PREFACE

Since the beginning of quantitative physical chemistry the study of electrolyte solutions has occupied a central position in that subject and constituted the early basis of electrochemistry. The success of the Debye-Hückel theory in 1923 tended to diminish attention to specific properties of electrolytes in solution by emphasis on the ionic-strength principle but the specificity of ionic interactions was recognized by Bjerrum. The Debye-Hückel theory placed emphasis on the long range ion-ion interactions as sources of non-ideality and the role of ion-solvent interactions was only discussed in rather later literature.

Work in this field was extended from aqueous solutions to other solvents as soon as the special nature of water was fully appreciated. This has led to more information regarding the specific nature of ion-solvent interactions normally associated with solvation and hydration. The problem of hydration has been approached mostly with regard to the properties of simple ions although studies have been extended in recent years to proteins, nucleic acids and poly-electrolytes.

One of the ways of investigating the specific nature of ion-solvent interactions is through the study of salting-out and salting-in. It is well known that the solubility of a non-electrolyte in an aqueous solution can be changed through the addition of a salt. This effect obviously depends on the type of electrolyte and non-electrolyte used.

On the other hand, the specific nature of ion-solvent interactions can also be evaluated through the study of partial molar volumes of the salts in solutions. In fact, the partial molar volume of ions and the associated electrostriction is an important factor determining the salting-out. The partial molar volume of an ion in the solution depends mainly on three factors: (a) the intrinsic volume of the ion; (b) the structural volume change and cavity occupation effect, and (c) the electrostriction (negative volume change). The latter effect provides information about electrostatic ion-solvent interactions since it depends on the volume change of the solvent due to entry of the ion into the solution.

The work presented in this thesis is concerned with experimental measurements of the solubility of argon in aqueous tetraalkylammonium bromide solutions and the measurement of the partial molal volumes of a series of tetraalkylammonium bromides in anhydrous methanolic solutions. The above salts are known as hydrophobic electrolytes and the cations show special structure promoting effects in water as well as in methanol. A new and convenient method for determination of gas solubilities was developed.

ACKNOWLEDGMENTS

The author is greatly indebted to Professor B. E. Conway, under whose direction and supervision this work was carried out. Professor Conway was always prepared to give freely of his time to discuss the problems that arose during the study and in preparation of the manuscript.

Thanks are also due to Dr. L.H. Laliberté for many helpful discussions and suggestions during the work, as well as for his assistance in the preparation of the thesis during the period of absence of Professor Conway.

The author also wishes to express her thanks to the University of Ottawa, Department of Chemistry, for the use of its research facilities and to the National Research Council of Canada and the Department of Mines, Energy and Resources for financial support of this work.

TABLE OF CONTENTS

Page No.

Page No.

Page No.

LIST OF TABLES

LIST OF FIGURES

LIST OF IMPORTANT SYMBOLS

C	concentration expressed in moles per litre (M)
d	density of a solution
d_o	density of the pure solvent
e	electronic charge (4.80×10^{-10} e.s.u.)
E	electric field
f_i	molar activity coefficient of a non-electrolyte in an aqueous salt solution
f_i^o	molar activity coefficient of a solute in a salt free solution
G	Gibb's free energy
k	Boltzmann constant ($.38 \times 10^{-16}$ erg degree^{-1}mole^{-1})
k_s	salting-out constant
K_H	Henry's law constant
m	concentration expressed in moles per 1000 grams of solvent (m)
M	molecular weight
n	optical refractive index
N	Avogadro's number (6.023×10^{23} kmole^{-1})
$\bar{P}_2$	molar polarisation of a non-electrolyte
R	gas constant (8.3144×10^7 erg degree^{-1}mole^{-1})
S	solubility of a non-electrolyte in a salt solution
S_o	solubility of a non-electrolyte in pure water
T	absolute temperature
v	molecular volume

V_s	molar volume of a salt
z_i	valency of an ion i
a	electronic polarisability
a_1	molar polarisability of the solvent
a_2	molar polarisability of a non-electrolyte
β	dielectric increment
β_o	compressibility of water
ε	dielectric constant
ε_o	dielectric constant at zero field strength (78.5 at 25°C)
ϕ_v	apparent molal volume
ϕ_v^o	apparent molal volume at infinite dilution

ABSTRACT

The solubility of argon in aqueous solutions of ammonium bromide and tetra-n-alkylammonium bromide salts has been determined at 25°C in order to evaluate the salting-out effects of these electrolytes. For this purpose, a new experimental technique was developed which did not require degassing of the solution under study and in which the determination of the gas solubility was based on a series of measurements rather than on a single one. The experimental solubility determinations were carried out up to relatively high concentrations and enabled an examination of the effects of the large hydrophobic salts on the solubility of argon to be made. The results thus obtained have been examined in the light of recent theories on salting-in and salting-out and also with regard to the special structural effects brought about by tetraalkylammonium salt in water.

The apparent molal volumes, ϕ_v, of ammonium bromide and of a series of tetra-n-alkylammonium bromides in anhydrous methanol have been measured down to 0.01 molal with a differential buoyancy balance. It is shown that the Debye-Hückel limiting law slope for $\bar{V}$ is maintained up to much higher concentrations in methanol than in water, an effect which is associated with smaller "hydrophobic" solvent structure changes in methanol than in water.

CHAPTER I

INTRODUCTION

A.

1. Definition of Salting-out and Salting-in

It is well known that the addition of a salt to an aqueous solution of a non-electrolyte will cause a change in the solubility of the non-electrolyte. The most common effect is salting-out which corresponds to a decrease in solubility of the non-electrolyte, while if the reverse behaviour is found, it is known as salting-in.

Essentially, salting-out is a result of the preferential attraction of the more polar component in the (binary) solution by the ion. In this case, the solvent will be thermodynamically less available to dissolve the non-electrolyte and the solubility will decrease. When the solute consists of non-polar or slightly polar molecules, as in the case of the noble gases, calculations of the decrease in solubility in terms of the inter-molecular forces can most easily be made. Through a study of salting-in and salting-out, it is possible to obtain important information about ion-solvent interactions in relation to interactions between ions and other neutral molecules. The case of ions in mixed solvents presents analogous problems arising from the preferential solvation of the ions by the more polar component in the solvent mixture.

2. Thermodynamics of Salting-out and Salting-in

The thermodynamic treatment of salting-out and salting-in can be given in terms of the condition for equilibrium between the solution of the substance and the pure substance in another phase. Thus in a system which consists of an aqueous salt solution and a non-electrolyte, an equilibrium will be established between the dissolved non-electrolyte and the undissolved pure substance.

At equilibrium, the chemical potential of the non-electrolyte must be the same in both phases, and for the solution, is given by:

$$\mu = \mu_i^o + RT \ln x_i f_i \qquad \text{I.1}$$

where μ_i^o is the chemical potential of the non-electrolyte species i in its standard state, R is the gas constant, T the absolute temperature, x_i the mole fraction of non-electrolyte i and f_i is the molar activity coefficient of the non-electrolyte in the salt solution.

The non ideal free energy contribution ΔG per mole associated with the dissolution of non-electrolyte in the aqueous salt solution can be expressed as

$$\Delta G = RT \ln \frac{f_i}{f_i^o} \qquad \text{I.2}$$

where f_i^o is the molar activity coefficient of the solute in a salt-free solution.

The molar activity coefficient f_i is a function of the concentrations of all solute species in the solution under consideration. Therefore, at a given temperature, $\log f_i$ is determined by the concentration of electrolyte C_s and the concentration of non-electrolyte C_i. At a given temperature, $\log f_i$ can be represented by a power series in C_s and C_i,

$$\log f_i = \sum_{mn \to 0} k\, m\, n\, C_s^{\,n}\, C_i^{\,m} \qquad \text{I. 3}$$

For low concentrations of electrolyte C_s and non-electrolyte C_i, and where there is no chemical interaction between solute species, only the linear terms are important, and equation I. 3 reduces to the following

$$\log f_i = k_s\, C_s + k_i\, C_i \qquad \text{I. 4}$$

where k_s is a salting-out parameter, while k_i refers to the non-electrolyte - non-electrolyte interactions. In gas solubility studies, C_i is often small enough so that the last term in equation I. 4 can be completely ignored and in effect most theories are concerned with the calculation of the salting-out parameter k_s. A useful correlation was found between the solubility of a non-electrolyte and its activity coefficient. The measurement of the solubility of a non-electrolyte in a pure solvent and in a salt solution gives the activity coefficient of the dissolved non-electrolyte. This is because the activity of the

non-electrolyte dissolved in the pure solvent and in the salt solution is usually regarded as the same*. That is

$$f_i S_i = f_i^o S_i^o \qquad \text{I. 5}$$

where S_i^o and S_i refer to the solubilities of the non-electrolyte in the pure solvent and in the salt solution, respectively and f_i^o and f_i are the corresponding activity coefficients. Equation I. 5 can be re-arranged to give

$$f_i = f_i^o \frac{S_i^o}{S_i} \qquad \text{I. 6}$$

which in logarithmic form is

$$\log f_i = \log f_i^o + \log \frac{S_i^o}{S_i} \qquad \text{I. 7}$$

---

* This is the usual assumption; however, it is strictly not correct from a thermodynamic point of view. Thus the condition for solubility equilibrium is

$$\mu_i^o + RT \ln x_i f_i = \mu_{o,i}^o + RT \ln x_i^o f_i^o$$

where the terms on the r. h. s. refer to the pure substance in equilibrium with the solution. It is obviously only an approximation to take $x_i f_i = x_i^o f_i^o$ and hence obtain the f_i as the concentration ratio x_i^o/x_i (with $f_i^o = 1$), since the μ_i^o terms on the l. h. s. and r. h. s. are not strictly identical. However, if the solubility is very small, the properties of the solvent will be almost unaffected by the non-electrolyte solute so that the assumption in eqn. I. 5 is usually satisfactory. The above limitation has not usually been appreciated in discussions of salting-out.

If I. 5 is equated to I. 4, then

$$\log f_i = \log f_i^o + \log \frac{S_i^o}{S_i} = k_s C_s + k_i C_i \qquad \text{I. 8}$$

Since $\log f_i^o = k_i^o S_i^o$,

$$\log \frac{f_i}{f_i^o} = \log \frac{S_i^o}{S_i} = k_s C_s + k_i (S_i - S_i^o) \qquad \text{I. 9}$$

and if S_i and S_i^o are small the last term can be neglected. Then

$$\log \frac{f_i}{f_i^o} = \log \frac{S_i^o}{S_i} = k'_s C_s \qquad \text{I. 10}$$

Equation I. 10 is the well known empirical Setchenow equation. Another form* of equation I. 10 is,

$$\frac{S_i^o - S_i}{S_i^o} = k_s C_s \qquad \text{I. 11}$$

where C_s is the concentration of the salt in moles per litre and k_s and k'_s are salting-out constants. In some systems, the term $k_i(S_i - S_i^o)$ cannot be ignored, for example when the solubility of the non-electrolyte in the pure solvent is large but in the presence of the salt is much smaller. Most of the results will be discussed in terms of eqn. I. 11 since the theoretical equations (see below) are derived in this form.

---

* Equation I. 11 is derived from I. 10 in Naperian form by expanding $\ln S_i^o/S_i$ to $1 - \frac{\Delta S_i}{S_i^o}$ for small values of $\Delta S_i/S_i^o$. Then k_s in I. 11 is limitingly equal to $2.3\, k'_s$ (cf. Table 6; the data in this table are, however, independently evaluated by linear and logarithmic plots of the basic solubility results).

Earlier work on the subject of salting-in and salting-out has been reviewed by Randall and Failey (1) and later by Long and McDevit (2). After 1950 several different approaches were made to the salting-out and salting-in problem. A discussion of these theories will be given later in this chapter.

3. Relation to Hydration and Solvent Activity

Hydration in solution results from interactions between solute and solvent molecules. Hydration will occur when the solute-solvent interactions are different from the normal solvent-solvent interactions. In general, solute-solvent interactions have been classified into three different categories, depending on the type of neutral solute under consideration. When the solute and solvent molecules differ only in their relative size, dipole moment or polarisability, the differences in interactions are usually small, but when the molecules are capable of forming hydrogen bonds the hydration is more significant.

In the case of ions as solutes, Bockris (3) has suggested that the region where the interactions are the strongest be called the primary hydration layer. In this region the solvent molecules are close to the ion and are strongly oriented by its electric field, so that the ion with its solvation sheath will move as one entity during its Brownian motion. The kinetic properties of aqueous solutions depend mainly on primary hydration, while for thermodynamic properties such as partial molar volumes it is difficult to separate the role of the primary solvation from that of the secondary and more distant interactions. Azzam (4) suggested that the energy of interaction between water molecules and ions should determine primary hydration. If this energy was larger than the kinetic energy (kT) of the water molecules in the bulk, then the water molecules would be considered as

involved in primary hydration according to Azzam. However, it is more correct to take the hydrogen bond energy between water molecules as the limiting quantity defining the condition for primary hydration. Frank and Evans (5) found that for dissolution of non-polar molecules in water the magnitude of the partial molar entropy of the solute could best be explained on the basis of the formation of a cage or "iceberg" by the solvent in the immediate vicinity of the solute. The interiors of the clusters contained quadruply-hydrogen bonded molecules while their surfaces contained less completely bonded water molecules.

As was mentioned above, the first hydration region is determined by the electrical field at the ion, which is usually strong enough to immobilize the water molecules rotationally and translationally in that region. But for large ions the intensity of the electric field at the periphery of the ion will be smaller and this will correspond to a looser primary hydration shell where the co-ordinated water molecules do not fit and bond into the water structure. Such a situation arises with cations of intermediate size and with most anions so that so-called "structure-breaking" effects arise.

The abnormal thermodynamic properties of aqueous solutions of non-electrolytes, compared with the properties of non-aqueous solutions have been related to the increase in the structure of water around non-polar solutes (5, 6). Recently, it has been found that the same kind of phenomena are also responsible for the peculiar behaviour of tetraalkylammonium (TAA) halides and long-chain organic salts (7). Experiments showed that the large negative entropies of solution or large positive partial molar heat capacities

of non-electrolytes should be ascribed to special structure formation effects in the solution. One of the principal ideas was the formation of a structural region (so-called "icebergs") around the solute molecules in water. This idea was later extended by Frank and Wen (7), who stressed the role of non-electrolyte stabilisation of the icelike clusters. A more quantitative explanation of the structure problem was given by Némethy and Scheraga (8). The non-polar molecule can be accepted by tetrahydrogen-bonded water molecules as a neighbour. This water molecule has complete coordination in the water structure but the non-polar molecule will be accepted with the gain of Van der Waals energy. Other less bonded water molecules suffer a net increase of energy by receiving the non-polar molecule as their neighbour but with loss of non-specific dipole-dipole interactions.

Another explanation was given by Clausen and Polglas (9), who suggested that the solvent structure around a non-electrolyte should be explained in terms of clathrates.

Although Wen and Saito (10) found that this explanation could be correct for the larger tetraalkylammonium salts, the real structure of the hydrate shell at these ions is still uncertain. It is obvious that this kind of hydration does not result from strong solute-solvent interactions but rather from a strengthening of already existing solvent-solvent interactions on account of the presence of the hydrophobic molecule. Therefore this kind of hydration has been called "hydrophobic" hydration.

Another and more common kind of hydration is called "hydrophilic" hydration. In this case, the hydration occurs because of strong solute-solvent interactions, usually arising from electrostatic ion-dipole interactions. In other words, the electrostatic field near the ion will be strong enough to immobilise a certain number of water molecules, although the water molecules in the hydration shell are usually in continuous rapid exchange with the water in the bulk of the solution, except in the case of some complexes, e.g. $[Cr \cdot 6H_2O]^{3+}$.

Another term "negative hydration" was introduced by Samoilov (11) to explain the anomalous kinetic properties of some ions in solution. For example, for halide ions, the Stokes radii were found to be smaller than the crystal radii (12). An explanation for this behaviour has been given also by Frank and Evans (5) and by Gurney (13) and was based on the assumption that near small ions the electric field is strong enough to orient the water molecules radially to the centre of the ion. When the orientating influence is of the same order of magnitude as the normal structural influence of the neighbouring molecules, the water molecules are in the state of higher disorder. This region is one where the structure is locally broken down and is characterised by a lower local viscosity of the solvent and an enhancement of the mobility of the ion. Thus, some ions can be structure makers while some behave as structure breakers. Vaslow (14) suggested that the small ions such as Li^+, Na^+ and H^+ may fit into the normal cavities in the water structure and stabilise the structure while the larger ions will disturb the structure, but this is questionable because the F^- ion is found to be a structure maker.

4. Brief Summary of Theories

(i) General

A number of approaches have been used to study the phenomena of salting-out and salting-in. One of the first was the theory of salting-out given by Debye and McAulay (15) in 1925. This electrostatic theory relates salt effects to the influence of non-electrolyte on the dielectric constant of the solvent. If the non-electrolyte decreases the dielectric constant of the solvent, the resultant effect will be salting-out. In 1929 Butler (16) considered molecular polarisabilities and volumes of non-electrolyte and solvent as the important terms determining the distribution of non-electrolyte and solvent in the region of the ions and thus the change of solubility leads to salting-out or salting-in.

The so-called Van der Waals' theories extended the electrostatic theories by introducing the influence of short range dispersion forces. The most detailed work was done by Bockris, Bowler-Reed and Kitchener (17). In 1952 Long and McDevit (2) developed the related thermodynamics for the problem of salt effects. Conway, Desnoyers and Smith (18) improved the above distribution theory by introducing the dielectric saturation effect, taking into account the existence of a discrete primary hydration shell about the ions and by introducing relations between the dielectric constant and molecular parameters such as the dipole moment, polarisability and molar volume through the theory of Kirkwood (19).

(ii) Electrostatic theory

Debye and McAulay's approach (15) was based on the consideration of the difference of energy ΔW of an ion in the pure solvent and in the non-electrolyte solution, arising from the change of dielectric constant brought about by the non-electrolyte. A simplified equation for the dielectric decrement β when n moles of non-electrolyte are added to the solution can be used, viz.

$$\varepsilon = \varepsilon_{\alpha} - \beta n \qquad \text{I.12}$$

where ε_{α} is the dielectric constant of a pure salt solution.
In this case the energy difference ΔW is

$$\Delta W = \sum_{i=1}^{i=i} \frac{z^2 e^2}{2 \varepsilon r_i} - \sum_{i=1}^{i=i} \frac{z^2 e^2}{2 \varepsilon_{\alpha} r_i} \qquad \text{I.13}$$

where z is the valency, r_i is the radius of the ion assumed spherical and e is the charge. As the change of energy depends on the concentration of non-electrolyte molecules through equations I.12 and I.13, the change of the chemical potential of the non-electrolyte caused by addition of the electrolyte can be calculated as

$$\Delta\mu = \frac{\partial \Delta W}{\partial n} = \frac{\beta}{2 \varepsilon_{\alpha}} \sum_{i=1}^{i=i} \frac{z^2 e^2}{r_i} = k\,T\,\ln f_i \qquad \text{I.14}$$

or

$$\ln f_i = \frac{\beta}{2\,kT\varepsilon_\alpha} \sum_{i=1}^{i=i} \frac{z^2e^2}{r_i} \qquad \text{I.15}$$

Equation I.15 is related to the salting-out coefficient, as can be seen through the thermodynamic approach given on page 4. It is seen that the direction of the solubility change is related to the sign of β which depends on the nature of the dissolved non-electrolyte. The value of $\ln f_i$ will be positive if β is positive, i.e. when the non-electrolyte decreases the dielectric constant of the solution. The overall effect will then be salting-out. Salting-in, the opposite case, occurs when β is negative.

(iii) Distribution theory

Butler (16) introduced the distribution type of theory showing the dependence of salting-out on the volume difference of pure solvent and non-electrolyte solute and the polarisation difference. Butler based the theory on evaluation of the work of bringing an element of volume containing non-electrolyte from infinity to a distance r from the ion with displacement of an equal volume of solvent. The ion will interact with this volume element with an energy determined by the polarisation difference. So the work done is

$$W = (a_1 - a_2)\,\frac{z^2e^2}{2\varepsilon^2 r^4} \qquad \text{I.16}$$

where a_1 and a_2 are the polarisabilities of the solvent and the non-electrolyte, calculated per unit volume, while the ionic field at the distance r is $ze/\varepsilon r^2$.

The distribution function for non-electrolyte molecules at a distance r from the ion is given by

$$n_{2,r} = n_2^o \exp[-\frac{(a_1 - a_2)\, e^2 z^2}{2\,\varepsilon^2\, r^4\, kT}] \qquad \text{I.17}$$

where $n_{2,r}$ is the concentration of the non-electrolyte in the ionic field at a distance r, while n_2^o is the concentration of non-electrolyte in the absence of the salt. Salting-out by the non-electrolyte will occur when the specific polarisability of the solvent is greater than that of the non-electrolyte, i.e. $a_1 > a_2$. This is analogous to the situation with the sign of the dielectric decrement β in Debye and McAulay's theory. After spherical integration of equation I.17 and linearisation of the exp. term, then

$$\log f_i = \log \frac{S_o}{S} = \frac{(a_1 - a_2)\, 4\pi}{k\, T\, \varepsilon^2} \sum_{i=1}^{i=i} \frac{z^2 e^2 c_i}{a_i} \qquad \text{I.18}$$

where c_i is the concentration of the ions of electrolyte per cc and a_i is the radius of the ion.

Butler's distribution theory gave a general basis for the calculation of the salting-out coefficient in terms of an electrostatic approach. The main attention was given to electric polarisation; the significance of the dielectric constant of the solvent which plays an important role in solvation and in particular the consequences of dielectric saturation were not, however, adequately explored. Also the presence of non-electrolyte in the salt solution and its role in causing structural changes in the solvent was not considered.

(iv) Electrostatic and Van der Waal's forces

In 1951 Bockris, Bowler-Reed and Kitchener modified Butler's distribution theory by considering the role of short range dispersion forces (20, 21) and treating in a more satisfactory way the electrostatic terms arising from molecular polarisation and electronic polarisability. By means of their improved theory they were able to explain "anomalous" salting-in effects which arise in tetraalkylammonium salt solutions with non-electrolytes, that on the basis of purely electrostatic theories, should be salted-out. The total molecular polarisation was defined as

$$P = \frac{(\varepsilon_s - 1)\, M}{4\pi d} \quad \frac{1}{N} \qquad \text{I.19}$$

and the electronic polarisability

$$a = \frac{(n^2 - 1)}{n^2 + 2} \quad \frac{3\, M}{4\pi\, d\ N} \qquad \text{I.20}$$

where M is the molecular weight, N is Avogadro's number, d is the density, ε_s is the dielectric constant of the pure solvent and n is the optical refractive index. The dispersion force is given by $6\lambda/r^7$ where λ is a quantity independent of r and can be calculated from the dispersion energy.

The concentration of non-electrolyte n_c at a distance r from the ion can be obtained again from a Maxwell-Boltzman distribution calculation in terms of above quantities, i.e.

$$n_c = n_c^o \exp\left[\frac{[(P_B v_C/v_B) - P_C] z^2e^2}{2 \varepsilon_s^2 r^4 k T} + \frac{[(\lambda_B v_C/v_B) - \lambda_C]}{r^6 k T}\right] \qquad \text{I. 21}$$

where v is the molecular volume while the indices B and C refer to solvent and non-electrolyte species.

Equation (I. 21) after integration gives the final equation for the salting-out ratio $\Delta S/S_o$ in terms of polarisation energy dependence and volume difference

$$\frac{\Delta S}{S_o} = m \left[(P_C - P_B \frac{v_C}{v_B}) \frac{2 \pi e^2 N}{1000 \varepsilon_s^2 kT} \left(\frac{1}{a_+} + \frac{1}{a_-}\right)\right.$$

$$\left. + \left(\frac{a_C \nu_C}{\nu_{A\pm} + \nu_C} - \frac{a_B \nu_B}{\nu_{A\pm} + \nu_B} \frac{v_C}{v_B}\right) \frac{2\pi N h}{1000 \varepsilon_o^2 kT} \left(\frac{a_{A^+} \nu_{A^+}}{a_+^3} + \frac{a_{A^-} \nu_{A^-}}{a_-^3}\right)\right] \qquad \text{I. 22}$$

where m is the concentration in g moles of salt per 1000 gms of solvent and the ν 's are the characteristic frequencies of the solvent and non-electrolyte.

Whether net salting-in or salting-out arises is seen to depend on the balance of the electrostatic and non-electrostatic forces and on the sign of the polarisation difference of the solvent and non-electrolyte solute. A simplified version of (I. 22) can be written if spherically symmetrical ions are considered so that $a_A = a_i^3$ and thus

$$\frac{\Delta S}{S_o m} = A\left(\frac{1}{a_+} + \frac{1}{a_-}\right) + B \qquad \text{I. 23}$$

where A and B are almost independent of a.

Conclusions about the dependence of $\Delta S/S_o$ on m can be made from equation (I. 23). At high concentrations, the variation of the static dielectric constant of the solution and the effect of the electrostatic field upon the ionic atmosphere will increase the value of $\frac{\partial}{\partial m}\left(\frac{\Delta S}{S_o}\right)$. On the other hand, at extremely low concentrations, the ion and non-electrolyte will be separated sufficiently that the dispersion energy will be reduced.

(v) Theory of Conway, Desnoyers and Smith

The treatment of Conway, Desnoyers and Smith that appeared in 1964, was based on Butler's method (16) but the following new factors were introduced : (a) dielectric saturation effects; (b) molecular structure of the primary hydration layer, and (c) the relation between the dielectric constant and the molecular parameters such as dipole moment and polarisation based on Kirkwood's (19) theory of dielectrics. The effective dielectric constant of the primary hydration layer was found to be around 2 while beyond the layer the normal value of about 80 is approached.

