# INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

**The quality of this reproduction is dependent upon the quality of the copy submitted.** Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

ProQuest Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

# ETHYLENE SOLUBILITY AND DIFFUSIVITY IN POLAR AND NON POLAR SOLVENTS AND SOLUTIONS

by

ASHOK SAHGAL

Thesis submitted to the School of Graduate Studies
of the University of Ottawa in partial fulfillment
of the requirements for the degree of

MASTER OF APPLIED SCIENCE

in the

DEPARTMENT OF CHEMICAL ENGINEERING

UNIVERSITY OF OTTAWA

1977


Research Director

M.A.Sc. Candidate

## ACKNOWLEDGEMENT

The author wishes to express his appreciation to Dr. W. Hayduk for his valuable assistance and guidance throughout this work.

Sincerest gratitude is extended to Mr. G. Gasperetti for his help in the construction and maintenance of the equipment and also to Mrs. Pamela Scrēve for her fine typing job.

## ABSTRACT

Solubilities of ethylene were measured in the solvents, n-hexane, dodecane, n-butanol, ethylene glycol and carbon disulphide as well as mixed solvent solutions composed of n-hexane-dodecane and n-butanol-ethylene glycol at 25°C and a total pressure of one atmosphere. In addition to this, ethylene solubilities were measured at five different temperatures over a range from -10°C to 70°C. The experimental results were compared with those predicted by theoretical correlations. Solubility variation with temperature was shown graphically by plotting log x versus log T and log x versus 1/T.

Diffusion coefficients of dissolved ethylene were measured in the solvents n-hexane, dodecane, n-butanol and ethylene glycol as well as in the mixed solvents hexane-dodecane and ethylene glycol-butanol at 25°C using the capillary cell method. Diffusivities were well described by a linear relation between the logarithm of diffusion coefficient and the logarithm of solvent viscosity except for the case of ethylene glycol and ethylene glycol-butanol solutions. The constancy of the product $D\sigma^2$ ($\sigma$ being the molecular diameter of the diffusing gas) was confirmed for the systems involving ethane, methane, propane and ethylene using n-hexane and dodecane as solvents. This result shows agreement with the concept that diffusion is controlled by the molecular size of diffusing species.

This work is presented in two parts; the first dealing

with ethylene solubilities and the second dealing with ethylene diffusivities in selected solvents and two component solvent solutions.

CONTENTS

# LIST OF TABLES

## LIST OF FIGURES

## LIST OF FIGURES

(continued)

## NOMENCLATURE

| | |
|---|---|
| $A_1$, $A_2$ | Cross-sectional areas of upper and lower capillaries respectively, $cm^2$ |
| A, B | Constants |
| $a_i$ | Activity of component i |
| $a_{1,3}$ | Interaction constant of pair 1,3 |
| $B_{11}$, $B_{22}$ | Second virial coefficients for pure components 1 and 2. |
| $B_{12}$ | Cross-coefficient for binary system |
| $B^0$, $B^1$ | Parameters (function of reduced temperature) |
| $D_{21}$, $D_{2M}$ | Diffusivity of gas, $cm^2/sec$ |
| $\Delta E$ | Internal energy change of vapourization |
| $f_i$ | Fugacity of component i |
| $f_{i,m}$ | Fugacity of component in solution |
| $H_i$, $H_{im}$ | Henry's constant in pure and mixed solvents respectively |
| $\Delta H$ | Enthalpy change of vapourization |
| h, hs | Slope cm/sec and $cm^3/cm^3$ respectively |
| $J_2$ | Molar flux, gm. mole/$cm^2$sec |
| L | Ostwald coefficient |
| $\ell$ | Diffusion path length, cm |
| $M_1$ | Molecular weight of solvent gm/gm. mole |
| $N_2$, $n_2$ | Mass and molar flux of gas respectively |
| P | Total pressure, mm of mercury |
| $p_i$ | Partial pressure, mm of mercury |
| $p_i^0$ | Vapour pressure of solvent, mm of mercury |
| R | Gas constant, cal/(gm.mole)°K |
| R.I. | Refractive index at 25°C |
| $\Delta S$ | Entropy change cal/°K |
| T | Absolute temperature, °K |
| $T_{cij}$ | Temperature parameter for binary system, °K |
| $V_2$, $V_1$ | Molar volumes of gas and solvent respectively |
| $V_{GS}$ | Volume of dissolved gas in solvent |
| $\overline{V}_2$ | Partial molal volume of gas ml/gm.mole |
| $X_1$ | Association parameter |
| $W_{AO}$, $W_{AL}$ | Mass concentrations gm/ml |

| | |
|---|---|
| $x_1$, $x_3$ | Mole fractions of solution components |
| $x_2$ | Solubility of gas in mole fraction |
| $y_1$, $y_2$ | Mole fractions in gas phase |
| $Z_{cij}$ | Compressibility parameter for binary system |

## Greek Letters

| | |
|---|---|
| $\mu$ | Viscosity c.p. |
| $\rho$ | Density gm/ml |
| $\sigma$ | Molecular diameter |
| $\phi$ | Fugacity coefficient |
| $\omega$ | Acentric factor |
| $\nu$ | Activity coefficient |
| $\delta$ | Solubility parameter $(cal/ml)^{\frac{1}{2}}$ |

# I GAS SOLUBILITY

## INTRODUCTION

(a) The solubility of a gas in a liquid is defined as the amount of gas that dissolves in a unit amount of liquid at equilibrium, the temperature and pressure of the system remaining constant.

To describe the behaviour of actual gas-liquid solutions, the concept of ideal solution has been found useful. Thermodynamically, an ideal solution is defined as one "in which the activity equals the mole fraction over the entire composition range and over a non-zero range of temperature and pressure"[1].

$$a_i = \frac{f_i}{f_i^\circ} = x_i \qquad (1)$$

Neglecting all gas phase non-idealities and also any non-idealities resulting from solute solvent interactions, equation (1) becomes Raoults' law[2] after substitution of vapour pressure for fugacity:

$$p_i = x_i p_i^\circ \qquad (2)$$

For gases above their critical temperature, the ideal solubility can be evaluated using a hypothetical value of vapour pressure by extrapolating the saturation pressure curve of the pure liquid beyond its critical temperature to the solution temperature.

The ideal solubility as determined from equation (2) suffers from two defects. Firstly, it predicts the same

solubility for a gas in all solvents at a constant temperature and pressure. This is contrary to observed behaviour. This equation also predicts that gas solubility always decreases with rising temperature at a constant pressure. This prediction is frequently correct but for many gases, it is not. Hence this equation is of limited use and is employed to obtain a rough estimate of gas solubility only.

Several corrollaries follow from the definition of ideal solutions. When an ideal solution is formed from the pure components at constant temperature and pressure:

i) there is no volume change on mixing

ii) there is no heat of mixing

iii) the entropy of the solution is ideal and is given by:

$$\Delta\bar{S}_i = -R\ell nx_i \qquad (3)$$

Many non-ideal solutions have positive heats of mixing but have approximately ideal entropies of mixing. These solutions have been termed regular solutions[3].

Hildebrand and Scott[3] have developed and tested equations which predict solubilities of those gases and liquids which form regular solutions. The first equation is for systems in which solute-solvent molecules do not differ greatly in size:

$$\ell nx = \ell nx_2^{i} - \frac{\bar{V}_2}{RT}(\delta_1 - \delta_2)^2 \qquad (4)$$

Correction terms were added for significant size differences between the solute and solvent molecules:

$$\ell n x_2 = \ell n x_2^{i} - \ell n \frac{\bar{V}_2}{V_1} - (1 - \frac{\bar{V}_2}{V_1}) - \frac{\bar{V}_2}{RT}(\delta_1 - \delta_2)^2 \quad (5)$$

where

$$\delta_1 = (\frac{\Delta E_1}{V_1})^{\frac{1}{2}} \approx (\frac{\Delta H - RT}{V_1})^{\frac{1}{2}} \quad (6)$$

These equations have proven to be useful in predicting solubilities for solutions where both solute and solvent were non polar. However, use of solubility parameters for polar systems is questionable as indicated by Burrell[4]. Gjaldbaek and Anderson[5] tried to use equations (4) and (5) to calculate the solubilities of carbon dioxide, oxygen and nitrogen in various polar solvents. The results were not satisfactory.

Gas solubility in mixed solvents:

With the aid of a simple thermodynamic model, it is possible to make a fair estimate of gas solubility in simple non-polar solvent solutions provided the solubility of the gas is known in each of the pure solvents. A procedure for the simplest case has been given by Krischevsky[6].

$$\ell n H_{2,m} = x_1 \ell n H_{2,1} + x_3 \ell n H_{2,3} \ldots \quad (7)$$

This equation has been derived from Wohl's expansion for the excess free energy[7] by assuming that all binaries form ideal mixtures.

Another form of the equation has been suggested by O'Connel and Prausnitz[8] which applies fairly well for non-polar solvents:

$$\ell n H_{2,m} = x_1 \ell n H_{2,1} + x_3 \ell n H_{2,3} - a_{13} x_1 x_3 \quad (8)$$

The constant $a_{13}$ is the characteristic of the 1,3 binary pair interaction and can be estimated using the regular solution theory:

$$a_{13} = \frac{(\delta_1 - \delta_2)^2 (V_1 + V_3)}{2RT} \qquad (9)$$

It may be observed from equation (8) that the logarithm of Henry's constant is a linear function of the solvent composition whenever the two solvents form an ideal solution, ($a_{13} = 0$). The equation then reduces to the Krischvesky equation.

O'Connell has derived Henry's constant in mixed solvents using an excess free energy expressed by the Wilson equation[9]. The resultant equation for a three component system is:

$$\ell n H_{2,m} = x_1 \ell n H_{2,1} + x_3 \ell n H_{2,3} - x_3 \ell n \left[ \frac{H_{2,3}}{H_{2,1}} \right] - \ell n \left[ x_1 + x_3 \frac{H_{2,1}}{H_{2,3}} \right] \qquad (10)$$

Various other correlations have been based on Wilson's equation, including Tassios'[10] modified form of the Wilson equation and the Prausnitz and Chueh equation[11]. The latter equations involve the evaluation of certain parameters which in turn require a substantial amount of vapour-liquid equilibrium data for a particular system. On the other hand, equations (7, 8 and 10) are relatively easy to use as shown by Puri and Ruether[12]. Their work involved hydrogen solubility in the solvent binaries: acetone-isopropanol, acetone-cyclohexane and acetone-benzene for which they recommend equation (7) to best represent their data. In their work,

they showed also that results predicted by other models were only marginally closer to experimentally measured solubilities than those obtained by means of equation (7).

Equations (7, 8 and 10) have been used in this work to predict solutibilities of ethylene for comparison with the experimentally determined values.

Henry's Law and Its Thermodynamic Basis:

In order to understand the significance, of Henry's constant, it is essential to understand the concept of fugacity coefficient. The fugacity coefficient is defined as the ratio of the fugacity of a material to its total pressure[41].

For a pure substance:

$$\phi_i = \frac{fi}{P} \quad \text{or} \quad \ell n\phi_i = \ell nf_i - \ell nP \qquad (11.a)$$

For a component in solution:

$$\phi_{i,m} = \frac{f_{im}}{x_i P} \quad \text{or} \quad \ell n\phi_{im} = \ell nf_{im} - \ell nx_i P \qquad (11.b)$$

Considering the Gibb's free energy for a component:

$$RTd\ell nf_i = V_i dp \text{ (at const. T)} \qquad (11.c)$$

Differentiating eq. 11.a and substituting for $d\ell nf_i$ in eq. 11.c

$$d\ell n\phi_i = \frac{PV_i}{RT}\frac{dP}{P} - \frac{dP}{P} = (\frac{PV_i}{RT} - 1)\frac{dP}{P} \qquad (11.d)$$

Integrating from zero-pressure state where $\phi_i = 1$ to the state of pressure at P:

$$\ell n\phi_i = \int_0^P (z_i - 1)\frac{dP}{P} \text{ (const. T)} \qquad (11.e)$$

An equation for $\phi_{im}$ can be derived in a similar manner.

Thus $$\ln\phi_{im} = \int_0^P (\bar{z}_i - 1)\frac{dP}{P} \quad (\text{const. } T, x) \qquad (11.f)$$

The relationship between the fugacity of a component in solution and its fugacity in the pure state at the same temperature and pressure is found from the difference between equation (11.e) and (11.f)

$$\frac{\ln\phi_{i,m}}{\phi_i} = \int_0^P (\bar{z}_i - z_i)\frac{dP}{P} \qquad (11.g)$$

$$z_i = \frac{PV_i}{RT} \quad \text{and} \quad \bar{z}_i = \frac{P\bar{V}_i}{RT},$$

Replacing $\phi_{i,m}$ and $\phi_i$ by their definitions in terms of $f_{i,m}$ and $f_i$:

$$\ln \frac{f_{i,m}}{f_i x_i} = \frac{1}{RT}\int_0^P (\bar{V}_i - V_i)dP \qquad (11.h)$$

Equation (11.h) is applicable in general but requires information about the mixture that is difficult to obtain: mainly the partial molar volume data. However if the mixture is an ideal solution i.e. $\bar{V}_i = V_i$, equation (11.h) reduces to

$$f_{i,m}^{id} = x_i f_i \qquad (11.i)$$

The limiting case of the curve represented by equation (11.i) is obtained by drawing a tangent to the curve at $x_i = 0$ and the mathematical condition thus imposed is expressed by:

$$\lim_{x_i \to 0} \frac{f_{i,m}}{x_i} = k_i = H_i \qquad (11.j)$$

Equation (11.j) is a statement of Henry's law and is approximately valid for the values of $x_i$ near zero.

Solubility of a gas in a liquid is determined by the

equation of phase equilibrium. If the gaseous phase and liquid phase are in equilibrium, then for the component i, the fugacities in both phases must be equal:

$$f_i^{gas} = f_i^{liq.} \qquad (11.k)$$

The thermodynamic significance of the Henry's constant can be established by comparing the liquid fugacity as given by Henry's law with that obtained by the conventional manner using the concept of activity coefficient $\nu$.[2]

$$f_i^{liq.} = H_i x_i = \nu_i x_i f_i^{\circ}$$

$$\text{or} \qquad H_i = \nu_i f_i^{0} \qquad (11.l)$$

The standard state fugacity $f_i^{\circ}$ is a constant at a given temperature and pressure and does not depend on the mole fraction of component i in the liquid phase. Since $H_i$ does not depend on $x_i$, it follows from equation (11.l) that $\nu_i$ must also be independent of $x_i$. This constancy of activity coefficient is the essential feature of Henry's law.

Estimation of Henry's Constant:

From solubility data at equilibrium, a value for Henry's constant can be estimated using the thermodynamic equilibrium relations in the following manner.

For a binary solute-solvent system:

$f_i^{\ell} = f_1^{V}$ and $f_2^{\ell} = f_2^{V}$:

$$f_1^{\ell} = (1 - x_2) P_1^{0} \qquad (12.a)$$

$$f_1^V = \phi_1 (1 - y_2) P \qquad (12.b)$$

$$f_2^V = \phi_2 y_2 P \qquad (12.c)$$

$$f_2^\ell = H_{2,1} \cdot x_2 \qquad (12.d)$$

The virial equation truncated after the second virial coefficeint can be used to relate $\phi_1$ and $\phi_2$ to temperature, pressure and composition.(41)

$$\ell n \phi_1 = \frac{P}{RT}(B_{11} + y_1^2 \delta_{12}) \qquad (12.e)$$

$$\ell n \phi_2 = \frac{P}{RT}(B_{22} + y_1^2 \delta_{12}) \qquad (12.f)$$

where $\delta_{12} = 2B_{12} - B_{11} - B_{22}$.

Pitzer's correlation for the second virial coefficient has been extended to mixtures by Prausnitz(41) and is given as:

$$B_{ij} = \frac{R.T_{cij}}{P_{cij}} (B^0 + \omega_{ij}.B^1)$$

where $B^0$ and $B^1$ are the functions of reduced temperature $T_r$. The mixing rules proposed by Prausnitz for the calculation of $\omega_{ij}$, $T_{cij}$ and $P_{cij}$ are:

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2}$$

$$T_{cij} = (T_{ci} \cdot T_{cj})^{1/2}$$

$$P_{cij} = \frac{z_{cij} R.T_{cij}}{V_{cij}}$$

where $z_{cij} = \frac{z_{ci} + z_{cj}}{2}$

and $V_{cij} = \left(\frac{V_{ci}^{1/3} + V_{cj}^{1/3}}{2}\right)^3$

Calculations for ethylene Henry's constant in hexane

at 25° are shown in Appendix III.

Treatment of Data:

(a) Some of the commonly used notations to express gas solubility in liquids are: 1. mole fraction solubility. 2. Ostwald coefficient. 3. Bunsen coefficient. 4. Weight percentage. 5. Moles solute per litre solvent. In this work, ethylene solubilities have been expressed in the form of mole fraction solubility and Ostwald coefficient. The main advantage of using the Ostwald coefficient to represent gas solubility is that the values thus obtained are independent of the actual gas partial pressure as long as Henry's law applies.

