The porosities, $\ln C^{*}_{NaCl}$, of the membranes were calculated as before and these are shown in Table 5-6. Other reverse osmosis data in the same concentration range were available for other salts. These were analyzed to give the $(D_{AM}/K\delta)$ values of Table 5-7 and in

Figure 5-1

Mass Transfer Coefficient with Solvent Permeability Constant for Cellulose Membranes and Aqueous NaCl Solutions

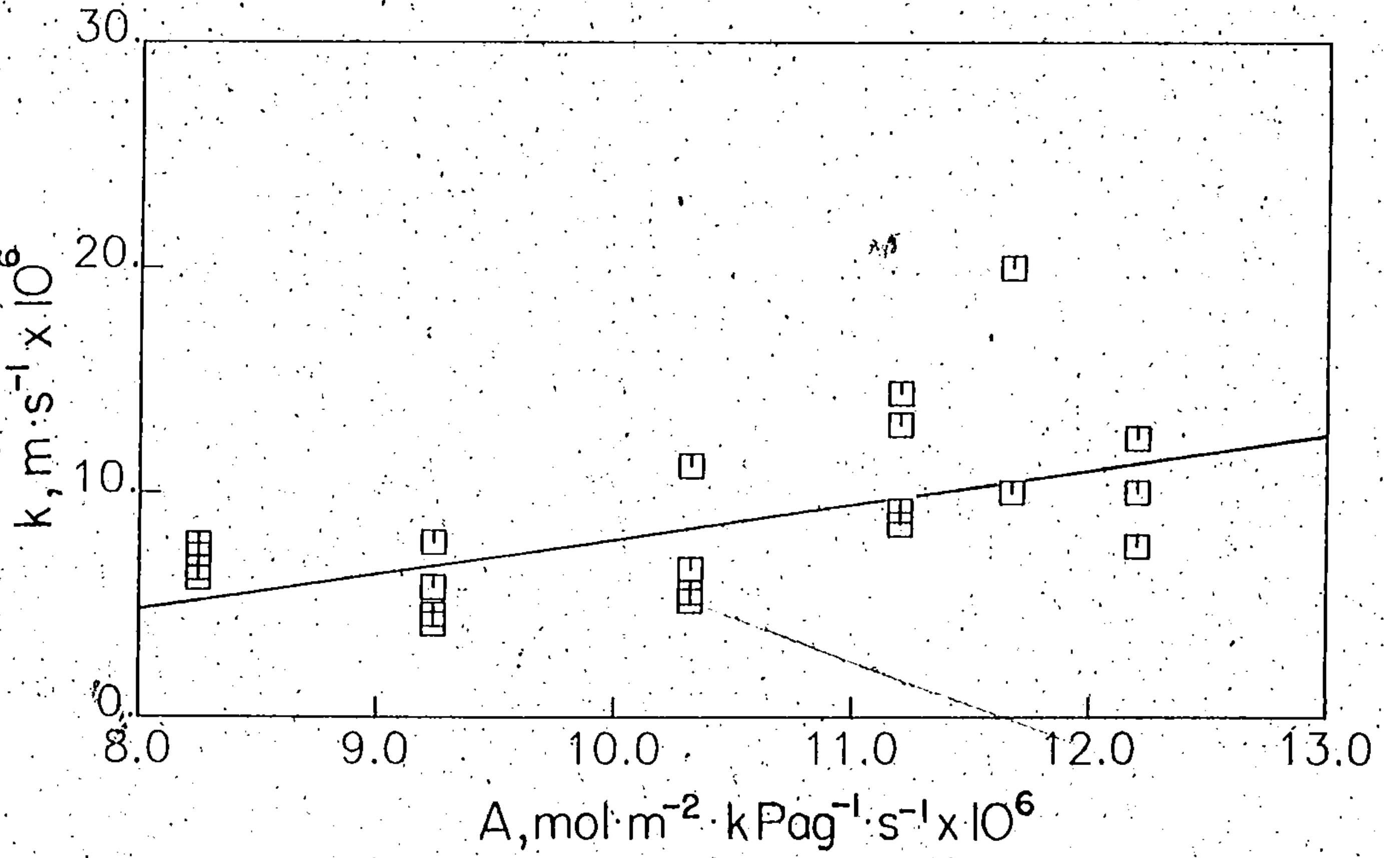

30
20
10
0
8.0
9.0
10.0
11.0
12.0
13.0
k, m·s⁻¹ x 10⁶
A, mol·m⁻²·kPag⁻¹·s⁻¹ x 10⁶

Table 5-2

$(D_{AM}/K\delta)$ for Alkali Metal Halide Salt in Aqueous Solutions with Cellulose Membranes at 6900 kPag, 25°C, and 0.0045 ± 0.0007 Molal

Salt	$(D_{AM}/K\delta) \times 10^7$, m/s					
	1	2	3	4	5	6
LiF	4.178	4.864	7.010	6.230	19.05	7.366
NaF	4.211	4.785	6.547	5.834	14.76	6.584
NaCl	9.480	8.634	10.88	10.02	27.83	12.39
NaBr	9.035	9.465	13.33	11.90	29.74	14.32
NaI	8.840	9.276	12.65	11.11	26.31	12.52
KCl	11.81	8.541	10.61	9.562	21.37	12.92
KBr	9.918	11.18	14.31	12.73	24.78	12.70
RbCl	8.334	9.077	11.84	10.44	22.24	11.32
CsCl	11.67	14.04	11.77	17.72	19.93	11.03
CsBr	9.771	11.88	16.52	13.25	25.25	12.16

Table 5-3

Diffusion Coefficients at Infinite Dilution for Salts in Aqueous Solutions

Salt	D°_{AB} [a], $m^2/s \times 10^{10}$
LiF	12.13
LiCl	13.67
LiBr	13.78
NaF	14.01
NaCl	16.11
NaBr	16.26
NaI	16.16
KF	16.83
KCl	19.95
KBr	20.19
RbCl	20.52
RbBr	20.76
CsCl	20.45
CsBr	20.70
NH_4Cl	19.93
$MgCl_2$	12.50
$CaCl_2$	13.36
$SrCl_2$	13.96
$BaCl_2$	13.87
$NaNO_2$	14.29
$NaNO_3$	15.68
$NaClO_3$	15.03
$NaBrO_3$	14.06
NaSCN	15.68
$NaIO_3$	11.93
Na_2SO_4	12.30
Na_2HPO_4	11.84
$MgSO_4$	8.49

[a] Matsuura et al., 1975.

Table 5-4

Modified Born Equation Parameters for Alkali Metal Halides in Aqueous Solutions at 6900 kPag, 25°C, Cellulose Membranes, and 0.0045 ± 0.0007 Molal

Ion	E_B[a], $\mathrm{kJ \cdot m \cdot mol^{-1} \times 10^{10}}$	Δ_B[a], $\mathrm{m \times 10^{10}}$	E_I, $\mathrm{kJ \cdot m \cdot mol^{-1} \times 10^{10}}$	Δ_I, $\mathrm{m \times 10^{10}}$
Alkali Metal Cations	761.5	0.890	748.1	0.873
Halide Anions	504.2	-0.200	518.0	-0.173

[a] Matsuura et al., 1975.

Table 5-5

$(-\Delta\Delta G/RT)_i$ for Ions in Aqueous Solutions with Cellulose Membranes at 25°C and 0.0045 ± 0.0007 Molal

Ion	r_i, m x 10^{10}	$(-\Delta\Delta G/RT)_i$
Li^+	0.60	-1.32[a]
Na^+	0.95	-1.42[a]
K^+	1.33	-1.40[a]
Rb^+	1.48	-1.37[a]
Cs^+	1.69	-1.33[a]
NH_4^+	1.48	-1.58
Mg^{++}	0.65	-1.83
Ca^{++}	0.99	-1.63
Sr^{++}	1.13	-1.43
Ba^{++}	1.35	-1.40
F^-	1.36	0.67[a]
Cl^-	1.81	1.30[a]
Br^-	1.95	1.36[a]
I^-	2.16	1.38[a]
NO_2^-	-	1.35
NO_3^-	-	1.21
SCN^-	-	0.95
ClO_3^-	-	0.83
BrO_3^-	-	0.78
IO_3^-	-	0.51
$SO_3^=$	-	0.98
$SO_4^=$	-	1.07

[a] Calculated by the Modified Born Equation Parameters of Table 5-4.

Table 5-6

Parameter ℓnC^* Representing the Porosity of Cellulose Membranes at 25°C and 6900 kPag

Membrane	ℓnC^*	(PSP)[a], g/h	A, $mol \cdot m^{-2} \cdot s^{-1} \cdot kPag^{-1} \times 10^6$
1	-13.75	5.45	9.239
2	-13.84	6.09	10.32
3	-13.61	6.91	11.81
4	-13.69	6.61	11.21
5	-12.67	7.19	12.35
6	-13.48	4.86	8.240

[a] for 13.2 cm^2 surface area.

Table 5-7

$(D_{AM}/K\delta)$ for Salts in Aqueous Solutions with Cellulose Membranes at 6900 kPag, 25°C and 0.0045 ± 0.0007 Molal

Salt	$(D_{AM}/K\delta) \times 10^7$, m/s					
	1	2	3	4	5	6
$MgCl_2$	29.68	21.33	36.63	32.17	58.48	25.01
$CaCl_2$	24.85	25.56	42.60	38.72	65.89	28.79
$SrCl_2$	27.42	48.46	48.59	64.28	79.17	31.28
$BaCl_2$	31.08	32.22	49.08	75.68	70.54	31.17
$NaNO_2$	51.27	8.615	12.68	22.84	33.29	11.53
$NaNO_3$	7.291	8.493	10.88	9.663	22.08	11.58
NaSCN	6.681	7.639	8.106	7.171	15.53	7.694
$NaClO_3$	4.753	7.176	7.465	12.63	16.31	7.371
$NaBrO_3$	7.341	5.807	7.298	7.125	14.47	7.140
$NaIO_3$	6.566	4.464	5.675	4.270	11.39	5.766
Na_2SO_3	1.353	1.623	2.019	1.721	6.933	1.872
Na_2SO_4	2.190	1.785	2.027	1.702	6.801	2.346
NH_4Cl	8.829	8.506	10.89	9.667	20.52	9.694
$MgSO_4$	1.880	2.224	4.249	6.787	12.87	4.055

conjunction with the ℓnC^*_{NaCl} and $(-\Delta\Delta G/RT)_i$ information of Tables 5-6 and 5-5, their $(-\Delta\Delta G/RT)_i$ values were calculated and included in Table 5-5. The data contained in these Tables was then used to calculate the reverse osmosis performance of these experiments and they are compared with the experimental separations in Table 5-8.

To demonstrate the unchanging surface porosity of the membranes, $\ln C^*_A$'s were compared for the alkali metal halide salts. As before, experimental $(D_{AM}/K\delta)$ data were used with eq 3-15 to determine the $\ln C^*_A$'s shown in Table 5-9. The agreement of the values shown in the table confirms the assumption of constant surface porosity used in the Kimura-Sourirajan analysis.

The free energy parameters for the ions studied were compared with the corresponding data for aqueous solutions and membranes made of cellulose acetate (39.8% acetylated) and polyamidohydrazide copolymer (PPPH 8273) (Sourirajan and Matsuura, 1979) in Fig 5-2 for the cations and Fig 5-3 for the anions. These figures show that for monovalent ions of either positive or negative charge there is either an identical relation or close analogy for the monovalent ions. However, the divalent cations are distinctly different where the cellulose membranes show positive $\Delta(-\Delta\Delta G/RT)_i$ values while the cellulose acetate membranes give negative ones. The effect of this is that divalent cation salt separation with respect to the NaCl reference salt would be less with cellulose membranes. A similar variation is observed for the divalent anion, $SO_4^{=}$,

Table 5-8

Comparison of Experimental and Calculated Reverse Osmosis Separations for Aqueous Solutions with Cellulose Membranes at 6900 kPag, 25°C, and 0.0045 ± 0.0007 Molal

Salt	1		2		3		4		5		6	
	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd
LiF	68.7	65.5	67.8	65.1	63.0	64.3	63.8	63.4	39.9	48.3	51.6	52.8
NaF	68.9	66.1	68.6	65.6	65.2	68.7	65.6	63.9	47.0	48.8	55.1	53.5
NaCl	55.2	53.9	55.9	53.3	53.7	52.3	53.7	51.5	33.0	36.3	41.5	41.0
NaBr	50.6	52.5	51.3	51.9	47.8	50.8	48.2	50.0	30.7	35.0	36.4	39.6
NaI	52.6	51.9	52.3	51.3	49.0	50.3	50.0	49.5	33.3	34.5	39.7	39.1
KCl	46.1	54.2	51.6	53.5	50.4	52.4	50.4	51.6	35.9	36.4	41.2	41.3
KBr	50.1	52.7	49.3	53.0	47.0	50.9	47.6	50.1	35.1	35.0	40.0	39.9
RbCl	54.0	53.5	54.2	52.8	51.6	51.7	52.4	50.9	37.9	35.7	43.1	40.7
CsCl	53.1	52.5	45.5	51.8	52.3	50.7	43.8	49.9	39.5	34.8	43.8	39.7
CsBr	50.3	52.5	47.5	51.8	43.3	50.7	46.6	49.9	34.8	34.8	41.0	39.8
$MgCl_2$	24.1	31.6	32.3	31.2	24.8	30.4	25.4	29.6	17.7	18.5	24.1	21.4
$CaCl_2$	27.5	27.7	28.6	27.2	21.9	26.5	21.9	25.8	16.1	15.8	21.2	18.4
$SrCl_2$	26.6	23.8	18.1	23.5	20.2	22.8	14.8	22.2	13.8	13.3	20.2	15.6
$BaCl_2$	25.2	23.4	25.0	23.0	22.4	22.3	22.4	21.8	10.9	13.0	12.8	15.3
$NaNO_2$	16.3	52.2	56.6	51.7	49.4	50.7	39.2	49.9	27.7	34.9	39.3	39.3
$NaNO_3$	56.8	56.1	55.5	55.5	53.0	54.5	53.6	53.6	36.6	38.3	40.7	43.1
NaSCN	58.3	61.5	59.2	61.0	60.6	60.2	60.9	59.3	44.6	44.0	50.5	48.5
$NaBrO_3$	57.2	65.9	64.8	65.4	63.0	64.5	61.3	63.7	47.6	48.6	53.1	53.3
$NaClO_3$	67.3	65.0	62.5	64.4	62.5	63.5	55.3	62.7	44.0	47.5	43.8	52.3
$NaIO_3$	61.8	71.1	70.3	70.7	68.2	69.9	72.1	69.2	52.2	54.8	57.4	59.1
Na_2SO_3	87.8	86.5	88.3	86.2	85.6	85.8	86.5	85.4	73.2	75.9	76.4	79.0
Na_2SO_4	80.7	85.4	87.1	85.1	85.5	84.7	86.5	84.2	64.7	74.2	74.8	77.5
NH_4Cl	52.7	58.6	56.3	57.9	53.8	56.8	54.4	56.0	39.4	40.6	46.2	45.7
$MgSO_4$	84.4	77.0	82.5	76.8	75.5	76.3	63.4	75.6	48.3	62.7	64.6	66.1

Table 5-9

Verification of the Constancy of $\ln C_A^*$ for Cellulose Membranes and Aqueous Salt Solutions at 25°C, 0.0045 molal, and 6900 kPag

Salt	$\ln C_A^*$ for Membrane No.					
	1	2	3	4	5	6
LiF	-14.04	-13.89	-13.52	-13.64	-12.52	-13.47
NaF	-13.93	-13.80	-13.49	-13.60	-12.68	-13.48
NaCl	-13.75	-13.84	-13.61	-13.69	-12.67	-13.48
NaBr	-13.86	-13.81	-13.47	-13.58	-12.67	-13.40
NaI	-13.90	-13.85	-13.54	-13.67	-12.81	-13.55
KCl	-13.55	-13.87	-13.66	-13.76	-12.96	-13.46
KBr	-13.78	-13.66	-13.42	-13.53	-12.87	-13.54
RbCl	-13.93	-13.84	-13.58	-13.70	-12.95	-13.62
CsCl	-13.63	-13.45	-13.62	-13.21	-13.10	-13.69
CsBr	-13.87	-13.67	-13.34	-13.56	-12.92	-13.65

Figure 5-2

Comparison of $\Delta(-\Delta\Delta G/RT)_i$ for Cations in Aqueous Solutions and Cellulose, Cellulose Acetate, and PPPH 8273 Membranes

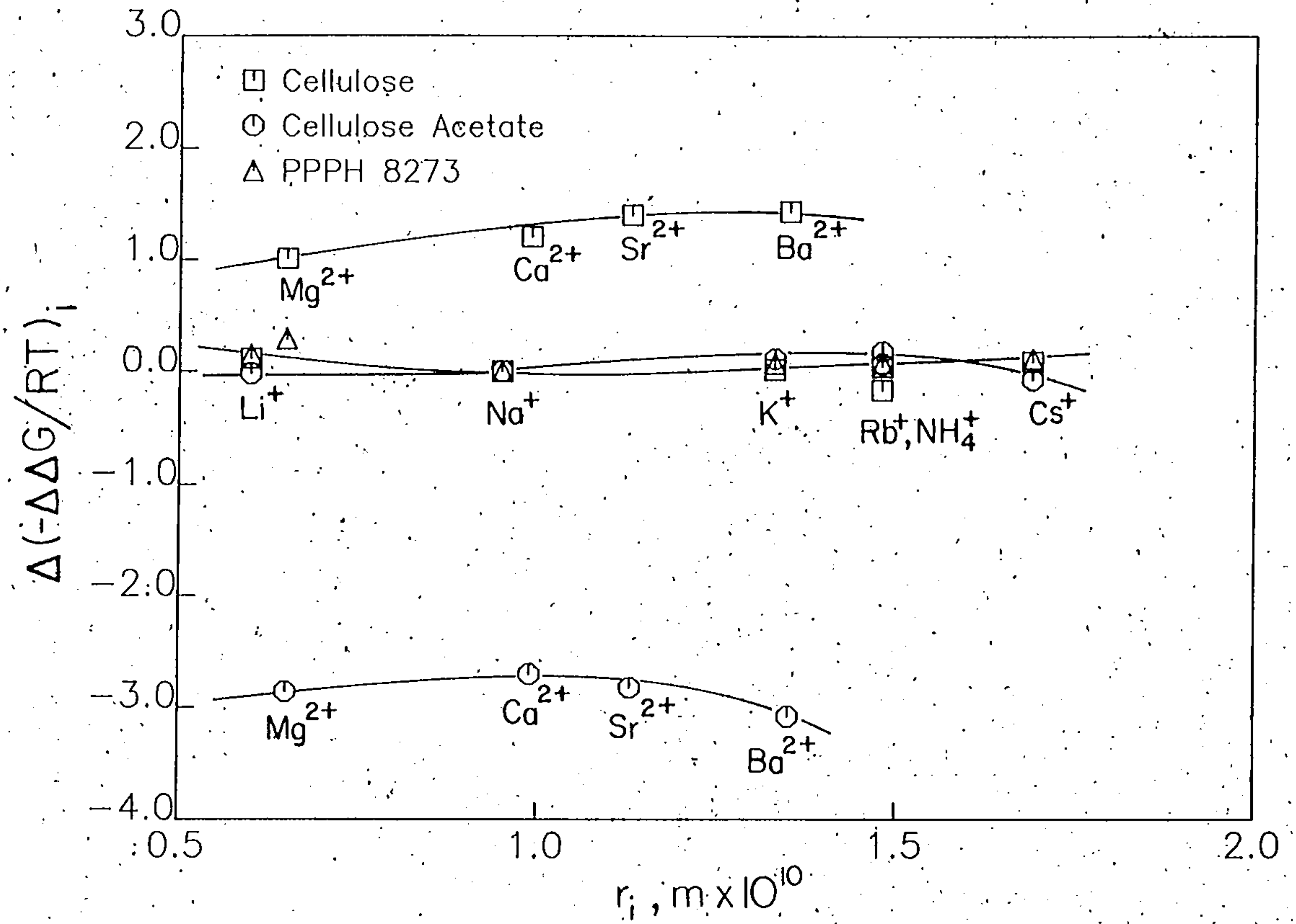
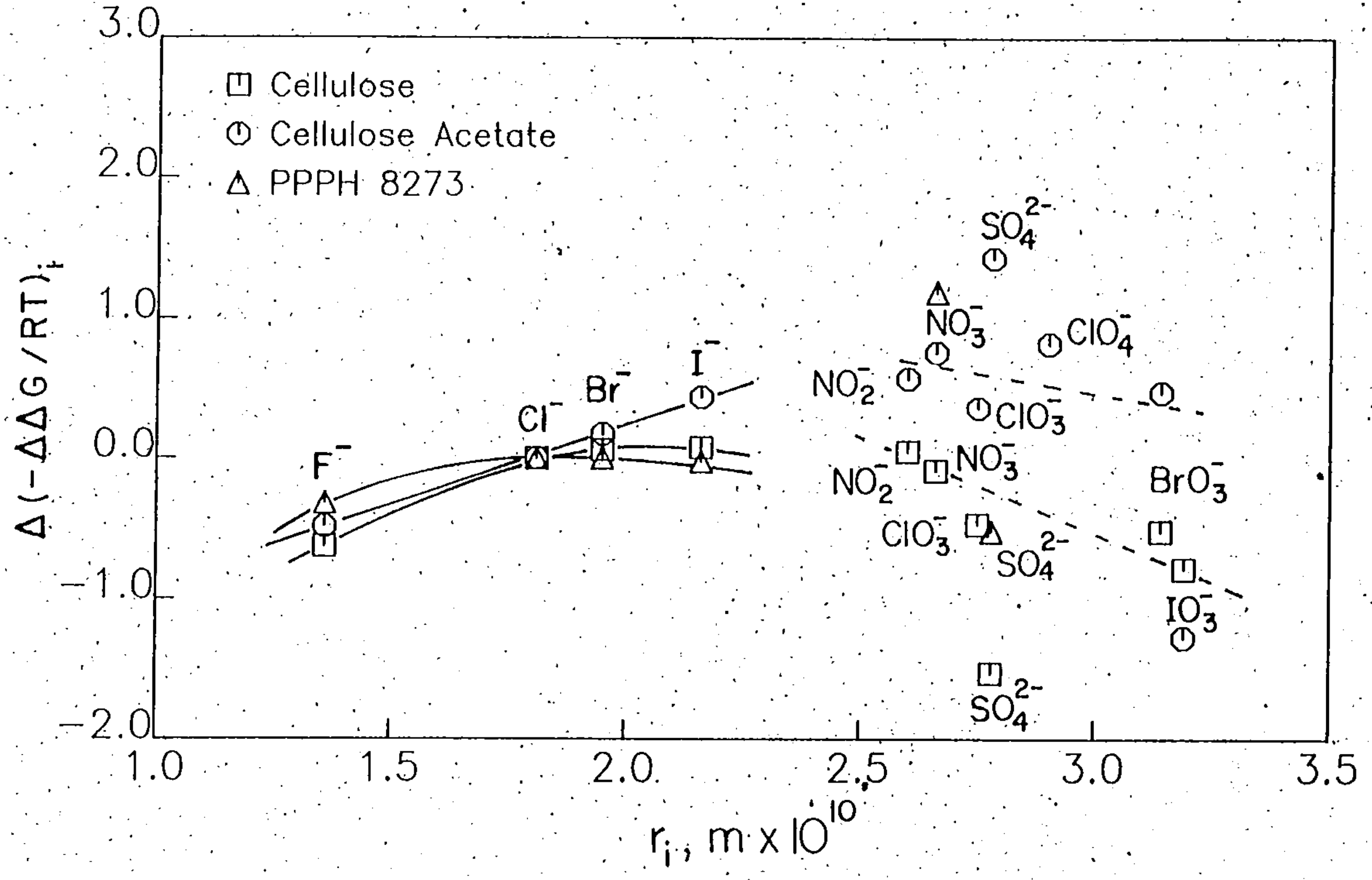

□ Cellulose
○ Cellulose Acetate
△ PPPH 8273
3.0
2.0
1.0
0.0
−1.0
−2.0
−3.0
−4.0
$\Delta(-\Delta\Delta G/RT)_i$
0.5
1.0
1.5
2.0
r_i, m x 10^{10}
Mg^{2+}
Ca^{2+}
Sr^{2+}
Ba^{2+}
Li^+
Na^+
K^+
Rb^+, NH_4^+
Cs^+
Mg^{2+}
Ca^{2+}
Sr^{2+}
Ba^{2+}

Figure 5-3

Comparison of $\Delta(-\Delta\Delta G/RT)_i$ for Anions in Aqueous Solutions and Cellulose, Cellulose Acetate, and PPPH 8273 Membranes


Cellulose
Cellulose Acetate
PPPH 8273
$\Delta(-\Delta\Delta G/RT)_i$
3.0
2.0
1.0
0.0
−1.0
−2.0
1.0
1.5
2.0
2.5
3.0
3.5
r_i, m x 10^{10}
F^-
Cl^-
Br^-
I^-
SO_4^{2-}
NO_3^-
ClO_4^-
NO_2^-
ClO_3^-
NO_2^-
NO_3^-
BrO_3^-
ClO_3^-
SO_4^{2-}
IO_3^-
SO_4^{2-}

with a reversal of the above trend with cellulose acetate membranes having positive values. Throughout, the PPPH 8273 membranes remain intermediate, but their data are limited.

The effect of concentration on $(D_{AM}/K\delta)$ for the salt solutions with the cellulose membranes is quite pronounced and appears to be related to the valence of the ions of which the salt is composed. This is demonstrated in Figs 5-4 to 5-7 for the solute transport parameters of NaCl, Na_2SO_4, $MgCl_2$ and $MgSO_4$. The $MgCl_2$ salt shows a large scatter of $(D_{AM}/K\delta)$ with boundary layer concentration, X_{A2}. It should be noted, however, that the scale in Fig 5-6 ($MgCl_2$) is magnified compared to Fig 5-4, -5, and -7. The other three salts show a change of $(D_{AM}/K\delta)$ with concentration which is similar to the observations of Yeager et al. (1981) for PPPH 8273 membranes. The same effect was not observed for cellulose acetate membranes as reported by Sourirajan (1970a).

Yeager et. al. (1981) described the variation of $(D_{AM}/K\delta)$ with a range of both X_{A2} and porosity, $\ell n C^*_{NaCl}$. Since the range of porosities for the cellulose membranes is small (see Table 5-6), this latter effect cannot be included. However, their analysis can be modified to describe the variation with concentration. The average slopes of the $\log(D_{AM}/K\delta)$ vs $\log(X_{A2})$ plots of Figs 5-4 to 5-7 are shown in Table 5-10. When they are combined with the value of $(D_{AM}/K\delta)$ at 0.0045 molal concentration they can be used to calculate reverse

Figure 5-4

Variation of $(\frac{D_{AM}}{K\delta})$ with Concentration for NaCl and Cellulose Membranes

Symbol	Membrane No.
□	1
○	2
△	3
+	4
×	6

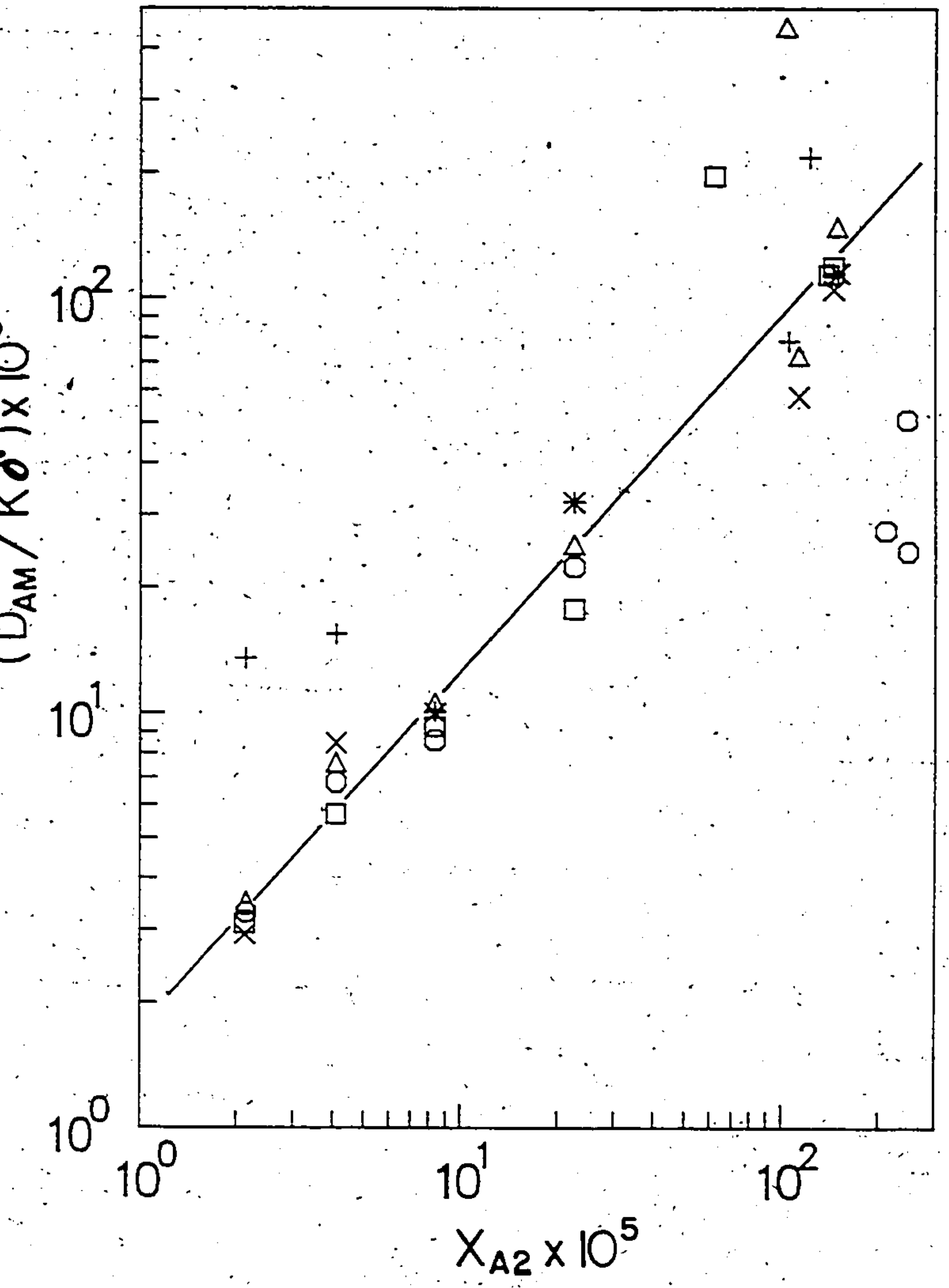
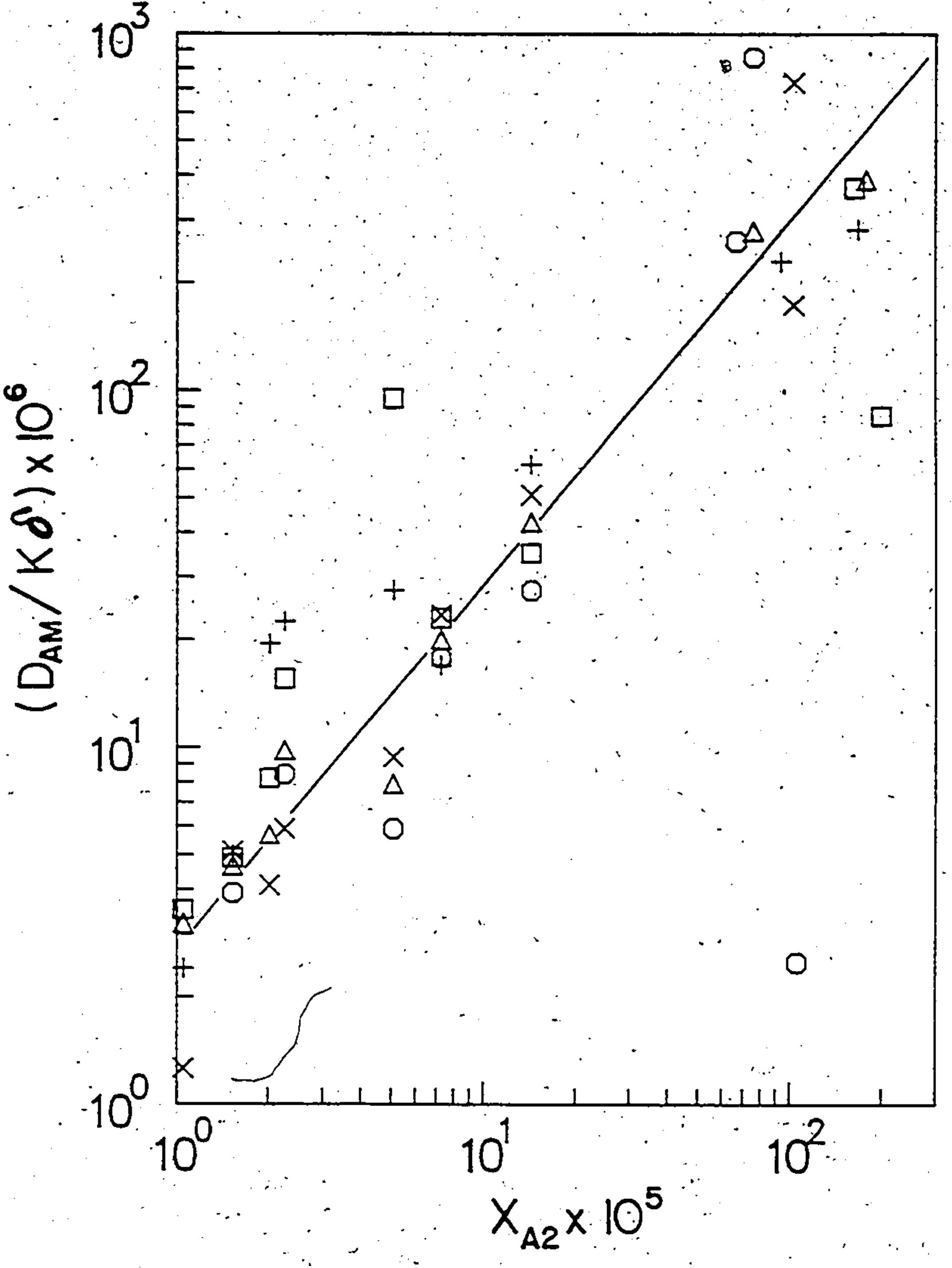

$(D_{AM}/K\delta) \times 10^5$
10^0
10^1
10^2
10^0
10^1
10^2
$X_{A2} \times 10^5$

Figure 5-5

Variation of $\left(\frac{D_{AM}}{K\delta}\right)$ with Concentration for Na_2SO_4 and Cellulose Membranes

Symbol	Membrane No.
□	1
○	2
△	3
+	4
×	6

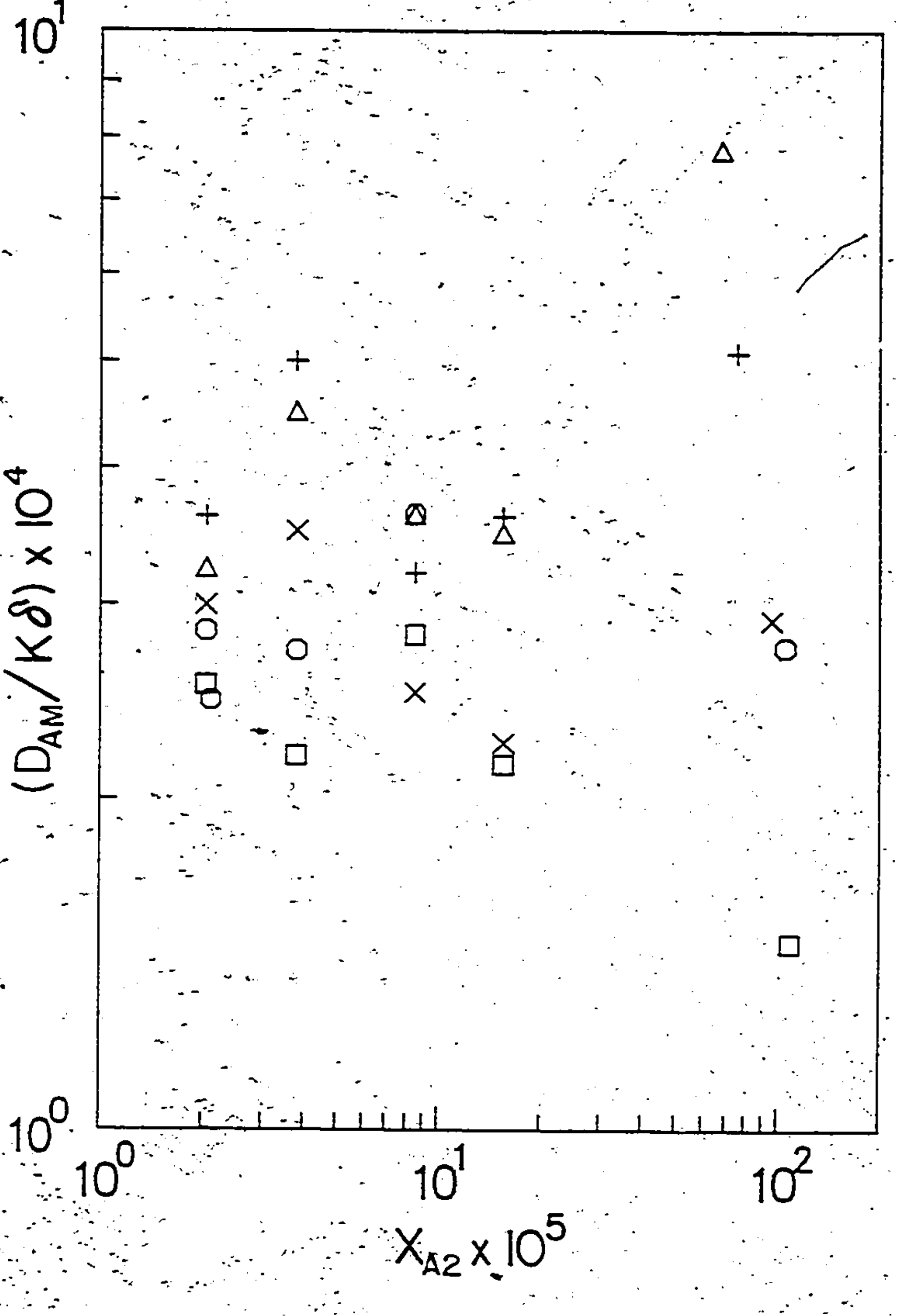


10^3
10^2
10^1
10^0
$(D_{AM}/K\delta)\times10^6$
10^0
10^1
10^2
$X_{A2}\times10^5$

Figure 5-6

Variation of $\left(\frac{D_{AM}}{K\delta}\right)$ with Concentration for $MgCl_2$ and Cellulose Membranes

Symbol	Membrane No.
□	1
○	2
△	3
+	4
×	6



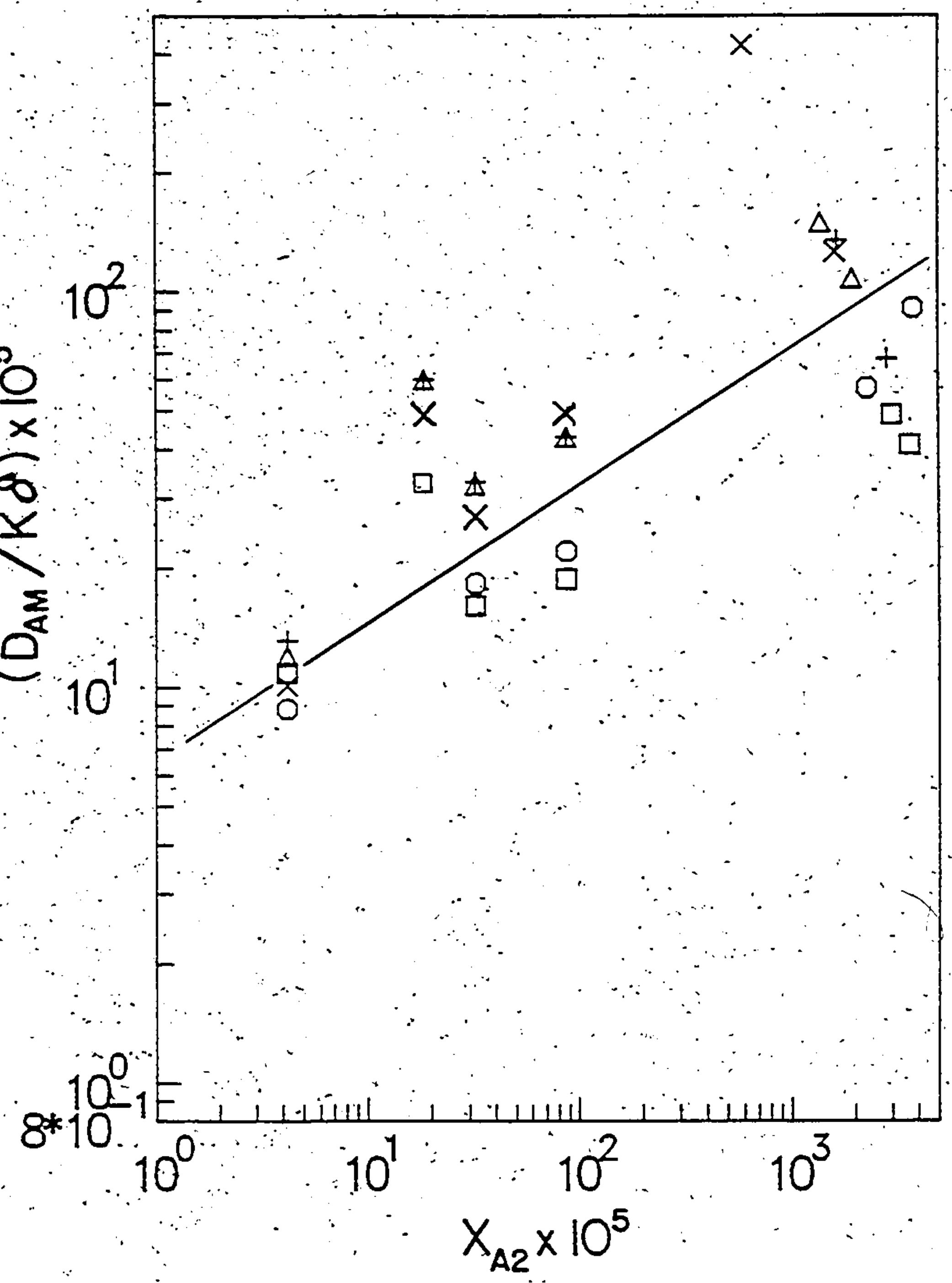
10^1
10^0
$(D_{AM}/K\delta) \times 10^4$
10^0
10^1
10^2
$X_{A2} \times 10^5$

Figure 5-7

Variation of $(\frac{D_{AM}}{K\delta})$ with Concentration for

$MgSO_4$ and Cellulose Membranes

Symbol	Membrane No.
□	1
○	2
△	3
+	4
×	6



$(D_{AM}/K\delta) \times 10^5$
10^2
10^1
10^0
$8*10^{-1}$
10^0
10^1
10^2
10^3
$X_{A2} \times 10^5$

Table 5-10

Slope of the Straight Line Correlation of $(D_{AM}/K\delta)$ with Concentration X_{A2}

Salt	Slope
NaCl	0.921
Na_2SO_4	1.024
$MgCl_2$	0
$MgSO_4$	0.375

osmosis performance for the range of concentrations included in this work. As an example of the calculation of $(D_{AM}/K\delta)$, consider the case of NaCl, membrane number 1 and an X_{A2} value of 10^{-3}. The value of $\ln C^*_{NaCl}$ from Table 5-6 for membrane number 1 is −13.75, the value of $(-\Delta\Delta G/RT)$ for NaCl from Table 5-5 is (−1.42 + 1.30) = −0.12 for $X_{A2} = 7.7 \times 10^{-5}$ (~ 0.0045 molal), and the appropriate value from Table 5-10 is 0.921. The value of $(D_{AM}/K\delta)$ is then calculated as

$$\begin{aligned}(D_{AM}/K\delta) &= \exp\left[\ell nC^* + (-\Delta\Delta G/RT)\right] \\ &\quad \times (X_{A2}/7.7 \times 10^{-5})^{0.921} \\ &= \exp\left[-13.75 - 0.12\right] \times (10^{-3}/7.7 \times 10^{-5})^{0.921} \\ &= 1.056 \times 10^{-5} \qquad (5\text{-}3)\end{aligned}$$

Equation 5-3 was used along with the equations of the Kimura-Sourirajan analysis to calculate reverse osmosis performance at concentrations other than 0.0045 molal for the 4 salts. These calculations are compared with experimental results in Table 5-11.