The change of electric energy ΔW that occurs when the non-electrolyte enters the salt solution can be expressed through the change of dielectric constants as

$$\Delta W = \frac{1000\, z^2 e^2}{8\pi r^4 N} \left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_o}\right) \frac{1}{c_2} \qquad \text{I. 24}$$

where c_2 is the concentration of the non-electrolyte. To find the local concentration of non-electrolyte in the presence of an ion in relation to the average concentration in its absence, the Boltzman distribution law was used, which after integration gives the relative solubility change as

$$\frac{S_o - S}{S_o m} = \frac{4\pi N}{1000} \int_a^R (1-\exp[-\Delta W/kT]) r^2 dr \qquad \text{I. 25}$$

The integration limits are (a) the ionic radius a and (b) a quantity R which is the critical radius corresponding to the volume available per ion in the solution and is defined by:

$$R = (3000/4\pi Nm)^{1/3} \qquad \text{I. 26}$$

Equation I.25 is very convenient for dealing with the question of ions. Thus if a radius r_h of the hydration shell is defined as that within which $\varepsilon \ll \varepsilon_o$, the field will be high and the function $\Delta W/kT$ will be large too. Beyond r_h, the value of $\Delta W/kT$ will be small. In the region where $r > r_h$ the Kirkwood theory of dielectrics can be employed, so that the function $\Delta W/kT$ can be expressed in terms of molar polarisation $\bar{P}_2$ and partial molar volume of non-electrolyte $\bar{V}_2$;

$$\Delta W/kT = \frac{E^2}{8\pi kTN} \left(\bar{V}_2 \varepsilon_o - \frac{9}{2} \bar{P}_2\right) \qquad \text{I. 27}$$

where E represents the ionic field. Finally, the salting-out constant can be expressed as

$$k_s = \frac{S_o - S}{S_o m} = \frac{4\pi N}{1000} \int_a^R \frac{z^2 e^2}{8\pi kTN\varepsilon^2} (\bar{V}_2 \varepsilon_o - \frac{9}{2} \bar{P}_2) \frac{1}{r^2} \, dr \qquad \text{I. 28}$$

from which predictions of the experimental behaviour can be made. If we take into account two hydration regions, the integrand of eqn. (I. 25) can be divided into two parts: from a to r_h (where $\varepsilon \ll \varepsilon_o$) and from r_h to R (where $\varepsilon \to 80$, the bulk value). Then having $e[-\Delta W/kT] \ll 1$ when $\varepsilon \ll \varepsilon_o$, integration gives

$$k_s = \frac{S_o - S}{S_o m} = \frac{4\pi N}{3000} (r_h^3 - a^3)$$

$$+ \frac{z^2 e^2}{2000\, kT\, \varepsilon_o^2} (\bar{V}_2 \varepsilon_o - \frac{9}{2} \bar{P}_2) [\frac{1}{r_h} - \frac{1}{R}] \qquad \text{I. 29}$$

The first term in equation I. 29 corresponds to the strong ion-solvent interactions associated with the primary hydration shell of the ion (where dielectric saturation effects are important) and is independent of the nature of the non-electrolyte, while the second term depends on the nature of the non-electrolyte and is related to its molar polarisation and partial molar volume. While the first term would, for most ions contribute a salting-out effect, the second term will lead to salting-out or salting-in depending on $\bar{V}_2$ and $\bar{P}_2$. Non-electrostatic effects will add further modifications to the predictions of equation (I. 29) depending on the role of dispersion forces and solvent structure effects.

(vi) Theory of Long and McDevit

A thermodynamic treatment of salting-out of non-electrolytes was given by Long and McDevit (2). The theory expressed the salting-out constant in terms of partial molar volumes of non-electrolyte $\bar{V}_2$ and salt $\bar{V}_s$, so that

$$k_s = \frac{\bar{V}_2(V_s - \bar{V}_s)}{\beta_o RT} \qquad \text{I.30}$$

where V_s is the molar volume of the salt and β_o is related to the compressibility of the solvent. An advantage of this thermodynamic approach was the introduction of the properties of the non-electrolyte and the ions through their partial molar volumes $\bar{V}_2$ and $\bar{V}_s$ which, in other theories were involved less explicitly. The factor $(V_s - \bar{V}_s)$ is seen to be related to the electrostriction and thus to the hydration of the ions. On the other hand, through $\bar{V}_s$, the theory satisfactorily accounts for specificities in salting-out by various kinds of salts. A disadvantage of the theory is that other properties of the salt were not considered.

5. Structural Effects in Salting-out

(i) Desnoyers and Jolicoeur

Much interest has been shown recently in the physico-chemical properties of the TAA salts solutions, because of their anomalous behaviour to be discussed later in this chapter. Normally, the presence of a salt in solution tends to decrease the solubility of the non-electrolyte, while TAA salts cause an increase in the solubility of some non-electrolytes (2, 17).

Desnoyers, Pelletier and Jolicoeur (22) studied the solubility of benzene, a large non-electrolyte, in symmetrical TAA salt solutions. They found that the salting-in effect was a linear function of the number of carbon atoms in the TAA cations. The same conclusion was not established in the study of non-symmetrical cations. This led to the conclusion that the k_s constants depend on the symmetry of the large ions. The difference between these two types of behaviour was explained in terms of the possibility of a certain amount of salting-out near the charge-bearing nitrogen atom when the large ions were not symmetrical. This indicated that the salting-in was principally caused by the hydrophobic parts of the ions.

On the other hand, a difference of k_s on TAA salt concentration was observed. It was found that for the lower members in the homologous series of TAA salts, k_s increased linearly with concentration, while with the higher members a rapid increase of solubility with concentration occured. This indicated that salting-in was a function of the length of the alkyl chain of the substituents on the nitrogen atom.

A possible explanation of these effects was found by the introduction of Diamond's suggestion (23) that the increase in the structure of water (7, 8) in the vicinity of the large ions plays an important role in salting-in by promoting the formation of an association complex between the non-electrolyte and the organic ion. The presence of a neutral molecule or the non-polar part of a molecule enhances the cluster lifetime in the vicinity of the neutral molecule. Therefore the presence of the neutral molecule tends to increase the ice-like structure of water. In the system considered, containing benzene, the large cation will tend to increase the water structure and the system will tend to minimise its free energy by formation of incipient micelles (24), thus minimising the water solute interfacial area. The solubility of benzene inside a micelle would be large. The critical micelle concentration decreases with increasing length of the organic chain. The lifetime of a micelle depends on the strength of Van der Waals forces between the large ion and the non-electrolyte. As the size of the particles increases, the Van der Waal's forces between them also become stronger, a situation which results in a large salting-in effect.

To verify the above hypothesis the partial and the apparent molar volumes of the hydrophobic salts have been measured (7). It was found that the hydrophobic character of TAA cations in an homologous series tends to cause mutual salting-in. In another study, Desnoyers and Arel (25) studied mutual salting-in through the concentration dependence of the apparent molar volumes in the alkylammonium (RNH_3^+) series of salts. The apparent molar volume decreases with increasing concentration until

the critical micelle concentration is reached, whereupon a large increase in volume is observed. This was attributed to the appearance of free space between the organic ions in the micelle. Before the critical concentration is reached there is little free space between hydrophobic ions and the surrounding water molecules. In a recent paper by Desnoyers and Ichhaporia (26), some more results for salting-in and salting-out of polar non-electrolytes have been presented.

The studies reviewed above took into account special structure effects and incipient association between the non-electrolyte solute and the hydrophobic quaternary ammonium cations. The separated quaternary ion and non-electrolyte tend to minimise the hydrophobic interactions by coming together and sharing a common region of solvent. The favourable energetic situation arising under these conditions leads to salting-in.

(ii) Entropy Effect

The entropy of ions in water is only rather distantly connected with the question of salting-out. More specific is the question of entropy effects that arise because of changes of properties of the solvent around the non-electrolyte; the transfer of a gaseous ion into an aqueous solution is connected with a decrease in free volume and thus with a decrease in the translational entropy of the ion. The hydration of an ion is associated with a large negative entropy change. This is because the neighbouring water molecules suffer a decrease in translational, vibrational and rotational freedom.

Changes in water structure also have an effect on the entropy (5), so that strengthening of the hydrogen bonds in the liquid results in a decrease in the entropy, while the breaking of hydrogen bonds will result in an increase in the entropy.

Usually, entropy of hydration is regarded as composed of two terms: (1) the entropy of "Born charging" ΔS_1 ,

$$\Delta S_1 = \frac{z^2 e^2}{2 r_e \varepsilon^2} \left(\frac{\partial \varepsilon}{\partial T} \right)_P \qquad \text{I. 31.}$$

where r_e is an effective radius of the ion, and ε is the dielectric constant, and (2) the entropy associated with the compressional or electrostriction effect ΔS_2

$$\Delta S_2 = \int_r^\infty \int_1^P \frac{1}{V_o} \left(\frac{\partial V}{\partial T} \right)_P dP \, 4\pi r^2 dr \qquad \text{I. 32.}$$

where V relates to the volume of the fluid, while $\frac{1}{V_o} \left(\frac{\partial V}{\partial T} \right)_P$

shows the dependence of the expansibilities on the pressure. In cases where no dielectric saturation occurs, ΔS_1 reduces to the expression derived from the Born equation. With the introduction of electrostriction effects, better agreement with experimental data was found, except for anions (27). This showed that the simplest approach to the calculation through the Born charging equation must be improved by the consideration of other factors such as local

compression of the solvent around the ions (28); the calculated results were very much higher than the experimental values. Eley and Evans (29) give a statistical-mechanical calculation of the entropy of hydration, including the compressional effect on the solvent, but it should be mentioned that none of these theories included any non-electrostatic effects.

(iii) Properties of R_4N^+ Ions in Solution

Aqueous solutions of TAA salts have unusual thermodynamic properties when compared with other 1:1 electrolytes. Knowing the size and the symmetry of these large cations, very little primary hydration was expected (12, 30). It has been found that the solutions containing R_4N^+ salts have high viscosities with large temperature coefficients (31), high apparent molal heat capacities (9), peculiar activity coefficients (32) etc. In general the activity coefficients decrease with increasing size of the anions for all R_4NX salts, where R is an alkyl group in the series methyl to n-butyl and X represents a halide anion in the series F^- to I^- (32). The activity coefficients were found to increase with increasing cation size in the fluoride and chloride series, but the opposite effects were observed in the bromide and iodide series. Similar effects were found in studies of apparent molal volumes and partial molal entropies (33, 34).

The large R_4N^+ ions have no hydrophobic hydration. All of the above mentioned properties for aqueous solutions of the $R_4N^+X^-$ salts point to the existence of a special structure of the solvent around these ions. Diamond (23) tried to explain the negative deviations from the limiting Debye-Hückel theory for activity coefficients in terms of a structure-enforced ion pairing between the hydrophobic ion (incipient micelleformation). Similar conclusions were reached by Levien (35) based on activity and conductivity studies. Lindenbaum and Boyd (34) suggested the role of micelles, a view which was later taken up by Desnoyers and Jolicoeur (36) in their interpretation of salting-in of benzene by tetraalkylammonium salts.

Most of the facts discussed above lead to the conclusion that structural influences are necessary for the interpretation of the specificities of the thermodynamic properties of ions at finite concentrations.

A study by Morrison and Johnstone (37) on the salting-out of inert gases in aqueous solutions containing electrolytes which varied in size over a wide range showed that the ions Me_4N^+ and Et_4N^+ caused slight salting-in of helium, krypton and sulphur hexafluoride and a stronger salting-in of n-butane.

The limiting slopes of the solubility plots for the two inert gases and SF_6 in aqueous solutions containing TAA salts, were compared with values predicted from the theories of Debye and McAulay, and Long and McDevit. The predicted slopes from the first theory are positive, as were the experimentally observed ones, while negative values appear to follow from Long and McDevit's theory.

The second theory failed to predict salting-in;in this case, better results were found for electrolytes that caused only salting-out (38, 39). Morrison and Johnston compared the behaviour of SF_6 and benzene which were approximately the same size, but are salted-in to different extents. The theory that predicts that the molecular volume is the main parameter determining the salting-out is evidently not borne out by the experimental results with these two compounds. These workers suggested that the difference between the polarisability of these molecules could be responsible for the differences of salting-out behaviour. The appreciable expansion in the volume of the solution found during dissolution of TAA salts (40) was ascribed to the more open structure that the solvent must assume. As the heat of solution was related to the polarisability of the solute (41), the conclusion was that the polarisability, together with Van der Waals forces, were the main factors responsible for salting-in effects.

(iv) Treatment of Efremov, Prokf'eva and Syrnikov

Efremov et al (42) stressed that the salting-out and salting-in effects depend on the change in potential energy of the non-electrolyte molecules in the ionic field as previously discussed by Butler (16). A method of employing chemical potentials was used to give the solubility equations for a non-electrolyte in a salt solution. The chemical potentials of the pure components 1 and 2, where 2 is the non-electrolyte can be represented by

$$\mu_1 = \mu_1^o + \Delta W_{11} + W_{12} + \alpha RT \ln N_1 \qquad \text{I. 33}$$

and

$$\mu_2 = \mu_2^o + \Delta W_{22} + W_{21} + RT \ln N_2 \qquad \text{I. 34}$$

where μ_1^o and μ_2^o are the chemical potentials of the pure components 1 and 2, N_1 and N_2 are the corresponding mole fractions in the solution, ΔW_{11} and ΔW_{22} are the changes in potential energy due to 1:1 and 2:2 interactions, while W_{12} and W_{21} are the energies of interaction of the unlike molecules 1 and 2 and α is a coefficient that decreases with increase of N_2. The non-electrolyte molecules are regarded as being spherical and larger than those of the solvent.

The chemical potential of the solvent containing the non-electrolyte and the salt can be written as

$$\mu_{(1)} = \mu_1^o + \Delta W_{11} + W_{12} - (\varepsilon_1 - 1)E^2/8\pi + \alpha' RT \ln N_1 \qquad \text{I. 35}$$

where ε_1 is the dielectric constant of the solvent and $(\varepsilon_1-1)E^2/8$ is a polarisation energy term related to the ionic field E.

Efremov considered that there could be a change in ε_1 corresponding to the concentration of N_2 because of the electrostatic interactions of the dissolved non-electrolyte. Thus, the chemical potential of dissolved non-electrolyte is given by

$$\mu_{(2)} = \mu_2^o + \Delta W_{22} + W_{21} - (\varepsilon_2 - 1)E^2/8\pi + RT \ln N_2 \qquad \text{I. 36}$$

When solubility equilibrium is attained, $\mu_1 = \mu_{(1)}$ and $\mu_2 = \mu_{(2)}$, so the solubility situation in the system can be expressed in terms of mole fractions as

$$\ln \frac{N_{(1)}^{a'}}{N_{(2)}} - \ln \frac{N_1^a}{N_2} = \frac{\Delta W}{RT} + \frac{(\varepsilon_1 - \varepsilon_2)E^2}{8\pi RT} \qquad \text{I. 37}$$

where ΔW is the sum of changes in potential energy of both kinds of molecules caused by the introduction of non-electrolyte into the solution. The condition for salting-out will be satisfied when $a' > a$ which automatically means that $V_2 > V_1$. However, if ΔW is equal to $(\varepsilon_1 - \varepsilon_2)E^2$ and the latter term is equal to zero, salting-out will be determined only by the entropy effect. By introducing a non-uniform distribution of a substance in a solution, the salting-out or salting-in effects are governed by the different relationships between energy and entropy factors for the system. Thus, if

$$\Delta W < 0 \text{ and } \left|\sum \Delta W\right| > \frac{(\varepsilon_1 - \varepsilon_2)E^2}{8\pi RT} \qquad \text{I. 38}$$

salting-out of the non-electrolytes will be replaced by salting-in. When ΔW is small and negative, the concentration of salt is high and $a' = a = 1$, so that eqn.(I.37) becomes similar to the well-known Setchenow equation.

Mikhailov (43) considered that dispersion interactions and the radius of the "salting-out sphere" were additional factors responsible for the observed effects. The system experimentally studied was tributyl phosphate in aqueous solution. Theoretical predictions from the treatments of McDevit and Long (2) and Debye and McAulay (15) show that tributyl phosphate should be salted-out of the aqueous solutions. In Mikhailov's experiments, the opposite effect was found, viz. salting-in. He attempted to explain this result using Debye's theory which predicts that 1/f should be a linear function of the salt concentration. Mikhailov found that this prediction was satisfactory only at quite low electrolyte concentrations. The Debye equation was therefore improved by introduction of the concept of a finite radius of the "salting-out sphere" [cf. the treatment of Conway, Desnoyers and Smith (18)]. The radius of the "salting-out sphere" was defined as

$$R = \left[\frac{3}{4\pi \sum n_i}\right]^{1/3} \qquad (I.39)$$

where n_i is the sum of "co-sphere" volumes of solution available per ion. By introducing eqn. (I.39) in Debye's equation (74), the only difference was that the integration was carried out from a to R, where a is radius of the ion. This means that at infinite dilution R tends to ∞ and Debye's equation applies. On the other hand Mikhailov took into account dispersion interactions according to the theory of Bockris et al (17). This relation agrees with the experimental data on salting-out and salting-in of tributyl phosphate.

It is to be noted that the choice of tributyl phosphate as the non-electrolyte solute is a very bad one owing to the multi-functional nature of the molecule. It contains large non-polar residues together with a relatively complex polar group, the phosphate. The molecule is also large compared with the solvent molecules and also with the distance over which the field of the ion is varying (0 - 15 Å). It is doubtful if Mikhailov's experiments lead to any improvement in the understanding of salting-out and ion-solvent interactions and a number of the theoretical ideas introduced had been published by other authors previously.

B. PARTIAL MOLAL VOLUMES

1. Introduction

Study of partial molal volumes $\bar{V}_2$ of ions in solution provides information complementary to that given by salting-out studies. The $\bar{V}_2$ data provide a measure of electrostriction and ion-solvent interaction that is required in the interpretation of salting-out behaviour.

Previous studies of partial molal volumes of TAA salts have been concerned with the relation between the ion-solvent interactions and volumes. Gilkerson and Stewart (45) studied the concentration dependence of the volume for the R_4NBr series by picnometric measurements and Wen and Saito (10) studied the partial and apparent molal volumes of five symmetrical TAA bromides. Through the dilatometric studies (46, 47) it was shown that the concentration dependence of the partial molar volumes of Me_4NBr and Bu_4NBr salts attains the Debye-Hückel limiting value at sufficiently low concentrations. The series of R_4N chlorides, bromides and iodides were studied by Conway and Verrall (48, 49) while Wirth was using dilatometric measurements to find out the partial molar volumes of the TAA bromide series (50).

It has been shown that the substitution of one methyl group in each alkyl chain in the TAA salt with a hydroxy methyl group removes the anomalous concentration dependence of the partial molar volumes (51).

Partial molal volume studies have also been made in methanol for the TAA bromide series and some of the chloride series (52). The apparent and partial molal volumes were found to increase with concentration. New measurements were made in methanol in order to establish a system of individual ionic contributions to volume in this solvent and to make comparisons with Padova's work.

2. Formulation of Equations used for Molal Volumes

Measurements of partial molal volumes can be made by determination of the apparent molal volume ϕ_v defined as

$$\phi_v = \frac{V - n_1 \bar{V}_1^o}{n_2} \qquad \text{I.41}$$

where n_1 is the number of moles of solvent of partial molal volume $\bar{V}_1^o$ and n_2 is the number of moles of solute.

If the concentration of solute is expressed as the number of moles of solute per 1000 grams of solvent, equation I.41 can be expressed as

$$\phi_v = \frac{1000\,(d_o - d)}{m\,d\,d_o} - \frac{M_2}{d} \qquad \text{I.42}$$

where d_o is the density of the pure solvent, d is the density of solution, m is the molality of the solution and M_2 refers to the molecular weight of the solute.

Because of the linear relationship that exists between ϕ_v and $m^{1/2}$ in dilute solutions, as is theoretically expected from the Debye-Hückel limiting law,

$$\phi_v = \phi_v^o + S_v\, m^{1/2} \qquad \text{I.43}$$

where S_v is the limiting slope. The most convenient calculation of

partial molar volume of solute makes use of the c-scale. The concentrations on the molal (m) scale can of course be converted to molar concentrations using the density data. The partial molar volumes $\bar{V}_2$ can be found from ϕ_v using the relation

$$\bar{V}_2 = \phi_v + \left[\frac{1000 - c\,\phi_v}{2000 + c^{3/2}(d\,\phi_v / d\,c^{1/2})} \right] \frac{c^{1/2}\phi_v}{d\,c^{1/2}} \qquad \text{I.44}$$

C. RELATION OF THE PRESENT WORK TO PREVIOUS RESEARCH

1. Salting-out

The previous work on salting-out reviewed in this chapter has been concerned mainly with the behaviour of small ions where coulombic interactions with the solvent determine the hydration and solvent polarisation, and hence the salting-out. In the present work, the aim has been to obtain new information on the solubility changes (salting-out or salting-in) for a simple non-polar non-electrolyte brought about by large organic ions where non-coulombic, structural hydration effects are as large (or larger) as the purely coulombic interactions. Such effects, for example, are indicated in other properties of such ions, e.g. their apparent molal volume and compressibility behaviour, their effect in changing the fluidity of water and their effect on the n.m.r. spin-lattice relaxation times of the solvent. Correspondingly, the relative role of van der Waals interactions, indicated in earlier work (17) with more complex non-electrolytes leading to a salting-in tendency requires further examination with non-electrolytes of simple structure which cannot interact with the solvent by dipole-dipole or specific H-bond effects. Finally, the role of entropy effects in salting-out requires more consideration as entropies of solution and solvation of solutes in the aqueous medium can be of great importance in determining the properties of aqueous solutions.

2. Partial Molal Volumes in Methanol

The solubility behaviour of non-electrolytes in ionic solutions in water is closely connected with the partial molal volumes which salts exhibit in that solvent. Previous work (2) by McDevit and Long has shown the thermodynamic basis of such relations. Hitherto, most studies on the partial molal volume of TAA salts have been concerned with the evaluation of the volume behaviour in water where electrostrictinn effects are evidently minimal with such ions. It is of interest, however, to evaluate, by comparison, the volume behaviour of TAA salts in methanol as solvent because of the much higher compressibility of this solvent than that of water - $130 \times 10^{-6} bar^{-1}$, compared with $44 \times 10^{-6} bar^{-1}$ for water at 30°C and 1 atm. This approach can also lead to an appreciation of how much the structural volume contribution in water may be compensated by non-specific polarisation volume changes due to electrostatic effects. In relation to the salting-out problem, the greater the electrostriction (manifested e. g. in volume or compressibility changes) the larger is the tendency for salting-out.

CHAPTER II

EXPERIMENTAL

A.

1. Methods for Determination of Gas Solubility

In the study of salting-out and salting-in of gases, various methods for the determination of gas solubility have been used. A general classification can be made by distinguishing the rarely used chemical methods from the well-known physical ones.

There are several reasons for omitting discussion of the chemical methods. They are usually specific for a particular gas and therefore do not have general applicability. For the noble gases, they are obviously inapplicable. It is also difficult in some cases to distinguish solubility arising from "chemical" absorption from that associated with purely physical equilibrium solubility because certain gas absorption processes are associated with some chemical equilibria. An example where a chemical method is useful is in evaluation of the solubility of oxygen in water, usually determined by means of Winkler's method (53).

The physical methods can be classified further into two groups: (i) saturation methods, based on absorption of gas in a previously degassed solvent up to the saturation solubility; (ii) extraction methods, where the gas dissolved in a previously saturated

solution is removed quantitatively from the system. In both cases the appropriate solubilities can be determined.

Various methods have been used to establish equilibrium in the two-phase system; for example equilibrium can be reached through shaking the mixture, bubbling the gas through the mixture or by flowing a stream of liquid through the gas, etc. (39, 54, 55). Qualitative determinations of the components in the gas and liquid phases can be made by manometric-volumetric and mass spectrometric methods, or by gas-chromatographic procedures.

The most frequently used method is the manometric-volumetric one, in which the solubility of a pure gas is determined by measurements of pressure, volume and temperature. In order to obtain satisfactory results, the following requirements must be satisfied: that (a) true equilibrium be attained; (b) the gas not be contaminated; (c) the solvent be completely degassed and (d) the quantity of gas dissolved can be accurately established. Some of these requirements depend only on the calibration and proper design of the apparatus and application of appropriate corrections. However, it should be stressed that the attainment of equilibrium is of prime importance for all solubility measurements. The design of the apparatus depends, of course, mainly on the method chosen for dissolution of the gas in the liquid.

As was mentioned above, mass spectrometric methods may be used for gas solubility determinations. The technique is based on out-gassing a sample of the gas-saturated solvent, then trapping the gas and analysing it by mass spectrometry. However,

the main advantage of this method is the determination of the ratios of dissolved gases in mixtures and isotope effects in dissolution of gases. In such cases, the solubility of one of the gases should be a "standard" quantity (56, 57).

Gas chromatographic methods have been employed and form the basis of liquid partition chromatography. Liquid and gas components are employed and the carrier gas continually bathes the liquid so that it can be assumed that an equilibrium exists between the passing carrier gas and the gas that is dissolved in the liquid phase. The mixture of vapours and gas is transported in the carrier gas and is partitioned between the carrier gas stream and the stationary liquid phase. Gas solubilities can be determined by introduction of a quantity of partitioning liquid, through the determination of the partition coefficient and from knowledge of the characteristics of the column. The method has been restricted to systems in which the liquid has a high boiling point, where the process involves a steady-state and where transient equilibria arise as the carried component is swept through the column.

Gas solubilities can be expressed in a number of different ways. Thus, according to Henry's law, the mass of gas dissolved by a given volume of solvent at constant temperature is proportional to the pressure of the gas with which the equilibrium is established. If n_s is the mass of gas dissolved by unit volume of solvent at the equilibrium pressure P,

$$n_s = K_H P \qquad \text{II.1}$$

where K_H is a constant that can satisfactorily be used to express the solubility. It should be stressed that Henry's law is a limiting law and therefore only applicable for a restricted range of dilute solutions or low gas solubilities where ideality can be assumed.

Another way of expressing gas solubility is in terms of Ostwald's solubility coefficient, which is in fact again a distribution equilibrium constant, completely independent of the partial pressure of the gas so long as ideality of the system obtains.

2. Development of the Method used in the Present Work

The method used in the present work was based on the determination of Henry's law constants (cf. eqn. II.1) for the solutions. If n_T is the total number of moles of gas in a closed system containing a liquid phase and a gas phase and, further, if n_g is the number of moles of gas in the gas phase then the following relations apply:

$$PV = n_g RT \qquad \text{II.2}$$

$$n_T - n_g = n_s \qquad \text{II.3}$$

$$n_s = K'_H P \qquad \text{II.1}$$

where n_s is the number of moles of gas in the liquid phase and K'_H is the Henry's law constant for the solution.