To determine solubility, the different data points for vapour free volumes of dissolved gas were linearly related to the accumulated solution volumes by the method of least squares using a NOVA computer. The true solvent volume was calculated by subtracting the volume of dissolved gas from the solution volume. The Ostwald coefficient is given by:

$$L = \frac{hs \cdot P}{P - P \cdot y_1} \times \frac{1}{1 - V_{GS}} \qquad (13.a)$$

where $V_{GS}$ is the volume of dissolved ethylene in solvent and is given by:

$$V_{GS} = hs \cdot P \cdot \frac{\overline{V}_2}{V_2}$$

The mole fraction solubility $x_2$, could be computed from the Ostwald coefficient using a unit volume of solvent as basis.

$$x = \frac{L}{L + \frac{V_2}{V_1}} \quad \text{or} \quad L = \frac{\alpha \cdot x_2}{1-x_2} \tag{13.b}$$

where $\alpha = \frac{V_2}{V_1}$

Equating (13.a) and (13.b):

$$\frac{hs}{y} \cdot \frac{1}{1-V_{GS}} = \frac{\alpha \cdot x_2}{1-x_2} \tag{13.c}$$

Using equilibrium relations to allow for the liquid phase non ideality:

$$f_1^{\ell} = f_1^{V} \quad \text{or} \quad (1-x_2)P_1^0 = \phi_1(1-y_2)P \tag{13.d}$$

Fugacity coefficient $\phi_1$ is related to temperature pressure and composition by the virial equation truncated after the second virial coefficient.[41]

$$\ell n \phi_1 = \frac{P}{RT}(B_{11} + y_2^2 \cdot \delta_{12})$$

where $\delta_{12} = 2B_{12} - B_{11} - B_{22}$

Substituting for $\phi_1$ from equation (13.d)

$$\ell n \left[\frac{(1-x_2)P^0}{(1-y_2)P}\right] = \frac{P}{RT}(B_{11} + y_2^2 \cdot \delta_{12}) \tag{13.e}$$

Using equations (13.c) and (13.e), $x_2$ and $y_2$ were calculated by trial and error method. This procedure was used to calculate ethylene solubilities in pure solvents except ethylene glycol at 25°C.

Results were also calculated by a simplified procedure of assuming Raoult's law for the calculation of solvent vapour pressure. In this case, the Ostwald coefficient is given by:

$$L = \frac{hs \cdot P}{P - P_1^0(1-x_2)} \times \frac{1}{1-V_{GS}} \tag{13.f}$$

and $$x_2 = \frac{L}{L + \frac{V_2}{V_1}} \qquad (13.g)$$

This method also involved a trial and error method for the calculation of L and $x_2$.

(b) Solubility in Mixed Solvents:

Solubilities in mixed solvents were determined by using equations (13.f) and (13.g). However, the vapour pressure and molal volume of mixed solvents were calculated differently. For the purpose of calculating the solution vapour pressure, the vapour pressure of dodecane in hexane-dodecane solution was ignored because of the vapour pressure of dodecane was 0.27 mm of mercury as compared to 151.2 mm of mercury for hexane at 25°C. The average molal volume of the solution was calculated with due regard for the solution density and its average molecular weight. The partial molal volume of ethylene was assumed to be the same (71.45 $cm^3$/gm.mole) in all solutions. The use of Raoult's law might have introduced an error of the order of less than one percent in case of solubility values in hexane-dodecane solutions. This error could be greater in case of ethylene gylcol-butanol solutions because of higher degree of non-ideality in their solutions. This inaccuracy in results could be avoided if vapour-liquid equilibrium data were available for the systems under consideration so that the results could be calculated without assuming Raoult's law.

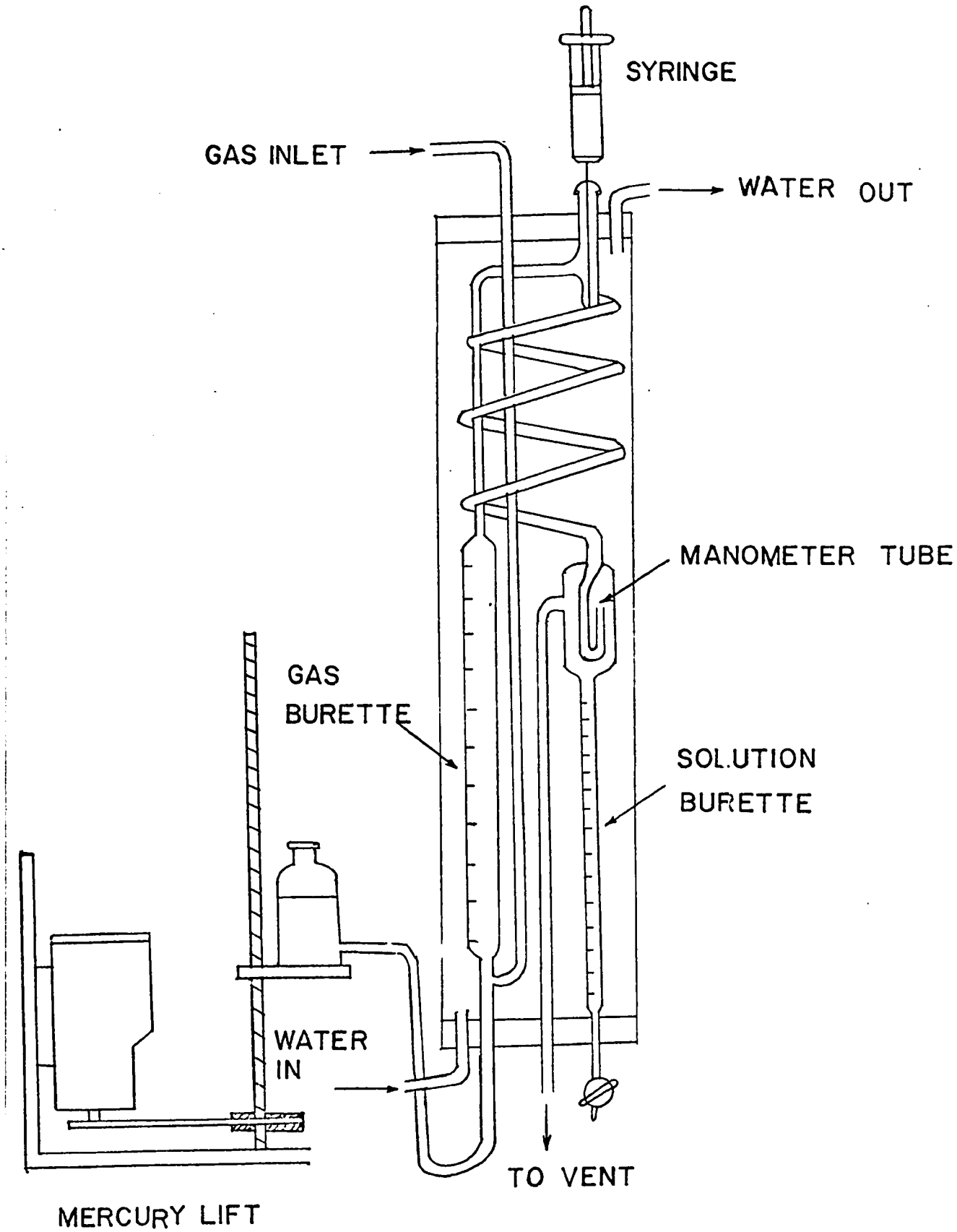


Fig. 1 Solubility Apparatus

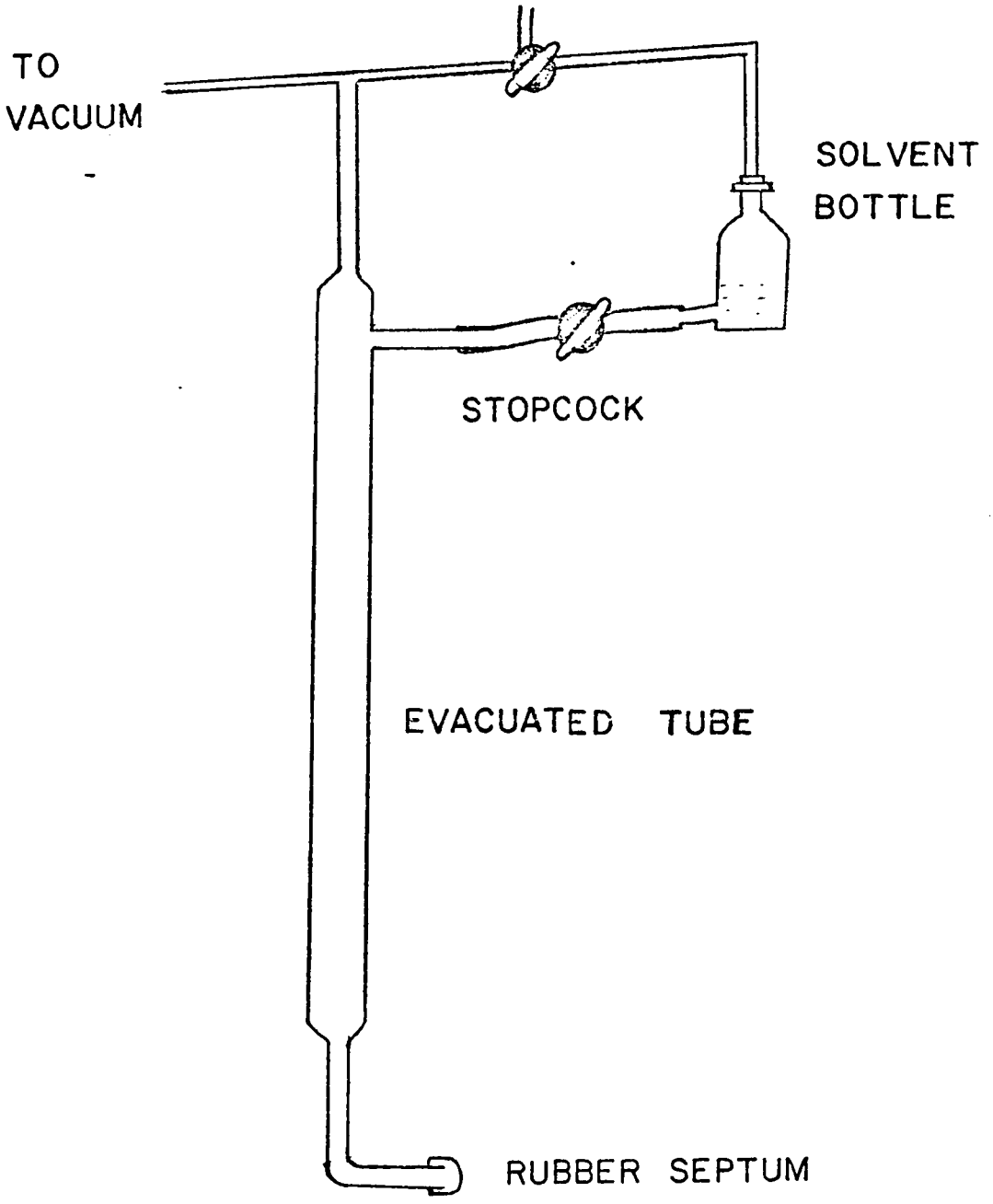


Fig. 2 Degassing Apparatus

Apparatus and Procedure:

The solubility apparatus used in this work was similar to the one developed by Hayduk and Cheng[13]. It consisted mainly of a gas burette, a contacting chamber in the form of a glass tube spiral, a small manometer and a solvent burette, all enclosed in a glass jacket through which water at constant temperature was circulated. The gas burette at its lower end was connected to a bottle filled with mercury thru a rubber tubing. The mercury-filled bottle could be raised by means of a variable speed motor. The top end of the glass tube spiral was closed with a rubber septum. The solvent was brought into the contacting chamber by the use of a syringe attached to a syringe pump.

For most experiments, the solubility apparatus used had a 20 ml gas burette and 20 ml solvent burette. For measuring lower solubilities at higher temperatures, a second apparatus equipped with a 5 ml gas burette and 10 ml solvent burette was used. Some modifications to the apparatus were introduced for measurements at temperatures above or below the ambient. The syringe was fitted with a syringe jacket through which water at the experiment temperature was circulated. In addition, the glass jacket of the apparatus was insulated by means of a transparent polythene sheet and the syringe needle was imbedded in styrofoam.

The water circulating in the jacket of the solubility apparatus was kept at constant temperature in a circulating bath purchased from the Fisher Scientific Company. The

temperature in the bath was controlled by a thermoregulator set at the experiment temperature. This thermoregulator controlled a heating element that kept the temperature constant. In the temperature range of 25°C to 50°C, tap water was circulated in a cooling coil inside the bath to avoid excessive heating. For temperatures above 50°C, no cooling was necessary since the heat lost by the system balanced the excessive heat input. For temperatures lower than the room temperature, a "Bath Cooler" regrigeration unit purchased from Neslab Instruments Inc. was used to cool a solution of water and ethylene glycol which was then circulated in the apparatus.

To carry out a solubility run, first of all the solvent to be used was decerated in the degassing apparatus shown in Fig. 2. It consisted of a bottle and a long glass column connected through a tygon tubing. The glass bottle equipped with a heating coil was filled with the desired solvent and warmed up. A vacuum was then applied to both the bottle and the glass column. Approximately one fourth of the solvent was allowed to boil away over a time period of about 5 minutes and the remaining liquid was accumulated in the glass column by opening the stop-cock connecting the bottle and the glass column. The vacuum was then released and the liquid was withdrawn into a syringe through the rubber septum at the bottom of glass column.

While the degassing process was going on, the solubility apparatus was purged with ethylene gas. The syringe containing degassed solvent was then fitted to the syringe

pump and the syringe needle was inserted through the rubber septum into the contacting chamber of the apparatus. It was verified at the beginning of each run that the end of the syringe needle was touching the walls of the spiral (contacting chamber) so as to ensure a smooth constant flow-rate of solvent down the tube. The solvent burette stop-cock was closed and the syringe infusion pump was started. Ethylene was still allowed to flow through the apparatus at a reduced flow rate until steady state was achieved. Then the mercury level was raised in the gas burette thus isolating a quantity of ethylene in the gas burette and contacting chamber. The gas was shut off and the gas feed line was then opened to the atmosphere. The pressure inside the apparatus, indicated by means of the small manometer, was maintained equal to the atmospheric pressure by adjusting the speed of the mercury lift. Volumes of solution accumulated along with volumes of gas absorbed were recorded at set intervals of time.

Properties of Test Fluids:

C.P. grade ethylene was supplied by Matheson of Canada. Relevant properties of the gas are presented in Table 1.a.

n-Hexane, ethylene glycol and n-butanol used were purchased from Fisher Chemicals. n-Hexane and n-butanol were specified to be olefin-free with a minimum purity of 99 mole%. Research grade dodecane supplied by Phillips Petroleum had a specified minimum purity of 99 mole%.

The density measurements of solvent mixtures were performed by means of a Digital precision density meter purchased from Anton Paar Austria. The procedure followed is the same as given by Picker[27].

Refractive indices were measured by means of a Bausch and Lomb refractrometer. Solvents for this purpose were n-hexane, dodecane, n-butanol and ethylene glycol and solutions composed of n-hexane-dodecane and n-butanol-ethylene-glycol. Viscosity measurements for butanol-ethylene glycol solutions were carried out by means of a Cannon-Fenske routine viscometer.

All pertinent properties of the liquids are listed in Table 1, 2(a) and 2(b) or shown graphically in Figures 3-7.

Results and Discussion:

Ethylene solubilities at 25°C in hexane, dodecane butanol, ehtylene glycol and carbon disulphide are given in Table 3. Calculations were carried out using two different methods, assuming Raoult's law and using equilibrium relations for fugacity. The latter method could not be used in case of ethylene glycol because the critical data required for calculations was not available. A comparison of solubility value s calculated by these two methods shows that assumption of Raoult's law introduced an insignificant error so long as the solvent vapour pressure was less than about one fifth of the total pressure of the system. An error of 3% in the value of $x_2$ was observed in case of ethylene solubility in carbon disulphide which has a vapour pressure of 348 mm mercury at 25°C.

For butanol and dodecane solvents, experiments were also carried out at four different temperatures in the range from -10°C to 70°C. The results were calculated by the method assuming Raoult's law and are listed in Table 4(a) and (b) and shown graphically in figures 9 and 10. Assumption of Raolt's could have introduced an error of less than one percent.

To test the accuracy of the apparatus and method used, the solubility of ethane was determined in hexane solvent for comparison with earlier data. A value of 6.105 was obtained for the Ostwald coefficient at 25°C which agreed with that found by Cheng [13] to within 0.3%. Duplicate and triplicate determinations showed reproducibility to within 1%.

Figure 8 shows a plot of logarithm mole fraction solu-

bility versus solvent solubility parameter at 25°C. It shows a trend similar to the one observed by Kubatake and Hildebrand[25] in their study of solubility of other gases. Ethylene solubility decreases with an increase in solvent solubility parameter. Hexane and dodecane have similar solubilities even though hexane has a lower solubility parameter. This type of behaviour has also been observed in the case of butane[26] and ethane solubility[13] in these solvents.

For the sake of comparison, ethylene solubilities were also calculated by the regular solution theory equations and by the ideal solubility equation. The comparison is shown in Table 3. The fact that equation (5) predicts results for hexane and dodecane better than equation (4) may be anticipated because of the large difference in solute and solvent molecular sizes. Equation (4) seems to predict solubilities that agree relatively well with experimentally determined ones for butanol and carbon disulphide. However, ethylene solubilities in ethylene glycol are not described well by either of the regular solution theory equations - a fact which may be expected because the regular solution theory applies only in the case of non-polar or slightly polar solvents. Both equations yield a difference from the experimental value of 300%. Hildebrand[1] had previously indicated that the use of $\delta$-values for polar solvents was rather questionable.

The solubilities of ethylene in dodecane are shown as the log mole fraction versus inverse absolute temperature. It is interesting to note that the solubility points for

dodecane fall on a straight line which can be extrapolated to the normal boiling point of ethylene (103.7°C) corresponding to a unit mole fraction solubility at this temperature. A comparable extrapolation for butanol is not linear. Similar behaviour has been observed for the other gases, butane[26] and ethane[13] in these same solvents. Additional solubility data at low temperatures are needed to establish with confidence that ethylene solubility in any solvent, when extrapolated to the normal boiling point of ethylene, corresponds to pure ethylene.