As with the methanol and ethanol free energy parameter determinations, the parameters for the alkali metal and halide ions were recalculated using a scheme to determine separation directly as opposed to the solute transport parameter. As well, all of the relevant experimental results were pooled together as opposed to separate regression for each membrane. As before, a package computer program of the SAS Institute based upon a derivative-free nonlinear regression was used (NLIN DUD). As well as determining the interfacial free energy parameters, their approximate standard deviations were determined and are shown in Table 5-12. The values reported in Table 5-12 for the interfacial parameters are similar to those calculated in Table 5-4 and lie within the approximate 95% confidence range.

The same computation recalculated ln C* directly for each membrane which is compared to the previous $\ln C^*_{NaCl}$ for each membrane in Table 5-13. As was seen in Chapter 3, only the trends of the ln C*'s are similar, which is consistent with its definition.

Table 5-11

Comparison of Experimental and Calculated Reverse Osmosis Performance at Various Concentrations of Aqueous Salt Solutions at 6900 kPag

Salt	Concn, molal	Membrane No.	(PR)		f, %	
			exptl	calcd	exptl	calcd
NaCl	0.01258	1	5.36	5.20	34.5	28.9
		2	6.15	5.84	32.8	33.8
		3	6.77	6.68	31.1	35.1
		4	6.90	6.35	26.8	34.9
		6	4.67	4.72	25.7	26.3
NaCl	0.002327	1	5.43	5.27	65.3	53.8
		2	6.28	5.91	63.7	60.3
		3	6.76	6.76	62.1	62.0
		4	7.24	6.42	45.2	61.5
		6	4.68	4.76	49.0	36.6
NaCl	0.001188	1	5.62	5.27	76.4	64.4
		2	6.08	5.91	77.2	70.7
		3	6.85	6.61	78.0	72.4
		4	7.33	6.44	53.2	72.0
		6	4.73	4.75	73.9	63.4
NaCl	0.0005427	1	5.44	5.29	70.4	75.6
		2	5.81	5.93	72.2	80.9
		3	6.67	6.77	75.4	81.2
		4	6.07	6.45	78.1	80.1
		6	4.65	4.78	76.4	70.1
Na_2SO_4	0.001130	1	5.42	5.27	92.3	87.3
		2	5.95	5.91	--	89.9
		3	6.65	6.76	73.5	90.9
		4	6.10	6.42	86.9	90.5
		6	4.65	4.76	95.1	83.2
Na_2SO_4	0.002862	1	5.70	5.22	91.0	90.9
		2	5.94	5.86	94.7	92.8
		3	6.81	6.71	94.0	93.5
		4	6.99	6.38	81.9	93.2
		6	4.65	4.72	89.7	87.8

Table 5-11 (cont'd)

Salt	Concn, molal	Membrane No.	(PR)		f,%	
			exptl	calcd	exptl	calcd
Na_2SO_4	0.008019	1	5.80	5.18	72.9	78.2
		2	5.85	5.81	78.5	82.1
		3	6.83	6.65	73.5	83.6
		4	6.67	6.33	66.6	82.9
		6	4.60	4.70	60.8	71.7
Na_2SO_4	0.001215	1	5.57	5.27	86.4	95.9
		2	5.90	5.91	92.7	96.9
		3	6.71	6.76	92.6	97.2
		4	6.69	6.42	84.6	97.1
		6	4.61	4.76	93.0	94.5
Na_2SO_4	0.008586	1	7.02	5.17	66.5	76.9
		2	5.86	5.82	77.0	81.0
		3	6.67	6.65	72.1	82.6
		4	6.06	6.32	70.5	81.9
		6	4.66	4.71	61.0	70.4
Na_2SO_4	0.01720	1	6.28	5.13	56.8	49.7
		2	5.96	5.74	62.3	56.1
		3	6.76	6.59	60.0	57.9
		4	6.47	6.26	56.0	57.4
		6	4.72	4.66	50.5	47.9
$MgCl_2$	0.002179	1	5.49	5.33	30.1	35.2
		2	5.96	5.92	28.2	41.3
		3	6.80	6.72	21.4	44.1
		4	6.99	6.44	19.8	42.9
		6	4.78	4.77	18.6	27.9
$MgCl_2$	0.001134	1	5.82	5.30	30.6	35.1
		2	5.87	5.93	31.3	41.3
		3	6.71	6.77	27.7	44.1
		4	6.54	6.44	25.0	42.9
		6	4.70	4.79	21.2	28.0
$MgCl_2$	0.008481	1	5.40	5.19	30.5	35.5
		2	5.92	5.84	30.0	41.6
		3	6.70	6.68	25.6	44.3
		4	6.27	6.34	23.5	43.2
		6	4.71	4.71	26.1	28.1

Table 5-11 (cont'd)

Salt	Concn, molal	Membrane No.	(PR)		f, %	
			exptl	calcd	exptl	calcd
$MgCl_2$	0.01763	1	5.64	5.07	35.3	36.2
		2	5.82	5.71	37.6	42.0
		3	6.68	6.55	30.7	44.6
		4	6.09	6.23	30.9	43.4
		6	4.72	4.64	30.9	28.5
$MgSO_4$	0.001809	1	5.47	5.23	82.9	75.7
		2	5.96	5.91	84.8	72.2
		3	6.77	6.75	78.4	75.2
		4	7.08	6.42	67.4	74.2
		6	4.71	4.77	70.3	70.9
$MgSO_4$	0.001021	1	5.44	5.29	72.0	79.4
		2	5.88	5.92	72.6	76.2
		3	6.67	6.76	65.6	78.9
		4	6.15	6.43	64.3	78.1
		6	4.67	4.78	57.7	75.1
$MgSO_4$	0.01971	1	5.61	5.27	67.1	62.2
		2	5.81	5.90	70.4	67.1
		3	6.61	6.75	63.6	68.3
		4	6.15	6.41	61.5	67.9
		6	4.63	4.77	49.4	44.4
$MgSO_4$	0.0002294	1	5.42	5.30	89.3	87.0
		2	5.80	5.94	92.0	84.8
		3	6.69	6.78	90.6	86.7
		4	6.14	6.44	88.3	86.2
		6	4.67	4.79	88.0	84.1
$MgSO_4$	0.02113	1	5.45	5.08	67.6	61.7
		2	5.70	5.69	69.6	66.7
		3	6.57	6.52	61.8	67.8
		4	6.11	6.20	61.8	67.3
		6	4.61	4.64	53.8	43.8

Table 5-12
Recalculated Interfacial Born Equation Parameters for Alkali Metal Halides with Cellulose Membranes in Aqueous Solutions[a]

Ion	E_I^- kJm/mol $\times 10^{10}$	Approximate Standard Error kJm/mol $\times 10^{10}$	Δ_I^- m $\times 10^{10}$	Approximate Standard Error m $\times 10^{10}$
Alkali Metal Cations	722.3	44.6	0.8389	0.0619
Halides	525.7	16.5	-0.1592	0.0257

[a] 60 data points

Table 5-13
Comparison of $\ln C^*_{NaCl}$ with Recalculated ln C*

Membrane	$\ln C^*_{NaCl}$	$\ln C^*_{recalcd}$
1	-13.75	-11.91
2	-13.84	-11.40
3	-13.61	-11.28
4	-13.69	-11.32
5	-12.67	-10.53
6	-13.48	-11.24

Determination of Interfacial Surface Force Parameters for Organic and Inorganic Solutes. Reverse osmosis experiments with organic solutes were performed and their surface potentials were calculated by the methods outlined in Chapter 4. This required the use of liquid chromatography data for the aqueous solution-cellulose system and physicochemical data as well, which are summarized in Table 5-14 for the solutes considered in this work. The calculation of surface excess concentration, Γ_A/c_A, required data for the surface area of the cellulose powder, which was reported by Matsuura et al. (1981) to be 242.9 m^2/g. The average pore sizes of the membranes used were calculated with data for isopropanol, n-hexanol and n-pentanol as reference solutes. This calculation consisted of equating the Stokes' radius of the solute with the solute size parameter, $\underset{\sim}{D}$, and with the Γ_A/c_A data for the solute, calculation of $\underset{\sim}{B}$ is made. These were then combined with reverse osmosis data to calculate the average pore radii of the membranes as shown in Table 5-15. These average pore radii were used with Γ_A/c_A data and reverse osmosis data for membrane number 3 to calculate the values of $\underset{\sim}{D}$ and $\underset{\sim}{B}$ shown in Table 5-14 for the organic solutes. Similar calculations were made with data for aqueous salt solutions and the values of $\underset{\sim}{D}$ and $\underset{\sim}{A}$ for these salts at 0.0045 ± 0.0007 molal concentration are shown in Table 5-16.

The parameters determined above were used to calculate reverse osmosis performance and the comparison with experimental reverse osmosis data is shown in Tables 5-17 and 5-18 for organic and inorganic solutes, respectively.

Table 5-14

Physicochemical Parameters for Organic Solutes in Aqueous Solutions and Cellulose Membranes

Solute	D°_{AB},[a] $m^2/s \times 10^9$	Γ_A/c_A, $m \times 10^{10}$	r_A,[a] $m^3 \times 10^{10}$	$\tilde{B}$, $m^3 \times 10^{30}$	$\tilde{D}$, $m \times 10^{10}$
Methanol	1.935	−5.87	1.45	—	—
Ethanol	1.460	−8.01	2.05	—	—
n-Propanol	1.206	−7.50	2.12	—	—
i-Propanol	1.206	−6.94	2.26	−164.8	3.600
n-Butanol	1.043	−8.01	2.33	−277.3	1.711
s-Butanol	1.043	−8.56	2.33	−328.9	2.182
i-Butanol	1.043	−6.42	3.05	−136.8	3.724
t-Butanol	1.043	−9.08	3.35	−371.3	2.535
n-Pentanol	0.930	−7.49	2.63	−201.8	3.505
n-Hexanol	0.842	−5.87	1.97	−102.7	3.874
n-Octanol	0.720	−3.74	—	0.0	4.543
Glycerol	1.091	−6.94	2.30	−165.2	3.643
Sucrose	0.489	−8.56	4.67	−289.4	3.993
d-Sorbitol	0.737	−4.81	3.30	−52.4	3.996
Methyl-i-Propyl Ketone	0.964	−5.35	2.59	−77.9	3.859
di-i-Butyl Ketone	0.689	−9.63	2.86	−450.8	4.230
Acetophenone	0.818	−4.28	—	−36.7	3.778
Phenetole	0.832	−5.35	—	−74.0	4.121
n-Butyl Ethyl Ether	0.834	−4.81	2.93	−20.0	5.021
Anisole	0.919	−5.87	—	−93.0	4.528
Phenol	1.189	5.87	2.10	187.8	4.345
p-Chlorophenol	0.947	29.40	—	340.5	4.399
Aniline	1.010	51.31	2.42	7.0	1.023
Benzene	1.156	6.94	—	—	—

[a] from Matsuura et al. (1981a)

Table 5-15

Average Pore Radii for the Cellulose Membranes

Solute	Pore Radius, m x 10^{10}				
	1	2	3	4	6
i-Propanol[a]	16.74	15.77	14.95	14.88	16.85
n-Hexanol[b]	14.69	14.55	16.94	17.79	15.02
n-Pentanol[c]	17.41	16.48	18.09	17.70	15.92
Average	16.28	15.60	16.66	16.79	15.93

[a] $\underset{\sim}{D} = r_A = 2.45 \times 10^{-10}$ m; $\underset{\sim}{B} = -250.91 \times 10^{-30}$ m^3 (calculated by eq 4-10)

[b] $\underset{\sim}{D} = r_A = 1.97 \times 10^{-10}$ m; $\underset{\sim}{B} = -149.09 \times 10^{-30}$ m^3 (calculated by eq 4-10)

[c] $\underset{\sim}{D} = r_A = 2.63 \times 10^{-10}$ m; $\underset{\sim}{B} = -322.02 \times 10^{-30}$ m^3 (calculated by eq 4-10)

Table 5-16

Physicochemical Parameters for Aqueous Salt Solutions and Cellulose Membranes at 0.0045 molal Salt Concentration

Salt	D^{o}_{AB}, $m^2/s \times 10^9$	Γ_A/c_A, $m \times 10^{10}$	$\underline{A}$, $m \times 10^{10}$	$\underline{R}$, $m \times 10^{10}$
LiBr	1.378	-11.76	2.686	3.998
NaF	1.401	-9.08	1.707	4.307
NaCl	1.611	-10.15	2.115	4.087
NaBr	1.626	-9.63	2.879	3.954
NaI	1.616	-9.63	1.951	4.035
KCl	1.995	-12.29	2.871	3.998
KBr	2.018	-11.22	3.987	2.501
RbCl	2.052	-8.56	1.578	4.124
CsCl	2.045	-14.43	3.646	3.976
CsBr	2.070	-13.90	3.474	3.854
NH_4Cl	1.993	-12.29	2.861	4.048
$NaNO_2$	1.429	-10.70	2.313	4.023
$NaNO_3$	1.568	-10.70	2.300	4.082
$NaClO_3$	1.503	-8.56	1.538	4.285
NaSCN	1.568	-12.83	3.036	4.140
$NaIO_3$	1.193	-9.63	1.876	4.357
$NaBrO_3$	1.406	-10.15	2.082	4.235
Na_2SO_4	1.230	-11.76	2.497	4.868
$MgCl_2$	1.250	-11.22	2.591	3.514
$CaCl_2$	1.336	-10.15	2.326	3.504

Table 5-17

Comparison of Experimental and Calculated Reverse Osmosis Performance for Cellulose Membranes in Aqueous Solutions at 25°C and 6900 kPag Operating Pressure

Solute	Concn, molal x 10^3	Memb. No.	$(PSP)^a$ exptl	$(PR)^a$ exptl	$(PR)^a$ calcd	f, % exptl	f, % calcd
i-Propanol	0.8857	1	6.71	5.72	6.71	36.5	30.9
		2	6.09	6.17	6.07	37.3	42.5
		3	6.80	6.81	6.78	33.2	32.1
		4	6.73	7.85	6.70	28.8	31.2
n-Butanol	0.798	1	5.53	5.60	5.53	36.3	27.8
		2	6.70	6.66	6.70	34.1	36.7
		3	6.70	6.66	6.70	34.1	32.9
		4	6.17	6.17	6.17	32.1	30.3
s-Butanol	0.797	1	6.18	5.51	6.18	40.8	35.3
		2	5.93	5.84	5.93	44.2	36.3
		3	6.78	6.70	6.78	37.7	36.5
		4	6.82	6.75	6.80	35.9	36.1
i-Butanol	0.815	1	5.56	5.34	5.54	42.2	32.5
		2	5.88	5.84	5.86	42.3	47.5
		3	6.72	6.68	6.70	34.3	33.2
		4	6.28	6.09	6.26	33.8	29.9
t-Butanol	0.797	1	5.64	5.47	5.62	49.7	32.5
		2	6.08	5.84	6.06	47.7	47.5
		3	6.88	6.69	6.85	40.5	33.2
		4	6.48	6.42	6.44	39.2	29.9
n-Pentanol	0.7014	1	6.08	6.38	6.08	31.3	31.8
		2	5.89	5.74	5.89	37.6	37.0
		3	6.79	6.73	6.79	33.3	33.2
		4	6.68	6.56	6.66	29.7	26.2
n-Hexanol	0.4132	1	5.40	6.43	6.08	31.1	43.2
		2	5.94	5.83	5.89	46.3	53.6
		3	6.69	6.69	6.79	39.9	35.9
		4	8.78	6.68	6.66	33.1	36.1

Table 5-17 (cont'd)

Solute	Concn, molal x 10^3	Memb. No.	$(PSP)^a$ exptl	$(PR)^a$ exptl	calcd	f, % exptl	calcd
n-Octanol	0.5234	1	5.68	5.75	5.64	72.1	69.0
		2	6.08	5.92	6.04	63.7	76.7
		3	6.92	6.81	6.88	68.7	68.7
		4	6.44	6.54	6.30	69.2	65.6
Sucrose	0.6521	1	6.32	5.82	6.31	61.9	64.5
		2	5.88	5.81	5.89	69.6	72.7
		3	6.80	6.61	6.79	58.5	63.8
		4	6.37	6.13	6.35	64.2	56.3
d-Sorbitol	0.6512	1	5.59	5.46	5.54	49.2	48.5
		2	5.96	5.88	5.91	51.2	58.8
		3	6.94	6.82	6.89	43.8	47.8
		4	6.56	6.23	6.48	44.1	38.7
Glycerol	0.3056	1	6.41	5.63	6.38	37.5	27.7
		2	6.85	6.07	6.82	37.4	40.4
		3	6.76	6.77	6.72	33.8	27.2
		4	8.77	7.75	6.48	17.0	15.0
Methyl-i-Propyl Ketone	0.3292	1	5.96	5.52	5.86	56.0	34.6
		2	6.02	5.83	5.96	56.5	49.5
		3	6.89	6.73	6.80	37.0	31.5
		4	8.86	8.96	6.48	36.2	24.3
di-i-Butyl Ketone	0.2037	1	6.89	6.25	6.80	75.5	77.8
		2	5.93	5.90	5.92	79.6	82.6
		3	6.71	6.78	6.60	77.3	73.6
		4	9.13	8.54	9.00	60.6	71.4
Acetophenone	0.4367	1	—	5.75	6.38	24.6	23.3
		2	—	5.76	6.82	28.4	38.3
		3	—	6.71	6.72	24.2	21.5
		4	—	6.75	6.48	18.7	19.8

Table 5-17 (cont'd)

Solute	Concn, molal x 10^3	Memb. No.	$(PSP)^a$ exptl	$(PR)^a$ exptl	$(PR)^a$ calcd	f,% exptl	f,% calcd
Phenetole	0.2479	1	5.62	5.52	5.50	60.9	53.8
		2	6.22	5.86	—	58.8	—
		3	7.01	6.88	6.90	56.3	50.1
		4	7.07	6.41	6.95	55.5	46.5
n-Butyl Ethyl Ether	0.2704	1	6.70	6.86	6.60	68.2	85.5
		2	6.03	5.90	5.90	73.8	87.9
		3	6.93	6.87	6.84	85.6	83.7
		4	7.73	8.68	7.60	71.8	83.4
Anisole	0.3863	1	5.49	5.42	6.60	49.9	75.8
		2	6.26	5.89	5.90	52.9	30.8
		3	6.89	6.76	6.84	42.2	61.7
		4	6.46	6.38	7.00	39.1	37.1
Phenol	0.4097	1	5.36	5.41	5.30	20.3	26.3
		2	5.80	5.87	5.71	23.7	34.0
		3	6.64	6.72	6.52	21.0	28.4
		4	6.52	6.31	6.40	18.6	26.2
p-Chlorophenol	0.4521	1	5.52	5.46	5.31	14.7	20.2
		2	6.40	5.85	6.22	14.7	26.8
		3	6.88	6.78	6.69	13.4	21.8
		4	6.45	6.43	6.18	10.0	20.0
Aniline	0.4257	1	5.57	5.49	5.57	2.4	-0.2
		2	5.90	5.92	5.90	2.4	-0.7
		3	6.70	6.85	6.70	-2.0	-1.8
		4	6.36	6.29	6.36	-0.3	-1.4

[a] g/h for 13.2 cm^2 membrane surface area.

Table 5-18

Comparison of Experimental and Calculated Reverse Osmosis Performance for Aqueous Salt Solutions and Cellulose Membranes at 25°C, 6900 kPag Operating Pressure and 0.0045 Molal Concentration

Solute	Concn, molal x 10^3	Memb. No.	$(PSP)^a$	$(PR)^a$		f,%	
			exptl	exptl	calcd	exptl	calcd
LiBr	3.725	1	5.46	5.32	5.46	55.2	43.8
		2	5.79	5.76	5.79	53.7	56.0
		3	6.39	6.74	6.39	50.5	52.6
		4	6.06	6.11	6.06	51.4	46.3
		6	4.71	4.82	4.70	38.5	45.8
NaF	4.399	1	5.33	5.25	5.33	68.9	54.7
		2	5.83	5.70	5.83	68.6	65.6
		3	6.73	6.62	6.72	65.2	63.1
		4	6.10	6.04	6.10	65.6	57.9
		6	4.77	4.72	4.75	55.1	57.2
NaCl	4.604	1	6.90	5.51	6.90	55.2	47.0
		2	6.05	5.64	6.05	55.9	56.7
		3	6.85	6.75	6.84	53.7	54.1
		4	6.32	6.10	6.32	53.7	46.9
		6	5.18	4.93	5.16	41.5	46.0
NaBr	4.426	1	5.17	5.26	5.17	50.6	37.9
		2	5.42	5.58	5.42	51.3	50.7
		3	6.59	6.66	6.58	47.8	48.4
		4	5.97	6.03	5.97	48.2	41.6
		6	4.73	4.73	4.72	36.4	41.7
NaI	5.204	1	5.55	5.33	5.55	52.6	36.5
		2	5.55	5.55	5.55	52.3	50.2
		3	6.56	6.71	6.55	49.0	46.3
		4	6.00	6.06	6.00	50.0	40.0
		6	4.73	4.77	4.71	39.7	40.2
KCl	4.631	1	5.59	5.38	5.59	46.1	43.4
		2	4.80	5.57	4.80	51.6	52.8
		3	5.63	5.00	5.62	50.4	50.6
		4	5.07	6.14	5.07	50.4	44.9
		6	–	4.91	4.90	41.2	44.1
KBr	4.185	1	5.49	5.34	5.49	50.1	40.7
		2	5.86	5.79	5.85	49.3	52.9
		3	6.75	6.67	6.75	47.0	48.9
		4	6.15	6.09	6.14	47.6	43.1
		6	4.77	4.64	4.75	40.0	42.9

Table 5-18 - (cont'd)

Solute	Concn, molal x 10^3	Memb. No.	$(PSP)^a$ exptl	$(PR)^a$ exptl	calcd	f,% exptl	calcd
RbCl	4.445	1	5.37	5.32	5.36	54.0	43.4
		2	5.77	5.69	5.76	54.2	55.4
		3	6.70	6.61	6.69	51.6	52.3
		4	6.10	6.05	6.09	52.4	46.1
		6	4.83	4.66	4.82	43.1	45.9
CsCl	4.839	1	7.73	5.55	5.67	53.1	45.4
		2	6.38	5.96	5.83	45.5	57.8
		3	6.87	6.76	6.80	52.3	52.4
		4	8.50	7.53	6.16	43.8	46.5
		6	4.85	4.68	4.70	43.8	46.2
CsBr	4.221	1	5.43	5.39	5.43	50.3	36.5
		2	5.77	5.96	5.76	47.5	49.0
		3	6.69	6.65	6.68	43.3	45.2
		4	6.14	6.05	6.13	46.6	38.7
		6	4.74	4.70	4.72	41.0	38.6
NH_4Cl	4.107	1	5.42	5.65	5.41	52.7	47.1
		2	5.92	5.66	5.91	56.3	58.6
		3	6.75	6.58	6.73	53.8	55.2
		4	6.14	6.00	6.13	54.4	49.3
		6	4.68	4.47	4.66	46.2	48.9
$NaNO_2$	4.092	1	5.78	5.40	5.78	16.3	43.7
		2	6.34	6.08	6.34	56.6	55.1
		3	6.79	6.66	6.78	49.4	49.7
		4	10.69	7.49	7.51	39.2	43.6
		6	4.28	4.63	4.70	39.2	43.2
$NaNO_3$	4.306	1	5.42	5.30	5.42	56.8	45.4
		2	5.84	5.72	5.84	55.5	56.8
		3	6.65	6.62	6.64	53.0	53.8
		4	6.05	6.05	6.05	53.6	47.7
		6	4.58	4.56	4.70	40.7	47.5
$NaClO_3$	4.236	1	5.59	5.36	5.58	67.3	55.6
		2	6.79	6.76	6.78	62.5	66.6
		3	6.79	6.76	6.78	62.5	61.8
		4	9.11	6.95	6.18	55.3	56.8
		6	4.76	4.66	4.70	52.5	55.7

Table 5-18 - (cont'd)

Solute	Concn, molal x 10^3	Memb. No.	(PSP)[a] exptl	(PR)[a] exptl	(PR)[a] calcd	f,% exptl	f,% calcd
NaSCN	3.907	1	5.40	5.97	5.40	58.3	57.3
		2	6.32	5.60	6.31	59.2	64.6
		3	6.92	6.78	6.91	60.6	62.2
		4	6.18	6.12	6.17	60.9	56.7
		6	4.66	4.63	4.68	50.5	56.1
$NaIO_3$	4.493	1	6.48	5.94	5.40	61.8	61.8
		2	6.04	6.00	6.04	70.3	68.8
		3	6.80	6.71	6.80	68.2	65.9
		4	6.16	6.07	6.16	72.1	61.4
		6	4.68	4.60	4.67	57.4	60.3
$NaBrO_3$	4.137	1	5.67	5.39	5.67	57.2	56.2
		2	5.83	5.82	5.83	64.3	64.8
		3	6.83	6.69	6.83	63.0	62.2
		4	6.20	6.12	6.20	61.3	57.0
		6	4.77	4.65	4.76	53.1	56.0
Na_2SO_4	4.092	1	5.32	6.15	5.67	80.7	82.3
		2	7.03	5.30	5.83	87.1	84.3
		3	6.63	6.48	6.80	85.5	83.8
		4	6.05	5.93	6.16	86.5	81.3
		6	4.58	4.42	4.76	76.6	80.5
$MgCl_2$	4.743	1	5.50	6.47	5.50	24.1	19.1
		2	5.73	5.74	5.73	32.3	20.7
		3	6.70	6.64	6.70	24.8	20.0
		4	6.07	6.03	6.07	25.4	18.0
		6	4.77	4.57	4.77	24.1	14.6
$CaCl_2$	4.036	1	5.44	5.38	5.44	27.5	15.2
		2	5.72	5.66	5.72	28.6	20.1
		3	6.56	6.61	6.56	21.9	19.6
		4	5.96	5.97	5.96	21.9	17.6
		6	4.56	4.56	4.56	21.2	13.9

[a] g/h for 13.2 cm^2 membrane surface area.

Discussion.

The cellulose membranes studied in this chapter can be used to give reverse osmosis separations of salts and small organic molecules and not just large molecules as with previous cellulose membranes. Their behaviour for the separation of aqueous solutions shows several characteristics which mark them as different from the cellulose acetate and PPPH 8273 membranes that were used for comparison. With respect to the salt solutions, the divalent anions are more strongly rejected from the membrane surface than the monovalent anions and the monovalent cations are more strongly rejected from the membrane surface than the divalent cations, as demonstrated by the free energy parameters in Figs 5-4 and 5-5. This trend was reversed for cellulose acetate membranes which suggests that the acetylation of cellulose changes the surface characteristics of the material. If the surface rejections listed above are valid, the two membranes behave as if they had induced surface charges, with the cellulose having a more negative induced charge.

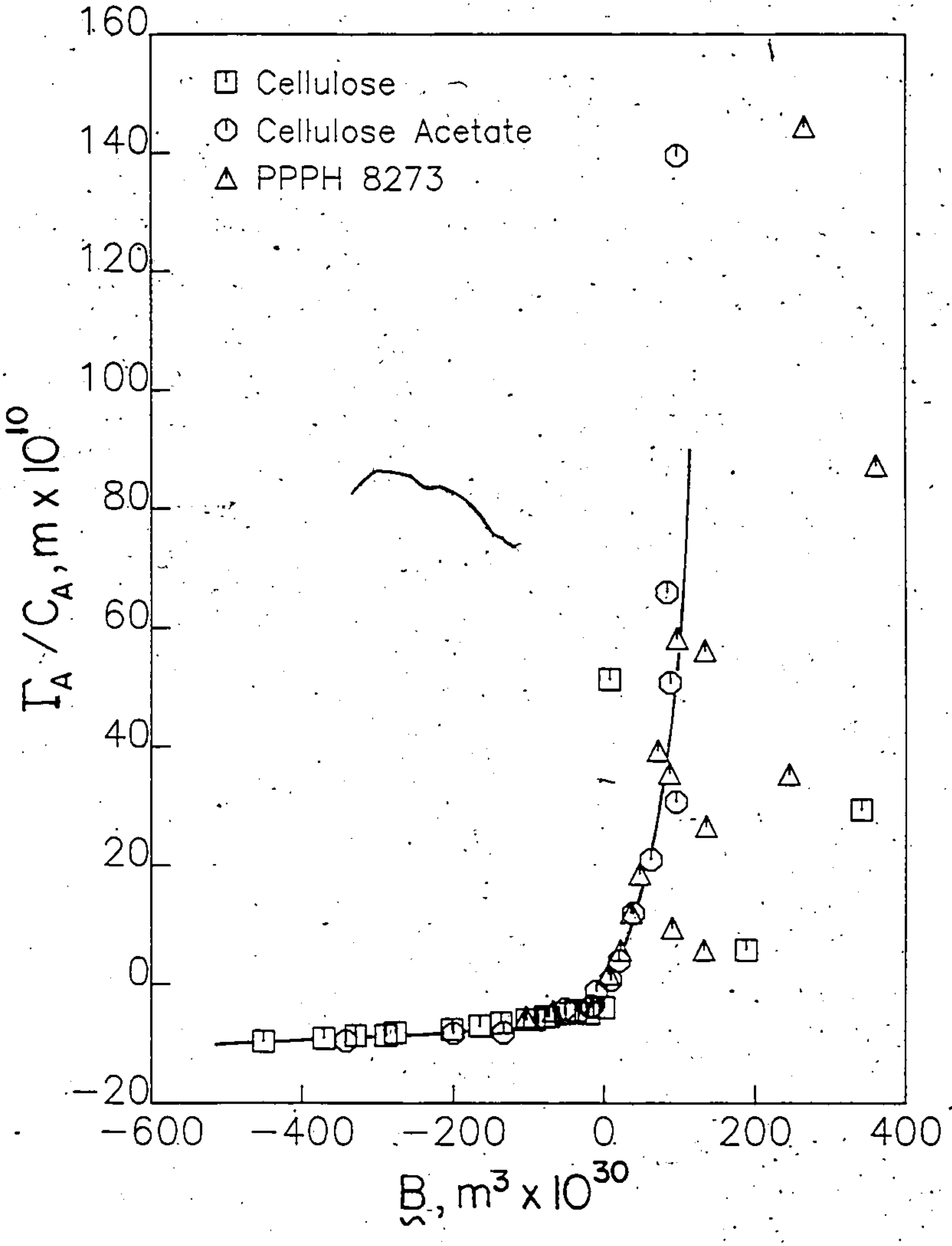
Another effect was observed for the cellulose membranes at higher solute concentrations where reverse osmosis separation showed an unusually large change with concentration, which was more pronounced for a 1:1 and a 1:2 salt than for a 2:1 and a 2:2 salt. While this investigation included only four salts at relatively dilute concentration, a similar effect as observed with PPPH 8273 membranes Yeager et al., 1981) did not show as pronounced an effect with respect to ion type, which was as much as an order of magnitude difference in the $(D_{AM}/K\delta)$ with X_{A2} slope. The poor agreement of calculated and experimental reverse osmosis performance in Table 5-11 for large concentration differences may be a result of oversimplifying the treatment used by Yeager et al. (1981) by not including the effect of porosity.

The comparison of calculated and experimental reverse osmosis separation in Table 5-8 for the constant concentration case shows good agreement which demonstrates the capability of the Kimura-Sourirajan analysis for the prediction of performance.

The surface potential-pore flow model's analysis of reverse osmosis performance included both organic and inorganic solutes and successfully compares experimental and calculated separations and product rates in Tables 5-17 and 5-18. When the $\underset{\sim}{B}$ parameters for the cellulose membranes were compared with Γ_A/c_A along with the $\underset{\sim}{B}$ parameters for polar organic solutes with cellulose acetate and PPPH 8273 membranes in Fig 5-8, it was found for the negative range of $\underset{\sim}{B}$ that there was a general agreement for all three membrane materials. However, for the positive $\underset{\sim}{B}$ range, several distinct effects are observed. For

Figure 5-8

Surface Excess Concentration for Dilute Aqueous Organic Solutes and Cellulose, Cellulose Acetate, and PPPH 8273 Materials With Surface Potential Parameters


160
140
120
100
80
60
40
20
0
−20
−600
−400
−200
0
200
400
□ Cellulose
○ Cellulose Acetate
△ PPPH 8273
Γ_A / C_A, m x 10^{10}
B, m^3 x 10^{30}

the cellulose membrane case there is a slow increase of Γ_A/c_A with $\underset{\sim}{B}$, but there is only limited data available. There is an overlap of the $\underset{\sim}{B}$ parameters for the cellulose acetate and PPPH 8273 membranes but there appears to be two different groups of $\underset{\sim}{B}$ for the PPPH 8273 membranes. These provide only inconclusive results for the positive $\underset{\sim}{B}$ values. However, it should be noted that Γ_A/c_A for these polar organic solutes tend to be smaller for the cellulose membranes than for the other two membranes.

When $\underset{\sim}{A}\cdot\varepsilon$ (ε of water) is compared for these three membranes and monovalent (1:1) salts in Fig 5-9, there is a very similar relation for all three cases but again the Γ_A/c_A values for the cellulose material are more negative than for the other two. This implies greater rejection of these salts from the cellulose surface than for the other two materials which should lead to greater values of $\underset{\sim}{A}$. While the relation of $\underset{\sim}{A}\cdot\varepsilon$ and Γ_A/c_A of Fig 5-9 may not be exact for all three materials, there is a definite trend of decreasing Γ_A/c_A for increasing $\underset{\sim}{A}\cdot\varepsilon$.

The residuals ($f_{exptl} - f_{calc}$) have been plotted with calculated separation in Fig 5-10 for the Kimura-Sourirajan model and Fig 5-11 for the surface potential-pore flow model. As well, the residuals have been plotted with $\sum_i(-\Delta\Delta G/RT)_i$ for the salts in Fig 5-12, and with $\underset{\sim}{B}$ and $\underset{\sim}{A}$ in Fig 5-13 and 5-14.

Figure 5-9

Surface Excess Concentration for Dilute Aqueous Salt Solutions and Cellulose, Cellulose Acetate, and PPPH 8273 Materials with Surface Potential Parameters

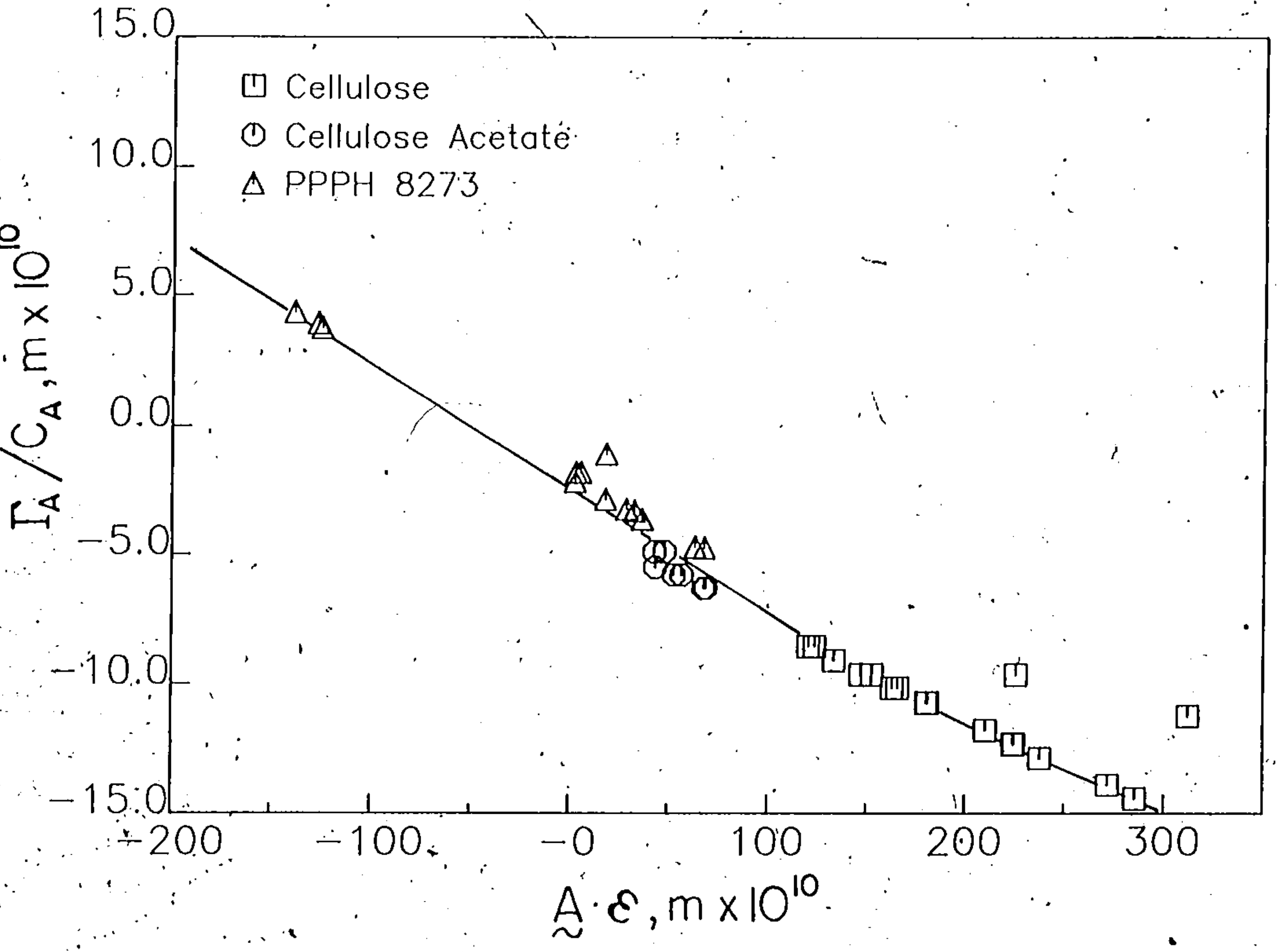

Cellulose
Cellulose Acetate
PPPH 8273
15.0
10.0
5.0
0.0
−5.0
−10.0
−15.0
Γ_A / C_A, m x 10^{10}
−200
−100
−0
100
200
300
$\underset{\sim}{A} \cdot \varepsilon$, m x 10^{10}

Figure 5-10

Residuals for Separation Plotted with the Kimura-Sourirajan Calculations for Separation