Appropriate substitution in the above equations yields the following expression

$$PV = (n_T - K'_H P) RT \qquad \text{II.4}$$

It should be mentioned that the pressure of the undissolved gas must be corrected for the vapour pressure of solvent over the solution and this results in a modification of eqn. (II.4) giving

$$V_T P_T = (n_T - K'_H P_{Ar})RT \qquad \text{II.5}$$

where V_T and P_T refer, respectively, to the total volume and total pressure in the system while P_{Ar} is the partial pressure of argon calculated from $P_T - P_{H_2O}$ using Raoult's law to estimate P_{H_2O}. By plotting $P_T V_T$ vs. P_{Ar} a straight line of slope $-K'_H RT$ is obtained from which the solubility of the gas can be calculated after K'_H is normalised to K_H, the Henry's law constant for 1 litre of solution.

3. Description of Apparatus used

A photograph of the apparatus used for the gas solubility measurements is shown in Figure 1 and a schematic diagram appears in Figure 2. The system consists of two closed, but mutually connected manometers, one of which (in the thermostat) is also used as a gas burette and is connected to a 500 ml flask containing the liquid solvent phase. Other equipment also shown was used to determine the dead volume of the apparatus.

The solubility measurements depend on four important factors: pressure, volume, temperature and attainment of equilibrium between the liquid and the gas phase. The solubilities were obtained by measuring the pressure in the gas phase and also the volume of the gas and liquid phase all at constant temperature.

The total pressure of the system was determined from the pressure differences shown by the two manometers. A second manometer was used to eliminate the effect of hour to hour changes in atmospheric pressure which were significant in these measurements, since attainment of equilibrium usually took up to twelve hours. The volume of the gas phase was determined from the burette reading on the inner manometer which had previously been calibrated in terms of dead space.

The experimental procedure consisted in preparing solutions of the TAA salts of known concentration in degassed water. The solution was then placed in the apparatus and saturated with gas by

Figure 1.

Photograph of the apparatus used for the gas solubility measurements

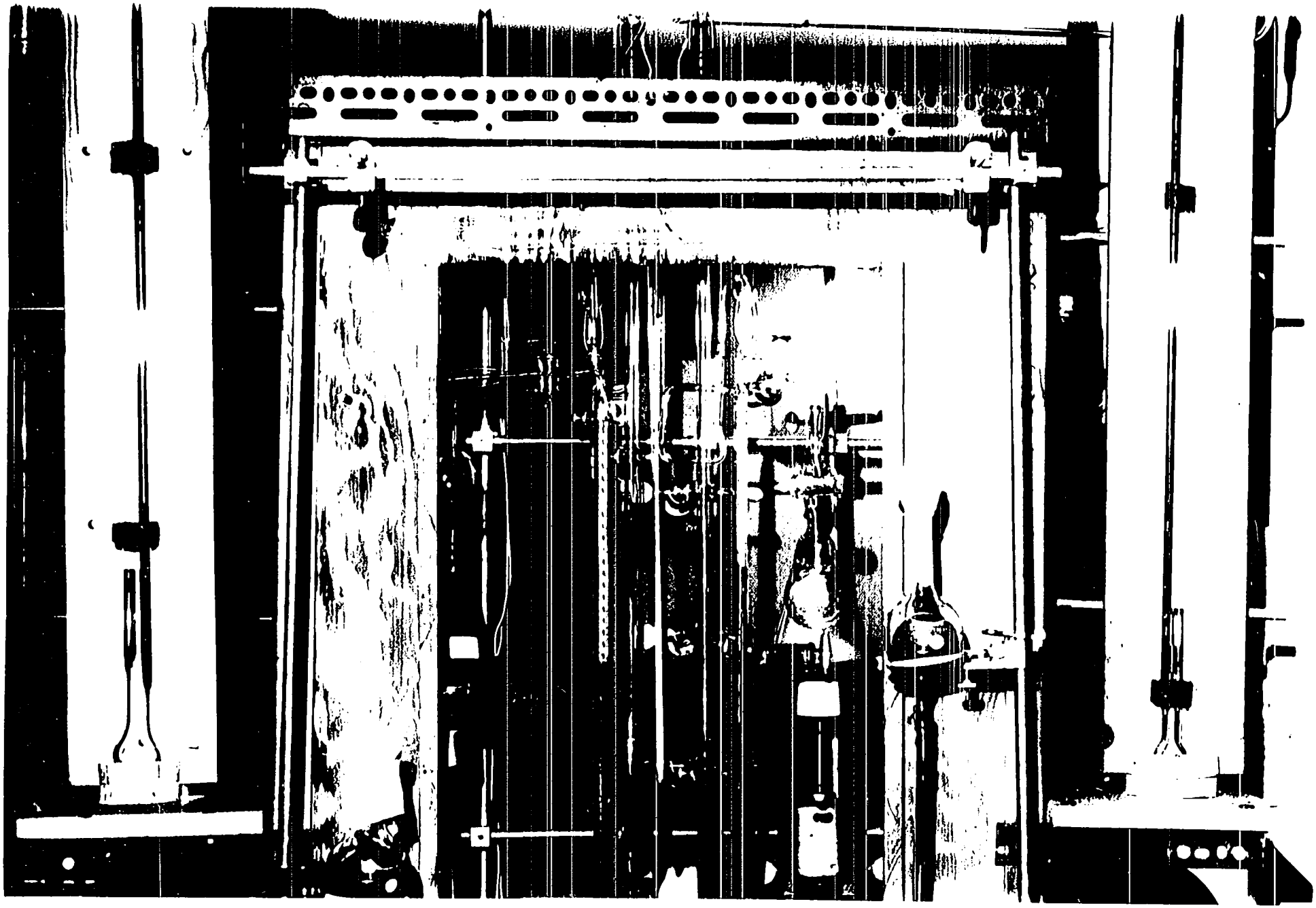
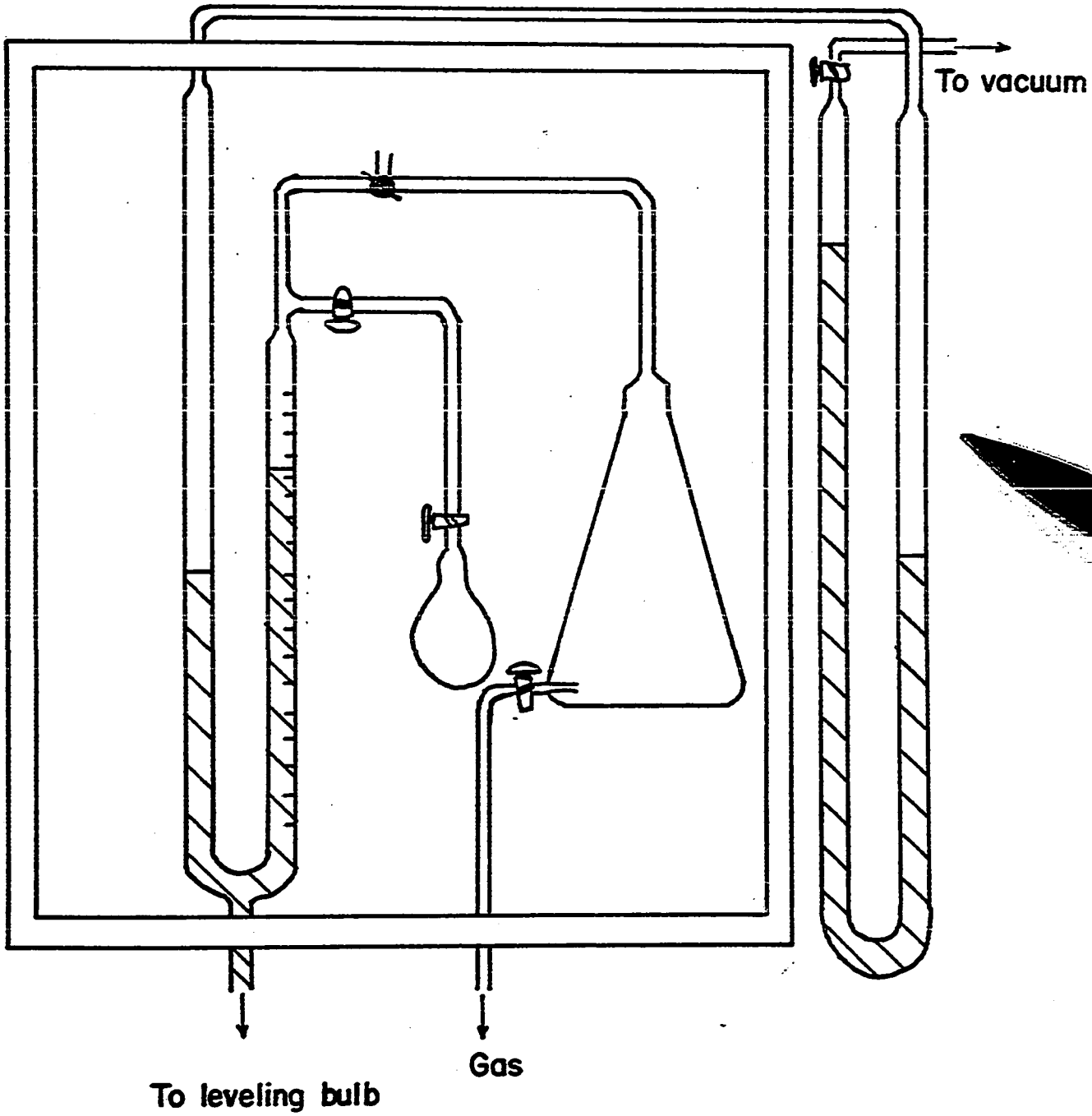


Figure 2.

Schematic diagram of the gas solubility apparatus


To vacuum
Gas
To leveling bulb

bubbling the desired gas through it for at least 30 minutes. This also served to displace other dissolved gases in the system. The system was then closed.

By fixing the pressure of argon over the liquid phase and stirring the system vigorously with a magnetic stirrer, equilibrium was attained after 12 hours. For the last six hours the solution was left unstirred to prevent super-saturation due to the presence of bubbles in which the gas would be above the measured bulk pressure. Final pressure and volume readings were than taken. This procedure was repeated to obtain 6 to 10 points for each solubility determination. The same gas sample was employed for this range of determinations and the present procedure allows a number of determinations of K_H on the given sample at various pressures without the requirement of renewing the solvent phase. Another advantage is that the method allows determination to be made successively at either increasing or decreasing gas pressures so that the successive equilibrium solubilities can be approached in either direction. The solubility determination is hence based on a number of points rather than on a single point as in some other methods (64, 65, 66).

The apparatus was enclosed in a thermostated air bath and all the experiments were carried out at 25°C.

The apparatus was checked by determining the solubility of argon in water. The results shown in the next chapter agreed to within 3 - 4% of those previously reported (58, 59, 60, 61, 62).

4. Advantages of the Present Method

The gas solubilities were evaluated with the aid of graphical plots where $V_T P_T$ was plotted against the partial pressure of argon P_{Ar}. Each of the plots was based on 6 - 10 points, so that the solubility was based on many points over a wide interval of pressures.

In solubility measurements it is of the utmost importance that equilibrium between dissolved and undissolved gas be reached. Vigorous agitation of the liquid phase ensured complete saturation of the liquid with the gas. Equilibrium could be approached by both dissolution and partial outgassing of the liquid phase using appropriate gas pressures. Equilibrium was assumed to have been reached when no further changes in the mercury levels in the manometers could be observed over a period of an hour.

A further advantage of this method is that it precludes the necessity of outgassing the liquid phase. The complete removal of gas from a liquid is important in the saturation methods where the solvent must be initially free of gas and for extraction methods, where the gas is to be completely extracted. The most frequently used method for degassing a liquid is to boil away a portion of it under vacuum. Another degassing procedure involves successively freezing the solution and pumping off the gas above the frozen liquid.

In the present case the solvent was roughly degassed with a water pump prior to making up the solutions. This procedure simply removes the bulk of the dissolved gases so that displacement of the remaining gas from the solution by bubbling of the experimental gas is achieved in less than 30 minutes.

5. Purification of Solvents and Salts used in the Solubility and Density Measurements

(i) Water

Water was used as solvent for all the solubility measurements. It was double distilled, the second distillation being made from alkaline potassium permanganate.

(ii) Methanol

Methanol was used as the solvent in all the density measurements (see below) carried out for determination of partial molal volumes. The methanol used was the Fisher "spectranalysed" grade having 99.95% purity.

(iii) Tetra-n-alkylammonium bromides

The salts employed were a series of symmetrical tetra-n-alkylammonium bromides with alkyl groups increasing in size from methyl to n-butyl. The salts were Eastman reagent grade materials and purification was carried out by recrystallisation using solvents and solvent mixtures recommended previously by Verrall (66) working in this laboratory. After purification, each salt was dried at 50 - 60°C in vacuo for at least two days prior to use.

(iv) NH_4Br

Merck ammonium bromide employed in both the salting-out and density measurements was the analytical reagent grade salt. It was used without further purification.

B.

1. Density Measurements for Evaluation of Partial Molal Volumes

The apparent molal volume ϕ_v of a solute in a solution can be obtained through eqn. (I. 42). It is obvious that ϕ_v depends almost entirely on the accuracy of the density difference $(d - d_o)$, where d_o is the density of the pure solvent while d refers to the solution.

An accurate method for determining the density of liquids is the hydrostatic balance method introduced by Kohlrausch (63) which is based on the Archimedian principle. When used differentially, density differences between solvent and solution can be determined, as shown by Wirth (64), with an accuracy of 2×10^{-6} g. ml^{-1}. This enables ϕ_v measurements to be made down to 0. 01 molal. To examine the densities of solutions at concentrations lower than 0. 01 molal an improved version of Stokes' dilatometer has been used, as developed by Laliberté (65) in this laboratory.

2. Apparatus used

A photograph of the differential buoyancy balance is shown in Figure 3. The apparatus used is similar to that described in detail by Verrall (66). The principle parts of the apparatus are shown in the schematic diagram, Figure 4. The vessels in which the solvent and solution are contained were made of Pyrex tubing of 48 mm i.d. and were placed beneath the balance in Plexiglass holders that could easily be moved to align the bulbs. An Oertling balance, model HO 3, modified for underpan weighting, was used. The floats were cylindrically shaped and had a volume of about 120 ml and were partly filled with mercury to give them an apparent density of about 1.12. The floats were attached to the balance pans with gold-chains and tungsten wires of 0.002" diameter. In order to prevent evaporation of the solution during the measurements, Plexiglass covers were placed on the top of each vessel.

All the measurements were made in a large, well-lagged water thermostat provided with an annular window and heated by means of a partially immersed electric bulb. The temperature of the thermostat was maintained at 25 ± 0.01°C and controlled by a large mercury thermo-regulator. A high speed stirrer provided good circulation in the bath.

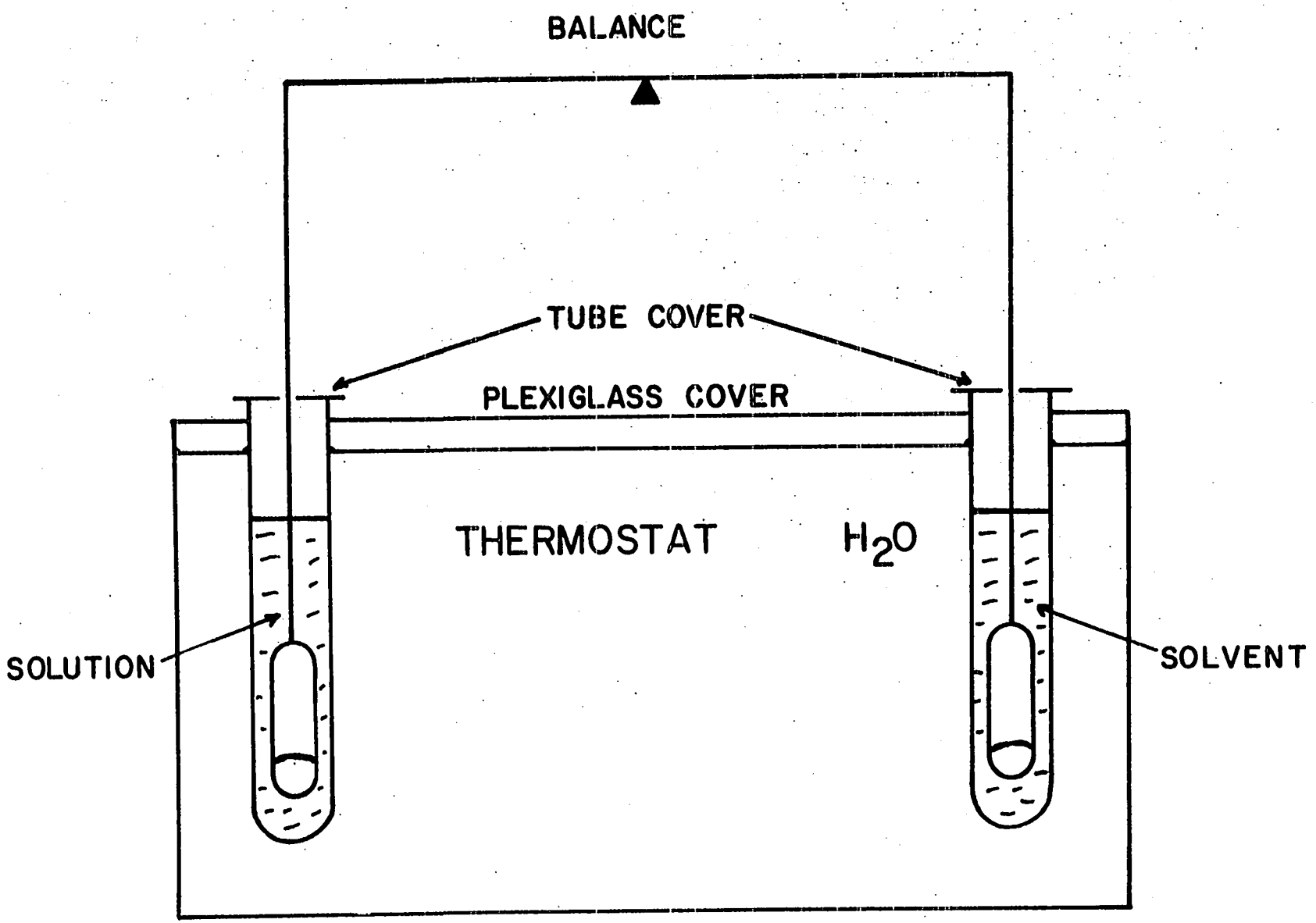
The dilatometer used to determine ϕ_v for the lowest concentrations of $(CH_3)_4NBr$ salt has been described in detail in a previous thesis by Laliberté (65).

Figure 3.

Photograph of differential buoyancy balance

Figure 4.

Schematic diagram of differential buoyancy balance


BALANCE
TUBE COVER
PLEXIGLASS COVER
THERMOSTAT
H_2O
SOLUTION
SOLVENT

3. Experimental Measurements

The following procedure was used to determine the density difference between the solvent and solution. A "zero" reading "wt_o" was first taken with the same liquid (solvent) in both vessels. This reading was taken since the volumes of the bulbs in the two vessels were not identical. A solution was then placed in one of the vessels and a second reading "wt" was taken. The density difference between the solution and solvent is then given by

$$d - d_o = \frac{wt - wt_o}{V_B} \qquad \text{II. 6}$$

where V_B is the volume of the bulb in the solution. The solutions were prepared in the test vessel by adding known weights of salt to a weighed amount of solvent giving the concentrations in molalities.

In order to prevent evaporation of the methanol, the vessels were kept covered during the measurements except for a hole of about 5 mm diameter in each cover. The density differences were reproducible to ca. $\pm 1 \times 10^{-5}$ g.mol^{-1} within a run.

The determination of ϕ_v of $(CH_3)_4NBr$ at low concentrations was necessitated by its relative insolubility in methanol. A dilution dilatometer was used for these measurements. In this technique, the difference in apparent molar volume between a concentrated starting solution and a final diluted one was measured. If $\phi_{v(init)}$ is the apparent molar volume of the salt in the initial concentrated solution and $\phi_{v(fin)}$ is the apparent molar volume of the

salt in the final diluted solution, then it can be shown that the following relation holds

$$\phi_{v(fin)} = \phi_{v(init)} + \frac{\Delta V}{n_2} \qquad \text{II. 7}$$

where ΔV is the change in volume upon dilution of the concentrated solution and n_2 is the number of moles of solute in the concentrated solution.

A capsule containing the concentrated solution was placed in the dilatometer filled with water. The whole apparatus was placed in a thermostat ($25. \pm 0.001^{o}C$) and the solvent was stirred for two hours. When thermal equilibrium had been established as indicated by observation of the liquid level in the capillary arm of the dilatometer, the contents of the capsule were allowed to mix with the solvent by releasing a magnetically operated valve. The change in volume ΔV upon mixing was determined by observing the change in level of the liquid in the calibrated capillary.

4. Accuracy of Apparatus and Reproducibilities of the Measurements

The density differences between solvent and solution can, in principle, be obtained to six decimal places. It was found that the scatter in the density determinations was slightly higher than that previously obtained in aqueous studies using this apparatus. This is due presumably to the greater volatility of the solvent which, although minimised, still occurred to a greater extent than with aqueous solutions. This results in an uncertainty of $\pm$ 0.050 ml(g.mole)$^{-1}$ in the ϕ_v determinations at moderate concentrations.

CHAPTER III

RESULTS

A. SALTING-OUT AND SALTING-IN

1. Test of the Apparatus

The apparatus was checked by determining the solubility of argon in water. As shown in Figure 5, a straight line of slope -16.30 ± 0.05 ml was obtained from which the solubility of argon in water could be calculated. The solubility of argon in water at 25°C determined by the above procedure was $1.31 \times 10^{-3} \pm 0.04 \times 10^{-3}$ mole.l^{-1}atm^{-1}.

A comparison of the values of the solubility of argon obtained by different authors in previous studies and that obtained in the present work is shown in Table 1. As can be seen, the present solubility data agree within the limits of the experimental errors, with the values listed, although the present value tends to be low by 3 - 4%.

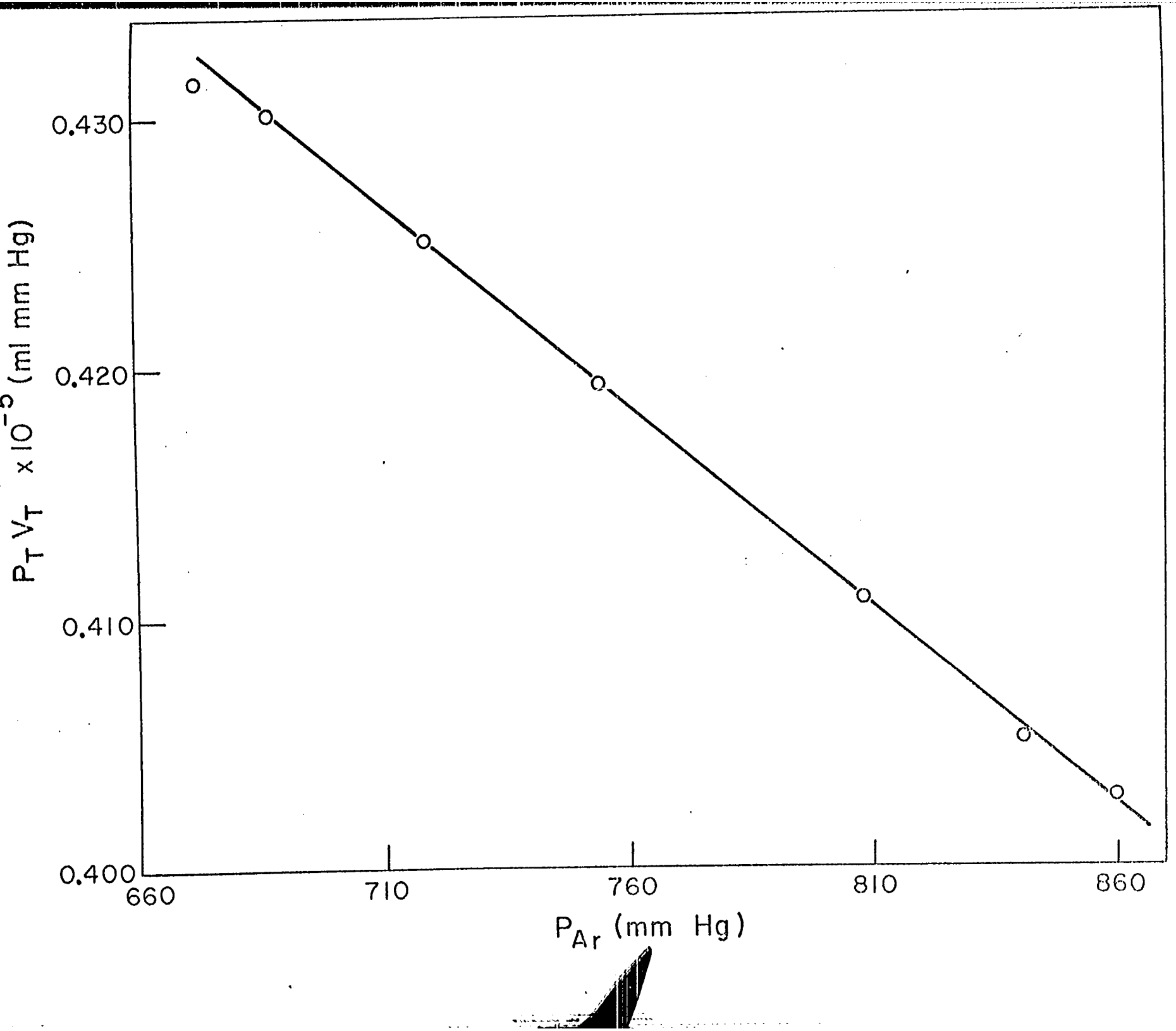
Table I

Summary of Previous Solubility Data for Ar in Water at 25°C

Author(s) and Reference	Solubility of argon in water (mole. l^{-1}. atm. $^{-1}$)
Ben-Naim (1965) (58)	$1.39 \times 10^{-3} \pm 0.02 \times 10^{-3}$
Hildebrand and Scott (1964) (59)	$1.38 \times 10^{-3} \pm 0.03 \times 10^{-3}$
Morrison and Johnstone (1954) (60)	$1.37 \times 10^{-3} \pm 0.02 \times 10^{-3}$
Douglas (1964) (61)	$1.39 \times 10^{-3} \pm 0.02 \times 10^{-3}$
Lannung (1934) (62)	$1.40 \times 10^{-3} \pm 0.02 \times 10^{-3}$
Present work	$1.31 \times 10^{-3} \pm 0.04 \times 10^{-3}$

Figure 5

Experimental data for argon in water at 25°C plotted according to eqn. (III. 5)


0.430
0.420
0.410
0.400
$P_T V_T \times 10^{-5}$ (ml mm Hg)
660
710
760
810
860
P_{Ar} (mm Hg)

2. Experimental Plots

The value of the Henry's law constant for each of the solutions was obtained by plotting the data according to equation (II. 5) from which a straight line of slope - $K'_H RT$ was obtained. The solubility was then calculated from the value of K'_H.