Gas solubilities at different temperatures are commonly plotted as log mole fraction versus log absolute temperature. According to Hildebrand, a linear plot is obtained for regular solutions where the slope represents the entropy change. This linearity was observed for the ethylene solubility in dodecane as shown in figure 10. The solubility line has been extrapolated to meet the reference at the critical temperature of dodecane ($x_o$ = 0.0019 at $T_c$ = 658°K)[28]. However, a comparable extrapolation for ethylene solubilities in butanol does not tend to the reference solubility of butanol. The solubility curve obtained is similar to those for inert gases dissolved in water as observed by Miller and Hildebrand[29]. Those workers, explained this behaviour in terms of hydrogen bonding and solute-solvent association as has also been stated by Prausnitz[2]. Prausnitz stated that "hydrogen bonding or solvation of solute solvent molecules is present in solvent such as ketones and alcohols for solutes such as ethylene and acytelene which are strong proton

acceptors". This is one of the several kinds of molecular interactions which occurs in gas-liquid solutions to complicate prediction of solubilities.

Solubility in Mixed Solvents

Ethylene solubilities in mixed solvents composed of hexane-dodecane and butanol-ethylene glycol at 25°C are listed in Table 3-5 as Ostwald coefficients and mole fraction. The results were calculated assuming Raoult's law (ideality of gaseous and liquid phases). Equilibrium relations for fugacity could not be used because the vapour-liquid equilibrium data for hexane-dodecane and butanol-ethylene glycol were not available. This could have introduced an error in the results particularly in case of butanol-ethylene glycol solutions because of higher degree of non-ideality as compared to hexane-dodecane solutions.

Solubilities predicted by means of equations (7, 8 and 10) have been compared with experimentally determined results. The results were also plotted as log mole fraction and log Ostwald coefficient versus mole fraction composition.

Table 5 shows a comparison of theoretically predicted and experimentally determined results for hexane-dodecane solutions. Equations (7) and (10) give an identical average absolute deviations of 3% while equation (8) gives a deviation of 4.5% from measured solubilities.

O'Connell and Prausnitz[8] have suggested as a result of their study with gas solubilities in non-ideal mixed solvents, that "in non-polar systems, the logarithm of the gas

solubility is, to a good approximation, a linear function of solvent composition". This was indeed found to correspond to actual ethylene solubilities in hexane-dodecane solutions as shown in figure 11(b). Similar behaviour had previously been observed in the case of ethane solubilities in hexane-dodecane solutions[13] but with a slightly increased degree of deviation.

Although equations (7, 8 and 10) are recommended for non-polar systems, an attempt was made using these equations to predict ethylene solubilities in the polar solutions of butanol and ethylene glycol. Equation (10) describes the results best showing an absolute average deviation of about 8%. Equations (7) and (8) show a 30% and 22.5% deviation respectively. These deviations could be greater depending on the error introduced by ignoring non idealities of the mixed solvents.

The plot of log mole fraction solubilities versus butanol mole fraction shows positive deviations from the ideal solubility line. A similar plot for Ostwald coefficient follows the same pattern. This type of behaviour is comparable to solubility results obtained by Puri and Ruether[12] in their study of hydrogen solubilities in polar solvent solutions.

More data, involving mixed solvents for which vapour liquid equilibria are known, must be available for a larger number of systems before firm conclusions can be made about the solubility behaviour of ethylene in mixed solvents.

TABLE 1a

Ethylene gas vol. cc/gm at 1 atm. Ref.(18)

| Temp.°C | Vol. cc/gm | Molar vol. cc/g.mole |
|---|---|---|
| 0 | 803.61 | 22,533.2244 |
| 25 | 878.71 | 24,639.0284 |
| 50 | 953.61 | 26,739.2244 |
| 75 | 1028.40 | 28,836.3360 |
| 100 | 1103.00 | 30,928.1200 |
| 125 | 1177.60 | 33,019.9040 |
| 150 | 1252.00 | 35,106.0800 |

TABLE 1b

Properties at 25°C

| Liquid | Solubility Parameter $(cal/cc)^{\frac{1}{2}}$ | R.I. Expt | R.I. Lit | Density Expt gm/cc | Density Lit gm/cc |
|---|---|---|---|---|---|
| Hexane | 7.30(14) | 1.3735 | 1.3722(15) | 0.6552 | 0.6548(15) |
| Dodecane | 7.84(14) | 1.4200 | 1.4149(15) | 0.7452 | 0.7451(15) |
| Butanol | 9.70( a ) | 1.3980 | 1.3950(17) | 0.8061 | 0.8060(15) |
| E.Glycol | 14.50( a ) | 1.4295 | 1.4290(17) | 1.1096 | 1.1101(16) |
| Carbon disulphide | 10.00(14) | | | | 1.2556(16) |

TABLE 1c

| Liquid | Molal Vol. ml/g. mole | Vap. Pr. mmHg | Viscosity cp |
|---|---|---|---|
| Hexane | 131.598(20) | 151.20(15) | 0.2985(15) |
| Dodecane | 228.579(20) | 0.27(15) | 1.3780(15) |
| Butanol | 91.814( b ) | 6.78(21) | 2.5820(23) |
| Ethylene glycol | 55.871( b ) | 0.13(22) | 16.0000(17) |
| Carbon disulphide | 60.640( b ) | 348.00(22) | |

(a) Calculated by Hildebrand's rule

(b) Found using $V_L = \frac{M}{\rho}$

TABLE 2(a)

Solution Densities and Refractive Indices at 25°C

Hexane-Dodecane:

| Dodecane m.f. | ρ gm/cc | R.I. |
|---|---|---|
| 0.0000 | 0.6552 | 1.3735 |
| 0.0600 | 0.6650 | 1.3790 |
| 0.1257 | 0.6748 | 1.3836 |
| 0.1977 | 0.6834 | 1.3889 |
| 0.2772 | 0.6912 | 1.3935 |
| 0.3651 | 0.7013 | 1.3985 |
| 0.4632 | 0.7089 | 1.4030 |
| 0.5730 | 0.7191 | 1.4075 |
| 0.8381 | 0.7367 | 1.4160 |
| 1.0000 | 0.7451 | 1.4200 |

Butanol-Ethylene glycol:

| Butanol m.f. | ρ gm/cc | R.I. |
|---|---|---|
| 0.0000 | 1.1096 | 1.4300 |
| 0.1320 | 1.0520 | 1.4245 |
| 0.2068 | 1.0190 | 1.4210 |
| 0.2886 | 0.9895 | 1.4181 |
| 0.3783 | 0.9596 | 1.4145 |
| 0.4772 | 0.9278 | 1.4112 |
| 0.5867 | 0.8968 | 1.4080 |
| 0.7085 | 0.8591 | 1.4051 |
| 1.0000 | 0.8060 | 1.3980 |

TABLE 2(b)

Viscosity of Butanol-Ethylene glycol solutions at 25°C

| Butanol m.f. | Viscosity c.p. |
|---|---|
| 0 | 16.264 |
| 0.1320 | 12.333 |
| 0.2886 | 8.749 |
| 0.4777 | 6.054 |
| 0.8450 | 3.175 |
| 1.0000 | 2.584 |

TABLE 3

Comparison of experimental solubility values of Ethylene with those predicted by theoretical equations at 25°C

| Solvent | Expt. Eqn. 13(c) | 13(g) | Eqn. 5 | Eqn. 4 | Ideal |
|---|---|---|---|---|---|
| n-Hexane | .02106 | .0208 | .0169 | .0145 | .0153 |
| Dodecane | .02129 | .0212 | .0244 | .0151 | .0153 |
| n-Butanol | .00823 | .00822 | .0105 | .0102 | .0153 |
| Ethylene glycol | — | .00070 | .0029 | .0028 | .0153 |
| Carbon disulphide | .00655 | .00635 | .0090 | .0089 | .0153 |

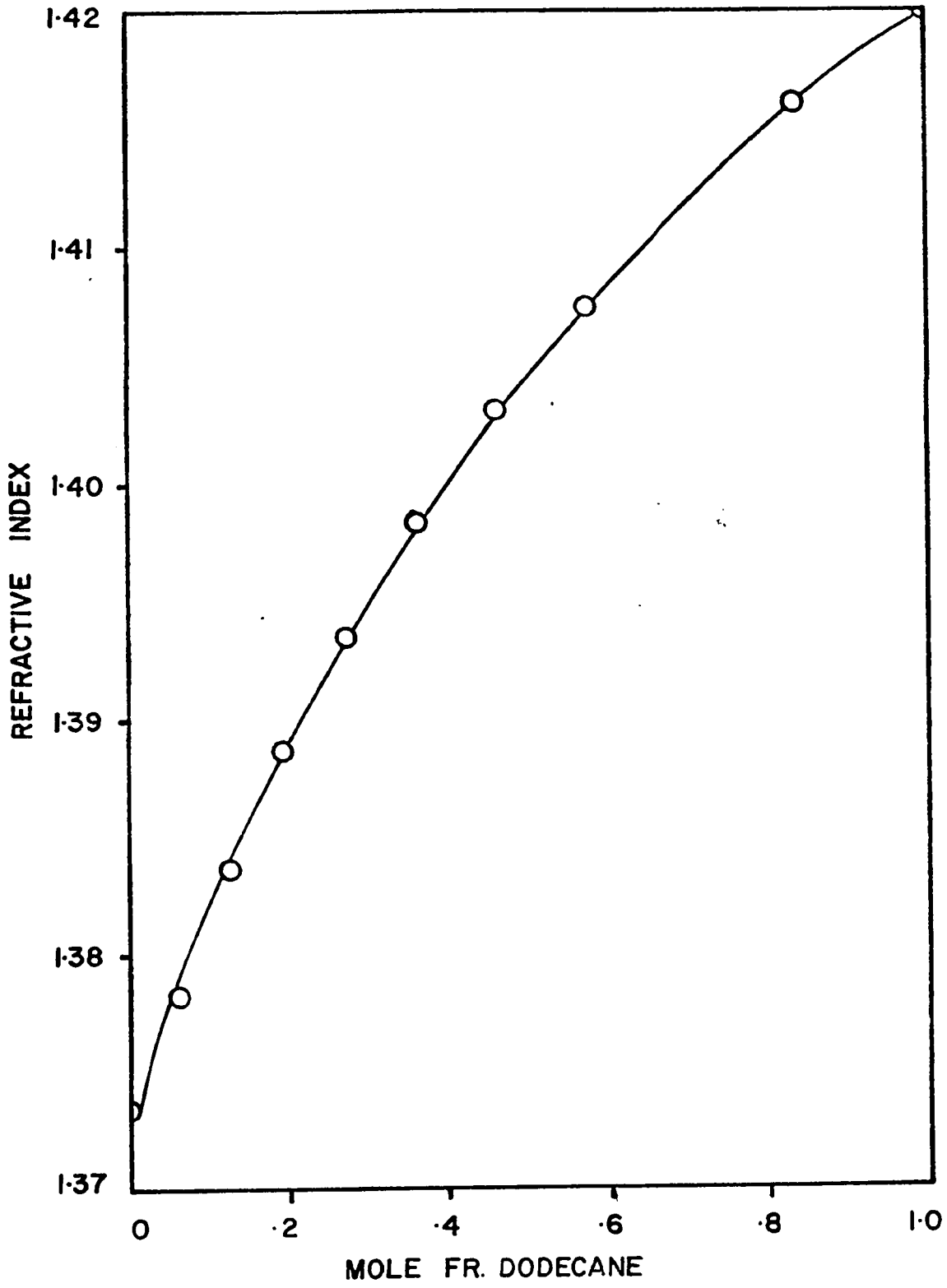


Fig. 3 Refractive index of hexane-dodecane solutions vs. solution composition at 25°C

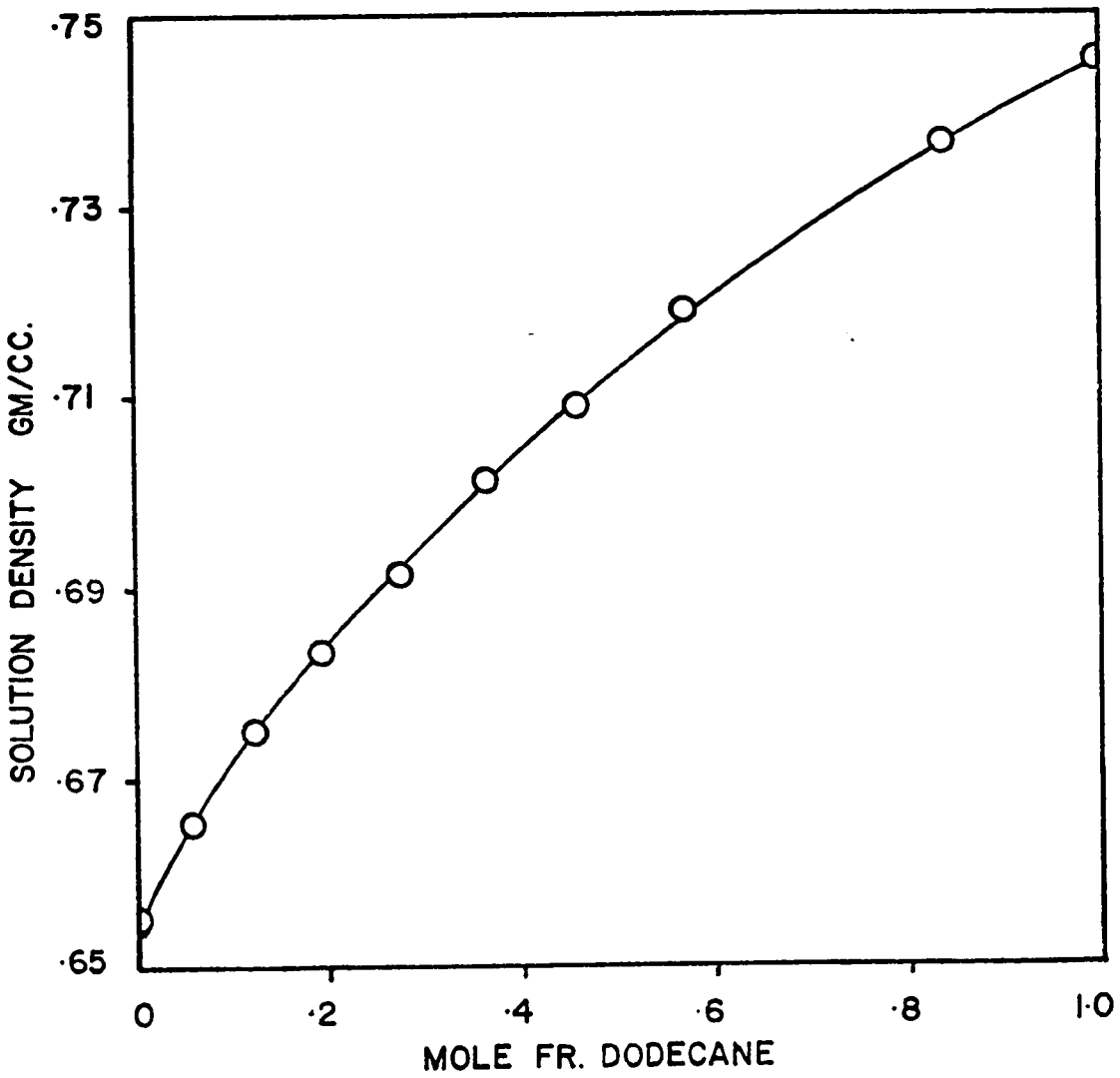


Fig. 4 Density of hexane-dodecane solutions vs. solution composition at 25°C

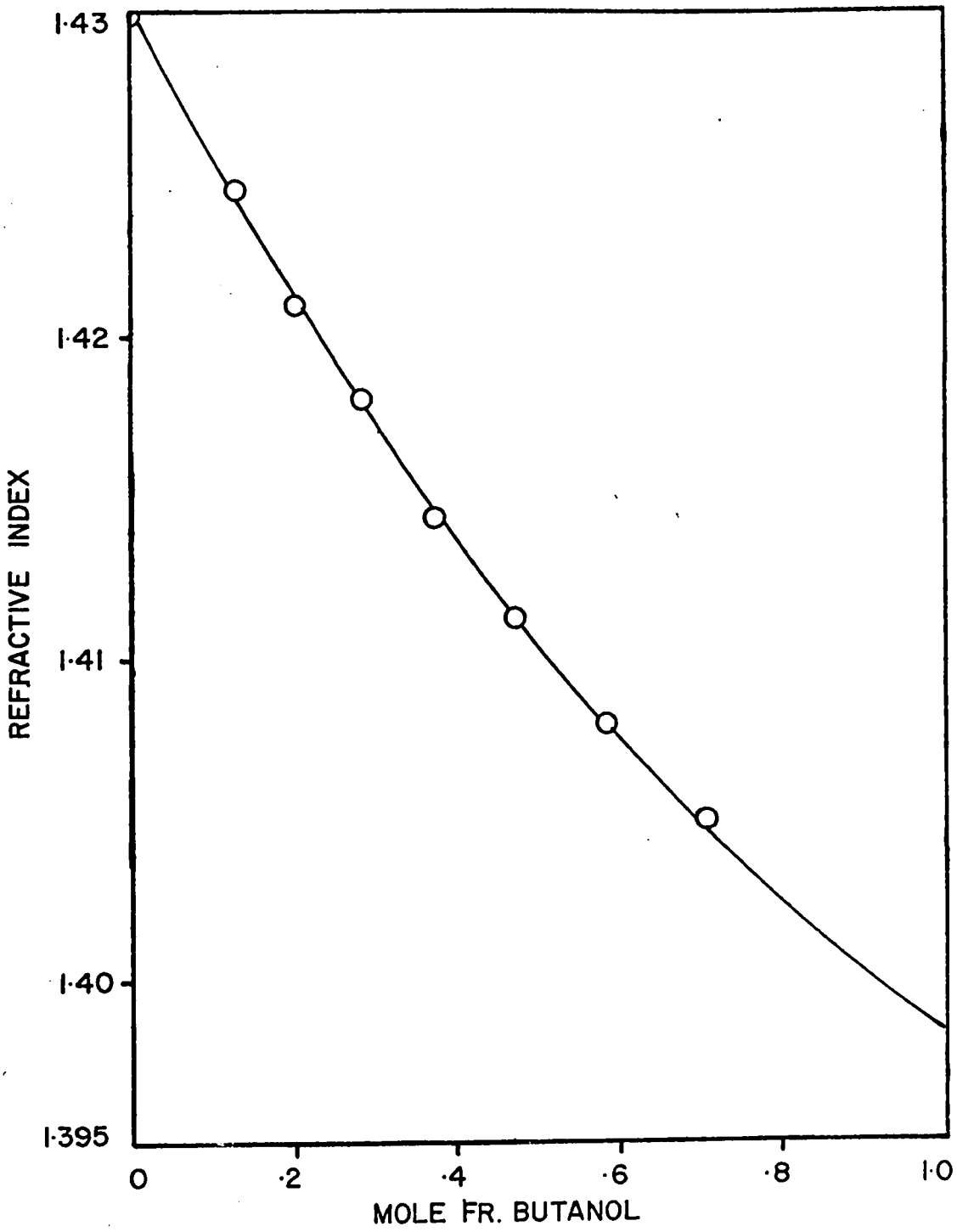


Fig. 5 Refractive index of ethylene glycol-butanol solutions vs. solution composition at 25°C

