THE UNIVERSITY OF MANITOBA

ACTIVITY AND DIFFUSION COEFFICIENTS OF LITHIUM AND OF SODIUM CHLORATE IN WATER AND WATER-DIOXANE MIXTURES

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TO MY WIFE, MARY ELLEN

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ABSTRACT

The vapour pressures of solutions of sodium chlorate and of lithium chlorate in water and in solvents consisting of 44.5% dioxane - 55.5% water and of 64.5% dioxane - 35.5% water, at 25°C, were determined using a differential manometer. The vapour compositions of the dioxane-water solutions were found using the air-saturation method.

From the vapour pressures and compositions the mean molal activity coefficients were calculated. The activity coefficients of the aqueous solutions were fitted to the theoretical equations of Stokes and Robinson and of Gleuckauf, yielding hydration numbers for the salts.

The minimum dioxanation numbers of sodium and lithium chlorate in the dioxane-water mixtures were calculated from the experimental activity coefficients by the method of Grunwald.

The diffusion coefficients of sodium chlorate and of lithium chlorate in water and in solvents consisting of 44.5% dioxane - 55.5% water and of 64.5% dioxane - 35.5% water were determined using the Stokes' diaphragm technique.

The diffusion coefficients of the aqueous solutions were treated by the extended Hartley-Crank analysis to obtain hydration numbers for the electrolytes.

Although experimental results indicated that dioxane was taking part in the solvation of the electrolytes, attempts to obtain a theoretical expression for the diffusion coefficients of the dioxane-water solutions and thus solvation numbers failed.

Results from both the vapour pressure and diffusion experiments proved conclusively that lithium chlorate is more highly solvated than sodium chlorate and that dioxane plays a major role in the solvation of both electrolytes in the dioxane-water mixtures.

GLOSSARY OF SYMBOLS

D	Differential diffusion coefficient
$\bar{\bar{D}}$	Diaphragm-cell integral diffusion coefficient
D^*	Self-diffusion or tracer-diffusion coefficient
F	Faraday
G	Gibbs free energy
I	Ionic strength
J	Flux of matter, in diffusion theory
M	Molecular weight
M_{12}	Mean Molecular weight of binary solvent
N	Avagadro's number
N_A, N_B	Mole fraction of components A and B
P	Pressure
R	Gas constant
S	Debye-Hückel limiting slope
T	Absolute temperature
$\bar{\bar{V}}_A$, $\bar{\bar{V}}_B$	Partial molal volumes of components A and B
W_A	Molecular weight of solvent
Z_1, Z_2	Algebraic valencies of cations and anions respectively
a	Distance of closest approach
a_A, a_B	Activity of components A and B
a_w	Water activity
c	concentration
d^o	Dioxanation number

e	Electronic charge
$f_{\pm}$	Mean rational activity coefficient
h, h^{o}	Hydration number
k	Boltzman constant
k_H	Henry law constant
m	Molality
n_A, n_B	Number of moles of substances A and B in system
n_D^{25}	Refractive index at 25°C
p	Partial pressure
r	Radius of the ions
$r_{\pm}$	Harmonic mean of r_+ and r_-
t	Time
t_1, t_2	Transport numbers of cations and anions respectively
u	Absolute mobility of particle
v	Velocity
$y_{\pm}$	Mean molar activity coefficient
ϕ	Molal osmotic coefficient
Π	Osmotic pressure
Δ	Penetration distance of ions
Δ_n	n^{th} order electrophoretic correction to diffusion coefficient
α_1	The partial pressure of component 1 of the binary solvent to which salt has been added, divided by, the partial pressure of component 1 of the binary solvent.
β	Diffusion cell constant
$\gamma = \gamma_{\pm}$	Mean molal activity coefficient

ν	Number of moles of ions formed from 1 mole of electrolyte
κ	Quantity proportional to square root of ionic strength (cm.$^{-1}$)
η	Viscosity
ε	Dielectric Constant

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INTRODUCTION

A. GENERAL INTRODUCTION

The modern theory of electrolytes dates from the work of Debye and Hückel in 1923, although it had begun to take shape many years earlier when Bjerrum, Jahn, Noyes, and Sutherland realized the importance of the electrostatic forces between free ions, and gave the first quantitative treatment of them.

Debye and Hückel[1] took as their model an electrolyte completely dissociated into rigid, spherically symmetrical ions. The interaction between these ions was computed by Coulomb's law, assuming the medium to have the dielectric constant of the pure solvent. The ions were assumed to be point masses of negligible dimensions. With suitable mathematical approximations, the theory led to an equation for the geometric mean activity coefficient of an electrolyte in dilute solution which contained no arbitrary constants. This familiar equation, the Debye-Hückel limiting law, predicted from first principles the thermodynamic behavior of dilute electrolyte and its dependence on valency, temperature and the properties of the solvent. The fact that values calculated from this equation were in agreement with the experimental data for many simple electrolytes in water showed that these electrolytes behaved in a manner consistent with the assumption of complete dissociation.

The conducting power of an electrolyte also is influenced by interionic forces, and here the treatment, modified by Onsager[2], led to another limiting law for dilute solutions - the Debye - Hückel - Onsager equation. The success of the theory in this direction was, if anything, even more striking, as the accurate data needed to test it became more abundant and were extended over a wide range of conditions. Once more the quantitative agreement between the predictions of the theory and the highly accurate experimental results for many salts seemed to indicate that these salts were completely dissociated in the extremely dilute region considered.

The main achievement of the Debye - Hückel - Onsager treatment was to draw attention to, and to show how to calculate, the effects of the long range electrostatic interactions in dilute solutions of electrolytes. This treatment not only showed that the older Arrhenius theory of electrolytic dissociation had to be modified, but it pointed the way to developments in the theory of electrolytes - their behavior in mixtures, their viscosity, reactivity, and so on - which dominated research in the field of solutions for many years. The demonstration that many salts in water were completely dissociated into ions in extremely dilute solutions was important but incidental, and it was not advanced as a rule of universal validity. Yet the new idea of complete dissociation was so attractively simple, and it harmonized so happily with the knowledge newly gained by x-ray methods of ionic structures in salt crystals and with the electronic theory of valency then in process of development, that it passed into popular science as 'the complete dissociation theory'. Simple electrolytes such as alkali metal chlorides were naturally chosen for study in following up and applying the new theories: for many years it was unfashionable to study electrolytes that deviated from ideal Debye - Onsager behavior, and the accumulation of information about them has consequently been slow.

From the beginning, however, it was known that such deviations were not uncommon; Onsager in his early paper quoted approximate dissociation constants for potassium nitrate and other electrolytes. Moreover, the cause, or at least one possible cause, of such deviations was clearly appreciated. In the mathematical simplification of the Debye - Hückel treatment it had to be assumed that the electrical energy of an ion is small compared with its mean thermal energy. This will not be true for small ions which can approach one another very closely, as can easily be seen by remembering that two point charges coming together would need infinite work to separate them again. Especially will this not be true for small ions of high valency and for solutions in organic media of low dielectric constant. A method allowing for this complication was proposed by Bjerrum[3] in 1926. Using the same model as Debye and Hückel, Bjerrum plotted the probability of finding an oppositely charged ion at a given distance from the central ion. The distribution curve shows a flat minimum at a distance where the work of separating the two oppositely charged ions is four times as great as the mean kinetic energy per degree of freedom. This distance is 3.5Å for univalent ions in water at 25°C. For ions so large that their centres cannot approach more closely than this, it is assumed that the Debye - Hückel limiting equation should be satisfactory. However, small ions can approach to distances varying from $r = 3.5\text{Å}$ to $r = a$, where 'a' is the sum of the radii of the ions - distances at which the work of separation increases rapidly and can become very large. Bjerrum regarded a pair of ions within this range as associated to form an 'ion-pair'. The associated ion pairs could be treated as neutral molecules of unit activity in equilibrium with free ions: $C^{+} + A^{-} \rightleftarrows [C^{+}A^{-}]^{o}$; and the law of mass action could be applied to give the dissociation constant of the ion-pair.

It does not follow that every deviation from the Debye - Hückel - Onsager equations is to be attributed to ionic association in the Bjerrum sense. Ion-solvent interactions must also be taken into consideration. The extent of this interaction for various electrolytes has been studied by Stokes and Robinson[3] and also by Gleuckauf[4]. Stokes and Robinson apply 'mole fraction statistics' to derive specific hydration numbers while Gleuckauf uses 'volume fraction statistics'. A more detailed discussion of their treatments will follow later in this thesis.

Another completely different approach to the problem of electrolytic solutions has been taken by Frank[5,6,7]. He believes that a model completely different from that of Debye - Hückel is needed. He bases his belief on the fact that real solutions obey a cube root law of the form $\log f_{\pm} = a - b\, c^{1/3}$ (where $f_{\pm}$ is the mean rational activity coefficient) over a range of concentration from 0.001M to 0.02 or 0.03M. Assuming that this equation is physically significant, Frank proposed that after conforming to the Debye - Hückel formulation from $C = 0$ to about 0.001M; the ion atmosphere goes over into a pseudo-lattice shape which results in the cube root form of the $\log f_{\pm}$ function in the observed range. Frank's diffuse-lattice cloud[6] seems to clear up some of the anomalies between experimental results and theory but at this stage of development it is very qualitative and lacks quantitative prediction.

A large variety of experimental methods have been used to provide information concerning ionic solutions and to test the theories mentioned. Three broad categories are: kinetic or transport phenomena, classical thermodynamics, and spectroscopic methods. In this thesis two major experimental methods were employed - vapour pressure and diffusion. Some conductance and viscosity work has also been done but I have given a complete theoretical treatment of these in my M.Sc. thesis[8]. In the next two sections of the introduction I shall give a complete theoretical interpretation of the activity and diffusion coefficients of electrolyte solutions.

B. THEORETICAL INTERPRETATION OF CHEMICAL POTENTIALS

The partial molal Gibbs free energies, or chemical potentials, of the solvent and solute are:

$$\bar{G}_A = \left(\frac{\partial G}{\partial n_A}\right)_{n_B,T,P} \qquad (1)$$

$$\bar{G}_B = \left(\frac{\partial G}{\partial n_B}\right)_{n_A,T,P} \qquad (2)$$

where n_A, n_B denote the number of moles of solvent and solute in the system. Since it is more interesting to study the variation of chemical potential with concentration than its absolute value, it is usual to express these quantities as a difference between the absolute value and that which holds in some specified standard state. The standard state is indicated by a superscript zero, G_A^o, G_B^o. The choice of the standard state is entirely arbitrary: it may be a pure component, a saturated solution or some entirely hypothetical solution. In the case of mixed liquids which are non-electrolytes, for example, the standard state for each component is usually taken to be the pure state; this choice preserves symmetry between the two components, which is useful in the study of these systems.

For electrolyte solutions, the standard state to which the free energy of the solvent is referred is invariably the pure solvent at the same temperature and pressure. The activity of the solvent, a_A, is then defined by:

$$\bar{G}_A - \bar{G}_A^o = RT \ln a_A \qquad (3)$$

Since the pure solvent can exist in equilibrium with its vapour at pressure p_A^o, and the solution with the solvent vapour at partial pressure p_A, assuming the vapour to be ideal:

$$\overline{G}_A^o = \overline{G}_A^o\ (v) + RT\ \ln p_A^o \tag{4}$$

and

$$\overline{G}_A = \overline{G}_A^o\ (v) + RT\ \ln p_A \tag{5}$$

where $\overline{G}_A^o$ (v) is the molal free energy of the vapour in the standard state of one atmosphere pressure at the temperature T.

It follows from (3), (4), and (5) that:

$$a_A = \frac{p_A}{p_A^o} \tag{6}$$

Strictly, the ratio p_A/p_A^o should be replaced by the ratio of the fugacities, p_A^*/p^{*o}_A . However, the vapour pressures of most commonly used electrolyte solutions are small enough to make this change negligible, i.e. the vapour may be assumed to be an ideal gas.

For electrolytes, however, the pure solute is not a very practical choice as a standard state, since it is frequently a solid or liquid with properties very different from those in solutions. Instead, it is the practice to use as standard states certain hypothetical solutions.

The standard state for a component considered as a solute B is based on Henry's Law. In the limit as $X_B \longrightarrow 0$, $a_B \longrightarrow X_B$, and the activity coefficient $\gamma_B \longrightarrow 1$. The departure of γ_B from unity is a measure of the departure of the behavior of the solute from that prescribed by Henry's Law.

Henry's Law implies the absence of interaction between molecules of solute. Therefore the deviations of the activity coefficients from unity measure the effects of interactions between solute species in solution. The limiting form of Henry's Law for an electrolyte which yields ν particles on dissociation is:

$$p_B^* = k_H \, a_B^{\nu} \qquad (7)$$

The usual standard state for an electrolyte is a hypothetical state in which the solute would exist at unit molality and one atmosphere pressure but would still have the environment typical of an extremely dilute solution that followed Henry's Law.

The free energy of the solute can be represented by the equation

$$\bar{G}_B = \bar{G}_B^o + RT \ln a_B \qquad (8)$$

where $\bar{G}_B^o$ is the free energy in the standard state, and a_B is the activity of the solute on the molal scale. Denoting the activity of the cation as a_+ and the activity of the anion as a_- one can write:

$$a_B = a_+ \, a_- = a_{\pm}^2 \qquad (9)$$

The quantity $a_{\pm}$, the geometric mean of a_+ and a_- is called the mean activity of the ions. The individual ionic activity coefficients γ_+ and γ_- may be defined as

$$a_+ = \gamma_+ \, m_+ \quad \text{and} \quad a_- = \gamma_- \, m_- \qquad (10)$$

In practice, since it is impossible to measure individual ion activities, only the geometric means of the coefficients ($\gamma_{\pm}$) will be measurable, where

$$\gamma_{\pm} = \gamma_{+}^{\nu+} \gamma_{-}^{\nu-} \qquad (11)$$

Equation (8) can then be written

$$a_B = m_{+}^{\nu+} m_{-}^{\nu-} \gamma_{+}^{\nu+} \gamma_{-}^{\nu-}$$

or

$$a_{\pm} = a_B^{1/\nu} = (m_{+}^{\nu+} m_{-}^{\nu-} \gamma_{+}^{\nu+} \gamma_{-}^{\nu-})^{1/\nu} \qquad (12)$$

When equation (11) is substituted into equation (12), $\gamma_{\pm}$ is obtained as

$$\gamma_{\pm} = \frac{a_{\pm}}{(m_{+}^{\nu+} m_{-}^{\nu-})^{1/\nu}} \qquad (13)$$

For the solution of a simple salt, of molality m, $m_{+} = \nu_{+} m$ and $m_{-} = \nu_{-} m$ hence,

$$\gamma_{\pm} = \frac{a_{\pm}}{m_{\pm}} \qquad (14)$$

The mean ionic activity coefficient $\gamma_{\pm}$ is used so often that it is abbreviated to γ.

To emphasize the departure from ideality indicated by the activity coefficient of the solute another useful quantity may be defined. This quantity is the molal osmotic coefficient which is given by the equation

$$\phi = - \frac{1000}{\nu m W_A} \ln a_A \qquad (15)$$

This molal osmotic coefficient is related to the osmotic pressure by:

$$\Pi = \frac{\nu R T W_A}{1000 \bar{V}_A} \phi m \qquad (16)$$

where $\bar{V}_A$ is the partial molal volume of the solvent.

Now that the basic concepts and definitions have been dealt with, it is possible to discuss the theoretical interpretation of chemical potentials. The problem of accounting for the thermodynamic properties of a solution is best regarded as that of finding a theoretical expression for the non-ideal part of the chemical potential (of either component) as a function of composition, temperature, dielectric constant and any other relevant variables. In practice, the activity coefficient of the solute is usually more convenient to handle than the chemical potential, and the problem accordingly becomes one of finding a theoretical expression for the activity coefficient. As has been previously stated, no adequate theoretical model based on the atomic characteristics of the ions has yet been developed which is able to account for the thermodynamic properties of aqueous solutions over wide ranges of concentration. For completely ionized electrolytes, however, expressions have been derived by Debye and Hückel[1] which predict exactly the limiting behavior of activity coefficients in very dilute solutions. Since the development of the Debye - Hückel theory has been covered so often in elementary texts, only the final result will be stated here. The expression is

$$\log \gamma_{\pm} = \frac{-A|Z_1 Z_2| (I)^{1/2}}{1 + Ba (I)^{1/2}} \qquad (17)$$

where Z_1 and Z_2 are the valencies of the ions, 'I' is the ionic strength, 'a' is the distance of closest approach, and A and B are constants that involve the absolute temperature and the dielectric constant of the solvent, as follows:

$$A = \left(\frac{2\pi N}{1000}\right)^{1/2} \cdot \frac{e^3}{2.303\ k^{3/2}} \cdot \frac{1}{(\epsilon\ T)^{3/2}} = \frac{1.8246 \times 10^6}{(\epsilon\ T)^{3/2}} \qquad (18)$$

$$B = \left(\frac{8\pi Ne^2}{1000k}\right)^{1/2} \frac{1}{(\varepsilon T)^{1/2}} = \frac{50.29 \times 10^8}{(\varepsilon\ T)^{1/2}} \qquad (19)$$

Since equation (17) contains the parameter 'a' defined as the 'distance of closest approach' of the ions, the formula for the activity coefficient is not expressible solely in terms of measurable quantities. However, it is clear that at very low values of $(I)^{1/2}$, the term $(Ba(I)^{1/2})$ will ultimately become negligible compared to unity, and (17) will approach the form:

$$\log \gamma_{\pm} = - A \mid Z_1 Z_2 \mid (I)^{1/2} \qquad (20)$$

This is the Debye - Hückel' limiting law according to which log $\gamma_{\pm}$ approaches linearity in the square root of the concentration at high dilutions. It is not to be expected that equation (20) will be obeyed accurately at any experimental concentration, since the product (Ba) is in practice always of the order of unity.

For many aqueous solutions the expression (17) is capable of representing the observed activity coefficients with very good accuracy by simply choosing a value of the parameter a, independent of concentration, and of a physically reasonable magnitude. This often holds up to an ionic strength of about $I = 0.1$, when the ions are separated on the average by no more than about 20Å . Here their mutual energy would be expected to be of the same order as kT; it appears, therefore, that the simple distribution - function used in deriving equation (17) is fairly adequate.

The derivation of equation (17) is such that the numerator of the right-hand side, $-A \; |Z_1 Z_2| \; (I)^{1/2}$, gives the effect of the long range coulomb forces, while the denomination $(1 + Ba\,(I)^{1/2})$ shows how these are modified by the short-range interactions between ions, which are represented on the crudest model, as non-deformable spheres of equal radii. In any actual solution there are short-range interactions between ions and solvent molecules, as well as other types of short-range interactions between ions, which cannot be adequately represented by the rigid-sphere model. These are all likely to be of a type giving an approximately linear variation of log $\gamma_{\pm}$ with concentration. Consequently they can be included, in a highly empirical fashion, by adding to (17) a term linear in the concentration, thus:

$$\log \gamma_{\pm} = \frac{-A\,|Z_1 Z_2|\,(I)^{1/2}}{1 + Ba\,(I)^{1/2}} + b\,I \qquad (21)$$

where, now, 'b' as well as 'a' is an adjustable parameter. Equations like (21) are widely used for the analytical representation of activity coefficients, especially for non-associated 1:1 electrolytes, where they are usually able to fit the data within experimental accuracy up to a concentration of at least one molal.

From comparisons of the ionic size parameter, a, necessary in the Debye - Hückel equation (17), with the dimensions of the crystallographic radii, it seems that there are good grounds for believing that the kinetic unit of the solute in many electrolyte solutions is an ion with several relatively firmly attached water molecules. This suggests that the activity coefficient predicted by the Debye - Hückel treatment is actually the mean molal activity coefficient of the hydrated ions. Taking this into consideration Robinson and Stokes[3] attempted to derive hydration numbers from the activity data available applying 'mole fraction statistics' as follows:

Consider a quantity of solution containing one mole of anhydrous solute, B, dissociated into ν_1 moles of cations and ν_2 moles of anions, dissolved in S moles of solvent A. The calculation of the fixed total free energy of the system, G, may be performed in two ways: (a) considering the solute as unsolvated; (b) considering that a total of 'h' moles of solvent are combined with the ν moles of ions (divided into h_1 moles of water combined with the ν_1 moles of cations, and h_2 moles of water combined with the ν_2 moles of anions). Let the solvent be denoted by a subscript A, and the chemical potentials and activity coefficients calculated on the basis of the solvated ions be distinguished by primes: G', f', etc.

In view of the arguments of the preceding paragraphs:

$$G = S\,\overline{G}_A + \nu_1\,\overline{G}_1 + \nu_2\,\overline{G}_2 \tag{22}$$

and

$$G = (S - h)\,\overline{G}_A + \nu_1\,\overline{G}'_1 + \nu_2\,\overline{G}'_2 \tag{23}$$

introducing for each chemical potential its expression in terms of the appropriate mole fraction and activity coefficient, and rearranging,

$$\nu_1\,(\overline{G}^o_1 - \overline{G}'^o_1)\,/RT + \nu_2\,(\overline{G}^o_2 - \overline{G}'^o_2)\,/RT + n\,\overline{G}^o_A\,/\,RT + h\ln a_A +$$

$$\nu\ \ln\frac{S + \nu - h}{S + \nu} + \nu_1\ln f_1 + \nu_2\ln f_2 = \nu_1\ln f_1' + \nu_2\ln f'_2 \tag{24}$$

Now as $S \longrightarrow \infty$ (i.e. at infinite dilution) all the activity coefficients become unity and a_A becomes unity, so that all the logarithmic terms are zero and hence the sum of the first three terms on the left of (24), involving the chemical potentials in the standard states is also zero. Introducing the mean ionic activity coefficients instead of the sums of the separate ionic activity coefficients:

$$\ln f'_{\pm} = \ln f_{\pm} + \frac{h}{\nu} \ln a_A + \ln \frac{S + \nu - h}{S + \nu} \qquad (25)$$

(In arriving at this result it has been assumed that the value of h in the actual solution is the same as at infinite dilution.) This result is in practice more useful when expressed in terms of the conventional mean molal activity coefficient $\gamma_{\pm}$ and the molality m; using the relations $S = \frac{1000}{W_A m}$, where W_A is the molecular weight of the solvent, and

$$f_{\pm} = \gamma_{\pm} (1 + 0.001 \ \nu W_A m)$$

$$\ln f'_{\pm} = \ln \gamma_{\pm} + \frac{h}{\nu} \ln a_A + \ln \ [1 + 0.001 \ W_A(\nu - h)m] \qquad (26)$$

Or, putting $\ln a_A$ in terms of the osmotic coefficient

$$\ln a_A = - \frac{\nu W_A m}{1000} \phi$$

$$\ln f_{\pm}' = \ln \gamma_{\pm} - 0.001 \ W_A h m \phi + \ln \ [1 + 0.001 \ W_A(\nu - h)m] \qquad (27)$$

Now ϕ or a_A can be calculated if $\gamma_{\pm}$ is known over the range of composition up to that considered, or alternatively $\gamma_{\pm}$ can be calculated if ϕ or a_A is similarly known. Hence the rational mean ionic activity coefficient of the solute in terms of the conventional activity coefficients has been derived. The solute is assumed solvated with h moles of solvent per mole of salt.

The only extra - thermodynamic assumption used in deriving equations (26) and (27) has been that the value of 'h' is unchanged on proceeding to infinite dilution. Therefore, the application of these equations to actual solutions is limited to cases where these are sufficient solvent molecules to solvate the solute particles, and where the forces between the latter, and those between solute and solvent are at least approximately of a saturable nature. While the forces between ions and water molecules are at least mainly electrostatic, and therefore are not strictly saturable in the same way that 'chemical' binding forces are, there is strong reason to believe that water molecules in direct contact with the ion are subject to much greater forces of attraction than those in subsequent layers, and there is a limit to the number of such molecules. Consequently, it is reasonable to expect the assumption of an 'h' value independent of concentration to apply to moderately high concentrations. In practice the limit is often reached when about a quarter of the solvent molecules are combined with ions.

It is possible to combine equation (25) with the Debye - Hückel equation (17), taking the latter to deal with interionic forces and the former to deal with the ion-solvent forces. Apart from the obvious advantage of using a model which certainly comes closer to the physical reality, this procedure goes a long way towards justifying another assumption implicit in the derivation of equation (17), namely, that the dielectric constant ε is that of the pure solvent. The work of Hasted, Ritson and Collie[9] has shown that most of the observed lowering of the bulk dielectric constant by ionic solutes arises from effects in the first layer of water molecules round the ion. If this layer is taken as part of the solute particle and if other ions do not penetrate it, the dielectric constant of the liquid outside may fairly be taken as that of the pure solvent.

The simplest treatment of the effect of ionic solvation on the activity coefficient would be, as suggested above, simply to combine equation (25) with the Debye - Hückel expression, where the latter gives the activity coefficient of the solvated ions, log $f_{\pm}'$. This course is consistent with the fact that the 'a' values of the Debye - Hückel expression correspond to the dimensions of solvated ions. The resulting expression is:

$$\log \gamma_{\pm} = \frac{- A \; |Z_1 Z_2| \; (I)^{1/2}}{1 + Ba \; (I)^{1/2}} - \frac{h}{\nu} \log a_A - \log [\, 1 + 0.001 \, W_A (\nu - h) m \,] \tag{28}$$

Equation (28) has been extensively tested and is remarkably successful with non-associated electrolytes. But, some anomalous behavior has been observed. Firstly, the largest anion is the most solvated, a conclusion at variance with both reasonable expectation and other experimental indications. Secondly, the solvation numbers 'h' are not additive for the separate ions. Thirdly, low values are obtained for potassium, ammonium and rubidium salts indicating that the chloride, bromide and iodide ions must be only slightly hydrated; it follows that, where high values of 'h' are found, most of the hydration must be attributed to the cation. This is quite reasonable since the anions studied have all been large and, therefore, have low surface charge. The resulting cation hydration numbers, however, do seem rather large. In particular, if the radius of spherical cations containing such amounts of water is estimated, one finds that the sum of this radius and the crystallographic radius of the anion exceeds the required value by about 0.7Å for 1:1 salts and 1.3Å for 2:1 salts. This rather unsatisfactory situation is dealt with by assuming that when the anion and cation meet, the anion can penetrate into the hydration sheath of the cation to the extent of these distances; the greater penetration when the cation is divalent (1.3Å against 0.7Å) would thus arise from the greater attraction it has for its anion.

Using the concept of a limited penetration of the anion into the hydration sheath of the cation, it has proved possible to obtain a relation between the parameters h and a, of sufficient accuracy to permit the calculation of the activity coefficients of the chlorides, bromides and iodides of the alkali and alkaline earth metals and hydrogen with quite good accuracy (better than one per cent) up to ionic strengths often as high as $I = 4$. The relation between "h" and "a" is obtained as follows: The volume occupied by a water molecule in liquid water at 25° is 30Å^3. The volume of the hydrated cation (taking the anion as unhydrated) is therefore $(30\ h + V_1)$, where V_1 is the apparent molal volume of the ion in Å^3. V_1 can be estimated from the apparent molal volume of the salt, V_{app}, in solution by means of the formula:

$$V_1 = V_{app} - 6.47 Z_1 r_2^{\ 3} \qquad (29)$$

where r_2 is the crystal radius of the anion (in Å). Since V_1 is usually only a small fraction of 30'h', it need not be calculated with great accuracy, and in practice it is sufficient to estimate the apparent molal volume at about 1 Molal and use this value at all concentrations. The radius of the hydrated cation, r_1', is then given by:

$$4\pi r_1'^{3}/3 = 30\,h + V_1 \qquad (30)$$

and the value of the mean distance of closest approach of the ions is given by:

$$a = r_1' + r_2 - \Delta \qquad (31)$$

where Δ is the 'penetration distance'. Since r_1' is a known function of 'h', 'a' can be calculated from 'h' and the known crystal radius of the anion. The resulting one-parameter equation for the activity coefficient (for aqueous solution at 25°) is:

$$\log \gamma_{\pm} = \frac{-\,0.5115\,|Z_1 Z_2|\,(I)^{1/2}}{1 + 0.3291\,(I)^{1/2}\left\{\frac{3}{4\pi}(30h + V_1)^{1/3} + r_2 - \Delta\right\}}$$

$$-\frac{h}{\nu}\log a_W - \log\left[1 - 0.018\,(h - \nu)m\right] \qquad (32)$$

It is, of course, not strictly a one-parameter equation, for it involves Δ as well as 'h'. However, Δ is constant for each class of salt (0.7 Å for 1:1 salts, 1.3 Å for 2:1 salts) so that only the parameter 'h' has to be specified to give the activity coefficient of a salt of one of these valency types. The limit of validity of this equation is generally reached when the product 'hm' ~ 12, i.e., when about one-fifth to one-quarter of the total water molecules are bound to ions as water of hydration.

Above this limit, equation (32) usually predicts values which are higher than those observed, which suggests that the hydration number is beginning to decrease as a result of competition between neighbouring cations.

Gleuckauf[4], recognizing the difficulty of interpreting the 'h' values of equations (28) and (32) as the actual sums of hydration numbers for the ions of the electrolytes proposed the following modification of the theory: If 'h_i' is the actual hydration number of an ion 'i', the partial molal volume of the hydrated ion $\bar{V}_i'$ is $(h_i \bar{V}_A + \bar{V}_i)$ where $\bar{V}_i$ is the partial molal volume of the unhydrated ion as ordinarily defined. He then assumes that the entropy of mixing of the hydrated ions and the 'free' solvent is given by the equation:

$$S^M = - R \left[N_A \ln \frac{N_A}{N_A + r_i N_B} + N_B \ln \frac{r_i N_B}{N_A + r_i N_B} \right] \qquad (33)$$

where $r_i = \dfrac{\bar{V}_i'}{\bar{V}_A}$. He then employs 'volume fraction statistics' instead of of the 'mole fraction statistics' which were used in deriving equation (28). His final expression for the mean molal activity coefficient is:

$$\ln \gamma_{\pm} = \frac{- A \mid Z_1 Z_2 \mid (I)^{1/2}}{1 + Ba (I)^{1/2}} + \frac{0.018 \; m \; r \; (r + h - \nu)}{\nu \; (1 + 0.018 \; mr)} +$$

$$\frac{h - \nu}{\nu} \ln (1 + 0.018 \; mr) - \frac{h}{\nu} \ln (1 - 0.018 \; mh) \qquad (34)$$

where the quantity r, now referring to the electrolyte as a whole, is $r = (\bar{V}_B + h \; \bar{V}_A)/\bar{V}_A$. Using 'h' and 'a' as parameters, this equation fits the experimental data as well as does equation (28). Robinson and Stokes[10] have shown that a simple relation between actual volumes and effective volumes in solution enables one to dispense with 'a' as an aribtrary parameter. The values of the hydration numbers required by equation (34) are considerably smaller than those of equation (28). Furthermore, the most serious anomaly in the earlier treatment now disappears: the new hydration numbers become nearly additive for separate ions.

In a recent paper Desnoyers and Conway[11] have attempted to improve the treatments of Stokes and Robinson and of Gleuckauf. They separate the experimental mean molal activity coefficients of simple electrolytes at concentrations below one molal into three main contributions arising from interionic coulombic forces, ion-solvent, and ion-cavity interactions. This separation is represented by the equation:

$$\log \gamma = \log f_c + \log f_h + \log f_{so} \qquad (35)$$

The ion-solvent contribution in the equation was claculated from the theory of Stokes and Robinson[3] using hydration parameters obtained from partial molal volume measurements. The ion-cavity contribution was based on a mutual salting-out effect in which each ion was assumed to interact with the cavities in the solvent associated with the presence of all other ions. Their expression for the mean salting-out activity coefficient contribution for a 1:1 salt of formula 'MA' is:

$$\log f_{so} = \frac{e^2 c}{4605 \quad kT} \quad \frac{1}{3} \; \frac{\bar{V}_A}{r_{h(M)}} + \frac{\bar{V}_M}{r_{h(M)}} + \frac{1}{3} \; \frac{\bar{V}_M}{r_{h(A)}} + \frac{\bar{V}_A}{r_{h(A)}} \qquad (36)$$

For a 2:1 salt their expression is:

$$\log f_{so} = \frac{e^2 c}{4605 \quad kT} \quad \frac{\bar{V}_A}{r_{h(M)}} + \frac{4\bar{V}_M}{r_{h(M)}} + \frac{\frac{4}{5}\bar{V}_M}{r_{h(A)}} + \frac{2\bar{V}_A}{r_{h(A)}} \tag{37}$$

where 'c' is the molar concentration, $\bar{V}_A$, $\bar{V}_M$ are the partial molal volumes of the ions A and M, and $r_{h(A)}$, $r_{h(M)}$, are the radii of the hydrated ions A and M.