Figures 6, 7, 8, 9 and 10 show some representative solubility data for argon in NH_4Br and four TAA bromide salt solutions. The straight lines obtained are characterized by the slopes - $K'_H RT$ which indicate the solubility of the desired gas in the actual volume of the solution (see below). Since the absolute values of the slopes in the lines in Figures 7, 8, 9 and 10 are lower than that for argon in pure water, salting-out is occurring in these solutions, while salting-in occurs with NH_4Br. The values of the slopes of the lines representing the experimental data in Figure 6 to 10 are:

for 0.5 M NH_4Br -16.60 ± 0.05 ml (509.4)

for 3.0 M $(Me)_4NBr$ -6.80 ± 0.05 ml (496.7)

for 1.0 M $(Et)_4NBr$ -10.26 ± 0.05 ml (499.7)

for 0.5 M $(\underline{n}\text{-}Pr)_4NBr$ -9.40 ± 0.05 ml (499.5)

for 0.75 M $(\underline{n}\text{-}Bu)_4NBr$ -11.40 ± 0.05 ml (497.7)

where the numbers in parentheses are the respective volumes V, of solution involved, i.e. $-\frac{\text{slope}}{RT} \times \frac{1000}{V} = S$ mole $(\text{atm.l})^{-1}$.

The uncertainties of the PV values are indicated by the sizes of the error circles.

Figure 6

Experimental data for argon in 0.5 molar NH_4Br solution at 25°C plotted according to eqn. (III. 5)

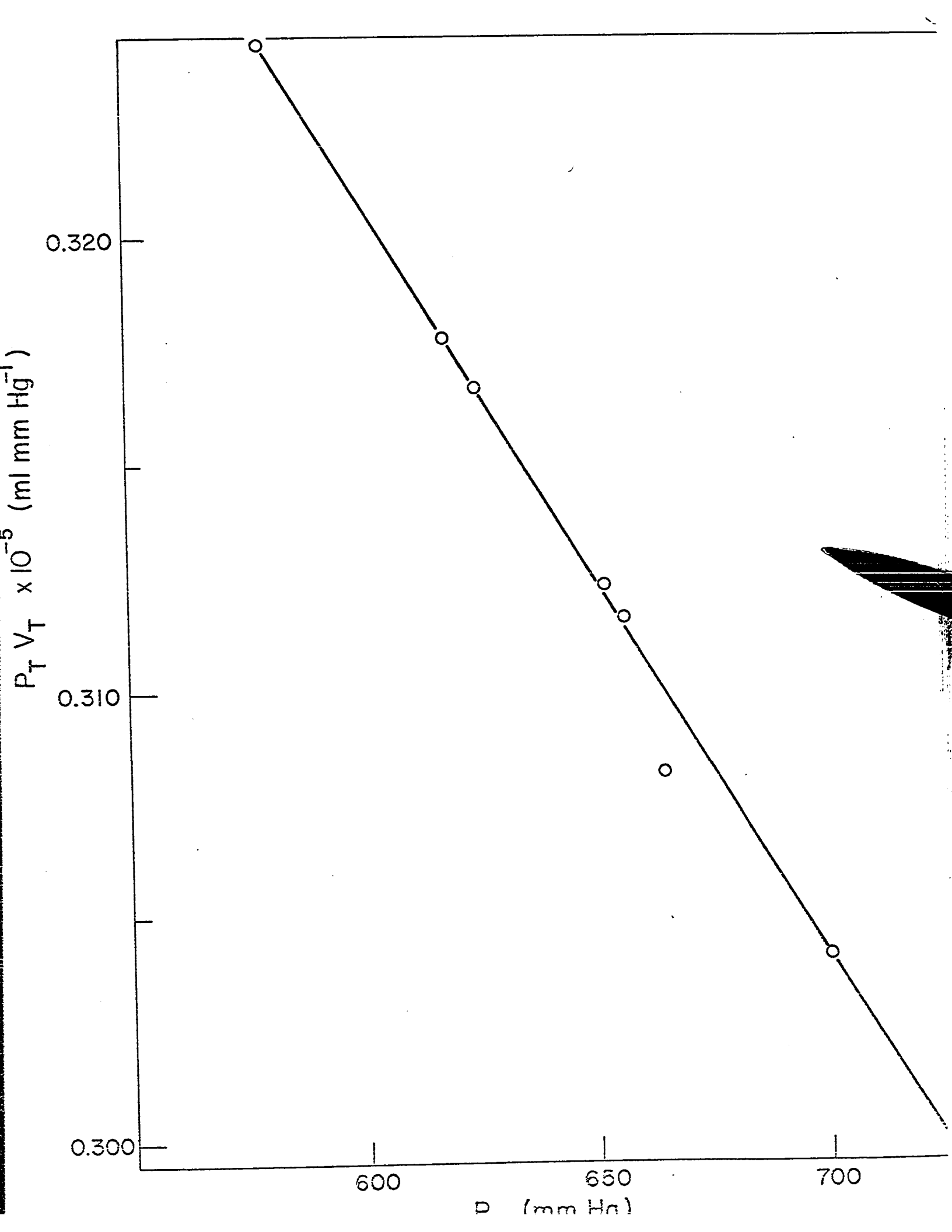

0.320
0.310
0.300
$P_T V_T \times 10^{-5}$ (ml mm Hg^{-1})
600
650
700
P (mm Hg)

Figure 7

Experimental data for argon in 3.0 molar $(Me)_4NBr$ solution at 25°C plotted according to eqn. (III. 5)

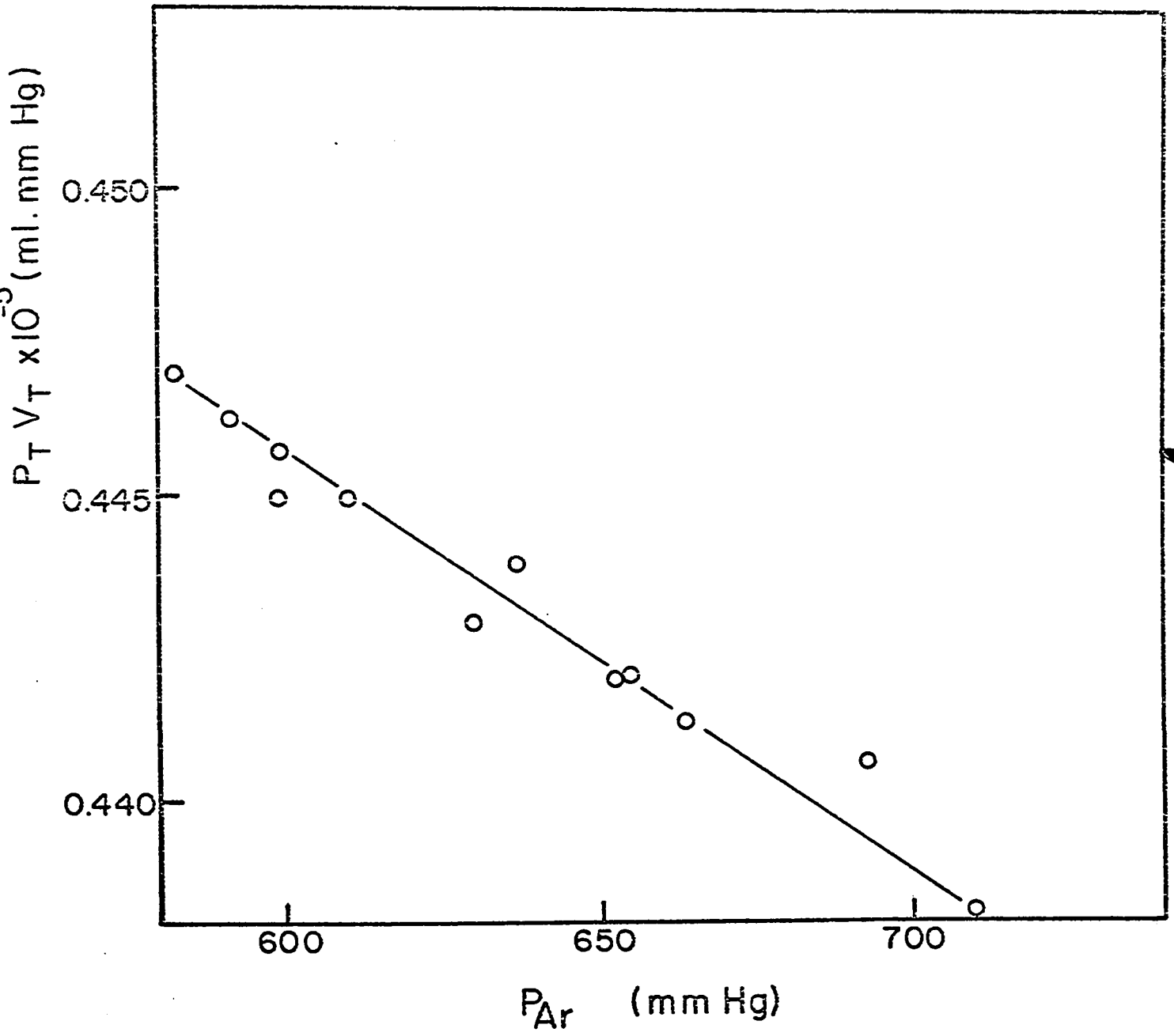

$P_T V_T \times 10^{-5}$ (ml. mm Hg)
0.450
0.445
0.440
600
650
700
P_{Ar} (mm Hg)

Figure 8

Experimental data for the solubility of argon in 1.0 molar $(Et)_4NBr$ solution plotted according to eqn. (III.5)

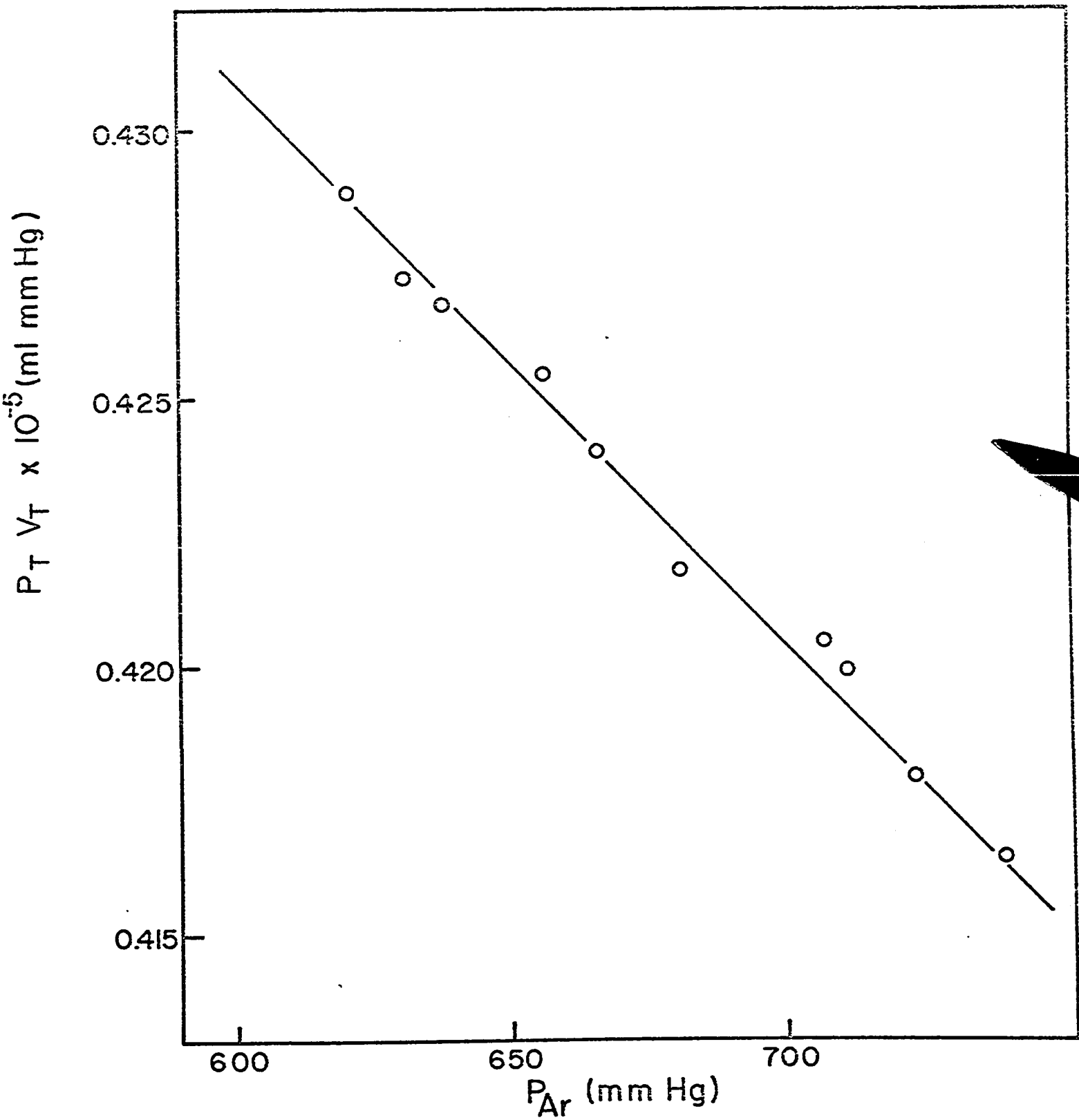

0.430
0.425
0.420
0.415
$P_T V_T \times 10^{-5}$ (ml mm Hg)
600
650
700
P_{Ar} (mm Hg)

Figure 9

Experimental data for argon in 0.5 molar $(\underline{n}\text{-Pr})_4NBr$ solution at 25°C plotted according to eqn. (III. 5)

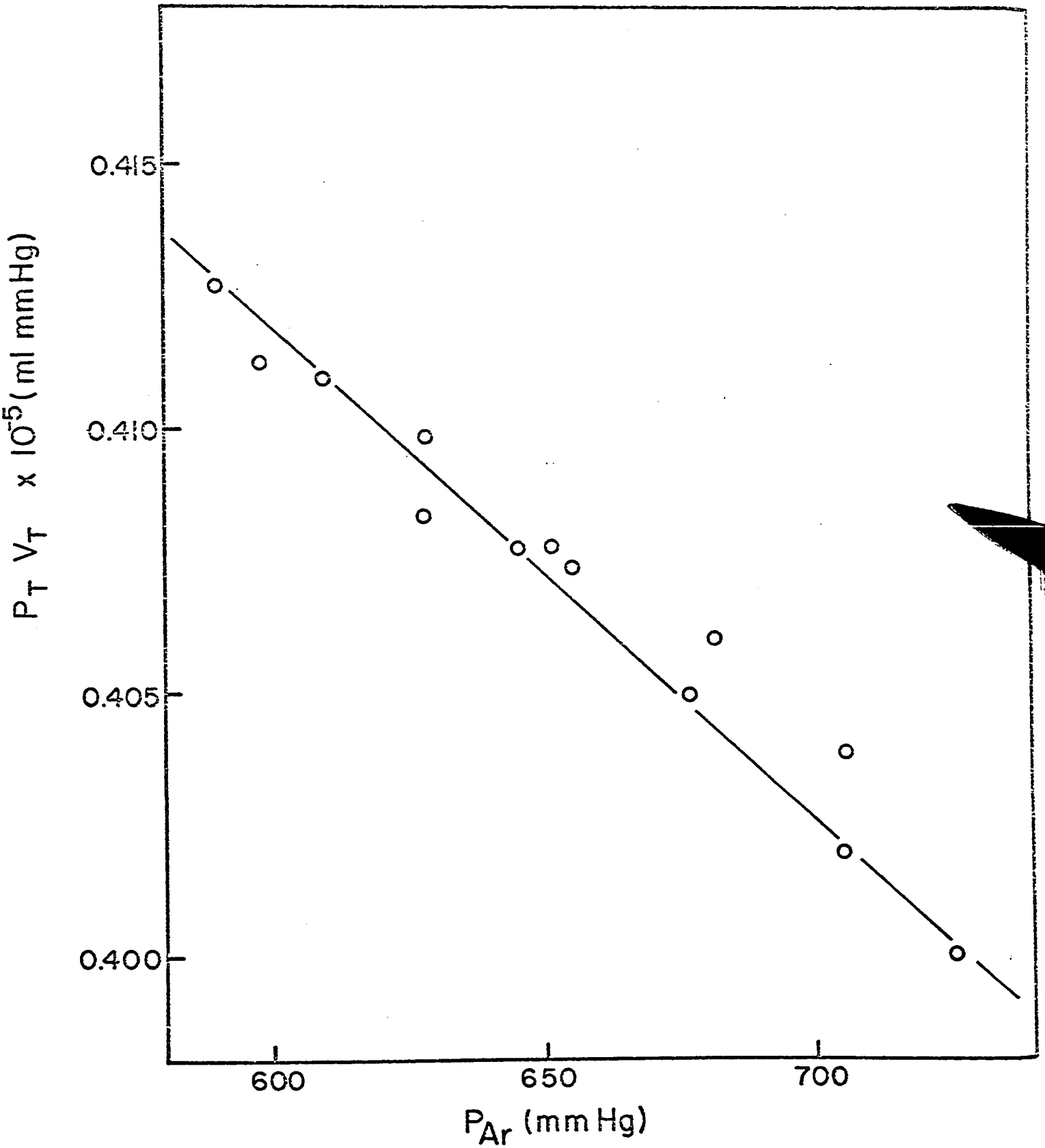
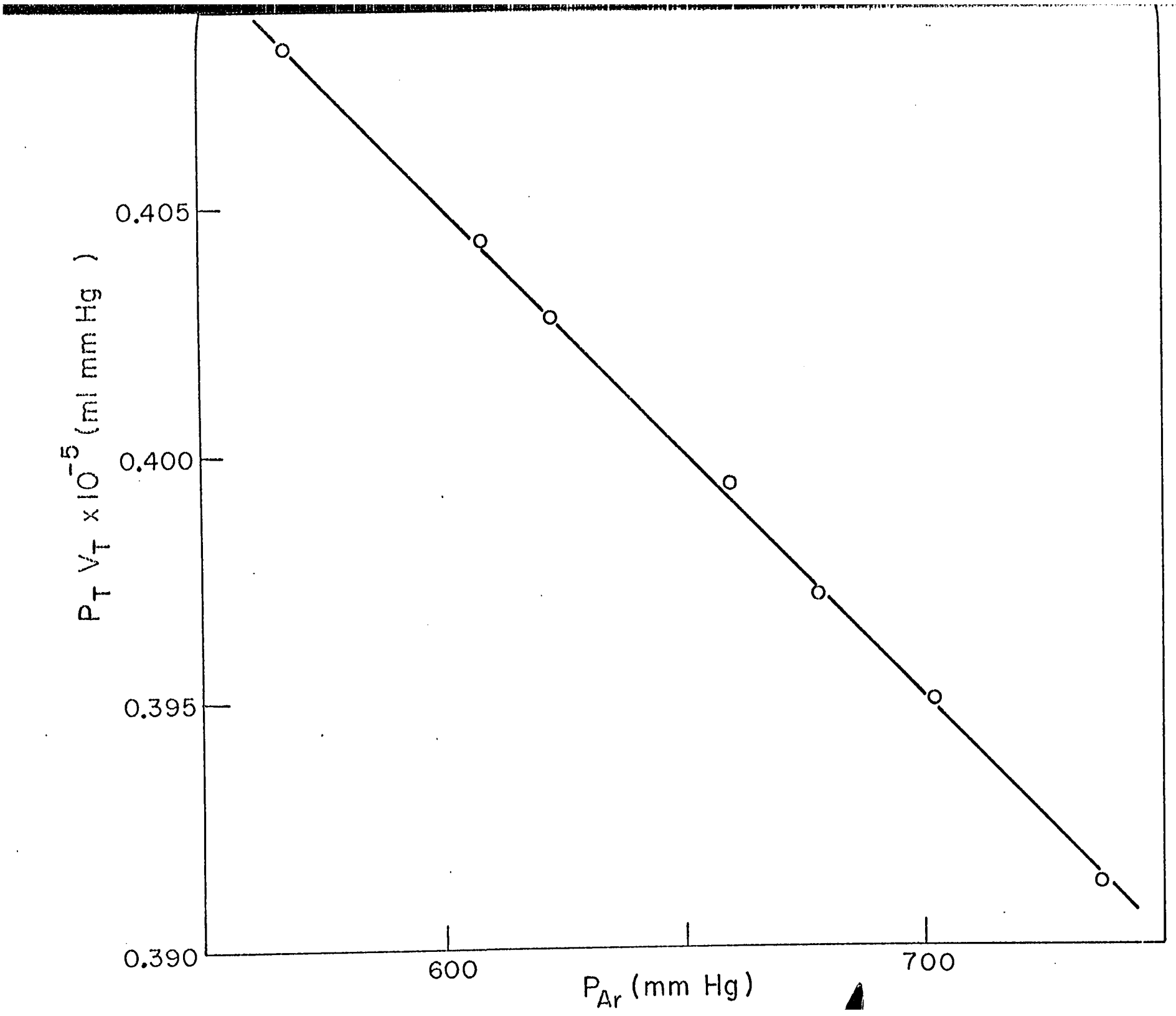

0.415
0.410
0.405
0.400
$P_T V_T \times 10^{-5}$ (ml mm Hg)
600
650
700
P_{Ar} (mm Hg)

Figure 10

Experimental plot for argon in 0.75 molar $(\underline{n}\text{-Bu})_4NBr$ solution at 25°C plotted according to eqn. (III. 5)


0.405
0.400
0.395
0.390
$P_T V_T \times 10^{-5}$ (ml mm Hg)
600
700
P_{Ar} (mm Hg)

3. Evaluation of Solubilities

A complete tabulation of the solubilities of argon and the Henry's law constants for the TAA salt solutions which were studied is given in Table 2. All the concentrations of electrolyte are expressed in mole $l.^{-1}$ (C). The solubilities of the non-electrolyte gas are given at one atmosphere gas pressure and are expressed in moles of gas dissolved at equilibrium in one litre of solution. The value for the solubility of argon in pure water is also listed in the same Table.

As can be seen, the solubilities decrease both with concentration and increasing size of the cation. The solubility values differ slightly for the lower concentrations of the TAA bromides, viz. < 0.5 M, but the differences between the solubility values become greater at higher concentrations.

Table 2

Solubilities of Argon in NH_4Br and TAA Bromide Solutions, 25°C

Salt	C mole l^{-1}	$10^6 K_H$ mole mm $Hg^{-1}l^{-1}$	$10^3 S$ mole l^{-1} $atm.^{-1}$
Argon in pure water at 25°C	$S_o = 1.31 \times 10^{-3} \pm 0.04 \times 10^{-3}$ mole. $l^{-1}atm^{-1}$		
NH_4Br	0.25	8.88	1.32
	0.50	8.93	1.33
	1.00	9.41	1.45
	2.00	9.85	1.47
$(Me)_4NBr$	0.25	1.70	1.29
	0.50	1.67	1.27
	1.00	1.62	1.23
	1.50	1.55	1.18
	2.00	1.32	1.00
	3.00	0.74	0.56
$(Et)_4NBr$	0.25	1.68	1.28
	0.50	1.52	1.16
	1.00	1.13	0.85
	1.50	0.79	0.61
	2.00	0.71	0.54
	2.50	0.70	0.55
	3.00	0.88	0.67

Table 2. (ctd.)

	C	$10^6 K_H$	$10^3 S$
	mole l^{-1}	mole mm $Hg^{-1}l^{-1}$	mole $l^{-1}atm.^{-1}$
$(n\text{-}Pr)_4NBr$	0.20	1.68	1.27
	0.30	1.62	1.23
	0.50	1.02	0.77
	1.00	0.76	0.59
	1.50	0.81	0.61
$(n\text{-}Bu)_4NBr$	0.20	8.29	1.25
	0.30	4.14	0.63
	0.50	4.36	0.67
	0.75	6.13	0.94

4. Concentration Dependence of $\Delta S/S_o$ and log S/S_o

The salting-out ratio $\Delta S/S_o$ and the log S/S_o values have been listed in Table 3 as a function of the concentration of the salt. The sign of the salting-out ratio indicates that salting-out is occurring. Figure 11 shows a complete summary of the results obtained in the present study. As can be seen, the three TAA bromides all exhibit strong salting-out. There is a linear section in the plots at low concentration as predicted by the Setchenow equation (I.10) and the slopes of these linear sections can be taken as the salting-out constants, k_s. For $(Et)_4NBr$, $(\underline{n}\text{-}Pr)_4NBr$ and $(\underline{n}\text{-}Bu)_4NBr$ at concentrations above *ca.* 0.3 molar, non-linear behaviour is observed in the log S/S_o *vs.* C plot and, in fact, the curves pass through a minimum at higher concentrations. This would seem to suggest that salting-in would eventually occur at even higher concentrations if such could be experimentally attained. However, experimental difficulties related to the surface active nature of these salts or to the limited solubility of some members of the series precluded the extension of these measurements to very high concentrations. In Figure 12, a plot of $\Delta S/S_o$ *vs.* concentration for the five salts studied is shown. In this case, the curves again exhibit a linear section at lower concentrations as predicted by the Setchenow equation. For the larger TAA cations, the maxima in the curves occur at higher concentrations.

Table 3

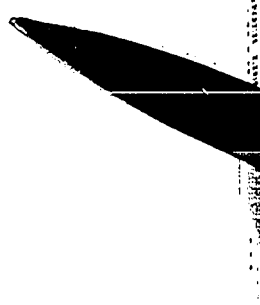
Salting-out of Argon by Tetraalkylammonium Bromides, 25°C, expressed in terms of log S/S_o and $\Delta S/S_o$

Salt	C mole l^{-1}	S mole $l^{-1}atm^{-1}$	log S/S_o	$\Delta S/S_o$
NH_4Br	0.25	1.32×10^{-3}	+0.0033	-0.0081
	0.50	1.33×10^{-3}	+0.0166	-0.0152
	1.00	1.45×10^{-3}	+0.0440	-0.1070
	2.00	1.47×10^{-3}	+0.0500	-0.2210
$(Me)_4NBr$	0.25	1.29×10^{-3}	-0.0070	0.0153
	0.50	1.27×10^{-3}	-0.0146	0.0305
	1.00	1.23×10^{-3}	-0.0287	0.0611
	1.50	1.18×10^{-3}	-0.0462	0.0992
	2.00	1.00×10^{-3}	-0.1158	0.2366
	3.00	0.56×10^{-3}	-0.3696	0.5725
$(Et)_4NBr$	0.25	1.28×10^{-3}	-0.0106	0.0229
	0.50	1.16×10^{-3}	-0.0545	0.1145
	1.00	0.85×10^{-3}	-0.1904	0.3511
	1.50	0.61×10^{-3}	-0.3354	0.5343
	2.00	0.54×10^{-3}	-0.3820	0.5878
	2.5	0.55×10^{-3}	-0.3757	0.5802
	3.0	0.67×10^{-3}	-0.2916	0.4885

Table 3. (ctd.)