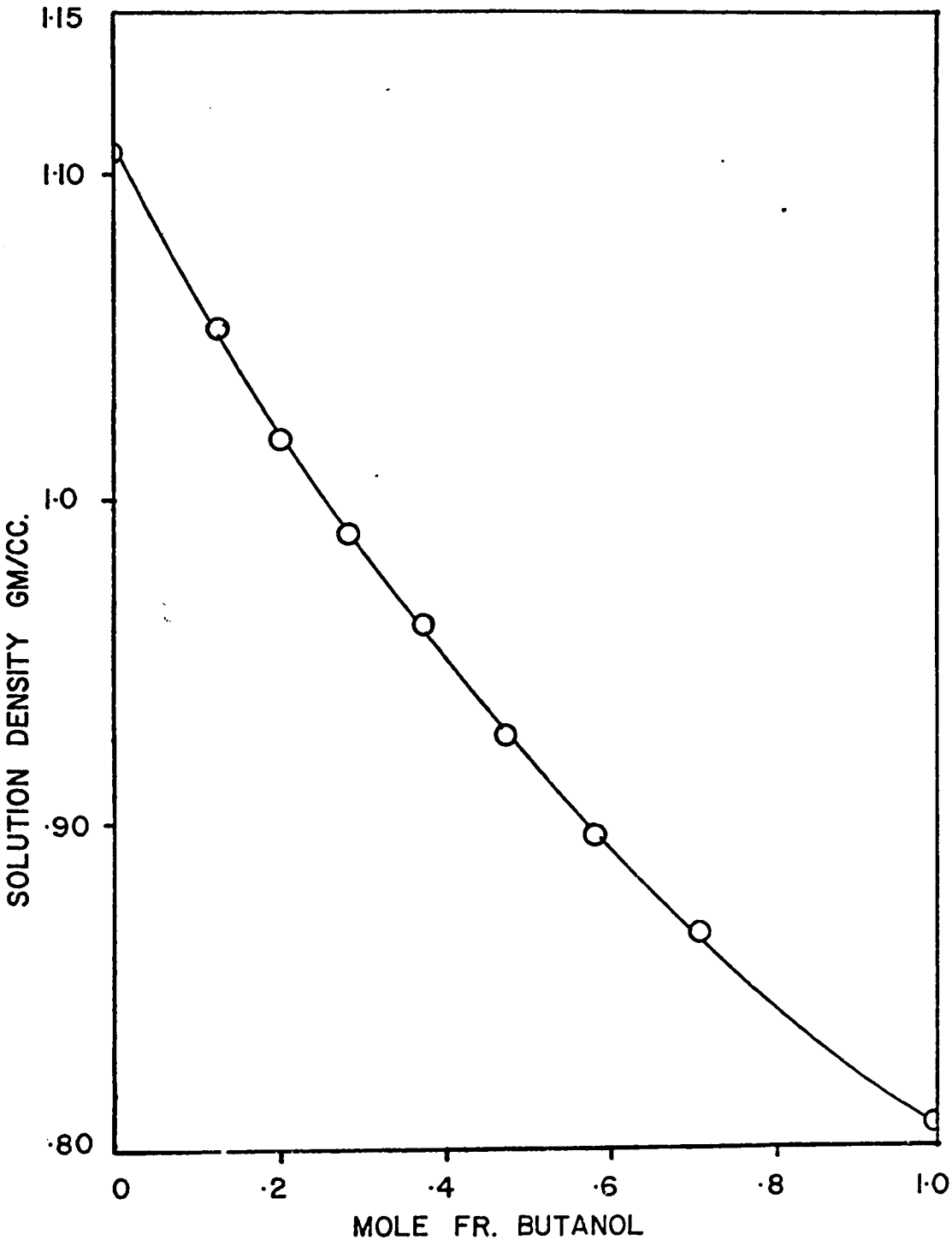


Fig. 6 Density of ethylene glycol-butanol solutions vs. solution composition at 25°C

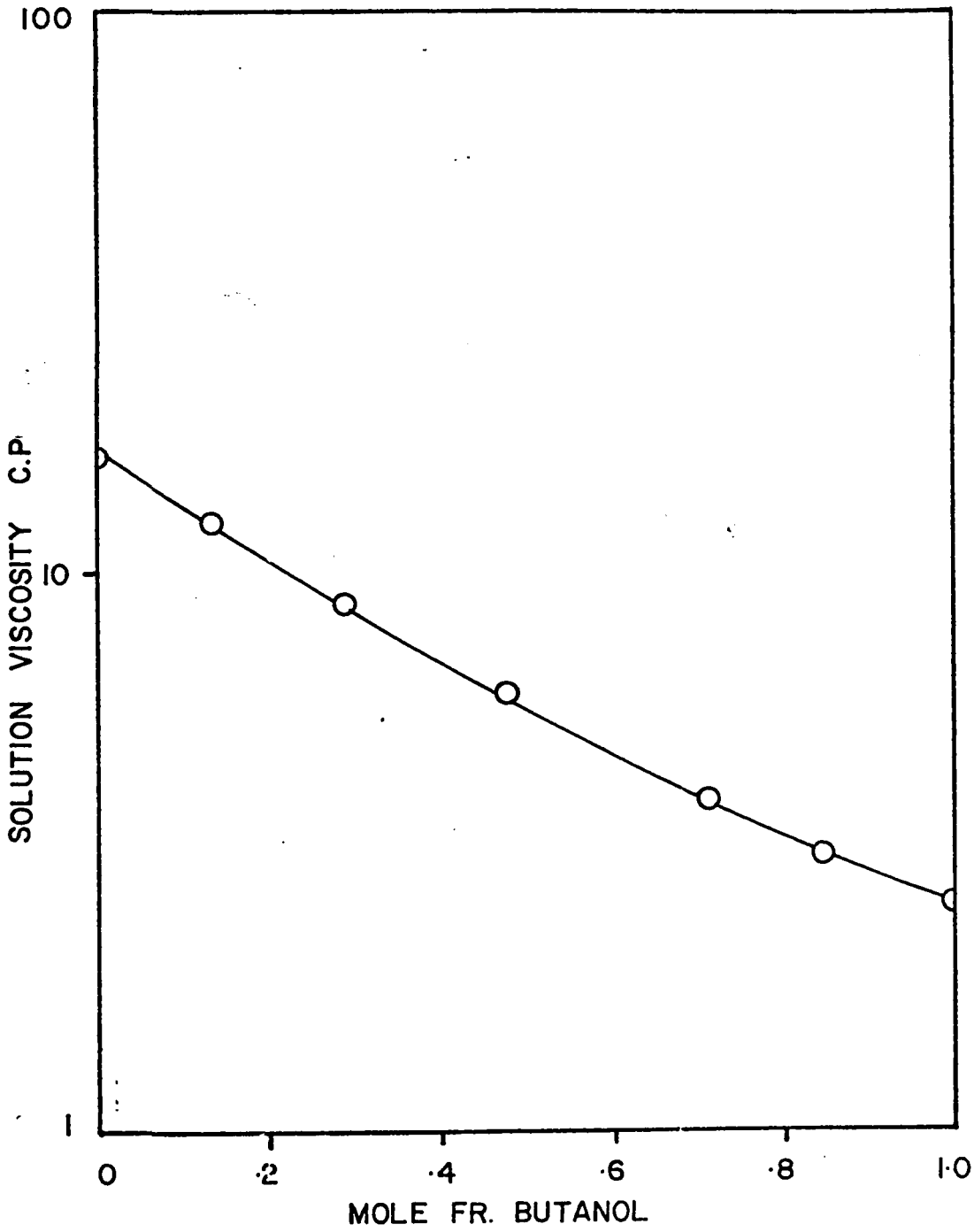


Fig. 7 Viscosity of ethylene glycol solutions vs. solution composition at 25°C

TABLE 4a

Solubility of Ethylene-Ostwald Coefficients

| Solvent | Temp.°C | L | L | L | Avg. |
|---|---|---|---|---|---|
| Hexane | 25 | 3.9213 | 3.9785 | 3.8787 | 3.9261 |
| Dodecane | 25 | 2.3454 | 2.3617 | | 2.3535 |
| Dodecane | 48 | 1.8121 | 1.7885 | | 1.8000 |
| Dodecane | 66 | 1.5460 | 1.5318 | | 1.5389 |
| Dodecane | -9.2 | 4.1413 | 4.0988 | | 4.1200 |
| Butanol | 25 | 2.2250 | 2.2411 | 2.2500 | 2.2387 |
| Butanol | 34 | 1.7890 | 1.8060 | | 1.7975 |
| Butanol | 49 | 1.7280 | 1.7190 | | 1.7235 |
| Butanol | 70 | 1.5059 | 1.4880 | | 1.4969 |
| Butanol | -9.2 | 3.6250 | 3.6120 | | 3.6185 |
| Carbon disulphide | 25 | 2.5986 | 2.6120 | | 2.6053 |
| Ethylene glycol | 25 | 0.3103 | 0.3132 | | 0.3117 |

TABLE 4b

Ethylene Solubility - Mole Fraction

| Solvent | Temp.°C | x | x | x | Avg. |
|---|---|---|---|---|---|
| Hexane | 25 | .020500 | .020800 | .02030 | .020500 |
| Dodecane | 25 | .021200 | .021400 | | .021300 |
| Dodecane | 48 | .015600 | .015400 | | .015500 |
| Dodecane | 66 | .013000 | .012800 | | .012900 |
| Dodecane | -9.2 | .040400 | .040000 | | .040200 |
| Butanol | 25 | .008220 | .008280 | .00831 | .008270 |
| Butanol | 34 | .006530 | .006590 | | .006560 |
| Butanol | 49 | .006090 | .006060 | | .006070 |
| Butanol | 70 | .005050 | .004990 | | .005020 |
| Butanol | -9.2 | .015000 | .014900 | | .014950 |
| Carbon disulphide | 25 | .006350 | .006380 | | .006360 |
| Ethylene glycol | 25 | .000703 | .000709 | | .000706 |

TABLE 5(a)

Solubility of ethylene in butanol-ethylene glycol solutions at 25°C

| Mole.Fr. Butanol | Ostwald Coeff. | Mole fraction solubilities: Experimental | Eqn.7 | Eqn.8 | Eqn.10 |
|---|---|---|---|---|---|
| 0.0000 | 0.3128 | .000705 | | | |
| 0.0425 | 0.4492 | .001040 | .00078 | .00087 | .00107 |
| 0.1350 | 0.6040 | .001510 | .00098 | .00137 | .00171 |
| 0.3820 | 1.1631 | .003270 | .00180 | .00355 | .00357 |
| 0.4700 | 1.3063 | .003840 | .00223 | .00457 | .00423 |
| 0.5350 | 1.5117 | .004580 | .00262 | .00536 | .00472 |
| 0.7420 | 1.7096 | .005680 | .00436 | .00756 | .00628 |
| 0.7850 | 1.8198 | .006160 | .00484 | .00787 | .00660 |
| 1.0000 | 2.2252 | .008220 | | | |

TABLE 5(b)

Solubility of ethylene in hexane-dodecane solutions at 25°C

| | | | | | |
|---|---|---|---|---|---|
| 0.0000 | 3.9785 | .02080 | | | |
| 0.1675 | 3.4819 | .02037 | .02088 | .02113 | .02088 |
| 0.2575 | 3.2539 | .02019 | .02092 | .02133 | .02092 |
| 0.2920 | 3.1635 | .02004 | .02094 | .02132 | .02094 |
| 0.3650 | 3.0019 | .01986 | .02097 | .02141 | .02097 |
| 0.5090 | 2.9238 | .02097 | .02104 | .02151 | .02104 |
| 0.8220 | 2.6001 | .02176 | .02120 | .02147 | .02120 |
| 1.0000 | 2.3454 | .02129 | | | |