In their treatment the experimental molal activity coefficients were first corrected for hydration and for the above mentioned mutual salting-out effects. Then the remaining coulombic contribution to the activity coefficients for most alkali halides was shown to follow the relation

$$\log f_c = a - b \ c^{1/3} \tag{38}$$

for concentrations lying between 0.1 and 1.0 molal. A theory capable of explaining the resulting dependence of $\log f_c$ on 'c' would have to based on Frank's disordered lattice model[5,6,7], previously discussed.

C. THEORETICAL TREATMENT OF DIFFUSION

One of the most fundamental of irreversible processes is that of diffusion, by which a difference of concentration is reduced by the spontaneous flow of matter. In a solution containing a single solute, the solute moves from the region of higher to that of lower concentration, while the solvent moves in the opposite sense. From the point of view of molecular kinetics, no individual solute particle shows a preference for motion in any particular direction, but a definite fraction of particles in an elementary unit volume may be considered to be moving in, say, the positive x-direction. In an adjacent volume-element, the same fraction may be considered as moving in the negative x-direction. Now if the concentration in the first volume-element is greater than that in the second, this means that more particles will be leaving the first element for the second than will be re-entering from the second to the first, so there will be a resultant flow of solute in the direction of lower concentration. Further, one would naturally expect, on the basis of this picture, that the rate of flow would be at least approximately proportional to the concentration difference existing between the two volume-elements.

Considering the one-dimensional case, the flux of matter, denoted by J, is defined as the amount of material crossing unit area of a plane perpendicular to the direction of flow in unit time.

The concentration gradient $\frac{\partial c}{\partial x}$ is the rate of increase of concentration with distance measured in the direction of the flow. It is usual to take the direction of flow as the positive direction of the distance x, to express the concentration c in the same units of moles, grams, etc., as are used in defining the flux, and to take the cube of the unit of distance 'x' as the volume unit for the concentration 'c'. Thus if J is expressed in moles cm^{-2} sec^{-1}, and x in cm, c will be expressed in moles cm^{-3}.

The diffusion coefficient 'D' is now defined by Fick's first law:

$$J = - D \frac{\partial c}{\partial x} \qquad (39)$$

the partial differential being necessary because 'c' is, in general, dependent on time as well as distance. The negative sign in equation (39) is introduced in order to make D a positive quantity, since $\frac{\partial c}{\partial x}$ is negative in virtue of our choice of sign for 'x', which increases as the concentration decreases. In c.g.s. units D is in units of cm^2 sec^{-1}. Equation (39) can be used in the study of diffusion only when steady-state methods, in which the concentration-gradient $\frac{\partial c}{\partial x}$ does not change with time, are employed.

In the theoretical treatment of diffusion it is usually assumed that the free energy change occurring when the solution mixes by diffusion is equal to the work done by the diffusing particles against the resistance of the medium. Each ion of the diffusing electrolyte can be regarded as moving under the influence of two forces, (a) the gradient of chemical potential for that ionic species, and (b) an electrical field produced by the motion of oppositely charged ions. The more mobile ions will tend to diffuse faster than the less mobile ones, but by doing so they will create on a microscopic scale a charge separation or gradient of electrical potential in the solution. This will have the effect of increasing the speed of the slower ion and decreasing that of the faster; the resultant speeds of both must finally be equal, since it is an experimental fact that a macroscopic charge separation does not occur.

For a single electrolyte, one molecule of which gives ν_1 cations of algebraic valency Z_1 and ν_2 anions of algebraic valency Z_2, the following argument is used. The chemical potentials $\overline{G}_1$ and $\overline{G}_2$ of the cations and anions may be considered separately (although they are not separately measurable) provided that the final equations contain only the chemical potential of the solute as a whole,

$$\overline{G}_B = \nu_1 \overline{G}_1 + \nu_2 \overline{G}_2 \tag{40}$$

The forces on single ions due to the gradient of chemical potential are therefore:

$$-\frac{1}{N} \frac{\partial \overline{G}_1}{\partial x} \quad \text{and} \quad -\frac{1}{N} \frac{\partial \overline{G}_2}{\partial x} \tag{41}$$

respectively, where N is the Avogadro number. The negative sign is used since the ionic motion is down the free energy gradient. The effect arising from the unequal mobilities of the ions may be represented as an electrical field of intensity E, which exerts on each ion an additional force, given by Z_1eE and Z_2eE respectively. The total forces are therefore:

$$F_1 = -\frac{1}{N} \frac{\partial \overline{G}_1}{\partial x} + Z_1eE \tag{42}$$

$$F_2 = -\frac{1}{N} \frac{\partial \overline{G}_2}{\partial x} + Z_2eE \tag{43}$$

These forces, acting respectively on ions of absolute mobilities u_1 and u_2, are required to produce equal velocities 'v' given by:

$$v = u_1 \left(-\frac{1}{N} \frac{\partial \bar{G}_1}{\partial x} + Z_1 eE\right) = u_2 \left(-\frac{1}{N} \frac{\partial \bar{G}_2}{\partial x} + Z_2 eE\right) \qquad (44)$$

From these equations eE can be eliminated giving:

$$\frac{1}{Z_1}\left(\frac{v}{u_1} + \frac{1}{N} \frac{\partial \bar{G}_1}{\partial x}\right) = eE = \frac{1}{Z_2}\left(\frac{v}{u_2} + \frac{1}{N} \frac{\partial \bar{G}_2}{\partial x}\right) \qquad (45)$$

whence, using the condition of electrical neutrality:

$$\nu_1 Z_1 + \nu_2 Z_2 = 0 \qquad (46)$$

there results:

$$v = -\frac{1}{N} \frac{u_1 u_2}{\nu_1 u_2 + \nu_2 u_1} \cdot \left(\nu_1 \frac{\partial \bar{G}_1}{\partial x} + \nu_2 \frac{\partial \bar{G}_2}{\partial x}\right) =$$

$$-\frac{1}{N} \frac{u_1 u_2}{\nu_1 u_2 + \nu_2 u_1} \frac{\partial \bar{G}_B}{\partial x} \qquad (47)$$

Now let 'c' be the concentration of solute in moles per unit volume at the point considered. Then the flux of solute is:

$$J = cv = -\frac{u_1 u_2}{\nu_1 u_2 + \nu_2 u_1} \cdot \frac{c}{N} \cdot \frac{\partial \bar{G}_B}{\partial c} \frac{\partial c}{\partial x} \qquad (48)$$

But the flux also defines the diffusion coefficient D in terms of the concentration gradient:

$$J = -D \frac{\partial c}{\partial x} \qquad (49)$$

Therefore, D is given by:

$$D = \frac{u_1 u_2}{\nu_1 u_2 + \nu_2 u_1} \frac{1}{N} \frac{\partial \bar{G}_B}{\partial \ln c} \qquad (50)$$

Also, from the definition of the mean molar activity coefficient, $y_{\pm} = a_{\pm}/c_{\pm}$, the differential in the equation (50) is

$$\frac{\partial \bar{\bar{G}}_B}{\partial \ln c} = RT\,(\nu_1 + \nu_2)\,\left(1 + \frac{d\ln y_{\pm}}{d\ln c}\right) \qquad (51)$$

and finally the absolute ionic mobilities 'u' may be expressed in terms of the limiting equivalent conductivities, λ^o, by the equation:

$$u = \frac{N\,\lambda}{|Z|\;F^2} \qquad (52)$$

where F is a Faraday giving:

$$D = \frac{(\nu_1 \pm \nu_2)\;\lambda_1^{\,o}\;\lambda_2^{\,o}}{\nu_1\;|Z_1|\;(\lambda_1^{\,o}\;\lambda_2^{\,o})}\;\frac{RT}{F^2}\;\left(1 + \frac{d\ln y_{\pm}}{d\ln c}\right) \qquad (53)$$

These formulae constitute the Nernst - Hartley relation. The limiting value of D at infinite dilution, where $\frac{d\ln y_{\pm}}{d\ln c} \longrightarrow 0$, is given by:

$$D^o = \frac{RT\,(\nu_1 + \nu_2)\;\lambda_1^{\,o}\;\lambda_2^{\,o}}{F^2\;\nu_1\;|Z_1|\;\lambda_1^{\,o} + \lambda_2^{\,o}} \qquad (54)$$

Equivalent forms of equation (53) obtained by using the condition of electrical neutrality $\nu_1\;|Z_1| = \nu_2\;|Z_2|$ and the definition of the transport numbers $t_1^{\,o} = \frac{\lambda_1^{\,o}}{\lambda_1^{\,o} + \lambda_2^{\,o}} = \frac{\lambda_1^{\,o}}{\Lambda_o}$ are:

$$D = \frac{RT}{F^2}\;\frac{|Z_1| + |Z_2|}{|Z_1\,Z_2|}\;\cdot\;\frac{\lambda_1^{\,o}\;\lambda_2^{\,o}}{\lambda_1^{\,o} + \lambda_2^{\,o}}\;\left(1 + \frac{d\ln y_{\pm}}{d\ln c}\right) \qquad (55)$$

$$D = \frac{RT}{F^2}\;\frac{|Z_1| + |Z_2|}{|Z_1\;Z_2|}\;\Lambda_o\;t_1^{\,o}\;t_2^{\,o}\;\left(1 + \frac{d\ln y_{\pm}}{d\ln c}\right) \qquad (56)$$

Since variations from the theory were observed at very low concentrations, Onsager and Fuoss[12] and Stokes[13] added a small electrophoretic effect to the above equations. Their final expression for the diffusion coefficient is:

$$D = (1 + c\,\frac{d \ln y}{dc})\ (D^{o} + \Sigma\,\Delta_{n}) \qquad (57)$$

where D^{o} is the Nernst limiting value of the diffusion coefficient given by:

$$D^{o} = \frac{RT}{F^2}\ \frac{\nu}{\nu_1\,|Z_1|}\ \frac{\lambda_1^{o}\,\lambda_2^{o}}{\lambda_1^{o} + \lambda_2^{o}} = \frac{RT}{F^2}\ \frac{|Z_1| + |Z_2|}{|Z_1\,Z_2|}\ \frac{\lambda_1^{o}\,\lambda_2^{o}}{\lambda_1^{o} + \lambda_2^{o}} \qquad (58)$$

and the electrophoretic terms Δ_n are given by:

$$\Delta_n = k\,T\,A_n\ \frac{(Z_1^{\,n}\,t_2^{o} + Z_2^{\,n}\,t_1^{o})^2}{a^{n}\ |Z_1\,Z_2|} \qquad (59)$$

where t_1 and t_2 are the transference numbers of cation and anion. The coefficients A_n are functions of the dielectric constant and viscosity of the solvent, the temperature and the dimensionless concentration-dependent quantity 'κ a'.

$$\kappa = (\frac{8\pi N e^2}{1000\,\varepsilon\,kT})^{1/2}\ (I)^{1/2} \qquad (60)$$

In the application of equation (57) to symmetrical salts $|Z_1| = |Z_2| = Z$. The factor $(Z_1^{\,n}\,t_2^{o} + Z_2^{\,n}\,t_1^{o})^2$ appearing in Δ_n then reduced to $|Z|^{2n}$ $(t_2^{o} - t_1^{o})^2$ for odd n, and $|Z|^{2n}$ for even n. Upon substituting n = 1 and n = 2 in the general formula for Δ_n:

$$\Delta_1 = -\frac{kT}{6\,\pi\,\eta}\ (t_2^{o} - t_1^{o})^2\ \frac{\kappa}{1 + \kappa a} \qquad (61)$$

$$\Delta_2 = \frac{kT}{12\pi \eta} \frac{e^2}{\varepsilon kT} (\kappa a)^2 \left(\frac{e^{\kappa a}}{1 + \kappa a}\right)^2 \cdot E_i(2\kappa a) \left(\frac{|Z|}{a}\right)^2 \qquad (62)$$

The function of '(κa)' appearing in Δ_2:

$$\phi_2 (\kappa a) = (\kappa a)^2 \left(\frac{e^{\kappa a}}{1 + \kappa a}\right)^2 \mathrm{Ei}\ (2\kappa a) \qquad (63)$$

has been tabulated[14]. In practice it is of interest to apply these formulae to 1:1 electrolytes at 25° in water, when they reduce to:

$$\Delta_1 = \frac{-\ 8.07 \times 10^{-6} (t_2^{\circ} - t_1^{\circ})^2 (c)^{1/2}}{(1 + \kappa a)} \qquad (64)$$

$$\Delta_2 = \frac{+\ 8.77 \times 10^{-21}\ \phi_2\ (\kappa a)}{a^2} \qquad (65)$$

where c is expressed in moles/liter and 'a' in cm.

The theory has been tested on various electrolytes and it has been found that it is obeyed up to concentrations of about 0.01 molar.

Hartley and Crank[67] have attempted to extend the theory to concentrated solutions. They consider a number of effects which were assumed to be negligible in dilute solution. Firstly, they consider the movement of the solvent molecules in the direction opposite to the solute molecules; secondly, the permanently attached layer of solvent molecules which is carried by the ions; and thirdly, the viscous forces which may be considerably modified by the presence of large numbers of ions.

Consider first a non-electrolyte solution containing only two types of diffusing entity, the molecules A and B, and let the treatment be restricted to the case where the partial volumes, $\overline{V}_A$ and $\overline{V}_B$, of both components are constant. In this case the diffusion coefficient measured experimentally is in terms of the flux across a plane P so fixed that the total volumes on each side of it remain constant. This measured diffusion coefficient is denoted by D_A^v, for component A, and by D_B^v for component B. Denoting the fluxes of moles of A and B across unit area of the plane P by J_A^v and J_B^v we have:

$$J_A^v = - D_A^v \frac{\partial C_A}{\partial x}, \quad J_B^v = - D_B^v \frac{\partial C_B}{\partial x} \tag{66}$$

C_A and C_B being the concentrations of A and B in moles per unit volume. The fluxes of volumes of A and B through the plane P are therefore:

$$- D_A^v \bar{V}_A \frac{\partial C_A}{\partial x} \quad \text{and} \quad - D_B^v \bar{V}_B \frac{\partial C_B}{\partial x} \tag{67}$$

Since there is no net transfer of volume across the plane P, it follows that the sum of these quantities is zero:

$$D_A^v \bar{V}_A \frac{\partial C_A}{\partial x} + D_B^v \bar{V}_B \frac{\partial C_B}{\partial x} = 0 \tag{68}$$

Also, since C_A and C_B are the numbers of moles of A and B in unit volume of solution:

$$\bar{V}_A C_A + \bar{V}_B C_B = 1 \tag{69}$$

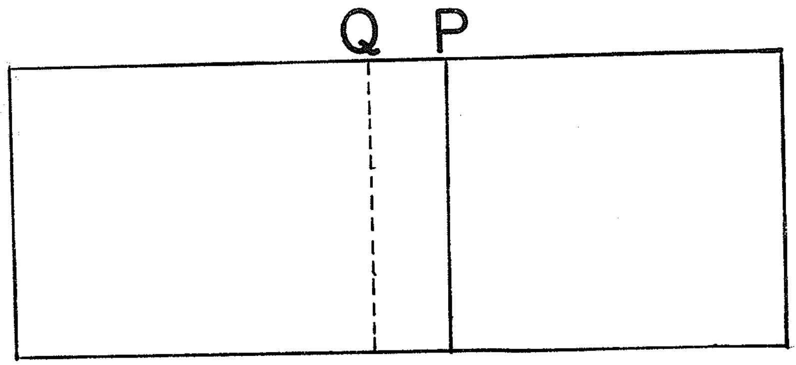
Differentiating this with respect to 'x' gives

$$\bar{V}_A \frac{\partial C_A}{\partial x} + \bar{V}_B \frac{\partial C_B}{\partial x} = 0 \tag{70}$$

and on comparing (68) and (70) it is evident that for both to hold it is necessary that:

$$D_A^{\ v} \equiv D_B^{\ v} \qquad (71)$$

except for the trivial cases where $\bar{V}_A = 0$ or $\bar{V}_B = 0$. Thus, the diffusion coefficient of a binary system where the partial volumes are constant can be described by a single diffusion coefficient, which may be called the mutual-diffusion coefficient, and denoted simply by D^v; the same value of D^v will be found whether one measures and calculates from the concentration of component A or component B.



$\longrightarrow$ X increasing

$\longrightarrow$ C_B increasing $\frac{\partial C_B}{\partial x}$ positive

$\longleftarrow$ C_A increasing $\frac{\partial C_A}{\partial x}$ negative

$\longrightarrow$ Direction of diffusion of A

$\longleftarrow$ Direction of diffusion of B

<u>Figure 1</u>

Next, Hartley and Crank introduce the idea of an 'intrinsic diffusion coefficient' of each component, here denoted by D_A' and D_B'. The passage of component A through the volume-fixed plane P just discussed must necessitate the passage of an equal volume of B in the opposite direction, in order to preserve the fixed volumes on each side of the plane. The total flow of each component is regarded as made up partly of a true diffusion-flux and partly of a 'bulk flow' which originates in the volume-difference between the two components. A plane Q may be imagined so that no 'bulk flow' occurs through it; and the 'intrinsic diffusion coefficients' D_A' and D_B' are defined in terms of the flux across unit area of such a plane.

Since the partial volumes are constant, the concentration gradients $\frac{\partial C_A}{\partial x}$ and $\frac{\partial C_B}{\partial x}$ must be opposite in sign; suppose that C_A increases to the left, and C_B to the right, and that the distance x is measured from left to right. Then on the right of the plane Q there will be a rate of increase of volume, due to the entry of A, given by $-\overline{V}_A D_A' \frac{\partial C_A}{\partial x}$ and a rate of decrease of volume, due to the outward passage of B, given by $+\overline{V}_B D_B' \frac{\partial C_B}{\partial x}$. The net rate of increase of the volume V' on the right of Q is therefore given by:

$$\frac{\partial V'}{\partial t} = -(\overline{V}_A D_A' \frac{\partial C_A}{\partial x} + \overline{V}_B D_B' \frac{\partial C_B}{\partial x}) \qquad (72)$$

This expression, considering unit cross-section of the plane Q, also gives the rate at which the plane Q moves away from the fixed plane P. Since no bulk flow occurs through Q, the motion of this plane with respect to P must be due to a bulk flow through P; so that expression (72) also represents the bulk flow through P from right to left. The bulk flow therefore involves a transport of component A from the left to the right of P given by:

$$J_A \text{ (bulk flow)} = - C_A \frac{\partial V'}{\partial t} \tag{73}$$

This transport of A across P by bulk flow is superimposed on the transport of A across P by 'pure diffusion', which is given by:

$$J_A \text{ (pure diffusion)} = - D_A' \frac{\partial C_A}{\partial x} \tag{74}$$

The total flux of A across P is therefore:

$$J_A \text{ (total)} = - D_A' \frac{\partial C_A}{\partial x} + C_A \left(\overline{V}_A D'_A \frac{\partial C_A}{\partial x} + \overline{V}_B D_B' \frac{\partial C_B}{\partial x} \right) \tag{75}$$

But the total flux J_A across the fixed plane P also defines the experimentally measured mutual diffusion coefficient D^v:

$$J_A \text{ (total)} = - D^v \frac{\partial C_A}{\partial x} \tag{76}$$

Combining equations (74, (75) and (70) now yields:

$$D^v = D_A' + \overline{V}_A C_A (D_B' - D_A') \tag{77}$$

Now the intrinsic diffusion coefficient D_A' of A at a finite concentration C_A is related to its value D_A^o at infinite dilution ($C_A = 0$) by the factor ($d \ln a_A / d \ln C_A$) which expresses the effect of the deviation of the solution from ideal behavior. It is also probable, but by no means certain, that the bulk viscosity of the solution compared with that of the pure liquid B should also be introduced; this relative viscosity is denoted by η / η°_B. The activity a_A in the thermodynamic factor may be expressed on any scale of concentration desired, since the logarithmic differentiation will eliminate any constant conversion factors; in terms of mole fraction:

$$D'_A = D^\circ_{AB} \frac{d \ln N_A f_A}{d \ln C_A} \frac{\eta^\circ_B}{\eta} \qquad (78)$$

$$D'_B = D^\circ_{BB} \frac{d \ln N_B f_B}{d \ln C_B} \frac{\eta^\circ_B}{\eta} \qquad (79)$$

where D°_{AB} is the diffusion coefficient of A at infinite dilution in B, and D°_{BB} is the (self) diffusion coefficient of B in pure B.

Since $C_A = \frac{N_A}{N_A \bar{V}_A + N_B \bar{V}_B}$, one finds on logarithmic differentiation, and using $N_A + N_B = 1.$,

$$\frac{d \ln C_A}{d \ln N_A} = 1 - \frac{N_A (\bar{V}_A - \bar{V}_B)}{N_A \bar{V}_A + N_B \bar{V}_B} = \frac{\bar{V}_B C_A}{N_A} \qquad (80$$

and similarly

$$\frac{d \ln C_B}{d \ln N_B} = \frac{\bar{V}_A C_B}{N_B} \qquad (81)$$

Hence equations (78) and (79) become:

$$D'_A = D^\circ_{AB} \frac{N_A}{\bar{V}_B C_A} \frac{d \ln N_A f_A}{d \ln N_A} \frac{\eta^\circ_B}{\eta} \qquad (82)$$

$$D'_B = D^\circ_{BB} \frac{N_B}{\bar{V}_A C_B} \frac{d \ln N_B f_B}{d \ln N_B} \frac{\eta^\circ_B}{\eta} \qquad (83)$$

Furthermore, the Gibbs-Duhem equation gives:

$$\frac{d \ln N_A f_A}{d \ln N_A} = \frac{d \ln N_B f_B}{d \ln N_B} \qquad (84)$$

Using, this along with equations (82), (83) and (77) gives for the mutual diffusion coefficient D^v:

$$D^v = \frac{d \ln N_A f_A}{d \ln N_A} \frac{\eta_B^o}{\eta} \left[D_{AB}^o N_A \left(\frac{1}{\bar{V}_B C_A} - \frac{\bar{V}_A}{\bar{V}_B}\right) + D_{BB}^o N_B \frac{C_A}{C_B} \right] \quad (85)$$

Since $N_A/N_B = C_A/C_B$ and $C_A \bar{V}_A + C_B \bar{V}_B = 1$, the expression in the square bracket simplifies giving finally:

$$D^v = \frac{d \ln N_A f_A}{d \ln N_A} \frac{\eta_B^o}{\eta} \left[N_B D_{AB}^o + N_A D_{BB}^o \right] \quad (86)$$

which, by symmetry, can also be written:

$$D^v = \frac{d \ln N_B f_B}{d \ln N_B} \frac{\eta_A^o}{\eta} \left[N_A D_{BA}^o + N_B D_{AA}^o \right] \quad (87)$$

This is the Hartley and Crank expression (in a slightly modified form) for the mutual diffusion coefficient at any concentration. If the volume effects and the counter-diffusion of the solvent are ignored, as was done in the derivation of the expressions for dilute solutions, one obtains an expression of the form:

$$D = D_{BA}^o \frac{d \ln N_B f_B}{d \ln C_B} \quad (88)$$

The theory is capable of straightforward extension to the case of the diffusion of a single electrolyte in solution, making allowance for the possible hydration of the ions. Let B denote the solvated electrolyte, one mole of which is associated with h moles of bound water, and let A denote the 'free' water. These are treated as the diffusing entities. In accordance with the notation used in the discussion of the chemical potential of solvated ions, primed symbols will be used to denote quantities in which account is taken of solvation. Equation (87) now becomes:

$$D^{v} = \frac{d \ln N_B' f_B'}{d \ln N_B'} \cdot \frac{\eta_A^{\circ}}{\eta_A} \left[N_A' D_{BA}^{\circ} + N_B' D_{AA}^{\circ} \right] \tag{89}$$

The only place in (87) at which consideration must be given to the fact of ionization is in the expression $d \ln N_B' f_B'$; this may be written $d \ln N_B' f_B' = d \ln a_B'$, since any scale of activity can be used legitimately. The solute is hydrated and ionized; let it produce ν ions per 'molecule' so that $a_B = (a\underline{+})^{\nu}$ denotes the conventional activity as computed for the unhydrated solute. Then, because of the hydration, and for an aqueous solution,

$$d \ln a_B' = d \ln a_B + h \, d \ln a_W \tag{90}$$

where a_W is the water activity. Also by the Gibbs-Duhem relation:

$$d \ln a_W = - \frac{m}{55.51} \, d \ln a_B \tag{91}$$

hence

$$d \ln a_B' = (1 - 0.018 \, h \, m) \, d \ln a_B =$$

$$(1 - 0.018 \, h \, m) \, \nu \, d \ln a\underline{+} \tag{92}$$

where $a\underline{+}$ is the mean activity coefficient of the unhydrated solute.

In formula (87), it is necessary to consider the meaning to be given to the limiting intrinsic diffusion coefficients D_{BA}° and D_{AA}°. For mixtures of liquids which are non-electrolytes their meaning is clear. For an electrolyte solution, however, it is necessary that formula (87) shall reduce to the Nernst limiting value as $N_B' \longrightarrow 0$. This means that because of the factor 'ν' in (92), $D^{o}_{BA} = D^{o}/\nu$ for electrolytes where D^{o} is the Nernst limiting value; or more completely, if the electrophoretic corrections are included, $D^{o}_{BA} = D^{o} + \Delta_1 + \Delta_2/\nu$. D^{o}_{AA} is the diffusion coefficient of water in the infinitely dilute solution, i.e., in the absence of any interfering non-ideal effects and volume restraints: it is, therefore, equal to the self-diffusion coefficient of pure water, D^{*}_{H20}. It is now convenient to convert from mole fraction to ordinary molality, taking into account the hydration number 'h':

$$N'_B = \frac{m}{55.51 - h\,m + m}, \quad N'_A = \frac{55.51 - h\,m}{55.51 - hm + m} \tag{93}$$

Hence

$$\frac{d \ln N'_B}{d \ln m} = \frac{1}{1 + 0.018\,(1 - h)\,m} \tag{94}$$

$$D^{v} = D^{o}_{BA}\, \frac{d \ln a'_B}{d \ln m} \cdot \frac{d \ln m}{d \ln N'_B}\, \left[\, N'_A + N'_B\, \frac{D^{o}_{AA}}{D^{o}_{BA}} \right] \frac{\eta^{o}_{A}}{\eta} \tag{95}$$

Putting $D^{o}_{BA} = D^{o}/\nu$, $D^{o}_{AA} = D^{*}_{H20}$, and substituting (92), (93), and (94)

$$D^{v} = D^{o}\, \left(\frac{d \ln a\pm}{d \ln m}\right) (1 - 0.018\,h\,m)\, \left[1 + 0.018\,m \left(\frac{\nu\, D^{*}_{H20}}{D^{o}} - h\right)\right] \frac{\eta^{o}_{A}}{\eta} \tag{96}$$

In(96), electrophoresis is neglected; to take this into account, substitute $(D^{o} + \Delta_1 + \Delta_2 + ---)$ for D^{o}. The activity factor $\dfrac{d \ln a\pm}{d \ln m}$ may be written in the alternative form $(1 + m\, d \ln \gamma / d\, m)$.

For a uni-univalent electrolyte at 'm' values small enough to justify neglecting the square of (0.018 hm), and including the electrophoresis corrections in the main D^o factor, but neglecting them in the small correction term $\frac{\nu D^*_{H20}}{D^o}$, (96) becomes:

$$D = (D^o + \Delta_1 + \Delta_2)\left(1 + m\frac{d \ln \gamma}{dm}\right)\left[1 + 0.036\, m \left(\frac{D^*_{H20}}{D^o} - h\right)\right]\frac{\eta^o}{\eta} \quad (97)$$

The bulk viscosity of the solution from the theory of non-electrolytes, has been taken over but it is by no means certain that this step is justified: the change of the bulk viscosity brought about by adding ions is not necessarily a fair measure of the change in frictional resistance experienced by the ions. For, this reason, it is of interest to calculate 'h' and 'h'' given by the equations:

a) $$\frac{\eta}{\eta_o} f(D) = 1 + 0.036\, m \left(\frac{D^*_{H20}}{D^o} - h\right) \quad (98)$$

where

$$f(D) = D_{obs} / \left[(D^o + \Delta_1 + \Delta_2)\left(1 + \frac{m\, d \ln \gamma}{dm}\right)\right] \quad (99)$$

and

b) $$f(D) = 1 + 0.036\, m \left(\frac{D^*_{H20}}{D^o} - h'\right) \quad (100)$$

Robinson and Stokes[14] tested these equations using the mean value of the self-diffusion coefficient of water ($D^*_{H20} = 2.44 \times 10^{-5}$) taken from the work of Parkington, Hudson, and Bagnall[15] and of Wang, Robinson and Edelmann[16]. They find that equations (98) and (100) represent the data to within about 0.5 percent up to a concentration of one molar. The value of 'h'', calculated by the equation in which the viscosity factor is omitted, is considerably larger than 'h' and seems to be more reasonable in the light of the trends observed.

In the case of salts, the interpretation of 'h' as the number of water molecules moving with the ion as part of the diffusing unit may be tentatively accepted. No surprise need be felt that these 'h' values from diffusion are smaller than those obtained from the treatment of activity data in terms of hydration, since in the latter treatment 'h' was introduced as the effective number of molecules bound by ion-solvent forces, and would therefore include contributions from water molecules beyond the first layer, which would not be firmly enough bound to move as a unit with the ion. These 'hydration numbers' 'h', are, however, somewhat lower than the majority of estimates of ionic hydration by other methods.

NATURE OF THE PROBLEM

NATURE OF THE PROBLEM

Two of the most powerful approaches used in the study of electrolyte solutionsare the studies of chemical potential and diffusion. Robinson and Stokes[14] in their book "Electrolyte Solutions" have shown how the study of these properties can give valuable information about the structure of these solutions.

More recently Grunwald and his associates[17,18,19] have used a dynamic vapour pressure technique to study the chemical potential of a number of electrolytes in a 50 wt.% dioxane-water mixture. They succeeded in deriving not only the activity of all three components in the system but also the hydration and dioxanation numbers.

In a recent monogram, Janz and Mayer[20] have given a comprehensive treatment of the Stoke's diaphragm technique for diffusion along with a complete literature survey of the work that has been done on diffusion in electrolyte solutions. Although no work has been done on diffusion in dioxane-water mixtures, Janz et al[21] have studied silver nitrate in acetonitrile and benzonitrile while Kulkarni and Lyons[22] have investigated the diffusion of dilute potassium chloride in methanol-water mixtures.

Since I had already studied the conductances of sodium chlorate and of lithium chlorate in water and in water-dioxane mixtures[23], I thought that a more thorough elucidation of their structure could be obtained by a study of the vapour pressures, vapour compositions, and diffusion coefficients of these solutions.

EXPERIMENTAL

A. EXPERIMENTAL TECHNIQUE

(a) Purity of Materials

1. Salts

Fisher certified sodium chlorate (major impurity 0.01 % bromate) was dried in an oven at 120°C for at least forty-eight hours before using.

Lithium chlorate was prepared by the method of Campbell and Griffiths[71]. Equimolar quantities of barium chlorate and lithium sulphate were mixed. After precipitation the barium sulphate was filtered off. The solution of lithium chlorate was then titrated with dilute lithium sulphate or barium chlorate, until equivalence was reached. The solution was then evaporated at about 80°C until a very viscous liquid was obtained. Finally, after further filtration, the mother liquor was dried under vacuum using barium oxide as the drying agent. The melting point of lithium chlorate 127.9°C was in agreement with the value reported by Campbell and Williams[24].

2. Solvents

Water of specific conductance 2×10^{-7} to 5×10^{-7} mhos/cm. was obtained by passing ordinary distilled water through a mixed-resin demineralizing column.