Salt	C mole l^{-1}	S mole $l^{-1}atm^{-1}$	log S/S_o	$\Delta S/S_o$
$(n\text{-}Pr)_4NBr$	0.20	1.27×10^{-3}	-0.0123	0.0305
	0.30	1.23×10^{-3}	-0.0273	0.0610
	0.50	0.77×10^{-3}	-0.2291	0.4122
	1.00	0.59×10^{-3}	-0.3439	0.5496
	1.50	0.61×10^{-3}	-0.3410	0.5343
$(n\text{-}Bu)_4NBr$	0.20	1.25×10^{-3}	-0.0204	0.0472
	0.30	0.63×10^{-3}	-0.3179	0.5191
	0.50	0.67×10^{-3}	-0.2916	0.4885
	0.75	0.94×10^{-3}	-0.1441	0.2824

Figure 11



Salting-out ratio (logarithmic plot) for change of solubility of argon caused by NH_4Br and TAA bromides at 25°C;

O $(Me)_4NBr$

Δ $(Et)_4NBr$

● $(\underline{n}\text{-}Pr)_4NBr$

□ $(\underline{n}\text{-}Bu)_4NBr$

▲ NH_4Br

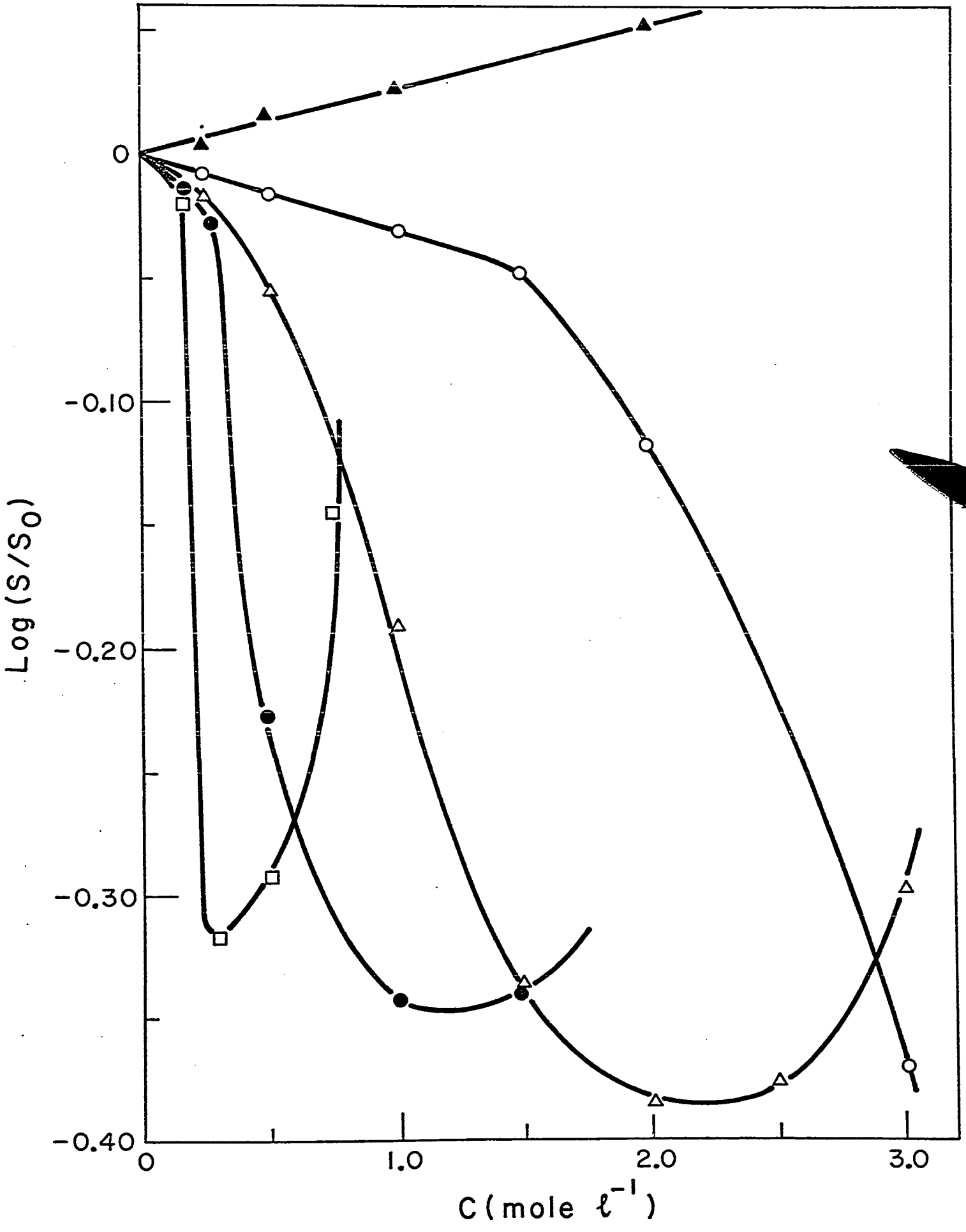

0
-0.10
-0.20
-0.30
-0.40
Log (S/S0)
0
1.0
2.0
3.0
C (mole ℓ-1)

Figure 12

Salting-out ratio for change of solubility of argon caused by NH_4Br and TAA bromides at 25°C;

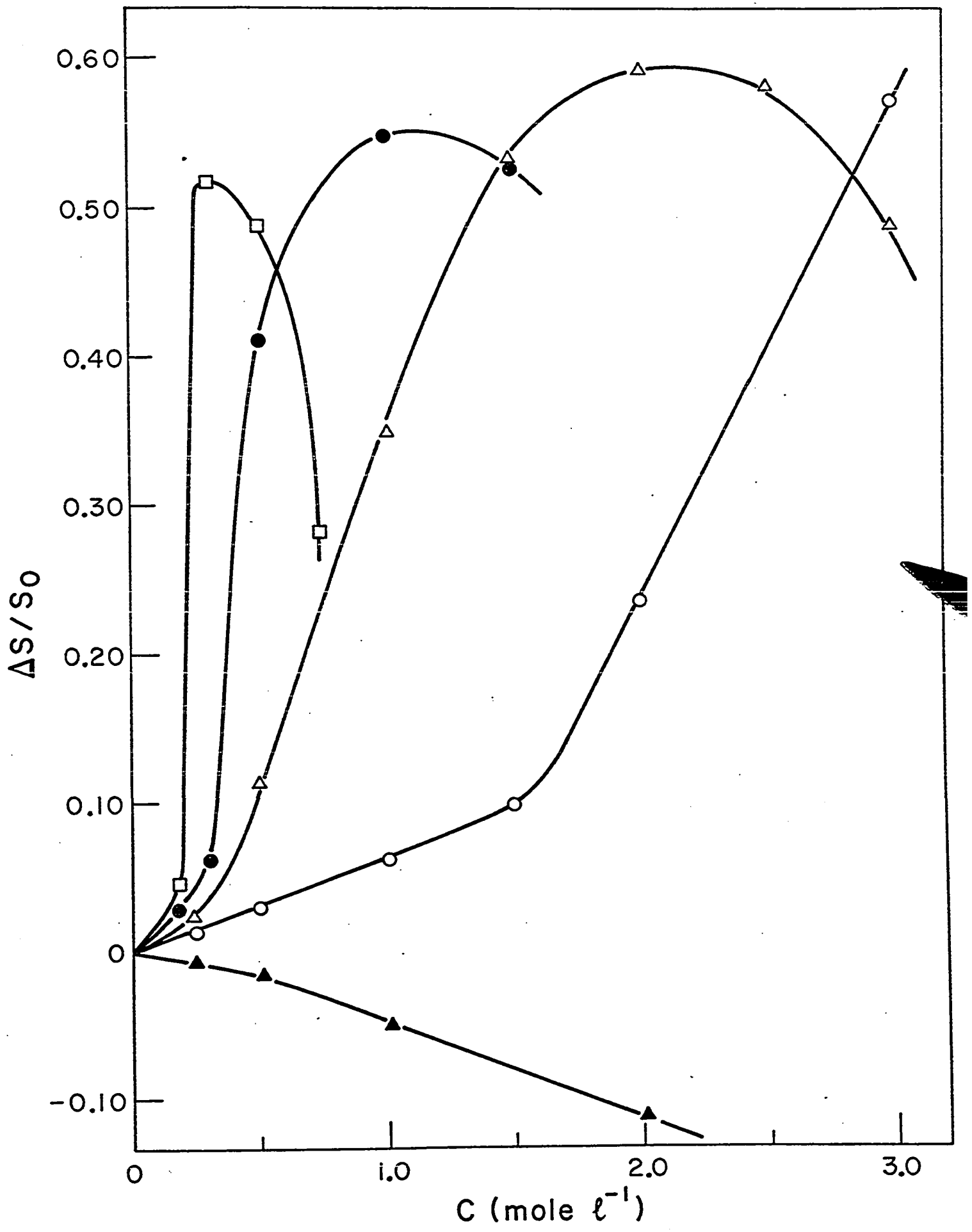
O $(Me)_4NBr$

Δ $(Et)_4NBr$

● $(\underline{n}\text{-}Pr)_4NBr$

□ $(\underline{n}\text{-}Bu)_4NBr$

▲ NH_4Br


0.60
0.50
0.40
0.30
0.20
0.10
0
-0.10
ΔS/S0
0
1.0
2.0
3.0
C (mole ℓ⁻¹)

B. PARTIAL MOLAR VOLUMES

1. Results of Density Determinations with R_4NBr Salts in Methanol

The densities of solutions of TAA bromides in methanol were measured in order to examine the influence of large hydrophobic cations on ion-solvent interactions in a relatively compressible solvent (contrast water) and to compare the results with those observed in previous studies in this laboratory in the aqueous medium (48, 49, 65).

The apparent molar volumes of a series of TAA bromides in methanol were evaluated from equation (II. 2). The measurements were carried out in the concentration range 0. 01 to $\gtrsim$ 0. 6 molal. The experimental data have been plotted according to equation (II. 3).

Measurements of the apparent molal volume of NH_4Br in anhydrous methanol were also made in order to compare the behaviour of the small cation NH_4^+ with that of large hydrophobic ions. Dilatometric measurements were also carried out with $(Me)_4NBr$ solutions in order to extend the concentration range to higher dilutions. This was necessary because the salt is relatively insoluble in MeOH.

In Figure 13, ϕ_v is shown plotted against $m^{1/2}$ for NH_4Br in the concentration range 0. 01 to 0. 06 molal. The relation is linear and has a slope of 11. 0 ± 0. 2 ml kg methanol$^{1/2}$ (g mole)$^{-3/2}$. Figure 14 shows the results for $(Me)_4NBr$ obtained with the dilatometer and the buoyancy balance. The concentration range is from 0. 01 to 0. 2 molal. The relation between ϕ_v and $m^{1/2}$ is linear and has a slope of 12. 5 ± 0. 2 ml kg methanol$^{1/2}$ (g mole)$^{-3/2}$.

Figure 13

A plot of apparent molal volume ϕ_v, against $m^{1/2}$ for NH_4Br in anhydrous methanol at 25°C

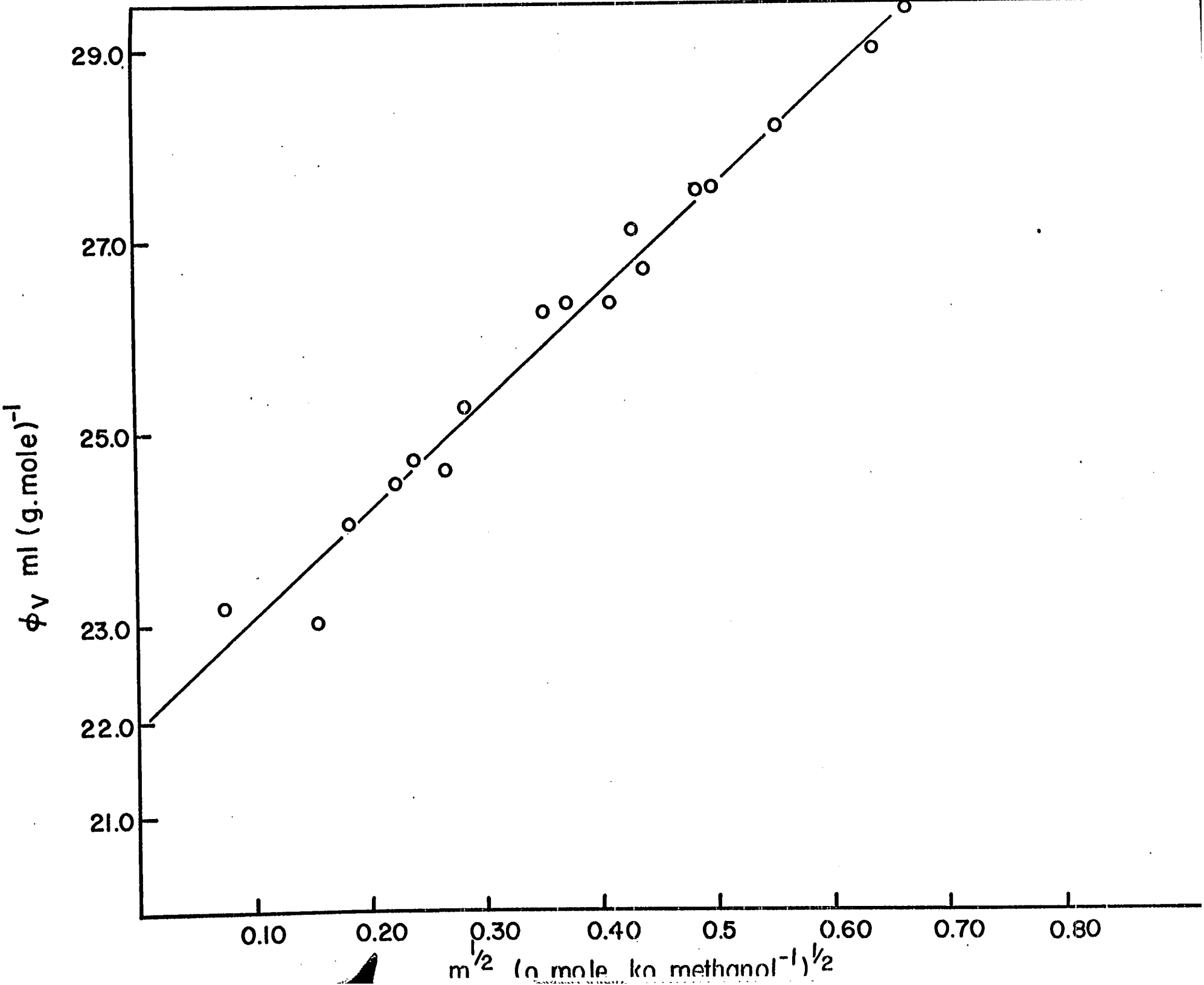
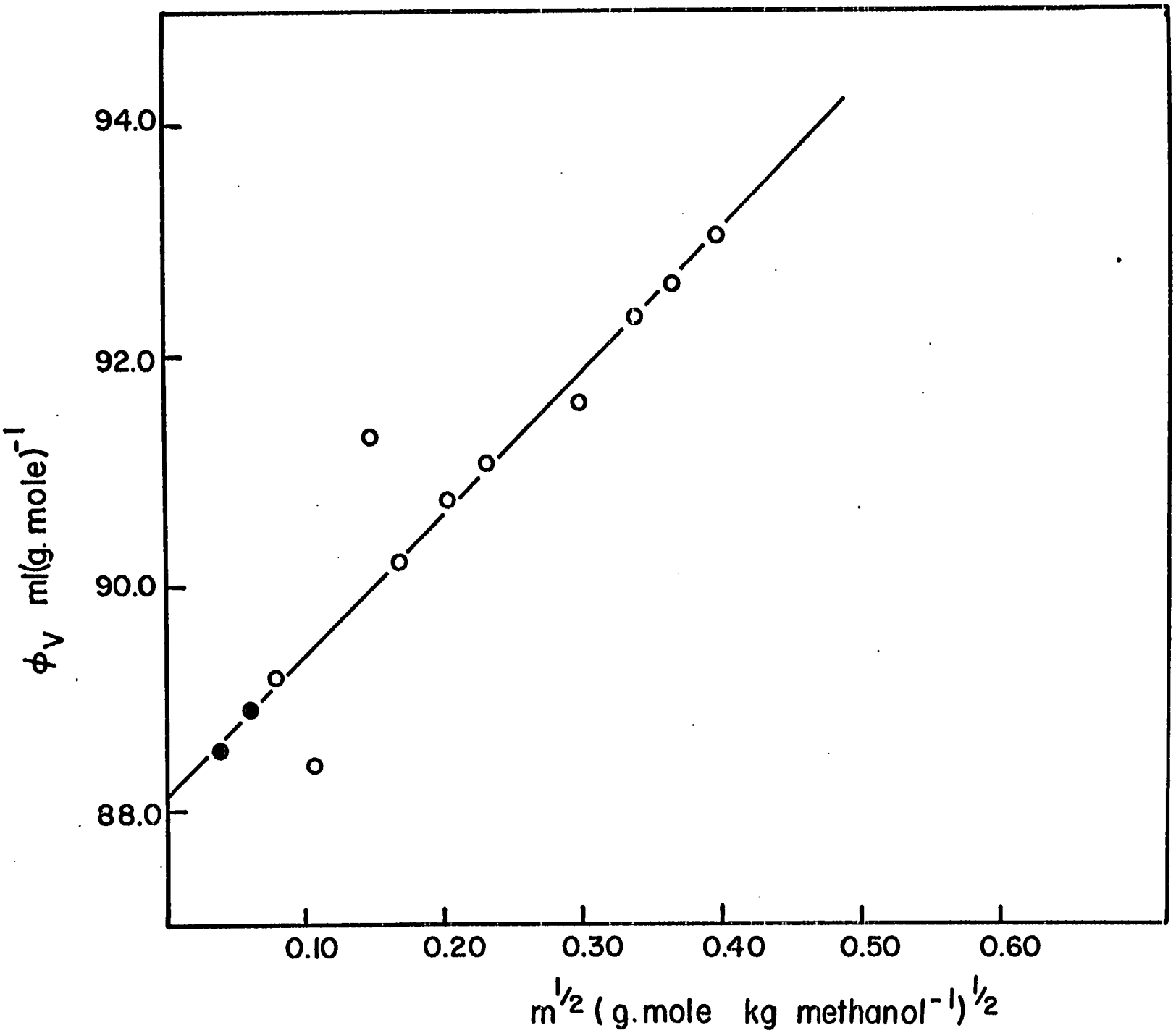

29.0
27.0
25.0
23.0
22.0
21.0
ϕ_V ml (g.mole)$^{-1}$
0.10
0.20
0.30
0.40
0.5
0.60
0.70
0.80
$m^{1/2}$ (g mole kg methanol^{-1})$^{1/2}$

Figure 14

A plot of apparent molar volume ϕ_v as a function of $m^{1/2}$ for $(Me)_4NBr$ in methanol at 25°C;

● results obtained by dilatometer

O results obtained with differential buoyancy balance


94.0
92.0
90.0
88.0
ϕ_V ml(g. mole)$^{-1}$
0.10
0.20
0.30
0.40
0.50
0.60
$m^{1/2}$ (g.mole kg methanol^{-1})$^{1/2}$

In Figures 15, 16 and 17 are shown the experimental results for $(Et)_4NBr$, $(\underline{n}\text{-}Pr)_4NBr$ and $(\underline{n}\text{-}Bu)_4NBr$ in anhydrous methanol plotted according to equation (II. 3). In these cases, the observed relations consist of two linear regions. The slope of the linear section at low concentrations deviates only slightly from that predicted by the Debye-Hückel limiting law, but the deviations are much higher at higher concentrations. The slopes obtained for the lower concentrations are:

for $(Et)_4NBr$, 14.0 ± 0.2 ml kg methanol$^{1/2}$ (g mole)$^{-3/2}$

for $(\underline{n}\text{-}Pr)_4NBr$, 13.5 ± 0.2 ml kg methanol$^{1/2}$ (g mole)$^{-3/2}$

for $(\underline{n}\text{-}Bu)_4NBr$, 14.7 ± 0.2 ml kg methanol$^{1/2}$ (g mole)$^{-3/2}$

The experimental data of densities and partial molal volumes of NH_4Br and TAA bromides in methanol are listed in Table 4.

The results for $\bar{V}_2^o$ obtained in this study on TAA bromides in anhydrous methanol are listed in Table 5, together with the experimental slopes $d\bar{V}_2/dc^{1/2}$.

In Figure 18 a Redlich and Meyer (67) plot is shown for $(\underline{n}\text{-}Pr)_4NBr$ in methanol. This type of plot removes the expected concentration dependence due to long range ionic interaction effects predicted by the Debye-Hückel theory, ie.

$$\phi_v - 15.77\, m^{1/2} = \phi_v^o + h\, m \qquad \text{(IV.1)}$$

and any resulting concentration dependence of the function plotted arises from deviations from the (limiting) Debye-Hückel behaviour.

As was found in the previous studies on aqueous solutions of TAA salts (33), the coefficient h is negative at higher concentrations although it becomes negligible at lower concentrations. The experimental determination of $\bar{V}_2$ for NH_4Br $(Et)_4NBr$, $(\underline{n}\text{-}Pr)_4NBr$ and $(\underline{n}\text{-}Bu)_4NBr$ and two of the chloride series, $(Me)_4NCl$ and $(Et)_4NCl$, were carried out in anhydrous methanol at 25°C (52). It was found that the apparent and partial molar volumes increased with concentration. This is the normal behaviour, but is to be contrasted with that exhibited in aqueous solutions of the TAA salts where (except at the very lowest attainable concentrations) $\bar{V}_2$ and ϕ_v decrease with concentration.

The concentration range investigated was from 0.1 to 2.0 M and it was found that within this range the apparent molar volumes of the salts studied varied linearly with $c^{1/2}$. The experimental values of S_v did not agree exactly with that predicted by the Debye-Hückel theory, which gives for methanol a value of 15.77 (65). The slopes of the second linear part covering the higher concentration range were found to be similar to those previously found by Padova and Abrahamer (52) except for $(\underline{n}\text{-}Bu)_4NBr$ where the slope found in the present work was smaller. The extrapolations of Padova and Abrahamer to obtain $\bar{V}_2^o$ were evidently made incorrectly since insufficiently low concentrations were employed in the measurements. Similar changes in the dependence of $\bar{V}_2$ on concentration at the lowest concentrations were also found previously by Laliberté (65) with salts of pyridine and its homologues in water and demonstrate the necessity of making measurements down to the lowest possible concentrations in the case of organic salt solutions where non-electrostatic effects have long range influence comparable to that of the Debye-Hückel coulombic effects.

Table 4

Apparent Molal Volumes and Densities of a Series of Tetra-n-alkylammonium Bromides in Methanol at 25°C

Salt	m g mole (kg methanol^{-1})	d g ml^{-1}	ϕ_v ml(g mole)$^{-1}$
NH_4Br	0.005922	0.786978	23.205
	0.016515	0.787661	21.364
	0.024755	0.788154	23.009
	0.034174	0.788726	24.062
	0.043813	0.789342	22.543
	0.048979	0.789626	24.602
	0.049688	0.789685	24.450
	0.057879	0.790173	24.728
	0.070534	0.790961	24.627
	0.079796	0.791492	25.283
	0.110368	0.793294	26.285
	0.125065	0.794184	26.313
	0.138877	0.795014	26.335
	0.172573	0.807012	26.338
	0.183015	0.797594	27.163
	0.193430	0.802246	26.698
	0.232506	0.800496	27.536
	0.242567	0.801180	27.567
	0.303355	0.804574	28.191
	0.404681	0.810330	28.934

Table 4. (ctd.)

Salt	m g mole (kg methanol^{-1})	d g ml^{-1}	ϕ_v ml(g mole)$^{-1}$
$(Me)_4NBr$	0.003920*		88.480*
	0.003930*		88.920*
	0.005083	0.786931	93.597
	0.0107010	0.787321	88.338
	0.020806	0.787954	91.281
	0.028082	0.788439	90.207
	0.041054	0.789272	90.741
	0.053027	0.790034	91.090
	0.087864	0.792244	91.559
	0.113922	0.793846	92.341
	0.132463	0.794944	92.606
	0.155781	0.796407	93.054
$(Et)_4NBr$	0.013420	0.787540	148.211
	0.025780	0.788410	150.344
	0.044140	0.789750	149.449
	0.053040	0.790380	149.781
	0.066058	0.791290	150.258
	0.069959	0.791600	150.334
	0.121707	0.795170	151.516
	0.169890	0.798420	152.291

* Points obtained dilatometrically

Table 4. (ctd.)

Salt	m g mole (kg methanol^{-1})	d g ml^{-1}	ϕ_v ml(g mole)$^{-1}$
$(Et)_4NBr$	0.0226900	0.802220	152.821
	0.286960	0.805160	153.345
	0.367090	0.811260	153.739
	0.426400	0.814970	154.036
	0.495380	0.819180	154.454
	0.547271	0.82234	154.566
$(\underline{n}\text{-}Pr)_4NBr$	0.003743	0.786797	217.466
	0.012820	0.787470	218.147
	0.018415	0.787914	218.380
	0.022950	0.788208	218.957
	0.029929	0.788750	219.558
	0.032160	0.788909	219.284
	0.035869	0.788158	219.053
	0.0523470	0.790370	219.789
	0.060475	0.790910	219.884
	0.066344	0.791366	220.055
	0.087216	0.792830	220.530
	0.102740	0.793830	221.412
	0.105960	0.794115	221.128
	0.125060	0.795429	221.379
	0.127564	0.795548	221.547
	0.142530	0.796397	221.832
	0.144168	0.796730	221.627

Table 4. (ctd.).