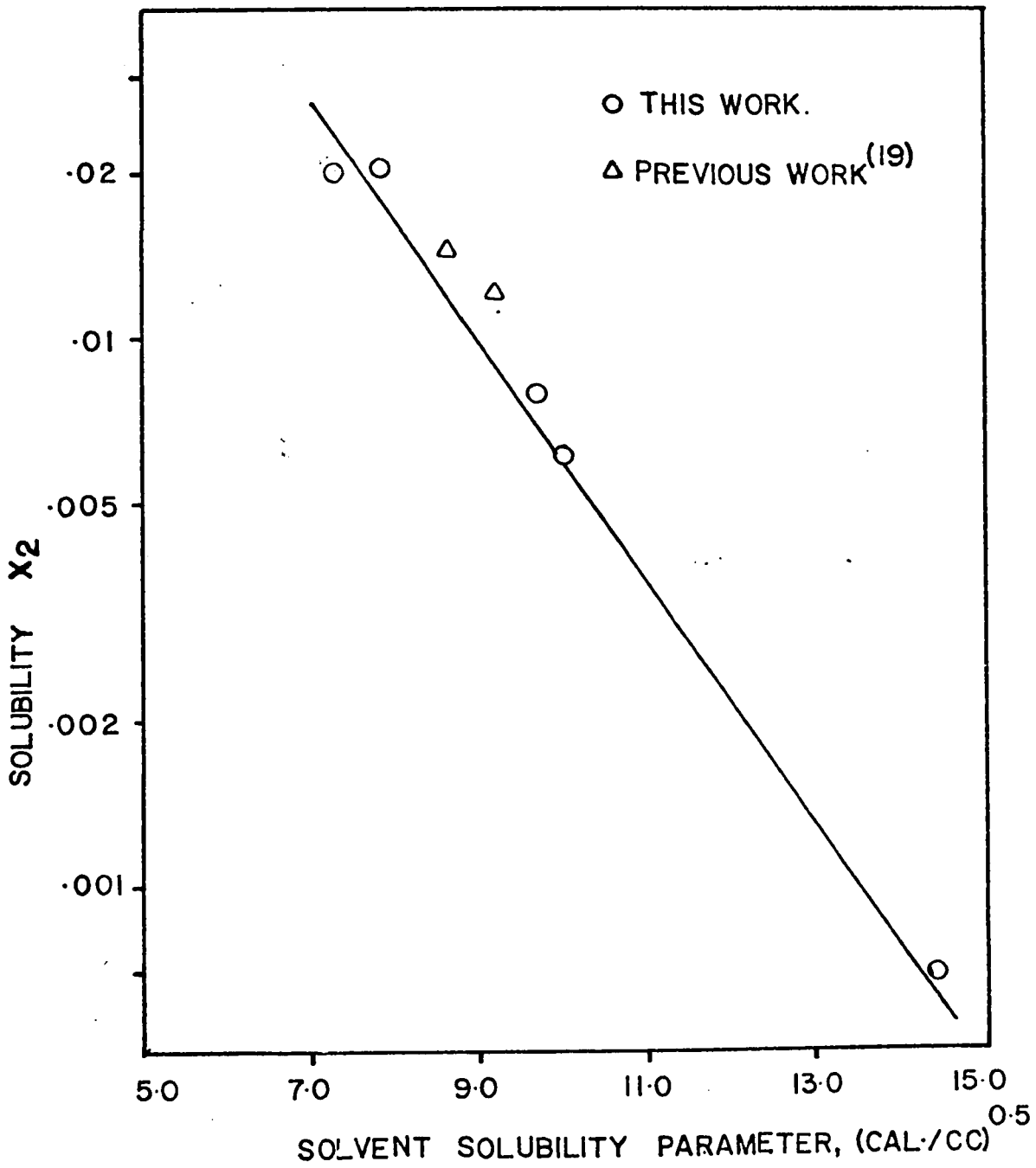


Fig. 8 Mole fraction solubility of ethylene vs. solvent parameter at 25°C

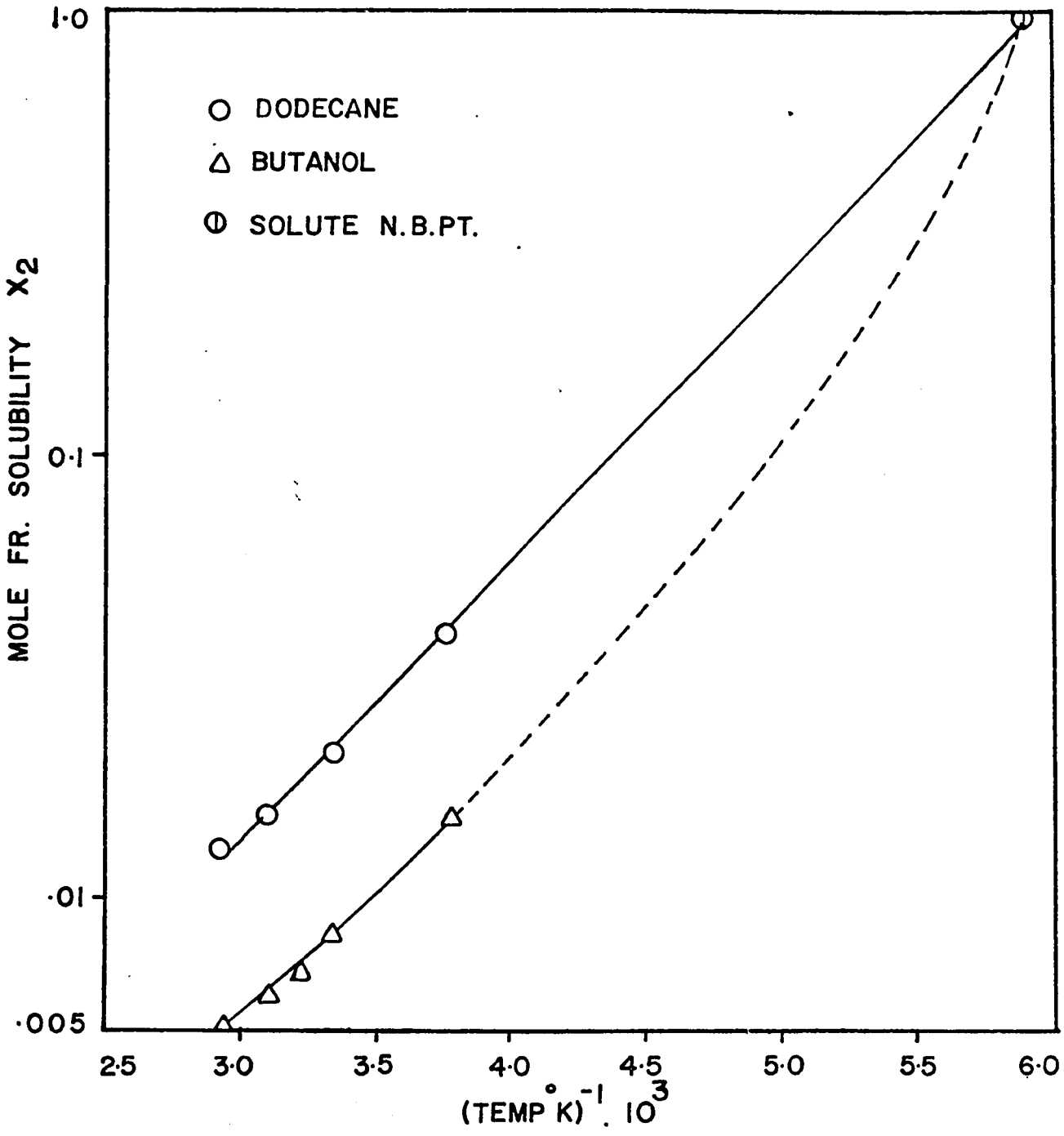


Fig. 9 Mole fraction solubility of ethylene vs. inverse temperature

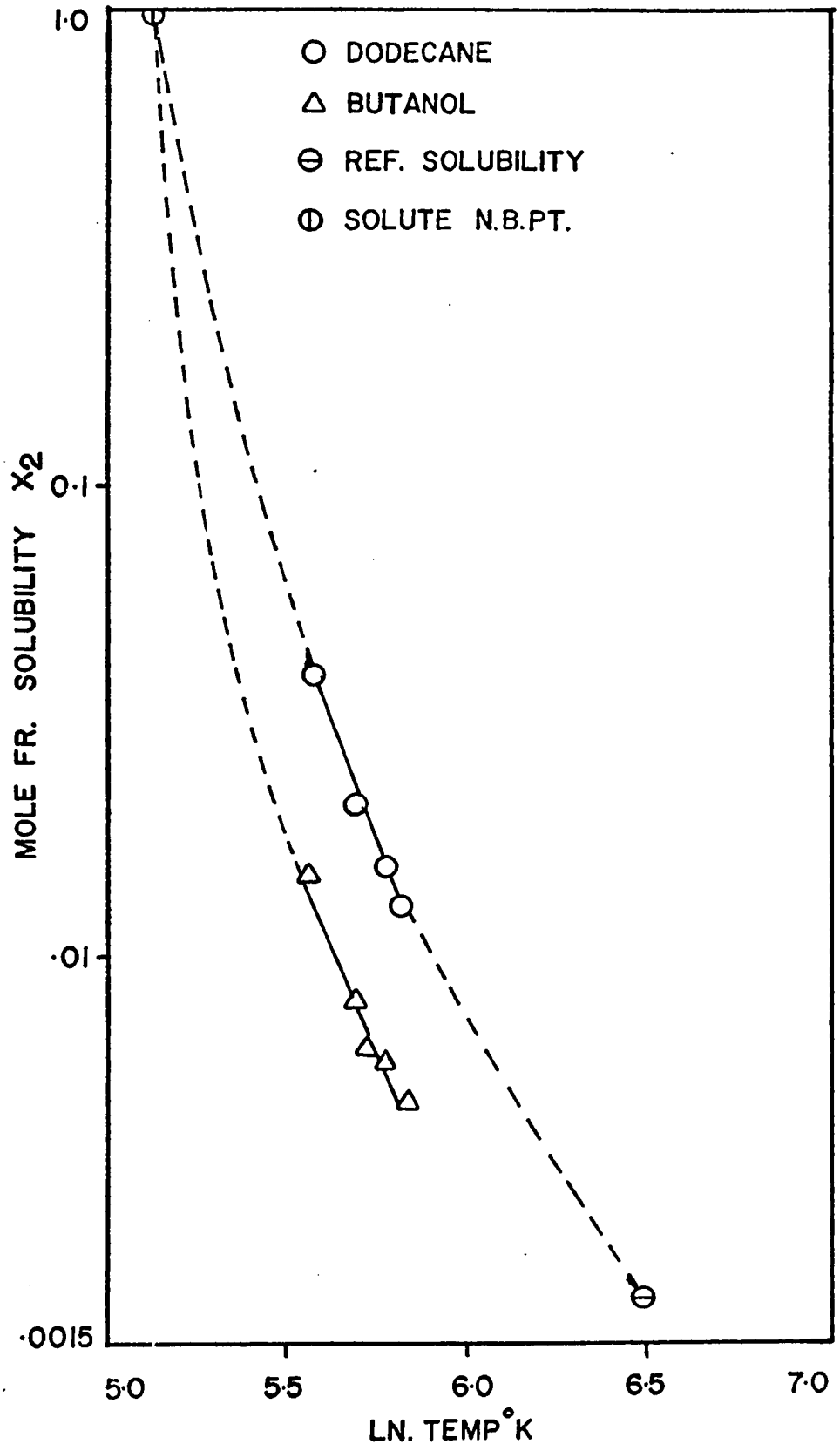


Fig. 10 Mole fraction solubility of ethylene vs ln temperature

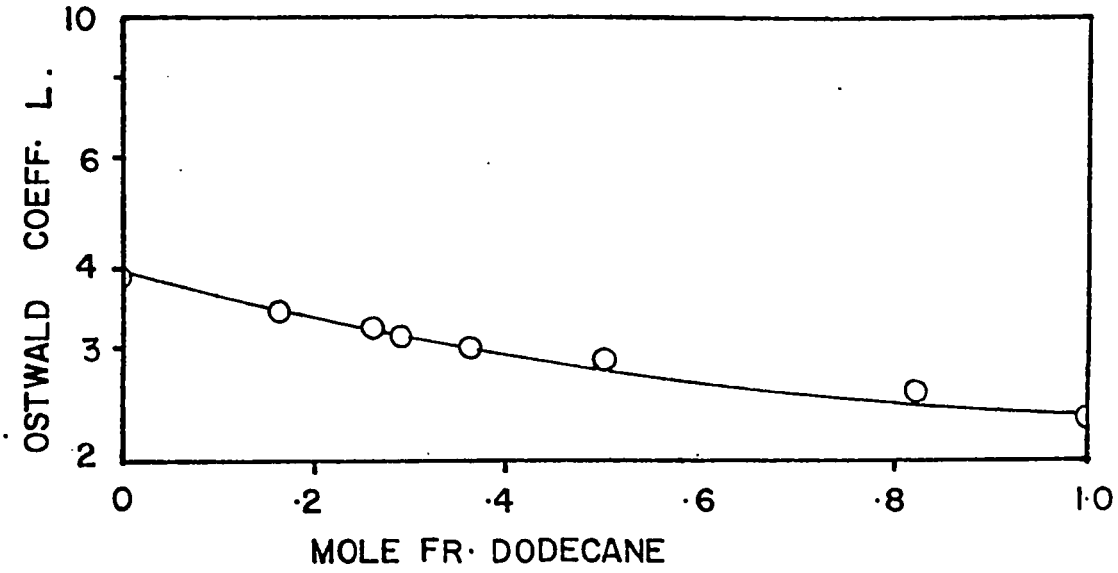


Fig. 11(a) Ostwald coefficient vs. hexane-dodecane solution composition at 25°C

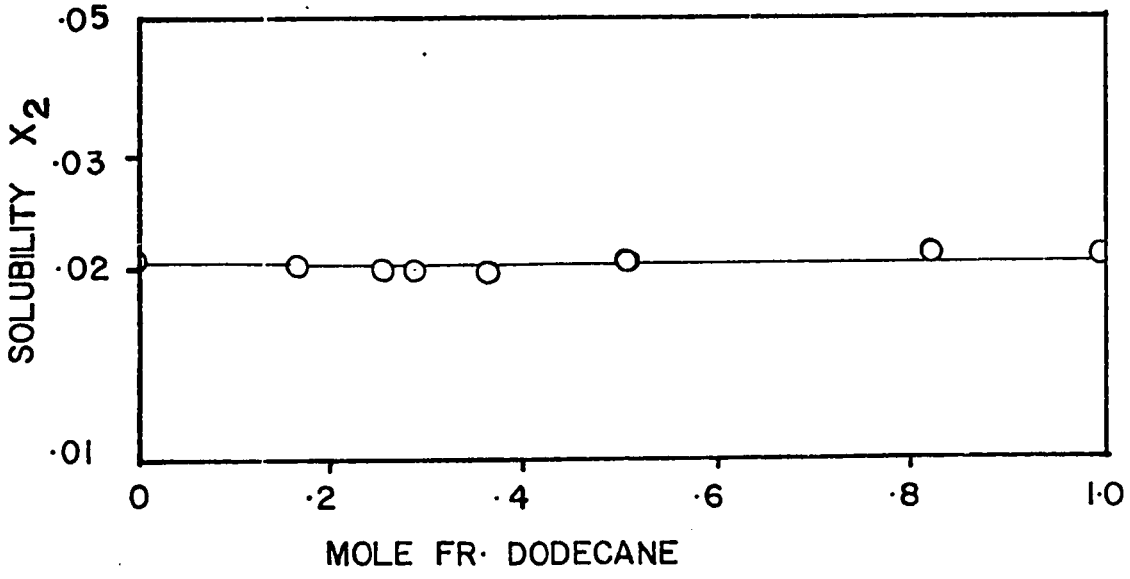


Fig. 11(b) Mole fraction solubility vs. hexane-dodecane solution composition at 25°C

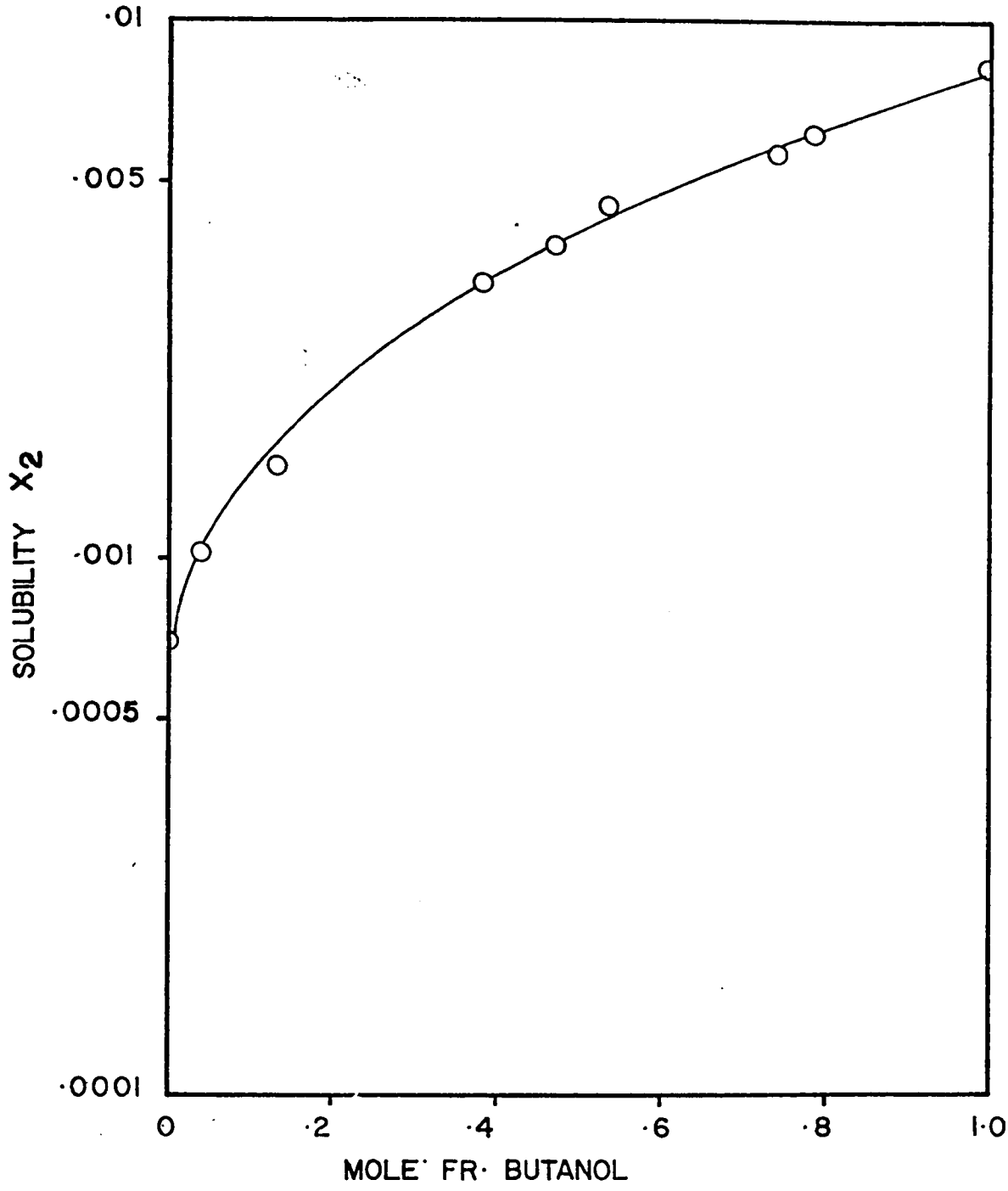


Fig. 12(a) Mole fraction solubility of ethylene in ethylene glycol solutions vs. solution composition at 25°C

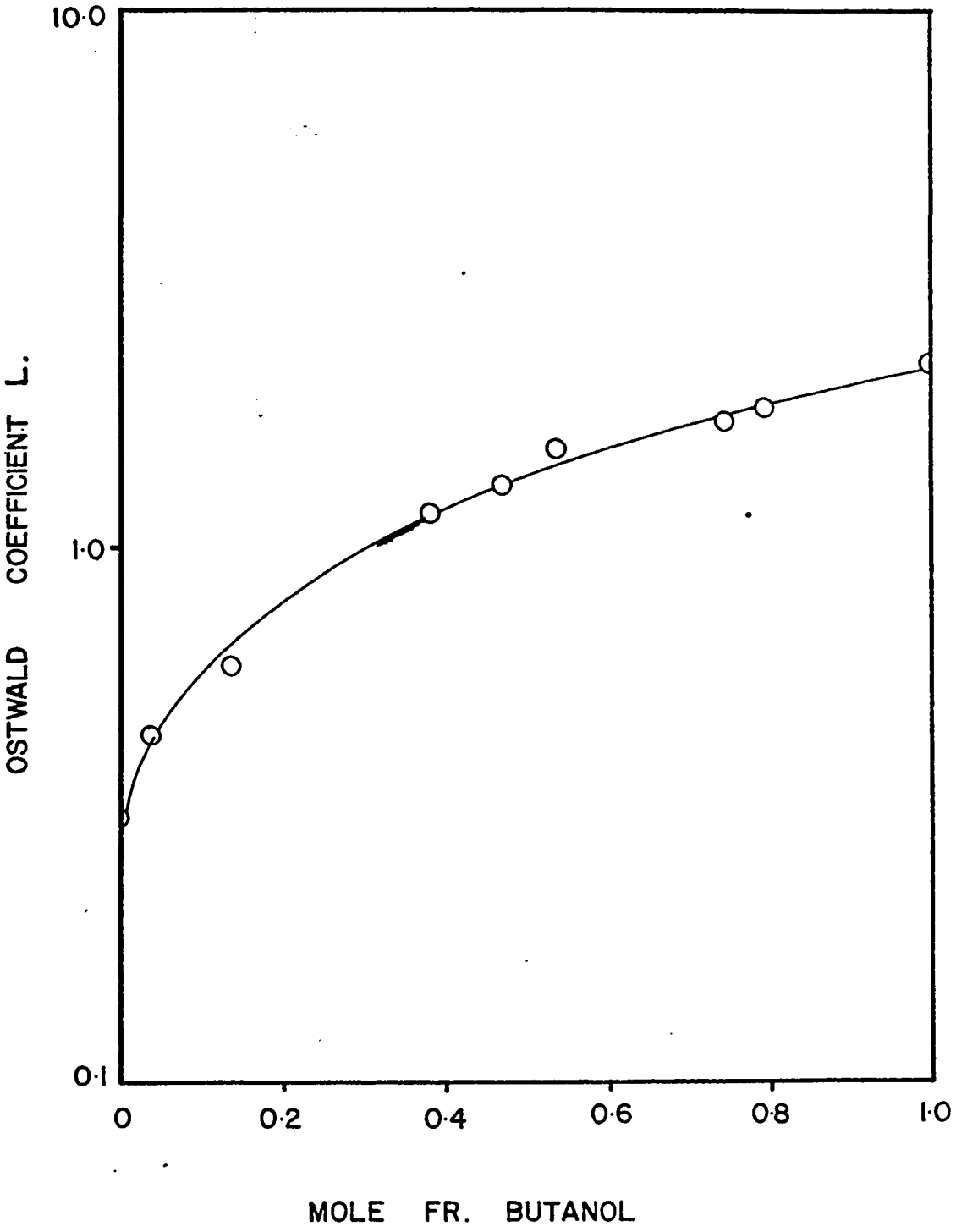


Fig. 12(b) Ostwald coefficients of ethylene in ethylene glycol-butanol solutions vs. solution composition at 25°C

## CONCLUSIONS

Solubility results for pure solvents at 25°C were compared for the two different methods; assuming Raoult's law and using equilibrium relations for ethylene fugacity. The latter method could not be used in case of ethylene glycol because the critical data required for calculations was not available. It was observed that the assumption of Raoult's law introduced an insignificant error so long as the solvent vapour pressure was less than one fifth of the total pressure of the system.