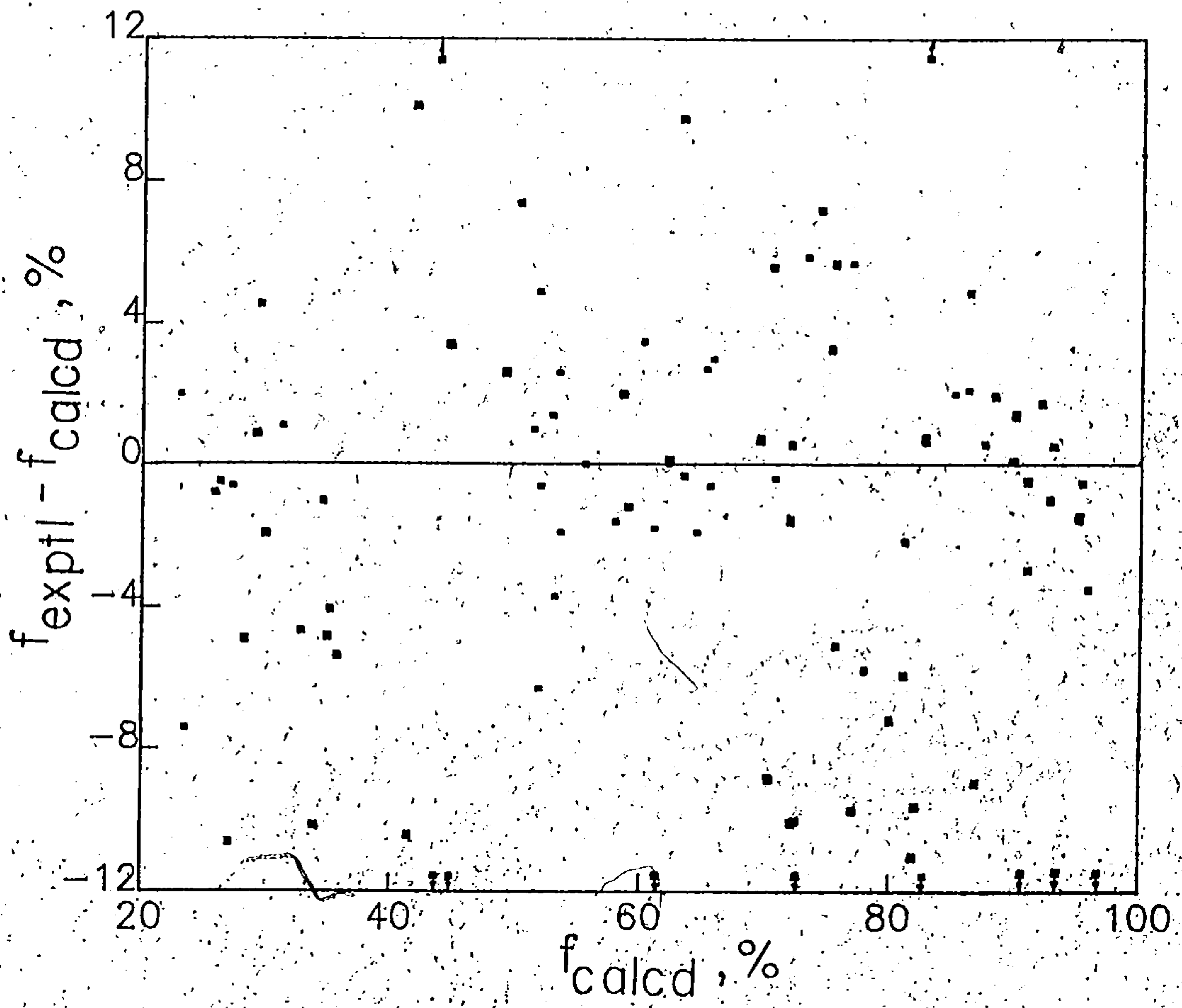

12
8
4
0
−4
−8
−12
20
40
60
80
100
$f_{exptl} - f_{calcd}$, %
f_{calcd} , %

Figure 5-11

Residuals for Separation Plotted with the

Surface Potential-Pore FlowCalculations for Separation

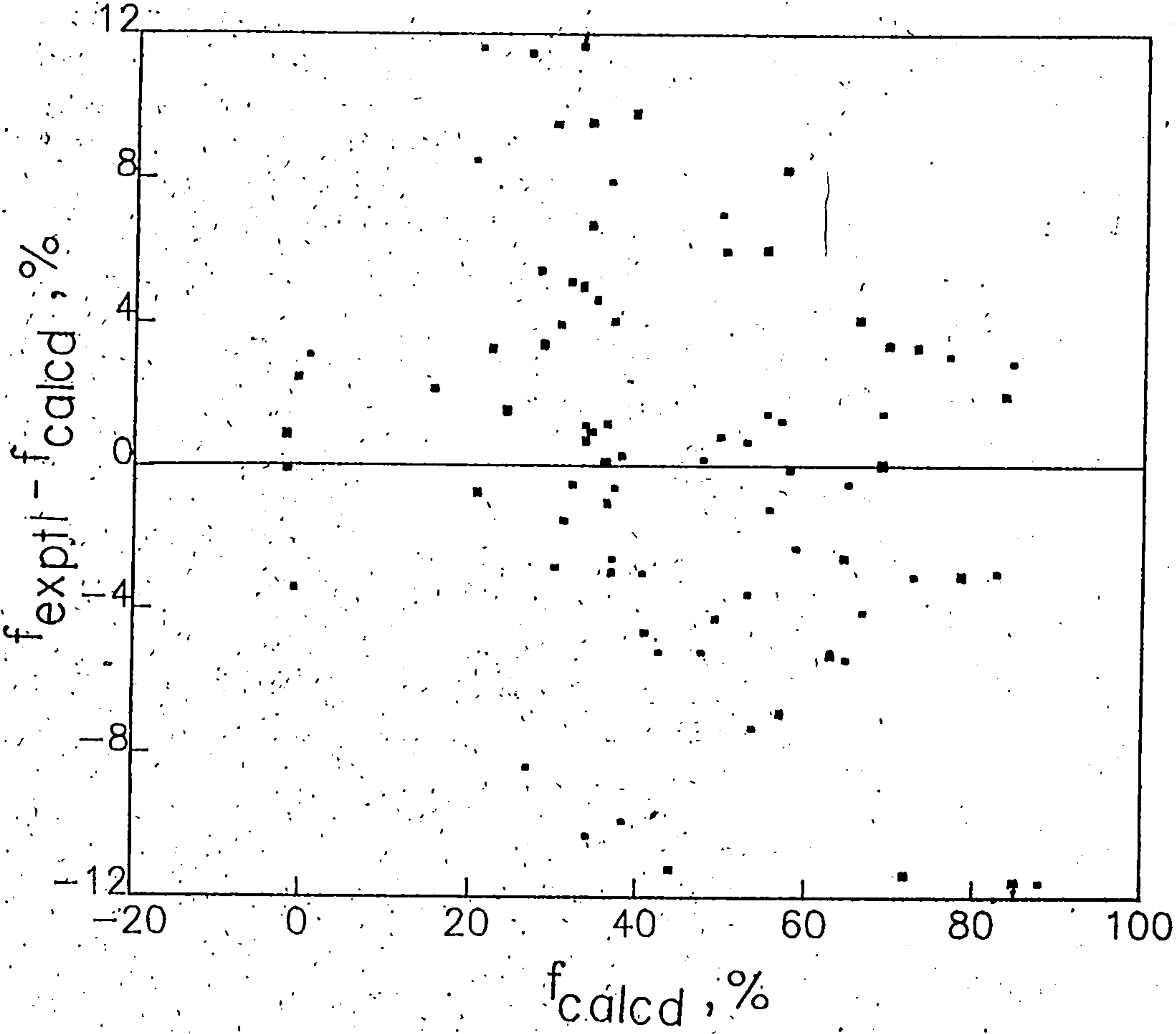

12
8
4
0
−4
−8
−12
−20
0
20
40
60
80
100
f_{calcd} , %
$f_{exptl} - f_{calcd}$, %

Figure 5-12

Residuals for Separation Plotted with
Free Energies for Salts

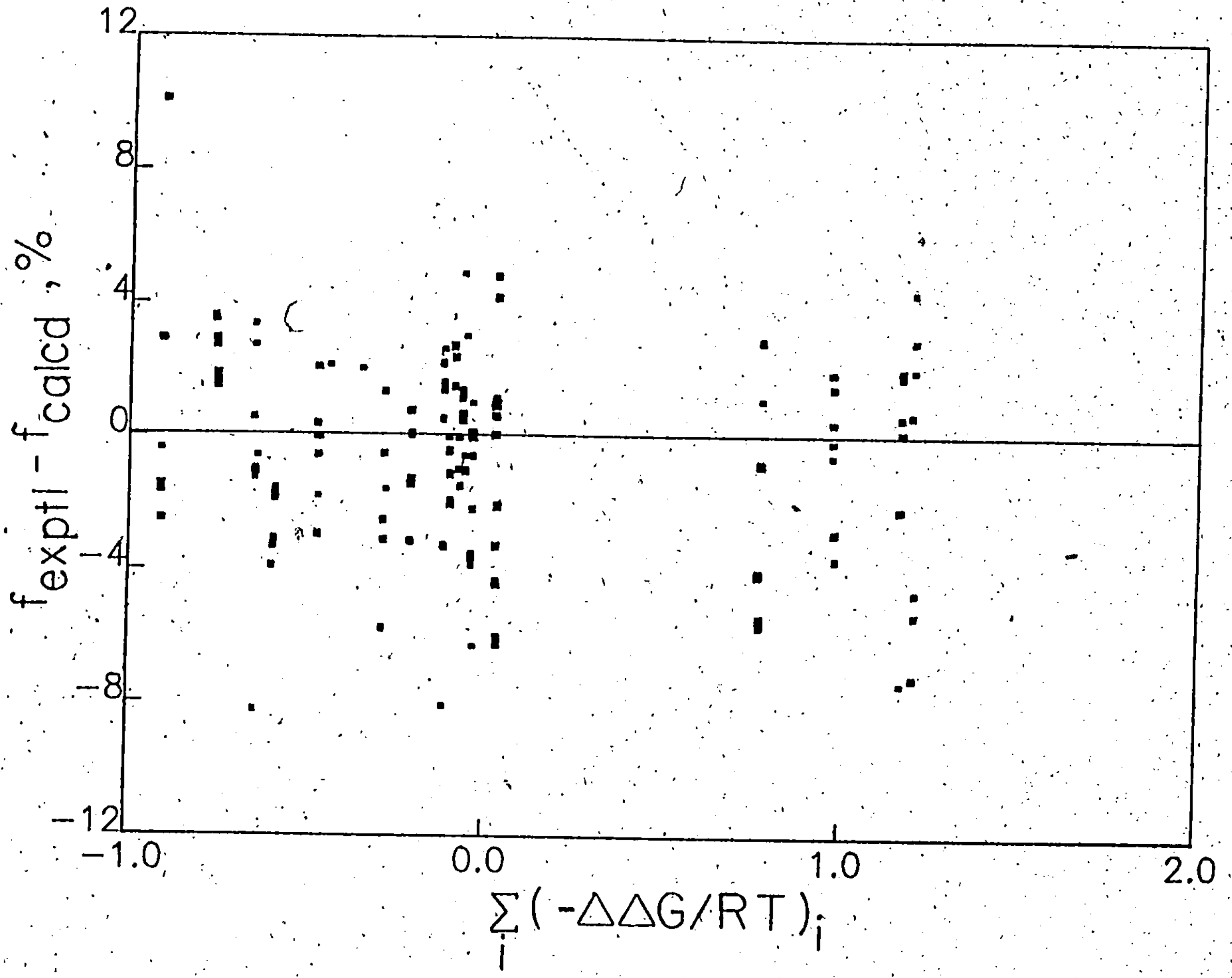

12
8
4
0
−4
−8
−12
−1.0
0.0
1.0
2.0
$f_{exptl} - f_{calcd}$, %
$\sum_i(-\Delta\Delta G/RT)_i$

Figure 5-13

Residuals for Separation Plotted with

Parameter $\underset{\sim}{B}$

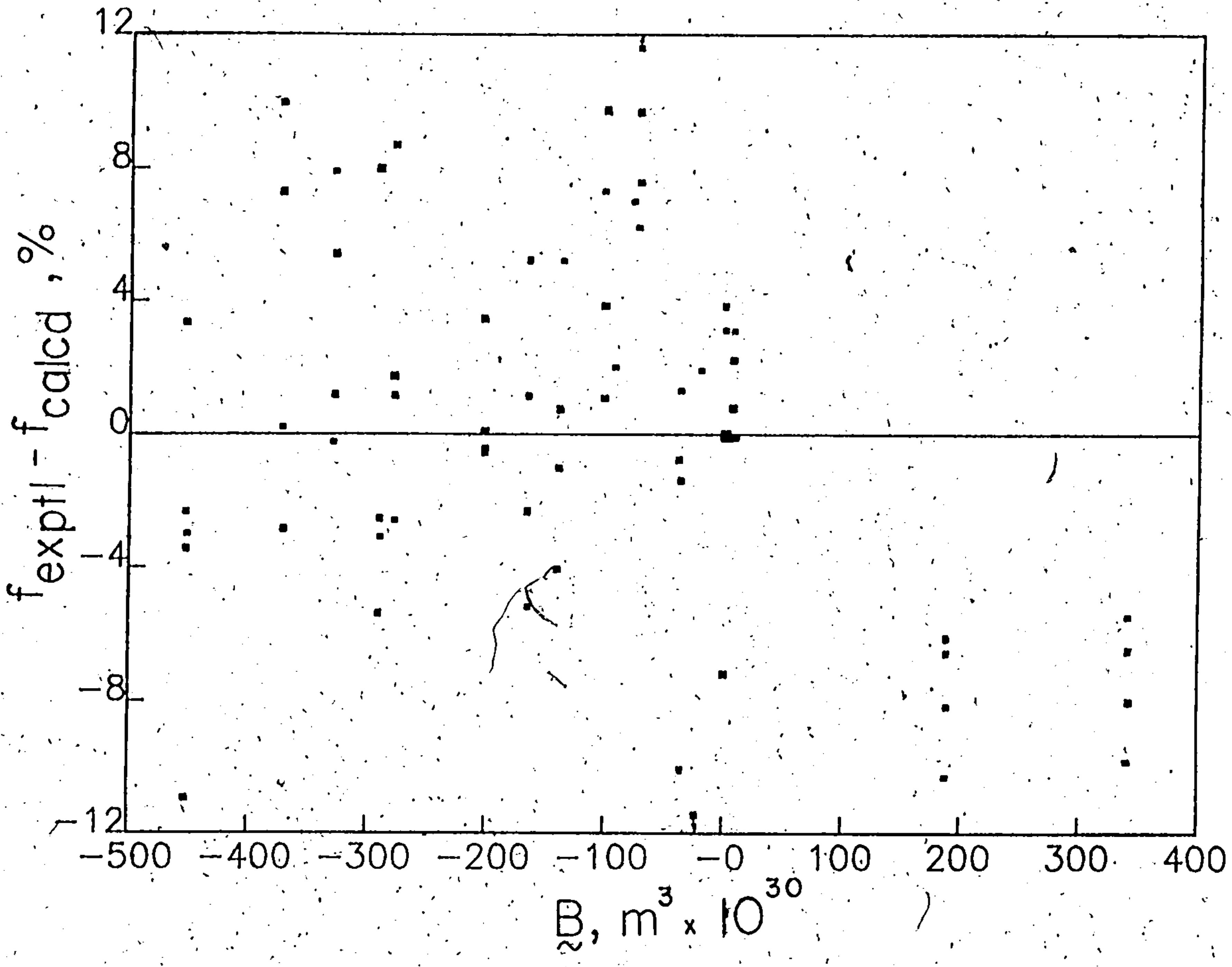
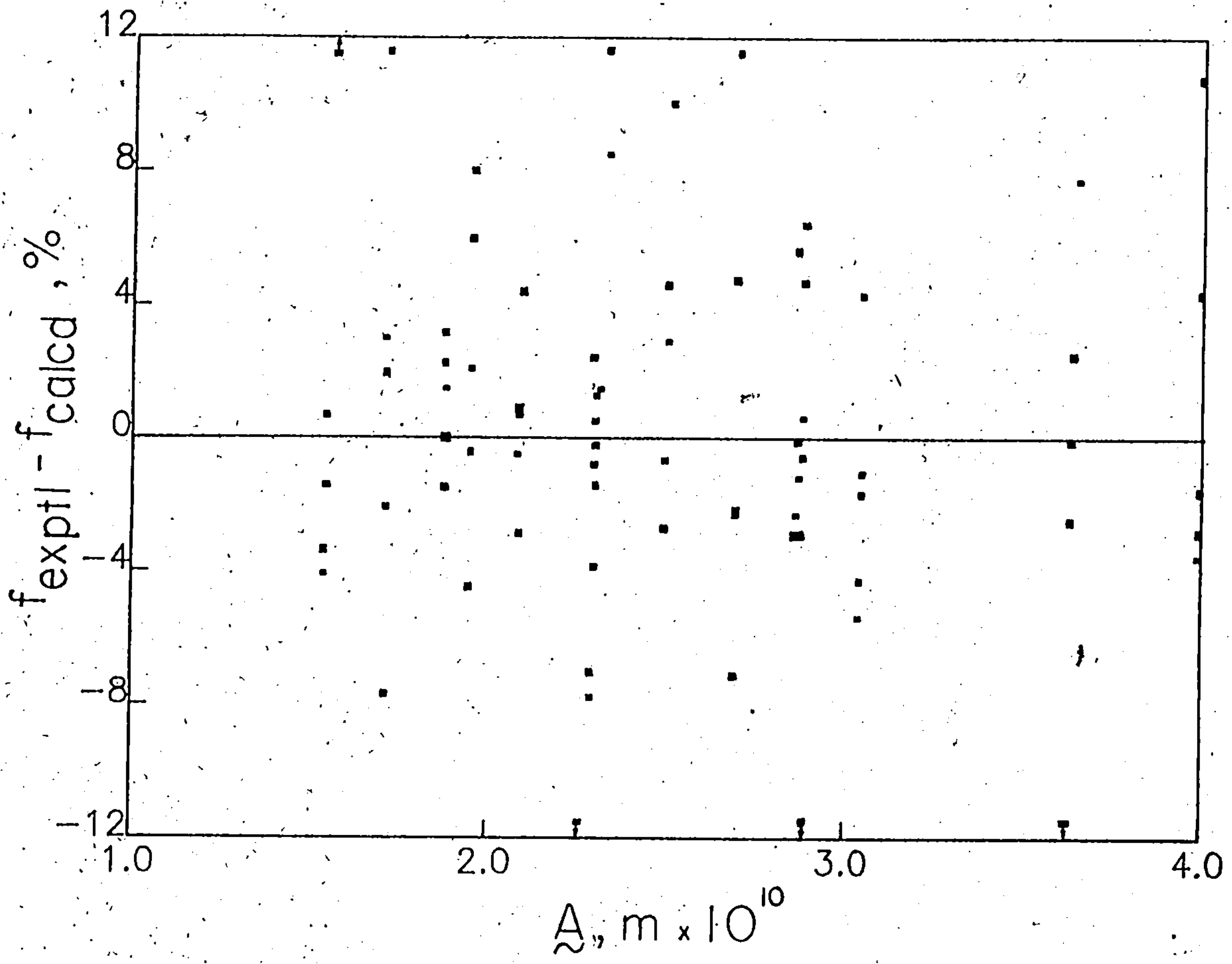

12
8
4
0
-4
-8
-12
$f_{exptl} - f_{calcd}$, %
-500
-400
-300
-200
-100
-0
100
200
300
400
$\underset{\sim}{B}$, $m^3 \times 10^{30}$

Figure 5-14

Residuals for Separation Plotted with

Parameter $\underset{\sim}{A}$


12
8
4
0
−4
−8
−12
1.0
2.0
3.0
4.0
$f_{exptl} - f_{calcd}$, %
$\underset{\sim}{A}$, m × 10^{10}

There are no trends in these plots, which is an indication of the adequacy of these two models for the calculation of separations.

As in Chapters 3 and 4, the F-test for model adequacy was included. To estimate the pure error variance, run number 5, 28 kand 69 for NaCl in Table A-1-8 were used. This gave a s_p^2 of 2.25 and γ_p of 11. For the alkali and metal halides and the Kimura-Sourirajan analysis, SSR was 421.5 for 58 residuals and a 5 parameter model. Equation 3-57 is calculated as

$$\left(\frac{421.5}{58-5}\right)/2.25 = 3.53$$

and $F_{53,11,.01}$ is estimated as 3.79. For the other salts, SSR is 5767 for 78 residuals and a 3 parameter model. Equation 3-57 is calculated as

$$\left(\frac{576.7}{78-3}\right)/2.25 = 3.42$$

and $F_{75,11,.01}$ is estimated as 3.77.

For the surface potential-pore flow model, the organic solutes had a SSR of 1089.6 with 55 residuals and a 3 parameter model, and when used in eq 3-57 gives

$$\left(\frac{1089.6}{55-3}\right)/2.25 = 9.31$$

and $F_{52,11,.01}$ is estimated as 3.80. For inorganic salts, SSR was 1148.3 for 79 residuals and 3 parameters, and when used in eq 3-57 gives

$$\left(\frac{1148.3}{79-3}\right)/2.25 = 6.72$$

and $F_{76,11,.01}$ is estimated as 3.75

It appears that the adequacy of the surface potential-pore flow model is questionable for both the organic and inorganic solutes at this level of significance of the F-test.

As in Chapter 4, a similar analysis of the ranges $\underset{\sim}{B}$, $\underset{\sim}{A}$ and $\underset{\sim}{D}$ that would give a range of ±0.03 for f_{calcd} was made. The same procedure was used where only dilute solutions were considered. The calculated ranges are shown in Table 5-19 for both organic and inorganic solutes. From these it can be seen that the ranges of $\underset{\sim}{B}$ and $\underset{\sim}{A}$ are large enough to have confidence in them for the purposes of modeling. As well, the ranges for $\underset{\sim}{B}$ can be seen to vary with the value of $\underset{\sim}{B}$ as shown in the cases of di-i-butyl ketone and n-octanol. As in the methanol and ethanol cases, the range of $\underset{\sim}{D}$ is small, which suggests that the value of $\underset{\sim}{D}$ has greater influence on the calculated result than the parameters $\underset{\sim}{B}$ and $\underset{\sim}{A}$.

One important observation from the point of view of commercial utility is the unusual positive separation of phenol, and the absence of strong adsorptions of the aromatic solutes onto the cellulose surface. This latter effect may be an indication of the cellulose membrane's resistance to fouling and its utility for the rejection of organic water pollutants.

Table 5-19

Parameter Ranges for Solutes in Dilute Aqueous Solutions that Calculate an Approximate Range of f_{calcd} of ±0.03

Solute	Parameter	Parameter's Value	f_{calcd}	f_{exptl}
di-i-Butyl Ketone	$+\underset{\sim}{B}$	-345	0.748	0.755
	$\underset{\sim}{B}^{c}$	-450.8	0.778	
	$-\underset{\sim}{B}$	-575	0.807	
	$+\underset{\sim}{D}$	4.30	0.807	
	$\underset{\sim}{D}^{c}$	4.23	0.778	
	$-\underset{\sim}{D}$	4.15	0.749	
n-Octanol	$+\underset{\sim}{B}$	5.5	0.660	0.721
	$\underset{\sim}{B}^{c}$	0.0	0.690	
	$-\underset{\sim}{B}$	-15.0	0.720	
	$+\underset{\sim}{D}$	4.62	0.721	
	$\underset{\sim}{D}^{c}$	4.54	0.690	
	$-\underset{\sim}{D}$	4.41	0.661	
$NaClO_3$	$+\underset{\sim}{A}$	2.2	0.586	0.673
	$\underset{\sim}{A}^{c}$	1.538	0.556	
	$-\underset{\sim}{A}$	1.0	0.528	
	$+\underset{\sim}{D}$	4.38	0.555	
	$\underset{\sim}{D}^{c}$	4.345	0.556	
	$-\underset{\sim}{D}$	4.29	0.527	

[a] $\underset{\sim}{B}$ has units of $m^3 \times 10^{-30}$, $\underset{\sim}{D}$ is in $m \times 10^{-10}$, and $\underset{\sim}{A}$ is in $m \times 10^{-10}$.

[b] For aqueous solutions and membrane number 1.

[c] As reported previously.

Conclusion

A method for the fabrication of small pore reverse osmosis membranes from a cellulose solution has been developed. These membranes show significant separations of both organic and inorganic solutes in aqueous solutions, as well as unusual positive separations of phenol. In general, they show a hydrophilic character as well as a large change of salt separation with concentration.

Free energy parameters for several salts and surface potential parameters for both salts and several organic solutes were developed. These were used to successfully predict reverse osmosis performance. Comparison has been made with the surface potential parameters obtained by these analyses for other membranes in aqueous reverse osmosis systems.

Chapter 6

Reverse Osmosis Fractionation of Ethanol-Heptane Mixtures Using Different Membranes

Introduction.

There are several examples in the literature of the uses of membranes to fractionate mixtures of binary liquids. One example is the work of Kammermeyer and Hagerbaumer (1955) who used sintered glass filters to separate several azeotropic liquid mixtures by permeation under pressure. Binning and coworkers (1960; 1961) demonstrated pervaporation through polymeric films for the separation of azeotropic mixtures. There have been many studies of pervaporation to separate binary liquid azeotropes (Cabasso et al., 1974; Paul and Carranza, 1973; Fels, 1972) but pervaporation is not compared to the reverse osmosis separations in this work because there is an induced vapour liquid phase transition involved in the process and the membrane involved is a nonporous film. Strathmann (1978) used data on the permeation of nonaqueous solvents through reverse osmosis membranes to test their strength and durability for use in seawater desalination. Nomura et al. (1978; 1979a; 1979b) investigated the permeation of multiple solvents through membranes of different polymers and reported different permeabilities of various alcohols and aromatic compounds. However, they experienced difficulties with solvent effects changing the membrane properties.

Sourirajan (1964) investigated reverse osmosis separations of azeotropes with various porous polymeric membranes and Kopecek and Sourirajan (1970) studied the reverse osmosis fractionation of several binary liquid mixtures with porous cellulose acetate membranes at all concentrations. They reported permeate-feed concentration and permeation rates for several operating pressures, and observed a collapse of the structure of the porous cellulose acetate membranes in hydrocarbon rich solutions. As well, Kopecek and Sourirajan (1969) observed what they described as an equisorptic effect analogous to vapour liquid azeotropy but at different concentrations.

This work studies the case of ethanol-heptane binary mixtures and their fractionation by reverse osmosis. This mixture was chosen for several reasons: it demonstrates an azeotropic mixture; sufficient analysis for concentration was by refractometry; the mixture was miscible at all concentrations; and dilute solution experiments with cellulose acetate membranes and alcohol solutions demonstrated the stability of these membranes in nonaqueous media. The three membrane types used in this work (PPPH 8273, cellulose acetate, and cellulose) were chosen because of existing fabrication methods and their performance with aqueous and other solutions.

Results and Discussion

The reverse osmosis experiments were performed at 6900 kPag with solutions that ranged from pure ethanol to pure heptane and back to pure ethanol, followed by a set performed at 3450 kPag from pure ethanol to pure heptane. Details of the membranes used are shown in Table 6-1. The results are shown graphically for representative membranes in Fig 6-1 for 6900 kPag and Fig 6-2 for 3450 kPag operating pressure where both the permeate rates and permeate concentrations are shown with the feed solution concentration. As well, Table 6-2 shows data for the reverse osmosis separation of LiCl in ethanol solutions before and after contact with the ethanol-heptane mixtures.

It can be seen from Figs 6-1 and 6-2 that there is a distinct difference between the cellulose and cellulose acetate membranes both in terms of permeation rates and the degree of separation. The PPPH 8273 membrane did not survive these experiments and data were not included beyond the point where a possible "pin hole" was found in the membrane. With respect to the product permeation rates, the cellulose acetate membrane showed a large decrease to almost no flow as the amount of heptane in the feed solution was increased with only partial recovery for the pure ethanol experiments. This decrease in permeation rate is the same as observed by Kopecek and

Table 6-1

Reverse Osmosis Membranes Used in Ethanol-Heptane System.

Membrane No.	1	2	3	4	5	6
Material	CE	CE	CE	CA	CE	PPPH 8273
Type	–	–	–	316(10/30)	–	–
Cellulose,g	17.96	17.96	17.96	–	17.53	–
DMSO,g	113.75	113.75	113.75	–	108.15	–
Paraformaldehyde,g	17.65	17.65	17.65	–	17.25	–
Evaporation Temp.,°C	135°	135°	137°	30°	122°	90°
Evaporation Time, min.	10	10	10	1	10	10
Gelation Solvent[a]	i-PrOH	i-PrOH	Toluene	H_2O	H_2O	H_2O
Gelation Time, min.	105	105	105	–	–	–
Regeneration	H_2O	H_2O	H_2O	–	H_2O	–
Shrinkage Temperature, °C	–	–	–	75	–	–

[a] Room Temperature; i-PrOH = i-propanol; H_2O = water.

7

Figure 6-1

Feed and Permeate Relation for the Ethanol-Heptane System at 6900 kPag and 25°C

△ Cellulose Acetate
□ PPPH 8273
○ Cellulose (No. 3)
◇ Cellulose (No. 5)

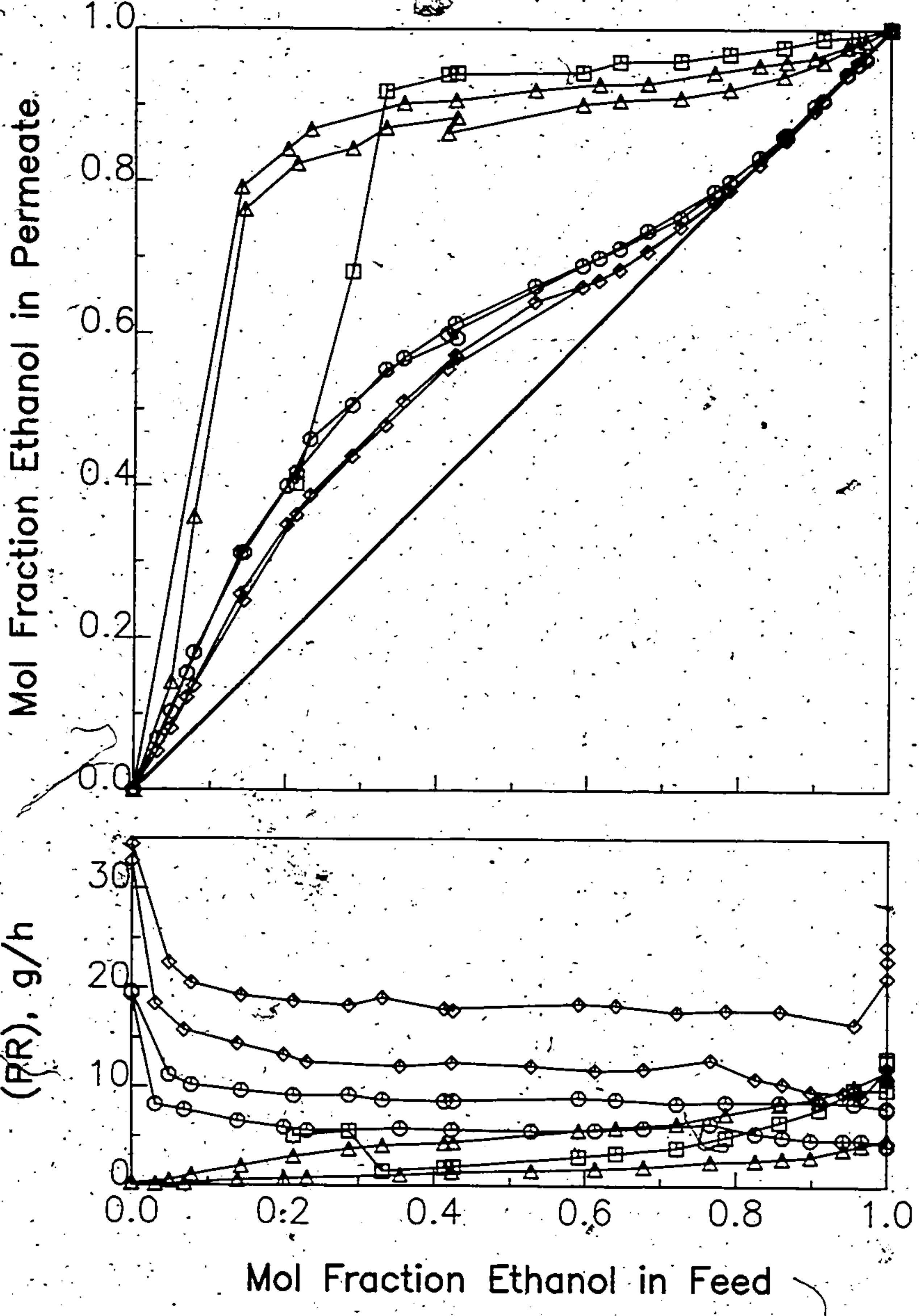
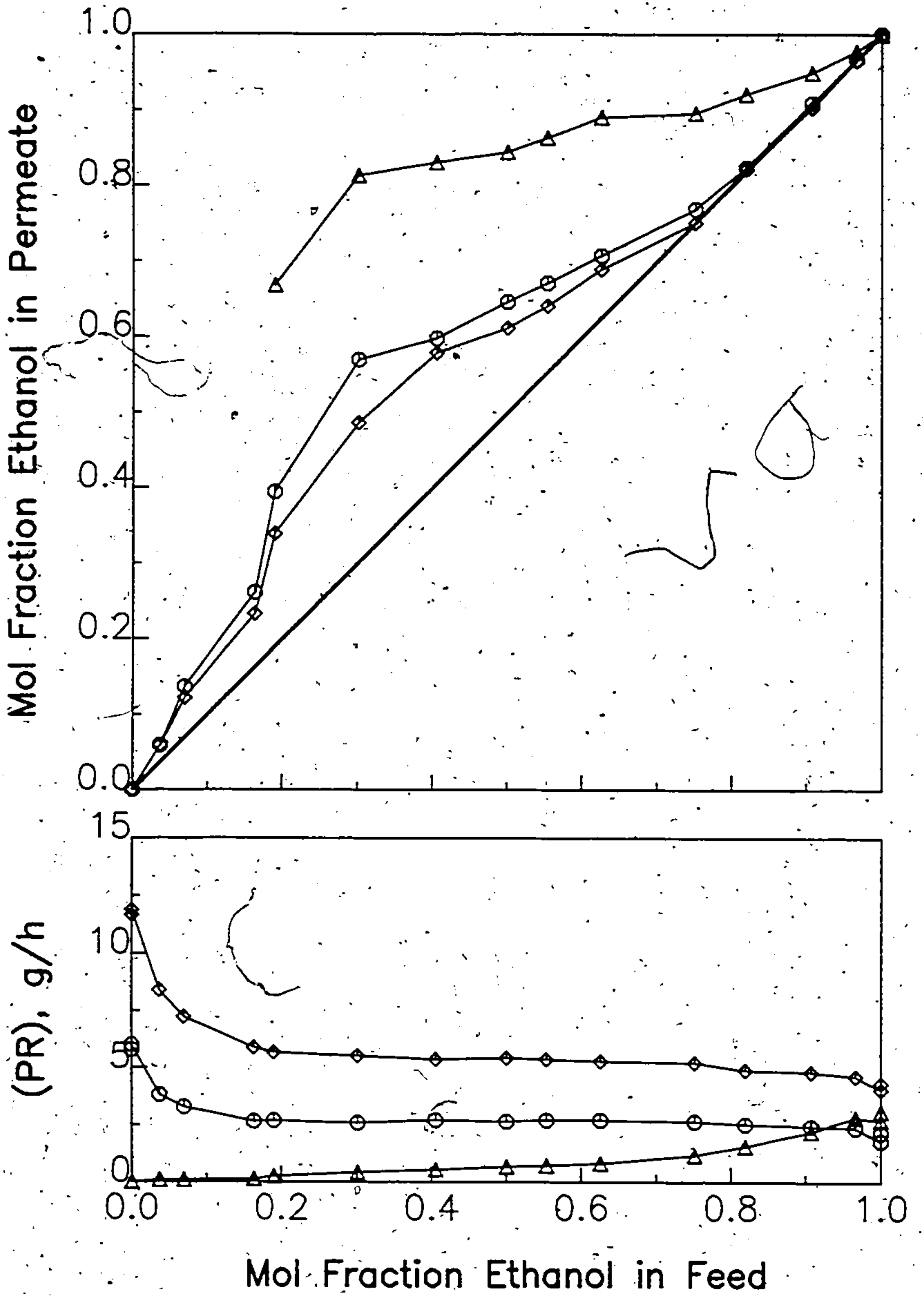

1.0
0.8
0.6
0.4
0.2
0.0
Mol Fraction Ethanol in Permeate
30
20
10
0
(PR), g/h
0.0
0.2
0.4
0.6
0.8
1.0
Mol Fraction Ethanol in Feed

Figure 6-2

Feed and Permeate Relation for the Ethanol-Heptane System at 3450 kPag and 25°C

△ Cellulose Acetate
○ Cellulose (No.3)
◇ Cellulose (No.5)


1.0
0.8
0.6
0.4
0.2
0.0
Mol Fraction Ethanol in Permeate
15
10
5
0
(PR), g/h
0.0
0.2
0.4
0.6
0.8
1.0
Mol Fraction Ethanol in Feed

Sourirajan (1970). This trend was also observed for the PPPH 8273 membrane for the concentration ranges which were available. The cellulose membranes did not show the same drastic decrease of permeation rate with heptane concentration and there was an almost complete recovery of permeation rate when the feed solution returned to pure ethanol. It is felt that the cellulose membranes show superior resistance to structural collapse in the ethanol-heptane binary mixture than the other two membranes.

The concentrations of the feed and permeate solution reported in Figs 6-1 and 6-2 also show a large difference between the membranes. The cellulose acetate and PPPH 8273 membranes (for the limited range available) show similar behaviours with a large excursion of permeate concentration from that of the feed solution. This was also reported by Kopecek and Sourirajan (1970). The cellulose membranes show smaller excursions of the permeate concentration from that of the feed and there is also the presence of an azeotrope analog condition similar to the observations of Kopecek and Sourirajan (1969) for cellulose acetate membranes and alcohol-aromatic solutions. This demonstrates that the azeotrope analog effect in reverse osmosis is related to the membrane material, and may not occur in some cases. When this work is combined with the results of Kopecek and Sourirajan (1969; 1970), it is also apparent that the azeotrope analog condition is related to the solution components' interactions. This is unlike vapour-liquid azeotropy where the azeotrope phenomena is dependent solely on the solution.

The effect of porosity on the separation is evident for the cellulose membranes. Table 6-2 contains the reverse osmosis separation data for LiCl-ethanol solutions both before and after the ethanol-heptane solutions were studied. In terms of the relative porosity of the cellulose membranes, the membranes which had higher LiCl separations showed greater differences in feed solution and permeate concentrations, as well as a lower permeation rate.

Another indication of the effect of changing solvents on the membranes is the calculation of pure liquid permeation rates modified for both viscosity and density of the liquids. These are shown sequentially in Table 6-3 for both 6900 kPag and 3450 kPag operating pressures. The modified permeation rates for the cellulose acetate membranes are almost nil for pure heptane and do not return to the original value for ethanol, while the cellulose membrane shows a similar modified permeation rate for all three cases. This is a further indication that the cellulose membrane structure is not severally affected by the heptane in the feed mixture and shows their superior capacity to handle hydrocarbon liquids when compared to cellulose acetate and the PPPH 8273 membranes.

Table 6-2

Experimental Reverse Osmosis Results with LiCl-Ethanol Solutions Before and After the Ethanol-Heptane Experiments, at 6900 kPag and 25°C.

Position	Concn molal × 10^3	Membrane No.	Membrane[a] Material	(PSP)[b]	(PR)[b]	f,%
Before	5.511	1	CE	5.03	4.61	15.2
		2	CE	3.07	2.79	40.9
		3	CE	7.75	7.60	33.4
		4	CA	10.94	10.80	>99.9
		5	CE	22.84	15.22	22.6
		6	PPPH	12.62	11.98	>99.9
After	6.643	1	CE	2.19	1.95	41.7
		2	CE	1.83	1.79	41.5
		3	CE	4.14	4.03	38.5
		4	CA	4.99	4.88	>99.9
		5	CE	11.97	11.14	24.0
Before	81.46	1	CE	5.19	4.37	24.7
		2	CE	3.03	2.54	31.4
		3	CE	7.98	6.60	22.3
		4	CA	11.62	9.94	97.6
		5	CE	21.08	13.31	14.4
		6	PPPH	13.19	9.83	97.8
After	74.09	1	CE	2.32	2.07	32.9
		2	CE	1.92	1.67	38.1
		3	CE	4.24	3.68	29.4
		4	CA	5.36	4.87	99.0
		5	CE	10.68	7.13	21.1

[a] CE = Cellulose; CA = Cellulose Acetate; PPPH = PPPH 8273.

[b] g/h for 13.2 cm^2 surface area.

Table 6-3

Modified Permeation Rates for Pure Ethanol and Pure Heptane at 25°C

Solvent	P, kPag	$\frac{(PR)}{(13.2)} \cdot \nu \cdot \frac{1}{(3600)} \cdot \frac{1}{P}$, m/s × 10^8, for Membrane Number					
		1^a	2^a	3^a	4^b	5^a	6^c
Ethanol	6900	37.3	22.8	57.5	81.1	169.3	93.6
		37.8	22.5	58.4	84.7	179.5	95.8
		36.7	22.5	59.2	86.1	156.3	75.2
Heptane	6900	34.9	26.5	60.4	0.7	106.1	–
		33.7	26.2	59.9	0.8	101.0	–
Ethanol	6900	16.2	14.2	31.6	35.5	71.3	–
		16.2	13.6	30.7	35.5	88.7	–
		15.8	14.4	31.7	38.2	64.0	–
		15.9	13.4	30.1	39.6	88.3	–
		17.2	14.2	31.3	39.7	79.2	–
Ethanol	3450	17.2	15.4	32.0	45.7	64.1	–
		14.4	9.3	26.7	40.2	60.2	–
Heptane	3450	18.3	14.5	36.9	0	73.2	–
		17.7	12.9	35.6	0	71.9	–

[a] Cellulose Membranes

[b] Cellulose Acetate Membranes

[c] PPPH 8273 Membranes

Conclusion

The use of reverse osmosis in a binary mixture fractionation has been demonstrated in a circulating feed solution system and with several different membranes. Each membrane type shows different permeation rates and separation characteristics as well as properties attributable to the variation of porosity. This is further evidence of the elementary principle of preferential adsorption and pore flow as the mechanism of reverse osmosis. Also, the presence of a vapour-liquid azeotrope condition had no visible relation to or effect upon reverse osmosis performance. The azeotrope analog has been demonstrated to be dependent upon the membrane material as well as the feed solution's nature. The resistance of the cellulose membranes to solvent degradation was observed, while the cellulose acetate and PPPH 8273 membranes showed greater separations. Quantification of parameters describing this type of reverse osmosis separation remains to be studied.

Chapter 7

Conclusion

A major contribution of this work is the extension of existing reverse osmosis literature to include nonaqueous solutions. This includes the separation of inorganic salts as well as organic solutes in their methanol and ethanol solutions. For the inorganic salts, free energy parameters were generated by the Kimura-Sourirajan analysis for the ions studied as well as for several ion pairs. These were used to successfully predict reverse osmosis performance in both the methanol and ethanol solutions. Combined with successful results in aqueous solutions, this demonstrates the validity of the Kimura-Sourirajan analysis, regardless of solvent. An attempt was made to correlate the ionic free energy parameters with a mobility term that would enable the prediction of reverse osmosis performance in other solutions.

Surface potential parameters were calculated for both the inorganic salts and the organic solutes in methanol and ethanol solutions by using the surface potential-pore flow model. The success of this model for the prediction of reverse osmosis performance including the enrichment of the solute (negative separation) as well as the enrichment of the solvent, demonstrates the validity of its use in both aqueous and nonaqueous solutions. Combined with the successful results of the Kimura-Sourirajan model, this leads to the conclusion that the reverse osmosis mechanism upon which the two models are based is the same in the alcohol cases as well as the aqueous case. Further, this mechanism should be the same for all other solution systems. An attempt to correlate surface potential parameters with suitable surface excess concentration terms demonstrates the effect of the interfacial properties on reverse osmosis performance.

Another contribution of this work has been the development of a cellulose reverse osmosis membrane. No comparable membrane has been described in the literature, both in terms of pore size (as measured by solute separation) and the degree of unaltered cellulose. These membranes were evaluated in aqueous reverse osmosis experiments to determine both surface potentials and free energy parameters of various salts and solutes. A concentration dependence of performance was also observed, and an attempt was made to measure this effect. The surface potentials and free energy parameters were compared with results for other membranes, which highlighted the unique properties of the cellulose membranes.

An experimental study of the reverse osmosis fractionation of binary mixtures of liquids has also been contributed to the literature by this work. It has been shown that vapour-liquid azeotropic conditions have no effect upon reverse osmosis performance. Also, confirmation of an azeotrope analogue condition has been made as well as an initial observation of the interfacial dependence of the azeotrope condition by changing the membrane material. The effect of porosity on membrane performance was demonstrated by using the same set of membranes throughout.

The primary conclusion that can be made from this work is that the physicochemical approach to the description of reverse osmosis can be used to anticipate and predict reverse osmosis performance in both nonaqueous as well as aqueous conditions. This work also supports the use of the physicochemical approach for the description of reverse osmosis in all of its forms.

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Nomenclature

A = pure solvent permeability constant, (mols solvent)$\cdot$ $m^{-2}\cdot s^{-1}\cdot kPag^{-1}$.

$\underset{\sim}{A}$ = constant characterizing electrostatic repulsive force, m.

A_p = specific surface area of polymer powder in the chromatography experiments, m^2/g.

A_1 = electrostatic interaction term in eq 3-52.

a_s = solvent activity.

B = solute membrane permeability.

$\underset{\sim}{B}$ = constant characterizing van der Waals' attractive force, m^3.

B_i = ionic viscosity coefficient parameter in eq 3-53.

B_1 = salt's viscosity coefficient parameter in eq 3-52.

b = solute friction in membrane pores.

c = molar density of solution, $mols/m^3$.

c_{AM} = concentration of solvent in the membrane.

c_{BM} = concentration of solute in the membrane.

c_B = solute concentration.

$\bar{c}$ = mean solute concentration in the membrane.

C^* = membrane porosity coefficient, m/s.

$\underset{\sim}{D}$ = distance associated with steric repulsion at the interface, m.

D_{1m} = diffusivity of solvent in the membrane.