Dioxane of spectro-quality was further purified by refluxing with sodium, according to the method of Hess and Frahm[25]. After purification, the dioxane had a refractive index $n_D^{25} = 1.4202$ and a density of 1.0278 gr/cc at 25°C. This was in close agreement with the refractive index of 1.42025 found by Frey and Gilbert[26] and the density of 1.02804 g/cc. found by Schott.[27]

(b) Thermostats

Three thermostats were used in this research. The vapour pressure measurements were made in a three foot high stainless steel bath fitted with glass windows. This bath permitted the differential manometer to be immersed completely. A $\frac{1}{4}$ horse power stirrer circulated the water so well that the temperature could be controlled at all heights to ± 0.005°C using a mercury-toluene regulator and a solid state relay.

The thermostats for diffusion and conductance were well-insulated containers of about six gallon capacity. The temperature control was effected by the use of a mercury-toluene regulator and solid state relay, as described by Swinehart[28]. For the diffusion work water was used as the thermostatic fluid while for conductance 'marcol' oil was used to avoid extraneous capacity effects[29].

The temperatures of all three baths were determined with Beckmann thermometers which had been calibrated against a standard platinum resistance thermometer using a Mueller Bridge. The temperature fluctuation in all cases was within ± 0.005°C.

(c) Vapour Pressure Measurement

The vapour pressure of the solution was measured by a static method in which the difference between the vapour pressure of a solution and that of pure solvent was determined with a differential manometer. This method has been used by many investigators, notably Gibson and Adams[30] and Shankman and Gordon[31]. The actual apparatus used is shown in Figure 2.

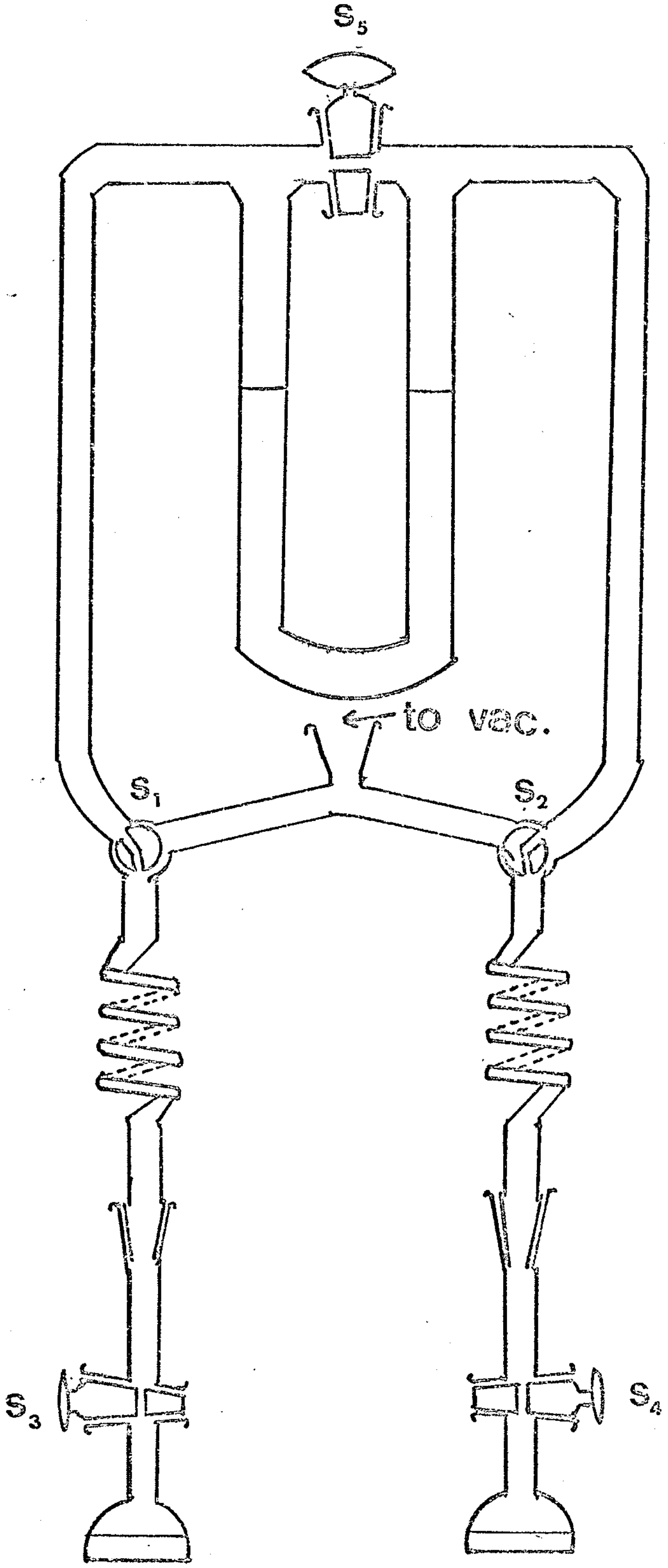
Two modifications of the apparatus described by Gibson and Adams[30] were made. Firstly, the auxiliary flasks used by Gibson and Adams to approach equilibrium by condensation of solvent vapour on the solution were dispensed with, the reason being that no appreciable difference between the vapour pressure determined by the evaporation of solution to fill the vapour space and that determined by the condensation of vapour from a state of supersaturation onto the solution was detected. Also it appeared that the presence of such flasks led to leakage errors. Secondly, spirals were added below the three-way stopcocks and to the vacuum line to remove strain from the system.

25cc. of solution were placed in the flasks, each of 75cc. capacity. The solution was stirred with a magnetic stirrer to hasten the attainment of equilibrium. The internal diameter of the manometer tubing, to avoid capillary effects, was 15 mm. The heights of the manometer liquid were measured with a cathetometer which could be read to ± 0.05 mm.

The manometer liquid used for the aqueous solutions was vacuum pump oil (density at 25°C, 0.8697) as recommended by Shankman and Gordon[31]. About 100cc. of the oil was placed in a liter flask with a magnetic stirring bar. The oil was then degassed by applying vacuum to the flask while the contents were stirred rapidly. The oil was then quickly transferred to the manometer through a side neck which was then sealed off. After refluxing in the manometer under high vacuum for several hours, the oil was ready for use. Although the oil proved fairly stable, it was

Figure 2

The Differential Manometer for Vapour Pressure Measurement


S_5
to vac.
S_1
S_2
S_3
S_4

necessary to change it after about five runs because of contamination of the oil and glass surface of the manometer with water.

Since the difference between the levels of liquid in the manometer could be read with an accuracy of ± 0.05 mm., considering the density difference between oil and mercury, it would appear that the vapour pressures could be measured with an accuracy better than ± 0.005 mm. of mercury. But, difficulties, such as slow drainage times and dissolved gases, as pointed out by McAllan[32], lead to much higher errors than anticipated. In this research the accuracy of my measurements is no better than ± 0.01 mm. of mercury.

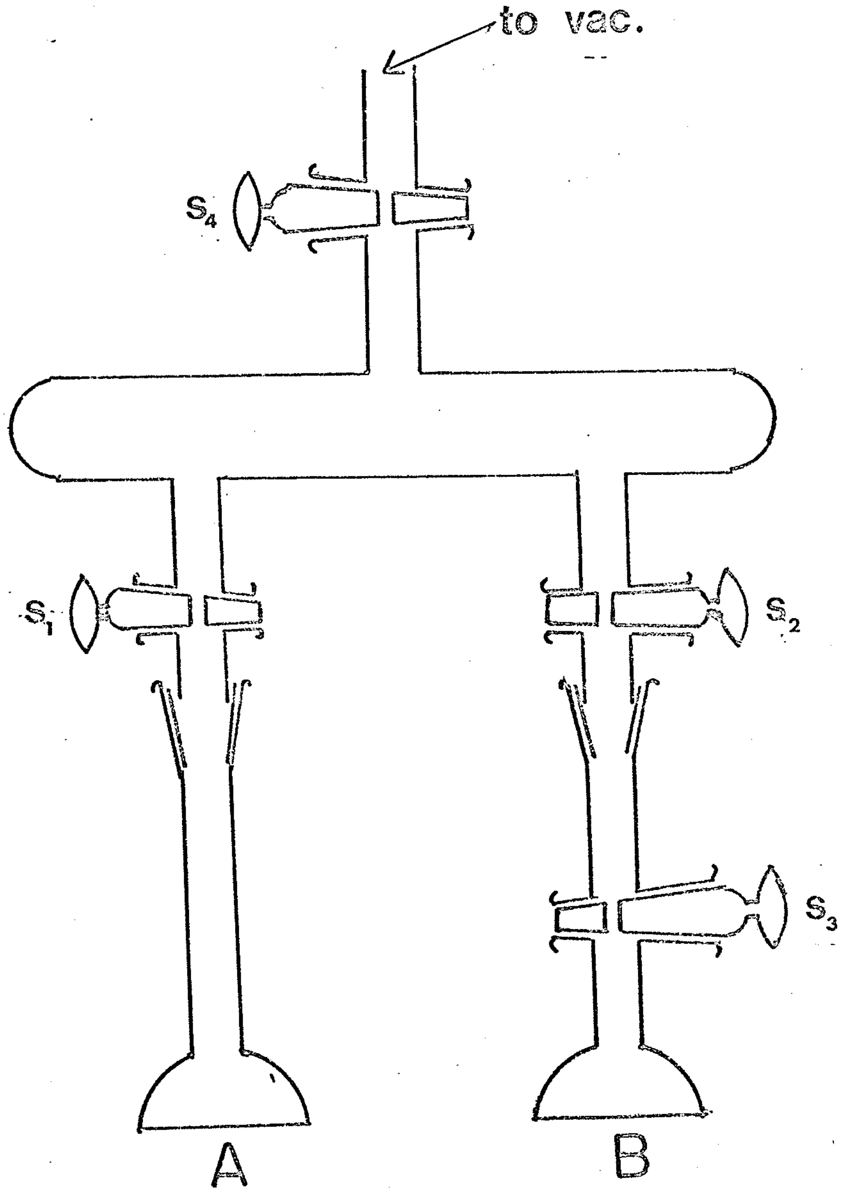
Since vacuum pump oil, diethyl phthalate, butyl phthalate and other manometric liquids are soluble in dioxane, it was necessary to employ mercury as the manometric liquid for the dioxane-water mixtures. The manometer tubing was changed to a diameter of 22 mm. so that no meniscus corrections were necessary. Thus, for the dioxane-water mixtures the accuracy of the vapour pressure measurements was reduced to ± 0.05 mm.

It should be noted that all the vapour pressure measurements were reduced to 0°C by the use of standard formulae.

A serious experimental difficulty in any static vapour pressure measurements is the removal of the residual air from the solution. This degassing was accomplished by freezing the solvent in a mixture of dry ice and acetone ($T = -80^\circ C.$), then evacuating till the residual pressure was less than 0.001 mm. or 1.0 micron as determined on a McLeod gauge. Stopcock S_1 in Figure 3 was then closed, the solvent melted, and the

Figure 3

The Apparatus for Vacuum Distillation


to vac.
S_4
S_1
S_2
S_3
A
B

freezing and evacuating procedure repeated four or five times. Finally, the solvent was vacuum distilled onto the salt using the following procedure: After the flasks containing the salt and degassed solvent had been evacuated, stopcock S_4 was closed. Next, flask B was placed in a dry ice-acetone bath while flask A was placed in a water bath at room temperature. After approximately four or five hours all the solvent had distilled to flask B. Any traces of air were then removed by evacuation to 1 micron. After stopcock S_3 was closed, flask B was removed from the vacuum line and attached to the differential manometer.

In a typical experiment the manometer was evacuated to about 1 micron. The entire manometer was then placed in a thermostat at 25°C and the stopcock to the solvent (S_3 in Figure 2) was opened. After one hour of equilibration, readings were taken until a steady value was obtained. Finally, the stopcock to the solution (S_4 in Figure 2) was opened and the difference in pressure measured. Stopcocks S_3 and S_4 were closed before the manometer was removed from the bath.

The concentrations of the solutions were determined by direct weighing. After the flask was weighed an appropriate amount of salt was added and the flask reweighed. Due to the hygroscopic nature of lithium chlorate it was necessary to transfer this salt in a nitrogen dry box. The concentration of the solution was then obtained by weighing the flask plus solution after measuring the vapour pressure. Although the evaporation of solvent in the manometer changed the concentration of the solution, no change in the mixed solvent composition was detected.

(d) Determination of Vapour Composition

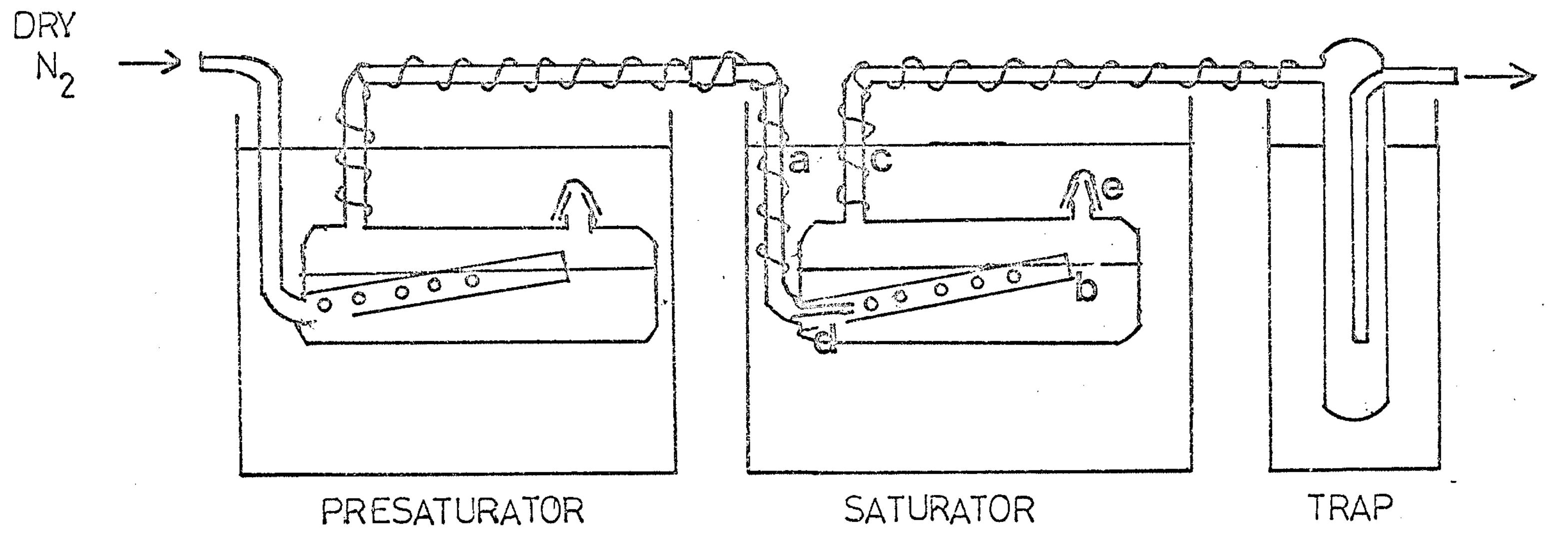
The compositions of the vapours given off by the dioxane-water solutions were determined by isothermal distillation. The apparatus designed originally by Bichowsky and Storch[33] was found to be satisfactory after slight modifications.

The apparatus shown in Figure 4 consisted of a series of eight units in the saturator part and six units in the presaturator part. Each unit in the saturator was constructed and used as follows: Dry nitrogen entered the unit through a short central tube "a" tapered down to a 2 mm. capillary. At the tip of the capillary the stream of nitrogen broke into bubbles which passed up a slightly inclined 5 mm. tube 80 mm. long and then broke at the end of the tube. An opening "d" was blown through the lower side of this inclined tube just back of the tip of the capillary. Through this opening liquid was drawn from the bottom of the saturator and carried by the nitrogen-bubbles up the slanting tube to the surface of the liquid, thereby maintaining a practically uniform vapour concentration. The gas liberated from the bubbles as they burst, then passed back over the surface of the liquid to the tube "c" leading either to a second saturator or finally to the absorber in the trap. Each tube in a saturator was provided with a vertical tube "e", for filling and emptying. This had a water-tight ground glass joint, thereby preventing water from mixing with the liquid when the saturators were immersed in the thermostat. The capacity of each container was 35 ml. when filled.

This type of saturator[33] has the advantage that the bubbles only have a short vertical movement in the liquid, whereas the contact with the liquid is comparatively long. This enables the nitrogen-bubbles to remain

Figure 4

The Isothermal Distillation Apparatus for Vapour Compositions


DRY
N$_2$
a
c
e
b
d
PRESATURATOR
SATURATOR
TRAP

saturated when they leave the liquid surface. The saturation is further facilitated because the bubbles again pass over the liquid surface, thereby having opportunity to come into equilibrium with the latter, before finally entering the absorber.

It was necessary to change the design of the presaturators previously used by Bichowsky and Storch[33] because of continual blockage of the capillary tubes by salt. This was caused by the dry nitrogen picking up solvent and leaving the solution supersaturated. For this reason the presaturator consisted of the following units: The first unit contained only a 10 mm. inclined tube with an opening in the bottom, the second unit contained a similar 7 mm. inclined tube, the third contained a 4 mm. capillary in a 5 mm. inclined tube which had an opening in the bottom as previously described, the fourth contained a 3 mm. capillary, and the fifth and sixth were of the same design as the saturators. This design eliminated the salt blockage by allowing the nitrogen to become almost saturated with vapour before it reached the small capillaries.

In a typical experiment nitrogen from a cylinder was passed through a calcium sulphate drying tube then into the presaturator which was maintained at a temperature of 30.00°C ± 0.05. The nitrogen then passed through a heated tube to the saturator, which was kept at a temperature of 25.00°C ± 0.01. After leaving the last unit of the saturator the nitrogen was led to a trap through a heated tube, (the connecting tubes outside the thermostat were heated to about 40°C by coiling the tubes with Nichrome resistance wire heated by a six volt copper oxide rectifier to avoid condensation of vapour).

The trap shown in Figure 4 consisted of a glass tube 200 mm. in length and 25 mm. in diameter with an internal tube 6 mm. in diameter. The trap was fitted with a ground glass joint to permit attachment and removal from the saturator and was maintained at a temperature of about - 80°C by an acetone-dry ice mixture. Tests showed that this trap gave quantitative condensation of the vapour.

After the vapour had condensed, the nitrogen passed out of the system through a calcium sulphate drierite drying tube. This drying tube prevented any condensation of water vapour from the air.

Although Campbell, Kartzmark and Gieskes[34] state that gas flows of 10 liters per hour give satisfactory saturation, a nitrogen speed of about 2 liters per hour was used to ensure complete saturation. After allowing distillation at this speed to continue for a sufficient period to obtain about 3 to 5 mls. of condensate, the liquid in the trap was analysized. A further analysis of the liquid in the final saturator showed that no change in its composition had occurred during the experiment.

The values of the vapour composition obtained by the above method were found to be reproducible to within ± 0.1 per cent.

(e) Diffusion Measurement

The diffusion coefficients were measured using a magnetically stirred diaphragm-cell as recommended by Stokes[35]. The cell is shown in Figure 5.

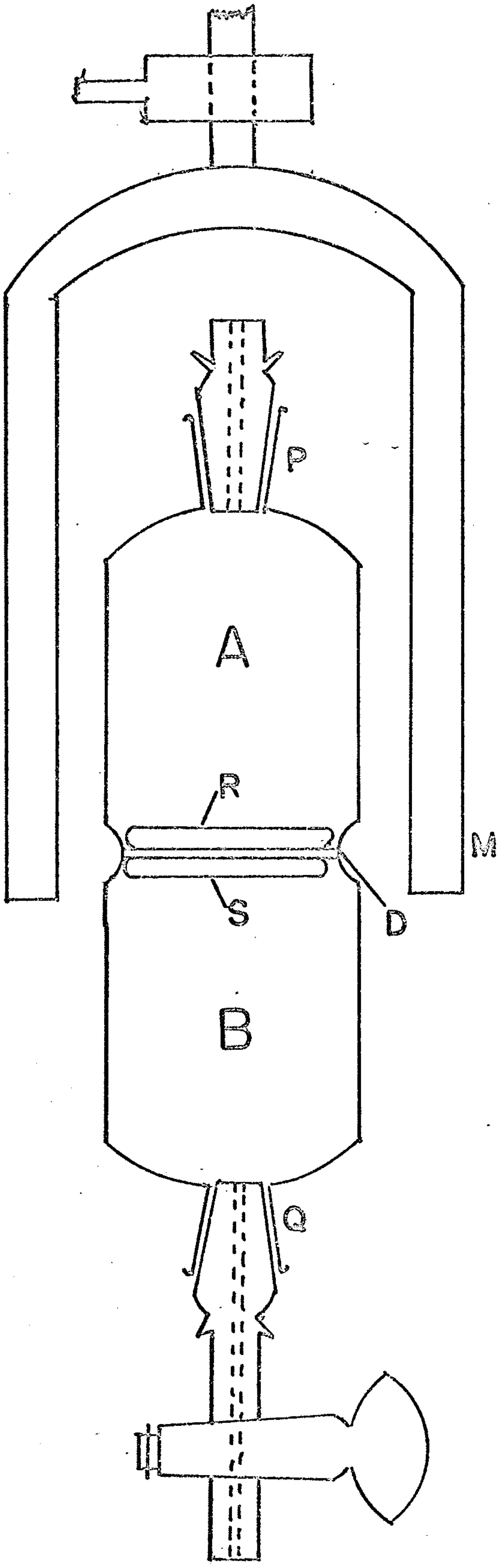
This cell was made of Pyrex glass and has two compartments each of about 50cc. capacity. The sintered glass diaphragms were of number 4 porosity, 40 mm. in diameter, and 2-3 mm. thick. Each compartment contained a stirrer of glass tubing, 3 mm. in diameter and of length slightly less than the diameter of the diaphragm. Inside each stirrer a length of iron wire was sealed, the thicknesses of the wire and the thickness of the tube walls were so adjusted that the stirrer in the upper compartment sank while that in the lower floated. It is advisable to use stirrers differing in density as little as possible from the densities of the solutions (but which do not "skip" or "bounce" in the cell) to avoid excessive wear of the diaphragm. The solutions in both compartments were stirred continuously by the rotation of a permanent magnet outside the cell to ensure homogeneity and to prevent the formation of stagnant layers on the diaphragm.

One slight modification of Stokes' cell was made. Instead of rubber stoppers, the necks of the cell were closed at the bottom with a capillary bore stopcock and at the top with a fine capillary plug. Both stoppers were lubricated with Dow Corning high vacuum silicone grease: no evaporation of solvent was observed.

Of utmost importance for valid diffusion measurements is the removal of all air from the pores of the diaphragm. In order to effect this removal of air it is necessary to have degassed solvents and solutions. In this research the pure water and aqueous solutions were degassed by evacuating the flask containing the solution for a period of about half an hour, while they were being heated. Since the solvent composition of the mixed solvents might be changed by such a procedure,

Figure 5

Magnetically Stirred Diaphragm Diffusion Cell:
M, Magnet; D, Porous Diaphragm; R,S, Glass
Stirrers Enclosing Iron Wire.


P
A
R
M
S
D
B
Q

these solutions were degassed by freezing the solution in an acetone-dry ice bath, then evacuating for about half an hour. The stopcock to the vacuum was then closed, the contents of the flask melted and the same procedure of freezing and pumping repeated. The degassed solvent was then placed in the diffusion cell and about 500cc. of solvent was sucked through the diaphragm. The cell was inverted and another 500cc. of degassed solvent was forced through the diaphragm.

After this procedure was completed the bottom compartment was stoppered, making sure that no air bubbles were trapped. Next about half the solvent in the upper compartment was removed and the upper compartment evacuated until the solvent boiled. The vacuum was released suddenly and atmospheric pressure then forced the solution into the diaphragm pores. This "vacuum thump" procedure was repeated several times, after which the top compartment was completely filled and stoppered. The cell was then inverted and the filling of the lower compartment completed.

To make certain that the diaphragm remained in the 'degassed' condition in all subsequent solution transfers to and from the cell compartments, special "side-hole" pipettes as recommended by Janz and Mayer[20] were used. In a "side-hole" pipette a hole about 1.5 mm. in diameter is made approximately 3 mm. above the sealed end of the lower pipette stem. The liquid delivery is thus effectively horizontal minimizing the possibility of air bubbles being forced into the diaphragm in rapid liquid transfers. This technique also minimizes the disturbance of any linear concentration gradient across the fritted disc in such solution transfer steps.

The diffusion cell must be cleaned with hot, concentrated nitric acid, and the compartment volumes must be measured prior to diffusion measurements.

The volumes of the cell and diaphragm were obtained by weight calibration with water. The dried diffusion cell and end plugs were weighed and the diaphragm was next "filled" with water (with the cell held horizontal water was added gradually from a 1cc. pipette; the capillary action of the diaphragm draws in water till its surface is shiny) and the assembly reweighed. Finally, the cell compartments were filled with water and weighed. After this volume calibration and after each experimental run the cell was kept filled with water.

The solutions to be diffused were prepared, filtered and degassed, preferably just prior to cell filling. The following cell-filling procedure was used in the diffusion measurements. The solvent-filled cell was placed in an inverted position, the stopcock plug was removed from the bottom compartment, and a side hole pipette was used to remove the solvent. This compartment was next rinsed three times with the more concentrated of the two solutions to be diffused. The 'floater' stirrer was then inserted, the filling of the half cell completed, and the compartment closed. The position of the cell was reversed and the procedure repeated for the upper compartment, using the less concentrated of the two solutions and the 'sinker' stirrer.

The filled cell was placed in the thermostat bath, magnetic stirring started, and the initial time of the 'diaphragm equilibration' period noted. After approximately three hours the cell was raised until the upper joint was just above the water level. The exposed plug was carefully dried and removed for the solution transfer step. The upper compartment solution was withdrawn, the compartment rinsed three times and refilled with the solution of the same concentration as used initially in the equilibration above. The time at which the final rinsing was completed was taken as the 'zero' for timing the diffusion experiment. The upper capillary plug, which was left open to the air to permit slight volume changes during the experiment, was placed in position and the magnetic stirring continued for the duration of the experiment.

When the diffusion experiment was completed, the cell was once more placed so as to expose partially the upper compartment. The solution in the top compartment was withdrawn for analysis. The cell was then removed from the bath and inverted. Next the stopcock on the lower plug was opened, prior to removal of the plug, to avoid disturbing the liquid in the diaphragm. Finally, the bottom stopper was removed and the solution withdrawn. The moment at which the latter compartment was opened was the final time or 'end' of the diffusion experiment.

The stirring rate within the cell must be sufficiently rapid to prevent the formation of stagnant solution layers in the vicinity of the cell diaphragm. In this research a rate of 60 r.p.m. was used, since Stokes[35] stated that any rate between 25 to 80 r.pm. is sufficient.

The alignment of the diffusion cell should be such that the diaphragm is in a horizontal plane. Since Stokes[35] has stated that deviations of one or two degrees from the horizontal in levelling the diaphragm result in a bulk flow error of less than 0.2% of the total transport, sufficiently accurate alignment of the cell could be made by eye.

The diaphragm cell was calibrated using potassium chloride solutions, which were approximately 0.5 molar in the lower compartment, and pure water in the upper compartment. The diffusion coefficients of potassium chloride used in this research have been tabulated by Stokes[36] from the data of Harned and Nuttall[37] and of Gosting[38].

Diaphragm wear by the action of the stirrers and enlargement of the pores from the flow of the solutions caused the cell constant to change with time. For this reason the cell was calibrated after every five runs and the cell constant interpolated for each experimental run.

When all the previously mentioned precautions had been made and the errors in analysis kept below about 0.1%, an accuracy of about ± 0.2% in the diffusion coefficient can be expected. But, the concentration of solutions must be kept above 0.05 molar becuase surface transport in the diaphragm cell leads to significant errors below this concentration.

(f) Analysis of Solutions

Since very accurate conductance data for sodium chlorate[23] in water were available, the compositions of the aqueous sodium chlorate solutions were determined by measuring their conductances. It was necessary, however, to dilute some of the more concentrated solutions because the specific conductance passes through a broad maximum beyond 2.5 molar. Analysis by this method was accurate to about ± 0.1%.

A volumetric method of analysis, taken from Vogel[39] and Talbot[40], was used to analyse the aqueous lithium chlorate solutions because sufficiently accurate conductance data were not available. A sample of lithium chlorate was diluted to a concentration appropriate for titration (approximately 0.075 molar). A ten c.c. aliquot was placed in a 250 ml. stoppered flask. To this was added 3cc. of concentrated hydrochloric acid and 15cc. of iodate-free solution containing about 5 grams of potassium iodide. This was followed by 22cc. of concentrated HCl and 0.1 gms. of sodium carbonate to exclude air from the flask. The mixture was stoppered and shaken and let stand for about ten minutes. The free iodine was titrated with standard sodium thiosulphate (approximately 0.1 molar) using starch solution as indicator. Standardization of this method using sodium chlorate which had been ground and dried at 120°C for several days, indicated a precision of better than 0.1%.

The water and dioxane content was determined refractometrically. Standard dioxane-water mixtures were prepared by weight using conductance water of refractive index $n_D^{25^\circ} = 1.3325 \pm 0.0001$ and freshly purified dioxane of refractive index $n_D^{25^\circ} = 1.4202 \pm 0.0001$. The results of the calibration are shown in Table 1. An Abbe refractometer capable of an accuracy of ± 0.0001 scale division was used. The accuracy in the refractive index corresponded to a probably error of ± 0.1% in the composition of the dioxane-water mixtures.

Since the solvent composition of the dioxane-water solutions used for diffusion changed during the experiment, it was necessary to analyse the solvent portion of the solution at the end of each run. To do this the solvent was separated from the solute by vacuum distillation. The solution was placed in a flask, frozen in a dry-ice-acetone bath, evacuated, then vacuum distilled, as previously described, into an empty flask kept in a dry-ice-acetone mixture. Complete separation required from twelve to twenty-four hours. This method gave the solvent composition of both sodium and lithium chlorate solutions with an accuracy of ± 0.1%.

Although the separation was sufficiently accurate for determining the solvent composition, enough liquid was left in the salt to make determination of its concentration by this method impossible. The concentration of sodium chlorate in the ternary solutions was obtained by evaporating a known quantity of solution in a platinum dish at 120°C for 24 hours. The accuracy of this technique was ± 0.1%.

This method could not be used for ternary solutions containing lithium chlorate, since lithium chlorate is too hygroscopic. The direct titration method used for aqueous solutions was unsuitable because dioxane interfered with the titration. It was necessary to remove all the dioxane by evaporation, and then titrate the remaining aqueous lithium chlorate solution.

A known quantity of solution in a platinum dish was diluted with about 50cc. of water, and evaporated nearly to dryness in an oven at 100°C. (It was necessary to make sure the dioxane content was less than 10% as Campbell, Kartzmark and Maryk[41] observed decomposition of lithium chlorate

Table 1

Calibration Data for Refractometric Analysis of Water-Dioxane Mixtures at 25°C.

Wt. % Dioxane	Refractive Index n_D^{25}
0.00	1.3325
4.94	1.3372
9.65	1.3417
17.66	1.3493
21.41	1.3533
30.15	1.3620
38.36	1.3697
44.16	1.3755
49.82	1.3808
60.01	1.3900
67.26	1.3961
76.42	1.4033
79.99	1.4061
82.54	1.4080
83.95	1.4090
84.99	1.4099
87.49	1.4115
90.00	1.4131
92.01	1.4146
92.88	1.4151
93.99	1.4159
100.00	1.4202

on heating above the composition.) To ensure complete removal of dioxane from the residue, a further 50cc. of water was added and the evaporation repeated. The salt was transferred quantitatively and titrated by the technique previously described. The concentration of lithium chlorate was obtained with an accuracy of about ± 0.1%.

(g) Conductance Measurement

A Leeds and Northrup Jones conductivity bridge was used to measure the resistance of the solutions. The latter is a modified version of the familiar Wheatstone resistance bridge, adapted to alternating current measurements. The modifications essentially consist of the replacement of the direct current resistor of the Wheatstone bridge by resistors designed for alternating current and by the inclusion of the "Wagner Ground"; a device which eliminates current leakage at the detector terminals. An Oscilloscope in series with a tuned amplifier and a frequency filter served as the detector. Measurements of resistance could be made well within one ohm in ten thousand.

Conductance cells of the type recommended by Jones and Bollinger[42] were used in this research. The cells were constructed of pyrex glass with the leads and filling tubes sufficiently far apart to eliminate errors due to the Parker effect[43]. Polarization errors were reduced by platinization.

The cell constants were determined by measuring the conductance of solutions of potassium chloride made up to the standards of Jones and Bradshaw[44].