Experimentally determined ethylene solubility results were compared with values predicted by the regular solution theory. It was observed that regular solution theory does not describe the ethylene solubility in polar solvents well.

Log x versus log T and logx versus 1/T plots for ethylene solubility in dodecane at different temperatures show a linearity as observed in case of other gases such as for butane[26] and ethane in dodecane. For ethylene solubilities in butanol at different temperatures, solubility curves similar to those for inert gasses in water[28] were obtained. This behaviour can be attributed to hydrogen bonding and solute-solvent association due to the polar nature of butanol, and results in lower solubility values.

Ethylene solubility in hexane-dodecane solutions when plotted against solution composition shows a linearity. This is similar to the behaviour observed by O'Connell and Prausnitz[8]

as a result of their study with gas solubilities in non-polar systems. A similar plot for ethylene glybol-butanol solutions shows a positive deviation from the ideal solubility line, a trend similar to the one observed in case of hydrogen solubility in polar solvents.

# II. GAS DIFFUSIVITY

## INTRODUCTION

Mass transfer of a gas through a liquid occurs in two consecutive steps; first the dissolution of the gas in the liquid, and then the travel of the dissolved gas molecules through the liquid molecules as a result of a concentration gradient. Fick's law[31] describes the second part of this process and relates the molar flux to the concentration gradient and the constant of proportionality which is called the diffusion coefficient.

$$J_2 = -D_{21} \cdot \frac{\partial C_2}{\partial Z} \tag{14}$$

The diffusion coefficient is characteristic of the diffusing component and its solvent. The mechanism of molecular diffusion in liquids is considered to be a complex phenomenon and no confirmed theory for it has yet been established. Some models based on physical properties of the substance involved and on emperical correlations have been developed, however, some of which are presented here:

### (i) Wilke-Chang Equation:

One of the best known correlations is the one proposed by Wilke and Change in 1955[32].

$$D_{21} = \frac{7.4 \times 10^{-8} (X M_1)^{\frac{1}{2}} T}{\mu_1 . V_2^{0.6}} \tag{15}$$

This equation gives reasonable predictions for many systems. The main limitations of this are the use of the association parameter, $x_1$, which has to be determined experimentally for associated solvents. It has a value of 1 for unassociated solvents. Another limitation is that accuracy of the equation decreases with increasing solvent viscosity.

(ii) Scheibel Correlation:

Scheibel[33] developed an equation eliminating the association parameter; but in other respects, it was very similar to the Wilke-Chang equation.

$$D_{21} = \frac{8.2 \times 10^{-8} \; T \; . \left[1 + \left(\frac{3V_2}{V_1}\right)^{2/3}\right]}{\mu_1 . V_2^{1/3}} \qquad (16)$$

(iii) Reddy Correlation:

Another modification of the Wilke-Chang equation proposed by Reddy et al[34] also overcomes the use of the association parameter.

$$D_{21} = \frac{K . M_1^{\frac{1}{2}} T}{\mu_1 . V_2^{1/3} . V_1^{1/3}} \qquad (17)$$

The value of the constant, K, was considered to depend on the ratio $V_1/V_2$.

If $V_1/V_2 \leq 1.5$, $K = 10 \times 10^{-8}$

$V_1/V_2 > 1.5$, $K = 8.5 \times 10^{-8}$

(iv) Hayduk and Cheng Relation:

Hayduk and Cheng[35] proposed a simple correlation for diffusivities in liquids which relates the diffusivity of a dissolved substance to the solvent viscosity by an equation of the form:

$$D_{21} = A.\mu_1^{B} \tag{18}$$

This equation is satisfactory for some systems.

Diffusivity in Mixed Solvents:

Several emperical or semi-emperical correlations proposed in the past to predict diffusivities of gases in mixed solvents have not been conclusively tested as to their general applicability because of the lack of data. Tang[36] developed two alternate expressions for predicting effective binary diffusion coefficients in mixed solvents, provided the diffusivities in the pure solvents are known:

$$\mu_M^{\frac{1}{2}}.D_{2M} = X_1 D_{2.1}\mu_1^{\frac{1}{2}} + X_3 D_{2.3}\mu_3^{\frac{1}{2}} \tag{19}$$

$$\log(D_{2M}.\mu_M^{\frac{1}{2}}) = X_1 \log(D_{21}.\mu_1^{\frac{1}{2}}) + X_3 \log(D_{23}.\mu_3^{\frac{1}{2}}) \tag{20}$$

Tang and Himmelblau[37] also suggested three other correlations.

$$D_{2M} = \frac{1 - X_A}{\frac{X_1}{D_{21}} + \frac{X_3}{D_{23}}} \tag{21}$$

$$D_{2M} = X_1 D_{21} + X_3 D_{23} \tag{22}$$

$$D_{2M} \cdot \mu_M = X_1 D_{21} \mu_1 + X_3 D_{23} \mu_3 \qquad (23)$$

From the appearance of these equations, it is evident that the relationship between the binary and multicomponent diffusivities of dissolved gases is not well understood.

Theory of the Capillary Cell Method:

Diffusion coefficients were measured using the steady state capillary cell method described earlier by Hayduk and Malik[38] and later modified by Hayduk and Cheng[35]. The mathematical analysis has been elaborated earlier[38]. Using Fick's first law of diffusion and assuming the mass density of solute in the liquid approximately equal to that of the solvent, the following equation results:

$$D_{21} = \frac{n_2 \cdot \ell}{\rho \cdot \ell n \left(\frac{1 + W_{AO}}{1 + W_{AL}}\right)} \qquad (24)$$

Another equation similar to the one above can be derived by assuming constant molar concentrations along the diffusion path.

$$D_{21} = \frac{N_2 \ell}{c \cdot \ell n \left(\frac{1 + X_{AO}}{1 + X_{AL}}\right)} \qquad (25)$$

Treatment of Data:

The descent rate of a bead in the capillary, when expressed as a function of time yielded a slope, h, based on a least square fit of the data. The mass and molar flux were expressed by:

$$n_2 = h.P_A \frac{M_A}{V_G} \cdot \frac{A_1}{A_2} \tag{26}$$

$$N_2 = h.\frac{P_A}{V_G} \cdot \frac{A_1}{A_2} \tag{27}$$

The mass fraction of dissolved gas at the interface was evaluated from its solubility.

$$W_{AO} = \frac{L.P_A(M_A/V_G)}{P_L + L.P_A.\frac{M_A}{V_G}} \tag{28}$$

The second term in the denominator of equation (28) is negligible when compared with the first, so the equation can be simplified to:

$$W_{AO} = \frac{L.P_A.M_A}{P_L.V_G} \tag{29}$$

The concentration at the end of the capillary tube leading to the reservoir was assumed to remain zero; that is, the solvent was considered to remain deaerated during the complete experiment.

Apparatus and Procedure:

Each diffusion cell consisted of a capillary sealed in a closed reservoir which could be filled with the desired solvent by means of two high vacuum stop cocks located on either side of the reservoir, figure 13. The capillary stem was made up of two diameters, the upper portion having a diameter of .016" and the lower portion having a diameter of .040". The end of the lower capillary was conically

ground to facilitate the dissipation of solute. The time period to achieve steady state ranged from 10 hours to 5 days for the different solvents. It was, therefore, expedient to use two cells simultaneously for the diffusion measurements. The cells were immersed in a constant temperature, full-visibility bath controlled to ±.01°C. A cathetometer was used to observe the bead position while an electric timer was used to measure the rate of travel of the bead.

Solvent was degassed according to a procedure similar to that followed for the solubility measurements. The only difference was that the rubber septum at the bottom of the accumulation tube was replaced by a piece of tygon tubing closed by a pinchcock. The diffusion cells were cleaned and stopcocks greased using water resistant silicone grease on the extremities and paraffin wax in the centre. The cells were purged with gas and then flushed with several volumes of degassed solvent. The diffusion path length within the lower capillary was adjusted between 2 to 3 cm and the cells were placed in the bath. The capillary tubing of the cell was connected to a glass tee arrangement through which ethylene gas, dried with anhydrous calcium sulphate, was allowed to flow. Crank's equation[30] was used to estimate the time required to reach steady state:

$$\frac{D_t}{L^2} = 0.45 \qquad (30)$$

After a steady state diffusion rate had been reached, a droplet of solvent, saturated with ethylene was injected at

the top of the capillary with a syringe. Then the rate of descent of bead was measured.

Results and Discussion

Diffusivity results for ethylene in various solvents are presented in Table 6. A comparison of experimentally determined values and those predicted by equations (15, 16 and 17) is also shown in Table 7. The Wilke-Chang relation appears successful in predicting ethylene diffusivities in hexane, dodecane and butanol solvents. Deviation in the case of the diffusivity in hexane is about 9% whereas it increases with an increase in solvent viscosity.

The results have also been plotted as log $D_{21}$ versus solvent viscosity as shown in figure 14. All diffusivity values except for those in glycol, fall on a straight-line. This may be the result of its high viscosity and polar nature.

According to Ross and Hildebrand[39], the product $D\sigma^2$ is constant for the diffusion of a series of gases in a particular solvent. This observation has been verified for the diffusion of methane, ethane, propane[26] as well as ethylene in hexane and dodecane as shown in Table 9. Exact values of $\sigma$ were obtained from Flynn and Thodos[40]. Analysis of the result confirm the constancy of product $D\sigma^2$ for the systems considered. As might have been expected, the diffusion of methane, ethane, propane and ethylene is primarily dependent on the size of the diffusing molecules.

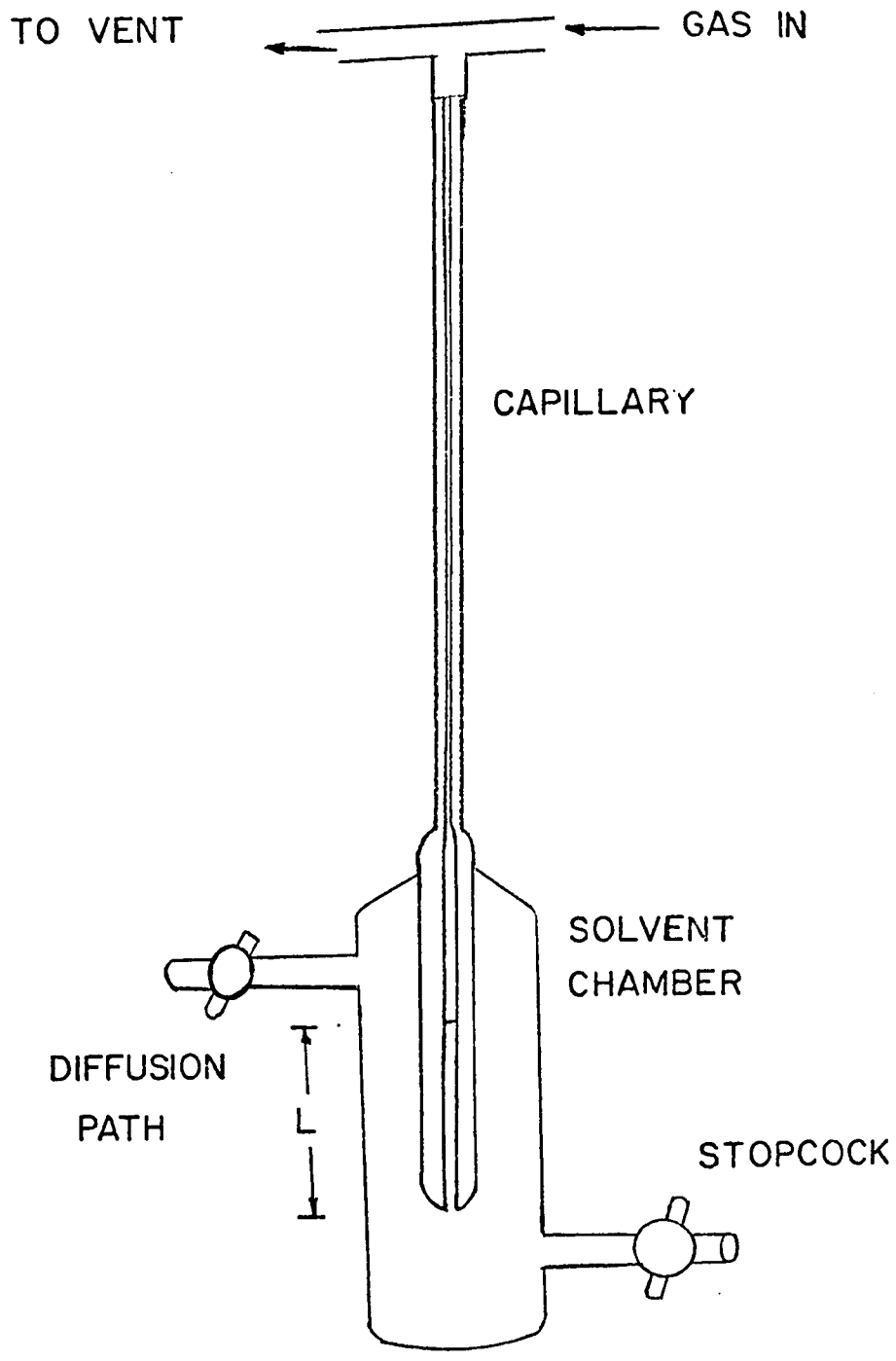


Fig. 13 Capillary Cell

TABLE 6

Diffusivity of dissolved ethylene at 25°C

| Solvent | D x $10^5$, $cm^2$/sec | | |
|---|---|---|---|
| | I | II | Average |
| Hexane | 7.795 | 7.532 | 7.663 |
| Dodecane | 3.060 | 3.115 | 3.087 |
| Butanol | 2.267 | 2.312 | 2.289 |
| Ethylene glycol | 0.371 | 0.365 | 0.368 |

TABLE 7

Comparison of ethylene diffusivities with correlations at 25°C

| Solvent | D x $10^5$, $cm^2$/sec | | | |
|---|---|---|---|---|
| | Experimental | Wilke | Scheibel | Reddy |
| Hexane | 7.663 | 6.979 | 4.541 | 4.254 |
| Dodecane | 3.087 | 2.125 | 0.815 | 1.047 |
| Butanol | 2.289 | 0.907 | 0.583 | 0.505 |
| Ethylene glycol | 0.368 | - | 0.107 | 0.083 |

TABLE 8

Comparison of predicted and experimental diffusion coefficients of ethylene in hexane-dodecane and butanol-ethylene glycol solutions at 25°C

| Mole fraction dodecane | $D_{2M} \times 10^5$ cm²/sec | | | |
|---|---|---|---|---|
| | Experimental | Equation 19 | Equation 21 | Equation 23 |
| .2350 | 5.774 | 5.645 | 5.998 | 6.036 |
| .4340 | 4.600 | 4.625 | 4.910 | 4.967 |
| .5331 | 4.194 | 4.243 | 4.521 | 4.550 |
| .8125 | 3.787 | 3.441 | 3.665 | 3.639 |
| **Mole fraction butanol** | | | | |
| .1800 | 0.549 | 0.434 | 0.545 | 0.567 |
| .3425 | 0.617 | 0.517 | 0.756 | 0.795 |
| .5150 | 0.695 | 0.648 | 1.059 | 1.101 |
| .7615 | 1.008 | 1.015 | 1.645 | 1.748 |
| .8280 | 1.249 | 1.199 | 1.836 | 1.834 |

TABLE 9

| σ,°A | Methane 3.808 | | Ethane 4.384 | | Propane 5.240 | | Ethylene 4.066 | |
|---|---|---|---|---|---|---|---|---|
| | D | Dσ² | D | Dσ² | D | Dσ² | D | Dσ² |
| Hexane | 8.64 | 125.4 | 5.79 | 111.28 | 4.48 | 123.01 | 7.66 | 126.63 |
| Dodecane | 3.94 | 57.2 | 2.73 | 52.46 | | | 3.08 | 50.92 |