D_{AM} = diffusivity of solute in the membrane.

D_{AB} = diffusivity of A in B, m^2/s.

$D_{AM}/K\delta$ = solute transport parameter, treated as a single variable, m/s.

d = density, kg/m^3.

d_s = membrane surface diameter (circular cells), m.

E = Born equation parameter, $kJ \cdot m \cdot mol^{-1}$.

e_o = electronic charge.

F = Faraday constant.

f = solute separation.

f' = solute separation based on the boundary layer concentration.

ΔG = free energy of solvation, kJ/mol.

$\Delta\Delta G$ = surface excess free energy of solvation, eq 3-13, kJ/mol.

h = characteristic cell dimension.

J_A = solvent flux through a membrane.

J_B = solute flux through a membrane.

K = distribution of solute between the bulk solution and the membrane.

K_D = ionic dissociation constant.

k = mass transfer coefficient on the high pressure side of the membrane, m/s.

$\underset{\sim}{k}$ = Boltzmann Constant.

L_p = hydraulic membrane permeability.

M_B = molecular weight of solute, g/mol.

N = mols of ion per mol of solute.

N_o = Avogadro's Number.

N_B = solvent flux through the membrane, $mol \cdot m^{-2} \cdot s^{-1}$.

N_{Re} = Reynold's number.

N_{Sc} = Schmidt's number.

N_{Sh} = Sherwood's number.

n_i = mols of ion i.

P = operating pressure, kPag.

(PR) = experimental product permeation rate, g/h for 13.2 cm^2 surface area.

(PSP) = experimental pure solvent permeation rate, g/h for 13.2 cm^2 surface area.

Q = high pressure side volumetric flow rate.

R = effective membrane pore radius, m.

$\underset{\sim}{R}$ = universal gas constant, 8.314×10^{-3} $J \cdot K^{-1} \cdot mol^{-1}$.

R_a = laminar flow pore radius, m.

R_b = "hard wall" pore radius, m.

r = radial distance from pore centerline, m.

r_A = Stoke's Law radius, m.

r_E = solvated ion size, m.

r_K = Kelvin radius, m.

S = effective membrane surface area, m^2.

T = temperature, K.

u_B = pore velocity.

V_s = molar volume of solution.

$\bar{V}_A$ = partial molar volume of the solvent.

$\tilde{V}$ = molar volume of pure solvent.

V'_R = experimental liquid chromatography retention volume.

v_E = solvated ion volume.

ΔW = excess energy of an ion inside a membrane pore, kJ/mol.

X = mol fraction.

X_A = mol fraction of solute.

x = distance, m.

Y = ratio of the dielectric constants of liquid and solid, eq (1-8).

Z_i = ion charge valence.

Greek Letters

α = degree of ionic dissociation.
α_g = defined in eq (1-9).
$\alpha(\rho)$ = dimensionless solution velocity profile in a pore.
β = concentration dependant parameter defined in eq 3-24.
β_1 = dimensionless quantity defined by eq 4-14.
β_2 = dimensionless quantity defined by eq 4-15.
Δ = parameter in modified Born equation, m.
δ = effective pore length.
γ = activity coefficient.
Γ = surface excess concentration, mol/m^2.
ε = dielectric constant.
κ = inverse of Debye-Huckel ionic cloud distance, m^{-1}.
η = viscosity, Pa•s.
λ_i = ionic conductivity, S•(equiv)$^{-1}$.
λ = dimensionless parameter defined in eq 4-26.
μ = chemical potential.
ν = kinematic viscosity, s/m^2.
Π = osmotic pressure, kPa.
ρ = dimensionless radial pore distance.
σ = reflection coefficient described by eq 1-6.
ϕ = potential function for the interfacial force exerted on the solute from the membrane pore wall, J•mol^{-1}.

Φ = dimensionless potential function.

χ_{AB} = $(\underset{\sim}{R}T/D_{AB})$, friction between solute and solvent, $J \cdot s \cdot m^{-2} \cdot mol^{-1}$.

ω = solute membrane permeability.

Superscripts

$^{\circ}$ = pure solution case.

Subscripts

^{1,2,3} = pertaining to bulk, concentrated boundary layer, membrane permeated solution concentrations, respectively.

A = pertaining to solute.

B = pertaining to solvent or bulk solution phase.

IP = pertaining to ion pairs.

s = pertaining to solvent.

i = pertaining to ion of type i.

+,- = pertaining to cations and anions, respectively.

$\pm$ = pertaining to the mean ionic property.

Appendix A

Sample Calculations of the Kimura-Sourirajan Transport Equations

An example of the calculation of $(D_{AM}/K\delta)$'s from experimental data is given here. The dilute solution case is considered here, with the experimental data from Run No. 9 for LiCl in ethanol solvent found in Table A-1-6. The results for membrane no. 1 are (PSP) of 17.52 g/h, (PR) of 17.33 g/h, an 83.4% separation, and a membrane surface area of 13.2 cm². Equation 3-7 can be used to determine $(D_{AM}/K\delta)$ since at the 0.0009453 molal concentration used in this experiment the osmotic pressure contribution is negligible. This equation also requires information on the density of ethanol, which was taken as 0.7892 g/mL.

The pure solvent transport parameter, A, is calculated by eq 3-1, where P is 1725 kPag, and M_B is 44 g/mol. This is shown as

$$A = \frac{17.52\ \mathrm{g/h}}{44\mathrm{g/mol} \cdot 13.2\ \mathrm{cm}^2 \cdot 3600\mathrm{s/h} \cdot 1725\ \mathrm{kPag}}$$

$$= 4.858 \times 10^{-9}\ \mathrm{mol/(cm^2 \cdot kPag \cdot s)}$$

$$= 5.858 \times 10^{-5}\ \mathrm{mol/(m^2 \cdot kPag \cdot s)}$$

With this value of A, the mass transfer coefficient can be determined by eq 3-45 as

$$k = 0.04951\ (4.858 \times 10^{-5}) + 5.962 \times 10^{-6}$$

$$= 8.371 \times 10^{-6}\ \mathrm{m/s}$$

Thus with eq 3-7, $(D_{AM}/K\delta)$ can be determined by

$$(D_{AM}/K\delta) = \frac{17.52\ g/h}{3600 s/h \cdot 13.2 cm^2 \cdot 0.7892\ g/mL} \cdot \frac{(1-0.902)}{0.902}$$

$$\times \left[\exp\left(\frac{17.52\ g/h}{3600 s/h \cdot 13.2 cm^2 \cdot 0.7892\ g/mL \cdot 8.371 \times 10^{-6} m/s}\right)\right]^{-1}$$

$$= 1.923 \times 10^{-6}\ m/s$$

For the calculation of reverse osmosis separation for dilute cases where osmotic pressure is not significant, eq 3-47 can be used. For the case of LiBr in run No. 6 and membrane No. 3 in Table A-1-6, the concentration was 0.001074 molal and the operating pressure was 1725 kPag. As well, the (PSP) for membrane No. 3 is 23.04 g/h for 13.2 cm^2 of membrane surface. From previous information (Table 3-13), the membrane porosity, ln C^*_{LiCl}, was taken as -9.38. On the basis of this information and the surface potential free energy parameters that are given in Table 3-10, the calculation can be made.

With the (PSP) and operating pressure information, A is calculated as

$$A = \frac{23.04\ g/h}{44 g/mol \cdot 13.2 cm^2 \cdot 3600 s/h \cdot 1725\ kPag}$$

$$= 6.389 \times 10^{-5}\ mol/(m^2 \cdot kPag \cdot s)$$

With this value of A, the mass transfer coefficient for LiCl can be calculated as

$$k_{ref} = 0.04951\ (6.546 \times 10^{-5}) + 5.962 \times 10^{-6}$$

$$= 9.125 \times 10^{-6}\ m/s$$

Unlike the previous example, because the reference case of the mass transfer coefficient is for dilute LiCl, a conversion must be made with eq 3-26 for LiBr. Because of the dilute concentration, the limiting diffusivities of Table 3-2 are used in eq 3-26, where $(D^\circ_{AB})_{LiCl}$ is 4.92×10^{-10} and $(D^\circ_{AB})_{LiBr}$ is 5.03×10^{-10}. The mass transfer coefficient of LiBr is then calculated as

$$\begin{aligned} k &= k_{ref}\,(D^\circ_{AB}/(D^\circ_{AB})_{ref})^{2/3} \\ &= 9.125 \times 10^{-6}\,(5.03/4.92)^{2/3} \\ &= 9.260 \times 10^{-6}\ \mathrm{m/s} \end{aligned}$$

This mass transfer coefficient was the one used in eq 3-47. A further requirement is the value of $(D_{AM}/K\delta)$ for LiBr. This is calculated as in eq 3-15 where the surface excess free energy parameters for the ions are taken from Table 3-10:

$$\begin{aligned} \ln(D_{AM}/K\delta) &= \ln C^*_{LiCl} + \sum_i n_i\,(-\Delta\Delta G/RT)_i \\ &= -9.38 + (-5.40) + (-0.43) \\ &= -15.21 \end{aligned}$$

and $(D_{AM}/K\delta)$ is 2.480×10^{-7} m/s.

Equation 3-47 is then calculated as

$$\begin{aligned} f &= \left[1 + (D_{AM}/K\delta)\cdot\frac{3600\cdot s\cdot d}{(PSP)}\exp\left[\frac{(PSP)}{3600\cdot s\cdot d\cdot k}\right]\right]^{-1} \\ &= \left[1 + 2.480 \times 10^{-7}\ \mathrm{m/s}\cdot\frac{3600\ \mathrm{s/h}\cdot 13.2\ \mathrm{cm}^2\cdot 0.7822\ \mathrm{g/mL}}{23.04\ \mathrm{g/h}}\right. \\ &\quad \left.\times \exp\left[\frac{23.04\ \mathrm{g/h}}{3600\ \mathrm{s/h}\cdot 13.2\ \mathrm{cm}^2\cdot 0.7822\ \mathrm{g/mL}\cdot 9.260\times 10^{-6}\ \mathrm{m/s}}\right]\right]^{-1} \\ &= 0.969 \end{aligned}$$

or 96.9% separation. This result can be compared with the experimental separation of 93.9% in Table A-1-6. As well, the assumption of equivalent (PSP) and (PR) is verified by the comparison of the two.

Appendix A-1

Experimental Results

Table A-1-1

Liquid Chromatography Retention Volumes for Cellulose Acetate Polymer and and Methanol and Ethanol Solutions.

Solute	Ethanol[a] $[V']_A$ m^3 x 10^6	Methanol[b] $[V']_A$ m^3 x 10^6
Acetonitrile	1.576	2.757
Propionitrile	2.327	2.631
Valeronitrile	1.880	2.491
Benzonitrile	2.105	2.477
Nitromethane	1.549	3.148
1-Nitropropane	2.181	2.658
2-Nitropropane	2.259	2.519
Propionamide	1.542	2.044
n-Butyramide	1.536	1.987
i-Butyramide	1.455	1.959
Aniline	2.816	2.728
Triethylamine	1.634	1.885
N,N-Dimethylbenzylamine	1.579	2.081
N,N-Dimethylaniline	1.996	2.449
Sucrose	1.627	1.708
Raffinose	1.741	--
Resorcinol	1.498	2.141
Ethylene Glycol	1.326	1.987
CCl_4	1.361	--
Polyacrylic Acid, 2k	1.442	--
Phenol	1.531	2.211
H_2O	1.458	2.038
Methanol	1.402	--
Methanol-d	--	1.994
Ethanol-d	1.285	--
Ethanol	--	1.903
Heptane	1.614	--
Benzene	1.619	2.225
Toluene	1.594	2.141
Ethylbenzene	1.482	2.057
o-Xylene	1.532	2.169
p-Xylene	1.472	2.099
Cumene	1.381	2.001
n-Propylbenzene	1.361	2.001
Mesitylene	1.397	2.029
n-Butylbenzene	1.270	1.959
s-Butylbenzene	1.257	1.917
i-Butylbenzene	1.217	1.917
t-Butylbenzene	1.278	1.932

Table A-1-1 (cont'd)

Solute	Ethanol[a] $[V']_A$ $m^3 \times 10^6$	Methanol[b] $[V']_A$ $m^3 \times 10^6$
$MgCl_2$	1.007	1.690
$CaCl_2$	1.060	1.715
$SrCl_2$	1.055	1.715
$BaCl_2$	--	1.739
LiF	0.757	--
LiCl	0.934	1.690
LiBr	0.956	1.715
NaCl	1.012	1.715
NaBr	1.179	1.714
NaI	1.289	1.910
KF	1.455	2.019
KCl	0.956	1.934
KBr	1.020	1.946
KI	0.997	2.056
RbCl	1.004	2.030
RbBr	1.020	--
RbI	1.174	--
CsCl	1.037	2.032
CsBr	1.075	2.080
$MgBr_2$	0.976	1.666
$MgSO_4$	1.510	--
$Sr(NO_3)_2$	1.192	--
Li_2SO_4	1.538	--
$NaNO_2$	1.510	--
$NaNO_3$	1.047	--
$NaClO_3$	1.009	--
$NaClO_4$	1.571	--
NH_4Cl	1.037	--
NH_4OH	0.764	--
HCl	0.918	--
$LiNO_3$	--	1.727

[a] Ethanol Flow Rate of 0.265 mL/min., 0.8715 g of cellulose acetate powder, 25°C.

[b] Data supplied by Taketani et al. (1981). Methanol Flow Rate of 0.267 mL/min., 0.92 g of cellulose acetate powder, room temperature (23-25°C).

Table A-1-2

Liquid Chromatography Retention Volumes for Aqueous Solutions and Cellulose Material[a]

Solute	$[V']_A$, $m^3 \times 10^6$
Na, K Tartate	1.995
Na Benzoate	2.038
Na Acetate	2.017
Na Succinate	2.022
Na Citrate	2.006
K-Biphthalate	2.142
Na Oxalate	2.440
Pimelic Acid	2.281
Citric Acid	2.244
Lactic Acid	2.188
i-Butyric Acid	2.173
Valeric Acid	2.223
Malonic Acid	2.355
Pivalic Acid	2.170
Adipic Acid	2.247
Malic Acid	2.305
Suberic Acid	2.257
Azelaic Acid	2.334
Benzoic Acid	2.064
Tartaric Acid	2.218
Succinic Acid	2.239
Acetic Acid	2.162
D_2O	2.290
Methanol	2.180
Ethanol	2.135
n-Propanol	2.154
i-Propanol	2.157
n-Butanol	2.135
s-Butanol	2.130
i-Butanol	2.170
t-Butanol	2.122
n-Pentanol	2.151
n-Hexanol	2.183

Table A-1-2 (cont'd)

Solute	$[V']_A$, $m^3 \times 10^6$
n-Octanol	2.218
n-Nonanol	2.265
Cyclohexanol	2.180
2,3-Butanediol	2.146
1,2,6-Hexanetriol	2.154
Glycerol	2.162
Ethylene Glycol	2.178
Polyethylene Glycol 200	2.104
PEG 300	2.067
PEG 600	2.048
PEG 1000	2.062
PEG 1500	2.033
PEG 3000	2.048
PEG 4000	2.067
PEG 6000	2.106
PEG 9000	2.064
PEG 15000	2.080
PEG 20000	2.075
Sucrose	2.125
Dextrose	2.167
Fructose	2.170
Glucose	2.175
d-Sorbitol	2.196
d-Xylitol	2.159
Lactose	2.149
Raffinose	2.128
PVA 2,000	2.054
PVA 10,000	2.043
PAA 5,000	2.014
PAA 50,000	2.003
PEI 1800	2.083
Phenol	2.397
p-Chlorophenol	2.841

Table A-1-2 (cont'd)

Solute	$[V']_A$ $m^3 \times 10^6$
o-Nitrophenol	2.737
m-Nitrophenol	2.763
p-Nitrophenol	2.837
Acetonitrile	2.088
Propionitrile	2.135
Acetamide	2.215
Propionamide	2.178
Nitromethane	2.315
1-Nitropropane	2.302
2-Chloropropane	2.231
Aniline	3.252
Methyl-Ethyl Ketone	2.328
Acetone	2.159
Methyl-i-Butyl Ketone	2.236
Methyl-i-Propyl Ketone	2.188
Di-i-Propyl Ketone	2.125
Di-i-Butyl Ketone	2.106
Cyclohexanone	2.188
Acetophenone	2.207
Anisole	2.183
n-Butyl Ethyl Ether	2.202
di-Ethyl Ether	2.275
Phenetole	2.191
Methyl Acetate	2.265
Ethyl Acetate	2.239
Propyl Acetate	2.244
n-Butyl Acetate	2.275
s-Butyl Acetate	2.498
i-Butyl Acetate	2.239
t-Butyl Acetate	2.244
Benzene	2.418
Toluene	2.328
Ethylbenzene	2.365

Table A-1-2 (cont'd)

Solute	$[V'_A]$[illegible], m^3 x 10^6
o-Xylene	2.281
m-Xylene	2.218
Cumene	2.302
n-Butylbenzene	2.384
s-Butylbenzene	2.344
i-Butylbenzene	2.463
t-Butylbenzene	2.218
$MgCl_2$	2.083
$CaCl_2$	2.104
$SrCl_2$	2.054
$BaCl_2$	2.035
$MgBr_2$	2.064
LiF	2.075
LiCl	2.130
LiBr	2.070
LiI	2.131
NaF	2.120
NaCl	2.098
NaBr	2.114
NaI	2.109
KF	2.059
KCl	2.064
KBr	2.083
KI	2.067
RbCl	2.130
RbBr	2.151
RbI	2.152
CsCl	2.022
CsBr	2.027
CsI	2.078
$NaNO_2$	2.090
$NaNO_3$	2.093
NaSCN	2.053

Table A-1-2 (cont'd)

Solute	$[V'_A]$, m^3 x 10^6
$NaClO_3$	2.130
$NaBrO_3$	2.098
$NaIO_3$	2.112
Na_2HPO_4	2.093
Na_2SO_4	2.067
Na_2SO_3	2.431
H_3BO_3	2.313
HCl	2.082
H_2SO_4	2.067
NaOH	2.083

[a] 0.7715 g (dry) cellulose powder, water flow rate of 0.266 mL/min., 25°C.

Table A-1-3

Peak Heights and Retention Times for Methanol on Cellulose Acetate Powder for Surface Area Determination

μL injected	Peak Height x 2.54, mm	Retention Time, cm	Peak Area, cm^2	Detector Attenuation Factor
2.0	23.3	2.10	11.73	8
2.5	24.5	1.80	14.97	8
5	26.3	1.30	14.17	16
10	30.8	0.80	3.193	32
10	16.0	0.90	7.028	64
20	44.5	0.50	1.337	64
30	18.0	0.36	4.799	256
40	28.5	0.25	7.258	256
60	46.7	0.18	10.23	256
70	54.0	0.20	11.10	256
80	53.3[b]	0.20	12.39	256
90	53.0[b]	0.30	12.35	256
100	53.5[b]	0.40	14.34	256
110	53.8[b]	0.45	14.44	256
120	53.9[b]	0.45	15.60	256
130	53.0[b]	0.40	16.80	256
140	53.0[b]	0.49	18.08	256
150	53.0[b]	0.50	19.81	256
250	54.0	1.45	21.16	256

[a] 63.0°C column temperature, 240 mm/hour chartspeed, 23.80 mL He/minute, 0.6205 g cellulose acetate powder.

[b] These values were considered to be 54.0.

Table A-1-4

Peak Heights and Retention Times for Ethanol on Cellulose Acetate Powder for Surface Area Determination

Injection Size µL	Attenuation Factor	Peak Height, cm	Retention Time, cm	Peak Area, cm^2
5	16	0.35	1.63	1.236
10	16	1.00	0.97	2.366
15	16	1.91	0.69	3.948
20	16	3.03	0.57	5.457
30	16	6.78	0.40	8.504
40	16	10.50	0.46	11.208
50	16	12.71	0.51	13.55
60	16	13.97	0.61	15.78
70	16	14.50	0.74	18.78
80	16	14.60	0.88	20.31
90	16	14.60	0.84	23.49
100	16	14.60	0.90	25.36
110	16	14.60	0.90	28.50
120	16	14.60	0.90	29.49
130	16	14.60	1.00	32.21
140	16	14.60	0.82	34.40
150	16	14.60	0.80	37.53
200	16	14.60	0.84	48.70
250	16	14.60	0.85	64.72

[a] Column Temperature, 67°C; 26.78 mL He/minute, 0.6205 g of cellulose acetate powder.

Table A-1-5

Experimental Reverse Osmosis Results for Dilute Methanol Solutions and Cellulose Acetate Membranes at 25°C

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f,%
1	NaCl	5.130	1725	13	17.44	17.28	78.2
				14	52.68	52.20	72.6
				15	47.68	47.48	70.7
				16	32.12	32.00	80.2
				17	38.24	38.08	78.9
				18	34.20	34.00	80.7
2	NaCl	5.591	1725	13	17.40	16.89	78.4
				14	52.67	51.41	72.7
				15	47.31	46.26	71.1
				16	31.83	31.14	80.9
				17	37.86	37.29	78.6
				18	33.91	33.09	81.1
3	$CaCl_2$	4.865	1725	13	17.36	17.12	99.6
				14	52.24	51.36	98.7
				15	47.40	46.92	97.9
				16	31.88	31.68	99.4
				17	37.62	37.56	99.1
				18	33.92	33.40	99.1
4	$LiNO_3$	5.707	1725	13	17.56	16.74	86.3
				14	53.12	51.00	81.6
				15	47.92	45.78	80.0
				16	32.28	31.14	86.3
				17	38.44	37.14	88.3
				18	34.00	32.91	88.3
5	$Sr(NO_3)_2$	5.592	1725	13	17.37	16.97	96.8
				14	52.73	50.87	91.1
				15	47.20	46.13	89.4
				16	31.97	30.97	93.4
				17	37.93	36.83	94.8
				18	33.60	32.50	95.2
6	NaCl	5.527	1725	13	16.94	16.60	77.1
				14	50.98	48.44	74.0
				15	46.20	44.54	70.3
				16	31.52	30.70	79.2
				17	37.10	36.44	77.8
				18	33.04	32.18	79.5

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	(PSP)^a, g/h	(PR)^a, g/h	f,%
7	KBr	5.270	1725	13	16.80	16.56	60.9
				14	50.36	50.16	54.1
				15	45.68	45.24	52.3
				16	30.96	30.60	62.8
				17	36.68	36.44	61.0
				18	32.44	32.04	64.1
8	NaCl	6.220	1725	13	17.08	16.65	77.8
				14	52.33	50.38	72.1
				15	47.23	45.55	70.6
				16	31.95	36.43	78.3
				17	37.88	30.70	79.7
				18	33.23	32.05	80.3
9	KBr	5.733	1725	13	16.95	16.62	60.5
				14	51.39	50.40	54.4
				15	46.53	45.63	52.1
				16	31.20	30.72	52.1
				17	36.96	36.54	60.8
				18	32.64	31.23	63.7
10	$MgCl_2$	4.319	1725	13	16.77	16.23	99.6
				14	51.30	49.26	99.4
				15	46.53	44.43	99.4
				16	31.14	30.09	99.5
				17	36.90	35.73	99.6
				18	32.16	31.23	99.5
11	$BaCl_2$	7.051	1725	13	16.53	15.90	99.6
				14	50.31	48.41	99.1
				15	45.24	43.64	98.7
				16	30.56	29.54	99.4
				17	36.37	35.15	99.4
				18	31.71	30.71	99.5
12	NaCl	4.897	1725	13	16.04	15.81	79.9
				14	48.96	49.06	72.4
				15	44.56	44.01	73.2
				16	30.00	29.72	81.1
				17	35.60	35.40	80.0
				18	31.04	30.95	82.1

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f, %
13	$SrCl_2$	5.257	1725	13	16.11	15.60	99.6
				14	49.77	48.03	99.0
				15	44.94	43.56	99.1
				16	30.33	29.84	99.3
				17	35.64	34.83	99.6
				18	30.84	30.06	99.4
14	LiCl	5.431	1725	13	16.05	15.79	87.9
				14	50.13	48.58	84.1
				15	45.15	43.85	84.0
				16	30.18	29.64	88.5
				17	35.88	35.06	88.1
				18	30.96	30.58	90.2
15	$NaClO_3$	5.759	1725	13	16.23	15.63	61.1
				14	49.83	48.81	73.5
				15	45.15	43.98	51.6
				16	30.57	29.58	27.0
				17	35.88	35.17	71.6
				18	31.26	30.49	82.0
16	$NaClO_4$	2.948	1725	13	16.08	15.54	75.9
				14	49.47	48.41	72.2
				15	44.73	43.41	75.9
				16	29.94	29.52	81.5
				17	35.67	34.77	83.3
				18	30.99	30.42	85.2
17	$NaNO_2$	7.151	1725	13	15.87	15.75	82.4
				14	49.23	48.66	82.4
				15	44.52	44.04	81.7
				16	29.91	29.64	86.3
				17	35.49	34.95	83.2
				18	30.75	30.51	87.0
18	$NaBrO_3$	8.990	1725	13	15.81	15.60	68.7
				14	48.48	47.61	74.2
				15	44.01	43.11	66.8
				16	29.61	29.19	78.8
				17	34.95	34.50	54.8
				18	30.21	29.85	76.0

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	(PSP)^a, g/h	(PR)^a, g/h	f,%
19	NaCl	5.110	1725	13	15.66	15.64	78.9
				14	48.75	47.94	73.5
				15	44.07	43.14	71.9
				16	29.82	28.97	80.5
				17	35.25	34.26	79.3
				18	30.64	29.88	82.0
20	$NaNO_3$	5.158	1725	13	16.04	15.57	76.7
				14	49.24	48.00	71.4
				15	44.60	43.41	71.4
				16	30.16	29.10	78.8
				17	35.56	34.68	77.8
				18	31.00	30.24	78.8
21	NH_4Cl	5.558	1725	13	15.91	15.67	76.9
				14	49.26	48.23	70.6
				15	44.14	43.67	67.0
				16	30.00	29.53	78.3
				17	35.09	34.70	77.4
				18	30.69	30.20	80.1
22	NaCl	4.989	1725	13	15.91	15.57	79.5
				14	44.24	43.11	73.8
				15	44.24	43.11	72.7
				16	30.00	29.20	80.6
				17	23.40	34.40	79.5
				18	30.78	29.74	82.4
23	Aniline	0.9101	1725	13	15.75	14.98	0.9
				14	48.63	48.53	0.1
				15	44.10	44.12	0.9
				16	29.67	29.70	2.4
				17	35.13	34.90	2.0
				18	30.72	30.53	−0.9

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f, %
24	N,N-Dimethylaniline	0.9299	1725	13	15.75	16.02	−0.1
				14	48.84	49.02	−0.3
				15	44.13	44.07	0.9
				16	29.55	29.37	0.2
				17	34.98	34.92	0.3
				18	30.51	30.54	−0.4
25	1-Nitropropane	1.033	1725	13	16.02	15.63	−3.0
				14	49.59	48.63	−3.9
				15	44.79	44.07	−2.1
				16	30.00	29.61	−1.1
				17	35.61	34.71	−5.9
				18	30.93	30.03	−7.2
26	Acetonitrile	0.8024	1725	13	15.87	15.81	3.4
				14	48.81	48.21	3.3
				15	44.34	43.80	−2.0
				16	29.46	29.22	−2.0
				17	34.71	34.98	2.8
				18	30.18	30.24	−4.7
27	Propionitrile	1.045	1725	13	16.03	15.46	0.1
				14	49.31	48.08	−1.2
				15	44.63	43.80	−1.2
				16	29.74	29.62	−0.3
				17	35.57	34.61	−0.9
				18	30.74	30.03	−0.9
28	Nitromethane	0.9991	1725	13	16.32	14.22	−1.7
				14	51.48	47.37	−2.8
				15	46.86	43.83	−2.4
				16	31.41	29.22	−4.1
				17	37.50	34.89	−4.1
				18	32.52	29.67	−4.5
29	Nitrobenzene	0.9138	1725	13	15.84	15.42	−3.1
				14	49.53	48.09	−3.5
				15	44.85	43.87	−1.6
				16	30.12	29.15	−1.7
				17	35.25	34.22	−0.9
				18	30.75	29.86	−4.8

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	(PSP)^a, g/h	(PR)^a, g/h	f,%
30	2-Nitropropane	0.9321	1725	13	15.93	15.54	-7.9
				14	49.02	48.24	2.4
				15	44.52	43.53	-5.3
				16	30.21	29.25	-2.3
				17	35.10	34.23	-8.5
				18	30.87	30.30	-1.9
31	Valeronitrile	0.8196	1725	13	15.88	15.38	0.3
				14	49.05	47.67	0.6
				15	44.35	44.10	0.6
				16	30.33	29.32	1.6
				17	35.30	34.58	3.5
				18	30.63	30.44	1.1
32	Benzonitrile	0.9113	1725	13	15.76	15.30	-1.5
				14	48.14	48.06	0.7
				15	43.36	43.32	6.2
				16	29.56	28.92	4.8
				17	34.20	34.74	3.8
				18	29.92	29.76	4.3
33	n-Butyramide	0.9541	1725	13	15.66	15.53	16.7
				14	48.03	47.98	13.0
				15	43.68	43.34	13.8
				16	29.22	29.14	19.1
				17	34.44	34.37	18.7
				18	29.94	30.00	17.6
34	i-Butyramide	0.9111	1725	13	15.63	15.39	19.7
				14	48.20	47.56	15.0
				15	43.29	42.97	17.6
				16	29.03	28.77	20.9
				17	34.17	33.99	22.7
				18	30.03	29.58	21.9
35	NaCl	3.320	1725	13	15.49	14.50	81.0
				14	48.09	46.41	75.7
				15	43.31	41.91	74.2
				16	29.06	28.14	82.3
				17	34.80	32.46	80.9
				18	29.26	28.47	83.9
36	Propionamide	0.9161	1725	13	15.69	14.69	7.4
				14	48.85	46.39	5.8
				15	43.77	42.23	6.7
				16	29.21	28.28	7.4
				17	34.23	33.37	7.2
				18	30.25	29.40	8.6

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f, %
52	Benzene	4.977	1725	13	15.03	14.88	2.6
				14	46.71	45.69	0.4
				15	42.15	41.37	0.2
				16	28.56	28.14	0.9
				17	33.00	32.49	1.4
				18	29.22	28.89	1.5
53	Toluene	5.067	1725	13	14.91	14.76	1.1
				14	46.47	45.78	0.4
				15	41.97	41.31	0.7
				16	28.53	28.23	1.1
				17	32.94	32.67	0.9
				18	29.46	29.10	1.3
54	o-Xylene	4.938	1725	13	14.91	14.88	5.7
				14	45.93	45.81	4.0
				15	41.34	41.46	5.6
				16	27.99	28.35	5.4
				17	32.31	32.88	5.4
				18	28.53	29.28	6.1
55	p-Xylene	4.798	1725	13	15.03	14.85	2.8
				14	46.50	45.66	3.4
				15	42.18	41.31	2.8
				16	28.65	28.17	5.2
				17	33.06	32.67	5.2
				18	29.52	29.07	5.8
56	Cumene	4.832	1725	13	15.09	14.97	13.7
				14	46.35	45.72	9.9
				15	41.91	41.52	9.9
				16	28.41	28.32	13.0
				17	33.00	32.97	13.2
				18	29.22	29.19	15.0
57	Ethylbenzene	4.846	1725	13	14.91	15.00	4.8
				14	46.08	45.66	3.4
				15	42.06	41.79	2.8
				16	28.56	28.35	4.2
				17	33.00	32.73	4.0
				18	29.49	29.43	5.4

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	(PSP)[a], g/h	(PR)[a], g/h	f,%
58	t-Butylbenzene	4.802	1725	13	15.10	14.91	8.5
				14	46.85	46.05	6.9
				15	42.29	42.09	6.9
				16	28.70	28.47	8.5
				17	33.52	33.27	8.5
				18	30.99	29.55	10.0
59	Mesitylene	4.520	1725	13	15.06	14.20	16.1
				14	46.37	43.31	12.3
				15	42.11	39.63	12.1
				16	28.51	26.86	16.2
				17	33.06	31.24	16.4
				18	29.46	27.74	17.9
60	i-Butylbenzene	4.707	1725	13	14.97	14.91	18.8
				14	46.38	45.69	14.0
				15	42.27	41.57	14.7
				16	28.62	28.29	18.6
				17	33.03	32.66	19.2
				18	29.55	29.43	21.7
61	s-Butylbenzene	4.880	1725	13	15.05	14.91	23.2
				14	46.38	45.63	17.4
				15	42.45	41.60	18.2
				16	28.92	28.31	23.1
				17	33.33	32.91	23.5
				18	29.55	29.23	24.8
62	n-Propylbenzene	4.716	1725	13	15.11	14.91	6.5
				14	46.31	45.57	4.6
				15	42.25	41.70	4.2
				16	28.88	28.32	6.5
				17	33.05	33.00	6.5
				18	29.73	29.16	9.0
63	n-Butylbenzene	4.824	1725	13	15.24	14.94	8.8
				14	46.44	45.66	5.8
				15	42.33	41.57	5.4
				16	28.44	28.23	7.3
				17	33.27	32.83	8.8
				18	29.64	29.09	8.8

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	(PSP)[a], g/h	(PR)[a], g/h	f,%
64	NaCl	5.149	1725	13	15.09	14.75	79.8
				14	46.26	44.78	67.2
				15	42.18	40.85	73.2
				16	28.56	27.90	76.5
				17	33.12	32.29	80.3
				18	29.64	28.69	82.5
65	t-Butylbenzene	4.787	1725	13	15.06	14.86	22.5
				14	45.72	45.26	17.4
				15	41.73	41.11	17.8
				16	28.29	28.03	22.5
				17	33.00	32.42	23.0
				18	29.58	29.09	25.4
66	s-Butylbenzene	4.899	1725	13	15.00	14.91	20.3
				14	45.78	45.30	16.2
				15	41.52	41.31	16.2
				16	28.11	28.20	20.6
				17	32.84	32.55	20.8
				18	29.16	29.19	23.8
68	NaCl	5.526	1035	13	8.82	8.68	71.5
				14	26.98	26.61	61.2
				15	24.88	24.41	65.3
				16	16.60	16.28	71.0
				17	19.50	19.26	72.7
				18	17.56	17.19	75.9
69	NaCl	4.6878	1035	13	8.76	8.67	71.1
				14	27.00	26.46	61.8
				15	24.72	24.48	65.5
				16	16.32	16.20	71.8
				17	19.32	19.13	73.4
				18	—	17.21	76.5
70	Benzene	2.977	1035	13	8.90	8.94	4.9
				14	27.21	27.23	2.8
				15	24.81	25.01	1.1
				16	16.55	16.80	7.1
				17	19.55	19.71	4.9
				18	17.63	17.87	−1.5

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	(PSP)^a, g/h	(PR)^a, g/h	f,%
71	Toluene	4.756	1035	13	8.78	8.75	2.7
				14	27.04	26.84	0.9
				15	24.70	24.64	0.5
				16	16.36	16.41	2.7
				17	19.52	19.49	1.8
				18	17.34	17.45	1.8
72	Benzene	4.641	1035	13	8.92	8.85	0.7
				14	27.16	27.14	1.2
				15	25.04	24.99	0.7
				16	16.72	16.68	0.7
				17	19.76	19.62	1.8
				18	17.64	17.68	2.3
73	o-Xylene	4.769	1035	13	8.92	9.00	5.1
				14	27.36	27.38	4.3
				15	25.04	25.17	3.8
				16	16.84	16.82	5.3
				17	19.92	19.92	5.1
				18	17.84	17.96	5.7
74	p-Xylene	4.726	1035	13	8.96	8.99	3.9
				14	27.48	27.41	1.9
				15	25.26	25.13	1.5
				16	16.76	16.80	3.3
				17	19.82	20.07	2.7
				18	17.94	17.85	3.3
75	Cumene	4.758	1035	13	8.80	8.85	9.0
				14	27.00	26.67	6.7
				15	25.02	24.86	6.0
				16	16.54	16.58	9.2
				17	19.66	19.55	7.8
				18	17.78	17.66	10.6
76	t-Butylbenzene	4.951	1035	13	8.96	8.69	16.8
				14	27.20	26.63	13.3
				15	24.82	24.63	13.2
				16	16.52	16.38	17.5
				17	19.72	19.41	18.9
				18	17.70	17.30	19.5

Run	Solute	Concn molal x 10^3	P, kPag	Membrane No.	(PSP)^a, g/h	(PR)^a, g/h	f,%
77	Mesitylene	4.978	1035	13	8.92	8.79	11.1
				14	27.16	26.79	8.6
				15	25.18	24.68	8.1
				16	16.62	16.46	10.6
				17	19.90	19.53	11.3
				18	17.94	17.63	12.3
78	i-Butylbenzene	4.873	1035	13	8.86	8.78	12.5
				14	27.06	26.76	9.8
				15	25.00	24.84	9.8
				16	16.72	16.52	10.6 13.0
				17	19.80	19.65	12.8
				18	17.94 8	17.~~63~~ 72	~~12.3~~ 14.8
79	s-Butylbenzene	4.876	1035	13	8.80	—	15.4
				14	26.78	27.02	11.7
				15	24.85	24.95	11.4
				16	16.55	16.65	15.5
				17	19.75	19.71	15.2
				18	17.65	17.75	17.6
80	Propylbenzene	4.779	1035	13	8.94	8.82	6.5
				14	27.17	26.91	4.4
				15	25.10	24.74	4.2
				16	16.72	16.58	6.0
				17	19.66	19.55	5.7
				18	17.69	17.67	6.9
81	Ethylbenzene	4.717	1035	13	8.79	8.87	2.6
				14	26.98	26.96	1.6
				15	24.89	24.92	1.6
				16	16.66	16.64	2.6
				17	19.63	19.67	2.4
				18	17.62	17.73	3.2
82	n-Butylbenzene	4.843	1035	13	8.82	8.79	6.5
				14	26.78	26.73	6.0
				15	24.72	24.65	6.0
				16	16.48	16.35	7.7
				17	19.74	19.43	7.8
				18	17.76	17.48	9.5

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	(PSP)[a], g/h	(PR)[a], g/h	f, %
83	NaCl	5.543	1035	13	8.72	8.69	71.3
				14	26.92	26.47	61.7
				15	24.76	24.44	64.5
				16	16.44	16.22	71.2
				17	19.94	19.37	72.9
				18	17.90	17.40	75.7
84	NaCl	4.968	1725	13	15.57	15.17	79.6
				14	44.82	42.89	71.7
				15	43.44	41.77	66.3
				16	28.32	27.31	79.8
				17	35.07	30.31	81.8
				18	31.53	30.31	81.8
85	NaCl	5.084	1725	13	15.54	15.21	79.8
				14	44.07	43.34	71.1
				15	42.78	41.92	73.0
				16	27.72	27.81	80.1
				17	34.44	33.56	80.4
				18	30.28	30.84	81.6
87	t-Butylbenzene	1.244	1725	13	15.54	15.24	26.9
				14	44.13	43.48	24.0
				15	42.84	42.18	24.0
				16	27.39	27.36	29.9
				17	34.71	33.81	29.9
				18	31.29	30.60	32.3
88	t-Butylbenzene	9.620	1725	13	15.33	15.36	23.2
				14	43.74	42.96	19.8
				15	42.57	41.88	20.1
				16	27.75	27.18	25.5
				17	34.11	33.84	25.8
				18	30.84	—	26.1
89	Triethylamine	11.72	1725	13	15.48	15.23	47.8
				14	43.89	43.10	43.0
				15	42.84	42.08	44.6
				16	27.90	27.33	52.4
				17	34.44	33.88	51.4
				18	40.05	30.38	52.6

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f,%
91	Triethylamine	1.539	1725	13	15.36	15.16	40.7
				14	43.41	42.26	36.7
				15	42.45	41.69	37.3
				16	27.78	27.21	39.3
				17	34.02	33.68	38.8
				18	31.05	30.27	41.1
92	NaCl	5.021	1725	13	15.53	15.91	80.2
				14	43.27	41.23	72.4
				15	42.62	42.05	73.5
				16	27.82	28.20	79.8
				17	34.42	35.04	80.2
				18	31.30	31.63	81.8
93	N,N-Dimethylbenzylamine	10.34	1725	13	15.39	15.13	28.1
				14	42.84	41.07	23.3
				15	42.21	41.54	22.2
				16	27.42	26.93	28.0
				17	33.93	33.31	27.8
				18	30.63	30.05	30.0
94	N,N-Dimethylbenzylamine	1.128	1725	13	15.48	15.38	—
				14	43.08	41.94	22.0
				15	42.21	41.89	21.3
				16	27.45	27.39	25.9
				17	34.29	33.87	25.9
				18	30.72	30.45	29.2
96	t-Butylbenzene	5.268	1725	13	15.48	15.48	26.9
				14	43.69	42.83	20.9
				15	42.81	42.37	20.7
				16	27.90	27.48	27.6
				17	34.56	33.99	26.7
				18	31.17	30.62	29.1
97	N,N-Dimethylbenzylamine	5.018	1725	13	15.36	15.10	28.5
				14	42.72	42.28	23.9
				15	42.07	41.58	23.4
				16	27.29	26.94	29.4
				17	33.96	33.50	29.3
				18	30.29	30.12	31.3
98	NaCl	5.413	1725	13	15.21	15.36	77.7
				14	42.31	42.54	72.4
				15	41.55	42.13	72.5
				16	26.79	27.56	79.6
				17	33.28	34.46	80.2
				18	29.68	30.94	81.5

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	(PSP)^a, g/h	(PR)^a, g/h	f,%
99	Glycerol	1.096%^{b}	1725	13	—	14.28	26.4
				14	—	41.58	23.2
				15	—	41.18	21.6
				16	—	26.55	27.2
				17	—	33.15	27.1
				18	—	28.25	22.5
100	NaCl	4.928	1208	13	10.92	11.71	75.0
				14	31.10	30.61	67.2
				15	30.19	29.00	68.3
				16	19.51	19.35	74.7
				17	24.72	24.37	72.2
				18	25.20	24.83	63.3
101	NaCl	5.085	1208	13	11.10	10.95	74.7
				14	31.13	30.49	66.8
				15	30.53	29.77	68.6
				16	19.82	19.47	74.4
				17	25.20	24.38	72.0
				18	25.80	24.90	63.2
102	t-Butylbenzene	5.183	1208	13	11.18	10.99	21.5
				14	31.60	–	17.9
				15	30.88	–	17.5
				16	20.08	19.65	21.6
				17	25.55	24.86	19.6
				18	26.25	25.41	20.2
103	N,N-Dimethyl-benzylamine	5.159	1208	13	10.93	11.12	25.2
				14	30.68	31.40	18.9
				15	29.79	30.59	19.7
				16	18.81	15.70	25.6
				17	24.42	24.94	23.0
				18	24.99	25.57	22.2
104	Triethylamine	5.730	1208	13	10.71	10.69	36.8
				14	31.02	30.49	32.9
				15	30.66	30.03	32.1
				16	19.68	19.22	38.9
				17	24.75	24.40	35.0
				18	23.97	24.89	32.2
105	NaCl	5.242	1208	13	11.06	–	74.6
				14	31.06	–	66.1
				15	30.40	–	67.8
				16	19.66	–	74.5
				17	24.80	–	71.7
				18	25.40	–	62.5