Salt	m g mole (kg methanol^{-1})	d g ml^{-1}	ϕ_v ml(g mole)$^{-1}$
($\underline{n}$-Pr)$_4$NBr	0.160000	0.797740	223.275
	0.165180	0.798112	221.800
	0.166139	0.797201	222.247
	0.185020	0.799465	222.133
	0.189219	0.799523	222.347
	0.192300	0.799826	222.924
	0.204580	0.800710	222.407
	0.214190	0.801302	223.068
	0.231220	0.802968	223.262
	0.244630	0.803266	223.037
	0.255470	0.804316	224.366
	0.270530	0.804921	223.584
	0.279570	0.804475	223.834
	0.324340	0.808277	224.092
	0.349574	0.809603	224.870
	0.433910	0.814985	224.512
	0.438845	0.815077	225.278
	0.509370	0.819200	225.548
	0.583129	0.823970	225.893
	0.641287	0.826586	226.101

Table 4 (Ctd.)

Salt	m g mole (kg methanol^{-1})	d g ml^{-1}	ϕ_v ml(g mole)$^{-1}$
($\underline{n}$-Bu)$_4$NBr	0.005994	0.787100	286.115
	0.013233	0.787644	287.233
	0.020402	0.788186	287.071
	0.027293	0.788690	287.788
	0.029448	0.788819	288.245
	0.030098	0.78901	287.792
	0.0352554	0.789250	288.714
	0.046184	0.790071	288.562
	0.054440	0.790646	288.859
	0.067141	0.791543	289.478
	0.069991	0.791802	288.781
	0.075818	0.792155	289.419
	0.097075	0.793724	289.929
	0.103918	0.794143	290.035
	0.141576	0.796803	290.505
	0.144124	0.796929	290.412
	0.174528	0.798973	290.858
	0.182918	0.799578	291.078
	0.223719	0.802256	291.515
	0.256440	0.804372	291.750
	0.305584	0.807502	291.959
	0.363685	0.811089	292.275

Table 4 (ctd.)

Salt	m g mole (kg methanol^{-1})	d g ml^{-1}	ϕ_v ml(g mole)$^{-1}$
(n-Bu)$_4$NBr	0.425068	0.814750	292.643
	0.493137	0.818697	292.861
	0.567343	0.822893	293.161
	0.606708	0.825054	293.286

Table 5

Partial Molar Volumes of NH_4Br and TAA Bromides at Infinite Dilution in Methanol at 25°C

Salt	$\bar{V}_2^o$ ml(g mole)$^{-1}$	S_v ml kg methanol$^{1/2}$(g mole)$^{-3/2}$
NH_4Br	21.95	11.00
$(Me)_4NBr$	88.15	12.50
$(Et)_4NBr$	146.60	14.00
$(\underline{n}\text{-Pr})_4NBr$	216.65	13.50
$(\underline{n}\text{-Bu})_4NBr$	285.35	14.70

Figure 15

A plot of apparent molal volume ϕ_v against $m^{1/2}$ for $(Et)_4NBr$ in methanol at 25°C

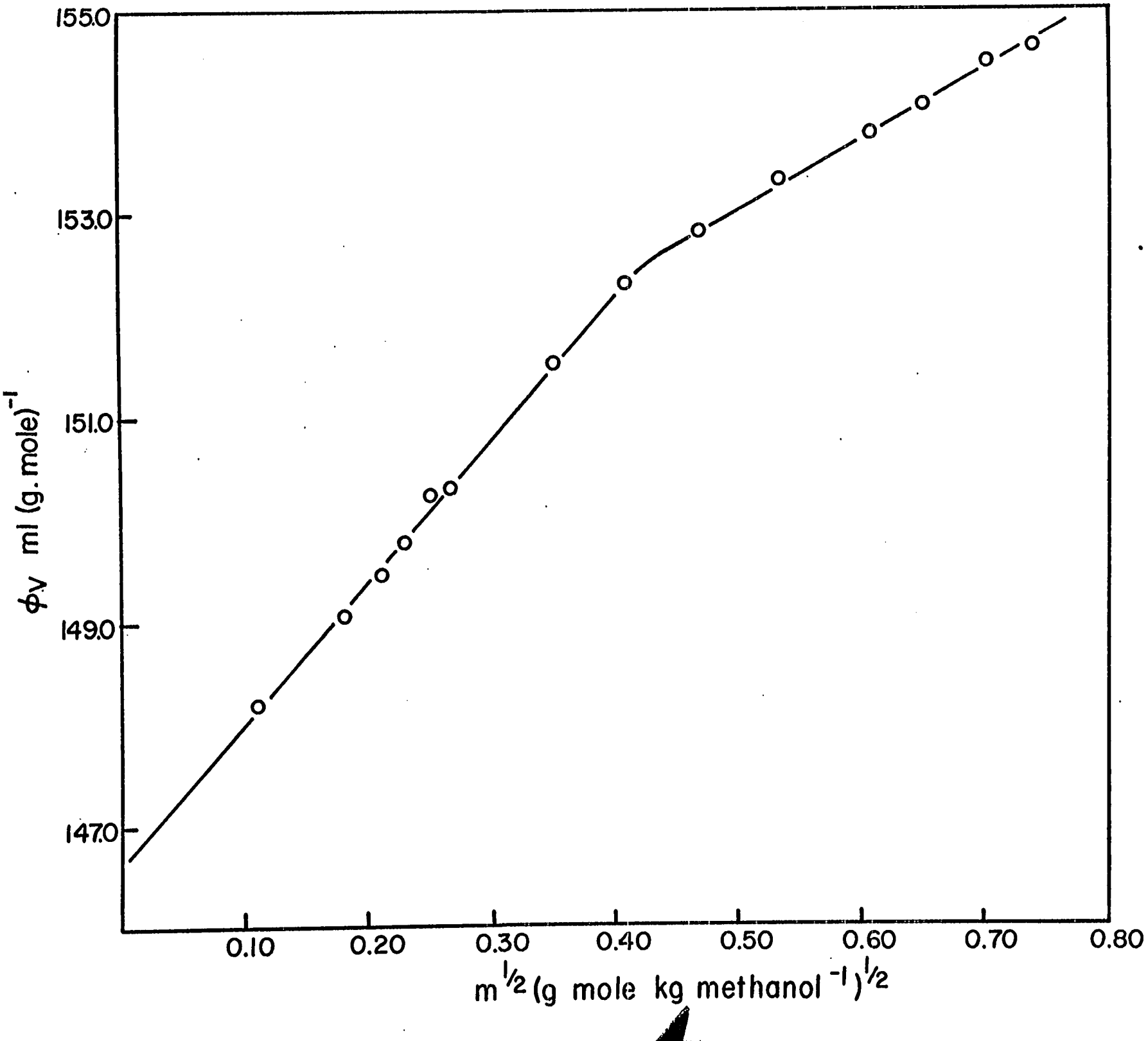

155.0
153.0
151.0
149.0
147.0
ϕ_V ml (g. mole)$^{-1}$
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
m$^{1/2}$ (g mole kg methanol^{-1})$^{1/2}$

Figure 16

A plot of apparent molal volume ϕ_v vs. $m^{1/2}$ for $(n\text{-}Pr)_4NBr$ in methanol at 25°C

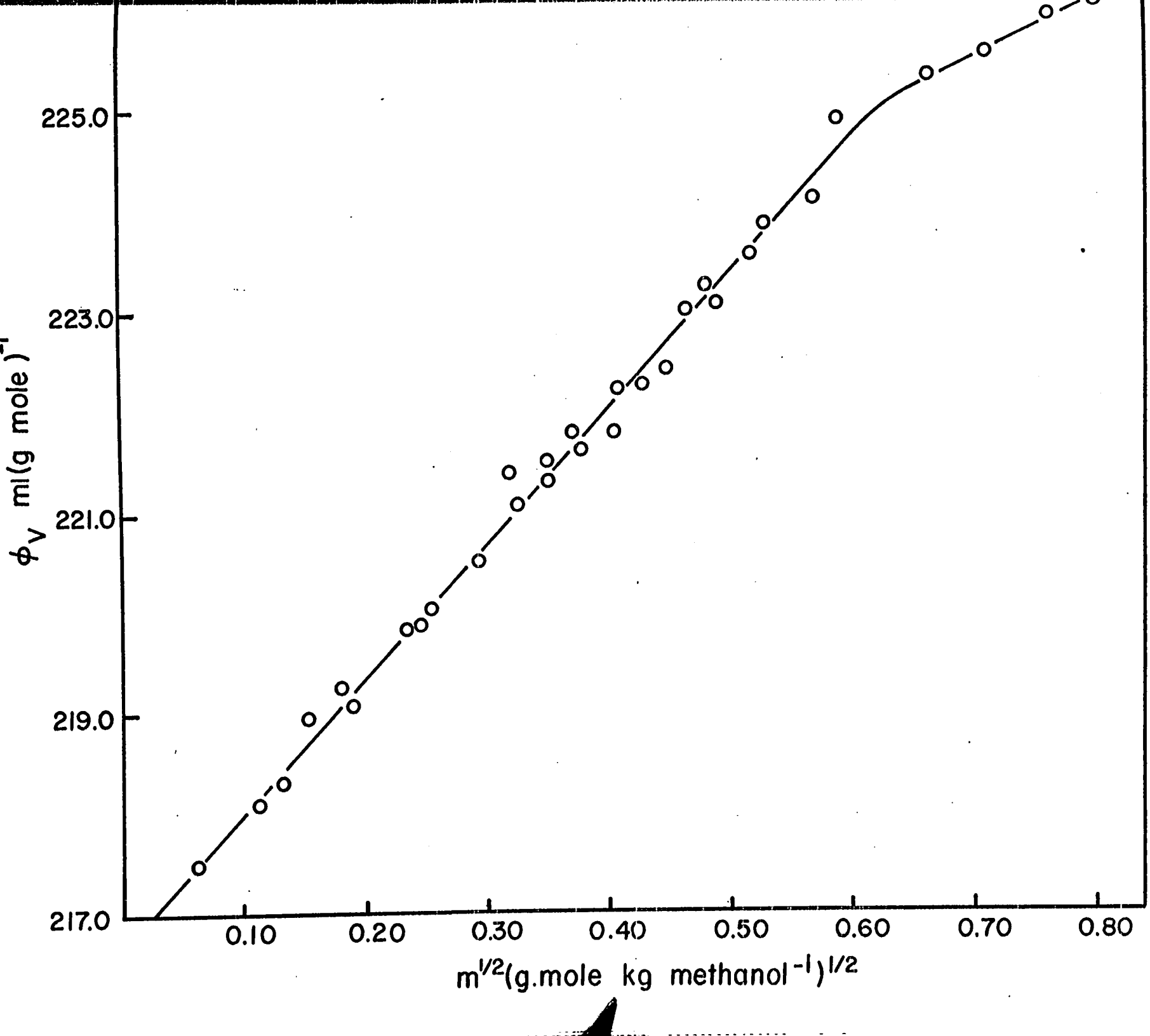

225.0
223.0
221.0
219.0
217.0
ϕ_V ml(g mole)$^{-1}$
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
$m^{1/2}$(g.mole kg methanol^{-1})$^{1/2}$

Figure 17

A plot of apparent molal volume ϕ_v as a function of $m^{1/2}$ for ($\underline{n}$-Bu)$_4$NBr in anhydrous methanol at 25°C

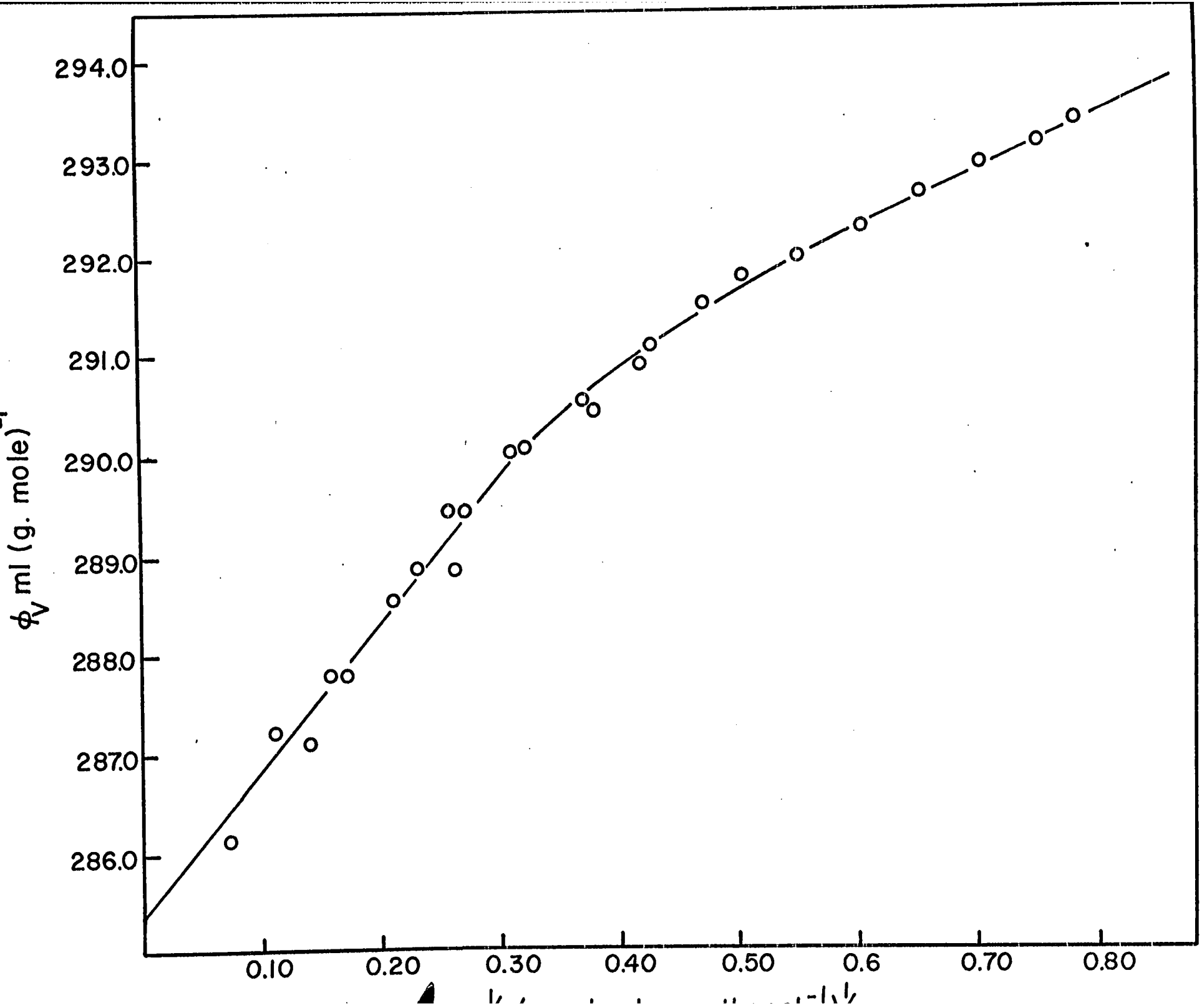
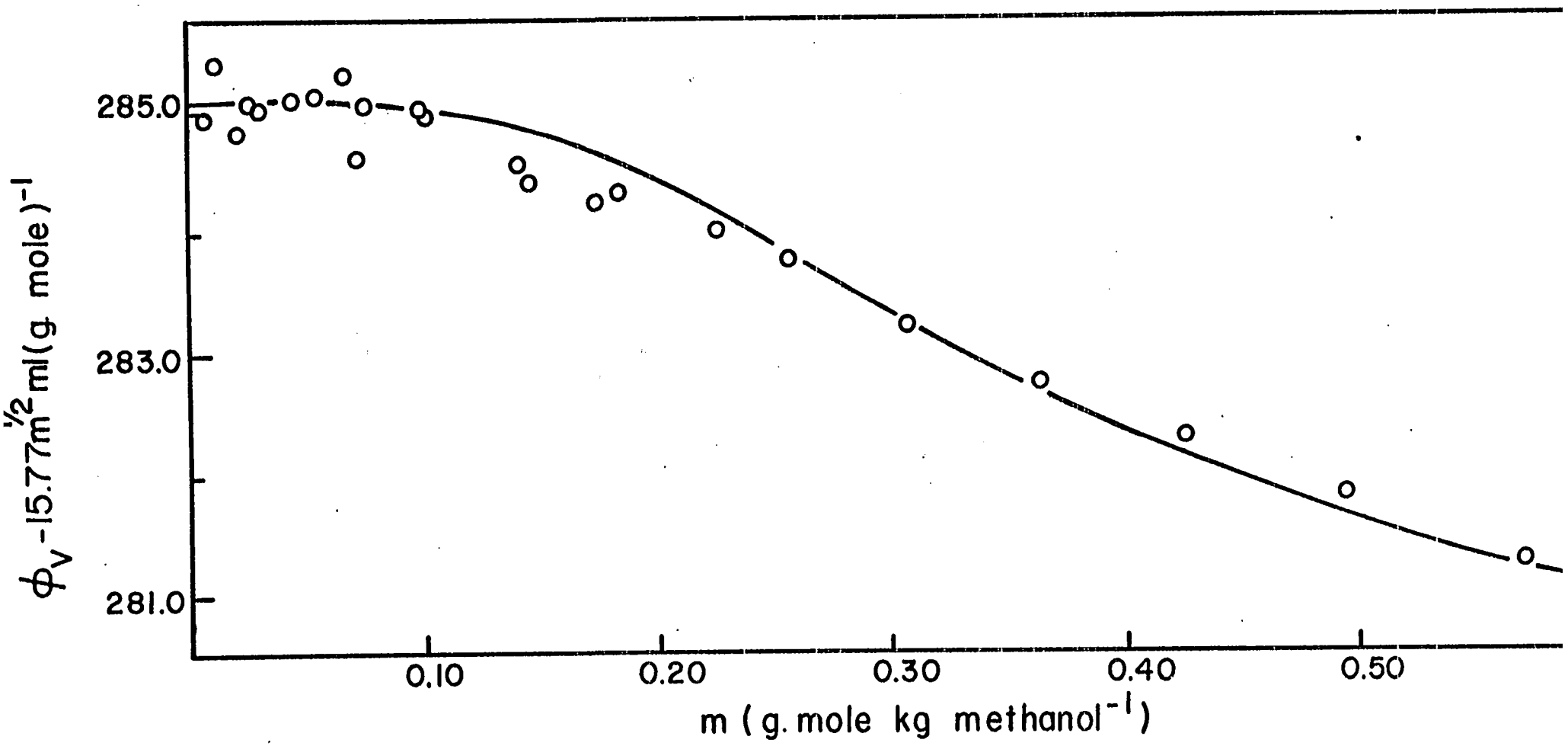

294.0
293.0
292.0
291.0
290.0
289.0
288.0
287.0
286.0
ϕ_V ml (g. mole)$^{-1}$
0.10
0.20
0.30
0.40
0.50
0.6
0.70
0.80

Figure 18

A plot of ϕ_v -15. 77 $m^{1/2}$ against concentration (m) for ($\underline{n}$-Pr)$_4$NBr in methanol at 25°C


285.0
283.0
281.0
$\phi_V - 15.77 m^{1/2}$ ml(g mole)$^{-1}$
0.10
0.20
0.30
0.40
0.50
m (g. mole kg methanol^{-1})

CHAPTER IV

DISCUSSION

A. SALTING-OUT AND SALTING-IN

1. Concentration Dependence of $\Delta S/S_o$

The significance of the salting-out behaviour of salts is normally considered at infinite dilution so that the effects of the isolated ions can be evaluated. Suitable extrapolations of k_s values obtained at finite moderate concentrations are usually possible on a linear basis with respect to salt concentration. The form of the concentration dependence of k_s was considered by Conway, Desnoyers and Smith (18) and by Efremov et al (42) in terms of an ionic co-sphere volume inversely proportional to concentration. This effect enters into the integration of the salting-out distribution equation (e.g. eqn. I. 29) and automatically leads to a concentration dependence of k_s (k_s decreasing with salt concentration) which is limitingly linear in m.

In the case of salting-out by TAA salts, the limiting k_s values are difficult to evaluate exactly as non-linear concentration dependence of $\Delta S/S_o$ already sets in at relatively low* salt concentrations. This non-linear behaviour (Figure 11 and 12) is, however, of intrinsic interest itself in relation to structural effects in the solution and to incipient micelle formation (see below). For example, co-sphere interaction effects amongst the ions are evidently substantially larger, with regard to the salting-out behaviour, than those which arise for simple electrostatic reasons [theories of Debye and McAulay (15); Butler (16); Conway, Desnoyers and Smith (18)] in the case of simple alkali halide salts. Such behaviour is consistent with other indications of long-range non-electrostatic interaction effects, e.g. as found in the volume behaviour [dependence of $\bar{V}_2$ on concentration for TAA salts (33)].

Within the limitations mentioned above, which cannot be avoided in the case of salting-out by the TAA salts, the limiting salting-out constants were obtained from the slopes of the $(S_o-S)/S_o$ vs. C curves at low concentrations, as shown in Figure 19. The same procedure was employed for the valuation of k'_s (eqn. I.10) from the slopes of the log S/S_o vs. concentration curves which are shown in Figure 20. The values of k_s (eqn. I.11) and k'_s are listed, together

---

* In relation to Debye-Hückel limiting law behaviour, the lowest concentration that can be used in studies of salting-out are relatively high. In relation, however, to the concentrations ($>$ ca. 2 m) where hydration effects with simple salts start to cause significant non-ideality by hydrate co-sphere interactions, the concentrations employed in salting-out measurements are "relatively low".

Figure 19

Plot showing the dependence of S/S_o on concentration using an enlarged concentration scale;
O $(Me)_4NBr$, Δ $(Et)_4NBr$, ● $(n\text{-}Pr)_4NBr$, □ $(n\text{-}Bu)_4NBr$, and ▲ NH_4Br.

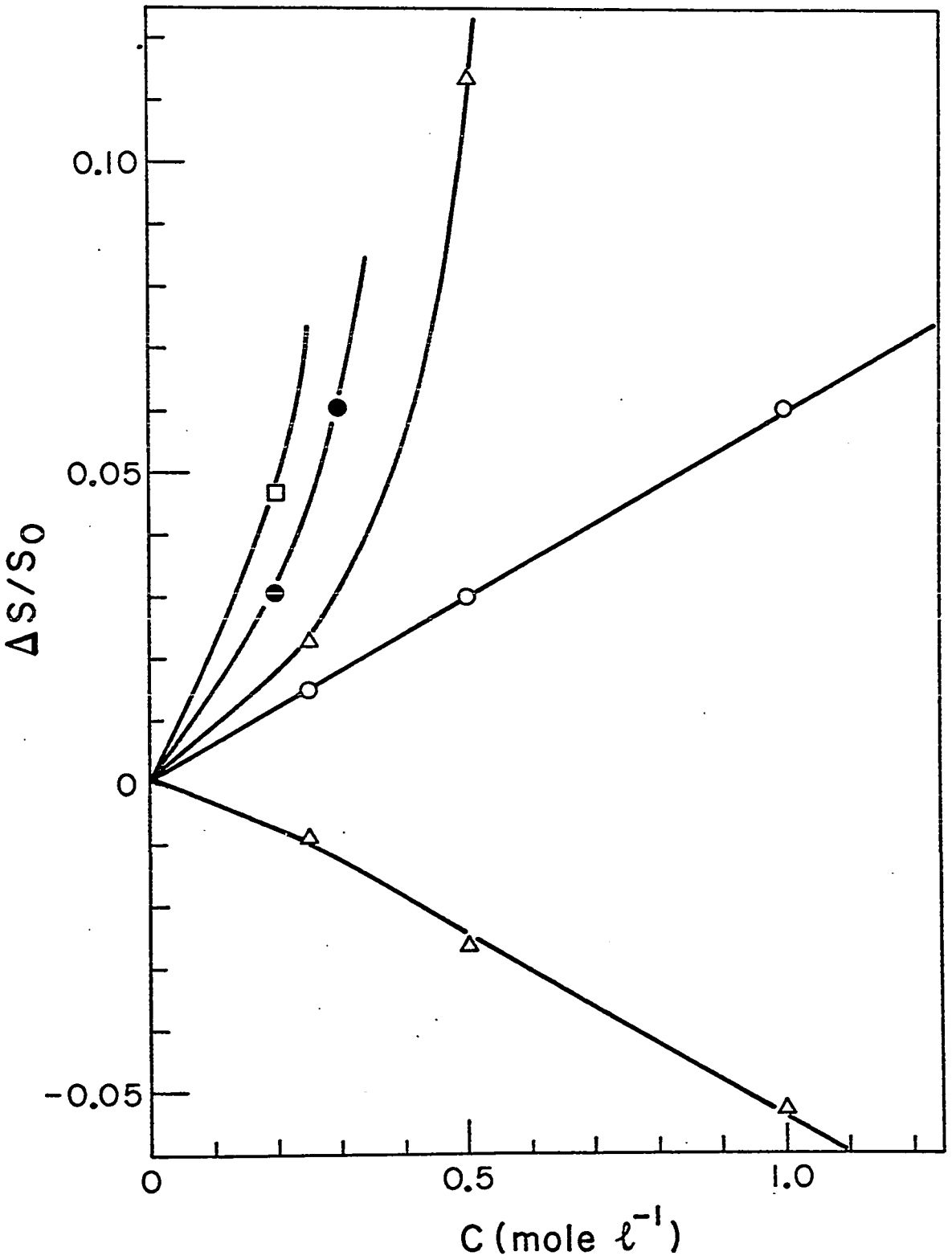
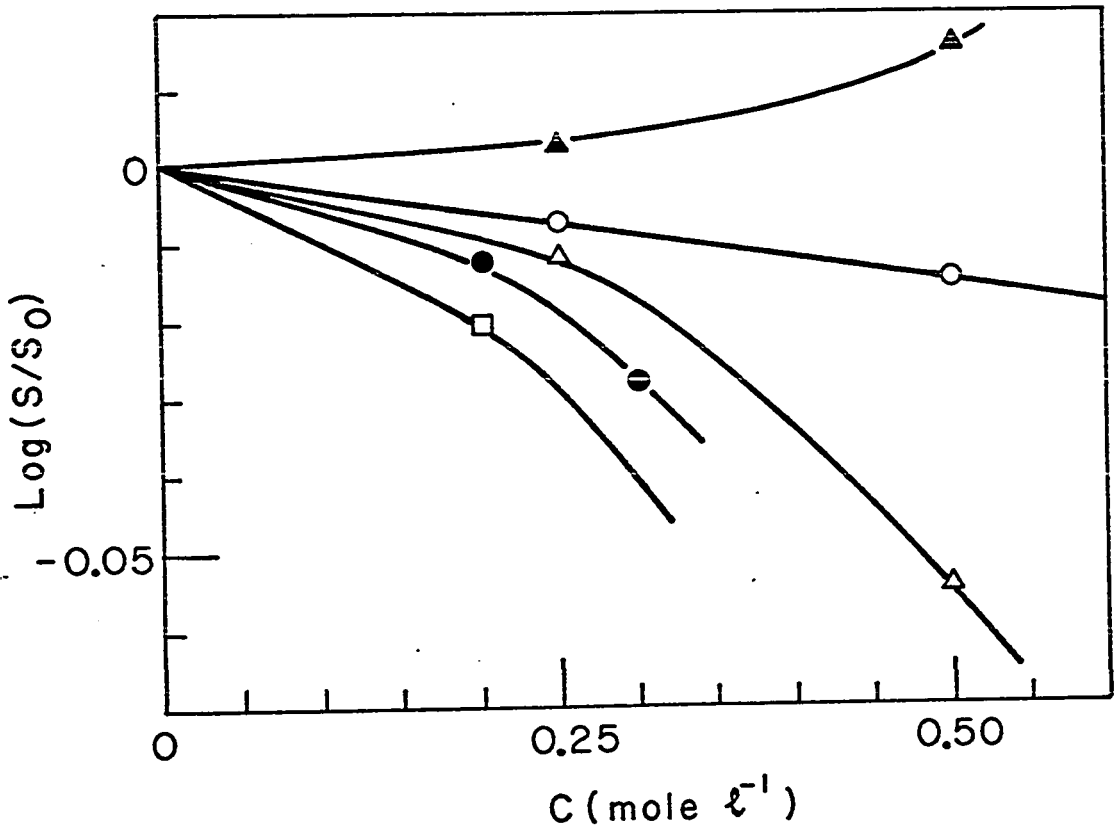

0.10
0.05
0
-0.05
ΔS/S0
0
0.5
1.0
C (mole ℓ⁻¹)

Figure 20

An experimental plot showing the dependence of $\log S/S_o$ on concentration, using an enlarged concentration scale: results of O $(Me)_4NBr$, Δ $(Et)_4NBr$, ● $(\underline{n}\text{-}Pr)_4NBr$, □ $(\underline{n}\text{-}Bu)_4NBr$ and ▲ NH_4Br.