(h) Viscosity Measurement

A viscometer of the Cannon and Fenske[45] type, having negligible drainage and kinetic energy corrections, was calibrated with water at 25°C. The run times were reproducible to 0.1%.

B. TREATMENT OF EXPERIMENTAL RESULTS

(a) Vapour pressure and vapour composition

The activity of the water in the aqueous solutions was calculated from the relation:

$$a_1 = \frac{p}{p^o} \qquad (101)$$

where p is the vapour pressure of the solution and p^o is the vapour pressure of pure water.

The activity of the solute was then calculated from the activity of the solvent by using the Gibbs-Duhem equation:

$$SdT - VdP + \Sigma\, n_i\, d\, \bar{G}_i = 0 \qquad (102)$$

which simplified to the form

$$d \ln a_2 = -(N_1/N_2)\, d \ln a_1 \qquad (103)$$

for the case in question. The actual method was taken from a paper by Randall and White[46].

They define a divergence function 'h' as follows:

$$h = \frac{55.51 \ln a_1}{\nu m} + 1 \qquad (104)$$

Differentiating

$$d\, h = \left(\frac{55.51}{\nu m}\right) d \ln a_1 - \left(\frac{55.51}{\nu\, m^2}\right) \ln a_1\, d\, m \qquad (105)$$

Substituting in equation (103) and rearranging

$$\frac{(d \ln a_2)}{\nu} = d \ln a_{\pm} = - d\, h - (h - 1)\, d \ln m \qquad (106)$$

Subtracting d ln $m_{\pm}$ from both sides of the equation, integrating and dividing by 2.303

$$\log \frac{a_{\pm}}{m_{\pm}} = \log \gamma = \frac{-h}{2.303} - \int_{o}^{m} h \, d \log m \tag{107}$$

'h' is then transformed to a more suitable form for graphical evaluation by making it a function of the square root of 'm':

$$\log \gamma = \frac{-h}{2.303} - \frac{2}{2.303} \int_{o}^{m} \frac{h}{m^{1/2}} \, d \, m^{1/2} \tag{108}$$

If $\frac{h}{m^{1/2}}$ is plotted against $m^{1/2}$, the integral in equation (108) is the area under the curve.

Because the data were not sufficiently accurate below.1 molal it was necessary to take the value of log γ at 1 molal as known and integrate to the desired concentration. The value of the integral was determined by plotting the function described above, cutting out the integral, and then weighing it on a balance.

The activity coefficient of sodium chlorate in water at a concentration of 1 molal was taken to be 0.589 from the data of Jones[47] who employed the isopiestic method.

It was necessary, in the case of lithium chlorate, to take the value γ = 0.809 from the freezing point data of Scatchard et al[48] assuming that the activity did not alter on changing the temperature from the freezing point to 25°C. But, even though such an assumption may lead to errors as great as 3%, when accurate data for the dilute region become available at 25°C it will be a simple matter to multiply by the appropriate factor to obtain the correct activities.

A different method must be used in the treatment of the dioxane-water-electrolyte solutions. Both the vapour pressure and vapour composition must now be determined in order to calculate the activity of the two components in the solvent. It was necessary to assume that Dalton's law of partial pressures for gaseous mixtures was applicable,

$$p_i = N_i P \qquad (109)$$

where p_i is the partial pressure of component 'i', N_i is the mole fraction of component 'i' in the vapour, and P is the total pressure above the solution. To calculate the activity of the ith component the following equation was used:

$$a_i = \frac{p_i}{p_i^o} \qquad (110)$$

where p_i is the partial pressure of component 'i' above the solution and p_i^o is the vapour pressure of component 'i' in the pure state. Denoting the components water, dioxane and electrolyte by the subscripts 1, 2, and 3, respectively, the addition of solute to a 2-component solvent at constant N_1 can be represented by the equation

$$N_1 \, d \ln a_1 + N_2 \, d \ln a_2 = - m_3 M_{12} \, d \ln a_3 /1000 \qquad (111)$$

where $M_{12} = N_1 M_1 + N_2 M_2$, the mean molecular weight of the binary solvent. If the solution is "ideal", a_1 and a_2 decrease by the same factor, $1 - N_3$, upon addition of electrolyte. If the solution is not "ideal" it follows from equation (111) that a_1 and a_2 may decrease by different factors. In fact, where there is strong preferential solvation of the solute by component 1, it is possible for the decrease in a_1 to be so pronounced that a_2 actually increases.

In the present method, developed by Grunwald and Bacarella[17], attention is focussed on d ln a_1/a_2 or, what is the same thing, on the experimental quantity d ln α_1/α_2. The quantities α_1 and α_2 are defined as

$$\alpha_1 = \frac{p_1}{p_1^*} \qquad \alpha_2 = \frac{p_2}{p_2^*} \tag{112}$$

where p_1 and p_2 are the partial pressures of water and dioxane over the solution containing solute and p_1^* and p_2^* are the partial pressures of water and dioxane over the solvent of composition N_1 in the absence of solute. The quantities α_1 and α_2 are introduced in addition to the conventional activities a_1, a_2 because α_1 and α_2 can be measured with higher precision. The following derivation will show how the measurement of α_1/α_2 can lead to the evaluation of the rate of change of the standard chemical potential with solvent composition:

Since $\partial^2 G/\partial n_1 \partial n_3 = \partial^2 G/\partial n_3 \partial n_1$,

$$\left(\frac{\partial \bar{G}_1}{\partial n_3}\right)_{n_1, n_2} = \left(\frac{\partial \bar{G}_3}{\partial n_1}\right)_{n_2, n_3} \tag{113}$$

It is convenient to express $\bar{G}_1$ and $\bar{G}_3$ as functions of the composition variables N_1 and m_3. Thus

$$\left(\frac{\partial \bar{G}_1}{\partial n_3}\right)_{n_1,n_2} = \left(\frac{\partial \bar{G}_1}{\partial N_1}\right)_{m_3} \left(\frac{\partial N_1}{\partial n_3}\right)_{n_1,n_2} + \left(\frac{\partial \bar{G}_1}{\partial m_3}\right)_{N_1} \left(\frac{\partial m_3}{\partial n_3}\right)_{m_1,m_2}$$

$$= \left(\frac{\partial \bar{G}_1}{\partial m_3}\right)_{N_1} \frac{1000}{(n_1 + n_2)\, M_{12}} \tag{114}$$

Similarly

$$\left(\frac{\partial \bar{G}_3}{\partial n_1}\right)_{n_2,n_3} = \left(\frac{\partial \bar{G}_3}{\partial N_1}\right)_{m_3} \frac{(1 - N_1)}{(n_1 + N_2)} - \left(\frac{\partial \bar{G}_3}{\partial m_3}\right)_{N_1} \frac{m_3\, M_1}{M_{12}\, (n_1 + n_2)} \tag{115}$$

Combining equations (113), (114) and (115)

$$\frac{1000}{M_{12}} \left(\frac{\partial \bar{G}_1}{\partial m_3}\right)_{N_1} = (1 - N_1) \left(\frac{\partial \bar{G}_3}{\partial N_1}\right)_{m_3} - \frac{m_3 M_1}{M_{12}} \left(\frac{\partial \bar{G}_3}{\partial m_3}\right) \tag{116}$$

Analogously, equation (117) is derived from the cross-differentiation identity, $\partial^2 G/\partial n_2\, \partial n_3 = \partial^2 G/\partial n_3\, \partial n_2$

$$\frac{1000}{M_{12}} \left(\frac{\partial \bar{G}_2}{\partial m_3}\right)_{N_1} = - N_1 \left(\frac{\partial \bar{G}_3}{\partial N_1}\right)_{m_3} - \left(\frac{\partial \bar{G}_3}{\partial m_3}\right)_{N_1} \frac{m_3\, M_2}{M_{12}} \tag{117}$$

Subtracting (117) from (116)

$$\frac{1000}{M_{12}} \left(\frac{\partial\, (\bar{G}_1 - \bar{G}_2)}{\partial\, m_3}\right)_{N_1} = \left(\frac{\partial \bar{G}_3}{\partial N_1}\right)_{m_3} - m_3\, r \left(\frac{\partial \bar{G}_3}{\partial m_3}\right)_{N_1} \tag{118}$$

where $r = (M_1 - M_2)/M_{12}$ and finally

$$\frac{1000}{M_{12}}\, RT \left(\frac{\partial \ln \alpha_1/\alpha_2}{\partial\, m_3}\right)_{N_1} = \left(\frac{\partial \bar{G}_3}{\partial N_1}\right)_{m_3} - m_3\, r \left(\frac{\partial \bar{G}_3}{\partial m_3}\right)_{N_1} \tag{119}$$

Alternative expressions can be written for $\bar{G}_3$:

$$\bar{G}_3 = \bar{G}_3^o + RT \ln N_3 f_3 \tag{120}$$

$$\bar{G}_3 = \bar{G}_{3m}^o + RT \ln m_3 \gamma_3 \tag{121}$$

$\bar{G}_3$ is completely defined by the variables N_1 and m_3. The activity coefficients f_3 and γ_3 are defined by the following choice of reference state. For any given value of m_3 and N_1, the reference state is chosen as the extremely dilute state ($m_3 = 0$) of the given solute in a binary solvent of the same composition N_1. By this definition, the reference state varies with N_1, and hence $\bar{G}_3^o$ and $\bar{G}_{3m}^o$ are functions of N_1.

It is convenient to solve equation (119) using $\bar{G}_3$ as given by equation (121). Then

$$\frac{1000}{M_{12}} \left(\frac{\partial \ln \alpha_1/\alpha_2}{\partial m_3}\right)_{N_1} = \frac{1}{RT} \frac{d\,\bar{G}_3^o}{d\,N_1} + \left(\frac{\partial \ln \gamma_3}{\partial N_1}\right)_{m_3} - r\,m_3 \left(\frac{\partial \ln \gamma_3}{\partial m_3}\right)_{N_1} \tag{122}$$

Equation (122) can be simplified slightly since equations (120) and (121) are related by

$$\bar{G}_{3m}^o = \bar{G}_3^o + RT \ln (M_{12}/1000) \tag{123}$$

Hence

$$\frac{1000}{M_{12}} \left(\frac{\partial \ln \alpha_1/\alpha_2}{\partial m_3}\right)_{N_1} = \frac{1}{RT} \frac{d\,\bar{G}_3^o}{d\,N_1} + \left(\frac{\partial \ln \gamma_3}{\partial N_1}\right)_{m_3} - r\,m_3 \left(\frac{\partial \ln \gamma_3}{\partial m_3}\right)_{N_1} \tag{124}$$

It is obvious from equation (124) that the measurement of α_1/α_2 can lead to the value of the rate of change of the standard chemical potential with solvent composition. Integration of values obtained at different N_1 leads to a knowledge of $\bar{G}_3^o$ as a function of N_1.

Equations analogous to (111) and (124) are obtained readily for 1-1 electrolytes. The particular equations that are most useful are:

$$\frac{1000}{M_{12}} \left(\frac{\partial \ln \alpha_1/\alpha_2}{\partial m}\right)_{N_1} = \frac{2}{RT} d\, G^o_{\pm} + 2 \left(\frac{\partial \ln \gamma_{\pm}}{\partial N_1}\right)_m - 2\, m\, r \left(\frac{\partial \ln \gamma_{\pm}}{\partial m}\right)_{N_1} \qquad (125)$$

$$\frac{1000}{M_{12}} (N_1\, d \ln \alpha_1 + N_2\, d \ln \alpha_2) = - 2\, d\, m - 2\, m\, d \ln \gamma_{\pm} \qquad (126)$$

Here m is expressed in formula weights of electrolyte per kg. of binary solvent, and $G^o_{\pm}$ is the mean value of G^o for cation and anion.

It is useful to expand $\ln \gamma_{\pm}$ in a power series in $m^{1/2}$ according to Scatchard and Prentiss[49]

$$\ln \gamma_{\pm} = - S\, m^{1/2} + Bm + Cm^{3/2} + Dm^2 + Em^{5/2} + \ldots \qquad (127)$$

In equation (127), S is the Debye-Huckel limiting slope and B, C, D, E, ... are adjustable constants. The latter are evaluated from the experimental data as follows. Substitution of (127) into (126) and integration leads to

$$- \frac{1000}{M_{12}} (N_1 \ln \alpha_1 + N_2 \ln \alpha_2) = 2\, m - \frac{2}{3} Sm^{3/2} + Bm^2 + \frac{6}{5} Cm^{5/2} + \frac{4}{3} Dm^3 + \frac{10}{7} Em^{7/2} + \ldots \qquad (128)$$

The terms on the left and the first two terms on the right involve only experimental data and known solvent properties. The adjustable constants in the remainder are evaluated by standard least squares methods using a computer. Once the constants are obtained it is a simple matter to insert them into equation (127) in order to calculate the activity coefficients. In no case were terms higher than Dm^2 found to be necessary.

(b) Diffusion

The theory for calculating the diffusion coefficient for concentration-dependent systems was outlined by Gordon[50] and extended by Stokes[51]. The principal assumptions of the theory are as follows. The diaphragm is considered to be equivalent to a collection of parallel pores, i.e., the diffusion process is assumed unidirectional. The concentrations of the solutions are assumed uniformly constant up to the diaphragm (i.e. there are no stagnant layers on the surface of the diaphragm). Transport from one compartment to the other is only by diffusion; there is no streaming through the pores or surface transport effects along the pore walls. The diaphragm assumes a steady state throughout the experiment (i.e. there is no gain or loss of solute from the diaphragm). The volumes of the two solutions are assumed constant during the experiment.

The following symbols are used throughout this discussion. The volume of the lower compartment of the diaphragm cell is V_1, the volume of the upper compartment is V_2, and the pore volume of the diaphragm is V_3. The pores have a total effective cross-sectional area 'A', and an average length, 'L'. The concentration of the lower compartment is c' and that of the upper is c''. At time $t = t_o$, $c' = c_1$ and $c'' = c_2$; at time $t = t$, $c' = c_3$ and $c'' = c_4$.

It should be noted that the initial concentration in the bottom compartment, c_1, is calculated by the characteristic cell equation

$$c_1 = c_3 + (c_4 - c_2)\left(\frac{V_2 + 1/2\ V_3}{V_1 + 1/2\ V_3}\right) \qquad (129)$$

The rates of change of the concentrations of the upper and lower compartments are related to the flux J(t) by:

$$\frac{dc'}{dt} = - J(t) \frac{A}{V_1} \qquad (130)$$

$$\frac{dc''}{dt} = + J(t) \frac{A}{V_2} \qquad (130a)$$

Hence $\frac{d(c' - c'')}{dt} = - J(t) A(\frac{1}{V_1} + \frac{1}{V_2})$ (131)

The average value of the diffusion coefficient D with respect to concentration over the concentration range c' to c'' prevailing at the time considered is now introduced. This quantity which is also a function of time is denoted by $\bar{D}(t)$. Then

$$\bar{D}(t) = \frac{1}{c' - c''} \int_{c''}^{c'} D \, d c = \frac{-1}{c' - c''} \int_{x=0}^{L} D \left(\frac{\partial c}{\partial x}\right) d x = \frac{L J(t)}{c' - c''}, \qquad (132)$$

since $J(t) = - D \frac{\partial c}{\partial x}$ is a constant for all points within the diaphragm at time t, x being the distance of the plane considered from the lower surface of the diaphragm. Combining equations (131) and (132) gives:

$$- \frac{d \ln (c' - c'')}{dt} = \frac{A}{L} \left(\frac{1}{V_1} + \frac{1}{V_2}\right) \bar{D}(t) \qquad (133)$$

Hence integrating between initial and final conditions:

$$\ln \frac{c_1 - c_2}{c_3 - c_4} = \frac{A}{L} \left(\frac{1}{V_1} + \frac{1}{V_2}\right) \int_{t=0}^{t=t} \bar{D}(t) \, dt \qquad (134)$$

Denoting the time average of $\bar{D}(t)$ by $\bar{\bar{D}}$, i.e., let

$$\bar{\bar{D}} = \frac{1}{t} \int_{o}^{t} \bar{D}(t) \, dt \qquad (135)$$

and also writing β for the cell constant $(A/L)\left(\frac{1}{V_1}+\frac{1}{V_2}\right)$, the following equation is obtained

$$\bar{\bar{D}} = \frac{1}{\beta t} \ln \frac{c_1 - c_2}{c_3 - c_4} \qquad (136)$$

The value $\bar{\bar{D}}$ calculated from equation (136) is a rather complicated double average known as the diaphragm-cell integral diffusion coefficient, which is not readily convertible into the more fundamental differential diffusion coefficient D. Fortunately it has been demonstrated by Gordon^{50} that a negligible error is introduced in all ordinary cases if instead of using the exact relation:

$$\bar{\bar{D}} = \frac{1}{t}\int_0^t \bar{D}(t)\,dt \qquad (135)$$

the integrand is treated as having a constant value equal to its value when the concentrations c' and c'' are half-way between their initial and final values. This constant value is then clearly equal to $\bar{\bar{D}}$ as defined above and given by equation (136), and is related to the differential diffusion coefficient by:

$$\bar{\bar{D}} = \frac{1}{c_{m'} - c_{m''}} \int_{c_{m''}}^{c_{m'}} D\,dc \qquad (137)$$

where $c_{m'} = \frac{c_1 + c_3}{2}$ and $c_{m''} = \frac{c_2 + c_4}{2}$

The differential diffusion coefficient D commonly varies with concentration in a manner shown in Figure 6, where the full ordinates are drawn at the concentrations for the beginning and end of a run, and the dashed ordinates correspond to $c_{m'}$ and $c_{m''}$ as defined above. Figure 6 refers to the case where $c_2 = 0$.

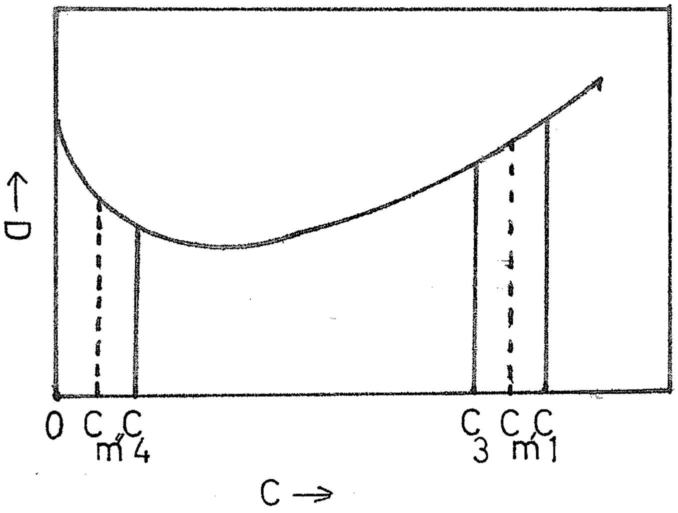


Figure 6 - Initial and final conditions in a diaphragm-cell diffusion.

Now a new integral diffusion coefficient $\bar{\bar{D}}^o$ is defined as that which would be found in a run of vanishingly short duration, with initial concentrations c and zero on opposite sides of the diaphragm. From equation (137)

$$\bar{\bar{D}}o = \frac{1}{c} \int_o^c D \, d \, c \tag{138}$$

The values of $\bar{\bar{D}}^o$ in such hypothetical experiments with initial concentrations $c_{m'}$ and $c_{m''}$ are denoted by $\bar{\bar{D}}^o(c_{m'})$ and $\bar{\bar{D}}^o(c_{m''})$ respectively. The geometry of Figure 6 shows that

$$\bar{D}^{o}(c_{m'}) = \bar{D} - (c_{m''}/c_{m'}) \;\; [\, \bar{D} - \bar{D}^{o}{}_{c_{m''}}] \qquad (139)$$

Hence from the observed integral diffusion coefficient $\bar{D}$ it is possible to calculate $\bar{D}^{o}$ for the concentration $c_{m'}$, provided it is known for the lower concentration $c_{m''}$. In practice the curve of $\bar{D}^{o}(c_{m'})$ against $c_{m'}$ lies within 1% of that of $\bar{D}$ against c_1, and this makes possible the solution of equation (139) by a short series of approximations. First the curve of $\bar{D}$ against $c_1^{1/2}$ is plotted and extrapolated smoothly to the Nernst limiting value at infinite dilution. From this curve, a first approximation to $\bar{D}^{o}(c_{m''})$ is read for each run, and substituted into the square bracket of equation (139). The resulting values of $\bar{D}^{o}(c_{m'})$ are then plotted against $c_{m'}^{1/2}$, and this curve gives a second approximation to $\bar{D}^{o}(c_{m''})$ which is again substituted into equation (139). This procedure is repeated until there is no change in $\bar{D}^{o}(c_{m'})$ on continuing the process. Usually, two series of approximations are sufficient.

From these $\bar{D}^{o}$ data the differential diffusion coefficient D is readily obtained, since equation (138) is immediately differentiable to yield

$$D = \bar{D}^{o} + c\,\frac{d\,\bar{D}^{o}}{d\,c}$$

or

$$D = \bar{D}^{o} + \frac{c^{1/2}}{2}\,\frac{d\,\bar{D}^{o}}{d\,c^{1/2}} \qquad (140)$$

(This differentiation is of course not possible in equation (137), since there the integral has a variable lower limit). The slopes $d\,\bar{D}^{o}/dc$ or d $\bar{D}^{o}$/d $c^{1/2}$ of (140) are obtained by graphical means yielding the differential diffusion coefficients.

This method worked well for the aqueous solutions of sodium and lithium chlorate, but could not be used for the dioxane-water mixtures because the limiting ionic conductivities necessary to calculate the Nernst limiting value of the diffusion coefficient were not available. For this reason it was necessary to use another method developed by Hammond and Stokes[52] for these solutions.

The differential diffusion coefficient was assumed to be of the form

$$D = A + 2\,B\,c + 3\,E\,c^{2} + 4\,F\,c^{3} + \dots \qquad (141)$$

Now the observed integral diffusion coefficient $\bar{\bar{D}}$ is, to a close approximation, related to D by the expression

$$\bar{\bar{D}} = \frac{1}{c_{m'} - c_{m''}} \int_{c_{m''}}^{c_{m'}} D\,dc \qquad (137)$$

Using equation (141) in the integration of (137), the following equation is obtained

$$\bar{\bar{D}} = A + B\,(c_{m'} + c_{m''}) + E(c_{m'}^{2} + c_{m'}\,c_{m''} + c_{m''}^{2}) + F\,(c_{m'}^{3} + c_{m'}^{2}\,c_{m''} + c_{m'}\,c_{m''}^{2} + c_{m''}^{3}) + \dots \qquad (142)$$

Since $c_{m'}$ and $c_{m''}$ are known for each value of $\bar{\bar{D}}$ the constants A, B, E, F, .. may be determined by the method of least squares. Finally, substituting the values for the constants into equation (141) yields the differential diffusion coefficient D.

The calculations were done using a computer and in no case were more than four parameters required.

It was necessary to make another assumption for the dioxane-water mixtures, viz, that the solvent composition remained constant throughout the experiment. This is not strictly true since transport of dioxane to the upper compartment changed the compositions of solvent in both compartments in the extreme case by as much as 2.8%. But, in most cases the solvent composition changed by less than 1% so I believe that the assumption is a good one.

EXPERIMENTAL RESULTS

A. VAPOUR PRESSURE AND VAPOUR COMPOSITION

Table 2

Vapour Pressures, Water Activities, and Osmotic Coefficients of Sodium Chlorate in Water at 25°C.

(Vapour Pressure of Water = 23.756)

Concentration (moles / Kg. of solvent) m	Vapour Pressure (mm. Hg)	Water Activity a_W	Osmotic Coefficient ϕ
3.9724	20.915	0.8804	0.890
4.9677	20.208	0.8507	0.904
5.9874	19.513	0.8214	0.912
7.3200	18.647	0.7849	0.918
8.0386	18.197	0.7660	0.920
9.4319	17.279	0.7274	0.937

Table 3

Activity Coefficients of Sodium Chlorate in Water at 25°C. (for details of calculation see page 62)

Concentration ($\frac{\text{moles}}{\text{Kg. of solvent}}$) m	Molal Activity Coefficient γ
4.0	0.506
5.0	0.501
6.0	0.497
7.0	0.493
8.0	0.489
9.0	0.490
9.4319	0.491

Table 4

Vapour Pressures, Water Activities, and Osmotic Coefficients of Lithium Chlorate in Water at 25°C.

(Vapour Pressure of Water = 23.756)

Concentration (moles / Kg. of solvent) m	Vapour Pressure (mm. Hg.)	Water Activity a_W	Osmotic Coefficient ϕ
0.9143	22.940	0.9657	1.061
1.0701	22.778	0.9589	1.090
1.2630	22.577	0.9504	1.118
1.4251	22.409	0.9433	1.137
1.6302	22.196	0.9344	1.156
1.9650	21.843	0.9194	1.187
2.2861	21.490	0.9046	1.217
2.8850	20.814	0.8761	1.272
3.4305	20.175	0.8492	1.322
4.1480	19.307	0.8127	1.388
5.0307	18.205	0.7664	1.468
6.3738	16.479	0.6937	1.593
8.5025	13.738	0.5783	1.788
10.2740	11.680	0.4917	1.918
11.9558	9.992	0.4206	2.010
14.3953	8.072	0.3398	2.081
15.7749	7.159	0.3014	2.110
17.6402	6.083	0.2561	2.143
20.3290	4.838	0.2037	2.173
25.1763	3.637	0.1531	2.069
30.2305	2.779	0.1170	1.970
36.5241	2.145	0.09029	1.827
43.7577	1.380	0.05809	1.805

Table 5

Activity Coefficients of Lithium Chlorate in Water at 25°C (for details of calculation see page 62)

Concentration ($\frac{\text{moles}}{\text{Kg. of solvent}}$) m	Molal Activity Coefficient γ	Concentration ($\frac{\text{moles}}{\text{Kg. of solvent}}$) m	Molal Activity Coefficient γ
1.0	0.809	12.0	5.501
1.2	0.837	14.0	6.838
1.4	0.868	16.0	8.234
1.6	0.905	18.0	9.657
1.8	0.946	20.0	11.05
2.0	0.988	22.0	12.20
2.5	1.088	24.0	13.03
3.0	1.193	26.0	13.40
3.5	1.306	28.0	13.68
4.0	1.428	30.0	13.94
5.0	1.711	33.0	14.25
6.0	2.104	36.0	14.41
7.0	2.472	39.0	14.95
8.0	2.990	42.0	15.75
9.0	3.562	43.7577	16.25
10.0	4.161		

Table 6

Vapour Compositions of the System 44.5% Dioxane - 55.5% Water - Sodium Chlorate at 25°C.

Concentration of Sodium Chlorate $\left(\frac{\text{moles}}{\text{Kg. of solvent}}\right)$ m	Wt % Dioxane in Vapour	Mole % Dioxane in Vapour
0.0	81.40	47.23
0.3844	82.57	49.20
0.9947	83.90	51.59
1.9809	85.37	54.40
2.9986	86.90	57.56
4.0388	88.40	60.91

Table 7

Total Vapour Pressures, Vapour Compositions, and Partial Vapour Pressures of the System 44.5% Dioxane - 55.5% Water - Sodium Chlorate at 25°C.

Concentration of Sodium Chlorate ($\frac{\text{moles}}{\text{Kg. of solvent}}$) m	Total Vapour Pressure (mm. Hg.)	Mole % Dioxane in Vapour	Partial Vapour Pressure of Dioxane (mm. Hg.)	Partial Vapour Pressure of Water (mm. Hg.)
0.0	40.57	47.23	19.16	21.41
1.0332	41.22	51.66	21.29	19.93
1.4716	41.32	53.00	21.90	19.42
2.0795	41.47	54.76	22.71	18.76
2.4637	41.62	55.90	23.27	18.35
3.2081	41.72	58.23	24.29	17.43
3.4873	41.72	59.09	24.65	17.07
4.0314	41.72	60.89	25.40	16.32

Table 8

Water and Dioxane Activities of the System 44.5% Dioxane - 55.5% Water - Sodium Chlorate at 25°C.

Concentration of Sodium Chlorate (moles/Kg. of solvent) m	$a_1 = \frac{\text{partial pressure of water over the solution}}{\text{vapour pressure of pure water}}$ ($p_o = 23.756$)	$a_2 = \frac{\text{partial pressure of dioxane over the solution}}{\text{vapour pressure of pure dioxane}}$ ($p_o = 35.70$)	$\alpha_1 = \frac{\text{partial pressure of water over the mixed solvent containing salt}}{\text{partial pressure of water over the mixed solvent}}$	$\alpha_2 = \frac{\text{partial pressure of dioxane over the mixed solvent containing salt}}{\text{partial pressure of dioxane over the mixed solvent}}$
0.0	0.9012	0.5367	1.0000	1.0000
1.0332	0.8389	0.5964	0.9309	1.1112
1.4716	0.8175	0.6134	0.9071	1.1430
2.0795	0.7897	0.6361	0.8762	1.1853
2.4637	0.7724	0.6518	0.8571	1.2145
3.2081	0.7337	0.6804	0.8141	1.2677
3.4873	0.7186	0.6905	0.7973	1.2865
4.0314	0.6870	0.7115	0.7623	1.3257

Table 9

Molal Activity Coefficients of Sodium Chlorate in the Solvent 44.5% Dioxane - 55.5% Water at 25°C Calculated from the Equation

$$\ln \gamma = - S\, m^{1/2} + B\, m + C\, m^{3/2} + D\, m^2$$

(for details of calculation see page 64)

Constant	Deviation in Constant
S = 3.1545	---
B = 3.67692	---
C = - 2.14785	0.10278
D = 0.46257	0.03041

Concentration of Sodium Chlorate (moles/ Kg. of solvent) m	Molal Activity Coefficient γ
1.0	0.313
1.5	0.286
2.0	0.264
2.5	0.248
3.0	0.239
3.5	0.239
4.0	0.251
4.0314	0.252

Table 10

Vapour Compositions of the System 44.5% Dioxane - 55.5% Water - Lithium Chlorate at 25°C.

Concentration of Lithium Chlorate $\left(\frac{\text{moles}}{\text{Kg. of solvent}}\right)$ m	Wt % Dioxane in Vapour	Mole % Dioxane in Vapour
0.0	81.40	47.23
0.5212	82.30	48.74
1.0211	82.70	49.43
1.8496	83.20	50.31
2.9977	83.77	51.35
4.9952	84.32	52.37
8.1236	84.77	53.23
13.4825	85.07	53.81

Table 11

Total Vapour Pressures, Vapour Compositions, and Partial Vapour Pressures of the System 44.5% Dioxane - 55.5% Water - Lithium Chlorate at 25°C.

Concentration of Lithium Chlorate $\left(\frac{\text{moles}}{\text{Kg. of solvent}}\right)$ m	Total Vapour Pressure (mm. Hg.)	Mole % Dioxane in Vapour	Partial Vapour Pressure of Dioxane (mm. Hg.)	Partial Vapour Pressure of Water (mm. Hg.)
0.0	40.57	47.23	19.16	21.41
1.0863	39.58	49.50	19.59	19.99
2.0172	37.14	50.46	18.74	18.40
3.0094	34.35	51.33	17.63	16.72
4.1095	30.77	51.98	15.99	14.78
5.0434	27.78	52.37	14.55	13.23
6.7324	22.50	52.94	11.91	10.59
8.9653	17.28	53.40	9.23	8.05
11.5036	12.65	53.68	6.79	5.86
14.0631	9.96	53.79	5.36	4.60

Table 12

Water and Dioxane Activities of the System 44.5% Dioxane - 55.5% Water - Lithium Chlorate

at 25°C.