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f,%
106	NaCl	5.203	690	13	6.39	6.26	63.8
				14	18.12	17.93	56.9
				15	18.09	17.25	58.2
				16	11.73	11.36	65.8
				17	14.80	14.25	62.8
				18	15.39	14.78	55.9
108	t-Butylbenzene	4.880	690	13	6.64	6.27	13.9
				14	19.08	17.85	11.0
				15	18.78	17.48	11.6
				16	12.14	10.87	14.7
				17	15.56	14.25	13.6
				18	16.10	14.73	13.6
109	N,N-Dimethylbenzylamine	5.192	690	13	—	6.12	16.1
				14	—	18.05	13.1
				15	—	17.78	13.8
				16	—	11.46	17.9
				17	—	14.51	16.5
				18	—	15.10	16.1
110	Triethylamine	5.118	690	13	—	6.52	27.3
				14	—	18.83	23.6
				15	—	18.26	21.5
				16	—	11.58	28.8
				17	—	14.95	26.0
				18	—	15.60	25.9
111	o-Toluidine	0.9757	1725	13	15.20	15.12	16.4
				14	43.20	41.96	10.5
				15	42.30	41.31	11.4
				16	27.05	26.59	15.4
				17	33.93	33.30	15.1
				18	34.73	33.68	12.4
112	NaCl	5.328	1725	13	15.40	14.70	79.7
				14	42.88	41.19	71.6
				15	42.23	40.53	72.3
				16	27.28	25.86	78.6
				17	34.41	32.43	76.5
				18	34.12	32.46	66.1

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	(PSP)^a, g/h	(PR)^a, g/h	f,%
113	o-Toluidine	1.436	1725	13	15.25	14.61	17.5
				14	42.50	40.84	13.6
				15	41.08	39.66	13.4
				16	26.00	25.44	16.2
				17	33.35	31.56	15.6
				18	33.58	31.92	14.8
114	o-Toluidine	0.5530	1725	13	15.36	15.26	8.8
				14	42.81	42.38	7.4
				15	41.70	41.60	6.6
				16	26.85	26.68	9.2
				17	—	33.30	7.8
				18	29.55	33.34	7.4
115	o-Toluidine	0.9953	1208	13	11.30	10.89	13.8
				14	31.86	30.73	10.0
				15	30.82	29.69	10.1
				16	19.78	19.32	13.1
				17	25.14	24.26	13.4
				18	25.28	24.40	10.0
116	o-Toluidine	0.9350	690	13	—	6.27	5.9
				14	—	18.00	7.9
				15	—	17.46	8.9
				16	—	11.19	5.3
				17	—	14.25	6.1
				18	—	14.45	4.9
117	NaCl	5.252	1725	13	15.44	—	78.1
				14	43.46	43.06	71.3
				15	42.31	42.57	72.0
				16	27.34	27.30	78.6
				17	34.75	34.34	76.4
				18	34.85	34.53	66.9
118	Triethylamine	5.746	1725	13	15.81	15.21	42.5
				14	44.49	42.66	37.3
				15	43.20	41.76	37.8
				16	28.08	26.82	43.6
				17	34.75	33.60	44.1
				18	35.55	33.57	38.2
119	Triethylamine	2.670	1725	13	—	15.63	43.7
				14	—	43.59	36.5
				15	—	37.38	35.0
				16	—	27.72	42.9
				17	—	34.74	43.2
				18	—	34.26	36.2

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f,%
512	NaI	5.040	1725	1	22.00	21.39	54.3
				2	5.47	5.37	55.4
				3	4.31	4.19	67.4
				4	15.31	15.37	70.0
				5	20.49	20.13	58.8
				6	3.33	3.24	75.9
513	NaCl	5.002	1725	1	21.74	21.22	58.9
				2	5.40	5.32	72.9
				3	4.28	4.21	75.6
				4	15.54	15.37	66.5
				5	20.11	20.26	63.1
				6	–	3.31	80.3
514	CsCl	4.929	1725	1	21.80	21.59	43.7
				2	5.46	5.35	61.2
				3	4.32	4.21	61.2
				4	15.52	15.35	47.6
				5	20.58	20.15	45.6
				6	3.28	3.27	67.0
515	RbCl	4.916	1725	1	21.60	21.41	45.5
				2	5.40	5.31	62.3
				3	4.22	4.17	64.2
				4	15.16	15.30	50.6
				5	20.18	20.09	46.4
				6	3.32	3.24	73.2
519	NaCl	155.4	1725	1	21.64	17.75	46.9
				2	5.42	4.22	62.0
				3	4.18	3.34	66.8
				4	15.45	12.53	52.1
				5	20.66	16.24	47.8
				6	3.24	2.55	73.4
520	NaCl	152.5	1725	1	21.77	17.77	47.1
				2	5.40	4.39	64.1
				3	4.26	3.32	65.4
				4	15.45	12.53	51.5
				5	20.66	16.75	47.9
				6	3.32	2.58	72.9

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	(PSP)^a, g/h	(PR)^a, g/h	f, %
521	NaCl	152.2	1725	1	21.64	17.66	46.9
				2	5.56	4.25	63.0
				3	4.20	3.30	65.2
				4	15.38	12.43	51.2
				5	20.16	16.38	47.8
				6	–	2.54	72.9
522	NaCl	117.3	1725	1	22.02	18.88	49.1
				2	5.34	4.66	63.8
				3	4.20	3.52	67.3
				4	15.27	13.14	54.6
				5	20.78	17.65	51.3
				6	3.38	2.78	72.2
524	NaCl	118.1	1725	1	21.92	18.77	48.8
				2	5.40	4.53	64.0
				3	4.22	3.52	67.4
				4	15.08	12.86	53.7
				5	20.56	17.60	50.8
				6	3.24	2.74	71.5
525	NaCl	117.5	1725	1	21.54	18.28	48.6
				2	5.36	4.31	64.1
				3	4.10	4.31	67.5
				4	14.82	12.77	53.7
				5	20.00	17.22	50.3
				6	3.08	2.65	72.1
527	NaCl	4.990	1725	1	21.80	21.67	61.3
				2	5.34	5.25	71.8
				3	4.14	4.15	74.4
				4	15.08	14.98	65.7
				5	20.28	20.12	62.2
				6	3.24	3.24	77.5
530	NaCl	116.6	1725	1	21.84	18.49	50.9
				2	5.28	4.40	64.6
				3	4.20	3.46	67.8
				4	15.20	12.87	56.3
				5	20.42	21.39	53.0
				6	3.26	2.68	72.5

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	(PSP)^a, g/h	(PR)^a, g/h	f,%
531	NaBr	148.6	1725	1	21.70	18.16	43.4
				2	5.23	4.75	59.1
				3	4.14	3.36	61.2
				4	15.00	12.56	47.5
				5	20.28	17.06	44.3
				6	3.23	2.60	66.2
532	NaCl	158.6	1725	1	21.90	17.78	45.9
				2	5.26	4.13	60.1
				3	4.16	3.27	63.9
				4	15.14	11.24	50.0
				5	20.44	17.73	47.3
				6	3.24	2.53	68.2
533	NaBr	123.9	1725	1	21.29	18.59	44.0
				2	5.13	4.35	61.2
				3	4.11	3.45	62.2
				4	14.85	12.74	49.2
				5	20.11	17.41	44.9
				6	3.16	2.66	66.5
534	LiBr	149.3	1725	1	22.08	17.40	64.8
				2	5.15	3.37	74.7
				3	4.19	3.23	77.8
				4	15.24	12.08	68.6
				5	20.75	16.48	65.6
				6	3.30	2.51	81.7
535	LiCl	125.9	1725	1	22.00	17.34	68.0
				2	5.32	4.15	76.5
				3	4.20	3.25	79.9
				4	15.16	11.16	71.2
				5	20.62	16.32	68.9
				6	3.24	2.53	83.8
536	LiBr	108.4	1725	1	21.68	18.47	66.4
				2	5.20	4.40	75.5
				3	4.10	3.45	78.9
				4	14.86	12.76	70.3
				5	20.02	17.24	67.3
				6	3.14	2.67	82.6

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	(PSP)^a, g/h	(PR)^a, g/h	f,%
537	LiCl	95.52	1725	1	21.68	18.40	71.5
				2	5.22	4.38	78.6
				3	4.12	3.44	81.9
				4	14.84	12.51	74.1
				5	20.18	17.16	71.7
				6	3.14	2.67	85.2
538	NaBr	4.996	1725	1	22.00	21.92	56.8
				2	5.27	5.25	66.1
				3	4.19	4.14	67.2
				4	15.13	15.18	60.7
				5	20.49	20.43	57.7
				6	3.24	3.22	70.4
539	LiCl	4.610	1725	1	21.86	21.50	80.2
				2	5.24	5.20	88.1
				3	4.14	4.10	86.0
				4	—	14.86	82.8
				5	20.34	20.05	80.6
				6	3.20	3.17	87.6
541	LiBr	6.432	1725	1	21.78	21.27	78.2
				2	5.20	5.08	83.9
				3	4.14	4.03	85.9
				4	15.00	14.66	81.4
				5	20.42	19.68	78.9
				6	3.24	3.11	88.8
542	KCl	5.246	1725	1	21.76	21.62	46.1
				2	5.20	5.15	60.6
				3	4.14	4.08	63.1
				4	14.92	14.87	50.1
				5	20.26	20.11	47.0
				6	3.20	3.14	67.8
543	KBr	4.774	1725	1	22.00	21.76	43.5
				2	5.24	5.15	57.7
				3	4.14	4.10	60.6
				4	15.02	14.94	47.4
				5	20.52	20.21	44.3
				6	3.22	3.15	64.2
544	KI	5.308	1725	1	21.72	21.49	43.2
				2	5.11	5.05	56.3
				3	4.06	4.02	58.5
				4	14.77	14.68	45.2
				5	19.87	19.89	41.9
				6	3.03	4.04	62.3

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	(PSP)[a], g/h	(PR)[a], g/h	f,%
546	CsBr	4.940	1725	1	21.90	21.59	41.5
				2	5.14	5.06	56.6
				3	4.10	4.04	56.6
				4	14.94	14.73	45.2
				5	20.34	19.94	41.5
				6	3.16	3.11	62.3
547	KI	146.2	1725	1	22.00	17.72	18.7
				2	5.16	4.12	30.6
				3	4.12	3.26	32.2
				4	14.88	12.03	22.3
				5	20.20	16.50	20.1
				6	3.14	2.53	37.5
548	CsCl	76.19	1725	1	21.48	20.02	25.6
				2	5.05	4.66	40.7
				3	4.03	3.74	43.0
				4	14.65	13.73	33.7
				5	20.03	18.57	29.0
				6	3.16	2.91	47.6
550	KF	5.947	1725	1	22.48	22.01	60.3
				2	5.38	5.26	70.6
				3	4.20	4.14	73.9
				4	14.94	14.79	66.0
				5	20.68	20.39	61.4
				6	3.26	3.23	77.4

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	(PSP)[a], g/h	(PR)[a], g/h	f,%
603	NaCl	177.4	1725	7	15.49	12.12	68.6
				8	10.50	8.20	71.6
				9	8.89	6.96	71.7
				10	—	—	—
				11	9.51	7.32	73.2
				12	7.54	5.95	72.7
604	NaCl	143.2	1725	7	15.32	14.19	65.8
				8	10.28	8.26	69.4
				9	8.76	7.02	69.3
				10	—	—	—
				11	9.36	7.42	70.8
				12	7.44	6.02	68.1
608	NaCl	152.2	3450	7	21.36	16.64	72.9
				8	15.42	12.14	78.1
				9	12.30	9.71	76.8
				10	3.12	—	81.5
				11	12.84	10.08	79.7
				12	10.02	7.90	70.9
609	NaCl	154.1	3450	7	18.45	14.75	72.2
				8	13.50	10.89	77.8
				9	10.62	8.68	75.9
				10	2.84	2.33	82.3
				11	11.31	9.03	77.8
				12	8.64	7.10	70.1
611	NaBr	385.3	3450	7	18.51	11.48	55.4
				8	13.59	8.50	61.6
				9	10.65	6.73	60.0
				10	2.85	—	70.1
				11	11.16	6.91	61.7
				12	8.58	5.42	55.1
612	NaBr	377.8	3450	7	16.58	10.32	55.1
				8	12.20	7.60	60.3
				9	9.49	6.00	59.5
				10	2.63	—	72.2
				11	9.96	6.22	61.2
				12	7.62	4.75	55.1

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	(PSP)^a, g/h	(PR)^a, g/h	f,%
614	LiBr	409.3	3450	7	15.75	9.88	76.8
				8	11.58	7.29	81.4
				9	9.03	5.79	80.0
				10	2.37	1.49	87.7
				11	9.39	5.99	87.7
				12	7.23	4.84	72.9
616	LiCl	458.6	3450	7	15.42	9.17	80.1
				8	11.28	6.71	83.5
				9	8.79	5.38	82.0
				10	2.31	–	89.9
				11	9.09	5.51	83.9
				12	7.05	4.54	74.8
618	LiCl	447.6	3450	7	14.84	8.76	79.0
				8	10.93	6.41	83.3
				9	8.45	5.16	81.7
				10	2.22	1.30	90.0
				11	8.77	5.29	83.7
				12	6.54	4.38	74.2
620	NaCl	152.9	3450	7	14.70	12.80	73.4
				8	10.74	9.44	77.9
				9	8.37	7.43	76.7
				10	2.16	1.87	83.5
				11	8.64	1.87	78.5
				12	6.81	6.07	70.5
622	LiCl	493.0	3450	7	14.49	8.25	79.0
				8	10.71	6.10	82.8
				9	8.34	4.86	81.5
				10	2.13	–	91.8
				11	8.64	5.05	83.5
				12	6.81	4.16	73.7
624	LiBr	261.7	3450	7	14.43	11.10	82.1
				8	10.68	8.21	85.6
				9	8.34	6.53	84.0
				10	2.13	–	88.8
				11	8.70	6.71	86.1
				12	6.81	5.47	77.1

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	(PSP)^a, g/h	(PR)^a, g/h	f,%
626	NaBr	268.6	3450	7	14.49	11.04	58.3
				8	10.77	8.15	67.6
				9	8.13	6.45	66.1
				10	1.83	1.58	77.9
				11	8.73	6.72	68.4
				12	6.93	5.34	57.1
628	NaCl	162.9	3450	7	14.31	12.11	73.3
				8	10.50	8.97	78.6
				9	8.19	7.02	77.1
				10	2.01	1.79	86.2
				11	8.58	7.33	78.6
				12	6.72	5.85	70.7
630	NaCl	158.2	1725	7	7.53	6.37	61.5
				8	5.67	4.65	66.2
				9	4.38	3.69	64.6
				10	1.11	0.87	82.2
				11	4.59	3.72	82.2
				12	3.60	3.07	58.9
631	NaCl	158.7	1725	7	7.73	6.32	60.5
				8	5.70	4.61	65.8
				9	4.48	3.65	63.9
				10	1.13	0.87	81.5
				11	4.57	3.60	65.5
				12	3.72	3.03	58.4
632	KCl	6.564	1725	7	7.71	7.83	55.8
				8	5.69	5.74	59.2
				9	4.46	4.50	57.4
				10	1.06	1.11	27.2
				11	4.06	4.61	61.2
				12	3.69	3.70	49.5
633	LiCl	4.315	1725	7	7.74	—	83.6
				8	5.68	—	83.2
				9	4.50	—	83.2
				10	1.11	—	50.8
				11	4.63	—	86.6
				12	3.60	—	73.6
634	NaBr	5.053	1725	7	7.56	7.57	71.6
				8	5.59	5.57	75.5
				9	4.44	4.38	73.8
				10	1.10	1.08	71.3
				11	4.46	4.51	76.5
				12	3.55	3.60	66.5

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f, %
635	LiBr	4.905	1725	7	7.70	7.56	84.4
				8	5.58	5.48	87.3
				9	4.41	4.38	85.6
				10	1.10	1.09	80.0
				11	4.46	4.47	87.6
				12	3.57	3.57	78.7
637	KI	4.813	1725	7	7.39	7.38	56.7
				8	5.43	5.41	61.0
				9	4.25	4.24	59.8
				10	1.01	1.03	78.3
				11	4.34	4.31	61.0
				12	3.30	3.28	55.7
638	CsCl	72.22	1725	7	7.54	6.87	35.1
				8	5.46	4.99	41.7
				9	4.23	3.94	41.7
				10	1.03	0.93	78.8
				11	4.37	3.97	78.8
				12	3.40	3.15	37.7
639	NaCl	4.864	1725	7	7.38	7.43	70.2
				8	5.40	5.41	72.2
				9	4.17	4.26	72.9
				10	0.96	1.02	52.8
				11	4.20	4.24	75.6
				12	3.27	3.37	64.2
640	LiCl	144.4	1725	7	7.30	5.65	81.7
				8	5.32	4.08	84.8
				9	4.16	3.22	83.6
				10	0.99	0.76	92.8
				11	4.19	3.20	92.8
				12	3.17	2.61	76.9
641	LiBr	149.8	1725	7	7.40	5.75	78.0
				8	5.31	4.17	81.7
				9	4.20	3.30	80.5
				10	0.97	0.78	90.1
				11	4.26	3.31	90.1
				12	3.31	2.68	73.8
642	NaBr	153.0	1725	7	7.32	6.04	59.1
				8	5.40	4.37	63.9
				9	4.35	3.47	62.5
				10	1.05	0.81	84.0
				11	4.35	3.47	64.9
				12	3.39	2.77	58.3

Run	Solute	Concn, molal x 10^3	P, kPag	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f, %
643	RbCl	149.8	1725	7	7.40	5.75	78.0
				8	5.21	5.35	62.5
				9	4.12	4.11	62.5
				10	1.04	1.00	—
				11	4.20	4.29	65.6
				12	3.27	3.33	59.4
644	CsCl	5.070	1725	7	7.48	7.35	58.1
				8	5.43	5.38	60.0
				9	4.25	4.22	60.0
				10	1.03	1.01	—
				11	4.28	4.34	63.8
				12	3.33	3.34	56.2
645	CsBr	4.592	1725	7	7.37	7.43	39.6
				8	5.46	5.45	52.1
				9	4.26	4.26	54.2
				10	1.00	1.00	—
				11	4.37	4.31	54.2
				12	3.37	3.42	52.1
646	NaI	5.231	1725	7	7.44	7.36	69.9
				8	5.37	5.36	73.9
				9	4.26	4.22	72.2
				10	1.08	1.07	78.1
				11	4.32	4.27	73.1
				12	3.42	3.36	66.1
647	KI	152.4	1725	7	7.35	5.94	32.3
				8	5.37	4.39	36.1
				9	4.23	3.43	34.9
				10	0.81	0.81	72.7
				11	3.42	3.48	38.1
				12	3.36	2.68	33.5

Table A-1-6

Experimental Reverse Osmosis Results for Dilute Ethanol Solutions at 25°C, 1725 kPag, and Cellulose Acetate Membranes.

Run No.	Solute	Concentration, molal × 10^3	Membrane No.	(PSP)^a, g/h	(PR),^{a} g/h	f, %
1	Ethanol	Pure	1	19.70	—	—
			2	30.30	—	—
			3	23.22	—	—
			4	16.96	—	—
			5	24.14	—	—
			6	14.04	—	—
2	Ethanol	Pure	1	19.02	—	—
			2	29.76	—	—
			3	23.10	—	—
			4	16.98	—	—
			5	23.98	—	—
			6	13.92	—	—
3	Ethanol	Pure	1	19.31	—	—
			2	30.28	—	—
			3	23.42	—	—
			4	16.92	—	—
			5	24.14	—	—
			6	13.80	—	—
4	LiCl	5.231	1	18.88	18.80	82.8
			2	29.96	29.24	89.8
			3	23.16	22.98	94.7
			4	16.92	16.88	95.4
			5	23.96	23.60	91.6
			6	13.64	13.88	94.7
5	LiCl	1.074	1	18.44	18.30	83.4
			2	29.56	28.97	89.4
			3	23.00	22.85	96.2
			4	16.84	16.76	96.9
			5	23.56	23.39	91.1
			6	13.28	13.61	94.5
6	LiBr	0.9545	1	17.96	18.47	82.6
			2	29.40	29.55	89.1
			3	23.04	23.39	93.9
			4	16.80	17.18	96.8
			5	23.60	23.94	90.7
			6	13.32	14.00	94.3
8	NaBr	1.272	1	17.28	18.11	67.4
			2	29.00	29.63	78.2
			3	23.08	23.84	72.6
			4	17.08	17.55	85.2
			5	23.67	24.33	83.5
			6	13.64	14.30	82.6

Run No.	Solute	Concentration, molal × 10^3	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f,%
9	LiCl	0.9453	1	17.52	17.33	90.2
			2	29.12	28.35	91.5
			3	23.20	22.69	96.5
			4	16.84	16.69	97.3
			5	23.56	23.08	94.2
			6	13.52	13.51	96.1
10	NaI	1.066	1	17.00	17.73	79.5
			2	28.72	29.15	76.9
			3	22.76	23.48	82.6
			4	16.64	17.30	83.1
			5	23.44	23.99	70.3
			6	13.44	14.13	83.1
11	KI	1.319	1	17.04	17.15	67.7
			2	28.24	28.00	67.2
			3	22.64	22.54	70.1
			4	16.52	16.58	70.9
			5	23.00	22.87	66.9
			6	13.16	13.40	74.1
12	KBr	1.238	1	16.80	17.47	71.1
			2	28.50	28.65	71.6
			3	22.88	23.15	72.1
			4	16.75	17.06	77.4
			5	23.43	23.59	73.2
			6	13.31	13.89	77.9
13	KCl	1.108	1	17.08	17.13	74.1
			2	28.59	28.07	75.0
			3	23.12	22.65	77.1
			4	16.94	16.63	79.4
			5	23.54	22.87	76.5
			6	13.31	13.42	81.5
14	CsBr	1.169	1	16.91	17.28	59.8
			2	28.16	28.20	62.3
			3	22.54	22.76	64.8
			4	16.43	16.61	62.3
			5	22.84	22.96	62.3
			6	12.98	13.49	68.8
15	NH_4Cl	9.601	1	15.68	17.04	91.2
			2	26.88	27.67	86.2
			3	21.56	22.33	92.8
			4	15.28	16.35	94.5
			5	21.64	22.37	90.1
			6	12.04	13.12	96.7

Run No.	Solute	Concentration, molal × 10^3	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f, %
17	CsI	1.160	1	—	18.52	51.2
			2	—	30.90	48.8
			3	—	—	52.1
			4	—	16.94	50.4
			5	—	24.25	51.2
			6	—	14.02	54.5
18	CsCl	1.112	1	18.20	18.34	59.4
			2	30.92	30.86	51.7
			3	23.04	23.15	64.7
			4	17.20	17.22	60.3
			5	24.40	24.31	61.2
			6	13.64	14.11	61.2
19	RbI	0.8345	1	17.50	17.75	60.7
			2	29.97	29.66	55.4
			3	22.63	22.62	60.7
			4	16.80	16.82	62.5
			5	23.77	23.61	57.1
			6	13.07	13.68	66.1
20	RbBr	9.016	1	17.28	17.84	63.6
			2	29.64	29.81	58.7
			3	22.56	22.93	65.3
			4	16.80	17.08	68.6
			5	23.60	23.97	63.6
			6	13.28	13.96	70.2
21	LiCl	0.7664	1	17.12	17.28	76.5
			2	29.32	28.60	85.4
			3	22.44	22.19	94.7
			4	16.60	16.51	96.4
			5	23.24	22.99	91.8
			6	13.04	13.36	91.1
22	$CaCl_2$	0.8580	1	17.07	17.20	92.2
			2	29.27	28.47	91.3
			3	22.47	22.36	98.5
			4	16.53	16.65	98.7
			5	23.37	23.04	96.7
			6	13.27	13.43	97.2
24	$NaClO_3$	1.116	1	16.60	17.09	67.1
			2	28.30	28.28	52.6
			3	22.03	22.45	64.8
			4	16.57	16.75	70.6
			5	23.17	24.31	53.4
			6	13.10	13.57	67.5

Run No.	Solute	Concentration, molal × 10^3	Membrane No.	(PSP),^{a} g/h	(PR)^a, g/h	f, %
25	$NaClO_4$	1.888	1	16.54	16.81	40.0
			2	28.20	27.67	60.5
			3	22.35	22.00	65.8
			4	16.61	16.40	58.2
			5	23.03	22.58	53.7
			6	13.09	13.15	68.2
26	$SrCl_2$	1.110	1	16.52	16.84	93.9
			2	28.36	27.74	92.8
			3	22.72	22.39	97.4
			4	16.88	16.72	97.9
			5	23.68	22.97	96.2
			6	13.60	13.49	97.5
27	LiCl	0.8966	1	16.52	16.74	91.3
			2	28.12	27.52	91.3
			3	22.60	22.17	94.9
			4	16.72	16.52	96.2
			5	23.04	23.65	93.6
			6	13.20	13.29	95.1
28	KF	0.7558	1	16.41	16.63	88.4
			2	27.74	27.34	65.7
			3	22.45	22.01	88.3
			4	16.73	16.40	92.5
			5	23.15	22.47	66.2
			6	13.38	13.17	89.5
29	$NaNO_2$	1.042	1	16.67	16.96	73.6
			2	28.13	27.82	67.3
			3	22.60	22.30	74.0
			4	16.90	16.62	74.0
			5	23.17	22.81	70.8
			6	13.27	13.37	78.1
30	NaCl	1.116	1	16.44	17.09	82.7
			2	27.88	28.00	79.1
			3	22.28	22.44	85.3
			4	16.60	16.72	87.3
			5	22.96	22.98	81.4
			6	13.16	13.54	87.3
31	Triethylamine	0.9556	1	16.77	17.22	38.3
			2	27.83	28.20	43.1
			3	22.26	22.58	33.6
			4	16.63	16.83	42.2
			5	22.94	23.18	45.5
			6	13.17	13.67	47.4

Run No.	Solute	Concentration, molal × 10^3	Membrane No.	(PSP)[a], g/h	(PR)[a], g/h	f, %
32	Aniline	1.068	1	17.01	17.35	−18.3
			2	28.13	28.11	0
			3	22.41	22.57	−4.7
			4	16.38	16.83	1.7
			5	22.91	23.08	−20.2
			6	12.99	13.55	−0.5
33	Propionitrile	0.8673	1	16.88	17.27	−7.1
			2	28.12	28.03	−10.1
			3	22.60	22.54	−9.7
			4	16.80	16.76	−11.2
			5	23.20	23.06	10.7
			6	13.24	13.52	−22.3
34	N,N-Dimethylbenzylamine	1.003	1	17.04	16.63	16.1
			2	28.32	27.00	15.6
			3	22.77	21.56	6.8
			4	16.76	15.92	17.0
			5	23.12	21.80	−1.5
			6	13.16	12.70	16.1
35	1-Nitropropane	0.0827	1	—	17.16	−4.9
			2	27.29	27.99	−2.9
			3	22.11	22.54	−10.7
			4	16.49	16.81	−8.1
			5	22.69	23.08	−14.9
			6	12.80	13.59	−16.5
36	Valeronitrile	0.9375	1	17.20	16.99	−7.2
			2	28.36	27.70	−9.6
			3	22.40	22.34	−6.2
			4	16.68	16.63	−18.8
			5	20.96	22.78	−8.2
			6	13.16	13.42	−4.8
37	N,N-Dimethylaniline	0.9261	1	16.14	16.76	−3.7
			2	27.28	27.49	5.1
			3	21.60	21.99	−3.1
			4	15.88	16.38	−13.4
			5	22.07	22.41	−7.1
			6	12.19	13.16	−13.9
38	Benzonitrile	1.196	1	16.73	17.20	−11.0
			2	28.24	28.20	−3.0
			3	22.66	22.68	12.1
			4	16.94	16.90	−5.5
			5	23.29	23.14	8.0
			6	13.34	13.60	11.7

Run No.	Solute	Concentration, molal × 10^3	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f,%
39	Nitromethane	0.9375	1	16.16	16.73	8.2
			2	27.24	27.35	7.3
			3	21.76	22.02	5.3
			4	16.20	16.34	1.9
			5	22.08	22.31	-13.0
			6	12.56	13.07	-12.1
40	2-Nitropropane	0.7740	1	16.32	16.70	0
			2	27.18	27.33	-7.6
			3	21.78	21.97	-9.9
			4	16.02	16.36	-6.5
			5	22.02	22.21	-8.8
			6	12.30	13.04	-14.7
53	Acetonitrile	0.8130	1	15.79	16.19	3.6
			2	26.59	26.55	3.1
			3	21.60	21.75	-0.1
			4	16.06	16.19	4.2
			5	20.81	21.94	0.2
			6	12.60	12.92	0.1
54	n-Butyramide	0.8843	1	15.38	16.27	6.4
			2	27.03	26.57	8.0
			3	22.01	21.73	10.0
			4	16.42	16.18	11.6
			5	22.42	21.89	9.5
			6	12.95	12.89	0.3
55	i-Butyramide	1.093	1	16.17	15.93	4.7
			2	27.17	26.15	2.7
			3	22.26	21.37	3.5
			4	16.60	15.90	8.9
			5	22.34	21.51	8.9
			6	12.97	12.65	12.3
56	n-Propionamide	0.9738	1	15.72	16.25	0.5
			2	26.48	26.57	8.8
			3	21.56	21.77	0.5
			4	15.92	16.22	-0.4
			5	21.60	21.90	-2.3
			6	12.24	12.90	7.4
69	LiCl	7.428	1	14.78	14.61	86.6
			2	26.35	26.00	90.2
			3	14.09	13.80	96.6
			4	10.78	10.38	96.8
			5	21.98	21.48	92.7
			6	12.38	11.49	94.4

Run No.	Solute	Concentration, molal × 10^3	Membrane No.	(PSP)[a], g/h	(PR)[a], g/h	f,%
70	LiCl	7.972	1	14.36	13.95	88.6
			2	26.38	25.84	91.4
			3	13.98	13.05	96.4
			4	10.48	9.59	96.6
			5	21.82	20.50	93.2
			6	10.86	11.51	95.0
73	LiCl	149.8	1	14.72	10.84	85.2
			2	25.86	17.94	88.0
			3	14.04	9.96	94.4
			4	10.70	7.72	94.8
			5	21.58	14.85	89.7
			6	12.20	8.84	92.5
74	LiCl	163.6	1	14.04	10.36	84.4
			2	24.83	17.17	87.5
			3	13.41	9.57	94.0
			4	10.13	7.41	94.8
			5	20.43	14.07	90.3
			6	11.54	8.49	92.9
75	Benzene	4.013	1	14.46	14.76	-1.3
			2	25.94	16.51	17.0
			3	14.06	14.13	2.3
			4	10.77	10.78	3.0
			5	21.69	16.24	23.6
			6	12.23	12.47	0
76	Cumene	4.338	1	14.33	14.84	6.4
			2	25.88	26.07	11.0
			3	14.03	14.22	13.4
			4	10.69	10.89	11.0
			5	21.53	21.63	5.8
			6	12.26	12.62	5.2
77	Toluene	4.428	1	14.40	14.60	-8.9
			2	26.16	19.18	-7.8
			3	14.28	14.04	-4.9
			4	10.92	10.68	-8.9
			5	22.00	18.26	-8.4
			6	12.52	12.34	-3.4
78	Mesitylene	4.110	1	14.26	14.55	—
			2	25.60	25.62	12.3
			3	13.98	14.07	18.7
			4	10.62	10.79	19.5
			5	21.26	21.36	15.5
			6	11.63	12.47	15.7

Run No.	Solute	Concentration, molal × 10 ^{3}	Membrane No.	(PSP)^a, g/h	(PR)^a, g/h	f,%
79	Ethylbenzene	4.725	1	—	15.04	3.3
			2	—	26.64	3.9
			3	—	14.61	5.0
			4	—	9.59	3.4
			5	—	22.15	1.8
			6	—	27.63	2.2
80	o-Xylene	4.399	1	—	17.86	3.8
			2	—	25.83	4.3
			3	—	17.41	5.6
			4	—	13.31	5.6
			5	—	21.62	3.6
			6	—	15.49	3.2
81	p-Xylene	4.650	1	14.10	14.29	0.9
			2	25.64	25.24	0.9
			3	14.05	13.92	1.7
			4	10.64	10.62	0.4
			5	21.35	21.06	1.1
			6	11.45	12.28	-0.2
82	n-Propylbenzene	4.671	1	14.07	14.32	-11.5
			2	25.50	25.40	5.9
			3	13.93	13.95	6.7
			4	10.50	10.60	6.1
			5	21.27	21.14	2.7
			6	11.97	12.24	3.3
83	s-Butylbenzene	5.077	1	14.18	—	16.5
			2	25.31	—	17.2
			3	13.77	—	15.0
			4	10.45	—	22.7
			5	20.75	—	16.8
			6	11.86	—	18.7
84	n-Butylbenzene	4.399	1	13.92	14.22	2.3
			2	25.32	25.25	6.0
			3	13.92	13.98	7.0
			4	10.56	10.54	8.4
			5	21.28	21.34	6.5
			6	12.20	12.11	10.9
85	t-Butylbenzene	4.429	1	13.84	13.87	19.1
			2	25.56	25.51	11.2
			3	14.00	13.85	16.6
			4	10.56	16.16	24.1
			5	21.28	21.86	14.6
			6	12.08	13.67	10.8

Run No.	Solute	Concentration, molal × 10^3	Membrane No.	(PSP)[a], g/h	(PR)[a], g/h	f,%
86	i-Butylbenzene	2.086	1	13.88	14.14	7.9
			2	25.68	26.03	23.2
			3	14.16	10.39	19.6
			4	10.60	10.88	27.1
			5	21.56	20.49	21.1
			6	12.20	6.72	16.1
87	Phenol	3.779	1	14.10	11.26	2.5
			2	25.87	21.07	3.1
			3	14.13	8.65	4.8
			4	10.77	9.56	3.4
			5	21.60	20.81	3.4
			6	12.20	9.63	5.9
88	H_2O	6.65%[b]	1	—	12.92	-1.6
			2	—	23.04	-1.5
			3	—	13.15	-10.7
			4	—	9.65	-9.7
			5	—	19.02	-11.0
			6	—	10.75	-10.4
89	H_2O	10.09%[b]	1	14.23	12.49	-16.8
			2	25.15	22.23	-7.5
			3	14.73	12.81	-10.4
			4	10.91	9.49	-3.4
			5	20.73	18.32	-11.1
			6	11.84	10.54	-5.3

[a] for 13.2 cm^2 surface area.

[b] weight percent.

Table A-1-7

Experimental Reverse Osmosis Results for Dilute Aqueous Solutions at 25°C, 6900 kPag, and Cellulose Membranes.

Run No.	Solute	Concentration, molal × 10^3	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f,%
1	NaCl	56.29	1	5.32	5.05	21.6
			2	6.40	5.34	21.4
			3	7.68	6.41	18.5
			4	6.66	5.98	18.5
			5	8.02	7.05	15.9
			6	5.78	5.00	16.7
2	LiCl	6.407	1	6.28	5.50	47.3
			2	6.28	5.95	47.3
			3	6.88	6.57	45.8
			4	6.41	6.07	46.9
			5	7.62	6.95	26.5
			6	5.32	4.93	33.1
3	NaCl	4.604	1	6.90	5.51	55.2
			2	6.05	5.64	55.9
			3	6.85	6.75	53.7
			4	6.32	6.10	53.7
			5	7.45	7.17	33.0
			6	5.18	4.93	41.5
4	KCl	4.631	1	5.59	5.38	46.1
			2	4.80	5.57	51.6
			3	5.63	6.80	50.4
			4	5.07	6.14	50.4
			5	6.27	7.28	35.9
			6	3.79	4.31	41.12
5	NaCl	51.50	1	5.40	5.27	22.3
			2	5.63	5.27	25.3
			3	6.90	6.73	19.0
			4	6.27	6.18	19.4
			5	7.51	7.21	15.8
			6	5.02	4.90	17.8
6	RbCl	2.632	1	5.48	5.27	63.0
			2	5.80	5.58	66.2
			3	6.84	6.77	61.9
			4	6.24	6.13	62.6
			5	7.40	7.15	45.8
			6	4.96	4.81	54.2
7	NaBr	4.426	1	5.17	5.26	50.6
			2	5.42	5.58	51.3
			3	6.59	6.66	47.8
			4	5.97	6.03	48.2
			5	7.11	7.10	30.7
			6	4.73	4.73	36.4

Run No.	Solute	Concentration, molal × 10^3	Membrane No.	(PSP)^a, g/h	(PR)^a, g/h	f,%
8	NaI	5.204	1	5.55	5.33	52.6
			2	5.55	5.55	52.3
			3	6.56	6.71	49.0
			4	6.00	6.06	50.0
			5	7.09	7.15	33.3
			6	4.73	4.77	39.7
9	LiCl	5.654	1	4.07	5.32	53.5
			2	5.35	5.97	51.4
			3	6.70	6.82	48.3
			4	6.03	5.99	48.3
			5	7.16	7.11	32.6
			6	4.76	4.72	37.2
10	NaF	4.399	1.	5.33	5.25	68.9
			2	5.83	5.70	68.6
			3	6.73	6.62	65.2
			4	6.10	6.04	65.6
			5	7.17	7.04	47.0
			6	4.77	4.72	55.1
11	RbCl	4.445	1	5.37	5.32	54.0
			2	5.77	5.69	54.2
			3	6.70	6.61	51.6
			4	6.10	6.05	52.4
			5	7.20	7.03	37.9
			6	4.83	4.66	43.1
12	CsBr	4.221	1	5.43	5.39	50.3
			2	5.77	5.96	47.5
			3	6.69	6.65	43.3
			4	6.14	6.05	46.6
			5	7.14	7.04	34.8
			6	4.74	4.70	41.0
13	NaCl	27.68	1	5.38	5.44	21.5
			2	6.09	5.71	22.3
			3	6.75	6.58	19.6
			4	6.16	6.02	19.6
			5	7.22	6.97	14.2
			6	4.79	4.67	16.5
14	LiF	3.848	1	5.34	5.36	68.7
			2	5.80	5.86	67.8
			3	6.63	6.71	63.0
			4	6.11	6.13	63.8
			5	7.00	7.10	39.9
			6	4.73	4.71	51.6

Run No.	Solute	Concentration, molal × 10^3	Membrane No.	(PSP)^a, g/h	(PR)^a, g/h	f,%
15	LiBr	3.725	1	5.46	5.32	55.2
			2	5.79	5.76	53.7
			3	6.39	6.74	50.5
			4	6.06	6.11	51.4
			5	7.11	7.03	30.0
			6	4.71	4.82	38.5
16	$NaBrO_3$	4.137	1	5.67	5.39	57.2
			2	5.83	5.82	64.3
			3	6.83	6.69	63.0
			4	6.20	6.12	61.3
			5	7.20	6.99	47.6
			6	4.77	4.65	53.1
17	KF	3.968	1	6.81	5.49	67.5
			2	5.91	5.81	69.2
			3	6.72	6.69	67.3
			4	6.18	6.09	67.8
			5	7.11	6.95	52.7
			6	4.74	4.65	59.1
18	KBr	4.185	1	5.49	5.35	50.1
			2	5.86	5.79	49.3
			3	6.75	6.67	47.0
			4	6.15	6.09	47.6
			5	7.11	6.98	35.1
			6	4.77	4.64	40.0
19	NH_4Cl	4.107	1	5.42	5.65	52.7
			2	5.92	5.66	56.3
			3	6.75	6.58	53.8
			4	6.14	6.00	54.4
			5	7.08	6.80	39.4
			6	4.68	4.47	46.2
20	NaI	3.769	1	6.11	5.41	61.8
			2	5.73	5.73	61.4
			3	7.69	6.71	58.2
			4	6.11	6.09	58.9
			5	7.04	6.94	40.5
			6	4.64	4.59	47.6
21	$CaCl_2$	4.036	1	5.44	5.38	27.5
			2	5.72	5.66	28.6
			3	6.56	6.61	21.9
			4	5.96	5.97	21.9
			5	6.92	6.85	16.1
			6	4.56	4.56	21.2

Run No.	Solute	Concentration, molal x 10^3	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f,%
22	$MgCl_2$	4.747	1	5.50	6.47	24.1
			2	5.73	5.74	32.3
			3	6.70	6.64	24.8
			4	6.07	6.03	25.4
			5	6.93	6.84	17.1
			6	4.77	4.57	24.1
23	Na_2SO_4	4.092	1	5.32	6.15	80.7
			2	7.08	5.30	87.1
			3	6.63	6.48	85.5
			4	6.05	5.93	86.5
			5	6.87	6.71	64.7
			6	4.58	4.42	76.6
24	Na_2SO_3	4.036	1	5.75	5.35	87.8
			2	7.23	5.69	88.3
			3	6.66	6.62	85.6
			4	6.13	6.02	86.5
			5	6.92	6.77	64.4
			6	4.58	4.51	80.4
25	$NaNO_3$	4.306	1	5.42	5.30	56.8
			2	5.84	5.72	55.5
			3	6.65	6.62	53.0
			4	6.05	6.05	53.6
			5	6.87	6.79	36.6
			6	4.58	4.56	40.7
26	Na_2HPO_4	8.679	1	5.30	5.37	91.2
			2	7.43	6.13	88.9
			3	—	6.93	89.1
			4	6.03	6.09	90.6
			5	6.81	6.83	68.0
			6	4.57	4.63	82.4
27	NaSCN	3.907	1	5.40	5.97	58.3
			2	6.32	5.60	59.2
			3	6.92	6.78	60.6
			4	6.18	6.12	60.9
			5	6.85	6.81	44.6
			6	4.66	4.63	50.5
28	NaCl	51.40	1	5.40	6.27	18.6
			2	6.22	5.83	21.7
			3	6.66	6.61	18.6
			4	6.06	5.97	18.7
			5	6.79	6.67	14.3
			6	4.64	4.54	17.6

Run No.	Solute	Concentration, molal × 10^3	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f,%
29	$NaIO_3$	4.493	1	6.48	5.94	61.8
			2	6.04	6.00	70.3
			3	6.80	6.71	68.2
			4	6.16	6.07	72.1
			5	6.88	6.72	52.2
			6	4.68	4.60	57.4
30	$BaCl_2$	4.515	1	6.17	5.30	25.2
			2	6.03	5.82	25.0
			3	6.74	6.63	20.0
			4	18.74	8.88	12.9
			5	6.83	6.74	15.1
			6	4.71	4.57	20.4
31	$SrCl_2$	4.391	1	5.81	5.42	26.6
			2	6.04	5.97	18.1
			3	6.79	6.81	20.2
			4	10.46	8.82	14.8
			5	6.94	6.88	13.8
			6	4.69	4.66	20.2
32	$NaNO_2$	4.092	1	5.78	5.40	16.3
			2	6.34	6.08	56.6
			3	6.79	6.66	49.4
			4	10.69	7.49	39.2
			5	6.94	6.79	27.7
			6	4.28	4.63	39.2
33	$NaClO_3$	4.236	1	5.59	5.36	67.3
			2	6.79	6.76	62.5
			3	6.79	6.76	62.5
			4	9.11	6.95	55.3
			5	6.94	6.78	44.0
			6	4.76	4.66	52.5
34	CsCl	4.839	1	7.73	5.55	53.1
			2	6.36	5.96	45.5
			3	6.87	6.76	52.3
			4	12.03	7.53	43.8
			5	6.87	6.75	39.5
			6	4.85	4.68	43.8
35	$MgSO_4$	4.885	1	6.68	5.28	84.4
			2	6.36	5.90	82.5
			3	6.88	6.62	75.5
			4	8.52	7.04	63.4
			5	6.92	6.59	48.3
			6	4.76	4.58	64.6