0
-0.05
Log(S/S0)
0
0.25
0.50
C (mole ℓ⁻¹)

with the molecular weights of the cations in Table 6. Since the linear section of the $\Delta S/S_o$ vs. C curves did not extend to high concentrations, the precise determination of the limiting k_s values was not possible. The uncertainty associated with the k_s values was estimated at $\pm$ 0.005 moles^{-1}. Both k_s and k'_s values <u>increase</u> with increasing size of the cation. In Figure 21, the k_s values are plotted as a function of the molecular weight of the TAA cations. An approximately linear relation is observed between the k_s values and the molecular weights of the cations in the middle portion of the curve. The end points deviate significantly from linearity, with NH_4Br showing salting-in and $(n\text{-}Bu)_4NBr$ exhibiting strong salting-out. The behaviour of this latter salt will be discussed more fully later in this chapter.

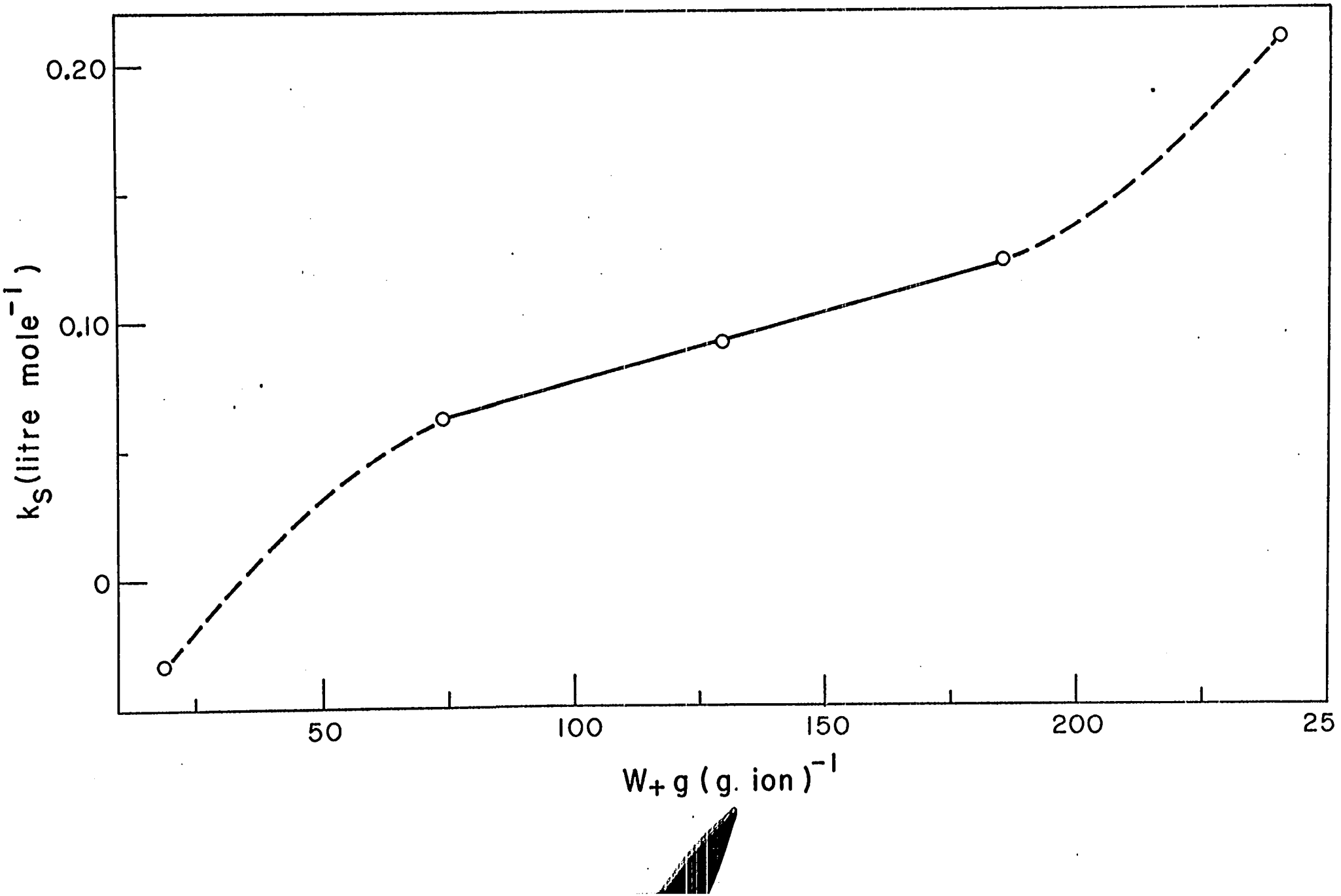
Table 6

Salting-out constants for Ar in aqueous NH_4Br and TAA bromide solutions at 25°C

Salt	Molecular weight of cation	k'_s ($l.mole^{-1}$) ± 0.005 $l.mole^{-1}$	k_s ($l.mole^{-1}$) ± 0.005 $l.mole^{-1}$
NH_4Br	18.05	-0.015	-0.035
$(Me)_4NBr$	74.04	0.030	0.061
$(Et)_4NBr$	130.08	0.041	0.091
$(n\text{-}Pr)_4NBr$	186.12	0.061	0.122
$(n\text{-}Bu)_4NBr$	242.16	0.100	0.210

Figure 21

Salting-out constants k_s and $\ldots_s$ for argon as a function of the molecular weight of NH_4^+ and four TAA cations


0.20
0.10
0
k_S(litre mole^{-1})
50
100
150
200
25
$W_+ g$ (g. ion)$^{-1}$

2. Comparison of Theoretical and Experimental Values of k_s

The values of k_s for the salting-out of argon by TAA bromide salts have been calculated and are listed in Table 7. For the theoretical evaluation of k_s, two theories were used, those of Conway, Desnoyers and Smith (18) and Long and McDevit (2). In the calculation of k_s by means of equation (I. 29), a limiting case was considered. As the concentration m tends to zero, R will tend to infinity and the field may then be represented simply as $-ze/\varepsilon r^2$. The salting-out equation (I. 29) therefore reduces to

$$k_s = \frac{S_o - S}{S_o m} = \frac{4\pi N}{3000}(r_h^3 - a^3) + \frac{z^2 e^2}{2000\, kT \varepsilon_o^2 r_h}(\bar{V}_2 \varepsilon_o - \frac{9}{2}\bar{P}_2) \qquad (IV.1)$$

The molar volume of the non-electrolyte Ar was taken from the tabulation of data for the noble gases given by Hildebrand and Scott (59) while the partial molar polarisability of argon was assumed to be the same as its molar polarisability and was taken from the data of Castellan (68). The crystal radii were those given by Pauling (69)*, while the hydration radii have been taken from Nightingale's (31) compilation.

---

* The Pauling ionic radii have been used here in order that calculated k_s values would have a basis comparable to that of salting-out parameters derived in previous publications. However, radii based on the recent compilation of Gourary and Adrian (70) are somewhat preferable.

Table 7

Salting-out constants for argon by NH_4Br and four TAA bromides at 25°C

Salt	k_s (l.mole^{-1}) Expt. ± 0.005 l.mole^{-1}	Eqn. (IV.1)	Eqn. (I.30)
NH_4Br	-0.035	0.2079	-0.00041
$(Me)_4NBr$	0.061	0.1211	0.01318
$(Et)_4NBr$	0.091	0.1129	0.01523
$(n\text{-}Pr)_4NBr$	0.122	0.1167	0.01963
$(n\text{-}Bu)_4NBr$	0.210	0.1151	0.02460

The values of k_s calculated from equation IV. 1 are for concentrations on the molal (m) scale. These k_s values were converted to k_s values on the molar (C) scale in order to compare them with the experimental k_s values and those of Long and McDevit (2).

Examination of Table 5 in which the calculated values of k_s are listed shows that equation (IV. 1) does not correctly predict the salting-out constants for argon in these solutions of TAA bromides. The theoretical values decrease, as expected, with increasing size of the cation. This can partially be explained in terms of the molecular picture of salting-out. The first term of equation (IV. 1) takes into account strong ion-solvent interactions associated with the primary solvation shell of the ion. As the size of the ion increases, the value of a tends to the value of r_h, so that the first term of equation (IV. 1) goes to zero. The second term is related only to long-range polarisation effects determined by the nature of the non-electrolyte. The special effects of the TAA salts on solvent structure which were discussed earlier, are of course, not taken into account in the electrostatic theories.

The second theory which was used for the calculation of salting-out constants is the more empirical one of Long and McDevit (2) and their equation (I. 30) was employed to obtain k_s values. The intrinsic volume of the salt V_s required in this treatment was calculated using the following equation (36)

$$V_{int} = 2.52\, a^3 + 3.15\, a^2 \qquad \text{(IV. 2)}$$

where V_{int} is the value of the intrinsic volume of the spherical ion in the solvent corrected for the amount of free space between the ion and the solvent molecules. The crystal radii taken were those given by Pauling (69). The values for the partial molar volumes of the TAA bromide salts were taken from the work of Conway and Laliberté (71) while the value of $\bar{V}_2$ for NH_4Br was calculated using the results of Laliberté (65) and Verrall (66) obtained in this laboratory.

A comparison of the theoretically predicted values of k_s calculated using Long and McDevit's theory, with the experimental values, shows that this theory leads to results which predict the correct trend in the k_s values although their absolute values are lower than the experimental ones. Although this relation fails to take into account the polarisability of the non-electrolyte (18), the theory does predict the dependence of k_s on the size of the cation much better than do the other theories. As can be seen in Table 5, the values of k_s which can be calculated for NH_4Br arise principally on account of the electrostriction term for the NH_4^+ ion. Insofar as an electrostriction or other volume change term $\bar{V}_s - V_s$ is considered in the above theory as an empirical experimental parameter some account is thereby automatically taken of the solvent "structure-making" properties of the TAA salts. The overall effect of "structure-making" in terms of volume is a decrease in volume (cf. 72, 73). This has an effect on the volume equivalent to that arising from ordinary (electrostatic) electrostriction although it arises for entirely different reasons related most probably to the occupation of solvent cavities

by the large cations and modification of the cavity distribution near the organic ions. Therefore the Long and McDevit theory gives a good prediction of the experimental behaviour but for the wrong reasons. Similar effects arise in the compressibility behaviour of TAA salts (74) where the larger cations cause negative compressibility changes in water like the small electrostricting cations, but for different reasons.

It should be stressed that the k_s values under discussion here are only for low concentrations of the salts. The behaviour of k_s at higher concentrations becomes more complex as shown in Figure 12. Such behaviour might be explained through effects arising from "negative" hydration, Van der Waals' repulsion forces and through incipient micelle formation (see below).

3. Estimation of Individual Ionic Salting-out Constants

Because of the strong salting-out effect which was observed in the present work with the TAA bromide salts, it was of interest to try to establish whether this effect was due primarily to the bromide ion or to the TAA cation. For this reason an attempt was made to estimate the salting-out constant of the individual Br^- ion.

The k_s value for the bromide ion was first calculated using the theory of Conway, Desnoyers and Smith (18) and gave a value of +0.098 l.mole^{-1}. An alternative method was also used to estimate $k_{s(Br^-)}$ and it was based on the assumption that two ions of opposite charge but of identical size should, in the first approximation, have the same k_s values. However, it has been shown (36) that two ions of the same size do not have the same properties as regards free energy of hydration and water orientation and that therefore a more realistic division of k_s could be made in terms of the ratio of the free energy of hydration of its ions.

Since the K^+ and F^- ions have identical ionic radii on the Pauling scale (69), KF was used. The salting-out constant of argon for aqueous KF solution is +0.330 l.mole^{-1}. On the above discussed basis a value of +0.140 l. mole^{-1} was obtained for the salting-out constant of the K^+ ion. Since no data was available in the literature for the salting-out of argon by any alkali metal bromides, the solubility of argon in an aqueous KBr solution was measured and thus its k_s value was determined as +0.210 ± 0.005 l.mole^{-1}. Taking the k_s value for the K^+ ion estimated above, a value of 0.07 ± 0.02 l.mole^{-1} was obtained

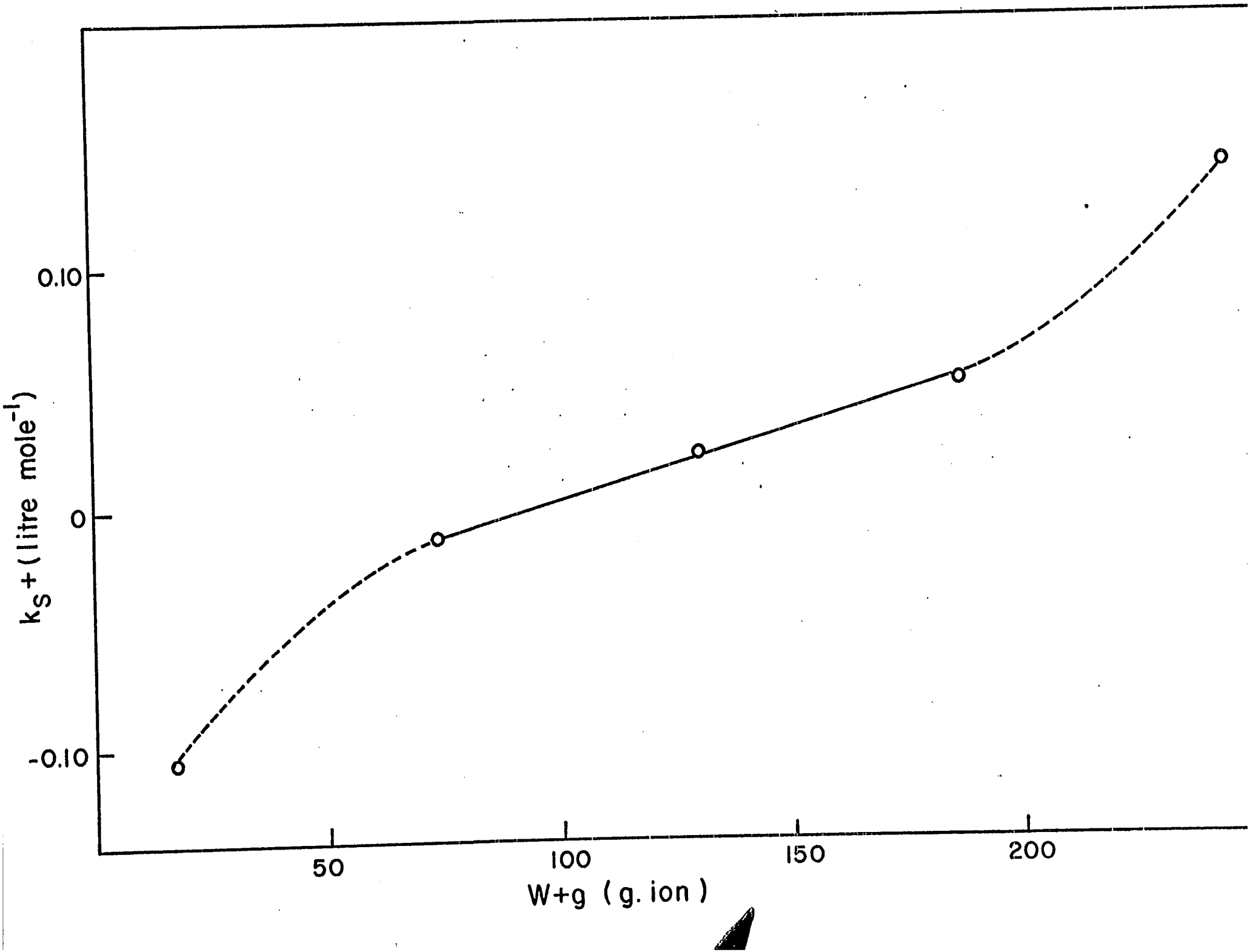
for the salting-out of argon by the bromide ion. The assigned uncertainty of ± 0.02 l.mole^{-1} includes an estimate of the possible error involved in the approximations used in the evaluation of k_s (Br^-).

The above estimate of k_s (Br^-) is in reasonable agreement with the a priori calculation of k_s (Br^-) using the theory of Conway et al (18).

In order to examine more closely the effect of the TAA cations on the solubility of Ar the k_s value for the Br^- ion was subtracted from the experimental k_s values for the TAA bromide salts. The k_s^+ values thus obtained were plotted as a function of the molecular weight of the cations as shown in Figure 22. As may be seen from this Figure, with the exception of the Me_4N^+ ion, the higher TAA ions cause an extent of salting-out of the non-electrolyte which increases with increasing size of the TAA cations. As is the case with other thermodynamic properties of the TAA ions (71) the change in the behaviour of these properties occurs between Me_4N^+ and Et_4N^+. In the present case, a transition from salting-in to salting-out occurs between these two ions.

Figure 22

Plot of k_s^+ cations vs. molecular weight for NH_4^+ and TAA cations


0.10
0
-0.10
k_S+ (litre mole^{-1})
50
100
150
200
W+g (g. ion)

4. Relation of the Present Results to those of Previous Studies

Two things are striking about the solubility behaviour of argon in TAA salt solutions. Firstly, salting-out rather than salting-in of the argon occurs and secondly the magnitude of the effect becomes greater with increasing size of the cations, whereas electrostatic salting-out effects would tend to become smaller. A recent study by Wen and Hung (75) of the solubility behaviour of hydrocarbon gases in TAA bromide solutions showed that salting-in was the predominant effect and that generally the salting-in increased with increasing size of the cation. There were, however, certain interesting exceptions to the above trends. Methane was salted-out by $(Me)_4NBr$ and $(\underline{n}\text{-}Bu)_4NBr$ at 5°C. Wen and Hung (75) postulated a series of competing effects related to the nature of the three components in the system under study.

The TAA ion can affect the solubility of the argon in two ways; firstly by acting on the solvent and secondly through direct "hydrophobic" contacts with the non-electrolyte solute. This term refers to ion/non-electrolyte contact with sharing of structured solvent regions initially existing around the two isolated species in the solution.

In relation to the first effect, that on the solvent, the TAA cation, through solvent structure formation, will increase the time average concentration of cavities (or modify their size distribution) in the solvent and will themselves occupy the cavities. The larger the cation the fewer will be the number of cavities left available for the non-electrolyte. Wen and Hung (75) have referred to this

as the "caging effect" and it seems to be most important, as might be expected, at lower temperatures. The size of the non-electrolyte evidently also plays an important role. It was found (75) that ethane was more soluble in a given TAA salt solution than either methane or propane, presumably since propane was too large for favourable cavity occupation while methane was too small.

Hydrophobic and Van der Waals' interactions between the TAA cations and the non-electrolyte would tend to decrease with decreasing size of the non-electrolyte so that little interaction energy could be gained by a hydrophobic contact between argon and the cations. It would seem therefore that these two effects can ultimately lead to the observed salting-out of argon by TAA bromides.

5. Entropy Effects in the Solubility Behaviour of Non-Electrolytes

In terms of the entropy of hydration of the cation and non-electrolyte solute, it is desirable to recall that the distribution of non-electrolyte and solvent about the ions is determined by the local free energy of the uncharged species in the fields of the ions. Normally, in the electrostatic theories of salting out, the electrical energy of polarisation of the non-electrolyte and an equal volume of solvent molecules is used in a distribution function, and this energy is taken as the relevant free energy. Any entropy component is implicitly associated with the temperature dependence of the dielectric constant of the solvent and dipole orientation of the non-electrolyte and solvent molecules near the ions. In the case of TAA cations, special consideration may have to be given to entropy factors in the salting-out since the formal electrostatic free energy of polarisation by the large ions is relatively small and non-electrostatic effects tend to become dominant.

In order to interpret the anomalously large salting-out of Ar which evidently occurs with the TAA bromide salts (cf. the behaviour of KBr) beyond that expected for purely electrostatic reasons (eg. as calculated from the theory of Conway, Desnoyers and Smith), it is necessary to postulate a non-electrostatic entropy factor in the distribution function of such a sign that the free energy of solvent replacement by the Ar near the ion is made larger (less negative or more positive) than it would otherwise be on the basis simply of electrostatic field effects; i.e. an increasingly negative entropy term is required for those Ar molecules which find themselves closer and closer to the ion. This could arise for several reasons:

(a) diminished free volume near the ion;

(b) diminished proportion of solvent cavities suitable for accommodating Ar atoms in the vicinity of the ion;

(c) decrease of the entropy of the solvent cage (mainly librational entropy of H_2O molecules) around the Ar atoms which are in the vicinity of the ion due to the presence of relaxationally less mobile water molecules (cf. the n.m.r. spin lattice relaxation behaviour) in the region of solvent near the ion. In water, the librational entropy is an important factor determining the molar entropy and is, of course, related to the specific heat behaviour of water and the partial molar heat capacities of ions and molecules in water.

With larger non-electrolytes, including benzene (22), salting-in tendencies outweigh these factors and presumably arise from (a) Van der Waals interactions (17), and (b) "hydrophobic contacts" (22).

At higher concentrations, the possibility of incipient micelle formation was already envisaged in the studies of Desnoyers et al (22). These hydrophobic micellar regions will be able to accommodate argon atoms and this will result in a relative increase in the solubility of the gas, as is in fact found at the higher concentrations. This is consistent with the fact that the minima in the curves tend to occur at lower concentrations as the size of the TAA cation increases, as shown in Figure 12. The formation of micelles with included non-electrolyte is the ultimate result of hydrophobic contacts referred to above for the more dilute solution conditions.

B. PARTIAL MOLAL VOLUMES

1. Introduction

The partial molal volumes of ions in solution are closely related to their salting-out behaviour as represented, for example, in the equations of Long and McDevit (eqn. I.30). Previous work had been carried out in this laboratory on the partial molal volumes and compressibilities of the TAA salts in water and interesting additivity effects were found in the volumes, indicating that positive structural volume changes just compensated cavity filling effects (see below). Since such effects are apparently important in determining the salting-out behaviour, further work of a comparative nature was carried out on the same series of TAA salts but in methanol where the electrostriction effect might be larger and the solvent lattice structure effects might be expected to be absent or smaller than in water.

2. Volume Behaviour and Density Measurements

The concentration dependence of the partial molar volumes, $\bar{V}_2$, of the TAA halides in aqueous solutions has been found (10, 33, 76) to be anomalous and large negative slopes are exhibited. It has been shown, however, that at very low concentrations, solutions of the TAA bromides and chlorides (33, 10) eventually exhibit positive slopes in the ϕ_v vs. $m^{1/2}$ curves and the values of these slopes are reasonably close to that expected from the Debye-Hückel limiting law

for water. Determinations of partial molal volumes on the series of TAA bromides have also been carried out in D_2O in this laboratory (65) and it was found that at high dilutions these salts also follow the Debye-Hückel limiting law. At higher concentrations, the non-ideality of such solutions becomes a major factor in their properties and is manifested in large deviations, usually negative, from the Debye-Hückel limiting slope S_v for ϕ_v as $f(m^{1/2})$. Therefore, in order first to obtain satisfactory values of the partial molar volume at infinite dilution, extrapolations should only be made from data in the Debye-Hückel limiting region.

The present study of partial molal volumes of the TAA bromides in anhydrous methanol differs from that previously carried out by Padova and Abrahamer (52) in that the apparent molal volumes have been measured down to 0.01 molal so that it becomes possible to obtain $\bar{V}_2^o$ data by reliable extrapolation to infinite dilution where no ion-ion interactions remain. Since the $\bar{V}_2^o$ results reported by Padova et al (52) were obtained by extrapolations from outside the Debye-Hückel limiting law region they are necessarily different from the present results and give $\bar{V}_2^o$ values which are higher than those reported here.

In the series of TAA bromides which were studied it was possible to approach the Debye-Hückel limiting slope in all cases thus ensuring an accurate extrapolation to infinite dilution. In contrast to the behaviour of the same salts in aqueous solutions, the limiting slope for the apparent molal volume is approached in methanol at a concentration which is fully an order of magnitude higher than in pure water. This indicates that methanol is a more "ideal" solvent

(from the point of view of volumes) for TAA salts than water. This is presumably due, amongst other things, to its inability to form three-dimensional hydrogen-bonded networks with the associated structural effects which are manifested thermodynamically in the anomalous volume, entropy, heat capacity and compressibility behaviour of ions in water.