Concentration of Lithium Chlorate (moles/Kg. of solvent) m	$a_1 = \frac{\text{partial pressure of water over the solution}}{\text{vapour pressure of pure water } (p_o = 23.756)}$	$a_2 = \frac{\text{partial pressure of dioxane over the solution}}{\text{vapour pressure of pure dioxane } (p_o = 35.70)}$	$\alpha_1 = \frac{\text{partial pressure of water over the mixed solvent containing salt}}{\text{partial pressure of water over the mixed solvent}}$	$\alpha_2 = \frac{\text{partial pressure o dioxane over the mixed solvent containing salt}}{\text{partial pressure o dioxane over the mixed solvent}}$
0.0	0.9012	0.5367	1.0000	1.0000
1.0863	0.8415	0.5487	0.9337	1.0224
2.0172	0.7745	0.5249	0.8594	0.9781
3.0094	0.7038	0.4938	0.7809	0.9201
4.1095	0.6222	0.4479	0.6903	0.8346
5.0434	0.5569	0.4076	0.6179	0.7594
6.7324	0.4458	0.3336	0.4946	0.6216
8.9653	0.3389	0.2585	0.3760	0.4817
11.5036	0.2467	0.1902	0.2737	0.3544
14.0631	0.1936	0.1501	0.2149	0.2797

Table 13

Molal Activity Coefficients of Lithium Chlorate in the Solvent 44.5% Dioxane - 55.5% Water at 25°C Calculated from the Equation

$$\ln \gamma = - S\, m^{1/2} + B\, m + C\, m^{3/2} + D\, m^2$$

(for details of calculation see page 64)

Constant	Deviation in Constant
S = 3.1545	---
B = 2.69531	---
C = -0.72993	0.03460
D = 0.06812	0.00635

Concentration of Lithium Chlorate (moles/ Kg. of solvent) m	Molal Activity Coefficient γ
1.0	0.326
2.0	0.422
3.0	0.573
4.0	0.758
5.0	0.966
6.0	1.185
7.0	1.406
8.0	1.622
9.0	1.829
10.0	2.029
11.0	2.223
12.0	2.418
13.0	2.623
14.0	2.848
14.0631	2.864

Table 14

Vapour Compositions of the System 64.5% Dioxane - 35.5% Water - Sodium Chlorate at 25°C.

Concentration of Sodium Chlorate $\left(\frac{\text{moles}}{\text{Kg. of Solvent}}\right)$ m	Wt % Dioxane in Vapour	Mole % Dioxane in Vapour
0.0	86.60	56.92
0.4810	87.80	59.54
1.0043	88.50	61.14
1.5813	89.40	63.30
2.1449	90.15	65.17

Table 15

Total Vapour Pressure, Vapour Compositions, and Partial Vapour Pressures of the System 64.5% Dioxane - 35.5% Water - Sodium Chlorate at 25°C.

Concentration of Sodium Chlorate (moles / Kg. of Solvent) m	Total Vapour Pressure (mm. Hg.)	Mole % Dioxane in Vapour	Partial Vapour Pressure of Dioxane (mm. Hg.)	Partial Vapour Pressure of Water (mm. Hg.)
0.0	45.50	56.88	25.88	19.62
0.8301	46.20	60.75	28.07	18.13
1.0200	46.23	61.35	28.36	17.87
1.2800	46.26	62.23	28.79	17.47
1.4665	46.25	62.83	29.06	17.19
1.6866	46.30	63.59	29.44	16.86
2.0000	46.27	64.64	29.91	16.36
2.3311	46.25	65.82	30.44	15.81

Table 16

Water and Dioxane Activities of the System 64.5% Dioxane - 35.5% Water - Sodium Chlorate at 25°C.

Concentration of Sodium Chlorate (moles/Kg. of solvent) m	$a_1 = \frac{\text{partial pressure of water over the solution}}{\text{vapour pressure of pure water}}$ (p_o = 23.756)	$a_2 = \frac{\text{partial pressure of dioxane over the solution}}{\text{vapour pressure of pure dioxane}}$ (p_o = 35.70)	$\alpha_1 = \frac{\text{partial pressure of water over the mixed solvent containing salt}}{\text{partial pressure of water over the mixed solvent}}$	$\alpha_2 = \frac{\text{partial pressure of dioxane over the mixed solvent containing salt}}{\text{partial pressure of dioxane over the mixed solvent}}$
0.0	0.8259	0.7249	1.0000	1.0000
0.8301	0.7632	0.7863	0.9241	1.0846
1.0200	0.7522	0.7944	0.9108	1.0958
1.2800	0.7354	0.8064	0.8904	1.1124
1.4665	0.7236	0.8140	0.8761	1.1229
1.6866	0.7097	0.8246	0.8593	1.1376
2.0000	0.6887	0.8378	0.8338	1.1557
2.3311	0.6655	0.8527	0.8058	1.1762

Table 17

Molal Activity Coefficients of Sodium Chlorate in the Solvent 64.5% Dioxane - 35.5% Water at 25°C. Calculated from the Equation

$$\ln \gamma = - S m^{1/2} + B m + C m^{3/2} + D m^2$$

(for details of calculation see page 64)

Constant	Deviation in Constant
S = 7.2091	---
B = 8.57917	---
C = -5.20461	0.24878
D = 1.22816	0.09166

Concentration of Sodium Chlorate (moles/ Kg. of Solvent) m	Molal Activity Coefficient γ
1.00	0.0738
1.25	0.0678
1.50	0.0634
1.75	0.0602
2.00	0.0581
2.25	0.0574
2.3311	0.0574

Table 18

Vapour Compositions of the System 64.5% Dioxane – 35.5% Water – Lithium Chlorate at 25°C.

Concentration of Lithium Chlorate $\left(\frac{\text{moles}}{\text{Kg. of Solvent}}\right)$ m	Wt % Dioxane in Vapour	Mole% Dioxane in Vapour
0.0	86.60	56.92
0.4123	87.66	59.23
1.0054	88.52	61.19
2.0071	89.70	64.04
3.7952	91.52	68.82
5.4522	92.40	71.31
7.6841	93.00	73.09

Table 19

Total Vapour Pressure, Vapour Composition, and Partial Vapour Pressures of the System 64.5% Dioxane - 35.5% Water - Lithium Chlorate at 25°C.

Concentration of Lithium Chlorate $\left(\frac{\text{moles}}{\text{Kg. of Solvent}}\right)$ m	Total Vapour Pressure (mm. Hg.)	Mole % Dioxane in Vapour	Partial Vapour Pressure of Dioxane (mm. Hg.)	Partial Vapour Pressure of Water (mm. Hg.)
0.0	45.50	56.88	25.88	19.62
1.0177	44.91	61.26	27.51	17.40
1.9613	42.47	63.99	27.18	15.29
3.0403	38.04	66.92	25.46	12.58
3.8451	34.60	68.90	23.84	10.76
5.0592	29.67	70.99	21.06	8.61
6.2070	25.19	72.20	18.19	7.00
7.6221	21.36	73.09	15.61	5.75

Table 20

Water and Dioxane Activities of the System 64.5% Dioxane - 35.5% Water - Lithium Chlorate at 25°C.

Concentration of Lithium Chlorate (moles/Kg. of solvent) m	$a_1 = \frac{\text{partial pressure of water over the solution}}{\text{vapour pressure of pure water}}$ (p_o = 23.756)	$a_2 = \frac{\text{partial pressure of dioxane over the solution}}{\text{vapour pressure of pure dioxane}}$ (p_o = 35.70)	$\alpha_1 = \frac{\text{partial pressure of water over the mixed solvent containing salt}}{\text{partial pressure of water over the mixed solvent}}$	$\alpha_2 = \frac{\text{partial pressure of dioxane over the mixed solvent containing salt}}{\text{partial pressure of dioxane over the mixed solvent}}$
0.0	0.8259	0.7249	1.0000	1.0000
1.0177	0.7324	0.7706	0.8869	1.0630
1.9613	0.6436	0.7613	0.7793	1.0502
3.0403	0.5296	0.7132	0.6412	0.9838
3.8451	0.4529	0.6678	0.5484	0.9212
5.0592	0.3624	0.5899	0.4391	0.8138
6.2070	0.2947	0.5095	0.3568	0.7029
7.6221	0.2420	0.4373	0.2931	0.6032

Table 21

Molal Activity Coefficients of Lithium Chlorate in the Solvent 64.5% Dioxane - 35.5% Water at 25°C Calculated from the Equation

$$\ln \gamma = - S\, m^{1/2} + B\, m + C\, m^{3/2} + D\, m^2$$

(for details of calculation see page 64)

Constant	Deviation in Constant
S = 7.2091	---
B = 7.71677	---
C = -3.07274	0.28952
D = 0.43970	0.06832

Concentration of Lithium Chlorate (moles/ Kg. of solvent) m	Molal Activity Coefficient γ
1.0	0.1194
2.0	0.1838
3.0	0.260
4.0	0.334
5.0	0.407
6.0	0.502
7.0	0.658
7.6221	0.818

B. DIFFUSION

Table 22

Diaphragm-Cell Integral Diffusion Coefficients of Sodium Chlorate in Water at 25°C.

Initial Concentration in Bottom Compartment (moles/liter) c_1	Initial Concentration in Top Compartment (moles/liter) c_2	Final Concentration in Bottom Compartment (moles/liter) c_3	Final Concentration in Top Compartment (moles/liter) c_4	Diaphragm-Cell Integral Diffusion Coefficient (cm^2 sec^{-1}) $\bar{D}$ x 10^5
0.1561	0.0	0.0943	0.0631	1.394
0.4351	0.0	0.2660	0.1740	1.375
0.6510	0.0	0.3990	0.2580	1.358
0.8748	0.0	0.5360	0.3460	1.351
1.4230	0.0	0.8780	0.5565	1.326
2.1615	0.0	1.3330	0.8460	1.305
3.9965	0.0	2.5050	1.5230	1.249
5.7752	0.0	3.6700	2.1400	1.190
4.9784	3.0100	4.2800	3.7200	1.102
5.9314	4.3400	5.4100	4.8700	0.961
6.4912	5.3880	6.1740	5.7105	0.774

Table 23

Integral Diffusion Coefficients for Runs of Vanishingly Short Duration and Differential Diffusion Coefficients of Sodium Chlorate in Water at 25°C. (for details of calculations see page 71).

$c = c_{m'} = \frac{c_1 + c_3}{2}$ (moles/liter)	$c_{m''} = \frac{c_2 + c_4}{2}$ (moles/liter)	Integral Diffusion Coefficient for Run of Vanishingly Short Duration ($cm^2\ sec^{-1}$) $\bar{D}^o(c_{m'}) \times 10^5$	Integral Diffusion Coefficient for Run of Vanishingly Short Duration ($cm^2\ sec^{-1}$) $\bar{D}^o(c_{m''}) \times 10^5$	Differential Diffusion Coefficient ($cm^2\ sec^{-1}$) $D \times 10^5$
0.0	0.0	---	---	1.502[a]
0.1252	0.0316	1.404	1.434	1.364
0.3506	0.0870	1.385	1.414	1.358
0.5250	0.1290	1.370	1.406	1.341
0.7054	0.1730	1.363	1.400	1.325
1.1505	0.2783	1.341	1.389	1.296
1.7473	0.4230	1.322	1.378	1.270
3.2508	0.7615	1.274	1.358	1.167
4.7226	1.0700	1.225	1.344	1.036
4.6292	3.3650	1.225	1.272	1.041
5.6707	4.6050	1.177	1.227	0.865
6.3326	5.5493	1.135	1.186	0.690

---

[a] Nernst limiting value

Table 24

Diaphragm-Cell Integral Diffusion Coefficients of Lithium Chlorate in Water at 25°C.

Initial Concentration in Bottom Compartment (moles/liter) c_1	Initial Concentration in Top Compartment (moles/liter) c_2	Final Concentration in Bottom Compartment (moles/liter) c_3	Final Concentration in Top Compartment (moles/liter) c_4	Diaphragm-Cell Integral Diffusion Coefficient $(\mathrm{cm}^2\ \mathrm{sec}^{-1})$ $\bar{D} \times 10^5$
0.1139	0.0	0.0708	0.0440	1.225
0.2442	0.0	0.1543	0.0918	1.208
0.4283	0.0	0.2687	0.1629	1.209
0.8670	0.0	0.5475	0.3263	1.240
1.9130	0.0	1.1990	0.7292	1.271
2.8850	0.0	1.7867	1.1210	1.283
8.1263	0.0	4.6745	3.5089	1.338
13.1332	0.0	8.4666	4.7438	1.104
15.0871	6.3838	13.5154	7.9908	0.573
15.1532	9.1562	14.0250	10.3076	0.381

Table 25

Integral Diffusion Coefficients for Runs of Vanishingly Short Duration and Differential Diffusion Coefficients of Lithium Chlorate in Water at 25°C (for details of calculations see page 71).

$c = c_{m'} = \frac{c_1 + c_3}{2}$ (moles/ liter)	$c_{m''} = \frac{c_2 + c_4}{2}$ (moles/liter)	Integral Diffusion Coefficient for Run of Vanishingly Short Duration ($cm^2\ sec^{-1}$) $\bar{D}^o(c_{m'}) \times 10^5$	Integral Diffusion Coefficient for Run of Vanishingly Short Duration ($cm^2\ sec^{-1}$) $\bar{D}^o(c_{m''}) \times 10^5$	Differential Diffusion Coefficient ($cm^2\ sec^{-1}$) $D \times 10^5$
0.0	0.0	----	---	1.288[a]
0.0923	0.0220	1.233	1.259	1.212
0.1993	0.0459	1.217	1.247	1.205
0.3485	0.0815	1.215	1.235	1.218
0.7073	0.1632	1.235	1.222	1.251
1.5560	0.3646	1.258	1.216	1.302
2.3359	0.5605	1.268	1.221	1.341
6.4004	1.7545	1.317	1.262	1.239
10.7999	2.3719	1.142	1.278	0.578
14.3013	7.1873	0.936	1.295	0.143
14.5891	9.7319	0.921	1.190	0.120

---

[a] Nernst limiting value

Table 26

Diaphragm-Cell Integral Diffusion Coefficients of Sodium Chlorate in 44.5% Dioxane - 55.5% Water at 25°C.

Initial Concentration in Bottom Compartment (moles/liter) c_1	Initial Concentration in Top Compartment (moles/liter) c_2	Final Concentration in Bottom Compartment (moles/liter) c_3	Final Concentration in Top Compartment (moles/liter) c_4	Wt. % Dioxane in Bottom Compartment at end of Experiment	Wt. % Dioxane in Top Compartment at end of Experiment	Diaphragm-Cell Integral Diffusion Coefficient (cm^2 sec^{-1}) $\bar{D} \times 10^5$
0.2189	0.0	0.1626	0.0576	44.20	44.80	0.635
1.0477	0.0	0.7751	0.2788	43.40	45.60	0.614
1.9563	0.0	1.4790	0.4881	42.80	46.10	0.588
3.5198	0.0	2.7030	0.8354	41.60	47.30	0.536
3.6925	2.9328	3.5200	3.1082	44.10	44.90	0.400

Table 27

Differential and Integral Diffusion Coefficients of Sodium Chlorate in 44.5% Dioxane - 55.5% Water at 25°C Calculated from the Equations

$$D = A + 2BC + 3EC^2$$

$$\bar{D} = A + B\,(C_{m'} + C_{m''}) + E(C_{m'}^2 + C_{m'}\,C_{m''} + C_{m''}^2)$$

(for details of calculation see page 74)

Constant	Deviation in Constant
A = 0.63802	---
B = -0.01840	0.00218
E = -0.00349	0.00040

$C = C_{m'} = \frac{C_1 + C_3}{2}$ (moles/liter)	$C_{m''} = \frac{C_2 + C_4}{2}$ (moles/liter)	Calculated Integral Diffusion Coefficient (cm^2 sec^{-1}) $\bar{D} \times 10^5$	Differential Diffusion Coefficients (cm^2 sec^{-1}) $D \times 10^5$
0.1908	0.0288	0.634	0.631
0.9114	0.1394	0.615	0.596
1.7177	0.2441	0.590	0.544
3.1114	0.4177	0.534	0.422
3.6063	3.0205	0.401	0.369

Table 28

Diaphragm-Cell Integral Diffusion Coefficients of Lithium Chlorate in 44.5% Dioxane - 55.5% Water at 25°C.

Initial Concentration in Bottom Compartment (moles/liter) c_1	Initial Concentration in Top Compartment (moles/liter) c_2	Final Concentration in Bottom Compartment (moles/liter) c_3	Final Concentration in Top Compartment (moles/liter) c_4	Wt. % Dioxane in Bottom Compartment at end of Experiment	Wt. % Dioxane in Top Compartment at end of Experiment	Diaphragm-Cell Integral Diffusion Coefficient (cm^2 sec^{-1}) $\bar{D} \times 10^5$
0.1029	0.0	0.0775	0.0260	44.45	44.55	0.561
0.2113	0.0	0.1622	0.0502	44.35	44.65	0.552
0.5911	0.0	0.4424	0.1521	44.20	44.80	0.570
1.3289	0.0	1.0088	0.3274	44.10	44.90	0.590
2.0431	0.0	1.5085	0.5467	43.90	45.10	0.604
4.6903	0.0	3.4878	1.2281	43.35	45.65	0.592
8.6908	0.0	6.8184	1.9040	42.90	46.10	0.463
8.7741	6.2267	8.4132	6.5950	44.00	45.00	0.211

Table 29

Differential and Integral Diffusion Coefficients of Lithium Chlorate in 44.5% Dioxane - 55.5% Water at 25°C Calculated from the Equations

$$D = A + 2Bc + 3Ec^2 + 4Fc^3$$

$$\bar{D} = A + B(c_{m'} + c_{m''}) + E(c_{m'}^2 + c_{m'}c_{m''} + c_{m''}^2) + F(c_{m'}^3 + c_{m'}^2 c_{m''} + c_{m'}c_{m''}^2 + c_{m''}^3)$$

(for details of calculations see page 74)

Constant	Deviation in Constant
A = 0.54390	---
B = 0.04708	0.00393
E = -0.01065	0.00101
F = 0.00045	0.00007

$c = c_{m'} = \frac{c_1 + c_3}{2}$ (moles/liter)	$c_{m''} = \frac{c_2 + c_4}{2}$ (moles/liter)	Calculated Integral Diffusion Coefficient (cm² sec⁻¹) $\bar{D} \times 10^5$	Differential Diffusion Coefficient (cm² sec⁻¹) $D \times 10^5$
0.1868	0.0251	0.554	0.552
0.5168	0.0761	0.569	0.565
1.1689	0.1637	0.591	0.585
1.7758	0.2734	0.604	0.596
4.0891	0.6141	0.593	0.589
7.7546	0.9520	0.464	0.478
8.5937	6.4109	0.215	0.448

Table 30

Diaphragm-Cell Integral Diffusion Coefficients of Sodium Chlorate in 64.5% Dioxane - 35.5% Water at 25°C.

Initial Concentration in Bottom Compartment (moles/liter) c_1	Initial Concentration in Top Compartment (moles/liter) c_2	Final Concentration in Bottom Compartment (moles/liter) c_3	Final Concentration in Top Compartment (moles/liter) c_4	Wt. % Dioxane in Bottom Compartment at end of Experiment	Wt. % Dioxane in Top Compartment at end of Experiment	Diaphragm-Cell Integral Diffusion Coefficient (cm^2 sec^{-1}) $\bar{D} \times 10^5$
0.2264	0.0	0.1691	0.0585	64.00	65.00	0.452
0.4890	0.0	0.3936	0.0974	63.80	65.20	0.445
0.9382	0.0	0.7622	0.1796	63.20	65.80	0.437
1.3597	0.0	1.0316	0.3356	62.60	66.40	0.426
1.0560	0.6909	0.9703	0.7785	64.00	65.00	0.423
1.1662	0.9685	1.1193	1.0165	64.20	64.80	0.417
1.9218	1.5998	1.8682	1.6546	64.00	65.00	0.349

Table 31

Differential and Integral Diffusion Coefficients of Sodium Chlorate in 64.5% Dioxane - 35.5% Water at 25°C Calculated from the Equations

$$D = A + 2Bc + 3Ec^2 + 4Fc^3$$

$$\bar{D} = A + B(c_{m'} + c_{m''}) + E(c_{m'}^2 + c_{m'}c_{m''} + c_{m''}^2) + F(c_{m'}^3 + c_{m'}^2 c_{m''} + c_{m'} c_{m''}^2 + c_{m''}^3)$$

(for details of calculations see page 74)

Constant	Deviation in Constant
A = 0.46191	---
B = -0.04782	0.01258
E = 0.03264	0.01137
F = -0.01130	0.00301

$c = c_{m'} = \frac{c_1 + c_3}{2}$ (moles/liter)	$c_{m''} = \frac{c_2 + c_4}{2}$ (moles/liter)	Calculated Integral Diffusion Coefficient (cm^2 sec^{-1}) $\bar{D} \times 10^5$	Differential Diffusion Coefficient (cm^2 sec^{-1}) $D \times 10^5$
0.1978	0.0293	0.452	0.446
0.4413	0.0487	0.444	0.435
0.8502	0.0898	0.435	0.424
1.1957	0.1678	0.428	0.410
1.0132	0.7347	0.423	0.418
1.1428	0.9925	0.416	0.413
1.8950	1.6272	0.349	0.325

Table 32

Diaphragm-Cell Integral Diffusion Coefficients of Lithium Chlorate in 64.5% Dioxane - 35.5% Water at 25°C.

Initial Concentration in Bottom Compartment (moles/liter) c_1	Initial Concentration in Top Compartment (moles/liter) c_2	Final Concentration in Bottom Compartment (moles/liter) c_3	Final Concentration in Top Compartment (moles/liter) c_4	Wt. % Dioxane in Bottom Compartment at end of Experiment	Wt. of Dioxane in Top Compartment at end of Experiment	Diaphragm-Cell Integral Diffusion Coefficient (cm^2 sec^{-1}) $\bar{D} \times 10^5$
0.1073	0.0	0.0868	0.0210	64.40	64.60	0.401
0.2164	0.0	0.1776	0.0397	64.30	64.70	0.406
0.6168	0.0	0.4868	0.1330	63.80	65.20	0.418
1.1353	0.0	0.9211	0.2191	63.65	65.35	0.433
1.8124	0.0	1.4388	0.3821	63.20	65.80	0.427
4.0171	0.0	3.3035	0.7298	62.50	66.50	0.395
5.5560	1.9071	4.9484	2.5250	62.80	66.20	0.264
6.0333	4.8601	5.9375	4.9579	64.10	64.90	0.157

Table 33

Differential and Integral Diffusion Coefficients of Lithium Chlorate in 64.5% Dioxane - 35.5% Water at 25°C Calculated from the Equations

$$D = A + 2Bc + 3Ec^2 + 4Fc^3$$

$$\bar{\bar{D}} = A + B(c_{m'} + c_{m''}) + E(c_{m'}^2 + c_{m'}c_{m''} + c_{m''}^2)$$
$$F(c_{m'}^3 + c_{m'}^2 c_{m''} + c_{m'} c_{m''}^2 + c_{m''}^3)$$

(for details of calculations see page 74)

Constant	Deviation in Constant
$A = 0.39569$	---
$B = 0.04830$	0.00542
$E = -0.01868$	0.00176
$F = 0.00138$	0.00016

$c = c_{m'} = \frac{c_1 + c_3}{2}$ (moles/liter)	$c_{m''} = \frac{c_2 + c_4}{2}$ (moles/liter)	Calculated Integral Diffusion Coefficient (cm^2 sec^{-1}) $\bar{\bar{D}} \times 10^5$	Differential Diffusion Coefficient (cm^2 sec^{-1}) $D \times 10^5$
0.0871	0.01049	0.400	0.400
0.1970	0.01985	0.405	0.405
0.5518	0.0665	0.419	0.417
1.0282	0.1096	0.430	0.427
1.6256	0.1911	0.434	0.431
3.6603	0.3649	0.388	0.390
5.2522	2.2161	0.267	0.334
5.9854	4.9090	0.155	0.312

C. CONDUCTANCE, DENSITY, AND VISCOSITY

Table 34

Densities, Viscosities, and Conductances of Sodium Chlorate in 44.5% Dioxane - 55.5% Water at 25°C.

Concentration (moles/liter)	Density (gm/c.c.)	Relative Viscosity to water (Water = 1.00)	Specific Conductance (mhos/cm) x 10^3	Equivalent Conductance (mhos)
0.0	1.0310	2.0041	---	57.75[a]
0.01007	1.0316	2.0121	0.5103	50.68
0.0995	1.0375	2.0356	4.202	42.24
0.3900	1.0560	2.1200	14.026	35.96
0.9837	1.0937	2.3242	29.963	30.46
1.8817	1.1502	2.7478	46.567	24.75
2.7354	1.2034	3.2912	56.106	20.51
3.5404	1.2535	4.0163	59.975	16.94

---

[a] Limiting equivalent conductance interpolated from the data of Accascina and D'Aprano[53].

Table 35

Densities, Viscosities, and Conductances of Lithium Chlorate in 44.5% Dioxane - 55.5% Water at 25°C.

Concentration (moles/liter)	Density (gm/c.c.)	Relative Viscosity to water (Water = 1.00)	Specific Conductance (mhos/cm) x 10^3	Equivalent Conductance (mhos)
0.0	1.0310	2.0041	----	52.05[a]
0.01804	1.0318	2.0108	0.7886	43.71
0.1101	1.0365	2.0619	4.177	37.94
0.5262	1.0571	2.2446	16.328	31.03
1.0103	1.0808	2.4908	27.174	26.90
2.7484	1.1653	3.7072	46.877	17.06
4.9544	1.2734	7.1275	44.480	8.978
6.7555	1.3586	13.065	35.666	5.280
8.8705	1.4598	28.099	26.278	2.962

---

[a] Limiting equivalent conductance interpolated from the data of Accascina, D'Aprano, and Triolo[54].

Table 36

Densities, Viscosities, and Conductances of Sodium Chlorate in 64.5% Dioxane - 55.5% Water at 25°C.

Concentration (moles/liter)	Density (gm/c.c.)	Relative Viscosity to water (Water = 1.00)	Specific Conductance (mhos/cm) x 10^3	Equivalent Conductance (mhos)
[a]0.0	1.0366	2.159	----	46.69
[a]0.01870	1.0378	2.172	0.5792	30.98
[a]0.05209	1.0400	2.193	1.4110	27.09
[a]0.09818	1.0428	2.229	2.4289	24.74
[a]0.2787	1.0545	2.329	5.9605	21.39
[a]0.5757	1.0736	2.505	10.811	18.78
[a]1.0290	1.1019	2.823	16.752	16.28
[a]1.2681	1.1168	3.009	19.275	15.20
1.5343	1.1336	3.260	21.156	13.79
2.0336	1.1646	3.804	24.315	11.96

---

[a] From Campbell, Karzmark, and Oliver[23].

Table 37

Densities, Viscosities and Conductances of Lithium Chlorate in 64.5% Dioxane - 35.5% Water at 25°C.

Concentration (moles/liter)	Density (gm/c.c.)	Relative Viscosity to Water (Water = 1.00)	Specific Conductance (mhos/cm) x 10^3	Equivalent Conductance (mhos)
0.0	1.0366	2.159	---	43.10[a]
0.01571	1.0377	2.186	0.4827	30.73
0.1025	1.0421	2.257	2.478	24.18
0.4207	1.0583	2.548	8.350	19.85
1.0024	1.0876	3.127	15.746	15.71
1.9258	1.1336	4.506	21.222	11.02
3.4093	1.2065	8.777	20.498	6.012
6.0521	1.3347	33.19	12.064	1.993

---

[a] Limiting equivalent conductance from Campbell, Kartzmark and Oliver[23].

A. VAPOUR PRESSURE AND COMPOSITION

The graphs of activity coefficients, γ, versus molality for sodium and lithium chlorates in water at $25^\circ C$ are shown in Figure 7. The accuracy of the activity coefficients plotted on this graph and calculated by the method described on page 62 of this thesis is ± 0.5%. The curve for lithium chlorate lies considerably above that of sodium chlorate over the entire concentration range. This is consistent with the idea that the smaller lithium ion ($r = 0.68\mathring{A}$) is more extensively hydrated in aqueous solution than the larger sodium ion ($r = 0.97\mathring{A}$). The extremely high value reached by the activity coefficient ($\gamma = 16.25$ at 43.7577 molal) is probably due to the extensive hydration of the lithium ion.

Attempts were made to treat these experimental results with the theoretical equations of Stokes and Robinson[3] mentioned earlier in the thesis.

Their equation is:

$$\log \gamma_{\pm} = \frac{- A \mid Z_1 \, Z_2 \mid I^{1/2}}{1 + B\, a\, I^{1/2}} - \frac{h}{\nu} \log a_A - \log \left[1 + 0.001\, W_A(\nu - h)m\right] \tag{28}$$

This equation contains two adjustable parameters: 'h' and 'a'. Earlier in this thesis a method of dispensing with 'a' as an arbitrary parameter was described. But, in a more recent paper, Stokes and Robinson[55] have stated that this method is invalid. Therefore, I have employed the equation for 'a' developed in their later paper.[55]

Stokes and Robinson's derivation of an expression for 'a' is

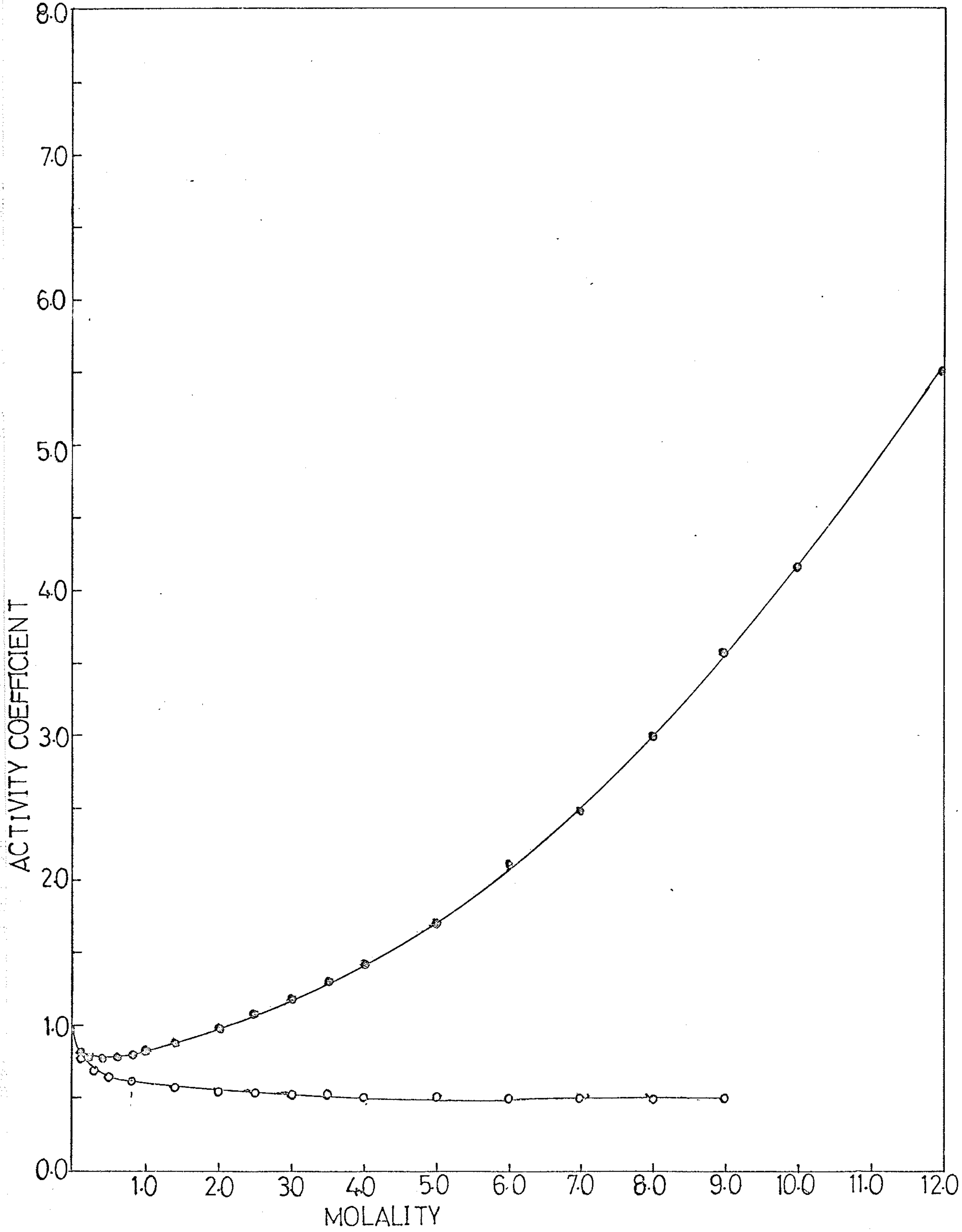
DISCUSSION

Figure 7

Mean Molal Activity Coefficient Versus Molality for Sodium Chlorate and of Lithium Chlorate in Water at 25°C.

○ Sodium Chlorate

● Lithium Chlorate.