Run No.	Solute	Concentration, molal × 10^3	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f,%
36	NaCl	12.58	1	5.23	5.36	34.5
			2	6.10	6.15	32.8
			3	6.27	6.77	31.1
			4	6.43	6.90	26.8
			5	6.30	6.70	20.8
			6	4.40	4.67	25.7
37	NaCl	2.327	1	6.13	5.43	65.3
			2	6.28	6.02	63.7
			3	6.92	6.67	62.1
			4	7.13	7.24	45.2
			5	6.92	6.62	45.2
			6	4.66	4.68	49.0
38	Ethanol	2.129	1	5.88	5.57	25.0
			2	6.06	5.95	22.3
			3	6.72	6.77	14.9
			4	7.12	6.58	13.9
			5	6.68	6.66	13.9
			6	4.68	4.69	18.4
39	i-Propanol	0.8857	1	6.71	5.72	36.5
			2	6.09	6.17	37.3
			3	6.80	6.81	33.2
			4	6.73	7.85	28.8
			5	6.68	6.60	29.4
			6	4.71	4.72	36.3
40	n-Propanol	0.7868	1	5.46	5.49	31.5
			2	6.00	6.05	30.5
			3	6.79	6.81	27.3
			4	4.20	6.98	21.3
			5	6.63	6.58	17.2
			6	4.74	4.64	19.7
41	NaCl	1.188	1	5.79	5.62	76.4
			2	6.16	6.08	77.2
			3	6.78	6.85	78.0
			4	8.79	7.33	53.2
			5	6.64	6.61	68.9
			6	4.68	4.73	73.9
42	$MgCl_2$	2.179	1	5.52	5.49	30.1
			2	6.08	5.96	28.2
			3	6.84	6.80	21.4
			4	7.04	6.99	19.8
			5	6.66	6.57	11.6
			6	4.82	4.78	18.6

Run No.	Solute	Concentration, molal × 10^3	Membrane No.	(PSP)^a, g/h	(PR)^a, g/h	f,%
43	$MgSO_4$	1.809	1	5.63	5.47	82.9
			2	—	5.96	84.8
			3	6.92	6.77	78.4
			4	7.48	7.08	67.4
			5	6.65	6.52	56.1
			6	4.75	4.71	70.3
44	Na_2SO_4	2.862	1	5.64	5.70	91.0
			2	5.94	5.94	94.7
			3	6.87	6.81	94.0
			4	7.29	6.99	81.9
			5	6.66	6.52	82.7
			6	4.80	4.65	89.7
45	Na_2SO_4	1.130	1	5.86	5.62	92.3
			2	—	—	—
			3	6.79	6.76	95.5
			4	7.36	6.79	86.9
			5	6.56	6.46	89.3
			6	4.72	4.65	95.1
46	Na_2SO_4	8.019	1	5.90	5.80	72.9
			2	6.05	5.85	78.8
			3	6.83	6.71	73.5
			4	7.02	6.67	66.6
			5	6.60	6.43	51.3
			6	4.77	4.60	60.8
47	Na_2SO_4	1.215	1	6.03	5.57	86.4
			2	6.09	5.90	92.7
			3	6.85	6.71	92.6
			4	6.95	6.69	84.6
			5	6.63	6.39	85.3
			6	4.77	4.61	93.0
48	NaCl	50.55	1	6.21	5.39	25.0
			2	5.91	5.90	21.8
			3	6.72	6.71	19.8
			4	6.57	6.40	18.6
			5	6.45	6.36	16.3
			6	4.69	4.68	19.4
49	$MgSO_4$	1.538	1	5.64	6.40	53.2
			2	6.04	6.05	67.3
			3	6.88	6.87	60.1
			4	7.28	6.81	65.2
			5	15.36	10.42	36.2
			6	4.76	4.79	49.7

Run No.	Solute	Concentration, molal × 10^3	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f, %
50	$MgCl_2$	1.134	1	6.99	5.82	30.6
			2	7.90	5.87	31.3
			3	6.86	6.71	27.7
			4	6.92	6.54	25.0
			5	13.97	6.34	13.0
			6	4.80	4.70	21.2
51	$MgCl_2$	8.481	1	5.64	5.40	30.5
			2	6.08	5.92	30.0
			3	6.67	6.70	25.6
			4	6.72	6.27	23.5
			5	23.76	7.79	14.1
			6	4.76	4.71	26.1
52	$MgSO_4$	1.021	1	5.52	5.44	72.0
			2	6.26	5.88	72.6
			3	6.79	6.67	65.6
			4	6.60	6.15	64.3
			5	14.51	9.29	30.8
			6	4.81	4.67	57.7
53	Na_2SO_4	8.586	1	5.72	7.02	66.5
			2	7.92	5.86	77.0
			3	6.80	6.67	72.1
			4	6.64	6.06	70.5
			5	10.48	8.51	36.0
			6	4.80	4.66	61.0
54	$MgSO_4$	19.71	1	6.00	5.61	67.1
			2	5.79	5.81	70.4
			3	6.55	6.61	63.6
			4	5.95	6.15	61.5
			5	38.56	7.28	31.6
			6	4.59	4.63	49.4
55	Na_2SO_4	17.20	1	6.24	6.28	56.8
			2	6.12	5.96	62.3
			3	6.96	6.76	60.0
			4	8.70	6.47	56.0
			5	7.02	6.39	39.6
			6	4.92	4.72	50.5
56	$MgCl_2$	17.63	1	6.23	5.69	35.3
			2	6.08	5.82	37.6
			3	6.83	6.68	30.7
			4	6.26	6.09	30.9
			5	21.08	9.12	15.5
			6	4.73	4.72	30.9

Run No.	Solute	Concentration molal x 10^3	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f, %
57	Ethanol	0.791	1	6.38	5.68	24.9
			2	6.15	5.87	24.9
			3	6.71	6.70	23.3
			4	6.26	6.18	26.2
			5	14.81	9.34	14.1
			6	4.76	4.72	26.7
58	n-Butanol	0.798	1	5.53	5.60	36.3
			2	6.70	6.66	34.1
			3	6.70	6.66	34.1
			4	6.17	6.17	32.1
			5	16.03	15.14	13.2
			6	4.70	4.69	29.8
59	i-Butanol	0.815	1	5.56	5.34	42.2
			2	5.88	5.84	42.3
			3	6.72	6.68	34.3
			4	6.28	6.09	33.8
			5	25.60	21.18	9.0
			6	4.68	4.68	35.0
60	t-Butanol	0.797	1	5.64	5.47	49.7
			2	6.08	5.84	47.7
			3	6.88	6.69	40.5
			4	6.48	6.42	39.2
			5	29.48	23.30	5.9
			6	4.84	4.68	39.1
61	s-Butanol	0.797	1	6.18	5.51	40.8
			2	5.93	5.84	44.2
			3	6.78	6.70	37.7
			4	6.82	6.75	35.9
			5	45.56	33.56	6.3
			6	4.76	4.69	38.7
62	Na_2SO_4	42.97	1	6.32	5.95	49.9
			2	5.96	5.92	54.4
			3	6.80	6.82	49.7
			4	6.80	6.38	48.2
			5	37.48	32.71	6.3
			6	4.72	4.72	44.2
63	$MgSO_4$	21.13	1	5.91	5.45	67.6
			2	5.91	5.70	69.6
			3	6.51	6.57	61.8
			4	6.51	6.11	61.8
			5	43.91	14.80	-17.0
			6	4.77	4.61	53.8

Run No.	Solute	Concentration, molal × 10^3	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f,%
64	Na_2SO_4	0.5859	1	6.69	5.55	78.2
			2	5.91	5.83	80.8
			3	6.72	6.60	79.0
			4	6.41	6.07	82.6
			5	21.71	13.07	43.8
			6	4.68	4.67	86.2
65	NaCl	0.5427	1	5.20	5.44	70.4
			2	5.92	5.81	72.2
			3	6.76	6.67	75.4
			4	6.36	6.07	78.1
			5	22.40	17.85	25.7
			6	4.80	4.65	76.4
66	$MgSO_4$	2.294	1	5.75	5.42	89.3
			2	5.95	5.80	92.0
			3	6.75	6.69	90.6
			4	6.30	6.14	88.3
			5	20.60	16.32	27.8
			6	4.75	4.67	88.0
68	1-Octanol	5.234	1	5.68	5.75	72.1
			2	6.08	5.92	63.7
			3	6.92	6.81	68.7
			4	6.44	6.54	69.2
			6	5.36	4.74	73.9
69	NaCl	52.47	1	5.54	5.45	22.6
			2	5.81	5.76	21.2
			3	6.72	6.69	19.6
			4	6.29	6.49	17.5
			6	4.73	4.67	19.1
70	Methanol	11.45	1	5.69	5.51	15.2
			2	5.95	5.78	14.1
			3	6.83	6.66	12.8
			4	6.70	6.23	13.4
			6	4.72	4.65	20.5
71	1-Pentanol	0.7014	1	6.08	6.38	31.3
			2	5.89	5.74	37.6
			3	6.79	6.73	33.3
			4	6.68	6.56	29.7
			6	4.80	4.69	28.7

Run No.	Solute	Concentration, molal × 10^3	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f,%
72	Methanol	3.283	1	6.46	5.74	13.7
			2	5.81	5.90	16.0
			3	6.66	6.77	13.1
			4	6.41	6.35	12.4
			6	4.69	4.71	13.2
73	Sucrose	0.6521	1	6.32	5.82	61.9
			2	5.88	5.81	69.6
			3	6.80	6.61	58.5
			4	6.37	6.13	64.2
			6	4.74	4.61	48.9
75	d-Sorbitol	0.4644	1	5.59	5.46	49.2
			2	5.96	5.88	51.2
			3	6.94	6.82	43.8
			4	6.56	6.23	44.1
			6	4.80	4.73	38.1
77	Anisole	0.0911	1	5.49	5.42	76.5
			2	6.26	5.89	84.3
			3	6.89	6.76	77.8
			4	6.46	6.38	67.3
			6	4.80	4.72	84.3
78	Phenol	0.4097	1	5.36	5.41	20.3
			2	5.80	5.87	23.7
			3	6.64	6.72	21.0
			4	6.52	6.31	18.6
			6	4.68	4.70	19.5
79	p-Chlorophenol	0.4521	1	5.52	5.46	14.7
			2	6.40	5.85	14.7
			3	6.88	6.78	13.4
			4	6.40	6.43	10.0
			6	4.80	4.80	13.2
80	Benzene	0.1646	1	5.53	5.97	85.6
			2	5.97	—	—
			3	6.77	6.67	84.8
			4	6.67	6.20	78.9
			6	4.87	4.65	91.6

Run No.	Solute	Concentration, molal × 10^3	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f,%
81	Anisole	0.3863	1	5.48	5.48	49.9
			2	—	—	52.9
			3	6.84	6.80	42.2
			4	6.40	6.40	39.1
			6	4.80	4.73	53.8
82	Benzene	0.3924	1	5.51	5.57	61.8
			2	5.96	5.95	67.1
			3	6.81	6.84	69.6
			4	6.35	6.45	83.2
			6	4.76	4.77	73.5
83	Aniline	0.4257	1	5.57	5.49	2.4
			2	5.90	5.92	2.4
			3	6.70	6.85	-2.0
			4	6.33	6.32	-0.3
			6	4.73	4.79	2.4
84	Acetone	0.4813	1	5.60	5.54	24.2
			2	6.04	5.72	29.7
			3	6.88	6.83	19.5
			4	6.36	6.29	22.9
			6	4.92	4.75	20.8
85	Phenetole	0.2479	1	5.62	5.52	60.9
			2	6.22	5.86	58.8
			3	7.01	6.88	56.3
			4	7.07	6.41	55.5
			6	4.86	4.82	65.1
86	n-Butyraldehyde	0.2771	1	—	5.51	61.7
			2	—	5.58	64.3
			3	—	6.67	46.6
			4	—	6.44	45.9
			6	—	4.71	57.1
87	Benzaldehyde	0.4344	1	6.12	6.60	31.3
			2	5.97	6.04	40.5
			3	6.84	6.77	38.3
			4	6.66	6.92	28.1
			6	4.77	4.70	30.3

Run No.	Solute	Concentration, molal × 10^3	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f,%
88	n-Butyl Ethyl Ether	0.2704	1	6.70	6.86	68.2
			2	6.03	5.90	73.8
			3	6.93	6.87	85.6
			4	7.73	8.68	71.8
			6	4.83	4.78	87.2
89	t-Butyl Ethyl Ether	0.2966	1	6.43	6.21	73.1
			2	5.83	5.71	77.1
			3	6.67	6.75	64.9
			4	8.37	7.14	49.4
			6	4.67	4.73	69.6
90	t-Butyl-i-Propyl Ether	0.2244	1	6.54	5.81	82.5
			2	5.91	5.50	83.6
			3	6.75	6.62	76.1
			4	6.95	6.64	90.5
			6	4.76	4.68	82.0
91	i-Propyl Ether	0.2875	1	6.23	5.74	63.8
			2	5.95	5.72	65.7
			3	6.78	6.63	73.4
			4	6.97	7.61	52.2
			6	4.71	4.63	70.5
92	i-Valeraldehyde	0.3250	1	—	5.74	61.8
			2	—	5.71	48.7
			3	—	6.67	56.4
			4	—	6.97	44.9
			6	—	4.65	57.3
93	i-Butylaldehyde	0.2276	1	—	5.90	61.1
			2	—	5.83	66.1
			3	—	6.70	46.0
			4	—	6.36	50.6
			6	—	4.67	50.6
94	Acetophenone	0.4367	1	—	5.57	24.6
			2	—	5.76	28.4
			3	—	6.71	24.2
			4	—	6.75	18.7
			6	—	4.68	22.5

Run No.	Solute	Concentration, molal × 10 ^{3}	Membrane No.	(PSP)^a, g/h	(PR)^a, g/h	f,%
95	Methyl Ethyl Ketone	0.6514	1	5.73	5.76	36.2
			2	5.90	5.81	31.9
			3	6.78	6.71	35.3
			4	6.85	12.67	18.4
			6	4.73	4.70	34.0
96	Methyl i-Propyl Ketone	0.3292	1	5.96	5.52	56.0
			2	6.02	5.83	56.6
			3	6.89	6.73	37.0
			4	13.13	8.96	36.2
			6	4.82	4.74	43.8
97	di-i-Propyl Ketone	0.3048	1	5.33	6.08	59.0
			2	5.86	5.75	61.7
			3	6.71	6.65	61.7
			4	8.86	10.21	53.1
			6	4.69	4.66	60.0
98	Benzyl Methyl Ketone	0.3958	1	6.39	6.66	33.9
			2	5.93	5.77	38.0
			3	6.81	6.66	34.5
			4	10.09	8.63	25.9
			6	4.73	4.61	33.3
99	di-i-Butyl Ketone	0.2037	1	6.89	6.25	75.5
			2	5.93	5.90	79.6
			3	6.71	6.78	77.3
			4	9.13	8.54	60.6
			6	4.76	4.72	73.8
100	NaCl	54.32	1	6.68	5.38	22.3
			2	6.12	5.82	21.7
			3	6.92	6.66	20.0
			4	10.24	7.69	15.5
			6	4.84	4.60	19.9
101	n-Hexanol	0.4132	1	5.40	6.43	31.1
			2	5.94	5.83	46.3
			3	6.69	6.69	39.9
			4	7.74	7.89	33.1
			6	4.62	4.63	36.3

Run No.	Solute	Concentration, molal × 10^3	Membrane No.	(PSP)[a], g/h	(PR)[a], g/h	f,%
102	Ethylene Glycol	0.5469	1	6.76	6.36	17.7
			2	6.03	5.87	22.3
			3	6.85	8.20	8.6
			4	8.78	6.68	15.4
			6	4.77	4.59	15.4
103	di-Ethylene Glycol	0.3600	1	6.60	5.56	35.7
			2	5.96	5.73	38.1
			3	6.60	6.53	32.9
			4	8.12	7.96	21.3
			6	4.76	4.51	23.0
104	PEG[b]200	39.0[c]	1	5.70	5.58	58.7
			2	6.65	6.93	52.8
			3	6.80	6.57	55.3
			4	9.50	18.58	38.4
			6	4.70	4.56	47.7
105	PEG[b]300	62.7[c]	1	5.63	5.91	68.1
			2	7.00	5.89	71.7
			3	6.67	6.67	67.9
			4	7.63	7.91	51.7
			6	4.70	4.63	72.2
106	PEG[b]400	65.8[c]	1	5.76	5.60	74.6
			2	6.12	6.16	74.5
			3	6.76	6.85	71.4
			4	6.88	7.18	61.3
			6	4.76	4.76	59.5
108	PEG[b]1000	52.8[c]	1	5.55	5.58	82.7
			2	6.85	6.48	77.3
			3	6.55	6.73	80.4
			4	6.70	7.38	66.2
			6	4.53	4.68	77.8
109	PEG[b]600	56.2[c]	1	5.77	5.62	83.7
			2	6.67	6.46	77.1
			3	6.70	6.77	83.0
			4	7.73	7.49	67.4
			6	4.70	4.69	73.3

Run No.	Solute	Concentration, molal × 10^3	Membrane No.	(PSP)^a, g/h	(PR)^a, g/h	f,%
110	PEG^b 2,000	62.7^c	1	5.70	5.94	88.5
			2	6.54	6.21	92.6
			3	6.48	6.73	95.6
			4	6.96	6.47	87.8
			6	4.50	4.74	93.0
111	PEG^b 3,000	58.0^c	1	6.17	5.96	88.6
			2	6.66	6.33	93.5
			3	6.85	6.75	96.2
			4	6.95	6.65	91.7
			6	4.82	4.70	99.9
112	PEG^b 4,000	165.5^c	1	5.65	8.08	63.1
			2	6.25	6.89	83.0
			3	6.73	6.82	97.6
			4	6.93	7.75	78.5
			6	4.74	4.74	98.5
113	PEG^b 1,500	64.8^c	1	8.54	5.55	94.2
			2	7.66	6.38	90.4
			3	6.92	6.81	96.0
			4	8.12	7.36	81.9
			6	4.85	4.70	92.6
114	PEG^b 4,000	61.5^c	1	5.66	6.05	89.1
			2	6.43	6.42	92.9
			3	6.77	6.77	97.7
			4	13.07	12.46	28.1
			6	4.71	4.72	98.0
115	PEG^b 6,000	58.1^c	1	—	5.51	96.7
			2	—	6.05	96.6
			3	—	6.67	99.0
			4	—	8.02	72.5
			6	—	4.66	99.6
116	PEG^b 1,000	48.0^c	1	—	5.58	80.6
			2	—	5.59	83.8
			3	—	6.73	80.4
			4	—	12.55	33.1
			6	—	4.70	73.5

Run No.	Solute	Concentration, molal x 10^3	Membrane No.	(PSP)[a], g/h	(PR)[a], g/h	f, %
117	Aniline	0.500	1	—	5.44	3.3
			2	—	5.90	11.4
			3	—	6.67	8.9
			4	—	6.30	9.7
			6	—	4.66	11.1
118	Phenol	3.750	1	5.54	5.46	18.7
			2	6.00	6.05	17.6
			3	6.67	6.73	16.1
			4	7.84	6.59	12.4
			6	4.62	4.69	12.1
119	Glycerol	0.3056	1	6.41	5.63	17.5
			2	6.85	6.07	37.4
			3	6.76	6.77	33.8
			4	8.72	7.75	17.0
			6	4.74	4.73	25.6
120	Glycerol	0.5924	1	—	5.64	37.6
			2	—	6.09	38.1
			3	—	6.87	33.4
			4	—	7.05	21.2
			6	—	4.81	25.4
121	PEG[b]1,000	56.5[c]	1	5.68	5.44	90.3
			2	6.08	5.90	88.1
			3	6.67	6.72	88.5
			4	6.92	6.78	79.6
			6	4.80	4.70	80.9
122	NaCl	53.33	1	6.03	5.62	22.6
			2	5.40	6.07	20.9
			3	7.02	6.93	20.4
			4	7.33	6.92	18.5
			6	4.93	4.82	18.0

[a] for 13.2 cm^2 surface area.

[b] Polyethylene glycol.

[c] ppm by weight.

Table A-1-8

Experimental Reverse Osmosis Results for the Ethanol-Heptane System at 6900 kPag and 25°C.

Membrane No. 1 (Cellulose)

Run No.	X_1^a	(PR), g/h	X_3^b
1	1.000	5.03	--
2	1.000	5.10	--
3	1.000	5.19	--
4	0.956	5.54	0.954
5	0.910	4.54	0.907
6	0.857	4.38	0.863
7	0.786	5.48	0.807
8	0.722	5.28	0.757
9	0.641	5.07	0.712
10	0.592	5.01	0.694
11	0.414	5.17	0.623
12	0.425	5.21	0.615
13	0.332	5.36	0.561
14	0.287	5.23	0.524
15	0.214	5.75	0.444
16	0.144	5.75	0.326
17	0.078	5.18	0.195
18	0.049	6.35	0.110
19	0.000	11.31	--
20	0.000	10.95	--
21	0.031	3.21	0.079
22	0.069	2.82	0.173
23	0.139	2.80	0.354
24	0.201	2.55	0.449
25	0.232	2.12	0.503
26	0.355	2.42	0.604
27	0.424	2.49	0.638
28	0.528	2.35	0.683
29	0.614	2.66	0.710
30	0.678	2.77	0.744
31	0.766	3.41	0.793
32	0.825	2.47	0.837
33	0.861	2.33	0.865
34	0.898	2.27	0.901
35	0.942	2.16	0.944
36	0.966	2.26	0.965
37	1.000	2.18	--
38	1.000	2.19	--
39	1.000	2.13	--
40	1.000	2.14	--
41	1.000	2.32	--
42	0.933	2.34	0.936
43	0.860	2.39	0.870

Membrane No. 1 (Cellulose) (cont'd)

Run No.	X_1[a]	(PR), g/h	X_3[b]
44	0.736	2.96	0.784
45	0.672	3.05	0.752
46	0.567	3.15	0.706
47	0.497	3.31	0.684
48	0.470	--	0.674
49	0.477	3.40	0.676
50	0.478	3.25	0.679
51	0.482	3.26	0.680

[a] mol fraction of ethanol in feed.

[b] mol fraction of ethanol in permeate.

Membrane No. 2 (Cellulose)

Run No.	X_1^a	(PR), g/h.	X_3^b
1	1.000	3.07	--
2	1.000	3.04	--
3	1.000	3.03	--
4	0.956	3.26	0.955
5	0.910	3.32	0.908
6	0.857	3.38	0.862
7	0.786	3.53	0.810
8	0.722	3.66	0.767
9	0.641	3.65	0.731
10	0.592	3.64	0.709
11	0.414	3.50	0.638
12	0.425	3.50	0.626
13	0.332	3.55	0.600
14	0.287	3.76	0.563
15	0.214	3.78	0.496
16	0.144	3.90	0.377
17	0.078	3.38	0.233
18	0.049	4.14	0.137
19	0.000	8.61	--
20	0.000	8.49	--
21	0.031	2.72	0.095
22	0.069	2.64	0.205
23	0.139	2.45	0.387
24	0.201	2.26	0.485
25	0.232	2.21	0.537
26	0.355	2.37	0.624
27	0.424	2.43	0.659
28	0.528	2.38	0.700
29	0.614	2.44	0.727
30	0.678	2.45	0.751
31	0.766	2.67	0.803
32	0.825	2.33	0.837
33	0.861	2.18	0.867
34	0.898	2.07	0.900
35	0.942	2.11	0.940
36	0.966	2.02	0.965
37	1.000	1.92	--
38	1.000	1.83	--
39	1.000	1.94	--
40	1.000	1.81	--
41	1.000	1.92	--
42	0.933	2.09	0.932
43	0.860	2.15	0.874

Membrane No. 2 (Cellulose) (cont'd)

Run No.	X_1[a]	(PR), g/h	X_3[b]
44	0.736	2.32	0.791
45	0.672	2.37	0.762
46	0.567	2.33	0.718
47	0.497	2.32	0.698
48	0.470	--	0.691
49	0.477	2.40	0.693
50	0.478	2.36	0.694
51	0.482	2.36	0.693

[a] mol fraction of ethanol in feed.

[b] mol fraction of ethanol in permeate.

Membrane No. 3 (Cellulose)

Run No.	x_1^a	(PR), g/h	x_3^b
1	1.000	7.75	--
2	1.000	7.88	--
3	1.000	7.98	--
4	0.956	8.37	0.955
5	0.910	8.54	0.907
6	0.857	8.47	0.859
7	0.786	8.46	0.800
8	0.722	8.34	0.752
9	0.641	8.78	0.712
10	0.592	8.90	0.689
11	0.414	8.55	0.599
12	0.425	8.56	0.594
13	0.332	8.70	0.553
14	0.287	9.15	0.505
15	0.214	9.11	0.416
16	0.144	9.58	0.311
17	0.078	10.17	0.180
18	0.049	11.22	0.103
19	0.000	19.59	--
20	0.000	19.44	--
21	0.031	8.19	0.067
22	0.069	7.62	0.154
23	0.139	6.52	0.311
24	0.201	5.85	0.399
25	0.232	5.59	0.461
26	0.355	5.80	0.568
27	0.424	5.69	0.614
28	0.528	5.52	0.663
29	0.614	5.67	0.700
30	0.678	5.91	0.735
31	0.766	6.32	0.787
32	0.825	5.29	0.832
33	0.861	5.00	0.862
34	0.898	4.72	0.900
35	0.942	4.67	0.942
36	0.966	4.66	0.962
37	1.000	4.26	--
38	1.000	4.14	--
39	1.000	4.28	--
40	1.000	4.06	--
41	1.000	4.24	--
42	0.933	4.53	0.934
43	0.860	4.66	0.867

Membrane No. 3 (Cellulose) (cont'd)

Run No.	X_1[a]	(PR), g/h	X_3[b]
44	0.736	5.13	0.787
45	0.672	5.08	0.738
46	0.567	5.25	0.693
47	0.497	5.25	0.666
48	0.470	--	0.653
49	0.477	5.38	0.649
50	0.478	5.36	0.654
51	0.482	5.32	0.653

[a] mol fraction of ethanol in feed.

[b] mol fraction of ethanol in permeate.

Membrane No. 4 (Cellulose Acetate)

Run No.	X_1^a	(PR), g/h	X_3^b
1	1.000	10.94	--
2	1.000	11.42	--
3	1.000	11.62	--
4	0.956	10.15	0.981
5	0.910	8.95	0.957
6	0.857	8.24	0.938
7	0.786	7.29	0.921
8	0.722	6.30	0.910
9	0.641	5.89	0.906
10	0.592	5.61	0.901
11	0.414	4.27	0.863
12	0.425	4.36	0.884
13	0.332	4.03	0.870
14	0.287	3.69	0.843
15	0.214	2.91	0.823
16	0.144	1.93	0.762
17	0.078	1.07	0.358
18	0.049	0.52	0.142
19	0.000	0.23	--
20	0.000	0.25	--
21	0.031	0.12	--
22	0.069	0.20	--
23	0.139	0.53	0.792
24	0.201	0.72	0.842
25	0.232	0.87	0.868
26	0.355	1.13	0.903
27	0.424	1.41	0.906
28	0.528	1.56	0.920
29	0.614	1.72	0.928
30	0.678	1.99	0.929
31	0.766	2.44	0.944
32	0.825	2.56	0.953
33	0.861	2.77	0.957
34	0.898	2.98	0.963
35	0.942	3.79	0.977
36	0.966	4.17	0.985
37	1.000	4.79	--
38	1.000	4.79	--
39	1.000	5.15	--
40	1.000	5.34	--
41	1.000	5.36	--
42	0.933	4.65	0.970
43	0.860	3.81	0.951

Membrane No. 4 (Cellulose Acetate) (cont'd)

Run No.	X_1[a]	(PR), g/h	X_3[b]
44	0.736	2.79	0.934
45	0.672	2.38	0.929
46	0.567	2.00	0.919
47	0.497	1.81	0.911
48	0.470	--	0.908
49	0.477	1.81	0.911
50	0.478	1.79	0.914
51	0.482	1.77	0.909

[a] mol fraction of ethanol in feed.

[b] mol fraction of ethanol in permeate.

Membrane No. 5 (Cellulose)

Run No.	X_1[a]	(PR), g/h	X_3[b]
1	1.000	22.84	--
2	1.000	24.22	--
3	1.000	21.08	--
4	0.956	16.35	0.954
5	0.910	--	0.907
6	0.857	17.74	0.856
7	0.786	17.80	0.789
8	0.722	17.57	0.740
9	0.641	18.26	0.684
10	0.592	18.41	0.661
11	0.414	17.92	0.554
12	0.425	17.70	0.568
13	0.332	19.04	0.479
14	0.287	18.28	0.438
15	0.214	18.68	0.361
16	0.144	19.28	0.248
17	0.078	20.53	0.136
18	0.049	22.51	0.081
19	0.000	34.43	--
20	0.000	32.78	--
21	0.031	18.41	0.051
22	0.069	15.75	0.122
23	0.139	14.38	0.257
24	0.201	13.24	0.348
25	0.232	12.50	0.387
26	0.355	12.11	0.511
27	0.424	12.46	0.572
28	0.528	12.13	0.642
29	0.614	11.69	0.670
30	0.678	11.83	0.708
31	0.766	12.74	0.773
32	0.825	10.87	0.823
33	0.861	10.35	0.855
34	0.898	9.58	0.894
35	0.942	9.42	0.940
36	0.966	9.05	0.963
37	1.000	9.62	--
38	1.000	11.97	--
39	1.000	8.63	--
40	1.000	11.91	--
41	1.000	10.68	--
42	0.933	9.01	0.932
43	0.860	9.44	0.862

Membrane No. 5 (Cellulose) (cont'd)

Run No.	X_1[a]	(PR), g/h	X_3[b]
44	0.736	10.08	0.756
45	0.672	10.27	0.714
46	0.567	10.53	0.649
47	0.497	10.74	0.616
48	0.470	--	0.604
49	0.477	10.93	0.611
50	0.478	11.01	0.609
51	0.482	--	0.605

[a] mol fraction of ethanol in feed.

[b] mol fraction of ethanol in permeate.

Membrane No. 6 (PPPH 8273)

Run No.	X_1[a]	(PR), g/h	X_3[b]
1	1.000	12.62	--
2	1.000	12.92	--
3	1.000	9.83	--
4	0.956	9.81	0.991
5	0.910	7.80	0.987
6	0.857	6.41	0.976
7	0.786	4.93	0.967
8	0.722	3.86	0.958
9	0.641	3.28	0.957
10	0.592	2.95	0.943
11	0.414	1.79	0.940
12	0.425	1.87	0.942
13	0.332	1.44	0.918
14	0.287	5.52	0.681
15	0.214	5.01	0.403

[a] mol fraction of ethanol in feed.

[b] mol fraction of ethanol in permeate.

Table A-1-9

Experimental Reverse Osmosis Results for the Ethanol-Heptane System at 3450 kPag and 25°C.

Membrane No. 1 (Cellulose)

Run No.	X_1[a]	(PR), g/h	X_3[b]
60	1.000	1.16	--
61	1.000	0.97	--
62	0.967	1.37	0.967
63	0.907	1.37	0.908
64	0.819	1.43	0.835
65	0.751	1.57	0.772
66	0.625	1.49	0.720
67	0.554	1.71	0.686
68	0.500	1.63	0.663
69	0.405	1.30	0.616
70	0.301	1.52	0.570
71	0.190	1.34	0.420
72	0.163	1.30	0.286
73	0.070	1.67	0.134
74	0.037	1.91	0.042
75	0.000	2.97	--
76	0.000	2.87	--

[a] mol fraction of ethanol in feed.

[b] mol fraction of ethanol in permeate.

Membrane No. 2 (Cellulose)

Run No.	X_1[a]	(PR), g/h	X_3[b]
60	1.000	1.04	--
61	1.000	0.63	--
62	0.967	1.13	0.966
63	0.907	1.14	0.909
64	0.819	1.19	0.837
65	0.751	1.21	0.781
66	0.625	1.19	0.728
67	0.554	1.22	0.696
68	0.500	1.22	0.673
69	0.405	1.22	0.633
70	0.301	1.13	0.587
71	0.190	1.09	0.448
72	0.163	0.95	0.313
73	0.070	1.11	0.148
74	0.037	1.45	0.061
75	0.000	2.35	--
76	0.000	2.10	--

[a] mol fraction of ethanol in feed.

[b] mol fraction of ethanol in permeate.

Membrane No. 3 (Cellulose)

Run No.	X_1[a]	(PR), g/h	X_3[b]
60	1.000	2.16	--
61	1.000	1.80	--
62	0.967	2.36	0.967
63	0.907	2.43	0.909
64	0.819	2.53	0.824
65	0.751	2.63	0.768
66	0.625	2.69	0.706
67	0.554	2.70	0.670
68	0.500	2.65	0.645
69	0.405	2.71	0.597
70	0.301	2.58	0.569
71	0.190	2.66	0.394
72	0.163	2.63	0.261
73	0.070	3.27	0.136
74	0.037	3.80	0.059
75	0.000	5.99	--
76	0.000	5.78	--

[a] mol fraction of ethanol in feed.

[b] mol fraction of ethanol in permeate.

Membrane No. 4 (Cellulose)

Run No.	X_1[a]	(PR), g/h	X_3[b]
60	1.000	3.08	--
61	1.000	2.71	--
62	0.967	2.83	0.977
63	0.907	2.19	0.949
64	0.819	1.56	0.921
65	0.751	1.18	0.895
66	0.625	0.80	0.890
67	0.554	0.72	0.863
68	0.500	0.66	0.844
69	0.405	0.55	0.830
70	0.301	0.43	0.813
71	0.190	0.23	0.667
72	0.163	0.13	--
73	0.070	0.10	--
74	0.037	0.09	--
75	0.000	0.01	--
76	0.000	0	--

[a] mol fraction of ethanol in feed.

[b] mol fraction of ethanol in permeate.

Membrane No. 5 (Cellulose)

Run No.	X_1[a]	(PR), g/h	X_3[b]
60	1.000	4.32	--
61	1.000	4.06	--
62	0.967	4.61	0.965
63	0.907	4.81	0.903
64	0.819	4.90	0.822
65	0.751	5.22	0.750
66	0.625	5.27	0.688
67	0.554	5.38	0.640
68	0.500	5.44	0.611
69	0.405	5.36	0.578
70	0.301	5.51	0.485
71	0.190	5.68	0.338
72	0.163	5.87	0.233
73	0.070	7.24	0.122
74	0.037	8.39	0.059
75	0.000	11.87	--
76	0.000	11.67	--

[a] mol fraction of ethanol in feed.

[b] mol fraction of ethanol in permeate.

Table A-1-10

Experimental Reverse Osmosis Results for Dilute Solutions in Ethanol at 6900 and 3450 kPag, and 25°C with the Membranes used for Ethanol-Heptane Fractionation.

Run No.	Solute	Concn, m x 10^3	P, kPag	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/h	f,%
1	LiCl	5.511	6900	1	5.03	4.61	15.2
				2	3.07	2.79	40.9
				3.	7.75	7.60	33.4
				4	10.94	10.80	>99.9
				5	22.84	15.22	22.6
				6	12.62	11.98	>99.9
2	LiCl	5.026	6900	1	5.10	4.75	33.5
				2	3.04	3.05	42.4
				3	7.88	7.62	30.0
				4	11.42	11.10	>99.9
				5	24.22	17.36	19.6
				6	12.92	12.35	>99.9
3	LiCl	81.46	6900	1	5.19	4.37	24.7
				2	3.03	2.54	31.4
				3	7.98	6.60	22.3
				4	11.62	9.94	97.6
				5	21.08	13.31	14.4
				6	13.19	9.83	97.8
37	LiCl	6.643	6900	1	2.19	1.95	41.7
				2	1.83	1.79	47.5
				3	4.14	4.03	38.5
				4	4.99	4.88	>99.9
				5	11.97	11.14	24.0
38	LiCl	6.107	6900	1	2.13	2.78	37.1
				2	1.94	1.91	43.1
				3	4.28	4.23	36.8
				4	5.15	5.09	>99.9
				5	8.63	8.58	35.2
39	LiCl	6.680	6900	1	2.34	1.99	43.1
				2	1.43	1.87	48.5
				3	4.63	4.13	38.9
				4	5.38	5.34	>99.9
				5	9.17	8.50	29.9

Run No.	Solute	Concn, m x 10^3	P, kPag	Membrane No.	$(PSP)^a$, g/h	$(PR)^a$, g/n	f,%
40	LiCl	8.085	6900	1	2.14	2.07	40.4
				2	1.81	1.86	46.7
				3	4.06	4.05	38.6
				4	5.34	5.33	>99.9
				5	11.91	12.75	19.3
41	LiCl	63.51	6900	1	2.21	—	33.8
				2	1.17	—	38.7
				3	4.18	—	29.9
				4	5.32	—	99.2
				5	8.90	—	23.0
42	LiCl	74.09	6900	1	2.32	2.07	32.9
				2	1.92	1.67	38.1
				3	4.24	3.68	29.4
				4	5.36	4.87	99.0
				5	10.68	7.13	21.1
54	N,N-Dimethylbenzylamine	4.022	6900	1	2.35	2.31	1.0
				2	1.86	1.88	1.7
				3	4.21	4.18	3.9
				4	5.45	5.36	61.5
				5	19.55	71.34	1.9
55	N,N-Dimethylbenzylamine	4.336	6900	1	1.73	2.53	6.0
				2	1.46	1.80	8.0
				3	3.43	4.02	7.8
				4	4.58	5.22	63.6
				5	10.26	12.59	9.1
56	Triethylamine	5.203	6900	1	2.76	2.72	15.9
				2	2.07	2.12	22.9
				3	4.48	4.47	19.2
				4	6.00	5.77	79.2
				5	14.76	10.72	8.0
57	Triethylamine	5.178	6900	1	2.65	2.70	15.7
				2	1.94	2.01	23.0
				3	4.32	4.23	17.4
				4	5.71	5.36	82.8
				5	12.84	8.15	3.6

Run No.	Solute	Concn, m x 10^3	P, kPag	Membrane No.	(PSP)^a, g/h	(PR)^a, g/n	f,%
59	Triethylamine	4.167	3450	1	1.16	1.31	14.1
				2	1.04	1.06	16.8
				3	2.16	2.18	13.5
				4	3.08	3.05	77.3
				5	4.32	4.16	7.03
60	Triethylamine	3.773	3450	1	0.97	1.15	16.4
				2	0.63	0.76	14.6
				3	1.80	1.82	12.8
				4	2.71	2.72	70.2
				5	4.06	3.92	11.9

Appendix B

A Detailed Reverse Osmosis Experimental Description

A more detailed description of a typical reverse osmosis experiment is given here as an elaboration. From Appendix A-1-5, run number 513 is taken as an example. The solute is NaCl at a nominal concentration of 0.005 molal in methanol. The membranes are of cellulose acetate numbered from 1 to 6 inclusively. The procedure is outlined as follows.

Step 1. It is considered that the entire ciculation system would have been standing with the tubing and pump filled with room temperature methanol, as well as 2 L of methanol in the feed reservoir. The pump and temperature controller are started, and the controls adjusted to give the flowrate (5×10^{-4} m^3/min) operating pressure (1725 kPag) and temperature (25°C).

Step 2. When the system reached operating conditions (usually temperature was the constraint), pre-weighed sample bottles were connected to the permeate outlet for each cell, and the time was recorded. These bottles were of 50 mL capacity, and were fitted with female ground glass joints for their necks. A special lid was used with a small hole through which a Teflon tube could be loosely fitted. This tube was connected directly to the permeate outlet. In this case, since six membranes were studied, six sample bottles were used.

Step 3. At the end of a suitable time period to obtain a weighable sample (31 minutes in this case) the sample bottles were removed. The exact time was not always the same, but was usually in the range of 15 to 30 minutes for these experiments. The samples were weighed and found to be 11.23, 2.79, 2.21, 8.03, and 10.39 grams for membranes 1 to 5, respectively (the (PSP) sample for membrane 6 was lost by a handling error).

Step 4. The pump was stopped and the pure methanol was removed. It should be noted that two separate feed solution reservoirs were used. The feed solution reservoir, which had previously been filled with a 3.8 L solution made up to the nominal concentration (0.005 molal) was attached. Instead of recycling, the circulation system was attached to a waste solvent tank. The pump was started and approximately 0.8 L were let run into the waste solvent tank. The pump was then stopped and the circulation system's closed cycle was reconnected. The pump was then restarted and the permeate from membrane 6 (lowest permeation rate) was collected in a small graduated cylinder.

Step 5. When 8 mL of permeate had been collected (a time period of approximately 2 hours), another set of preweighed sample bottles were connected to the permeate outlets and the time was recorded. As well, a sample of the feed solution was taken. After 60 minutes, the sample bottles were removed and another sample of the feed solution was collected. The permeate samples were then weighed and found to be 21.22, 4.21, 15.37 and 20.21 grams for membranes 5 to 8 respectively.

Step 6. The pump was stopped and the feed solution was replaced by pure methanol. The circulation system was connected to the waste solvent tank and the pump was started. After 2 L of pure methanol had been passed (sufficient to rinse the system), the pump was stopped and the circulation system was reconnected. If no more experiments were considered, the system was left standing as encountered in Step 1.

Step 7. The six samples (2 feed, 6 permeate) were then analyzed for concentration by an electrical conductance method. The two feed solution samples were 265 and 273.2 μg/mL, and the six permeate solution samples were 110.9, 72.95, 65.7, 90.1, 99.3 and 52.9 μg/mL, for membranes 1 to 6, respectively. The solute separations were then calculated for the six membranes: 58.9%, 72.9%; 75.6%; 66.5%;, 63.1%; and 80.3%, for membranes 1 to 6, respectively. Both (PSP) and (PR) were calculated. The (PSP)'s were 21.74, 5.40, 4.28, 15.54, and 20.11 g/h for 13.2 cm^2 surface areas for membranes 1 to 5, respectively. The (PR)'s were calculated as 21.22, 5.32, 4.21, 15.37, 20.21 and 3.31 g/h for 13.2 cm^2 surface areas for membranes 1 to 6, respectively.