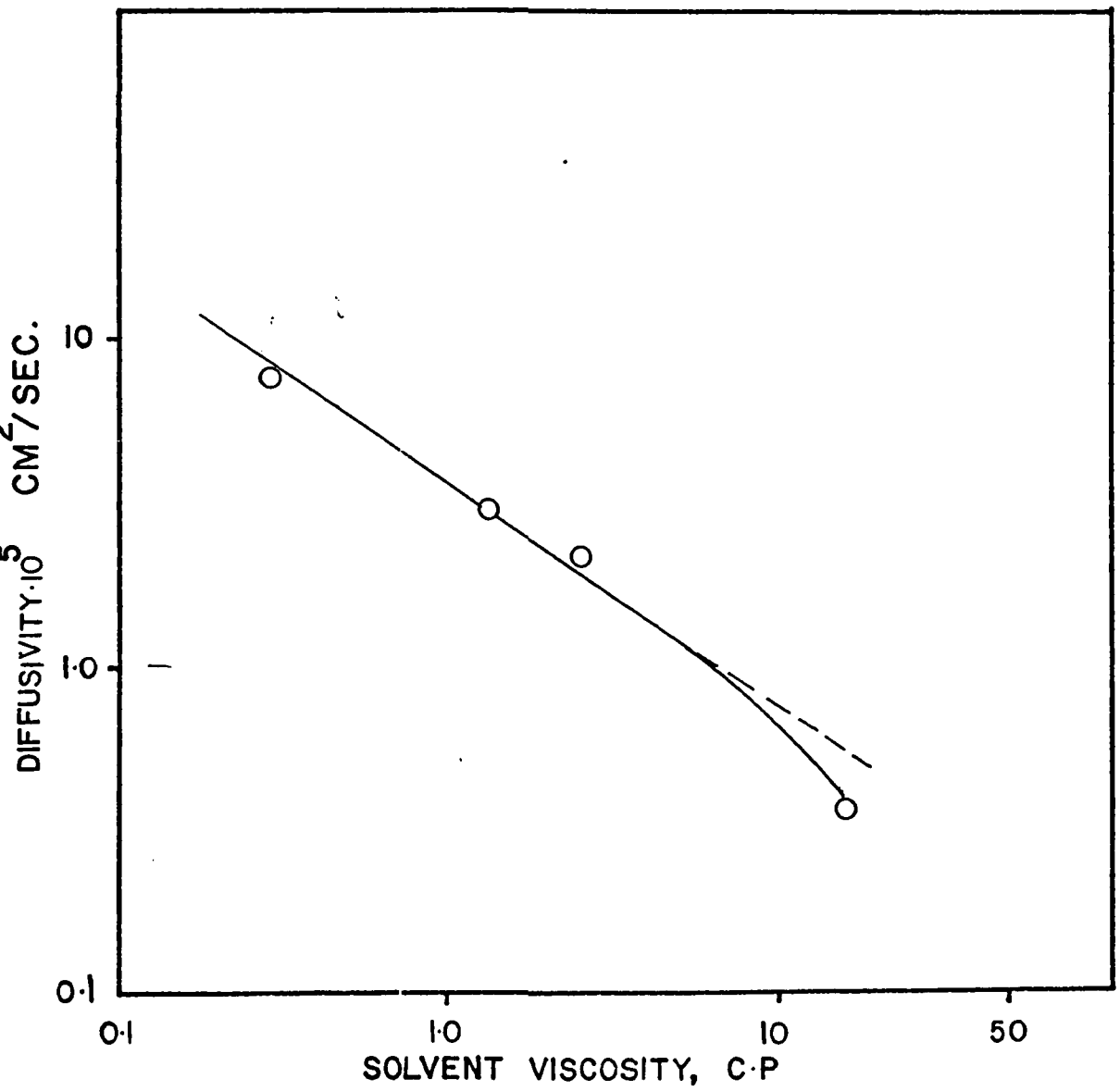


Fig. 14 Diffusivity vs. solvent viscosity at 25°C

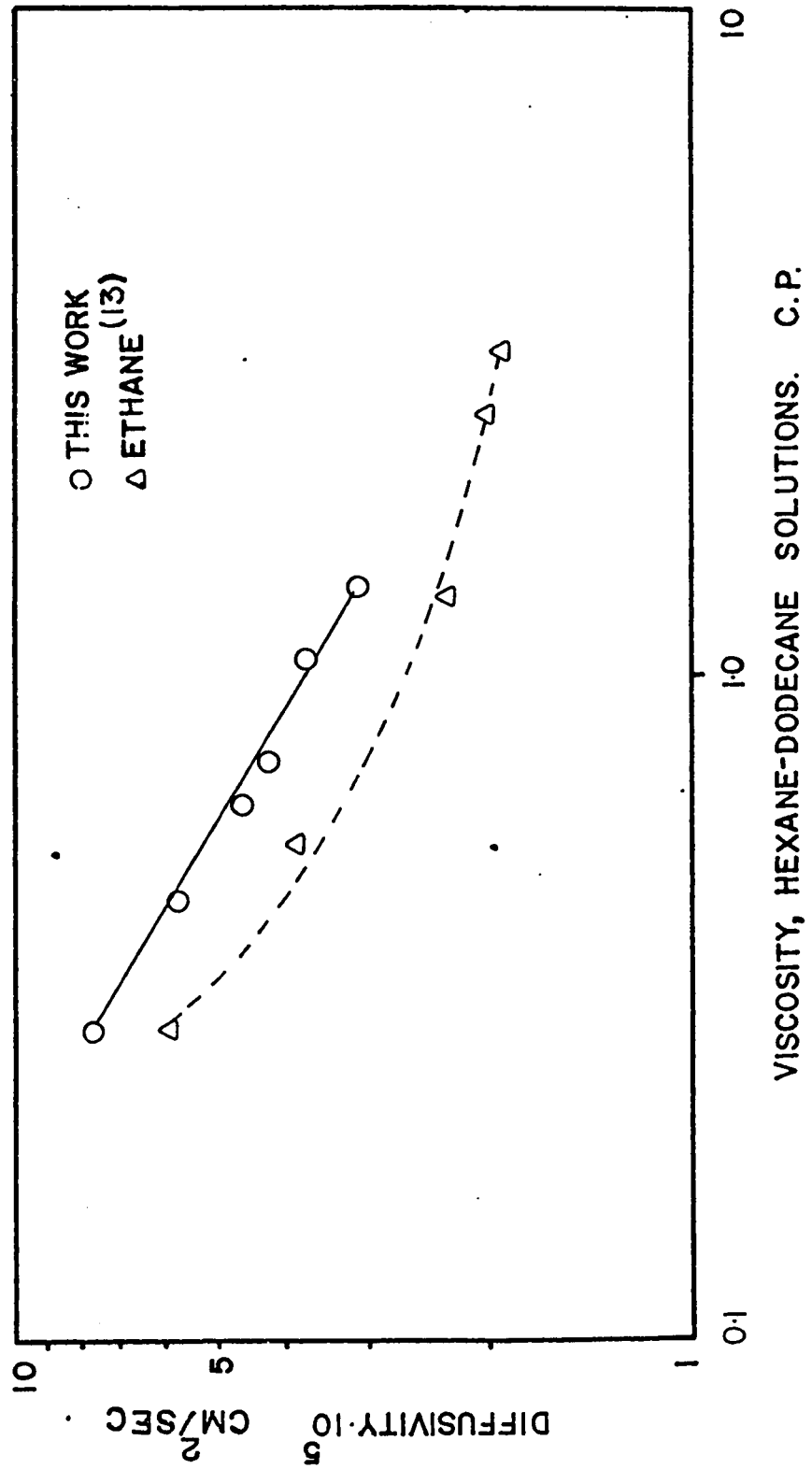


Fig. 15 Diffusivity vs. viscosity of hexane-dodecane solutions at 25°C

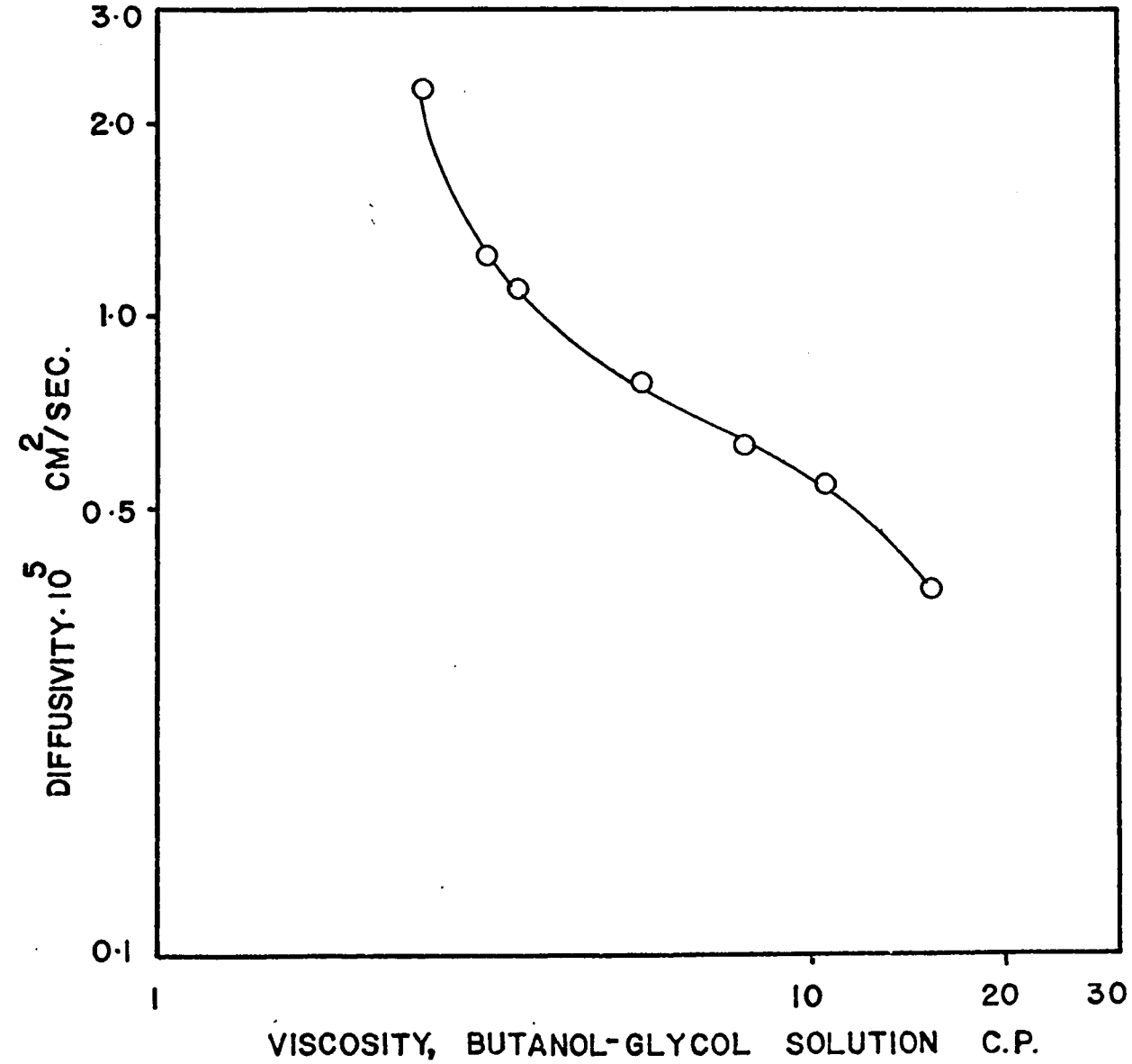


Fig. 16 Diffusivity vs. viscosity of ethylene glycol-butanol solutions at 25°C

Three of the several correlations suggested by Tang and Himmelblau[37], equations (19) and (21) and (23) for predicting ethylene diffusivities in solvent solutions were used. The remaining equations had previously been shown to be largely inapplicable by Cheng[13] for ethane diffusivities in mixed solvents.

The diffusion coefficients were calculated using experimental values for $D_{21}$ and $D_{23}$.

Although Tang and Himmelblau had studied gas diffusivities in several mixed solvents, yet their data showed only small differences in gas diffusivities in the particular solvent solutions. On the other hand, in this work, the solvent solutions were selected in such a manner that there was a significant difference in the viscosities of the solvent components. Hence the data obtained in this work should be more suited to test the validity of the correlations proposed.

Among the three equations tested, equation (19) was found to predict diffusivities most reliably. For hexane-dodecane solutions, an absolute average deviation of 3.2% was obtained and about 14% for the butanol-glycol solutions. Equations (21) and (23) predicted results for butanol glycol solutions with absolute average deviation of up to 50%, 60% respectively. Similar conclusions were drawn by Chang[13] while testing these equations for ethane diffusivities in mixed solvents in which case, equation (19) gave the best prediction of gas diffusivities.

Results have been plotted as log $D_{2M}$ versus log solution viscosity as shown in figures 15 and 16. It is interesting

to note that for the hexane-dodecane solution diffusivities lie on a straight line thereby reaffirming the model proposed by Hayduk and Cheng[35] that the diffusivity depends mainly on the solvent viscosity.

In the case of butanol-glycol solutions, however, a curve similar to the one obtained for $CO_2$ diffusivity in aqueous glycol solutions resulted. The diffusivity showed a large change with the addition of glycol in butanol-rich solutions and as the glycol content was increased, a linear relation was observed. Equation (19) appears to be more successful in predicting diffusivities in mixed polar solvents than does the relation of Hayduk and Cheng.

## CONCLUSIONS

A comparison of experimentally determined diffusivity results for ethylene in various solvents was made with those predicted by theoretical equations. The Wilke Chang relations appears to be the best and its accuracy decreases with increase in solvent viscosity.

Linearity of the plot log $D_{2,1}$ vs $\mu$ was observed with the exception of ethylene diffusivity in ethylene glycol. This may be expected due to high viscosity and polar nature of ethylene glycol.

Constancy of the product $D6^2$ was confirmed for systems involving ethane, methane, propane and ethylene. This shows that diffusion of these gases is primarily dependent on the size of the diffusing molecules.

Ethylene diffusivity results in hexane-dodecane solutions were plotted as log $D_{2,M}$ versus log $\mu_M$. Linearity of the plot reaffirms the model proposed by Hayduk and Cheng[35] that the diffusivity depends mainly on the solvent viscosity. However this model fails for the case of butanol-ethylene glycol solution. This may be due to the highly polar nature of these solvents which makes the diffusivity predictions more complicated.

## REFERENCES


1. Hildebrand, J.H. and Scott, R.L., "Regular Solutions" 14, Prentice Hall Inc., 1962.

2. Prausnitz, J.M., "Molecular Thermodynamics of Fluid Phase Equilibria", 352, Prentice Hall Inc., 1969.

3. Hildebrand, J.H. and Scott, R.L., "Solubilities of non-electrolytes", 46, Dover Publ. Inc., N.Y., 1964.

4. Burell, H., Interchem. Rev. 14, 31, 1955.

5. Gjaldbeck, J., Anderson, E.K., Ibid 8, 1398 (1954).

6. Krischevsky, I.R., Zh. Fiz. Khim. 9, 41 (1937).

7. Wohl, K., Trans. AIChE., 17, 658 (1971).

8. O'Connell, J.P. and Prausnitz, J.M., Ind. Eng. Chem. Fundamentals, 3, 347 (1964).

9. O'Connell, J.P., AIChE., 17, 658 (1971).

10. Tassios, D., AIChE., 17, 1367 (1971).

11. Prausnitz, J.M. and Chueh, P.L., "Computer Calculations for High Pressure Vapour-Liquid Equilibria", Prentice Hall, N.J. 1968.

12. Puri, P.S. and Ruether, J.A., Can. J. Chem. Eng., 52, 636 (1974).

13. John Cheng, MASc. Thesis, U. of Ottawa, 1969.

14. Hayduk, W. and Cheng, S.C., Can. J. Chem. Eng., 48, 93 (1970).

15. Rossini et al., Am. Pet. Inst. Research Project, 44, Circular of the Natl. Bur. Standards (1947).

16. Riddick, W.P., "Techniques of Organic Chemistry", (Organic Solvents), 1955.

17. Handbook Phy. and Chem., 52nd Edition, 1971-72.

18. Din., "Thermodynamic Functions of Gases", Vol. II, 1956.

19. Wilhelm, E. and Baltino, R., "Thermodynamic Functions of the Solubilities of Gases in Liquids at 25°C", Chem. Reviews, 73, (1973).

20. Rossini, D.F., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds", 1953.

21. Bulter et al., J. Chem. Soc., 138, 280 (1935).

22. Perry, J.H., "Chemical Engineers Handbook", 4th Ed., McGraw-Hill Book Co., New York (1963).

23. "International Critical Tables", McGraw-Hill Book Company, Inc., N.Y., 1928.