8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ACTIVITY COEFFICIENT
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
MOLALITY

based on the observation of Adler[56] that the fraction of volume occupied by spherical molecules is 58% of the total volume. Thus, spherical ions which dissolve without significant electrostriction of surrounding water molecules might be expected to contribute an amount $4\pi b^3/(3 \times 0.58)$ per ion of radius 'b' to the volume of the system, i.e., the molar volume for such ions should be

$$\bar{V}^{o} = \frac{4\ \pi\ N\ b^3}{3 \times 0.58} = 4.35 \times 10^{24}\ b^3 \qquad (143)$$

If an ion contained 'h' molecules of water of hydration, its volume would be $\bar{V}_h = (\bar{V}^o + 18\ h)\ cm^3\ mole^{-1}$, and if it obeyed equation (143) its radius 'b_h' would be

$$b_h = [(\bar{V}^o + 18\ h)/4.35 \times 10^{24}]^{1/3} \qquad (144)$$

Assuming that only the cation is hydrated the Debye-Hückel parameter 'a' is

$$a = [(\bar{V}^o_+ + 18h)/4.35 \times 10^{24}]^{1/3} + [\bar{V}^o_-/4.35 \times 10^{24}]^{1/3} \qquad (145)$$

The partial molal volumes of the sodium and lithium ions which were introduced into the above equation were obtained from the data of Mukerjee[57]. The value for the chlorate ion was obtained from Conture and Laidler[58]. Taking the partial molal volume of hydrogen ion to be $\bar{V}^o_{H^+} = -4.5$c.c./mole, the partial molal volumes of the other ions are $\bar{V}^o_{Na^+} = -5.7$c.c./mole $\bar{V}^o_{Li^+} = -5.2$c.c/mole $\bar{V}^o_{ClO_3^-} = +40.9$c.c./mole.

The values of the hydration number 'h' which best fit the experimental data, the 'a' values calculated by the above method, and the calculated activity coefficients are presented in Tables 38 and 39.

Table 38 shows good agreement between the experimental activity coefficients of sodium chlorate and the theory over the entire concentration range. This is to be expected, since sodium chlorate is only slightly hydrated ($h = 1.05$) and there are plenty of free water molecules even at saturation. On the other hand, the theory begins to break down at about 2 molal for lithium chlorate (Table 39). This also is not surprising, since lithium chlorate is highly hydrated ($h = 6.7$), and there are only a limited number of water molecules available. In fact, Stokes and Robinson[3] have stated that in the majority of cases the equation breaks down when the product of the hydration number 'h' and the molality 'm' exceeds 10 or 15. Thus, the equation would not be expected to hold above 2 molal lithium chlorate because h x m is greater than 15. To proceed to higher concentrations it would be necessary to use a hydration number which was a suitably decreasing function of concentration.

Next the experimental activity coefficients were fitted to the equation developed by Gleuckauf[4].

$$\ln \gamma_{\pm} = \frac{- A \, |Z_1 \, Z_2| \, (I)^{1/2}}{1 + B \, a \, (I)^{1/2}} + 0.018 \, m \, r \, (r + h - \nu) + \frac{h - \nu}{\nu} \ln(1 + 0.018 \, m \, r) - \frac{h}{\nu} \ln(1 - 0.018 \, m \, h) \qquad (34)$$

This equation has two adjustable parameters 'h' and 'a'. The number of adjustable parameters was reduced to one by substitution of equation (145) for 'a'.

The values of the hydration number 'h' which fit the experimental data best, the 'a' values calculated by equation (145), and the calculated activity coefficients are shown in Tables 40 and 41.

Table 38

Activity Coefficients of Sodium Chlorate in Water at 25°C Calculated by the Stokes - Robinson Equation (28).

h = 1.05 a = 3.56

Concentration (moles/Kg. of solvent) m	γ observed	γ calculated	Deviation
1.0	0.589*	0.586	-0.003
1.2	0.575*	0.573	-0.002
1.4	0.563*	0.563	0.000
1.6	0.553*	0.554	+0.001
1.8	0.545*	0.547	+0.002
2.0	0.538*	0.540	+0.002
2.5	0.525*	0.528	+0.003
3.0	0.515*	0.518	+0.003
3.5	0.508*	0.511	+0.003
4.0	0.506	0.505	-0.001
5.0	0.501	0.496	-0.005
6.0	0.497	0.490	-0.007
7.0	0.493	0.485	-0.008
8.0	0.489	0.482	-0.007
9.0	0.490	0.480	-0.010
9.4319	0.491	0.479	-0.012

* From Jones[47].

Table 39

Activity Coefficients of Lithium Chlorate in Water at 25°C Calculated by the Stokes-Robinson Equation (28).

h = 6.7 a = 5.09

Concentration (moles/Kg. of solvent) m	γ observed	γ calculation	Deviation
1.0	0.809	0.806	-0.003
1.2	0.837	0.834	-0.003
1.4	0.868	0.866	-0.002
1.6	0.905	0.903	-0.002
1.8	0.946	0.943	-0.003
2.0	0.988	0.988	0.000
2.5	1.088	1.118	+0.030
3.0	1.193	1.279	+0.086
3.5	1.306	1.478	+0.172
4.0	1.428	1.727	+0.299
5.0	1.711	2.440	+0.729
6.0	2.104	3.614	+1.410
7.0	2.472	5.660	+3.188
8.0	2.990	9.534	+6.544
9.0	3.562	17.39	+13.828
10.0	4.161	36.34	+32.179

Table 40

Activity Coefficients of Sodium Chlorate in Water at 25°C. Calculated by Gleuckauf's Equation (34).

$h = 0.96$ $a = 3.50$ $r = 1.948$

Concentration (moles/Kg. of solvent) m	γ observed	γ calculated	Deviation
1.0	0.589*	0.587	-0.002
1.2	0.575*	0.574	-0.001
1.4	0.563*	0.565	+0.002
1.6	0.553*	0.556	+0.003
1.8	0.545*	0.549	+0.004
2.0	0.538*	0.544	+0.006
2.5	0.525*	0.532	+0.007
3.0	0.515*	0.523	+0.008
3.5	0.508*	0.516	+0.008
4.0	0.506	0.511	+0.005
5.0	0.501	0.503	+0.002
6.0	0.497	0.499	+0.002
7.0	0.493	0.495	+0.002
8.0	0.489	0.492	+0.003
9.0	0.490	0.491	+0.001
9.4319	0.491	0.490	-0.001

* From Jones[47].

Table 41

Activity Coefficients of Lithium Chlorate in Water at 25°C. Calculated by Gleuckauf's Equation (34)

h = 3.97　　a = 4.59　　r = 1.976

Concentration (moles/Kg. of solvent) m	γ observed	γ calculated	Deviation
1.0	0.809	0.808	-0.001
1.2	0.837	0.836	-0.001
1.4	0.868	0.868	0.000
1.6	0.905	0.904	-0.001
1.8	0.946	0.942	-0.004
2.0	0.988	0.983	-0.005
2.5	1.088	1.102	+0.014
3.0	1.193	1.242	+0.049
3.5	1.306	1.408	+0.102
4.0	1.428	1.605	+0.177
5.0	1.711	2.119	+0.408
6.0	2.204	2.865	+0.661
7.0	2.472	3.992	+1.520
8.0	2.990	5.788	+2.798
9.0	3.562	8.851	+5.289
10.0	4.161	14.66	+10.499

This equation represents the data as well as the Stokes-Robinson equation. In fact, it seems to be valid over the entire concentration range for sodium chlorate and up to 2.5 molal for lithium chlorate. The hydration numbers found by this method are lower than those obtained by the Stokes-Robinson equation in agreement with the findings of Gleuckauf[4].

The hydration numbers 'h' and the distance of closest approach 'a' obtained from both the Stokes-Robinson equation and the Gleuckauf equation seem to be of the right order of magnitude. Lithium chlorate is found to be more highly hydrated than sodium chlorate.

Although Gleuckauf's derivation takes into account the size differences between the hydrated ions and the water molecules, Gleuckauf, Stokes, and Robinson assume that all the differences between the experimental and the calculated activity coefficients can be ascribed to hydration. It is true that the resulting equations are remarkably useful in describing observed results, but this should not obscure the fact that, while hydration is a very important factor, it is not the only one which determines the complicated equilibria in an electrolyte solution. To put it briefly, the secondary hydration has been stretched to cover a number of effects, the quantitative nature of which requires a great deal of investigation.

I made attempts to get some information on the behavior of the concentrated lithium chlorate solutions using the concept of Stokes and Robinson[3] that the ions adsorb layers of water molecules in accordance with the Brunauer, Emmet, and Teller equation[59]. Modifying the notation of these authors to suit the present case, their equation is

$$\frac{m\ a_w}{55.51\ (1 - a_w)} = \frac{1}{b\ g} + \frac{(b - 1)}{b\ g}\ a_w \qquad (146)$$

where 'a_w' is the water activity of the solution; 'm' is the molality; 'g' is the number of molecules of water in the monomolecular hydration layer when it is complete; and 'b' is a constant related to the heat of adsorption E of the molecules in the layer given by the approximate relation $b = \exp\ (E - E_L)/RT$, E_L being the heat of liquéfaction of pure water. Equation (146) may be tested by plotting the left hand side (determined from experimental 'm' and a_w) against 'a_w'. It is evident from Figure 8 that a straight line is obtained for lithium chlorate in water at 25°C when the water activity of the solution is less than 0.420, i.e., above 12 molal. The best values of the parameters 'b' and 'g' were obtained from the slope and intercept of the line by the method of least squares. The values of 'b' and 'g', the calculated water activities, and the deviations are presented in Table 42.

The accuracy of the fit is fairly good over the range 12 to 44 molal. The value of 'g', 3.11, is between 3 and 4 in accordance with the values found by Stokes and Robinson[3] for other 1-1 electrolytes. The value of the parameter 'b', 8.75, is also reasonable, corresponding to $E - E_L$ = 1.29 Kcal. per mole. of water absorbed.

An unsatisfactory feature of equation (146) is that it demands a non-integral 'g' value. This can scarcely correspond to any physical reality, and has more likely arisen as a result of approximations in the Brunauer,

Figure 8

$\frac{m\ a_w}{55.51\ (1 - a_w)}$ Versus a_w for Lithium Chlorate in Water at 25°C.

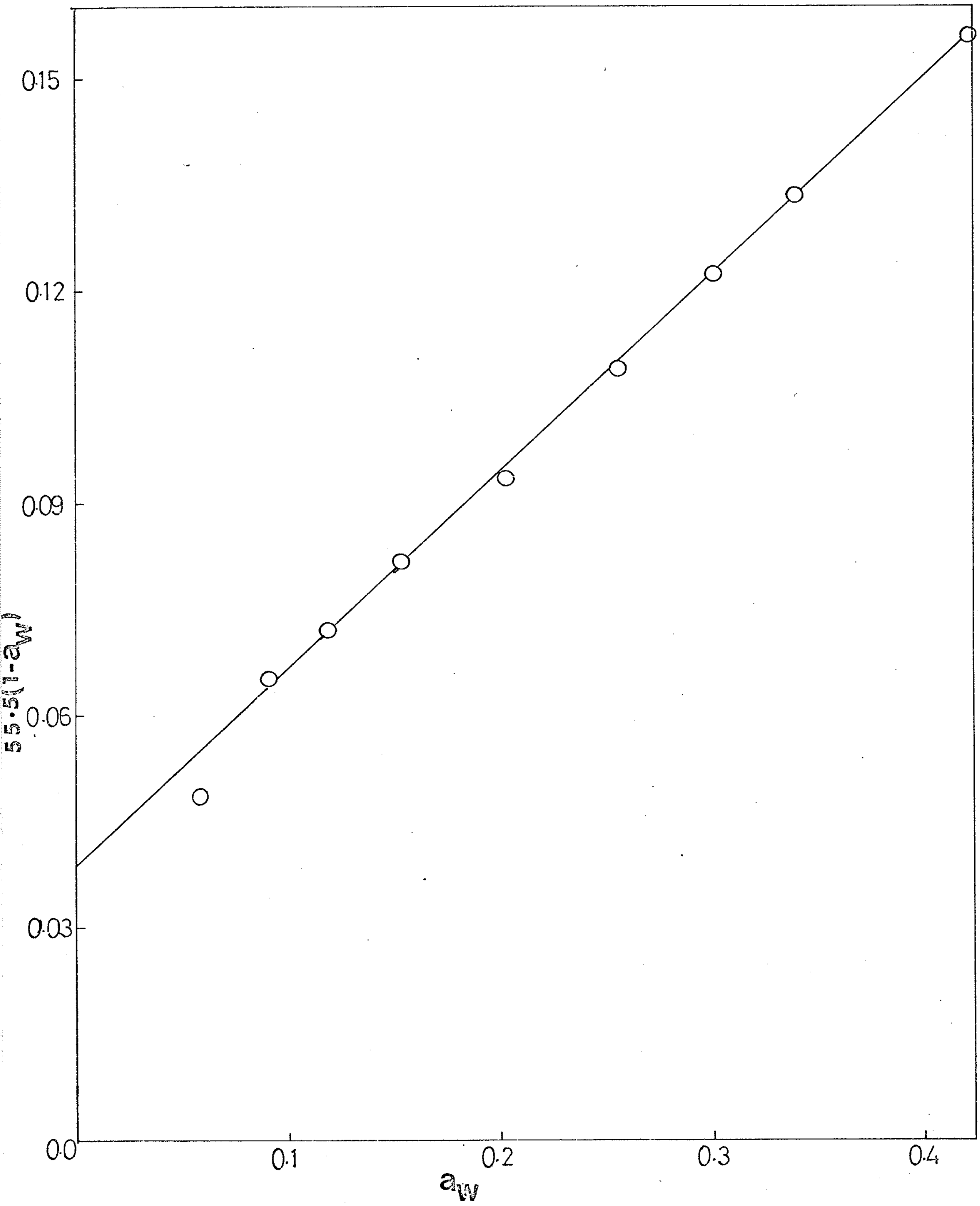

0.15
0.12
0.09
0.06
0.03
0.0
55.5(1-a_W)
0.0
0.1
0.2
0.3
0.4
a_W

Table 42

Water Activities of Concentrated Lithium Chlorate at 25°C, Fitted to the Equation

$$\frac{m\ a_w}{55.51\ (1 - a_w)} = \frac{1}{b\ g} + \frac{(b - 1)}{b\ g}\ a_w$$

$b = 8.75$ $g = 3.11$

Concentration (moles/Kg. of solvent) m	a_w observed	a_w calculated	Deviation
11.9558	0.4206	0.4208	+0.0002
14.3953	0.3398	0.3396	-0.0002
15.7749	0.3014	0.3010	-0.0004
17.6402	0.2561	0.2568	+0.0007
20.3290	0.2037	0.2071	+0.0034
25.1763	0.1531	0.1481	-0.0050
30.2305	0.1170	0.1117	-0.0053
36.5241	0.0903	0.0846	-0.0057
43.7577	0.0581	0.0657	+0.0076
		Average Deviation	0.0032

Emmett and Teller theory and its application to this case. The most drastic of these approximations is that of treating all water molecules beyond the first layer as held by ordinary liquid forces, with a heat of liquefaction E_L.

Anderson[60] has deduced a modification of the B-E-T equation in which the subsequent layers have a heat of adsorption less than that of water by 'd'. This has the effect of multiplying a_w, wherever it occurs in (146) by a factor $K = e^{-d/RT}$ leading to the equation

$$\frac{m\, a_w}{55.51\,(1 - K a_w)} = \frac{1}{bKg} + \frac{(b - 1)}{b\, g}\, a_w \tag{147}$$

To test the appropriateness of this equation the value of g is set at 4.0. Then equation (147) is written in the form

$$b = \left(\frac{1}{K} - a_w\right) \Big/ \left(\frac{g\, m\, a_w}{55.51(1 - K\, a_w)} - a_w\right) \tag{148}$$

and, by trial and error, the value of K which leads to a reasonably constant 'b' over the widest possible range of molality is found. The values of the parameters 'b' and 'K', the calculated water activities, and the deviations are shown in Table 43.

The average deviation of equation (147) is the same as that of equation (146), although the range fitted is slightly smaller (12 - 37 molal). The value of the parameter 'b', 6.9, is plausible and corresponds to $E - E_L = 1.14$ Kcal. per mole. of water absorbed. The K parameter, 0.785, corresponds to d = 0.14 Kcal. per mole. of water in the second and subsequent layers. This relatively small energy might easily correspond to a weak ordering effect on the water molecules

Table 43

Water Activities of Concentrated Lithium Chlorate at 25°C, Fitted to the Equation

$$\frac{m\, a_w}{55.51\,(1 - K a_w)} = \frac{1}{bKg} + \frac{(b - 1)}{b\, g}\, a_w$$

$b = 6.9$ $g = 4.0$ $K = 0.785$

Concentration (moles/Kg. of solvent) m	a_w observed	a_w calculated	Deviation from Experimental a_w
11.9558	0.4206	0.4230	+0.0024
14.3953	0.3398	0.3342	-0.0056
15.7749	0.3014	0.2952	-0.0062
17.6402	0.2561	0.2525	-0.0036
20.3290	0.2037	0.2065	+0.0028
25.1763	0.1531	0.1530	-0.0001
30.2305	0.1170	0.1192	+0.0022
36.5241	0.0903	0.0930	+0.0027
		Average Deviation	0.0032

concerned. The parameter b has a value of 4 which means that lithium chlorate has 4 sites available for occupation by water molecules in the inner layer, each being held with an energy some 1.14 Kcal./mole greater than the latent heat of evaporation of water, which is 10.48 Kcal./mole at 25°C.

The Stokes-Robinson approach used for lower concentrations and the Brunauer-Emmett-Teller approach used for higher concentrations are not self-contradictory. Between these concentrations the hydration number, 'h', is diminishing and the ions are tending to a quasi-crystalline structure with some of the water molecules imbedded in the remnants of crystal lattice (adsorbed water) and some present as "free" solvent. There is nothing contradictory in these two methods of approach, rather they are limiting cases of a more general theory which would cover the entire concentration range.

I undertook a study of the vapour pressures and vapour compositions of sodium and lithium chlorate in dioxane-water mixtures to see what effect changing the solvent would have on the activities of the salts. The systems studied are numbered and the physical properties of the solvents are shown in Table 44. As previously mentioned, it is possible to deduce the activities of all three components in these systems by a method developed by Grunwald and Bacarella[17]. Before discussing this procedure and the resulting activity coefficients of the salts it is interesting to examine some of the trends of the solvent activities in the various systems.

The variation of water and dioxane activity with salt concentration is shown in Figures 9 to 12. The accuracy of these results is ± 0.5%.

Table 44

The Systems Studied and the Densities, Dielectric Constants and Viscosities of the Solvents at 25°C.

Number	System	Density of Solvent (gr/cc.)	Dielectric Constant of Solvent	Viscosity (Centipoise)
1	Sodium Chlorate in Water	0.9971	78.3	0.890
2	Lithium Chlorate in Water	0.9971	78.3	0.890
3	Sodium Chlorate in 44.5% Dioxane - 55.5% Water	1.0310	40.6	1.784
4	Lithium Chlorate in 44.5% Dioxane - 55.5% Water	1.0310	40.6	1.784
5	Sodium Chlorate in 64.5% Dioxane - 35.5% Water	1.0366	23.4	1.923
6	Lithium Chlorate in 64.5% Dioxane - 35.5% Water	1.0366	23.4	1.923

Figure 9 gives the change of the water and dioxane activity upon addition of sodium chlorate to a solvent consisting of 44.5% dioxane - 55.5% water. It can be seen that the water activity decreases upon addition of salt whereas the dioxane activity increases. These results can be explained by considering sodium chlorate to be strongly preferentially solvated by water. As salt is added to the solution more water than dioxane is bound by the salt in the formation of a solvation sheath. Thus the remaining solvent becomes richer in dioxane and the partial pressure and activity of dioxane in the system rises.

Similar changes in the water and dioxane activities are found when sodium chlorate is added to a solvent consisting of 64.5% dioxane - 35.5% water (Figure 11), and a similar explanation applies.

The changes in water and dioxane activity for lithium chlorate in 44.5% dioxane - 55.5% water (Figure 10) and for lithium chlorate in 64.5% dioxane - 35.5% water (Figure 12) are quite different from those of sodium chlorate. The water activity in the lithium chlorate decreases but to a greater extent than is the case for the systems with sodium chlorate, while the dioxane activity at first shows a slight increase, then decreases. The larger decrease in water activity in the case of lithium chlorate is to be expected because of higher hydration of the lithium ion. The change in dioxane activity can be explained by considering lithium chlorate to be preferentially solvated by water.

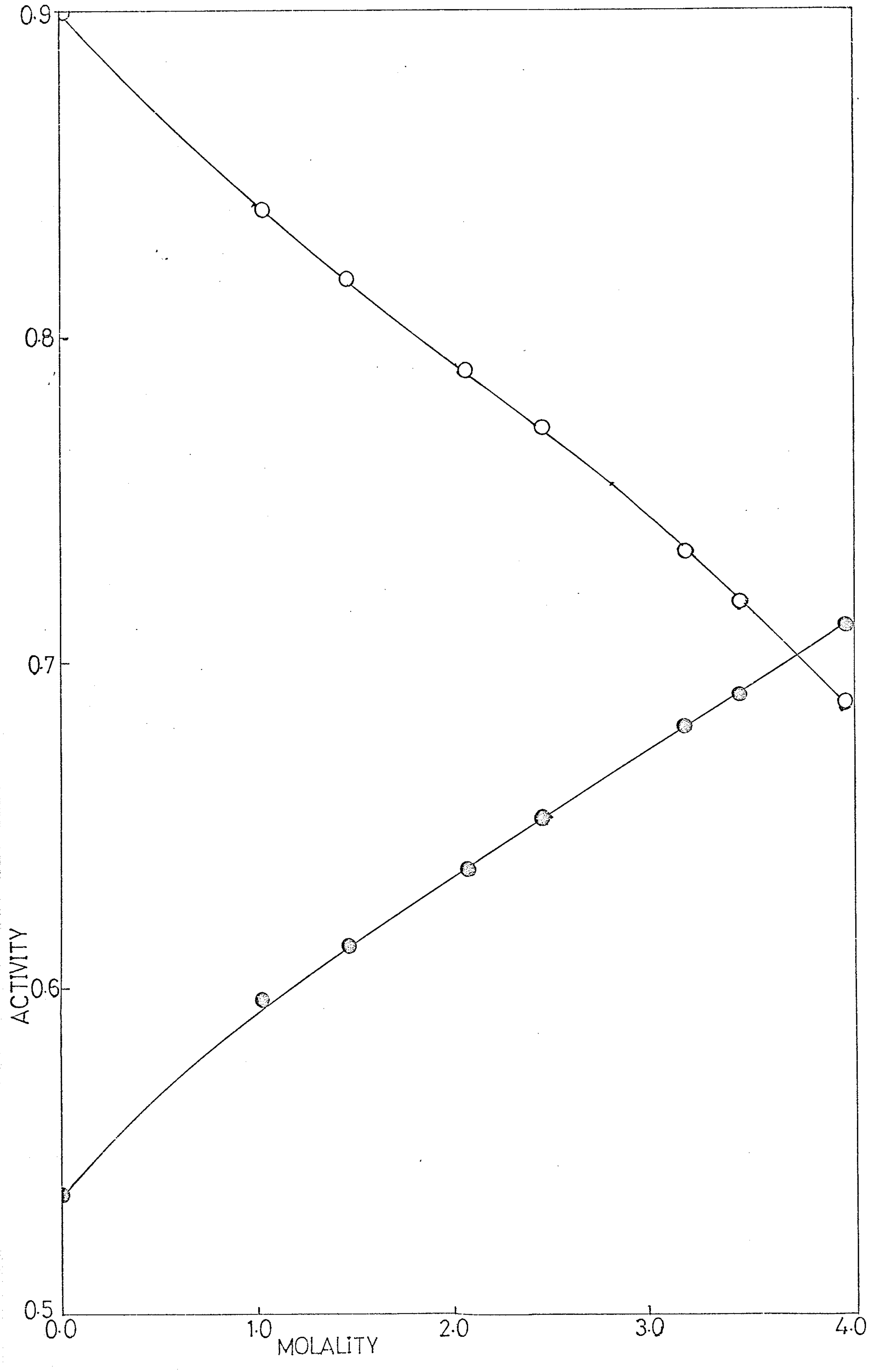
The activity coefficients of sodium and lithium chlorate in these

Figure 9

Water and Dioxane Activity Versus Molality for the System-Sodium Chlorate - 44.5% Dioxane - 55.5% Water at 25°C as Determined from Vapour Pressure and Composition.

○ Water Activity

● Dioxane Activity



0·9
0·8
0·7
0·6
0·5
ACTIVITY
0·0
1·0
2·0
3·0
4·0
MOLALITY

Figure 10

Water and Dioxane Activity Versus Molality for the System - Lithium Chlorate - 44.5% Dioxane - 55.5% Water at 25°C as Determined from Vapour Pressure and Composition.

○ Water Activity

● Dioxane Activity

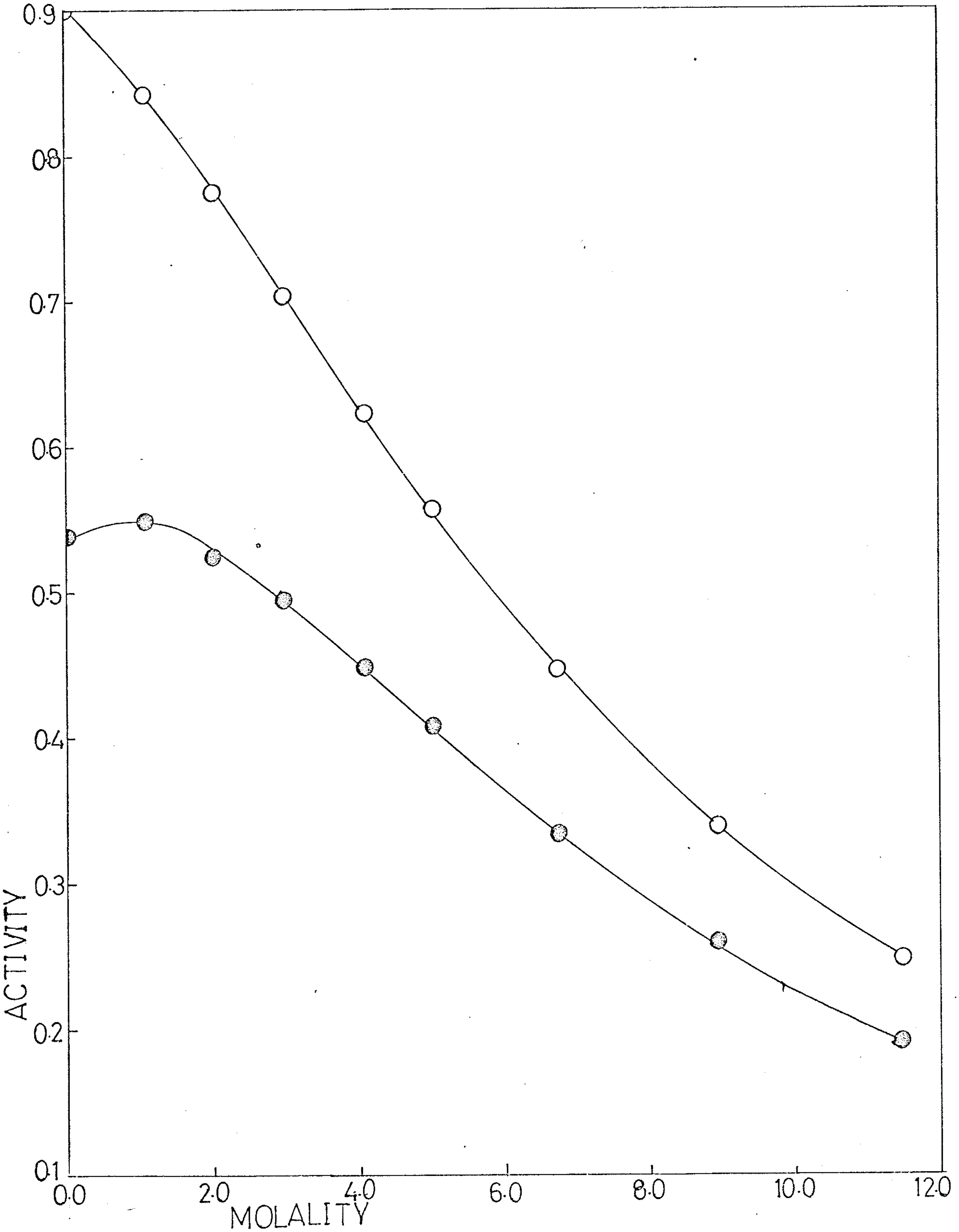

0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
ACTIVITY
0.0
2.0
4.0
6.0
8.0
10.0
12.0
MOLALITY

Figure 11

Water and Dioxane Activity Versus Molality for the System - Sodium Chlorate - 64.5% Dioxane - 35.5% Water at 25°C as Determined by Vapour Pressure and Composition

○ Water Activity

● Dioxane Activity

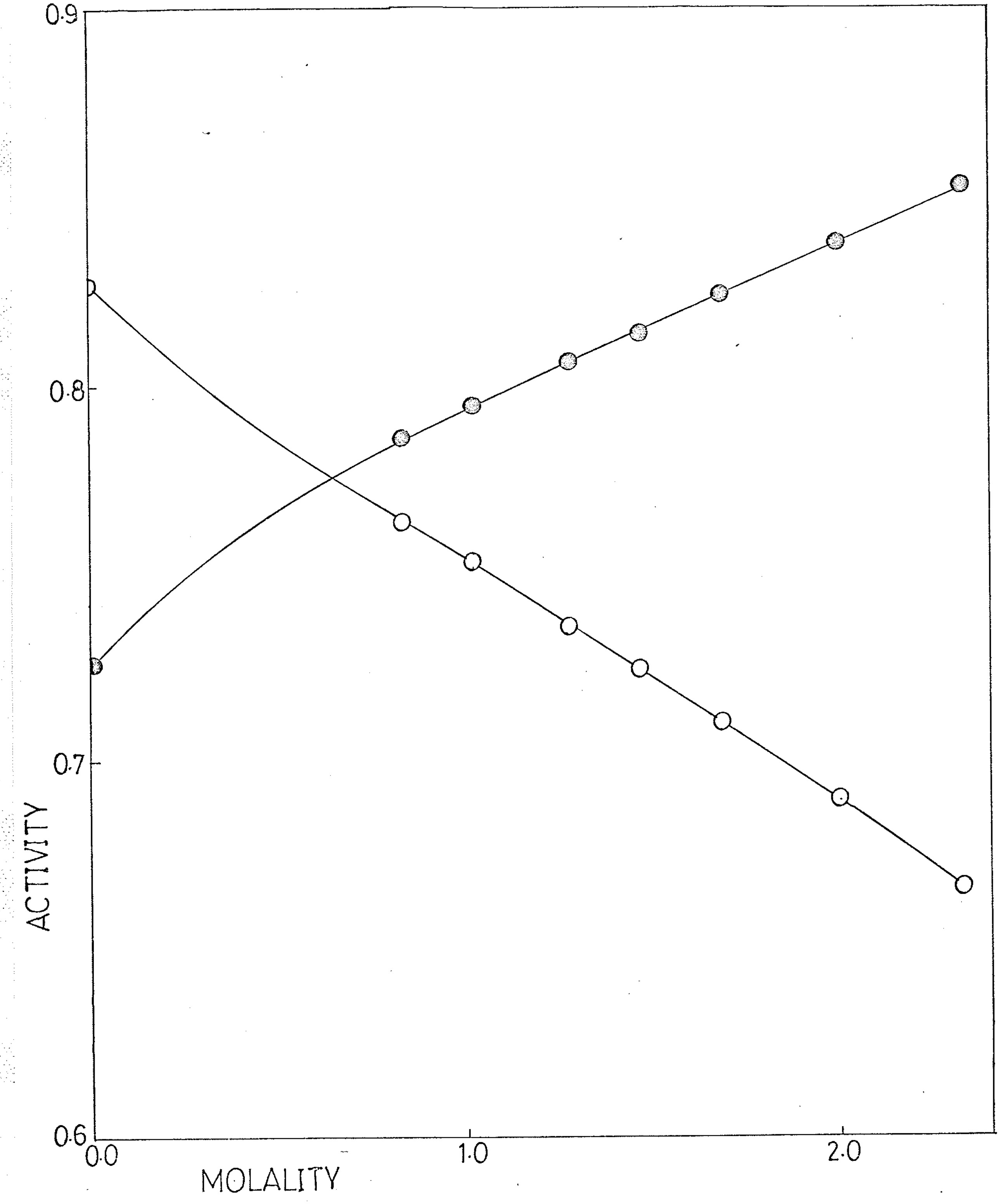
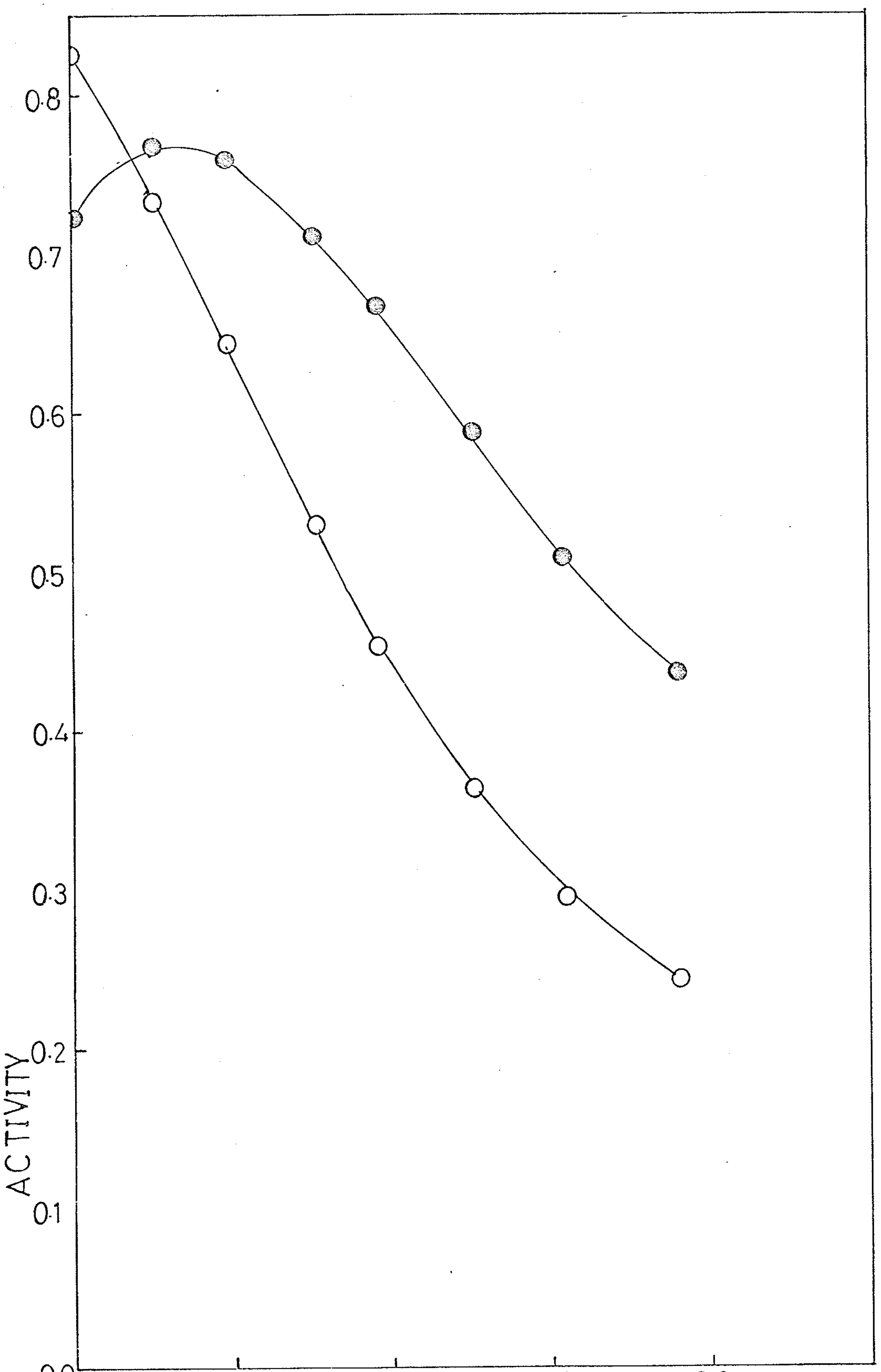

0.9
0.8
0.7
0.6
ACTIVITY
0.0
1.0
2.0
MOLALITY

Figure 12

Water and Dioxane Activity Versus Molality for the System - Lithium Chlorate - 64.5% Dioxane - 35.5% Water at 25°C as Determined by Vapour Pressure and Composition.