Appendix C

Fortran Program Listings

```
FORTRAN IV-PLUS V3.0-3            15:28:07     23-OCT-82          PAGE 1
CALA1.FTN;101                  /TR:BLOCKS/WR

C     ----------------------------------------------
C     THIS PROGRAM IS USED FOR FINDING BBAR OR ABAR FROM
C     CHROMATOGRAPHY DATA AND A GIVEN DBAR VALUE.
      EXTERNAL FCT14
      DIMENSION AUX(100)
      REAL*8 RES,SEKI,DFF,DELTA,DWATER,PARK,D00,D
      INTEGER IER II
      COMMON C,CC
      OPEN (UNIT=2,NAME='HAMAK.OUT',TYPE='NEW')
C   THESE ARE FOR THE ETHANOL - CA  CASE
C
C
        DELTA=15.5
        DWATER=0.87
        PARK=0.517
        D00=2.63
        D=13
        C=-11
        CC=0
C     DELTA=INTERFACIAL WATER THICKNESS
C     DWATER=MOLECULAR RADIUS OF WATER
C     PARK=K FROM CHROMATOGRAPHY DATA
C     D00=DBAR VALUE
C     D=UPPER INTEGRATION LIMIT
C     C=INITIAL GUESS OF BBAR
C     CC=USUALLY THIS IS ZERO.. INSERT ABAR VALUE ONLY WHEN
C        BOTH ELECTROSTATIC AND VAN DER WAALS FORCES ARE CONSIDERED.
   21 FORMAT(7D10.3)
      SEKI=(PARK-1.0D0)*DELTA+D00-DWATER
C        SEKI=(DELTA-DWATER)*PARK-DELTA+D00
C        WAS INITIALLY USED. THIS IS A WRONG FORM.
      II=1
   82 II=II+1
      CALL QATR2(D00,D,1.E-2,100,FCT14,RES,IER,AUX)
      DFF=DABS(RES-SEKI)
      IF(DFF.LE.0.001D0) GO TO 83
      IF(RES-SEKI) 84,84,85
   84 C=C*(1.0D0-0.5D0**II)
C         USE + WHEN C=BBAR IS +
C         USE - WHEN C=BBAR IS -
      TYPE*,'C',C
      CALL QATR2(D00,D,1.E-2,100,FCT14,RES,IER,AUX)
      IF(RES-SEKI) 84,84,86
   86 II=II+1
   85 C=C*(1.0D0+0.5D0**II)
C         USE - WHEN C=BBAR IS +
C         USE + WHEN C=BBAR IS -
      TYPE*,'C',C
      CALL QATR2(D00,D,1.E-2,100,FCT14,RES,IER,AUX)
      IF(RES-SEKI) 82,82,85
   83 WRITE(2,31) PARK,D00,C
   31 FORMAT(3D12.3)
      TYPE*,'C',C
      STOP
      END
```

```
FORTRAN IV-PLUS V3.0-3              15:25:29    23-OCT-82          PAGE 1
CALA7.FTN;17                 /TR:BLOCKS/WR
          C    THIS PROGRAM IS USED TO FIND A ENERGY POTENTIAL FUNCTION
          C    FROM A GIVEN SEPARATION DATA.IN THIS MODEL RADIUS IS (REAL RADIUS
          C    - RADIUS OF WATER MOLECULE)
          C        --------------------------------------------------
          C
          C
          C
          C                                                MODIFIED CALA7 FOR MEOH
          C
          C
          C        ALPHA : INSERT 1.0D0
          C        EH : INSERT 0.02D0
          C        CONST : INSERT 0.3D0
          C        RADIUS : PORE RADIUS
          C        PRESS : OPERATING PRESSURE AS ATM D05
          C        CONC : FEED CONCENTRATION AS GMOL/M3
          C        Q : SOLUTE DIFFUSIVITY CM2/S*10.0D05
          C        PWP : AS GP/HR
          C        K,L,M,KK : INSERT 0,0,3,1
          C        D01 : ASYMPTOTE OF HYPERBOLIC FUNCTION WHICH EXTENDS INTO INSIDE
          C               THE PORE WALL
          C        D00 : EFFECTIVE RADIUS OF SOLUTE
          C        D4 : DISTANCE WITHIN WHICH SOLUTE IS IMMOBILF
          C        D : UPPER LIMIT OF INTEGRATION = 100.0D0
          C        DELTA : THICKNESS OF BOUND WATER
          C        DWATER : RADIUS OF WATER MOLECULF = D01 = 0.87D0
          C        PARK : PARTITION COEFFICIENT FROM LC
          C        F4P CALA7=CALA7,CHR,QATR,FCT12,TRANS2,FDELT1,DERBE1,POTEN3,FPIC2
          C        IN TRANS2 X1=(581.0D02/1.61D0)*Q/RADIUS**2/CONC AND X2=686.0D0
          C        DONT FORGET TO INSERT Q WHEN TRANS2 IS CALLED
          C        --------------------------------------------------
                   REAL*8 D,PARK,DELTA,DWATER
                   REAL*8 ALPHO,CONST,RATIO,SEP,RADIUS,PRESS,CONC,D00,D01,
                  1D1,D2,D3,D4,P1,P2,P3,P4,Q,AM
                  2,CA1,CA2,CA3,SEP1,SEP2,APWP,PWP,TRANSN,TRANS,V,DIFF,DIFFF,SEPF
                   INTEGER MMM,NNN
                   COMMON X1,X2,EH,ALPHA(100),A,B,C,AA,K,L,M,KK,N,ROHO,ROHOO,POH1
                   OPEN (UNIT=1,NAME='CALA7.IN',TYPF='OLD')
                   READ(1,*) ALPHO,FH,CONST,PRESS,D01,ROHOO
                   READ(1,*) D,DELTA,DWATER
          C    21  FORMAT(6D10.3)
                   READ(1,*) K,L,M,KK,MMM,NNN
          C    33  FORMAT(6I3)
                   DO 41 J=1,MMM
                   READ(1,*) RADIUS,PWP
          C    35  FORMAT(2D10.3)
                   DO 42 IJ=1,NNN
                   READ(1,*) D00,C,Q,CONC,SEPF,PARK
          C    34  FORMAT(6D10.3)
                      CLOSE (UNIT=1,DISP='KEEP')
                   CALL CHR(DELTA,DWATER,PARK,D00,D)
                   TYPE*,'C',C
                   D1=0.0D0
                   D2=0.0D0
                   D3=0.0D0
                   D4=0.0D0
```

```
FORTRAN IV-PLUS V3.0-3             15:25:29    23-OCT-82          PAGE 2
CALA7.FTN;17                    /TR:BLOCKS/WR

      P1=0.0D0
      P2=0.0D0
      P3=0.0D0
      P4=0.0D0
      AM=FLOAT(M)
      C=C/(RADIUS**AM)
      APWP=PWP/13.2D-4/3600.0D0/46.04/(PRESS*1.0D-5*1.01325D02)*1.0D-3
   14 TRANSN=0.4951*(APWP*1.0D09+5.962)*1.0D-06
   16 TRANS=TRANSN*(Q/0.4916D0)**0.6667D0
      V=APWP*(PRESS*1.0D-5*1.01325D02)/21.74D0
      V=V/TRANS
      I=1
   22 I=I+1
      CA1=CONC
      CA2=CONC
      CALL TRANS2(ALPHO,CONST,RADIUS,PRESS,CONC,D00,D1,D2,D3,D4,
     1P1,P2,P3,P4,D01,Q,SEP,RATIO)
   18 SEP1=SEP
      CA3=(1.0D0-SEP1)*CA2
      CA2=CA3+(CA1-CA3)*DEXP(V)
      CONC=CA2
      CALL TRANS2(ALPHO,CONST,RADIUS,PRESS,CONC,D00,D1,D2,D3,D4,
     1P1,P2,P3,P4,D01,Q,SEP,RATIO)
      SEP2=SEP
      DIFF=DABS(SEP2-SEP1)
      IF(DIFF-0.001D0) 17,17,18
   17 SEP=CA2/CA1*SEP/DEXP(V)
      TYPE*,'SEP',SEP
      DIFF[illegible]=DABS(SEP-SEPF)
      IF(DIFFF.LE.0.001D0) GO TO 23
      IF(SEP-SEPF) 24,24,25
   24 D00=D00*(1.0D0+0.5D0**I)
      CALL CHR(DELTA,DWATER,PARK,D00,D)
      TYPE*,'C',C
      TYPE*,'D00',D00
      C=C/(RADIUS**AM)
      CONC=CA1
      CA2=CONC
      CALL TRANS2(ALPHO,CONST,RADIUS,PRESS,CONC,D00,D1,D2,D3,D4,
     1P1,P2,P3,P4,D01,Q,SEP,RATIO)
   58 SEP1=SEP
      CA3=(1.0D0-SEP1)*CA2
      CA2=CA3+(CA1-CA3)*DEXP(V)
      CONC=CA2
      CALL TRANS2(ALPHO,CONST,RADIUS,PRESS,CONC,D00,D1,D2,D3,D4,
     1P1,P2,P3,P4,D01,Q,SEP,RATIO)
      SEP2=SEP
      DIFF=DABS(SEP2-SEP1)
      IF(DIFF-0.001D0) 57,57,58
   57 SEP=CA2/CA1*SEP/DEXP(V)
      TYPE*,'SEP',SEP
      IF(SEP-SEPF) 24,24,26
   26 I=I+1
   25 D00=D00*(1.0D0-0.5D0**I)
      CALL CHR(DELTA,DWATER,PARK,D00,D)
      TYPE*,'C',C
```

```
      TYPE*,'D00',D00
      C=C/(RADIUS**AM)
      CONC=CA1
      CA2=CONC
      CALL TRANS2(ALPHO,CONST,RADIUS,PRESS,CONC,D00,D1,D2,D3,D4,
     1P1,P2,P3,P4,D01,Q,SEP,RATIO)
   68 SEP1=SEP
      CA3=(1.0D0-SEP1)*CA2
      CA2=CA3+(CA1-CA3)*DEXP(V)
      CONC=CA2
      CALL TRANS2(ALPHO,CONST,RADIUS,PRESS,CONC,D00,D1,D2,D3,D4,
     1P1,P2,P3,P4,D01,Q,SEP,RATIO)
      SEP2=SEP
      DIFF=DABS(SEP2-SEP1)
      IF(DIFF-0.001D0) 67,67,68
   67 SEP=CA2/CA1*SEP/DEXP(V)
      TYPE*,'SEP',SEP
      IF(SEP-SEPF) 22,22,25
   23 C=C*(RADIUS**AM)
      TYPE*,'SEP',SEP
      TYPE*,'D00',D00
      TYPE*,'PARK',PARK
      TYPE*,'C',C
      TYPE*,'RATIO',RATIO
   42 CONTINUE
   41 CONTINUE
      STOP
      END
```

```
FORTRAN IV-PLUS V3.0-3          15:25:55     23-OCT-82              PAGE 1
CALA9.FTN;22                   /TR:BLOCKS/WR

C
C
C                                    THIS PROGRAM IS CALA9.FTN, MODIFIED FOR MEOH
C
C
C
C      THIS PROGRAM IS USED TO FIND A ENERGY POTENTIAL FUNCTION
C      FROM A GIVEN SEPARATION DATA.IN THIS MODEL RADIUS IS (REAL RADIUS
C      - RADIUS OF WATER MOLECULE)
C         -------------------------------------------------------
C         ALPHA : INSERT 1.0D0
C         EH : INSERT 0.02D0
C         CONST : INSERT 0.3D0
C         RADIUS : PORE RADIUS
C         PRESS : OPERATING PRESSURE AS ATM D05
C         CONC : FEED CONCENTRATION AS GMOL/M3
C         Q : SOLUTE DIFFUSIVITY CM2/S*10.0D05
C         PWP : AS GR/HR
C         K,L,M,KK : INSERT 0,0,1,1
C         D01 : ASYMPTOTE OF HYPERBOLIC FUNCTION WHICH EXTENDS INTO INSIDE
C               THE PORE WALL
C         D00 : EFFECTIVE RADIUS OF SOLUTE
C         D4 : DISTANCE WITHIN WHICH SOLUTE IS IMMOBILE
C         F4P CALA9=CALA9,TRANS2,FDELT1,DERBE1,POTEN3,FRIC2
C         IN TRANS2 X1=(581.0D02/1.61D0)*Q/RADIUS**2/CONC AND X2=686.0D0
C         DONT FORGET TO INSERT Q WHEN TRANS2 IS CALLED
C         -------------------------------------------------------
          REAL*8 ALPH0,CONST,RATIO,SEP,RADIUS,PRESS,CONC,D00,D01,
         1D1,D2,D3,D4,P1,P2,P3,P4,Q,AM,C1
         2,CA1,CA2,CA3,SEP1,SEP2,APWP,PWP,TRANSN,TRANS,V,DIFF,DIFFF,SEPF
          INTEGER MMM,NNN
          COMMON X1,X2,EH,ALPHA(100),A,B,C,AA,K,L,M,KK,N,ROH0,ROH00,ROH1
          OPEN (UNIT=1,NAME='CALA9.IN',TYPE='OLD')
          OPEN (UNIT=2,NAME='CALA9.OUT',TYPE='NEW')
          READ(1,*) ALPH0,EH,CONST,PRESS,D01,ROH00
C      21 FORMAT(6D10.3)
          READ(1,*) K,L,M,KK,MMM,NNN
C      33 FORMAT(6I3)
          DO 41 J=1,MMM
          READ(1,*) RADIUS,PWP,PR
C      35 FORMAT(3D10.3)
          DO 42 IJ=1,NNN
          READ(1,*) D00,C1,Q,CA1,SEPF
C      34 FORMAT(5D10.3)
          D1=0.0D0
          D2=0.0D0
          D3=0.0D0
          D4=0.0D0
          P1=0.0D0
          P2=0.0D0
          P3=0.0D0
          P4=0.0D0
          AM=FLOAT(M)
          C=C1/(RADIUS**AM)
          APWP=PWP/13.2D-4/3600.0D0/32.03D0/(PRESS*1.0D-5*1.01325D02)*1.0D-3
C      ETOH  14 TRANSN=0.4951*(APWP*1.0D09+5.962)*1.0D-06
```

```
      14 TRANSN=0.920*(APWP*1.0D09+12.17)*1.0D-06
      16 TRANS=TRANSN*(Q/1.317D0)**0.6667D0
         V=APWP*PR/PWP*(PRESS*1.0D-5*1.01325D02)/31.25D0
         V=V/TRANS
         I=1
      22 I=I+1
         CONC=CA1
         CA2=CONC
         CALL TRANS2(ALPHO,CONST,RADIUS,PRESS,CONC,D00,D1,D2,D3,D4,
        1P1,P2,P3,P4,D01,Q,SEP,RATIO)
      18 SEP1=SEP
         CA3=(1.0D0-SEP1)*CA2
         CA2=CA3+(CA1-CA3)*DEXP(V)
         CONC=CA2
         CALL TRANS2(ALPHO,CONST,RADIUS,PRESS,CONC,D00,D1,D2,D3,D4,
        1P1,P2,P3,P4,D01,Q,SEP,RATIO)
         SEP2=SEP
         DIFF=DABS(SEP2-SEP1)
         IF(DIFF-0.001D0) 17,17,18
      17 SEP=CA2/CA1*SEP/DEXP(V)
         TYPE*,'SEP',SEP
         TYPE*,'RADIUS',RADIUS
         DIFFF=DABS(SEP-SEPF)
         IF(DIFFF.LE.0.001D0) GO TO 23
         IF(SEP-SEPF) 24,24,25
      24 RADIUS=RADIUS*(1.0D0-0.5D0**I)
         C=C1/(RADIUS**AM)
         TYPE*,'C1',C1
         CONC=CA1
         CA2=CONC
         CALL TRANS2(ALPHO,CONST,RADIUS,PRESS,CONC,D00,D1,D2,D3,D4,
        1P1,P2,P3,P4,D01,Q,SEP,RATIO)
      58 SEP1=SEP
         CA3=(1.0D0-SEP1)*CA2
         CA2=CA3+(CA1-CA3)*DEXP(V)
         CONC=CA2
         CALL TRANS2(ALPHO,CONST,RADIUS,PRESS,CONC,D00,D1,D2,D3,D4,
        1P1,P2,P3,P4,D01,Q,SEP,RATIO)
         SEP2=SEP
         DIFF=DABS(SEP2-SEP1)
         IF(DIFF-0.001D0) 57,57,58
      57 SEP=CA2/CA1*SEP/DEXP(V)
         TYPE*,'SEP',SEP
         TYPE*,'RADIUS',RADIUS
         IF(SEP-SEPF) 24,24,26
      26 I=I+1
      25 RADIUS=RADIUS*(1.0D0+0.5D0**I)
         C=C1/(RADIUS**AM)
         TYPE*,'C1',C1
         CONC=CA1
         CA2=CONC
         CALL TRANS2(ALPHO,CONST,RADIUS,PRESS,CONC,D00,D1,D2,D3,D4,
        1P1,P2,P3,P4,D01,Q,SEP,RATIO)
      68 SEP1=SEP
         CA3=(1.0D0-SEP1)*CA2
         CA2=CA3+(CA1-CA3)*DEXP(V)
```

```
      CONC=CA2
      CALL TRANS2(ALPHO,CONST,RADIUS,PRESS,CONC,D00,D1,D2,D3,D4,
     1P1,P2,P3,P4,D01,Q,SEP,RATIO)
      SEP2=SEP
      DIFF=DABS(SEP2-SEP1)
      IF(DIFF-0.001D0) 67,67,68
   67 SEP=CA2/CA1*SEP/DEXP(V)
      TYPE*,'SEP',SEP
      TYPE*,'RADIUS',RADIUS
      IF(SEP-SEPF) 22,22,25
   23 C=C*(RADIUS**AM)
      TYPE*,'SEP',SEP
      TYPE*,'RADIUS',RADIUS
      TYPE*,'C',C
      TYPE*,'RATIO',RATIO
   42 CONTINUE
   41 CONTINUE
      STOP
      END
```

```
FORTRAN IV-PLUS V3.0-3              15:24:41     23-OCT-82            PAGE 1
CALA11.FTN;30              /TR:BLOCKS/WR

C   THIS PROGRAM IS USED TO FIND A ENERGY POTENTIAL FUNCTION
C   FROM A GIVEN SEPARATION DATA.IN THIS MODEL RADIUS IS (REAL RADIUS
C   - RADIUS OF WATER MOLECULE)
C       --------------------------------------------------------
C
C
C
C                                                 CAL11MEOH IS CALA11 MODIFIED FOR
C
C
C
C       ALPHA : INSERT 1.0D0
C       EH : INSERT 0.02D0
C       CONST : INSERT 0.3D0
C       RADIUS : PORE RADIUS
C       PRESS : OPERATING PRESSURE AS ATM D05
C       CONC : FEED CONCENTRATION AS GMOL/M3
C       Q : SOLUTE DIFFUSIVITY CM2/S*10.0D05
C       PWP : AS GR/HR
C       K,L,M,KK : INSERT 0,0,3,1
C       D01 : ASYMPTOTE OF HYPERBOLIC FUNCTION WHICH EXTENDS INTO INSIDE
C             THE PORE WALL
C       D00 : EFFECTIVE RADIUS OF SOLUTE
C       D4 : DISTANCE WITHIN WHICH SOLUTE IS IMMOBILE
C       F4P CALA10=CALA10,TRANS2,FDELT1,DERBE1,POTEN3,FRIC2
C       IN TRANS2 X1=(581.0D02/1.61D0)*Q/RADIUS**2/CONC AND X2=686.0D0
C       DONT FORGET TO INSERT Q WHEN TRANS2 IS CALLED
C       ------------------------------------------------------------
        REAL*8 ALPHO,CONST,RATIO,SEP,RADIUS,PRESS,CONC,D00,D01,
      1D1,D2,D3,D4,P1,P2,P3,P4,Q,AM
      2,CA1,CA2,CA3,SEP1,SEP2,APWP,PWP,TRANSN,TRANS,V,DIEF,DIFFF,SEPF
        INTEGER MMM,NNN
        COMMON X1,X2,EH,ALPHA(100),A,B,C,AA,K,L,M,KK,N,ROHO,ROHOO,ROH1,Z
        OPEN (UNIT=1,NAME='CALA11.IN',TYPE='OLD')
        OPEN (UNIT=3,NAME='CALA11.OUT',TYPE='NEW')
        READ(1,*) ALPHO,EH,CONST,PRESS,D01,ROHOO
C   21  FORMAT(6D10.3)
        READ(1,*) K,L,M,KK,MMM,NNN
C   33  FORMAT(6I3)
        DO 41 J=1,MMM
        READ(1,*) D00,C,Q,CONC,SEPF,Z
C   34  FORMAT(6D10.3)
        DO 42 IJ=1,NNN
        READ(1,*) RADIUS,PWP
C   35  FORMAT(2D10.3)
        TYPE*,'RADIUS',RADIUS
        TYPE*,'C',C
        TYPE*,'M',M
        TYPE*,'PWP',PWP
        D1=0.0D0
        D2=0.0D0
        D3=0.0D0
        D4=0.0D0
        P1=0.0D0
        P2=0.0D0
        P3=0.0D0
```

```
FORTRAN IV-PLUS V3.0-3          15:24:41     23-OCT-82          PAGE 2
CALA11.FTN;30              /TR:BLOCKS/WR

      P4=0.0D0
      AM=FLOAT(M)
      TYPE*,'AM',AM
      C=C/RADIUS**M
      TYPE*,'C',C
      APWP=PWP/13.2D-4/3600.0D0/46.04D0/(PRESS*1.0D-5*1.01325D02)*1.0D-3
      TRANSN=0.4951*(APWP*1.0D09+5.965)*1.0D-06
   16 TRANS=TRANSN*(Q/0.4916D0)**0.6667D0
      V=APWP*(PRESS*1.0D-5*1.01325D02)/21.74D0
      V=V/TRANS
      TYPE*,'V',V
      CA1=CONC
      CA2=CONC
      CALL TRANS2(ALPHO,CONST,RADIUS,PRESS,CONC,D00,D1,D2,D3,D4,
     1P1,P2,P3,P4,D01,Q,SEP,RATIO)
   18 SEP1=SEP
      CA3=(1.0D0-SEP1)*CA2
      CA2=CA3+(CA1-CA3)*DEXP(V)
      CONC=CA2
      CALL TRANS2(ALPHO,CONST,RADIUS,PRESS,CONC,D00,D1,D2,D3,D4,
     1P1,P2,P3,P4,D01,Q,SEP,RATIO)
      SEP2=SEP
      DIFF=DABS(SEP2-SEP1)
      IF(DIFF-0.001D0) 17,17,18
   17 SEP=CA2/CA1*SEP/DEXP(V)
      C=C*(RADIUS**AM)
      TYPE*,'SEP',SEP
      TYPE*,'ROHOO',ROHOO
      TYPE*,'C',C
      TYPE*,'RATIO',RATIO
      SEP=100.0 * SEP
      RATIO=PWP*RATIO
      WRITE(3,999) IJ,SEP,PWP,RATIO
  999 FORMAT(1X,'NUMBER=',I2,'  SEPARATION=',F6.1, '  PWP=',F5.2,
     &'    RATIO=',F5.2)
   42 CONTINUE
   41 CONTINUE
      STOP 'CAL11MEOH'
      END
```

```
FORTRAN IV-PLUS V3.0-3                  15:30:05    23-OCT-82           PAGE 1
CHR.FTN;64              /TR:BLOCKS/WR

              SUBROUTINE CHR(DELTA,DWATER,PARK,D00,D)
        C
        C
        C
        C
        C                                            PART OF CALA SERIES
        C
        C
              EXTERNAL FCT12
              DIMENSION AUX(100)
              REAL*8 RES,SEKI,DFF
              INTEGER IER II
              COMMON X1,X2,EH,ALPHA(100),A,B,C,AA,K,L,M,KK,N,ROHO,ROHOO,ROH1
              SEKI=(DELTA-DWATER)*PARK-DELTA+D00
              II=1
                J=1
           82 II=II+1
                IF(II.GT.13) GO TO 83
              CALL QATR(D00,D,1.E-2,100,FCT12,RES,IER,AUX)
              DFF=DABS(RES-SEKI)
              IF(DFF.LE.0.001D0) GO TO 83
              IF(RES-SEKI) 84,84,85
        C       CHANGE SIGN HERE FOR LC K VALUES > OR < 1
           84 C=C*(1.0D0+0.5D0**II)
                J=J+1
                IF(J.GT.150) GO TO 83
              CALL QATR(D00,D,1.E-2,100,FCT12,RES,IER,AUX)
              IF(RES-SEKI) 84,84,86
           86 II=II+1
        C       CHANGE SIGN HERE FOR LC K VALUES > OR < 1
           85 C=C*(1.0D0-0.5D0**II)
                J=J+1
                IF(J.GT.150) GO TO 83
              CALL QATR(D00,D,1.E-2,100,FCT12,RES,IER,AUX)
              IF(RES-SEKI) 82,82,85
        C  83 TYPE *,'II',II,'  J',J,'  DFF',DFF
          83    TYPE*,'C',C
              RETURN
              END
```

```
FORTRAN IV-PLUS V3.0-3             15:33:49     23-OCT-82              PAGE 1
DAMDIS.SUB;231                /TR:BLOCKS/WR

0001            SUBROUTINE DAMDIS(XA2,NOFILM,ALFA,GAM,DAMBKD)
0002            IMPLICIT DOUBLE PRECISION(A-H,O-Z)
          C
0003            DIMENSION PORO(6)
          C   THIS IS FOR THE CELLULOSE-WATER CASE
          C   FOR THE CHANGE OF DAMBKD WITH CONCENTRATION
0004            DATA PORO/-9.09,-8.93,-8.74,-8.76,-8.04,-8.72/
0005            DDGION=-0.99
0006            DAMBKD=PORO(NOFILM)+DDGION
0007            DAMBKD=DEXP(DAMBKD)
          C
          C   THIS IS WHERE THE MODIFICATION IS INSERTED
          C     DAMBKD=((0.298*(XA2-4.6E-05))/1.3E-05)*((DAMBKD)/1.601E-04)
          C     DAMBKD=DAMBKD+0.00101*(XA2-7.36E-05)
          C     TEST=0.298*(XA2-7.36E-05)
          C     TYPE 9090, XA2
          C
          C
0008            DAMBKD=DAMBKD*((XA2/7.7E-05)**0.375)
          C9090 FORMAT ('+',T40,'XA2',D15.5)
          C DAMBKD IS RETURNED
          C
0009            RETURN
0010            END
```

```
FORTRAN IV-PLUS V3.0-3              15:29:46    23-OCT-82           PAGE 1
DAMKD.FTN;10                  /TR:BLOCKS/WR
             C   THIS PROGRAM GENERATES DAM/K(DELTA) VALUES FOR SALTS
             C   IN DILUTE MEDIA FROM THE DIFFUSIVITY RATIO(2/3 POWER)
             C   , THE EXPERIMENTAL VALUS FOR SEPERATION AND THE AVERAGE
             C   PURE SOLVENT RATE
             C
             C
             C
             C   THIS PROGRAM IS AN UNRELATED VERSION OF DIDAM.FTN
             C   IN ACCOUNT 100,007, DRMATSUURA
             C
             C
             C
0001                   REAL KSALT(6,15),VPERM(6),DAMKD(16,6,15),RTIO(15),KNACL(6)
0002                   REAL SALT(15),PALCP(6),SEPN(6)
0003                   DATA KNACL/8.323E-04,9.818E-04,9.000E-04,8.222E-04
                 &,9.104E-04,7.798E-04/
0004                   DATA PALCP/17.50,28.58,22.49,16.76,23.29,13.61/
0005                   DATA RTIO/1.000,1.022,1.094,1.113,1.145,1.160,1.182,1.221
                 &,1.0,1.220,1.242,1.0,1.0,1.0,1.0/
0006                   DATA SALT/'LICL','LIBR','NACL','NABR','NAI','KCL','KBR','KI',
                 &'RBCL','CSCL','CSBR','NIL','KF','NIL','NIL'/
             C
0007                   JJ=0
0008                   OPEN(UNIT=3,NAME='DAMKD.OUT')
0009                   WRITE(3,11) (I,I=1,6)
0010            11     FORMAT(1X,'ENTRY',2X,'SALT',2X,6('CELL # ',I2,4X)/)
             C
             C
             C   CALC THE VALUES OF KSALT
             C
             C
0011                   DO 100,I=1,6
0012                   DO 100 J=1,15
0013            100    KSALT(I,J)=RTIO(J)*KNACL(I)
             C
             C
             C   CALC THE PERMEATION VELOCITIES FOR EACH FILM
             C   THESE ARE CONSTANTS
             C
             C
0014                   DO 200 K=1,6
0015                   AREA=13.2
0016                   VPERM(K)=PALCP(K)/(3600*AREA*0.7885)
0017            200    CONTINUE
             C
             C
             C
             C         THE PROGRAM NOWREQUIRES "LIVE" INTERACTION WITH THE USER
             C
             C
0018            250    TYPE *,' GET YOUR DATA READY'
0019                   TYPE *,' TYPE IN THE SALTS NUMBER(SEE CODE SHEET)'
0020                   ACCEPT *,ISALT
0021                   IF(ISALT.EQ.0) GO TO 350
0022                   TYPE *,' TYPE IN THE SIX SEPERATIONS, FROM CELL1 - 6'
```

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FORTRAN IV-PLUS V3.0-3              15:29:46     23-OCT-82          PAGE 2
DAMKD.FTN;10                    /TR:BLOCKS/WR

0023                ACCEPT *,(SEPN(I),I=1,6)
          C
          CC
          C
          C         CALC THE DAM/K(DELTA)
          C
          C
0024                JJ=JJ+1
0025                DO 300 I=1,6
0026                DAMKD(JJ,I,ISALT)=VPERM(I)*(1-SEPN(I))/(SEPN(I))
                   &/EXP(VPERM(I)/KSALT(I,ISALT))
0027                TYPE *,'CELL',I,'DAMKD',DAMKD(JJ,I,ISALT)
0028         300    CONTINUE
0029                GO TO 250
          C
          C
          C
          C   THE CALC'N IS COMPLETE
          C   WRITE ON PAPER FOR POSTERITY
          C
          C
0030         350    DO 500 J=1,15
0031                DO 500 K=1,JJ
0032                IF(DAMKD(K,1,J).EQ.0.0) GO TO 500
0033                WRITE(3,101) K,SALT(J),(DAMKD(K,I,J),I=1,6)
0034         101    FORMAT(1X,I2,3X,A4,6(G13.4))
0035         500    CONTINUE
0036                CLOSE(UNIT=3,DISP='PRINT')
0037                STOP
0038                END
```

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FORTRAN IV-PLUS V3.0-3              15:33:21     23-OCT-82               PAGE 1
DERBE1.FTN;26              /TR:BLOCKS/WR

0001             SUBROUTINE DERBE1(ROH,ALPH,BET,FUNCG)
          C
          C
          C
          C                                     PART OF CALA SERIES
          C
0002             REAL*8 FUNCK,FUNCB,ALPH
0003             COMMON X1,X2,EH,ALPHA(100),A,B,C,AA,K,L,M,KK,N,ROH0,ROH00,ROH1
0004             CALL POTEN1(ROH,FUNCK)
0005             CALL FRIC1(ROH,FUNCB)
0006             IF(ALPH.GT.13)ALPH=DMIN1(13.0D00,DMAX1(DSQRT(ALPH),ALPH/1.0D05))
0007             FUNCG=-BET/ROH-X2/X1-(1.0D0-FUNCK)/X1*(DEXP(ALPH)/(1.0D0+FUNCB
                1/FUNCK*(DEXP(ALPH)-1.0D0))-1.0D0)+(FUNCB-1.0D0)*ALPH*DEXP(ALPH)
                2/(1.0D0+FUNCB/FUNCK*(DEXP(ALPH)-1.0D0))/X1
0008             RETURN
0009             END
```

```
FORTRAN IV-PLUS V3.0-3          15:33:04    23-OCT-82          PAGE 1
FCT12.FTN:22                 /TR:BLOCKS/WR

0001                FUNCTION FCT12(X)
          C
          C
          C
          C                                          PART OF CALA SERIES
          C
          C
0002                REAL*8 XX
0003                COMMON X1,X2,EH,ALPHA(100),A,B,C,AA,K,L,M,KK,N,ROH0,ROH00,ROH1
0004                XX=-C/X**(FLOAT(M))
0005                IF(XX+13.0D0) 21,21,22
0006             22 FCT12=DEXP(-XX)-1.0D0
0007                GO TO 23
0008             21 FCT12=DEXP(13.0D0)-1.0D0
0009             23 RETURN
0010                END
```

```
FORTRAN IV-PLUS V3.0-3          15:32:38     23-OCT-82          PAGE 1
FCT14.FTN;3                 /TR:BLOCKS/WR

              FUNCTION FCT14(X)
              REAL*8 XX
              COMMON C,CC
              XX=-C/X**3.0D0+CC/X**1.0D0
              IF(XX+10.0D0) 21,21,22
           22 FCT14=DEXP(-XX)-1.0D0
              GO TO 23
           21 FCT14=DEXP(10.0D0)-1.0D0
           23 RETURN
              END
```

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FORTRAN IV-PLUS V3.0-3          15:29:19     23-OCT-82            PAGE 1
FDELT1.FTN;11               /TR:BLOCKS/WR

          SUBROUTINE FDELT1(ALPH0,ALPH1)
C
C
C                                           PART OF CALA SERIES
C
C
          REAL*8 ROH,BETA(100),STEP,ALPH,BET,FUNCG,CA1,CA2,CA3,CA4,
         1CB1,CB2,CB3,CB4
          COMMON X1,X2,EH,ALPHA(100),A,B,C,AA,K,L,M,KK,N,ROH0,ROH00,ROH1
          STEP=1.0D0/EH+0.1D0
          N=IDINT(STEP)
          ALPHA(1)=ALPH0
          BETA(1)=0.0D0
          ROH=0.0D0
          DO 12 I=1,N
          ALPH=ALPHA(I)
          BET=BETA(I)
          CA1=EH*BET
          IF(I.GE.2) GO TO 14
          CB1=0.0D0
          GO TO 15
       14 CALL DERBE1(ROH,ALPH,BET,FUNCG)
          CB1=EH*FUNCG
       15 ROH=ROH+EH*0.5D0
          ALPH=ALPHA(I)+CA1*0.5D0
          BET=BETA(I)+CB1*0.5D0
          CA2=EH*BET
          CALL DERBE1(ROH,ALPH,BET,FUNCG)
          CB2=EH*FUNCG
          ALPH=ALPHA(I)+CA2*0.5D0
          BET=BETA(I)+CB2*0.5D0
          CA3=EH*BET
          CALL DERBE1(ROH,ALPH,BET,FUNCG)
          CB3=EH*FUNCG
          ROH=ROH+EH*0.5D0
          ALPH=ALPHA(I)+CA3
          BET=BETA(I)+CB3
          CA4=EH*BET
          CALL DERBE1(ROH,ALPH,BET,FUNCG)
          CB4=EH*FUNCG
          ALPHA(I+1)=ALPHA(I)+(CA1+2.0D0*CA2+
         12.0D0*CA3+CA4)/6.0D0
          BETA(I+1)=BETA(I)+(CB1+2.0D0*CB2+2.0D0*CB3+CB4)/6.0D0
       12 CONTINUE
          ALPH1=ALPHA(N+1)
          RETURN
          END
```

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FORTRAN IV-PLUS V3.0-3                 15:32:09     23-OCT-82              PAGE 1
FRIC2.FTN;17                    /TR:BLOCKS/WR

                SUBROUTINE FRIC1(ROH,FUNCB)
      C
      C
      C                                                   PART OF CALA SERIES
      C
      C
                REAL*8 FUNC,RAMDA
                COMMON X1,X2,EH,ALPHA(100),A,B,C,AA,K,L,M,KK,N,ROH0,ROH00,ROH1
                RAMDA=1.0D0-ROH0/ROH1
                IF(RAMDA-0.2D0) 12,12,13
             13 FUNCB=44.57D0-416.2D0*RAMDA+934.9D0*RAMDA**2+302.4D0*
               1RAMDA**3
                GO TO 14
             12   FUNCB=1.0
             14 RETURN
                END
```

```
FORTRAN IV-PLUS V3.0-3          15:13:52     23-OCT-82          PAGE 1
KIMWATER.FTN;7               /TR:BLOCKS/WR

          C
          C
          C          KIMURA-SOURIRAJAN ANALISIS FOR REVERSE OSMOSIS
          C          ==============================================
          C
          C          THIS PROGRAM USES THE EXPERIMENTAL DATA FROM REVERSE OSMOSIS
          C  AND RELEVENT PHYSIO-CHEMICAL DATA OF THE SOLUTE TO CALCULATE THE SOLUTE
          C  TRANSPORT PARAMETER (DAM/KD),THE MASS TRANSFER COEFFICIENT (K),THE PURE
          C  WATER PERMEABILITY CONSTANT (A) AND OTHER MASS TRANSFER PARAMETERS.
          C
          C
          C
          C
0001                 IMPLICIT DOUBLE PRECISION (A-H,O-Z)
0002               DIMENSION A(50),ERROR(5),AVDEN1(50),
                  1TRANSC(50),XA1(50),XA2(50),XA3(50),
                  2DENSML(100),DAMBKD(50),FRACML(100),OSMPRS(100),
                  3PAIXA2(50),PAIXA3(50),YNB(50),YNA(50),
                  4REYNO(50),SCHNO(50),SHERNO(50),PARAMT(50),
                  5VISCOS(100),Q(50),SSS(50),DIFFSN(100)
0003               DIMENSION AVETRA(50),AVDE22(50),PRESSS(50),
                  1AVDE33(50),FEEDMM(50),SEPRTT(50),PROD(50)
                  &,RTIO(50),DAMKD(50),CORRK(6),AVGA(6)
0004                DIMENSION FFABS(50),NRUN(50),ICOUNT(50)
          C
          C    A(50).....................PURE SOLVENT FLUX (GMOLE/SQ.CM.*SEC.)
          C    AREA......................MEMBRANE AREA (SQ.CM.)
          C    AVDEN1(50)................MOLAR DENSITY OF FEED SOLUTION (GMOLE/CC)
          C    AVDEN2(50)................MOLAR DEN. OF BOUNDARY SOL'N (GMOLE/CC)
          C    AVDEN3(50)................MOLAR DEN. OF PRODUCT SOL'N (GMOLE/CC)
          C    AVDENX(50)................DUMMY PARAMETER FOR MOLAR DENSITY
          C    B1,B2,B3..................DUMMY PARAMETERS FOR LINEAR INTERPOLATION
          C    C,C1,C2,C3................DUMMY PARAMETERS FOR SOLUTE-SOLVENT FLUX
          C    DAMBKD(50)................SOLUTE TRANSPORT PARAMETER
          C    DENSML(50)................MOLAR DENSITY
          C    DIA.......................DIAMETER OF MEMBRANE
          C    DIFFCO....................DIFFUSION COEFFICIENT
          C    DIFFSN(100)...............DIFFUSIVITY OF SOLUTE
          C    FDPPM.....................FEED CONCENTRATION (PPM)
          C    FEEML.....................FEED MOLALITY
          C    FEEDRT....................FEED RATE (CC/MIN)
          C    FRACML(100)...............CONCENTRATION (MOLALITY)
          C    NRUN(50)..................RUN NUMBER
          C    OSMPRS(100)...............OSMOTIC PRESSURE DATA
          C    PARAMT(50)................A TRANSPORT PARAMETER
          C    PIAXA2(50)................OSMOTIC PRESSURE OF BOUNDARY SOLUTION
          C    PIAXA3(50)................OSMOTIC PRESSURE OF PRODUCT SOLUTION
          C    PRESS.....................OPERATING PRESSURE (ATM)
          C    PWP.......................PURE SOLVENT PERMEATION RATE (G/H)
          C    Q(50).....................FLOW RATE PARAMETER
          C    REYNO(50).................REYNOLD'S NUMBER
          C    SCHNO(50).................TRANSPORT PARAMETER
          C    SEPRTN....................SEPARATION
          C    SHERNO(50)................SHERWOOD'S NUMBER
          C    SOL1,SOL2,SOL3............NAME(S) OF SOLUTE(S)
          C    SSS(50)...................DUMMY PARAMETER
          C    TRANSC(50)................MASS TRANSFER (K)
```

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FORTRAN IV-PLUS V3.0-3                  15:13:52     23-OCT-82               PAGE 2
KIMWATER.FTN;7                  /TR:BLOCKS/WR