Information about ion-solvent interactions can be obtained by considering the behaviour of the large hydrophobic cations of the TAA series in methanol. The sign and magnitude of the slope of the plot of $\phi_v - S_v m^{1/2}$ against m reflects mainly the concentration dependence of ion-solvent interactions or in other words deviations from the Debye-Hückel limiting-law for ϕ_v as $f(m^{1/2})$ can be ascribed to long range ion-solvent interactions, particularly when such deviations occur already at quite high dilutions.

It has been suggested (72, 76) that structure formation effects occur to a much smaller extent in methanol than in water and this is fully supported by the shape of the ϕ_v vs. $m^{1/2}$ curves which only begin to show deviations from the Debye-Hückel limiting law at concentrations $>$ 0.1 molal.

3. Linear Additivity Relations and Volume Structural Effects in Methanol

It has been found (49, 33) for the series of aqueous TAA bromide salts that the values of $\bar{V}_2^o$ are additive in the homologous series of these ions. In the case of R_4NX salts in aqueous solutions, electrostriction is negligible for the larger cations so that additivity

can be ascribed to the fact that the large cations are not hydrated in the usual sense or, if hydration exists, it has the same character for all of the members in the series. In the case of methanol, a strict additivity effect is not found, as will be discussed below.

The partial molal volume $\bar{V}_2^o$ of the salt consists of the partial molar volume of the anion and cation at infinite dilution and can be written as

$$\bar{V}_2^o = \bar{V}_+^o + \bar{V}_-^o \qquad \text{(IV.3)}$$

Conway, Verrall and Desnoyers (49) developed a procedure for determining the individual partial g. ionic volume of an anion in a series of TAA salts. The individual volume of an ion can be represented as the sum of three factors, so that eqn. (IV.3) can be expressed as

$$\bar{V}_2^o = V_{in(+)} + V_{e(+)} + V_{str(+)} + \bar{V}_-^o \qquad \text{(IV.4)}$$

where $V_{in(+)}$ is the intrinsic volume of the ion and is always positive, $V_{e(+)}$ is the electrostriction of the solvent caused by the field of the ion and is always negative and $V_{str(+)}$ is the structural contribution to the volume depending on the structural changes in the vicinity of the ion.

In the case of TAA salts, $V_{e(+)}$ tends to zero because the strength of the electric field at the periphery of these ions is quite negligible in terms of electrostrictive effects. All the ions are hydrophobic and show a tendency to enhance the solvent structure or, in terms of kinetic effects, to increase the solvent lattice

relaxation times (77). The $V_{str(+)}$ term is negative but it is difficult to estimate its value quantitatively; it was found to become important only for $(\underline{n}\text{-Bu})_4NBr$ (72). Assuming, therefore, that $V_{e(+)}$ and $V_{str(+)}$ can be neglected, $V_{in(+)}$ is evidently the most important factor.

The intrinsic volume is proportional to the molecular weight and can be written as

$$V_{in(+)} = \frac{W_+}{d_+} \qquad \text{(IV. 5)}$$

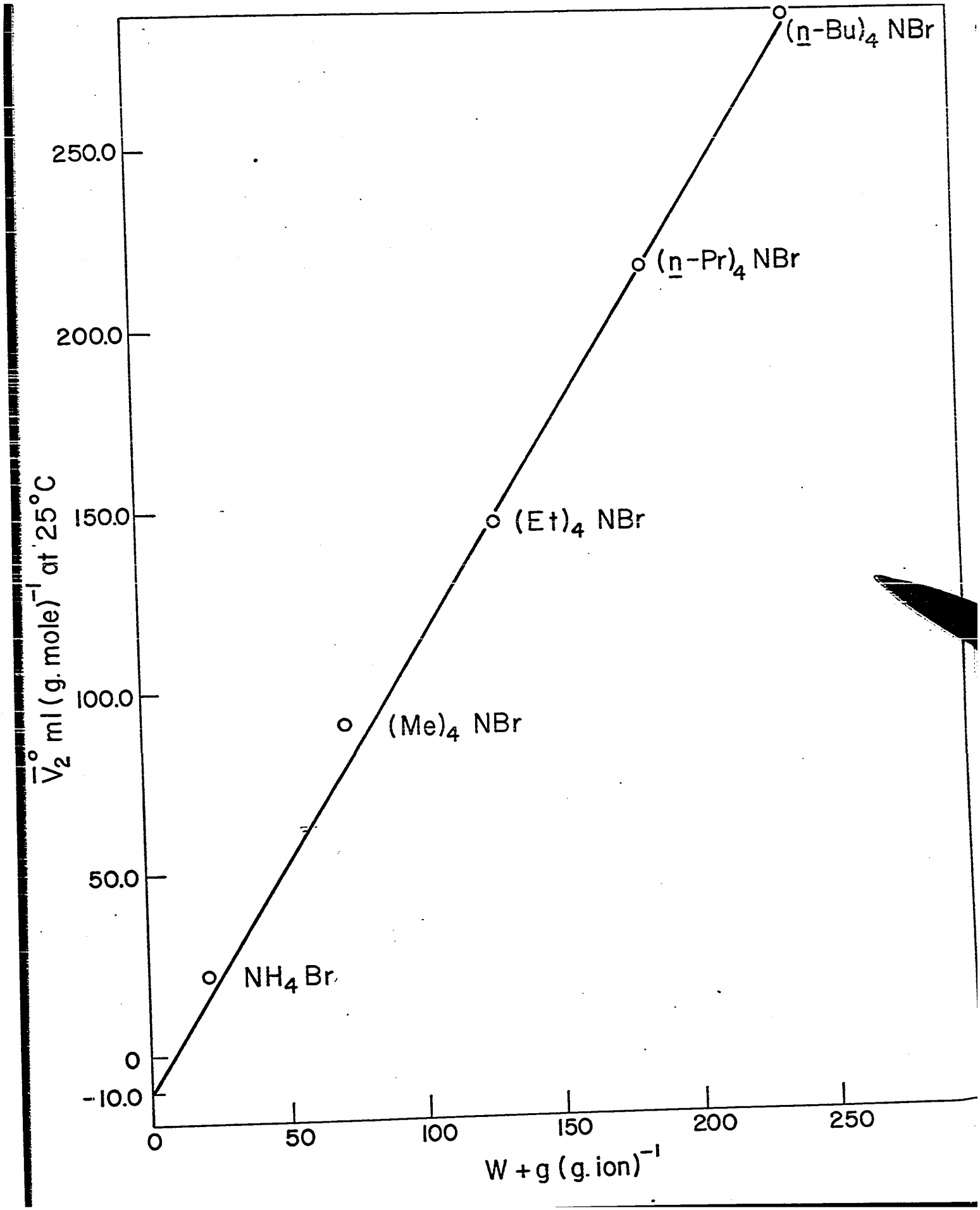
where d_+ is a proportionality constant with the dimensions of density; it is the mean density of the cation. In Figure 23 a plot of $\bar{V}_2^o$ against W_+ the molecular weight of the cation, is shown for the series of TAA bromides in methanol. For the three larger bromides, $(Et)_4NBr$, $(\underline{n}\text{-Pr})_4NBr$ and $(\underline{n}\text{-Bu})_4NBr$, a straight line was obtained which when extrapolated to zero W_+ gives the value for $\bar{V}^o_{Br^-}$ in methanol.

4. Individual Partial Gram Ionic Volumes in Methanol

In order to evaluate if the structural effects of the TAA bromide salts were significant in methanol in relation to those exhibited in water, a comparison between the partial molal volumes in water and methanol was made. From the point of view of liquid structure, the main difference between H_2O and MeOH molecules can be considered in terms of their ability to form hydrogen bonds;

Figure 23

Values of $\bar{V}_2^o$ for NH_4Br and TAA bromide salts as a function of the molecular weight of the cations


(n-Bu)4 NBr
(n-Pr)4 NBr
(Et)4 NBr
(Me)4 NBr
NH4 Br
250.0
200.0
150.0
100.0
50.0
0
-10.0
0
50
100
150
200
250
$\bar{V}_2^\circ$ ml (g. mole)$^{-1}$ at 25°C
W + g (g. ion)$^{-1}$

in the case of methanol, two-dimensional (78) rather than the three-dimensional tetrahedral structures (characteristic of water) are formed. This suggests that the structure-forming effects of alkyl groups, manifested in water solutions, are quite weak in methanol. This is confirmed by NMR relaxation time measurements (77) which show that the tendency for structure formation (enhancement of the relaxation times) decreases from water to methanol, ethanol and acetone and, in fact, does not significantly exist in the latter solvent.

Therefore the difference $\Delta\bar{V}^{\circ}_{MeOH\text{-}H_2O}$ for an ion in the two solvents can be regarded as largely arising from the difference between the electrostriction or structure formation volume in H_2O and MeOH. Thus, if the partial molal volume of the ion in water is represented as

$$\bar{V}_{2(H_2O)} = V_{in(H_2O)} + \Delta V_{e(H_2O)} , \qquad (IV.6)$$

the partial molal volume in methanol is

$$\bar{V}_{2(MeOH)} = V_{in(MeOH)} + \Delta V_{e(MeOH)} \qquad (IV.7)$$

The difference between (IV.6) and (IV.7) is then

$$\Delta\bar{V}^{\circ}_{2(MeOH\text{-}H_2O)} = -\Delta V_{e(MeOH\text{-}H_2O)} + V_{in(MeOH\text{-}H_2O)} \qquad (IV.8)$$

and neglecting $V_{in(MeOH\text{-}H_2O)}$

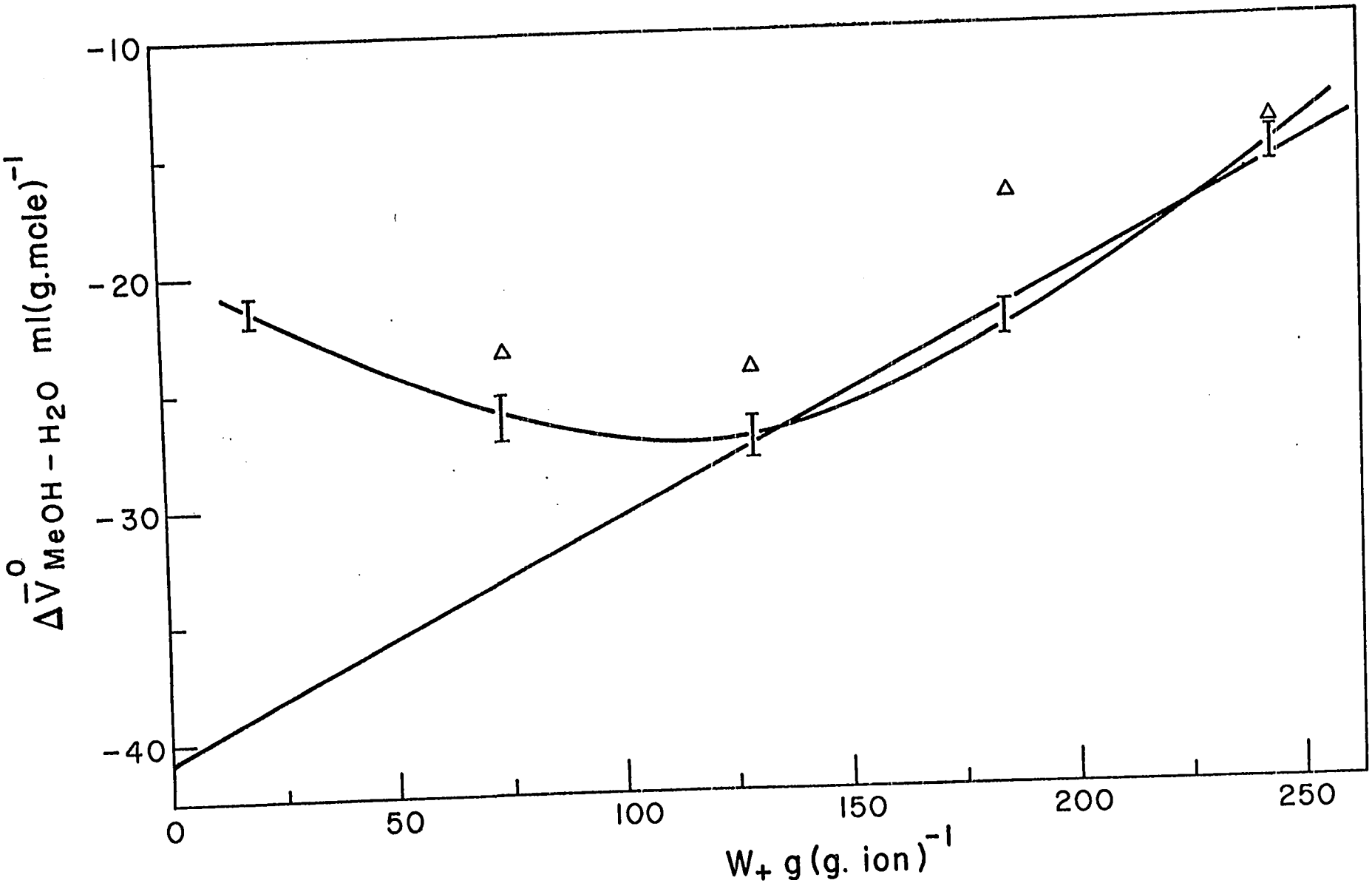
$$\Delta\bar{V}^{\circ}_{2(MeOH\text{-}H_2O)} = \Delta V_{e(MeOH)} - \Delta V_{e(H_2O)} \qquad (IV.9)$$

As $\Delta V_{e(H_2O)}$ is found to be almost zero for the TAA bromides in water, the value of $\Delta V_{e(MeOH)}$ is evidently larger than zero or, in other words, ΔV_e is greater in methanol than in water. Figure 24 shows a plot of $\Delta \bar{V}^o_{2(MeOH-H_2O)}$ vs. W_+, the molecular weight of the cation. The curve can be interpreted in terms of the ideas discussed above where the difference in electrostriction and structure formation which occurs in the two solvents was considered. The most important feature of Figure 24 is that the values of $\Delta \bar{V}_{2(MeOH-H_2O)}$ are all negative. This means that for NH_4Br and Me_4NBr the electrostriction term in the partial molar volume is larger in methanol than in H_2O. The curve exhibits a minimum between Me_4NBr and Et_4NBr which presumably results from a competition between the structure-forming and the electrostrictive effects of the ions in the two solvents.

The NH_4^+ ion which has a relatively small radius will be capable of electrostricting rather effectively in both water and methanol. However, when the next higher (TAA) ion, Me_4N^+, in the series is considered, the previous results (33, 48) indicate that it does not significantly electrostrict in aqueous solutions. In methanol, on the other hand, because of the less extensive hydrogen bonding, electrostriction will occur. Expressed in another way, larger electrostriction will be expected in methanol than in water because of the substantially higher compressibility of the former solvent than the latter. For example, the isothermal compressibility of methanol at 1 atm. is $130 \times 10^{-6} bar^{-1}$ (30°C) (79) compared with

Figure 24

Values of $\Delta\bar{V}^{o}_{(MeOH\text{-}H_2O)}$ for NH_4Br and TAA bromide salts as a function of the molecular weight of the cations, present results I , results of Padova and Abrahamer Δ (52).


-10
-20
-30
-40
0
50
100
150
200
250
$\Delta\bar{V}^{o}_{MeOH-H_2O}$ ml(g.mole)$^{-1}$
W_+ g (g. ion)$^{-1}$

$44 \times 10^{-6} bar^{-1}$ for water (80) under the same conditions. The difference in the electrostrictive ability of a given ion in the two solvents leads to the observed decrease in $\Delta\bar{V}^{o}_{2(MeOH-H_2O)}$ in going from NH_4^+ to Me_4N^+. For Et_4N^+ and the larger ions in the symmetrical TAA series, the regular increase in $\Delta\bar{V}^{o}_{2(MeOH-H_2O)}$ will be due to the difference in structure-forming ability of the ions in the two solvents.

Using the plot of $\Delta\bar{V}^{o}_{2(MeOH-H_2O)}$ vs. $\bar{W}_+$, another extrapolation can be made to determine the value of $\Delta\bar{V}^{o}_{2(MeOH-H_2O)}$ for the bromide ion. The section of the curve passing through the points for the largest cations where insignificant electrostriction occurs can be extrapolated to zero molecular weight of the cation. This leads to a value of -40.8 ml $(g.mole)^{-1}$ for $\Delta\bar{V}^{o}_{Br^-(MeOH-H_2O)}$. Using the value of $\bar{V}^{o}_{Br^-(H_2O)}$ previously reported (65), a value of -9.9 ml$(g.mole)^{-1}$ for the partial molal volume of the bromide ion in methanol can be calculated. Previously a value of +6 ml. $mole^{-1}$ had been reported by Padova and Abrahamer (52) for $\bar{V}^{o}_{Br^-}$ in methanol. This value was derived from considerations of the solvated radius of the Br^- ion in methanol as calculated from results of viscosity experiments. This treatment involved a knowledge of the hydration number which, however, is not likely to be the same in a comparative treatment of kinetic and thermodynamic properties. The method used in the present work has been shown, in the case of

aqueous solutions, to give a result which is in very close agreement with an independently derived value for $\bar{V}^{o}_{Br^-(H_2O)}$ (81) based on measurements of ultrasonic potentials. Therefore, in methanol, the procedure should be at least as reliable since structure-formation effects are less likely to introduce an error in the results for that solvent.

CONTRIBUTIONS TO ORIGINAL RESEARCH

1. A new experimental technique based on an application of Henry's law was developed.

2. The solubility of argon in aqueous ammonium bromide and tetraalkylammonium bromide salt solutions was determined over a wide range of concentrations of the salts.

3. A method has been proposed to evaluate individual ionic Setchenow constants (k_s).

4. The partial molal volume of ammonium bromide and of a series of four tetraalkylammonium bromide salts has been determined in anhydrous methanol. The measurements were extended into the Debye-Hückel limiting law region.

5. An evaluation of the partial molar volume of the bromide ion in methanol has been made, thus establishing an absolute scale of individual ionic partial molar volumes in methanol.

REFERENCES

1. M. Randall and C. F. Failey, Chem. Rev. 4, 271 (1927).
2. F. A. Long and W. F. McDevit, Chem. Rev. 51, 119 (1952).
3. J. O'M. Bockris, Quart. Rev. 3, 179 (1949).
4. A. M. Azzam, Can. J. Chem. 38, 993 (1960).
5. H. S. Frank and M. W. Evans, J. Chem. Phys. 13, 507 (1945).
6. D. D. Eley, Trans. Faraday Soc. 35, 1281 (1939).
7. H. S. Frank and W.-Y. Wen, Disc. Faraday Soc. 24, 133 (1957).
8. G. Némethy and H. A. Scheraga, J. Chem. Phys., 36, 3401 (1962).
9. W. F. Clausen and M. F. Polglas, J. Amer. Chem. Soc., 74, 4817 (1952).
10. W.-Y. Wen and S. Saito, J. Phys. Chem. 68, 2639 (1964).
11. O. Ya. Samoilov, Structure of Electrolyte Solutions and Hydration of Ions (Engl. Translation), Consultants Bureau Enterprises Inc., New York (1965).
12. E. R. Nightingale, Jr., J. Phys. Chem. 63, 1381 (1959).
13. R. W. Gurney, Ionic Processes in Solution, Chap. 9 and 16, McGraw-Hill Book Company, New York (1954).
14. F. Vaslow, J. Phys. Chem. 67, 2773 (1963).
15. P. Debye and J. McAulay, Physik. Z. 26, 22 (1925).
16. J. A. V. Butler, J. Phys. Chem. 33, 1015 (1929).
17. J. O'M. Bockris, J. Bowler-Reed and J. A. Kitchener, Trans. Faraday Soc. 47, 184 (1951).
18. B. E. Conway, J. E. Desnoyers and A. C. Smith, Phil. Trans. Roy. Soc. London, Ser. A. 256, 389 (1964).

19. J.G. Kirkwood, J. Chem. Phys. 7, 911 (1939).

20. H. Margenau, Rev. Mod. Phys. 11, 1 (1939).

21. B. Chu, Molecular Forces, Interscience Publishers, John Wiley and Sons, New York (1967).

22. J.E. Desnoyers, G.E. Pelletier and C. Jolicoeur, Can. J. Chem. 43, 3232 (1965).

23. R.M. Diamond, J. Phys. Chem. 67, 2513 (1963).

24. H.B. Klevens, Chem. Rev. 47, 1 (1950).

25. J.E. Desnoyers and M. Arel, Can. J. Chem. 45, 359 (1967).

26. J.E. Desnoyers and F.M. Ichhaporia, Can. J. Chem. 47, 4639 (1969).

27. K.J. Laidler and C. Pegis, Proc. Roy. Soc. (London), A241, 80 (1957).

28. W.M. Latimer and C. Kasper, J. Am. Chem. Soc. 51, 2293 (1929).

29. D.D. Eley and M.G. Evans, Trans. Faraday Soc. 34, 1093 (1938).

30. R.A. Robinson and R.H. Stokes, Electrolyte Solutions, Chapter 6, Butterworths, London (1959).

31. E.R. Nightingale, Jr., J. Phys. Chem. 66, 894 (1962).

32. H.S. Frank, J. Phys. Chem. 67, 1554 (1963).

33. B.E. Conway, R.E. Verrall and J.E. Desnoyers, Trans. Faraday Soc. 62, 2738 (1966).

34. S. Lindenbaum and G.E. Boyd, J. Phys. Chem. 68, 911 (1964).

35. B.J. Levien, Austral. J. Chem. 18, 1161 (1965).

36. J.E. Desnoyers and C. Jolicoeur, Modern Aspects of Electrochemistry, Vol. 5, Eds. J.O'M. Bockris and B.E. Conway, Plenum Press, New York (1969).

37. T.J. Morrison and N.B. Johnstone, J.Chem.Soc. 3655 (1955).

38. T.J. Morrison, J.Chem.Soc. 3814 (1952).

39. T.J. Morrison and F. Billett, J.Chem.Soc. 3819 (1952).

40. J.D. Bernal and R.H. Fowler, J.Chem.Phys. 1, 515 (1933).

41. D.D. Eley, Disc. Faraday Soc. 15, 150 (1953).

42. I.F. Efremov, T.A. Prokf'eva and Yu.P. Syrnikov, Russ.J.Phys.Chem.(Engl.Transl.) 38, 1389 (1964).

43. A. Mikhailov, Russ.J.Phys.Chem.(Engl.Transl.) 36, 153 (1962).

44. P. Debye, Z.Physik.Chem. 130, 56 (1927).

45. W.R. Gilkerson and J.L. Stewart, J.Phys.Chem. 65, 146 (1961).

46. L.G. Hepler, J.M.Stokes and R.H. Stokes, Trans.Faraday Soc. 61, 20 (1965).

47. L.A. Dunn, Trans.Faraday Soc. 64, 1898 (1968).

48. B.E. Conway and R.E. Verrall, J.Phys.Chem. 70, 3961 (1966).

49. B.E. Conway, R.E. Verrall and J.E. Desnoyers, Zeit.Phys.Chem., 230, 157 (1965).

50. H.E. Wirth, J.Phys.Chem. 71, 2922 (1967).

51. W.-Y. Wen and S. Saito, J.Phys.Chem. 69, 3569 (1965).

52. J. Padova and I. Abrahamer, J.Phys.Chem. 71, 2112 (1967).

53. L.W. Winkler, Ber. 22, 1764 (1889); see also R. Battino and H.L. Clever, Chem.Rev. 66, 395 (1966).

54. M.W. Cook and D.N. Hanson, Rev.Sci.Instr. 28, 370 (1957).

55. A. Ben-Naim and S. Baer , Trans.Faraday Soc. 60, 1736 (1964).

56. B.B. Benson and P.D.M. Parker, J.Phys.Chem. 65, 1489 (1961).

57. C.E. Klots and B.B. Benson, J.Phys.Chem. 67, 890 (1963).

58. A. Ben-Naim, J.Phys.Chem. 69, 3245 (1965).

59. J.H. Hildebrand and R.L. Scott, Solubility of Non-Electrolytes, 3rd. Edition, Dover Publications Inc. New York (1964).

60. T.J. Morrison and N.B. Johnstone, J. Chem. Soc. 3441 (1954).

61. E. Douglas, J. Phys. Chem. 68, 169 (1964).

62. A. Lannung, J. Am. Chem. Soc. 52, 68 (1934).

63. F. Kohlrausch and W. Hallwachs, Weid. Ann. d. Phys. 50, 118 (1893).

64. H.E. Wirth, J. Am. Chem. Soc. 59, 2549 (1937).

65. L.H. Laliberté, Ph. D. Thesis, University of Ottawa (1969).

66. R.E. Verrall, Ph. D. Thesis, University of Ottawa (1966).

67. O. Redlich and D.M. Meyer, Chem. Rev. 44, 221 (1964).

68. G.W. Castellan, Physical Chemistry, Addison-Wesley Publishing Company, Inc., Reading, Mass. (1964).

69. L. Pauling, Nature of Chemical Bond, Cornell University Press, 2nd Edition, Ithaca, New York (1948).

70. B.S. Gourary and F.J. Adrian, Solid State Physics, 10, 127 (1960).

71. B.E. Conway and L.H. Laliberté, Trans. Faraday Soc. (1970) submitted.

72. F.J. Millero and W. Drost-Hansen, J. Phys. Chem. 72, 1758 (1968).

73. M.E. Friedman and H.A. Scheraga, J. Phys. Chem. 69, 3795 (1965).

74. R.E. Verrall and B.E. Conway, J. Phys. Chem. 70, 3952 (1966).

75. W.-Y. Wen and J.H. Hung, J. Phys. Chem. 74, 170 (1970).

76. B.E. Conway and R.E. Verrall, J. Chem. Phys. 440, 1473 (1966).

77. H.G. Hertz and M. D. Zeidler, Ber. Bunsenges. Physik. Chem. 68, 821 (1964).

78. W. H. Zachariasen, J. Chem. Phys. 3, 158 (1935).

79. E. B. Frever, J. C. Habbard and D. H. Andrew, J. Am. Chem. Soc. 51, 759 (1929).

80. G. S. Kell, J. Chem. Eng. Data. 12, 66 (1967).

81. R. Zana and E. Yeager, J. Phys. Chem. 70, 954 (1966); 71, 521 (1967).