○ Water Activity

● Dioxane Activity


0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
ACTIVITY
2.0
4.0
6.0
8.0
MOLALITY

dioxane-water mixtures were calculated by the method of Grunwald and Bacarella[17]. The activity coefficients are represented by the power series

$$\ln \gamma_{\pm} = - S\ m^{1/2} + B\ m + C\ m^{3/2} + D\ m^2 \tag{127}$$

The Debye-Hückel limiting slope, S, is calculated from the known solvent properties while the constants B, C and D are found by applying the following equation to the data.

$$\frac{-1000}{M_{12}} (N_1 \ln \alpha_1 + N_2 \ln \alpha_2) = 2\ m - \frac{2}{3} S\ m^{3/2} + B\ m^2 + \frac{6}{5} C\ m^{5/2} + \frac{4}{3} D\ m^3 \tag{128}$$

The values of the constants calculated by the method of least squares on a computer are given in Tables 9, 13, 17, and 21. These constants reproduce the experimental quantity ($N_1 \ln \alpha_1 + N_2 \ln \alpha_2$) for systems 3,4,5, and 6 over the entire concentration range studied with a maximum deviation of 2%. Therefore, the activity coefficients tabulated in Table 9,13,17, and 21 are accurate to about 2%.

Graphs of the activity coefficient of sodium and lithium chlorate in 44.5% dioxane - 55.5% water and in 64.5% dioxane - 35.5% water are shown in Figures 13, and 14. The curve for lithium chlorate lies considerably above that of sodium chlorate over the entire concentration range. This behavior is similar to that in aqueous solution and can again be explained as due to a higher degree of solvation of the lithium ion.

Graphs of the variation in the activity coefficients of sodium and lithium chlorate with solvent composition are given in Figures 15 and 16. It can be seen that the activity coefficients of both sodium chlorate

Figure 13

Mean Molal Activity Coefficient Versus Molality for Sodium Chlorate and Lithium Chlorate in the Solvent – 44.5% Dioxane – 55.5% Water at 25°C.

○ Sodium Chlorate

● Lithium Chlorate

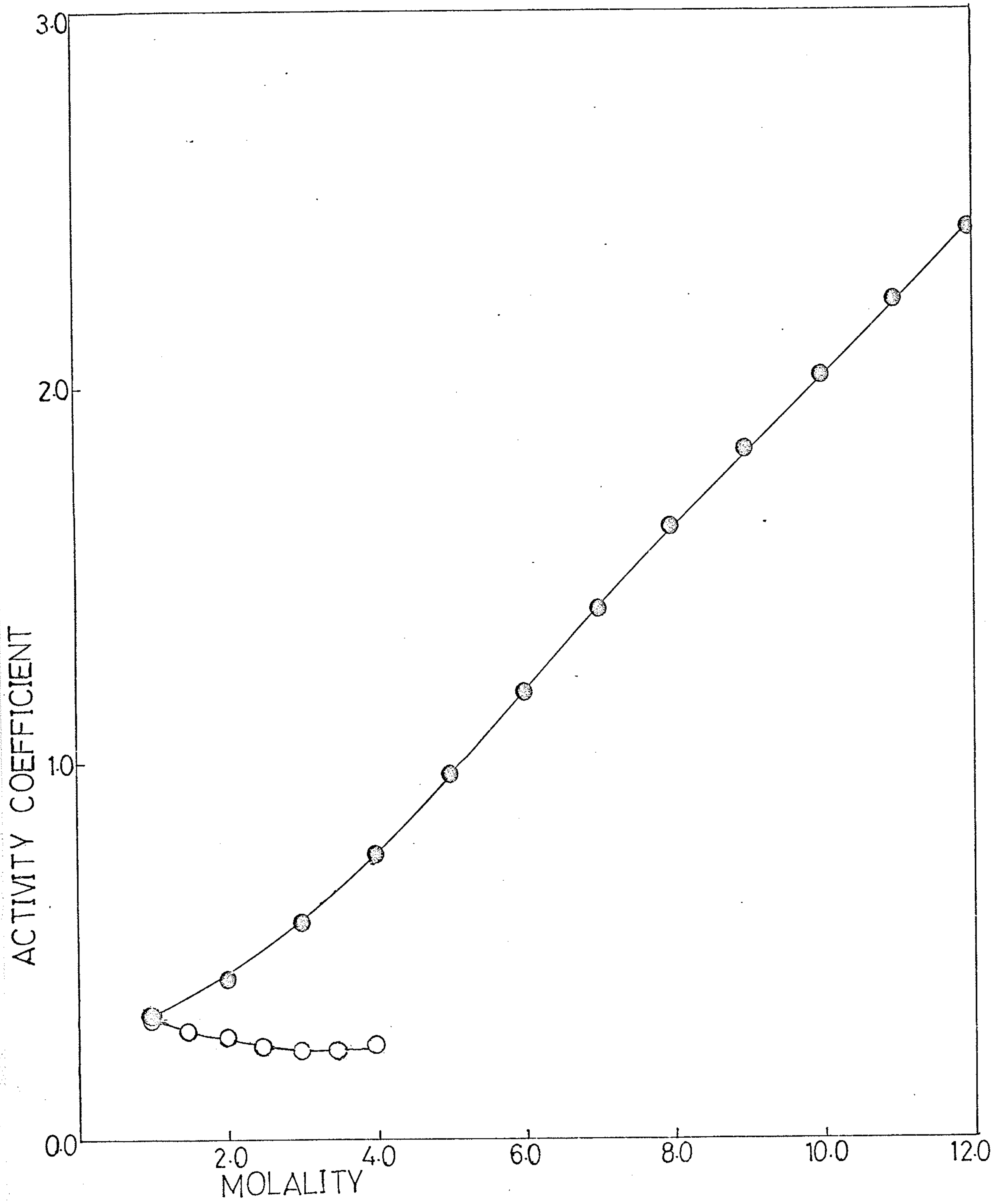

3.0
2.0
1.0
0.0
ACTIVITY COEFFICIENT
2.0
4.0
6.0
8.0
10.0
12.0
MOLALITY

Figure 14

Mean Molal Activity Coefficient Versus Molality for Sodium Chlorate and Lithium Chlorate in the Solvent - 64.5% Dioxane - 35.5% Water at 25°C.

○ Sodium Chlorate

● Lithium Chlorate

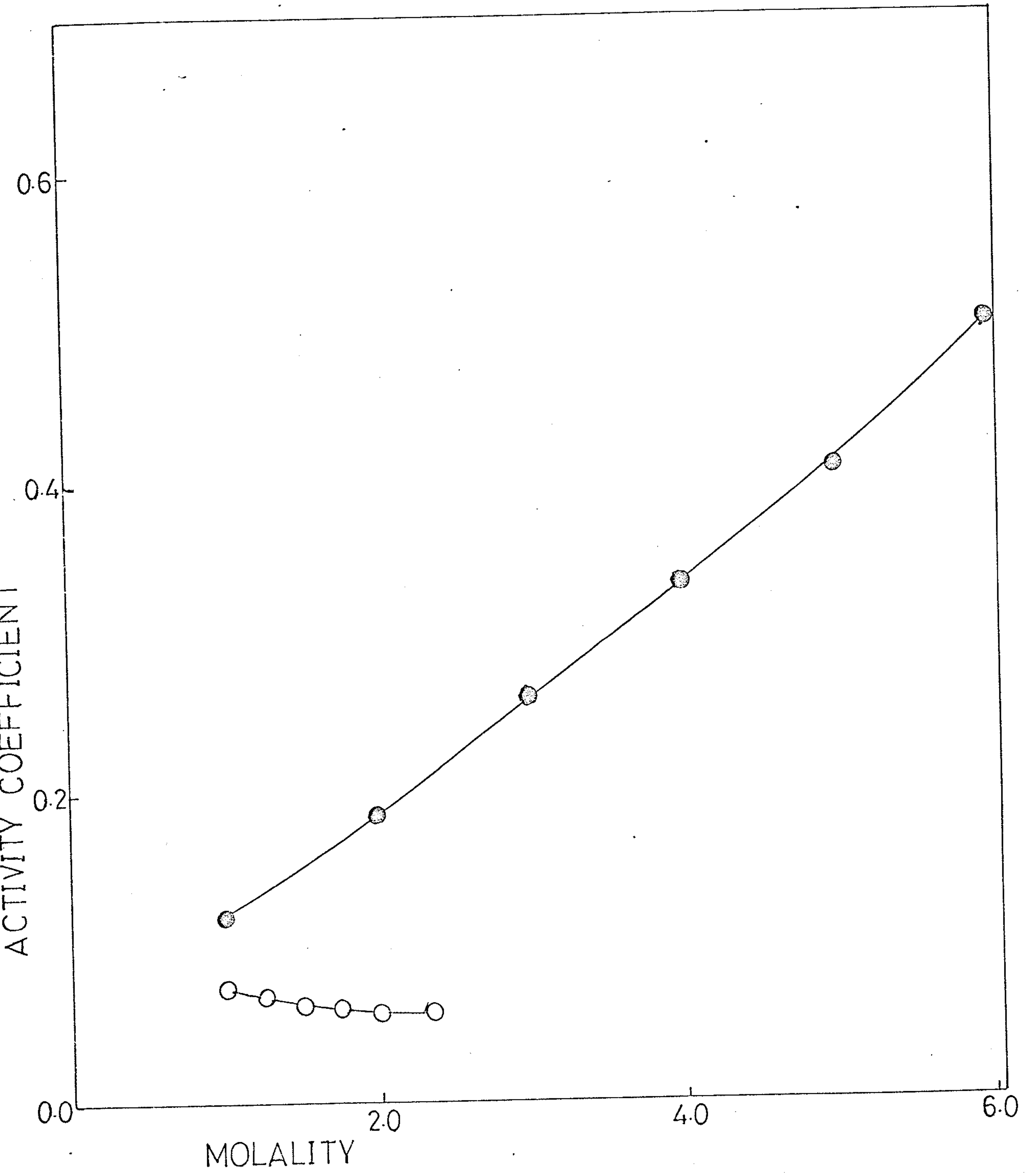

ACTIVITY COEFFICIENT
0.6
0.4
0.2
0.0
2.0
4.0
6.0
MOLALITY

Figure 15

Mean Molal Activity Coefficient Versus Molality for Sodium Chlorate in Water, 44.5% Dioxane - 55.5% Water, and 64.5% Dioxane - 35.5% Water at 25°C.

○ in Water

◓ in 44.5% Dioxane - 55.5% Water

● in 64.5% Dioxane - 35.5% Water

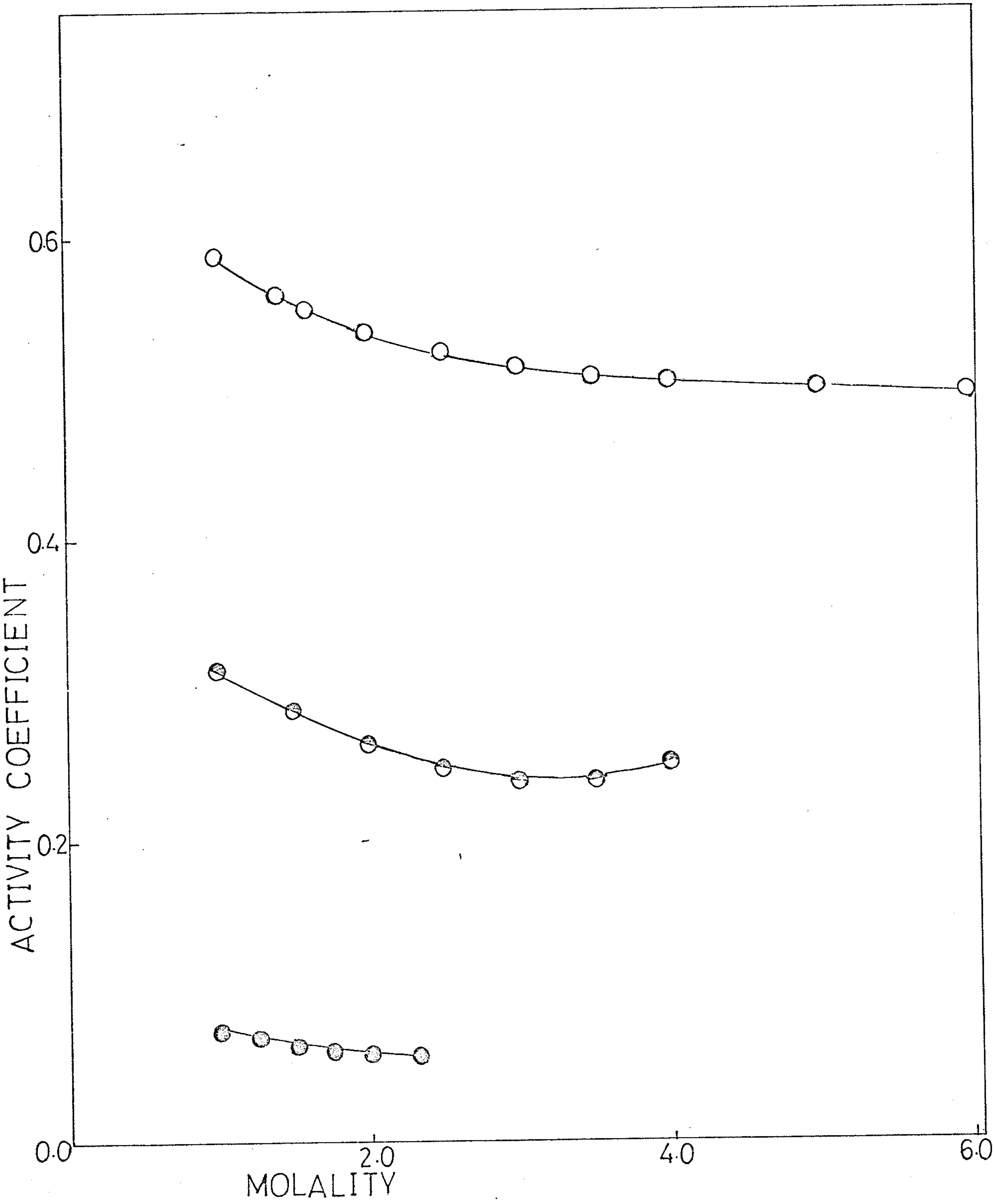

ACTIVITY COEFFICIENT
0.6
0.4
0.2
0.0
2.0
4.0
6.0
MOLALITY

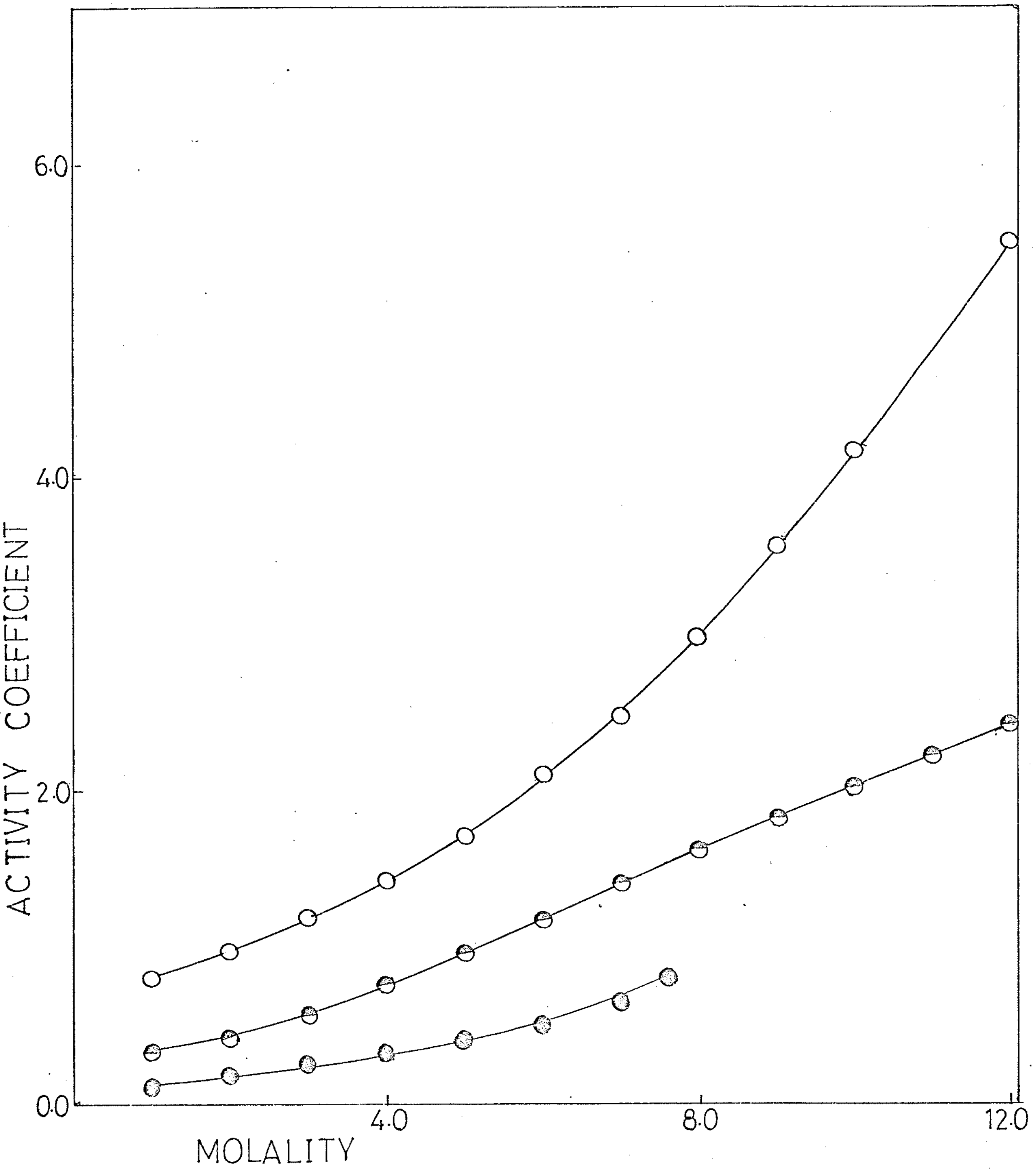
Figure 16

Mean Molal Activity Coefficient Versus Molality for Lithium Chlorate in Water, 44.5% Dioxane - 55.5% Water, and 64.5% Dioxane - 35.5% Water at 25°C.

○ in Water

◓ in 44.5% Dioxane - 55.5% Water

● in 64.5% Dioxane - 35.5% Water


6.0
4.0
2.0
0.0
ACTIVITY COEFFICIENT
4.0
8.0
12.0
MOLALITY

and lithium chlorate are greatly reduced on changing the solvent from water to 44.5% dioxane - 55.5% water and finally to 64.5% dioxane - 35.5% water. Much of the decrease can be ascribed to the large change in dielectric constant. Along with this decrease in dielectric constant an increased tendency toward ion pair formation in the mixed solvents undoubtly reduces the activity of the salts.

Many inconsistencies appear in the literature as to the nature of solvation in dioxane-water mixtures. Grunwald[19], in a study of a variety of electrolytes in 50% dioxane-water mixtures by a vapour pressure technique, observed partial solvation of the electrolytes by dioxane. Fratiello and Douglass[61] used nuclear magnetic resonance to show that the chlorides of Li, Na, K, Mg, Ca, Zn, and Cd, along with the sodium salts of I, NO_3, $Cl\ O_4$, and SO_4 are preferentially solvated by water in 50% dioxane-water mixtures. They found no evidence for solvation by dioxane. Other N.M.R. evidence by Hinton, McDowell and Amis[62] indicates solvation of aluminum perchlorate by dioxane. Analysis of conductance data by Hyne[63] also indicated interaction between dioxane and electrolyte in similar mixtures.

To clarify the situation I made attempts to determine the nature of solvation in systems 3,4,5 and 6 by the method developed by Grunwald[17,18,19].

Substitution of equation (127) into equation (125) and integration leads to the equation

$$\frac{1000}{M_{12}} \ln \frac{\alpha_1}{\alpha_2} = \frac{2}{RT} \left(\frac{dG^o_\pm}{d\ N_1}\right)m - m^{3/2} \left(\frac{4}{3} \frac{d\ S}{d\ N_1} - \frac{2}{3} S\ r\right) +$$

$$m^2\left(\frac{d\ B}{d\ N_1} - B\ r\right) + m^{5/2}\left(\frac{4}{5}\frac{d\ C}{d\ N_1} - \frac{6}{5}\ C\ r\right) +$$

$$m^3\left(\frac{2}{3}\frac{d\ D}{d\ N_1} - \frac{4}{3}\ D\ r\right) + m^{7/2}\left(\frac{4}{7}\frac{d\ E}{d\ N_1} - \frac{10}{7}\ E\ r\right) \qquad (149)$$

where $r = (M_1 - M_2)/M_{12}$.

The coefficients of the $m^{5/2}$ term and the $m^{7/2}$ term are found to be negligibly small. The equation, therefore, reduces to

$$\frac{1000}{M_{12}} \ln \frac{\alpha_1}{\alpha_2} = \frac{2}{RT}\left(\frac{d\ G^{o}_{\pm}}{d\ N_1}\right) m - m^{3/2}\left(\frac{4}{3}\frac{d\ S}{d\ N_1} - \frac{2}{3}\ S\ r\right)$$

$$+ m^2\left(\frac{d\ B}{d\ N_1} - B\ r\right) + m^3\left(\frac{2}{3} \cdot \frac{d\ D}{d\ N_1} - \frac{4}{3}\ D\ r\right) \qquad (150)$$

The coefficient of the $m^{3/2}$ term was calculated from the Debye-Hückel limiting slope, S, along with the slope of the curve of S plotted against N_1. The values of the other coefficients on the right in equation (150) were obtained by fitting the data by the method of least squares on a computer. The constants which reproduced the experimental quantity $\ln\frac{\alpha_1}{\alpha_2}$ over the entire concentration range, with a maximum deviation of 2%, are presented in Table 45. Other useful quantities are shown in Table 46. The values of $\frac{d\ G^{o}_{\pm}}{d\ N_1}$ were calculated from the values of $\frac{2}{RT}\frac{d\ G^{o}_{\pm}}{d\ N_1}$ of Table 45. The values of the quantities $\frac{d\ \ln\ \varepsilon}{d\ N_1}$, $\frac{d\ \ln\ a_1}{d\ N_1}$, and $\frac{d\ \ln\ a_2}{d\ N_1}$ were calculated by plotting $\ln \varepsilon$, $\ln a_1$, and $\ln a_2$ against N_1 and evaluating the slopes at the appropriate N_1. The required data on the dielectric constants of various dioxane - water mixtures were obtained from Critchfield, Gibson and Hall[64], while the required data for the activities of water and dioxane in water - dioxane mixtures were obtained from Bacarella, Finch and Grunwald[65].

Table 45

Constants for Equation (150).

System	$\frac{2}{RT}\frac{d\,G^{\circ\ddagger}}{d\,N_1}$	$\left(\frac{4}{3}\frac{d\,S}{d\,N_1} - \frac{2}{3}\,S\,r\right)$	$\left(\frac{d\,B}{d\,N_1} - B\,r\right)$	$\left(\frac{2}{3}\frac{d\,D}{d\,N_1} - \frac{4}{3}\,D\,r\right)$
3	-20.56456	24.59	-11.00845	0.66085
4	-22.06514	24.59	- 7.74068	0.19668
5	-28.03932	48.62	-28.33023	2.85783
6	-35.78041	48.62	-19.70203	0.85889

Table 46

Derived Quantities for Sodium and Lithium Chlorate in 44.5% Dioxane - 55.5% Water and 64.5% Dioxane 35.5% Water at 25°C.

System	$\frac{d\,G^{o}\pm}{d\,N_1}$ (Kcal./mole)	$\frac{d\,\ln\,\varepsilon}{d\,N_1}$	$\frac{d\,\ln\,a_1}{d\,N_1}$	$\frac{d\,\ln\,a_2}{d\,N_1}$
3	-6.1	4.49	0.737	-4.396
4	-6.5	4.49	0.737	-4.396
5	-8.3	4.16	0.445	-1.035
6	-10.6	4.16	0.445	-1.035

If the coulombic free energy is given by the Born equation[66], then

$$\frac{d\ G^{o}_{el}}{d\ N_1} = -\frac{N\ e^2}{2}\left(\frac{1}{r_+} + \frac{1}{r_-}\right)\frac{d\ \ln \varepsilon}{d\ N_1} \qquad (151)$$

where 'r' is the ionic radius, 'e' is the ionic charge, ε is the dielectric constant, and N is Avogadro's number. For 44.5% dioxane - 55.5% water at $25^{o}C$, $\varepsilon = 40.6$ and $\frac{d\ \ln\ \varepsilon}{d\ N_1} = 4.49$. Thus one obtains equation (152) for univalent electrolytes, where $r_{\pm} = 2\ r_+\ r_-/r_+ + r_-$ the harmonic mean of r_+ and r_-

$$\frac{d\ G^{o}_{el}}{d\ N_1} = -\frac{36.7}{r_{\pm}(\overset{o}{A})}\ \text{Kcal.} \qquad (152)$$

Sample values of $-36.7/r_{\pm}$ are as follows: sodium chlorate, -29.2 Kcal and lithium chlorate, -37.3 Kcal. In both cases, $-36.7/r_{\pm}$ is appreciably more negative than the experimental value of $d\ G^{o}/d\ N_1$. Similar results are obtained for sodium and lithium chlorate in 64.5% dioxane - 35.5% water.

In the preceding calculations, the electrolyte was regarded as unsolvated, and $r_{\pm}$ referred to the unsolvated ions. It is not surprising that such a model does not fit the data. In order to remove this discrepancy, the ions are assumed to be solvated.

Firstly, it is assumed that the solute is present at extreme dilution, and that it exists as an equilibrium mixture of molecular complexes of the type S. i H_2O. j dioxane. The fraction of the total formula weights of solute which exists in the form of S. i H_2O. j dioxane under these conditions will be denoted by ϕ^{o}_{ij}. Then the average hydration number per formula weight is defined by equation (153) and the average dioxanation number per formula weight by equation (154)

$$h^o = \sum_i \sum_j i\, \phi^o_{ij} \qquad (153)$$

$$d^o = \sum_i \sum_j j\, \phi^o_{ij} \qquad (154)$$

If the rate of change of the standard partial molal free energy of the actual molecular species $S \cdot i\, H_2O \cdot j$ dioxane is denoted by $d\, G^{o'}_{ij}/d\, N_1$, then the experimental value, $d\, G^o_{\pm}/d\, N_1$ is related to the former by means of equation

$$\sum_i \sum_j \phi^o_{ij} \frac{d\, G^{o'}_{ij}}{d\, N_1} = \frac{d\, G^o_{\pm}}{d\, N_1} + h^o RT \frac{d \ln a_1}{d\, N_1} + d^o RT \frac{d \ln a_2}{d\, N_1} \qquad (155)$$

In this equation, $d \ln a_1/d\, N_1$ and $d \ln a_2/d\, N_1$ refer to the activities of the solvent components in the absence of solute.

Assuming that the Born equation applies separately to each solvation complex that is formed between solute and solvent, the following equation is obtained

$$\frac{d\, G^{o'}_{ij}}{d\, N_1} = - \frac{N e^2}{2 \varepsilon\, b_{ij}} \left(\frac{d \ln \varepsilon}{d\, N_1}\right) \qquad (156)$$

where $b_{\pm}$ is the solvated radius; then equation (155) can be written in the form

$$- \frac{N e^2}{b_{\pm} \varepsilon} \left(\frac{d \ln \varepsilon}{d\, N_1}\right) = \frac{d\, G^o_{\pm}}{d\, N_1} + h^o RT \frac{d \ln a_1}{d\, N_1} + d^o RT \frac{d \ln a_2}{d\, N_1} \qquad (157)$$

where $b_{\pm}$ is a harmonic average, defined by the equation

$$\frac{1}{b_{\pm}} = \Big[\underset{\text{cations}}{\sum_i \sum_j} \phi^o_{ij}/b_{ij} + \underset{\text{anions}}{\sum_i \sum_j} \phi^o_{ij}/b_{ij} \Big]/2 \qquad (158)$$

The average solvation numbers h° and d° in equation (157) are defined as the sums of h° and d° for cations and anions.