              C     V...........................KINEMATIC VISCOSITY OF FEED SOLUTION
              C     VISCOS(100).................KINEMATIC VISCOSITY DATA
              C     WEITM.......................MOLECULAR WEIGHT OF SOLUTE
              C     XA1.........................MOLE FRACTION SOLUTE IN FEED SOL'N
              C     XA2.........................MOLE FRACTION SOLUTE IN BOUNDARY SOL'N
              C     XA3.........................MOLE FRACTION SOLUTE IN PRODUCT SOL'N
              C     X1,X2,X3,X4.................DUMMY PARAMETERS FOR K CALCULATION
              C     XXX.........................DUMMY PARAMETER FOR DENSITY CALCULATION
              C     YNA(50).....................SOLUTE FLUX (GMOLE/SQ.CM*SEC)
              C     YNB(50).....................SOLVENT FLUX (GMOLE/SQ.CM.*SEC)
              C
              C           THESE CORRELATED MASS TRANSFER COEFF'TS ARE AVERAGED(250PSI)
              C  SREIES A       DATA CORRK/9.774D-04,3.319D-04,2.872D-04,7.178D-04,
              C      &9.221D-04,2.504D-04/
0005                    DATA CORRK/4.164D-04,3.380D-04,2.9204D-04,1.2742D-04,
                     &2.9401D-04,2.5785D-04/
              C   THESE ARE AVERAGE 'A' VALUES
              C   SERIES A      DATA AVGA/84.25D-08,20.58D-08,16.17D-08,58.64D-08,78.80D-
              C      &12.53D-08/
              C           DATAAVGA/28.908D-08,21.179D-08,16.65D-08,4.054D-08,16.8389D-08
              C      &,13.272D-08/
              C
              C   ERRROR MESSAGES
0006                    DATA ERROR/' XA3  ','PAIXA2','DENSTY',' DIFF ','K.VISC'/
              C
              C
0007                    DO 2222 I=1,10
0008            2222    TYPE *,'WARNING!!!!!!! FOR WATER ONLY!!!!!!!'
              C
0009                    OPEN (UNIT=1,NAME='SOLUTION.DAT',TYPE='OLD')
0010                    OPEN (UNIT=2,NAME='EXPRMNTL.DAT',TYPE='OLD')
0011                    OPEN (UNIT=3,NAME='KIMWATER.OUT',TYPE='NEW')
              C
              C         READ THE SOLUTE DATA
0012                  READ(1,99) IMAX,WEITM,SOL1,SOL2,SOL3
0013              99  FORMAT(I2,3X,D10.4,9X,3A4)
0014                  READ(1,*)(FRACML(I),DENSML(I),OSMPPS(I),VISCOS(I),DIFFSN(I),
                     &I=1,IMAX)
              C
              C
              C
              C   ADJUST THE DIFFUSION COEFFICIENT
              C
              C
              C
              C
              C
0015                    DO 321 I=1,IMAX
0016             321    DIFFSN(I)=DIFFSN(I)*(1.000D-05)
              C
              C
              C         READ THE EXPERIMENTAL DATA
              C
0017               9  READ(2,*) NOFILM,MAXNU
0018               1  NU=1
0019                    TYPE *,'FILM # ',NOFILM
```

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FORTRAN IV-PLUS V3.0-3          15:13:52    23-OCT-82          PAGE 3
KIMWATER.FTN;7              /TR:BLOCKS/WR

              WRITE(3,105) NOFILM,SOL1,SOL2,SOL3
       105    FORMAT(1H1,'FILM NO.',5X,I3,10X,3A4///)
              IC=1
         2    READ(2,*) NORUN,PWP,PRODRT,SEPRTN,PRESS,FEEDML,XA1(NO),FEEDRT
              AREA=13.2D0
                TYPE *,'XA1',XA1(NO)
              NRUN(NO)=NORUN
C
C
C   IF NORUN=0 STOP
C
                IF(NORUN.LE.0) GO TO 7777
              PRESSS(NO)=PRESS
              FEEDMM(NO)=FEEDML
              SEPRTT(NO)=SEPRTN
C
C CALCULATE SOLVENT FLUX AND SOLUTE FLUX
C
       999    PRODML=(1.0D0-SEPRTN)*FEEDML
                XA3(NO)=XA1(NO)*(1-SEPRTN)
                YNB(NO)=PRODRT*(1-XA3(NO))/(((1-XA3(NO))*18.02+XA3(NO)*WEITM)
           &*3600*AREA)
                YNA(NO)=YNB(NO)*XA3(NO)/(1-XA3(NO))
C
C USING SOLUTION DATA, CALCULATE THE OSMOTIC PRESSURE OF PRODUCT FROM
C ITS MOLAL CONCENTRATION,BY LINEAR INTERPOLATION.
C
                CALL LNTERP(XA3(NO),PAIXA3(NO),FRACML,OSMPRS,IMAX,MESS)
                IER=1
                IF(MESS.EQ.0) GO TO 4444
C
C CALCULATE "A" AND OSMOTIC PRESSURE OF XA2
C
        60    A(NO)=PWP/(3600*AREA*18.02*PRESS)
              PAIXA2(NO)=PRESS+PAIXA3(NO)-YNB(NO)/A(NO)
C
C USING SOLUTION DATA, CALCULATE MOLAL CONCENTRATION OF XA2 FROM
C ITS OSMOTIC PRESSURE, BY LINEAR INTERPOLATION.
C
                CALL LNTERP(PAIXA2(NO),XA2(NO),OSMPRS,FRACML,IMAX,MESS)
                IER=2
                IF(MESS.EQ.0) GO TO 4444
C
C USING THE SOLUTION DATA,CALCULATE THE MOLAR DENSITY OF XA1,XA2&XA3
C BY LINEAR INTERPOLATION.
C
                CALL LNTERP(XA1(NO),AVDEN1(NO),FRACML,DENSML,IMAX,MESS)
                IER=3
                IF(MESS.EQ.0) GO TO 4444
                CALL LNTERP(XA2(NO),AVDEN2,FRACML,DENSML,IMAX,MESS)

                IF(MESS.EQ.0) GO TO 4444
                CALL LNTERP(XA3(NO),AVDEN3,FRACML,DENSML,IMAX,MESS)
                IF(MESS.EQ.0) GO TO 4444
C CALCULATE DAM/KD
C
```

```
           DAMBKD(NO)=YNB(NO)*XA3(NO)/((AVDEN2*XA2(NO)-AVDEN3*XA3(NO))
         &*(1-XA3(NO)))
      C
            AVDE33(NO)=AVDEN3
      C CALCULATE MASS TRANSFER (K)
      C
           X1=XA1(NO)-XA3(NO)
           X2=XA2(NO)-XA3(NO)
           X4=X2/X1
           IF(X4)777,777,778
       777 TRANSC(NO)=-0.0D0
           GO TO 3333
       778 TRANSC(NO)=(YNA(NO)+YNB(NO))/(AVDEN1(NO)*DLOG(X4))
      C
      C USING SOLUTION DATA, CALCULATE THE DIFFUSIVITY OF THE SOLUTE FROM THE
      C MOLAL CONCENTRATION OF THE FEED SOLUTION, BY LINFAP INTERPELATION.
      C
      C
            CALL LNTERP(XA1(NO),DIFFCO,FRACML,DIFFSN,IMAX,MESS)
            IER=4
            IF(MESS.EQ.0) GO TO 4444
      C
      C  THE CORRECTION FOR MASS TRANSFER COEFF REQUIRES THE
      C   DIFFUSIVITY THAT WAS USED TO DETERMINF IT.
      C USING SOLUTION DATA, CALCULATE THE KINEM. VISC. OF THE FEEP SOLUTION
      C FROM ITS MOLAL CONCENTRATION, BY LINEAR INTERPOLATION.
      C
            CALL LNTERP(XA1(NO),V,FRACML,VISCOS,IMAX,MESS)
            IER=5
            IF(MESS.EQ.0) GO TO 4444
      C
      C
      C  DETERMINE THE RATIO OF DIFF. AND VISCO. FOR SCMIDT & SHERWOOD
      C  FOR MASS TRANSFER
      C
      C
      C
      C
           REYNO(NO)=Q(NO)/(1.43D0*V)
           IF(DIFFCO)9999,9999,199
       199 SCHNO(NO)=V/DIFFCO
           SSS(NO)=SCHNO(NO)**0.33D0
           DIA=DSQRT(4.0D0*AREA/3.141593D0)
           SHERNO(NO)=(TRANSC(NO)*DIA      )/DIFFCO
           PARAMT(NO)=SHERNO(NO)/SSS(NO)
           GO TO 1999
      9999 SCHNO(NO)=0.0D0
           SSS(NO)=0.0D0
           SHERNO(NO)=0.0D0
           PARAMT(NO)=0.0D0
      1999 IF(IC-1) 200,200,220
       200 WRITE(3,210)
       210 FORMAT(/1X,'RUNNO',T11,'PRESS',T25,'FEEDML',T36,'FEEDRT',
          1T50,'PSP',T63,'PRODRT',T75,'SEPRTN',T88,'DIFFCO',T101,
          2'KINE.VISC',T113,'MOLDENST2',T124,'MOLDENST3'//)
       220 WRITE(3,230) NORUN,PRESS,FEEDML,FEEDRT,PWP,PRODRT,SEPRTN,DIFFCO,
          1V,AVDEN2,AVDEN3
       230 FORMAT(1X,I3,6F13.5,D12.5,F13.5,2F12.5)
```

```
      IC=2
  235 IF(MAXNO-NO)240,245,240
  240 NO=NO+1
      GO TO 2
  245 NOFINL=NO
  250 WRITE(3,260)
  260 FORMAT(///1X,'RUNNO',T12,'DAM',T22,'MASSTRANS',T38,'A',
     1T51,'XA1',T63,'XA2',T77,'XA3',T88,'PAIXA2',T102,'PAIXA3',
     2T116,'NA',T128,'NB'//)
      DO 290  NO=1,NOFINL
  270 WRITE(3,280) NRUN(NO),DAMBKD(NO),TRANSC(NO),A(NO),XA1(NO),XA2(NO),
     1XA3(NO),PAIXA2(NO),PAIXA3(NO),YNA(NO),YNB(NO)
  280 FORMAT(1X,I3,8D13.4,2D12.4)
  290 CONTINUE
  300 WRITE(3,310)
  310 FORMAT(///1X,'RUNNO',T11,'SHERWOOD',T24,'REYNOLDS',T37,
     1'SCHMIDT',T51,'SCH**0.33',T63,'NSH/NSC',T78,'MOLDEN1',T92,'Q',
     2 T106,'AREA'//)
      DO 340 NO=1,NOFINL
      WRITE(3,330) NRUN(NO),SHERNO(NO),REYNO(NO),SCHNO(NO),SSS(NO),
     1PARAMT(NO),AVDEN1(NO),Q(NO),AREA
  330 FORMAT(2X,I3,9F13.4)
        GO TO 340
 4444   WRITE(3,26) NRUN(NO),ERROR(IER)
   26   FORMAT(2X,I3,'VALUE OF ',A6,' HAS EXCEEDED THE TABLE DATA')
        GO TO 340
 3333   WRITE(3,27) NRUN(NO)
   27   FORMAT(2X,I3,' THERE IS SOMETHING WRONG WITH XA2,XA3,XA1')
  340 CONTINUE
C
        GO TO 9
C
C
C***********************************************************
C***********************************************************
C***********************************************************
C***********************************************************
C***********************************************************
C***********************************************************
C
 7777   CONTINUE
        STOP 'KIMWATER'
        END
```

```
FORTRAN IV-PLUS V3.0-3          15:23:25    23-OCT-82           PAGE 1
OHYA.FTN;126                 /TR:BLOCKS/WR

        IMPLICIT DOUBLE PRECISION(A-H,O-Z)
        DIMENSION DENSML(100),FRACML(100),OSMPRS(100),INDEX(2)
      OPEN (UNIT=3,NAME='CALC.RES',TYPE='NEW')
C       OPEN(UNIT=4,NAME='PARAM.DAT',TYPE='OLD')
C 888   READ(4,*) DAMBKD,TRANSC,A
  888   TYPE *,'TYPE IN DAM/KD,K'
        ACCEPT *,DAMBKD,TRANSC
        A=1.032E-06
        IF(DAMBKD.EQ.0) GO TO 9999
        DAMBKD=DAMBKD*1.0E-06
        TRANSC=TRANSC*1.0E-04
        OPEN(UNIT=1,NAME='SOLUTE.DAT',TYPE='OLD')
        WRITE(3,100)
  100   FORMAT(8X,'FILM',3X,'FEED',9X,'SEPN',8X,'PROD',9X,'XA2',10X,
     &'RESF',9X,'RESP',8X,'SEPOLD',8X,'PROLD')
      READ(1,99) IMAX,WEITM
  99  FORMAT(I2,3X,D10.4)
      READ(1,33)(FRACML(I),I=1,IMAX)
      READ(1,33)(OSMPRS(I),I=1,IMAX)
      READ(1,33)(DENSML(I),I=1,IMAX)
  33  FORMAT(7D10.4)
        CLOSE(UNIT=1)
        SSR1=0
        SSR2=0
        SSRHYB=0
        OPEN(UNIT=2,NAME='RO.DAT',TYPE='OLD')
   39 READ(2,*,END=5000) NOFILM,PRESS,FEEDML,FOLD,PROLD
        AREA=26.8
      XA1=FEEDML/(FEEDML+55.506D0)
      SIGMA=TRANSC/DAMBKD
 320  EB=0.01D0
      J=1
      E2=1.0D0+EB
 330  E31=0.05
      Z=1.0D0
      ZZ=1.0D0
 340  EE=(E2-E31)/(1.0D0-E31)
        IF(EE.LE.0) EE=ABS(EE)
      EEE=Z+SIGMA*DLOG(EE)
      E32=ZZ*E2/EEE
      S=E31-E32
      SA=DABS(S)
      BB=E32/500.0D0
      IF(SA-BB) 360,360,350
  350   E3DER=1+ZZ*E2/(Z+SIGMA/(EE)*(E2-1)/(1-E31)**2)
        E31NEW=E31-S/E3DER
        E31=E31NEW
       -IF(E31.GT.0.99) E31=0.9
        IF(E31.LT.0) E31=0
C350  E31=E32
        E32=E31
      XA2=E2*XA1
      XA3=E31*XA1
C**************************************************************
C
        CALL LNTERP(XA1,AVDEN1,FRACML,DENSML,IMAX,ERR1)
```

```
FORTRAN IV-PLUS V3.0-3          15:23:25     23-OCT-82             PAGE 2
OHYA.FTN;126              /TR:BLOCKS/WR

        CALL LNTERP(XA2,AVDEN2,FRACML,DENSML,IMAX,ERR2)
        CALL LNTERP(XA3,AVDEN3,FRACML,DENSML,IMAX,ERR3)
        LINERR=100
        IF(ERR1.EQ.0.OR.ERR2.EQ.0.OR.ERR3.EQ.0) TYPE*,'ERROR ',LINERR
C
C************************************************************
      Z=AVDEN3/AVDEN1
      ZZ=AVDEN2/AVDEN1
      GO TO 340
 360  XA2=E2*XA1
      XA3=E32*XA1
      X3=(1.0D0-XA3)/XA3
      ENB=DAMBKD*X3*(AVDEN2*XA2-AVDEN3*XA3)
C*************************************************************
C
        CALL LNTERP(XA2,PAIXA2,FRACML,OSMPRS,IMAX,ERR1)
        CALL LNTERP(XA3,PAIXA3,FRACML,OSMPRS,IMAX,ERR2)
        LINERR=101
        IF(ERR1.EQ.0.OR.ERR2.EQ.0) TYPE*,'ERROR AT LINERR=',LINERR
C
C*************************************************************
      ENBP=A*(PRESS-PAIXA2+PAIXA3)
      SSA=ENBP-ENB
      SSAA=DABS(SSA)
      BBB=ENBP/500.0D0
      IF(SSAA-BBB) 2000,2000,500
C500    ENBDER=A*(PAIXA2-PAIXA3)/(XA2-XA3)-DAMBKD*X3*AVDEN2
C       XA2NEW=XA2-SSA/ENBDER
C       E2=XA2NEW/XA1
C       GO TO 330
 500  IF(SSA) 600,2000,700
 600  INDEX(J)=1
      GO TO 800
 700  INDEX(J)=-1
 800  IF(J-1) 900,900,850
 850  IF(INDEX(2)-INDEX(1)) 1000,900,1000
 900  E2=E2+EB
      J=2
      GO TO 330
 1000  E2=E2-EB
      EB=EB*0.1D0
      E2=E2+EB
      GO TO 330
2000  Y1=XA1/(1.0D0-XA1)
      Y3=XA3/(1.0D0-XA3)
      SEPRTN=1.0D0-Y3/Y1
      Y4=FEEDML*WEITM*(1.0D0-SEPRTN)
      Y5=1.0D0+1000.0D0/Y4
      Y6=1.0D0-1.0D0/Y5
      PRODRT=ENB*AREA*18.02*3600./Y6
 2602   FORMAT(5X,I5,8D13.4)
C
C       COMPUTE THE RESIDUALS
        RES1=SEPRTN-FOLD
        RES2=PRODRT-PROLD
        SSR1=SSR1+(RES1)**2
```

```
                SSR2=SSR2+(RES2)**2
                SSRHYB=SSRHYB+(RES1*RES2)
        C
        C       WRITE THESE OUT
                WRITE(3,2602)NOFILM,FEEDML,SEPRTN,PRODRT,XA2,RES1,RES2,FOLD,
             &PROLD
        C
                TYPE *,'SSRHYB',SSRHYB
         2998 GO TO 39
         5000   DSPRN=SSR1*SSR2-SSRHYB**2
                WRITE(3,2699) SSR1,SSR2,DSPRN,DAMBKD,TRANSC,A
         2699   FORMAT(///,5X,'SSR1',9X,'SSR2',8X,'DSPRSN',10X,'DAM',
             &8X,'TRANSC',8X,'A',/,1X,6D13.4,//)
                TYPE 2699,SSR1,SSR2,DSPRN,DAMBKD,TRANSC,A
                CLOSE(UNIT=2)
                GO TO 888
         9999   STOP 'OUTPUT IN CALC.RES'
        6000  WRITE(3,7000)
        7000  FORMAT(1H0,2X,'OVER FLOW')
                TYPE *,'OVER FLOW FILM NO.',NOFILM
              GO TO 39
              END
```

```
FORTRAN IV-PLUS V3.0-3          15:26:52     23-OCT-82               PAGE 1
POTENBF.FTN;41              /TR:BLOCKS/WR

C
C
C
C                                                    PART OF THE CALA SERIES
C
C
      SUBROUTINE POTEN1(ROH,FUNCK)
C
      REAL*8 FUNC,FUNCK
      COMMON X1,X2,EH,ALPHA(100),A,B,C,AA,K,L,M,KK,N,ROHO,ROHOO,
     1ROH1
      IF(ROH.EQ.ROH1) GO TO 5
      AM=FLOAT(M)
      FUNC=-C/(ROH1-ROH)**AM
      IF(FUNC.LT.-10.0) FUNC=-10.0
      IF(FUNC.GT.13.0) FUNC=13.0
      FUNCK=DEXP(-FUNC)
      RETURN
    5 FUNCK=DEXP(-10.0D0)
      RETURN
      END
```

```
FORTRAN IV-PLUS V3.0-3           15:31:30    23-OCT-82          PAGE 1
QATR.FTN;4                  /TR:BLOCKS/WR
C
C
C
C                                         PART OF CALA SERIES
C
C
C
      SUBROUTINE QATR(XL,XU,EPS,NDIM,FCT,Y,IER,AUX)
C
C
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DIMENSION AUX(1)
         COMMON X1,X2,EH,ALPHA(100),A,B,C,AA,K,L,M,KK,N,ROH0,ROH00,ROH1
C
C     PREPARATIONS OF ROMBERG-LOOP
      AUX(1)=.5*(FCT(XL)+FCT(XU))
      H=XU-HL
      IF(NDIM-1)8,8,1
    1 IF(H)2,10,2
C
C     NDIM IS GREATER THAN 1 AND H IS NOT EQUAL TO 0.
    2 HH=H
      E=EPS/ABS(H)
      DELT2=0.
      P=1.
      JJ=1
      DO 7 I=2,NDIM
      Y=AUX(1)
      DELT1=DELT2
      HD=HH
      HH=.5*HH
      P=.5*P
      X=XL+HH
      SM=0.
      DO 3 J=1,JJ
      SM=SM+FCT(X)
    3 X=X+HD
      AUX(I)=.5*AUX(I-1)+P*SM
C     A NEW APPROXIMATION OF INTEGRAL VALUE IS COMPUTED BY MEANS OF
C     TRAPEZOIDAL RULE.
C
C     START OF ROMBERGS EXTRAPORATION METHOD.
      Q=1.
      JI=I-1
      DO 4 J=1,JI
      II=I-J
      Q=Q+Q
      Q=Q+Q
    4 AUX(II)=AUX(II+1)+(AUX(II+1)-AUX(II))/(Q-1.)
C     END OF ROMBERG-STEP
C
      DELT2=ABS(Y-AUX(1))
      IF(I-5)7,5,5
    5 IF(DELT2-E)10,10,6
    6 IF(DELT2-DELT1)7,11,11
    7 JJ=JJ+JJ
```

```
    8 IER=2
    9 Y=H*AUX(1)
      RETURN
   10 IER=0
      GO TO 9
   11 IER=1
      Y=H*Y
      RETURN
      END
```

```
FORTRAN IV-PLUS V3.0-3         15:28:42     23-OCT-82          PAGE 1
QATR2.FTN;3                 /TR:BLOCKS/WR
          C
          C
          C                                                       PART OF CALA SERIES
          C
0001            SUBROUTINE QATR2(XL,XU,EPS,NDIM,FCT,Y,IER,AUX)
          C
          C
0002            DIMENSION AUX(1)
0003                COMMON X1,X2,EH,ALPHA(100),A,B,C,AA,K,L,M,KK,N,ROHO,ROHOO,ROH1
               1,Z,CC
          C
          C     PREPARATIONS OF ROMBERG-LOOP
0004            AUX(1)=.5*(FCT(XL)+FCT(XU))
0005            H=XU-XL
0006            IF(NDIM-1)8,8,1
0007          1 IF(H)2,10,2
          C
          C     NDIM IS GREATER THAN 1 AND H IS NOT EQUAL TO 0.
0008          2 HH=H
0009            E=EPS/ABS(H)
0010            DELT2=0.
0011            P=1.
0012            JJ=1
0013            DO 7 I=2,NDIM
0014            Y=AUX(1)
0015            DELT1=DELT2
0016            HD=HH
0017            HH=.5*HH
0018            P=.5*P
0019            X=XL+HH
0020            SM=0.
0021            DO 3 J=1,JJ
0022            SM=SM+FCT(X)
0023          3 X=X+HD
0024            AUX(I)=.5*AUX(I-1)+P*SM
          C     A NEW APPROXIMATION OF INTEGRAL VALUE IS COMPUTED BY MEANS OF
          C     TRAPEZOIDAL RULE.
          C
          C     START OF ROMBERGS EXTRAPORATION METHOD.
0025            Q=1.
0026            JI=I-1
0027            DO 4 J=1,JI
0028            II=I-J
0029            Q=Q+Q
0030            Q=Q+Q
0031          4 AUX(II)=AUX(II+1)+(AUX(II+1)-AUX(II))/(Q-1.)
          C     END OF ROMBERG-STEP
          C
0032            DELT2=ABS(Y-AUX(1))
0033            IF(I-5)7,5,5
0034          5 IF(DELT2-E)10,10,6
0035          6 IF(DELT2-DELT1)7,11,11
0036          7 JJ=JJ+JJ
0037          8 IER=2
0038          9 Y=H*AUX(1)
0039            RETURN
```

```
FORTRAN IV-PLUS V3.0-3            15:28:42    23-OCT-82           PAGE 2
QATR2.FTN;3                  /TR:BLOCKS/WR

0040         10 IER=0
0041            GO TO 9
0042         11 IER=1
0043            Y=H*Y
0044            RETURN
0045            END
```

```
FORTRAN IV-PLUS V3.0-3            15:27:35     23-OCT-82           PAGE 1
SEPN.FTN;112              /TR:BLOCKS/WR

      C   THIS PROGRAM BACK CALCS THE SEP'N FOR THE MEOH SYSTEM GIVEN
      C   THE DDG/RT FOR EACH SALT AND THE POROSITY(PORO=LN(C*))
      C
      C
      C
      C
      C
      C
      C
              REAL KSALT(6,15),VPERM(6),DAMKD(6,15),RTIO(15),KNACL(6)
              REAL SALT(15),PALCP(6),SEPN(6,15)
              REAL PORD(6),DDGRT(15)
      C
              DATA PALCP/16.41,50.38,45.53,30.75,36.30,31.79/
              DATA KNACL/5.16E-04,14.67E-04,13.37E-04,9.43E-04,
         &10.91E-04,9.71E-04/
              DATA RTIO/.8416,.8555,.8555,.8586,1.1319,.9918,.8555,
         &1.0886,1.1389,1.0684,1.0684,1.1002,1.0,1.0,1.0/
              DATA SALT/'MGCL','CACL','SRCL','BACL','NHCL','LNO3','SNO3',
         &'CLO3','CLO4','NO2','NO3','BRO3','NACL','NIL','NIL'/
              DATA DDGRT/-6.34,-5.72,-6.01,-6.02,-1.90,-2.78,-4.01,-1.20,
         &-2.12,-2.47,-1.85,-1.84,-2.14,1.0,1.0/
              DATA PORO/-7.71,-6.39,-6.45,-7.27,-7.03,-7.31/
              OPEN(UNIT=3,NAME='SEPN.OUT')
      C
      C
      C   CALC THE VALUES OF KSALT
      C
      C
              DO 100,I=1,6
              DO 100 J=1,15
          100     KSALT(I,J)=RTIO(J)*KNACL(I)
      C
      C
      C   CALC THE PERMEATION VELOCITIES FOR EACH FILM
      C   THESE ARE CONSTANTS
      C
      C
              DO 200 K=1,6
              AREA=13.2
              VPERM(K)=PALCP(K)/(3600*AREA*0.7866)
          200     CONTINUE
      C
      C
      C
      C
      C   CALC THE DAM/KD AND SEP'N FOR EACH CASE
      C
              DO 500 I=1,6
              DO 500 J=1,15
              DAMKD(I,J)=EXP(PURO(I)+DDGPT(J))
              SEP=DAMKD(I,J)/(VPERM(I)/EXP(VPERM(I)/KSALT(I,J)))
              SEPN(I,J)=1/(SEP+1)
          500     CONTINUE
      C   BEGIN WRITING
      C
              WRITE(3,1000) (I,I=1,6)
```

```
FORTRAN IV-PLUS V3.0-3            15:27:35     23-OCT-82            PAGE 2
SEPN.FTN;112                /TR:BLOCKS/WR

0025      1000    FORMAT(35X,'VALUES OF SEPARATION',//,10X,6('CELL # '
              &,I2,6X)/)
0026              DO 1075 J=1,15
0027      1075    WRITE(3,1050) SALT(J),(SEPN(I,J), I=1,6)
0028      1050    FORMAT(3X,A4,3X,6(F5.4,10X)/)
          C
          C
          C
          C
0029              STOP
0030              END
```

```
FORTRAN IV-PLUS V3.0-3            15:23:54    23-OCT-82              PAGE 1
SURET.FTN;7               /TR:BLOCKS/WR
      C     THIS PROGRAM IS TO CALCULATE ADSORPTION ISOTHERM AND SURFACE AREA
      C     DISTRIBUTION AS A FUNCTION OF PORE RADIUS.
      C
      C
      C
      C     THIS IS THE MODIFIED VERSION FOR ETHANOL
      C
      C
             REAL*8 SAMSIZ(20),PEAKH(20),RETTIM(20),PEAKA(20),SENSIT(20)
            1,CHATSP(20),FLWRT(20),SEKI(20),ALPHA,FCTER,FCTER1,PREMAX,
            2PREPAR(20),PREREL(20),WATABS(20),TEMP(20),PRESS(20),
            3B1,B2,B3,TEMPR,RELMOI(25),THICK(25),TEMPA(20),FCT(20),
            4FCTR,LAYNUM(25),RADKEL(25),RADSUM(25),WATER,WATVOL(25),
            5AVELAY(25),AVERAS(25),VOLUM(25),PORSUR(25),A2,DIFRAD(25),
            6SMALLF(25),DIFF1,DIFF2,TVOLM,TPORSU,TVOLRD,TSUFRD,PPOB(25),
            7AVERD1,AVERD2,BOWATH,VOLSPC,CONST,DIFF,TVOLBE,WEIT
             INTEGER M,N,JMAX,KMAX,LMAX,NNN
      C        SAMSIZ IS THE SAMPLE SIZE
      C        PEAKH IS THE PEAK HEIGHT IN UNITS OF  CM
      C        RETTIM IS THE RETENTION TIME IN CM
      C        PEAKA IS THE PEAK AREA, MM*MM
      C        SENSIT IS THE DETECTOR ATTENUATOR
      C        CHATSP IS CHART SPEED MM/HOUR
      C        FLWRT IS THE CARRIER FLOWRATE, IN SEC/10CC
      C        SEKI IS THE LOCUS AREA
      C        M IS THE NUMBER OF INJECTIONS
      C        WEIT IS THE WEIGHT OF POLYMER IN THE COLUMN
      C        KMAX IS THE # OF DATA POINTS IN PI/PO VS THICKNESS
      C
      C
      C                       READ IN THE DATA
      C
      C
            OPEN (UNIT=1,NAME='SURARE.IN',TYPE='OLD')
            OPEN (UNIT=3,NAME='SURARE.OUT',TYPE='NEW')
            OPEN (UNIT=2,NAME='PHYSS.DAT',TYPE='OLD')
            READ(1,*) M,NNN,WEIT
      C 101 FORMAT(5I3,5X,E10.3)
      C     READ(1,*)(SAMSIZ(I),I=1,M)
      C     READ(1,*)(PEAKH(I),I=1,M)
      C     READ(1,*)(RETTIM(I),I=1,M)
      C     READ(1,*)(PEAKA(I),I=1,M)
      C     READ(1,*)(SENSIT(I),I=1,M)
      C     READ(1,*)(CHATSP(I),I=1,M)
      C     READ(1,*)(FLWRT(I),I=1,M)
      C     READ(1,*)(SEKI(I),I=1,M)
      C 102 FORMAT(7D10.3)
      C
            DO 102 I=1,M
        102 READ(1,*) SAMSIZ(I),PEAKH(I),RETTIM(I),PEAKA(I),SENSIT(I),
           &CHATSP(I),SEKI(I),FLWRT(I)
      C
      C     CALCULATION OF RELATIVE PRESSURE
      C     FROM MOHLIN AND GRAY, EQ 2(A)
      C
      C
```

```
      ALPHA=0.0D0
      DO 303 I=1,M
      ALPHA=ALPHA+60.0D0*FLWRT(I)/CHATSP(I)
  303 CONTINUE
      ALPHA=ALPHA/FLOAT(M)
      ALPHA=82.05*300.0/ALPHA
      FCTER=0.0D0
      DO 313 I=M-2,M
      FCTER=FCTER+SAMSIZ(I)*1.625D-5/(PEAKA(I)*SENSIT(I)/16.0D0)
  313 CONTINUE
      FCTER=FCTER/3.0D0
      FCTER1=FCTER*ALPHA
      PREMAX=(PEAKH(M)*SENSIT(M)/16.0D0)*FCTER1
      DO 304 I=1,M
      PREPAR(I)=(PEAKH(I)*SENSIT(I)/16.0D0)*FCTER1
      PREPEL(I)=PREPAR(I)/PREMAX
  304 CONTINUE
C
C
C    CALCULATION OF AMOUNT OF WATER ADSORBED
C    MOHLIN AND GRAY EQ 2(B)
C
C
      DO 305 I=1,M
      WATABS(I)=SEKI(I)*FCTER*1000.
  305 CONTINUE
C
C
C    CALCULATION OF COLUMN TEMPERATURE
C    BASED ON THE VAPOUR PRESSURE DATA
C    THIS IS ANTOINES EQUATION    REID, SHEERWOOD, PRAUSNITZ
C
C
C     READ(2,108)(TEMP(J),J=1,JMAX)
C     READ(2,108)(PRESS(J),J=1,JMAX)
C 108 FORMAT(7D10.3)
      PREMAX=PREMAX*760.0D0
C     DO 306 J=2,JMAX
C     IF(PREMAX-PRESS(J)) 6,7,306
C 306 CONTINUE
C   6 IF(J-JMAX) 77,75,75
C  75 IF(PREMAX-PRESS(J)) 77,7,600
C  77 B1=(TEMP(J)-TEMP(J-1))/(PRESS(J)-PRESS(J-1))
C     B2=PREMAX-PRESS(J-1)
C     B3=TEMP(J-1)
C     TEMPR=B1*B2+B3
C     GO TO 501
C   7 TEMPR=TEMP(J)
    7 TEMPR = -231.48-3803.98/(DLOG(PREMAX)-18.919)
C
        TYPE *,'TEMPR',TEMPR
C
C
C
C
C
```

```
C     CALCULATION OF KELVIN RADIUS
C  .  BASED ON JOHN AND BUHRA FROM HERE ON.
C
C
C
C
      READ(2,*) KMAX
  501 READ(2,*)(RELMOI(K),K=1,KMAX)
      READ(2,*)(THICK(K),K=1,KMAX)
C 109 FORMAT(7D10.4)
C
C    THIS SECTION REPLACED BY JASPER EQ FOR SURFACE TENSION
C
CC    READ(2,121)(TEMPA(L),L=1,LMAX)
C     READ(2,121)(FCT(L),L=1,LMAX)
C 121 FORMAT(7D10.3)
C     DO 307 L=2,LMAX
C     IF(TEMPR-TEMPA(L)) 16,17,307
C 307 CONTINUE
C  16 IF(L-LMAX) 87,85,85
C  85 IF(TEMPR-TEMPA(L)) 87,17,600
C  87 B1=(FCT(L)-FCT(L-1))/(TEMPA(L)-TEMPA(L-1))
C     B2=TEMPR-TEMPA(L-1)
C     B3=FCT(L-1)
C     FCTR=B1*B2+B3
C     GO TO 502
C  17 FCTR=FCT(L)
   17 FCTR = (24.05-0.0832*TEMPR)*4.353D-1
C
C
  502 DO 308 K=1,KMAX
      THICK(K)=THICK(K)*(4.78/1.91)
      LAYNUM(K)=THICK(K)/4.78
      RADKEL(K)=-FCTR/DLOG(RELMOI(K))
      RADSUM(K)=THICK(K)+RADKEL(K)
  308 CONTINUE
C    CALCULATION OF ADSORBED WATER IN VOLUME
      DO 309 K=1,KMAX
      DO 310 I=1,M
      IF(RELMOI(K)-PREREL(I)) 26,27,310
  310 CONTINUE
   26 IF(I-M) 97,95,95
   95 IF(RELMOI(K)-PREREL(I)) 97,27,600
   97 B1=(WATABS(I)-WATABS(I-1))/(PREREL(I)-PREREL(I-1))
      B2=RELMOI(K)-PREREL(I-1)
      B3=WATABS(I-1)
      WATER=B1*B2+B3
      GO TO 503
   27 WATER=WATABS(I)
  503 WATVOL(K)=22.4D0*WATER
  309 CONTINUE
C    CALCULATION OF PORE SIZE DISTRIBUTION
      AVELAY(1)=(LAYNUM(1)+LAYNUM(2))/2.0D0
      AVERAS(1)=200.0D0
      DIFRAD(1)=AVERAS(1)-RADSUM(2)
      VOLUM(1)=(WATVOL(1)-WATVOL(2))/(1.0D0-AVELAY(1)
```

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     1/AVERAS(1)*7.44)
      PORSUR(1)=(VOLUM(1)/AVERAS(1))*54.90
      A2=0.0D0
      DO 311 K=2,KMAX
      AVELAY(K)=(LAYNUM(K)+LAYNUM(K+1))/2.0D0
      AVERAS(K)=(RADSUM(K)+RADSUM(K+1))/2.0D0
      DIFRAD(K)=RADSUM(K)-RADSUM(K+1)
      A2=A2+PORSUR(K-1)
      SMALLF(K)=(LAYNUM(K)-LAYNUM(K+1))*A2*0.1355
      DIFF1=1.0D0-AVELAY(K)/AVERAS(K)*7.44
      IF(DIFF1) 402,402,401
  401 DIFF2=(WATVOL(K)-WATVOL(K+1))-SMALLF(K)
      IF(DIFF2) 402,402,403
  403 VOLUM(K)=DIFF2/DIFF1
      PORSUR(K)=(VOLUM(K)/AVERAS(K))*54.90
  311 CONTINUE
      GO TO 404
  402 KMAX=K-1
  404 TVOLM=0.0D0
      TPORSU=0.0D0
      TVOLRD=0.0D0
      TSUFRD=0.0D0
      DO 312 K=1,KMAX
      TVOLM=TVOLM+VOLUM(K)
      TPORSU=TPORSU+PORSUR(K)
      TVOLRD=TVOLRD+VOLUM(K)*AVERAS(K)
      TSUFRD=TSUFRD+PORSUR(K)*AVERAS(K)
      PROB(K)=PORSUR(K)/DIFRAD(K)
  312 CONTINUE
      AVERD1=TVOLRD/TVOLM
      AVERD2=TSUFRD/TPORSU
      READ(1,*) BOWATH,VOLSPC,CONST
C 131 FORMAT(7D10.3)
      IF(NNN) 23,23,2
    2 I=1
   22 I=I+1
      CALL VOLCAL(KMAX,BOWATH,AVERAS,PORSUR,VOLUM,
     1TVOLBW)
      DIFF=DABS(TVOLBW-VOLSPC)
      IF(DIFF.LE.0.0001D0) GO TO 23
      IF(TVOLBW-VOLSPC) 24,24,25
   24 BOWATH=BOWATH*(1.0D0+CONST/2.0D0**I)
        DIFF=(TVOLBW-VOLSPC)
        TYPE *,'TVOLBW',TVOLBW,'DIFF',DIFF,'BOWATH',BOWATH
      CALL VOLCAL(KMAX,BOWATH,AVERAS,PORSUR,VOLUM,
     1TVOLBW)
      IF(TVOLBW-VOLSPC) 22,24,36
   36 I=I+1
   25 BOWATH=BOWATH*(1.0D0-CONST/2.0D0**I)
      CALL VOLCAL(KMAX,BOWATH,AVERAS,PORSUR,VOLUM,
     1TVOLBW)
      IF(TVOLBW-VOLSPC) 22,22,25
   23 WRITE(3,601)
  601 FORMAT(/1X,'P/P0'//)
      WRITE(3,602)(PREREL(I),I=1,M)
  602 FORMAT(7D12.4)
```

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FORTRAN IV-PLUS V3.0-3             15:23:54    23-OCT-82              PAGE 5
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                WRITE(3,603)
            603 FORMAT(///1X,'ABSORBED WATER IN MMOL'//)
                DO 701 I=1,M
                WATABS(I)=WATABS(I)/WEIT
            701 CONTINUE
                WRITE(3,604)(WATABS(I),I=1,M)
            604 FORMAT(7D12.4)
                WRITE(3,605)
            605 FORMAT(///1X,'COLUMN T',T12,'MAX PRESS'//)
                WRITE(3,606) TEMPR,PREMAX
            606 FORMAT(7D12.4)
                WRITE(3,607)
            607 FORMAT(///1X,'PORE SIZE DISTRIBUTION'//)
                DO 702 K=1,KMAX
                PROB(K)=PROB(K)/WEIT
            702 CONTINUE
                WRITE(3,608)(PROB(K),K=1,KMAX)
            608 FORMAT(7D12.4)
                WRITE(3,609)
            609 FORMAT(///1X,'PORE SIZE IN A'//)
                WRITE(3,610)(AVERAS(K),K=1,KMAX)
            610 FORMAT(7D12.4)
                WRITE(3,611)
            611 FORMAT(///1X,'TOTAL VOL',T11,'TOTAL SUR',T24,'VOLRAD',T37,
               1'SUR RAD'//)
                TVOLM=TVOLM/WEIT
                TPORSU=TPORSU/WEIT
                WRITE(3,612) TVOLM,TPORSU,AVERD1,AVERD2
            612 FORMAT(7D12.4)
                WRITE(3,613)
            613 FORMAT(///1X,'VOL BWTER',T12,'THI BWTER'//)
                WRITE(3,614) VOLSPC,BOWATH
            614 FORMAT(7D12.4)
            600 STOP
                END
```

```
C
C
C
C                                              PART OF CALA SERIES
C
C
C    THIS PROGRAM CALCULATE SEPARATION AND FLUX WHEN POTENTIAL AND FRICTION
C    ARE GIVEN AS FUNCTIONS OF RADIUS.
          SUBROUTINE TRANS2(ALPHO,CONST,RADIUS,PRESS,CONC,D00,D1,D2,D3,D4,
        1P1,P2,P3,P4,D01,Q,SEP,RATIO)
          REAL*8 ALPH1,DIFF,SEKI1,SEKI2,ALPH,SEP,RATIO,
        1FUNCK,FUNCB,DAM,DIST(100),ALPHI(100),FUNCI(100),FUNBI(100),
        2RO(100),A1,A2,A3,B1,B2,B3,
        3C1,C2,C3,AAA,BB,CC,DD
          COMMON X1,X2,EH,ALPHA(100),A,B,C,AA,K,L,M,KK,N,ROHO,ROH00,ROH1
          X1=(193.8D02/0.4916D0)*Q/RADIUS**2/CONC
          X2=686.0D0/17.0D05*PRESS/CONC
          NNN=K+L+M
          IF(NNN.EQ.1) GO TO 54
          IF(NNN.EQ.18) GO TO 52
          IF(NNN.EQ.21) GO TO 53
          IF(NNN.EQ.3) GO TO 54
     51   A=P1*(D1+D01)**K
          A=A/RADIUS**K
          B=0.0D0
          C=0.0D0
          GO TO 61
     52   A1=1.0D0/(D1+D01)**K
          A3=1.0D0/(D3+D01)**K
          C1=-1.0D0/(D1+D01)**M
          C3=-1.0D0/(D3+D01)**M
          A=(P1*C3-P3*C1)/(A1*C3-A3*C1)
          B=0.0D0
          C=(-P1*A3+P3*A1)/(A1*C3-A3*C1)
          A=A/RADIUS**K
          C=C/RADIUS**M
          GO TO 61
     53   A1=1.0D0/D1**K
          A2=1.0D0/D2**K
          A3=1.0D0/D3**K
          B1=1.0D0/D1**L
          B2=1.0D0/D2**L
          B3=1.0D0/D3**L
          C1=-1.0D0/D1**M
          C2=-1.0D0/D2**M
          C3=-1.0D0/D3**M
          P1=-P1
          P2=-P2
          P3=-P3
          AAA=B1*(C2*P3-C3*P2)-B2*(C1*P3-C3*P1)+B3*(C1*P2-C2*P1)
          BB=A1*(C2*P3-C3*P2)-A2*(C1*P3-C3*P1)+A3*(C1*P2-C2*P1)
          CC=A1*(B2*P3-B3*P2)-A2*(B1*P3-B3*P1)+A3*(B1*P2-B2*P1)
          DD=A1*(B2*C3-B3*C2)-A2*(B1*C3-B3*C1)+A3*(B1*C3-B3*C1)
          A=-AAA/DD
          B=BB/DD
          C=-CC/DD
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TRANS2.FTN;46                /TR:BLOCKS/WR

       A=A/RADIUS**K
       B=B/RADIUS**L
       C=C/RADIUS**M
       GO TO 61
    54 A=0.0D0
       B=0.0D0
    61 AA=P4*(D4+D01)**KK
       AA=AA/RADIUS**KK
       ROH1=1.0D0+D01/RADIUS
       ROH0=1.0D0-D00/RADIUS+D01/RADIUS
       ROH00=ROH00
C   THIS SECTION FINDS A SUITABLE ALPHA0 SO THAT ALPHA=0IS AT RO=0
C
       I=0
    22 I=I+1
       CALL FDELT1(ALPH0,ALPH1)
         TYPE *,'ALPH0',ALPH0,'ALPH1',ALPH1
       DIFF=DABS(ALPH1)
       IF(DIFF.LE.0.0001) GO TO 23
       IF(ALPH1) 24,24,25
    24 ALPH0=ALPH0+CONST/2.0D0**I
       CALL FDELT1(ALPH0,ALPH1)
         IF(DABS(ALPH1).LT.0.0001) GO TO 23
       IF(ALPH1) 24,24,26
    26 I=I+1
    25 ALPH0=ALPH0-CONST/2.0D0**I
       CALL FDELT1(ALPH0,ALPH1)
         IF(DABS(ALPH1).LT.0.0001) GO TO 23
       IF(ALPH1) 22,22,25
C   END OF THAT SECTION
C
C
    23 ROH=0.5D0*EH
       SEKI1=0.0D0
       SEKI2=0.0D0
       DO 27 I=1,N
       ALPH=(ALPHA(I)+ALPHA(I+1))/2.0D0
       CALL POTEN1(ROH,FUNCK)
       CALL FRIC1(ROH,FUNCB)
       SEKI1=SEKI1+(DEXP(ALPH)/(1.0D0+FUNCB/FUNCK*(DEXP(ALPH)-
      11.0D0)))*ROH*EH*ALPH
       SEKI2=SEKI2+ALPH*ROH*EH
       RO(I)=ROH
       DIST(I)=RADIUS*(1.0D0-ROH)+D01
       ALPHI(I)=ALPH
       ROH=ROH+EH
    27 CONTINUE
       SEP=1.0D0-SEKI1/SEKI2
       RATIO=2.0D0*SEKI2*8.0D0*X1/X2
       RETURN
       END
```

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FORTRAN IV-PLUS V3.0-3          15:30:40    23-OCT-82            PAGE 1
VOLCAL.SUB;11              /TR:BLOCKS/WR

0001            SUBROUTINE VOLCAL(KMAX,BOWATH,AVERAS,PORSUR,VOLUM,
               1TVOLBW)
          C    THIS IS SUBROUTINE FOR CALCULATING TOTAL VOLUME OF BOUND WATER
          C    WHEN THE THICKNESS IS GIVEN.
          C
          C
          C
          C                   MODIFIED FOR ETHANOL
          C
0002            REAL*8 TVOLBW,VOLBW
0003            REAL*8 AVERAS(25),PORSUR(25),VOLUM(25)
0004            TVOLBW=0.0D0
0005            DO 313 K=1,KMAX
0006            IF(AVERAS(K)-BOWATH) 711,711,712
0007        711 VOLBW=VOLUM(K)*46.0D0/22.4D03
0008            GO TO 713
0009        712 VOLBW=PORSUR(K)*(BOWATH-BOWATH**2/AVERAS(K)/2.0D0)*1.0D-4
0010        713 TVOLBW=TVOLBW+VOLBW
0011        313 CONTINUE
0012            RETURN
0013            END
```