24. Fleury, D., MASc. Thesis, U. of Ottawa, 1973.

25. Kobatake, Y. and Hildebrand, J.H., J. Phys. Chem., 65, 331 (1961).

26. Castenada, R., MASc. Thesis, U. of Ottawa, 1971.

27. Picker, P., Tremblay, E. and Jolicoeur, C., "Journal of Solution Chemistry", Vol. 3, No. 5, (1974).

28. Hayduk, W. and Buckley, W.D., Can. J. Chem. Eng., 49, (1971).

29. Miller, K.W. and Hildebrand, J.H., J. Am. Chem. Soc., 90, 3001 (1968).

30. Crank, J. "Mathematics of Diffusion", Clarendon Press, Oxford, England, 1957.

31. Treybal, R.E., "Mass Transfer Operations", 2nd Ed., McGraw-Hill, N.Y., 1968.

32. Wilke, C.R. and Chang, P., AIChE., 1, 264 (1954).

33. Sheibel, E.G., Ind. Eng. Chem., 46, 2007 (1954).

34. Reddy, K.A. and Doraiswamy, L.K., Ind. and Eng. Chem. Fundamentals, 6, 77 (1967).

35. Hayduk, W. and Cheng, S.C., Chem. Eng. Sci., 26, (1971).

36. Tang, Y.P., PhD. Dissertation, U. of Texas, (1963).

37. Tang, U.P. and Himmelblau, D.M., Chem. Eng. Sci., 20. 7 (1965).

38. Malik, V.K. and Hayduk, W., Can. J. Chem. Eng., 46, 462 (1968).

39. Ross, M. and Hildebrand, J.H., J. Chem. Phys., 40, 2397 (1964).

40. Flynn, L.W. and Thodos, G., AIChE., 8, 362 (1962).

# APPENDIX I

## Raw Experimental Data for Solubility Measurements at 25°C.

Run No. : 1

System : Ethylene-Hexane

Temperature : 25°C

Bar. Pressure : 753 ml

| Solution Volume c.c. | Vol. of Gas Absorbed c.c. |
|---|---|
| 0.0 | 0 |
| 0.42 | 1.35 |
| 0.58 | 1.90 |
| 0.96 | 2.80 |
| 1.28 | 3.75 |
| 1.60 | 4.70 |
| 1.92 | 5.65 |
| 2.24 | 6.50 |
| 2.55 | 7.40 |
| 2.86 | 8.40 |
| 3.18 | 9.35 |
| 3.50 | 10.35 |
| 3.80 | 11.25 |

Ostwald coefficient = 3.9785

mole fraction solubility = 0.0208

## SAMPLE CALCULATIONS:

### Ethylene solubility in ethylene glycol-butanol solution at 25°C

R.I. solution = 1.4035

$\rho_{SOLN}$ = 0.8510 gm/ml

Butanol mole fraction = .785

Glycol mole fraction = .215

Molecular weight (Avg) = .785 x 74 + .215 x 62 = 71.42

Molar volume of solution = $\frac{M_{AVG}}{\rho_{SOLN}} = \frac{71.42}{.851} = 83.92479 \frac{ml}{gm.mole}$

Slope, $h_s$ = $1.79774 \frac{ml.gas}{ml.soln}$

Atmospheric pressure = 753 mmHg

Butanol vapour pressure = 678 mmHg

Ethylene molar volume = 24639.0284ml/gm.mole

Ethylene partial molar volume = 71.4531 ml/gm./mole

Assuming x = .00616

$$L = \frac{1.79774 \times 753}{753 - 678 \times .785(1 - .00616)} \times \frac{1}{1 - \frac{1.79774 \times 753 \times 71.4531}{760 \times 24639.0284}}$$

$$= 1.81986$$

$$x = \frac{1.81986}{1.81986 + \frac{24639.0284}{83.92479}}$$

$$= .00616$$

# APPENDIX II

## Raw Experimental Data for Diffusivity Measurements at 25°C:

Run No. : A-1
System : Ethylene, n-Hexane
Bar. Pressure: 763 mmHg
Diffusion Path Length: 2.469 cm

| Time Sec. | Bead Movement cm |
|---|---|
| 1000 | .820 |
| 2000 | 1.625 |
| 3000 | 2.321 |
| 4000 | 3.132 |
| 5000 | 3.975 |
| 6000 | 4.689 |

Slope : $.777 \times 10^{-3}$ cm/sec
$D = 7.795 \times 10^{-5}$ cm$^2$/sec

Run No. : A-2
System : Ethylene-n-Hexane
Bar. Pressure: 763 mm
Diffusion Path Length: 2.220 cm

| Time Sec. | Bead Movement cm |
|---|---|
| 1000 | .841 |
| 2000 | 1.661 |
| 3000 | 2.592 |
| 4000 | 3.367 |
| 5000 | 4.163 |

Slope : $.835 \times 10^{-3}$ cm/sec
$D = 7.532 \times 10^{-5}$ cm$^2$/sec

Run No. : B-1
System : Ethylene-Dodecane
Bar. Pressure: 746 mmHg
Diffusion Path Length: 2.003 cm

| Time Sec. | Bead Movement cm |
|---|---|
| 1000 | .225 |
| 2000 | .458 |
| 3000 | .668 |
| 4000 | .902 |
| 5000 | 1.122 |
| 6000 | 1.341 |
| 7000 | 1.582 |

Slope : $.224 \times 10^{-3}$ cm/sec
$D = 3.060 \times 10^{-5}$ cm$^2$/sec

Run No. : B-2
System : Ethylene-Dodecane
Bar. Pressure: 746 mm
Diffusion Path Length: 2.066 cm

| Time Sec. | Bead Movement cm. |
|---|---|
| 1000 | .217 |
| 2000 | .429 |
| 3000 | .648 |
| 4000 | .879 |
| 5000 | 1.108 |
| 6000 | 1.326 |
| 7000 | 1.532 |

Slope : $.221 \times 10^{-3}$ cm/sec
$D = 3.115 \times 10^{-5}$ cm$^2$/sec

Run No. : C-1
System : Ethylene-Butanol
Bar. Pressure: 753.5 mmHg
Diffusion Path Length: 2.214 cm

| Time Sec. | Bead Movement cm |
|---|---|
| 1500 | .207 |
| 3200 | .441 |
| 4500 | .619 |
| 6100 | .872 |
| 7500 | 1.068 |
| 9000 | 1.281 |
| 11000 | 1.542 |

Slope : $.142 \times 10^{-3}$ cm/sec

$D = 2.267 \times 10^{-5}$ $cm^2$/sec

Run No. : C-2
System : Ethylene-Butanol
Bar. Pressure: 753.5 mm
Diffusion Path Length: 2.094

| Time Sec. | Bead Movement cm |
|---|---|
| 1500 | .220 |
| 3100 | .452 |
| 4600 | .678 |
| 5500 | .829 |
| 7000 | 1.072 |
| 8300 | 1.262 |
| 9500 | 1.433 |
| 11000 | 1.669 |

Slope : $.153 \times 10^{-3}$ cm/sec

$D = 2.312 \times 10^{-5}$ $cm^2$/sec

Run No. : D-1
System : Ethylene-Ethylene Glycol
Bar. Pressure: 748.5 mmHg
Diffusion Path Length: 2.394 cm

| Time Hrs. | Bead Movement cm |
|---|---|
| 25 | .243 |
| 50 | .489 |
| 75 | .731 |
| 100 | .976 |
| 125 | 1.229 |

Slope : .00983 cm/hr

$D = 0.371 \times 10^{-5}$ $cm^2$/sec

Run No. : D-2
System : Ethylene-Ethylene Glycol
Bar. Pressure: 758.5 mmHg
Diffusion Path Length: 2.322 cm

| Time Hrs. | Bead Movement cm |
|---|---|
| 25 | .249 |
| 50 | .500 |
| 75 | .746 |
| 100 | .997 |
| 125 | 1.247 |

Slope : .00997 cm/hr

$D = 0.365 \times 10^{-5}$ cm /hr

Run No. : E-1
System : Ethylene, n-Hexane and Dodecane
Solvent comp.: 0.2350 mf Hexane
0.7650 mf Dodecane
Bar. Pressure: 763.5 mmHg
Diffusion Path Length: 2.266 cm

| Time Sec. | Bead Movement cm |
|---|---|
| 900 | .364 |
| 1500 | .658 |
| 2500 | 1.122 |
| 3300 | 1.511 |
| 4000 | 1.902 |
| 4800 | 2.258 |
| 5500 | 2.620 |

Slope : $.4905 \times 10^{-3}$ cm/sec
$D = 5.749 \times 10^{-5}$ $cm^2$/sec

Run No. : E-2
System : Ethylene, n-Hexane and Dodecane
Solvent comp.: 0.235 mf Dodecane
0.765 mf Hexane
Bar. Pressure: 763.5 mmHg
Diffusion Path Length: 2.323 cm

| Time Sec. | Bead Movement cm |
|---|---|
| 1000 | .437 |
| 1800 | .815 |
| 2500 | 1.182 |
| 3300 | 1.510 |
| 4000 | 1.878 |
| 4500 | 2.118 |
| 5000 | 2.381 |

Slope : $.4826 \times 10^{-3}$ cm/sec
$D = 5.7989 \times 10^{-5}$ $cm^2$/sec

Run No. : F-1
System : Ethylene, n-Hexane and Dodecane
Solvent comp.: 0.434 mf Dodecane
0.566 mf Hexane
Bar. Pressure: 762.25 mm
Diffusion Path Length: 2.170

| Time Sec. | Bead Movement cm |
|---|---|
| 1000 | .363 |
| 1750 | .642 |
| 2500 | .985 |
| 3300 | 1.286 |
| 4000 | 1.545 |
| 4750 | 1.818 |
| 6000 | 2.350 |

Slope: $.3913 \times 10^{-3}$ cm/sec
$D = 4.600 \times 10^{-5}$ $cm^2$/sec

Run No. : G-1
System : Ethylene, n-Hexane and Dodecane
Solvent comp.: 0.533 mf Dodecane
0.467 mf Hexane
Bar. Pressure: 753.5 mm
Diffusion Path Length: 2.325

| Time Sec. | Bead Movement cm. |
|---|---|
| 1000 | .366 |
| 1900 | .698 |
| 2900 | 1.084 |
| 4000 | 1.521 |
| 4750 | 1.792 |
| 5500 | 2.055 |
| 6000 | 2.224 |

Slope: $.370 \times 10^{-3}$ cm/sec
$D = 4.2066 \times 10^{-5}$ $cm^2$/sec

Run No. : G-2
System : Ethylene, n-Hexane and Dodecane
Solvent comp.: 0.533 mf Dodecane
0.467 mf Hexane
Bar. Pressure: 753.5 mmHg
Diffusion Path Length: 2.116 cm

| Time Sec. | Bead Movement cm |
|---|---|
| 1000 | .358 |
| 1800 | .659 |
| 2500 | .941 |
| 3500 | 1.356 |
| 4250 | 1.642 |
| 5000 | 1.955 |
| 6000 | 2.362 |
| 6500 | 2.584 |

Slope: $.404 \times 10^{-3}$ cm/sec

$D = 4.182 \times 10^{-5}$ $cm^2/sec$

Run No. : H-1
System : Ethylene, n-Hexane and Dodecane
Solvent comp.: 0.812 mf Dodecane
0.188 mf Hexane
Bar. Pressure: 758.25 mmHg
Diffusion Path Length: 2.384 cm

| Time Sec. | Bead Movement cm |
|---|---|
| 1000 | .252 |
| 2000 | .522 |
| 2900 | .738 |
| 3750 | .992 |
| 4500 | 1.172 |
| 5000 | 1.275 |
| 5500 | 1.401 |
| 6300 | 1.587 |

Slope: $.252 \times 10^{-3}$ cm/sec

$D = 3.787 \times 10^{-5}$ $cm^2/sec$

Run No. : I-1
System : Ethylene, Butanol and Ethylene Glycol
Solvent comp.: 0.180 mf Butanol
0.920 mf Glycol
Bar. Pressure: 756.5 mmHg
Diffusion Path Length: 2.690 cm

| Time Min. | Bead Movement cm |
|---|---|
| 200 | .113 |
| 325 | .167 |
| 425 | .228 |
| 500 | .284 |
| 600 | .312 |
| 700 | .375 |
| 800 | .417 |
| 1350 | .722 |

Slope: $.528 \times 10^{-3}$ cm/min

$D = 0.549 \times 10^{-5}$ $cm^2/sec$

Run No. : J-1
System : Ethylene, Butanol and Ethylene Glycol
Solvent comp.: 0.3425 mf Butanol
0.6575 mf Glycol
Bar. Pressure: 754.5 mmHg
Diffusion Path Length: 2.384 cm

| Time Min. | Bead Movement cm |
|---|---|
| 90 | .088 |
| 180 | .187 |
| 275 | .282 |
| 350 | .369 |
| 400 | .400 |
| 500 | .517 |
| 590 | .615 |
| 675 | .678 |

Slope: $1.020 \times 10^{-3}$ cm/min

$D = 0.636 \times 10^{-5}$ $cm^2/sec$

Run No. : J-2
System : Ethylene, Butanol and Ethylene Glycole
Solvent comp.: 0.3425 mf Butanol
0.6575 mf E.Glycol
Bar. Pressure: 754.5 mmHg
Diffusion Path Length: 2.625 cm

| Time Min. | Bead Movement cm |
|---|---|
| 100 | .101 |
| 180 | .161 |
| 275 | .260 |
| 400 | .379 |
| 500 | .453 |
| 580 | .512 |
| 650 | .579 |

Slope: $.872 \times 10^{-3}$ cm/min
$D = 0.598 \times 10^{-5}$ $cm^2/sec$

Run No. : K-1
System : Ethylene, Butanol and Ethylene Glycol
Solvent comp.: 0.515 mf Butanol
0.485 mf E.Glycol
Bar Pressure: 762.25 mmHg
Diffusion Path Length: 2.245 cm

| Time Min. | Bead Movement cm |
|---|---|
| 100 | .150 |
| 200 | .301 |
| 290 | .453 |
| 380 | .594 |
| 450 | .698 |
| 550 | .872 |
| 665 | 1.302 |

Slope: $1.910 \times 10^{-3}$ cm/min
$D = 0.800 \times 10^{-5}$ $cm^2/sec$

Run No. : K-2
System : Ethylene, Butanol and Ethylene Glycol
Solvent comp.: 0.515 mf Butanol
0.485 mf E.Glycol
Bar. Pressure: 762.25 mmHg
Diffusion Path Length: 3.065 cm

| Time Min. | Bead Movement cm |
|---|---|
| 100 | .145 |
| 175 | .260 |
| 275 | .400 |
| 350 | .516 |
| 450 | .645 |
| 540 | .752 |
| 625 | .877 |

Slope: $1.380 \times 10^{-3}$ cm/min
$D = .789 \times 10^{-5}$ $cm^2/sec$

Run No. : L-1
System : Ethylene, Butanol and Ethylene Glycol
Solvent comp.: 0.7615 mf Butanol
0.2385 mf E.Glycol
Bar. Pressure: 758.25 mmHg
Diffusion Path Length: 2.680 cm

| Time Min. | Bead Movement cm |
|---|---|
| 120 | .311 |
| 200 | .549 |
| 290 | .803 |
| 350 | .965 |
| 430 | 1.178 |
| 510 | 1.401 |
| 600 | 1.630 |

Slope: $2.743 \times 10^{-3}$ cm/min
$D = 1.008 \times 10^{-5}$ $cm^2/sec$

Run No. : M-1

System : Ethylene, Butanol and
Ethylene Glycol

Solvent Comp.: 0.828 mf Butanol
0.172 mf E.Glycol

Bar. Pressure: 760.5 mmHg

Diffusion Path Length: 2.941 cm

| Time Min. | Bead Movement cm. |
|---|---|
| 90 | .281 |
| 175 | .582 |
| 250 | .865 |
| 300 | 1.025 |
| 325 | 1.151 |
| 400 | 1.427 |
| 500 | 1.761 |

Slope: $3.644 \times 10^{-3}$ cm/min

$D = 1.249 \times 10^{-5}$ $cm^2$/sec

## SAMPLE CALCULATIONS

Ethylene diffusivity in butanol-ethylene glycol solution at 25°C : Run No. : L-1

| | | |
|---|---|---|
| R.I. Solution | = | 1.4040 |
| $\rho_{SOLN}$ | = | 0.856 gm/ml |
| Butanol mole fraction | = | .7615 |
| Glycol mole fraction | = | .2385 |
| Solubility data | : | x = .0062, L = 1.80 |
| Ethylene molar volume | = | 24639.0284 ml/gm.mole |
| Butanol vapour pressure | = | 6.78 mm at 25°C |
| Diffusion path length | = | 2.704 cm |
| Atmospheric pressure | = | 758.25 mm |
| Slope, h | = | .0027434 cm/min |
| Ratio of capillary areas | = | $\frac{A_1}{A_2} = \frac{4}{25}$ |

$$W_{AO} = \frac{1.8 \{758.25 - 6.78 \times .7615(1 - .0062)\} 28.04}{760 \times 24639.0284 \times .856}$$

$$= .002371 \text{ gm/ml}$$

$$D = \frac{.0027434}{60} \times \frac{4}{25} \frac{\{758.25 - 6.78 \times .7615(1 - .0062)\} 28.04}{760 \times 0.856 \times 24639.00284}$$

$$\times \frac{2.704}{\ell n(1 + .002371)}$$

$$= 1.008 \times 10^{-5} \text{ cm}^2/\text{sec}$$

# APPENDIX II

Calculation of Henry's Constant:

System: Ethylene-Hexane at 25°C, 7'

$x = 0.0208 \quad P = 753$ mm Hg. $\quad P_1^0 = 151.2$ mm Hg.

$\omega_{ij} = 191$

$T_{cij} = 378.5368$

$V_{cij} = 228.69$

$z_{cij} = .270$

$P_{cij} = .4469R$

$B_{11} = -23.2165R$

$B_{22} = -1.7292R$

$B_{12} = -507.3245$

$\delta_{12} = 1032.1456$

$f_1^L = (1-x_2)P_1^0 = f_1^V = \phi_1(1-y_2)P$

$f_1^V = 148.055 = \phi_1(1-y_2)P$

$\phi_1(1-y_2)P = 148.055$

$\ln\phi_1 = \frac{P}{RT}(B_{11} + y_2^2\delta_{12})$

Solving these equations by trial and error for $\phi_1$ and $y_2$:

Assume $\quad y_2 = .793118 \quad$ or $\quad 1-y_2 = .206882$

$\phi_1 = .950397$

$\phi_2 = .99604$

$f_2^V = f_2^L = .78270$

$H_{2,1} = 37.62986$