In order to apply equations (157) and (158) to my data, it is convenient to represent $b_{\pm}$ as a function of $r_{\pm}$, h° and d°. It is assumed that the harmonic average of the b_{ij} values may be approximated by the radius calculated for a hypothetical 'average solvate', defined as ion with unsolvated radius $r_{\pm}$ complexed with $h^{\circ}/2$ water molecules and $d^{\circ}/2$ dioxane molecules. Assuming spherical molecules and closest packing of spheres, the following equation results.

$$(b_{\pm})^3 = 1.351 \; [\, r^3_{\pm} + (h^{\circ}/2)\, r_1^3 + (d^{\circ}/2)\, r_2^3 \,] \qquad (159)$$

where r_1 and r_2 were taken as 1.6Å and 2.7Å, respectively. (These radii are computed from the molar volumes of the pure liquids, assuming random packing of spheres, i.e., the actual volume occupied by the molecules is 58 per cent of the total volume.) Using the values quoted in Table 46 equations (157) and (159) can be simplified to the form:

$$\frac{d\, G^{\circ}_{\pm}}{d\, N_1} = - \frac{36.7}{b_{\pm}} - 0.437\, h^{\circ} + 2.605\, d^{\circ} \qquad (160)$$

$$b_{\pm} = 1.106\, (r^3_{\pm} + 2.05\, h^{\circ} + 9.84\, d^{\circ})^{1/3} \qquad (161)$$

for 44.5% dioxane 55.5% water, while for 64.5% dioxane 35.5% water the following simplified equations can be written

$$\frac{d\, G^{\circ}_{\pm}}{d\, N_1} = - \frac{59.0}{b_{\pm}} - 0.264\, h^{\circ} + 0.613\, d^{\circ} \qquad (162)$$

$$b_{\pm} = 1.106\ (r_{\pm}^3 + 2.05\ h^o + 9.84\ d^o)^{1/3} \qquad (161)$$

Equations (160), (161), and (162) can now be used to estimate solvation numbers. The first step is to show that d^o is greater than zero. An examination of Figure 17 in which $\frac{d\ G^o_{\pm}}{d\ N_1}$ for sodium chlorate in 44.5% dioxane - 55.5% water is plotted against 'h^o' reveals that the calculated value of $\frac{d\ G^o_{\pm}}{d\ N_1}$ is always more negative than the experimental value. This curve is typical and similar curves are obtained for sodium chlorate in 64.5% dioxane - 35.5% water, lithium chlorate in 44.5% dioxane - 55.5% water, and lithium chlorate in 64.5% dioxane - 35.5% water. Agreement between the experimental and calculated values is possible only if d^o is greater than zero.

This means that there are two unknown parameters, 'h^o' and 'd^o', but since there is only one experimental quantity, $d\ G^o_{\pm}/d\ N_1$, it is evidently not possible to obtain a unique solution. It is possible, however, by substituting all the values of 'h^o' and 'd^o' that are consistent with the experimental results, to find the smallest value of d^o which gives the experimental value for $d\ G^o_{\pm}/d\ N_1$. Minimum dioxanation numbers, calculated in this way, along with the corresponding value of 'h^o' are given in Table 47. The values presented here are of the same order of magnitude as those found by Grunwald[19] in 50% dioxane -water mixtures. As expected the minimum dioxanation number increases as the dioxane content of the solvent increases.

Thus dioxane plays a major role in the solvation of electrolytes in dioxane - water mixtures. This at first may appear unlikely since

Figure 17

$\frac{d\ G^{\circ}_{\pm}}{d\ N_1}$ Versus h° for Sodium Chlorate in 44.5% Dioxane - 55.5% Water at 25°C Calculated by Equations (160) and (161).

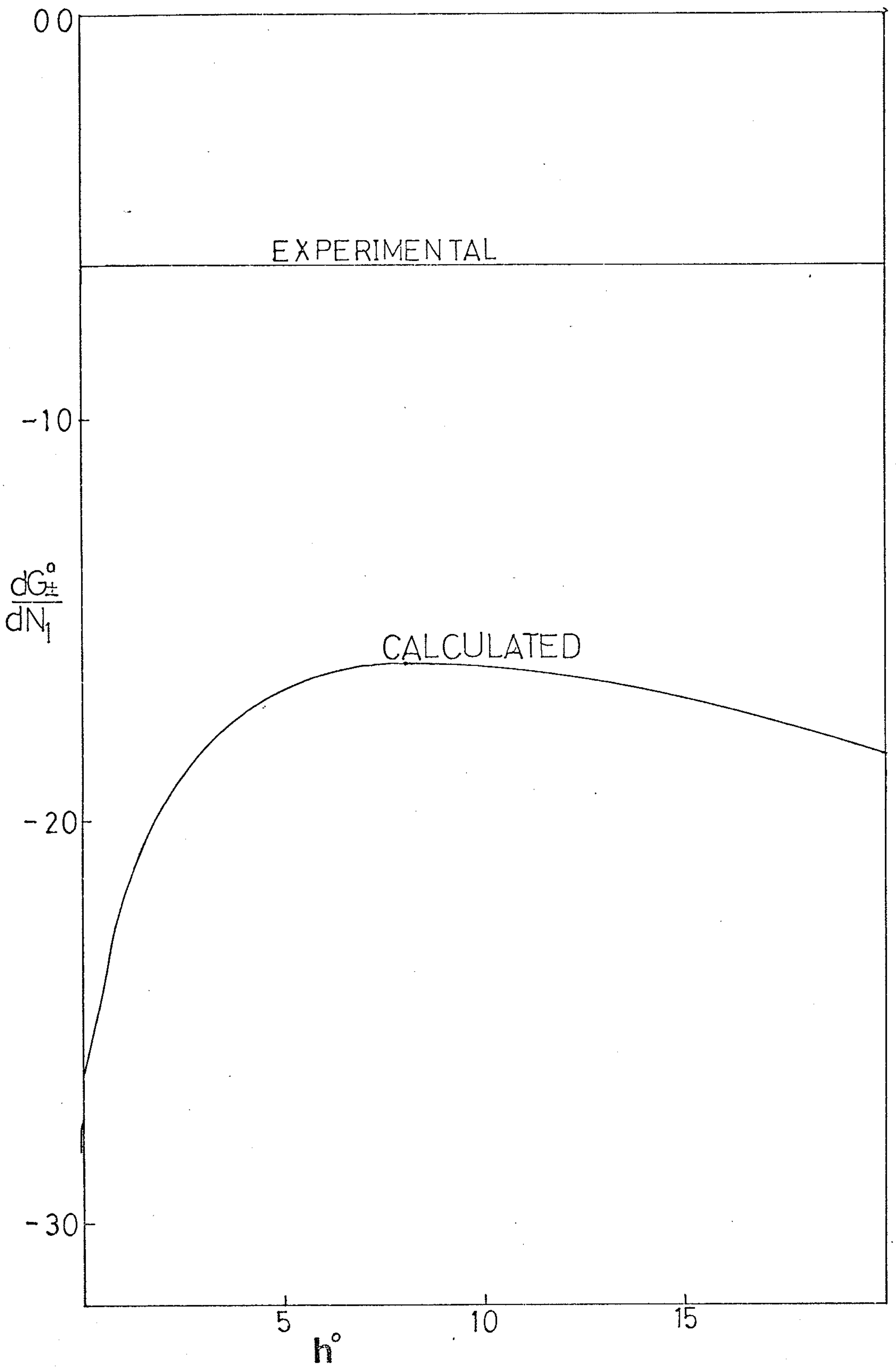
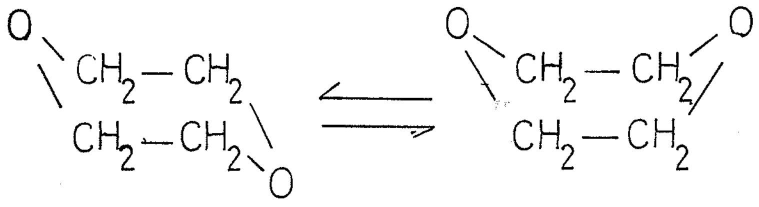

0.0
-10
-20
-30
$\frac{dG^{o}_{\pm}}{dN_1}$
EXPERIMENTAL
CALCULATED
5
10
15
h°

Table 47

Minimum Values for the Average Dioxanation Number for Sodium and Lithium Chlorate in 44.5% Dioxane - 55.5% Water and in 64.5% Dioxane - 35.5% Water at 25°C.

System	Minimum value of d^o	Corresponding value of h^o
3	2.14	0.0
4	2.08	0.0
5	7.25	0.0
6	5.53	0.0

pure dioxane has such a low dielectric constant (2.21 at 25°C) and, therefore, a low dipole moment. However, Hyne[63] has shown that addition of electrolyte to dioxane - water mixtures greatly increases the micro-dielectric constant over the bulk value. Such an increase in the micro-dielectric constant is in keeping with the displacement of the boat-chair equilibrium for dioxane toward the boat form under the influence of the coulombic field of the ionic species.



Due to the opposition of the bond moments in the chair form the preponderance of this conformation in pure dioxane results in a low dielectric constant value. But, the preponderance of the boat form, with its bond moments acting together, when electrolyte is added to the system would explain the strong interaction between dioxane and electrolytes in these systems.

B. DIFFUSION

The graphs of the differential diffusion coefficients of sodium and lithium chlorates in water versus the square root of the concentration are shown in Figure 18. There is a marked difference between the shape of the two curves, in fact, the differential diffusion coefficient of lithium chlorate is greater than that of sodium chlorate above 1.23 molar. A possible explanation of this is the thermodynamic non-ideality of these electrolytes. Division of the observed D values by the corresponding activity factor, $d \ln f_{\pm}/d \ln m$, gives a quantity proportional to the actual mobility of the diffusing solute, $D_{corr.}$. The $D_{corr.}$ values for lithium chlorate are below those of sodium chlorate over the entire concentration range indicating that much of the observed change is due to activity coefficient differences.

Attempts were made to fit the experimental diffusion coefficients to the theoretical equation of Hartley and Crank[67] extended to electrolytes by Wishaw and Stokes[68]. Their two equations, one including the viscosity correction and the other omitting it, are:

$$\frac{\eta}{\eta_0} f(D) = 1 + 0.036\, m \left(\frac{D^*_{H_2O}}{D^{\circ}} - h\right) \qquad (98)$$

where

$$f(D) = D_{obs.} / \left[(D^{\circ} + \Delta_1 + \Delta_2)\left(1 + m \frac{d \ln \gamma}{d\, m}\right)\right] \qquad (99)$$

and

$$f(D) = 1 + 0.036\, m \left(\frac{D^*_{H_2O}}{D^{\circ}} - h'\right) \qquad (100)$$

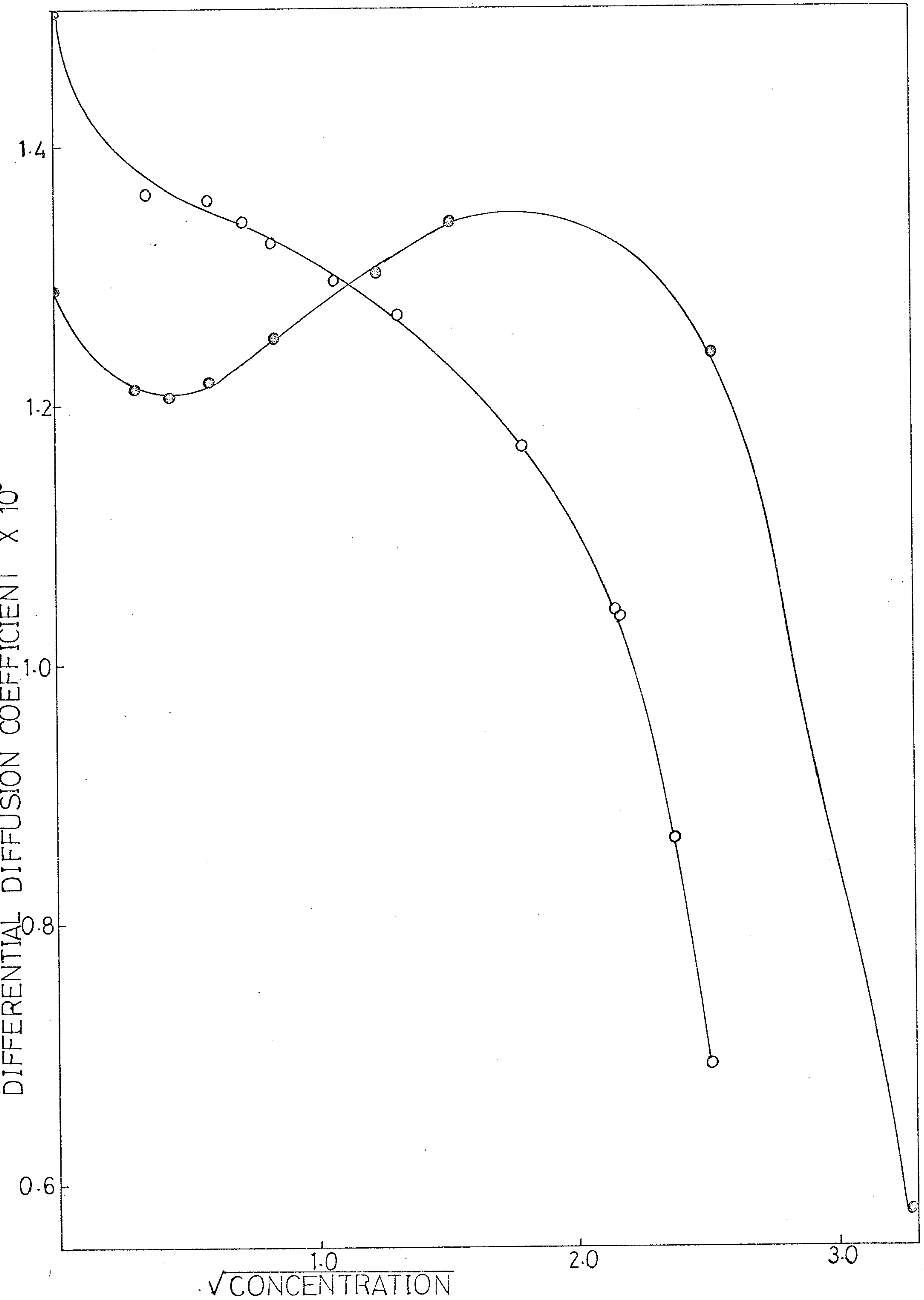
When applying these equations it should be noted that all the quantities except the hydration number are calculable from experimental limiting

Figure 18

Differential Diffusion Coefficient Versus the Square Root of Concentration for Sodium Chlorate and Lithium Chlorate in Water at 25°C.

○ Sodium Chlorate

● Lithium Chlorate


1.4
1.2
1.0
0.8
0.6
DIFFERENTIAL DIFFUSION COEFFICIENT X 10^5
1.0
2.0
3.0
√CONCENTRATION

mobilities and thermodynamic data; the terms Δ_1 and Δ_2 also involve assuming some value for the ion size parameter 'a', but since this appears only in small correction terms, the exact value chosen is not highly critical. The values a = 3.56 Å for sodium chlorate and a = 5.09 Å for lithium chlorate were taken from Tables 38, and 39, respectively. The values of the quantities in equations (98) and (100) used to fit the experimental data are shown in Table 48 and 49.

An examination of equation (98) shows that the plot of $\frac{\eta}{\eta_0}$ f(D) versus 'm' should be a straight line of slope $0.036\ (D^*_{H_2O}/D^\circ - h)$. Similarly, from equation (100), the plot of f(D) versus 'm' should be a straight line of slope $0.036\ (D^*_{H_2O}/D^\circ - h')$. The graphs of f(D) $\frac{\eta}{\eta_0}$ and f(D) versus 'm' for sodium and lithium chlorate in water at 25°C are shown in Figures 19 and 20. As can be seen from the figures straight lines are obtained below a concentration of 2 molal. The value of h and h' are obtained by the method of least squares from the slope of these plots taking the value of $D^*_{H_2O}$ (the self-diffusion coefficient of water) to be 2.44×10^{-5} cm^2 sec^{-1}[14]. The hydration numbers calculated in this way along with the corresponding calculated values of the differential diffusion coefficient are shown in Tables 50 and 51. It can be seen from the tables that equations (48) and (100) represent the experimental data fairly well with a maximum deviation of 2% up to a concentration of about 2 molar.

The values of the hydration numbers obtained by this technique are reasonable. Lithium chlorate is shown to be more highly hydrated than

Table 48

Application of Equations (98) and (100) to Sodium Chlorate in Water at 25°C.

Concentration (moles/liter)	$D_{observed}$ x 10^5	Δ_1 x 10^5	Δ_2 x 10^5	$1 + m \frac{d \ln \gamma}{d m}$	η/η_o	f(D) (Equation 99)	f(D) η/η_o
0.0	1.502	0.000	0.000	1.000	1.000	1.000	1.000
0.1252	1.364	-0.003	+0.039	0.905	1.008	0.980	0.988
0.3506	1.358	-0.005	+0.055	0.877	1.024	0.998	1.022
0.5250	1.341	-0.005	+0.060	0.870	1.040	0.990	1.030
0.7054	1.325	-0.005	+0.062	0.866	1.058	0.981	1.038
1.1505	1.296	-0.006	+0.065	0.870	1.104	0.954	1.053
1.7473	1.270	-0.007	+0.065	0.878	1.175	0.927	1.089
3.2508	1.167	-0.007	+0.063	0.931	1.470	0.805	1.183
4.6292	1.041	-0.008	+0.060	0.966	1.896	0.693	1.314
4.7226	1.036	-0.008	+0.060	0.967	1.932	0.689	1.331
5.6707	0.865	-0.008	+0.058	0.978	2.396	0.570	1.366
6.3326	0.690	-0.008	0.057	1.000	2.840	0.445	1.264

Table 49

Application of Equation (98) and (100) to Lithium Chlorate in Water at 25°C.

Concentration (moles/liter)	$D_{observed} \times 10^5$	$\Delta_1 \times 10^5$	$\Delta_2 \times 10^5$	$1 + m \frac{d \ln Y}{d m}$	η / η_0	f(D) (Equation 99)	f(D) η / η_0
0.0	1.288	0.000	0.000	1.000	1.000	1.000	1.000
0.0923	1.212	-0.010	+0.023	0.937	1.012	0.994	1.006
0.1993	1.205	-0.013	+0.028	0.961	1.025	0.962	0.986
0.3485	1.219	-0.015	+0.030	0.982	1.042	0.952	0.992
0.7073	1.251	-0.018	+0.032	1.074	1.090	0.895	0.975
1.5560	1.302	-0.021	+0.031	1.325	1.220	0.757	0.924
2.3359	1.341	-0.022	+0.029	1.495	1.360	0.693	0.942
6.4004	1.239	-0.025	+0.024	2.478	2.700	0.389	1.049
10.7994	0.578	-0.026	+0.020	2.265	8.20	0.199	1.632
14.3013	0.143	-0.026	+0.019	1.251	28.9	0.089	2.581
14.5891	0.120	-0.026	+0.018	1.308	32.6	0.072	2.337

Figure 19

$f(D)\,\frac{\eta}{\eta_0}$ and f(D) Versus Molality for Sodium Chlorate in Water at 25°C. Quantities Calculated by Equations (98) and (100).

○ $f(D)\ \eta/\eta_0$

● f(D)

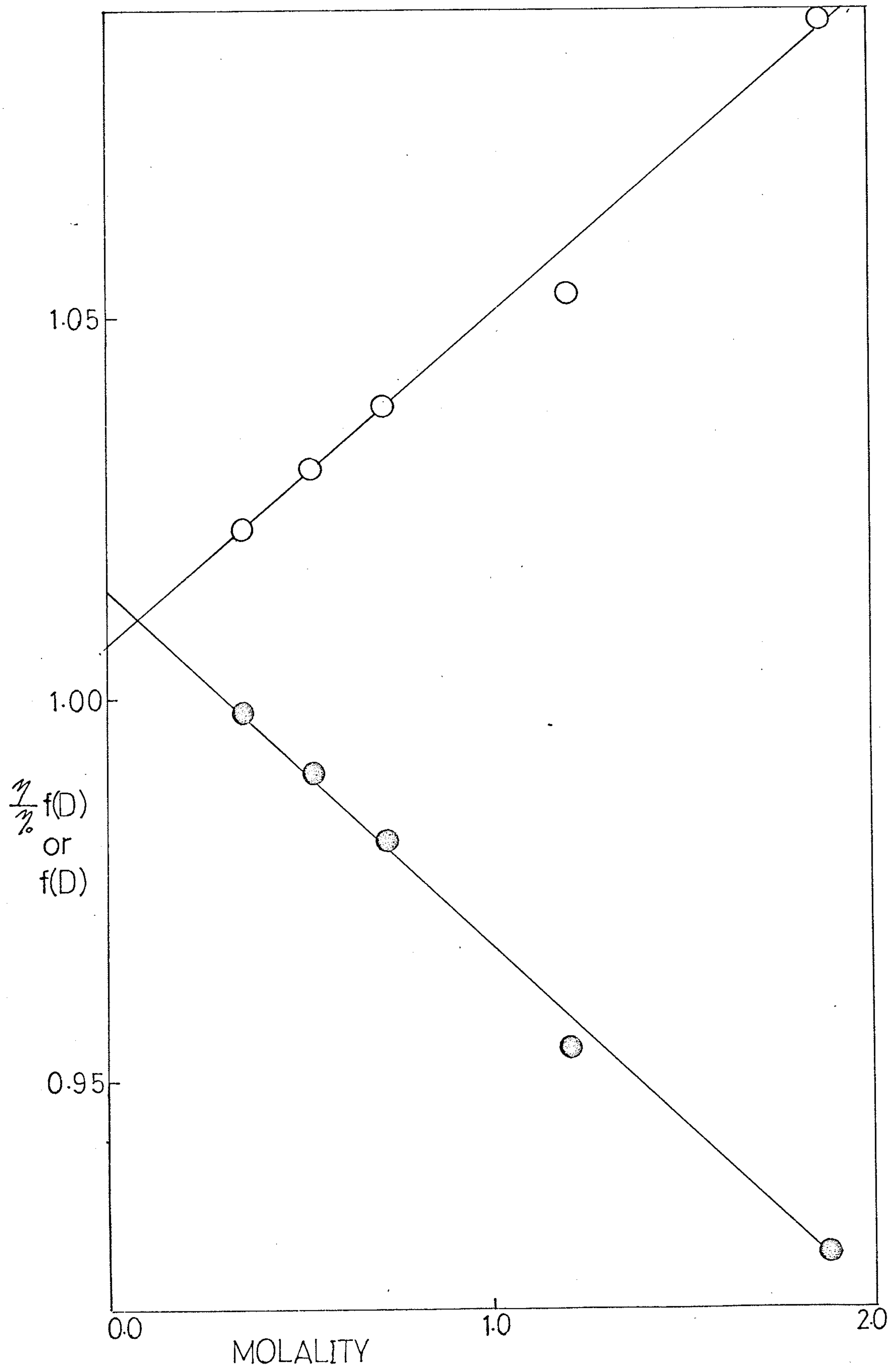

1.05
1.00
0.95
$\frac{\eta}{\eta_0}$ f(D)
or
f(D)
0.0
1.0
2.0
MOLALITY

Figure 20

$f(D)\frac{\eta}{\eta_0}$ and f(D) Versus Molality for Lithium Chlorate in Water at 25°C. Quantities Calculated from Equations (98) and (100).

○ $f(D)\,\eta/\eta_0$

● f(D)

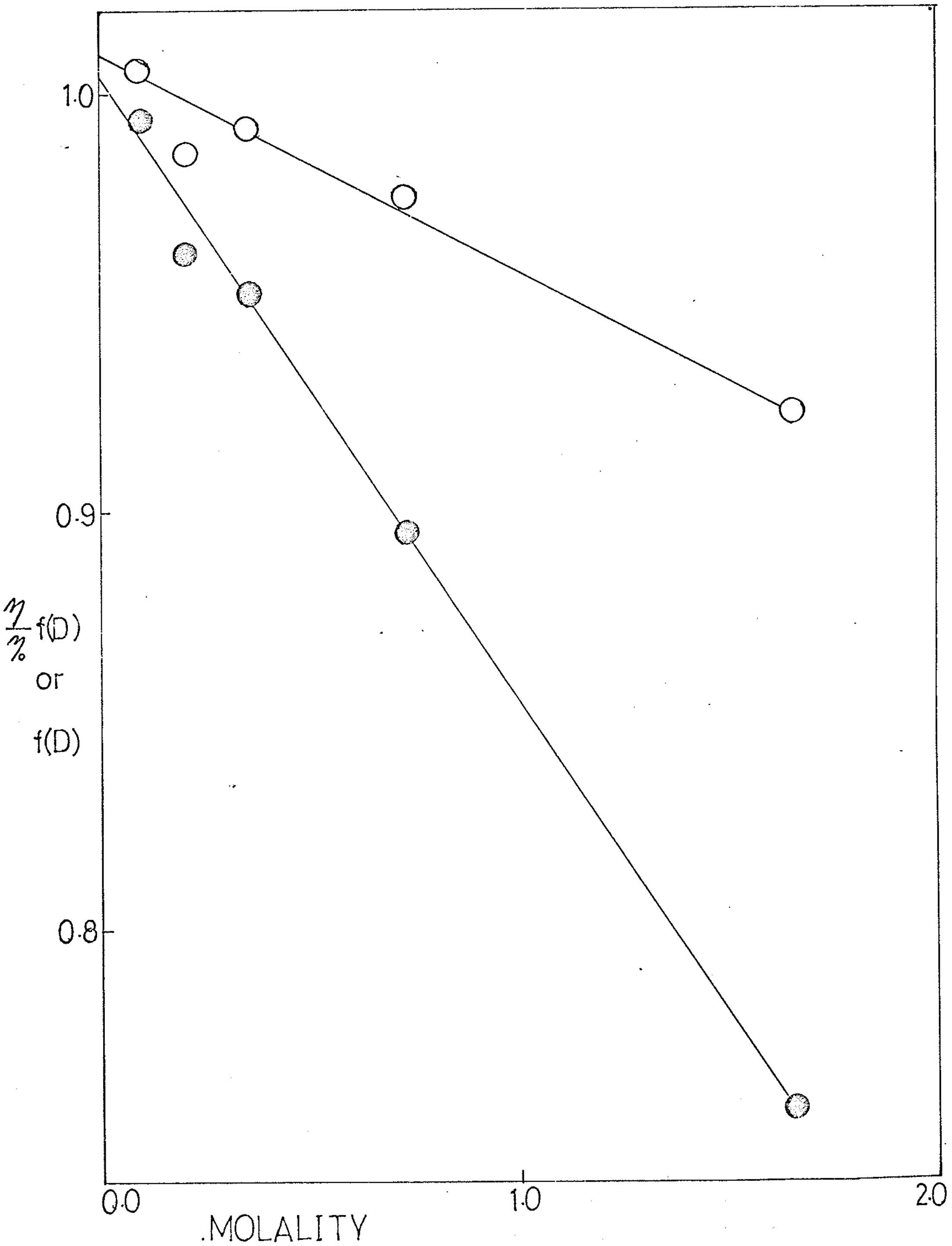

1.0
0.9
0.8
$\frac{\eta}{\eta_0}$ f(D)
or
f(D)
0.0
1.0
2.0
MOLALITY

Table 50

Differential Diffusion Coefficients of Sodium Chlorate in Water at $25^{\circ}C$ Calculated by Equation (98) and (100).

Concentration (moles/liter) c	Concentration (moles/Kg. of solvent) m	$D_{observed}$ (cm^2 sec^{-1})	D Calculated by Equation (100) $h' = 2.8$	D Calculated by Equation (98) $h = 0.6$
0.0	0.0	1.502	1.502	1.502
0.1252	0.1262	1.364	1.384	1.387
0.3506	0.3564	1.358	1.340	1.347
0.5250	0.5373	1.341	1.324	1.328
0.7054	0.7268	1.325	1.308	1.310
1.1505	1.2066	1.296	1.288	1.285
1.7473	1.8768	1.270	1.260	1.246
3.2508	3.7497	1.167	1.219	1.123
4.6292	5.6994	1.041	1.138	0.957
4.7226	5.8427	1.036	1.130	0.945
5.6707	7.3995	0.865	1.041	0.806
6.3326	8.5935	0.690	0.985	0.718

Table 51

Differential Diffusion Coefficients of Lithium Chlorate in Water at $25^{\circ}C$ Calculated by Equations (98) and (100).

Concentration (moles/liter) c	Concentration (moles/Kg. of solvent) m	$D_{observed}$ (cm^2 sec^{-1})	D Calculated by Equation (100) h' = 6.0	D Calculated by Equation (98) h = 3.2
0.0	0.0	1.288	1.288	1.288
0.0923	0.0929	1.212	1.202	1.199
0.1993	0.2013	1.205	1.215	1.210
0.3485	0.3540	1.218	1.213	1.207
0.7073	0.7288	1.251	1.248	1.239
1.5560	1.6582	1.302	1.298	1.299
2.3359	2.5702	1.341	1.200	1.251
6.4004	8.5748	1.239	- ve	0.767
10.7999	19.0232	0.578	- ve	0.704
14.3013	33.4764	0.143	- ve	0.036
14.5891	35.0120	0.120	- ve	- ve

sodium chlorate. But, the viscosity corrected equation (98) gives vastly different hydration numbers from those of the uncorrected equation (100). A comparison of these hydration numbers with those obtained from activity seems to indicate that the viscosity corrected equation gives values which are too low while the uncorrected equation gives values which are too high.

The determination of hydration by diffusion will be weighted in favour of the firmly bound water molecules, since the ion must carry the hydrating water molecules with it through the diaphragm. Thus diffusion will give a good approximation to the lower limit of the hydration number and should measure the primary hydration. The determination of hydration by activity, on the other hand, will include secondary hydration, since any interaction between the solvent and the ions should affect the activity coefficient. Therefore, the viscosity corrected equation (98) should give the minimum hydration number while the Stokes-Robinson equation (28) should give the maximum hydration number.

Table 52

Hydration Numbers of Sodium Chlorate and Lithium Chlorate in Water at $25^{o}C$.

Sodium Chlorate		Lithium Chlorate	
Equation	Hydration Number	Equation	Hydration Number
(28)	1.05	(28)	6.70
(34)	0.96	(34)	3.97
(98)	0.60	(98)	3.20
(100)	2.80	(100)	6.00

As previously mentioned the accuracy of the diaphragm integral diffusion coefficients is ± 0.2%. But, in converting this experimental value to the differential diffusion coefficient much accuracy is lost. For the aqueous solutions it was necessary to evaluate the slope of the $D^{o}_{(c_{m'})}$ versus $c_{m'}^{1/2}$ curve (see page 73) resulting in a further error of about 0.3%. Thus the overall accuracy of the differential diffusion coefficients is about ± 0.5%.

For the dioxane-water mixtures it was necessary to find an analytical expression which represented the data and to calculate the differential diffusion coefficient from this (see page 74). The analytical expressions obtained reproduced the experimental diaphragm cell integral diffusion coefficients with a maximum deviation of 2%. But, over most of the concentration range in all the solvents the error was less than 0.5%. Thus the accuracy of the differential diffusion coefficients derived from these analytical expressions is about 1% except in the extremely concentrated region where the accuracy is reduced to about 2%.

A consistency check of the two methods of determining the differential diffusion coefficient was made by fitting the aqueous sodium chlorate data to an analytical function similar to that used for the dioxane-water mixtures and then calculating the differential diffusion coefficients. Both methods were found to give the same results within 0.5%.

Graphs of the differential diffusion coefficients of sodium and lithium chlorates in 44.5% dioxane - 55.5% water and in 64.5% dioxane - 35.5% water are shown in Figures 21 and 22. Although the limiting

Figure 21

Differential Diffusion Coefficient Versus the Square Root of Concentration for Sodium Chlorate and Lithium Chlorate in 44.5% Dioxane - 55.5% Water at 25°C.

○ Sodium Chlorate

● Lithium Chlorate

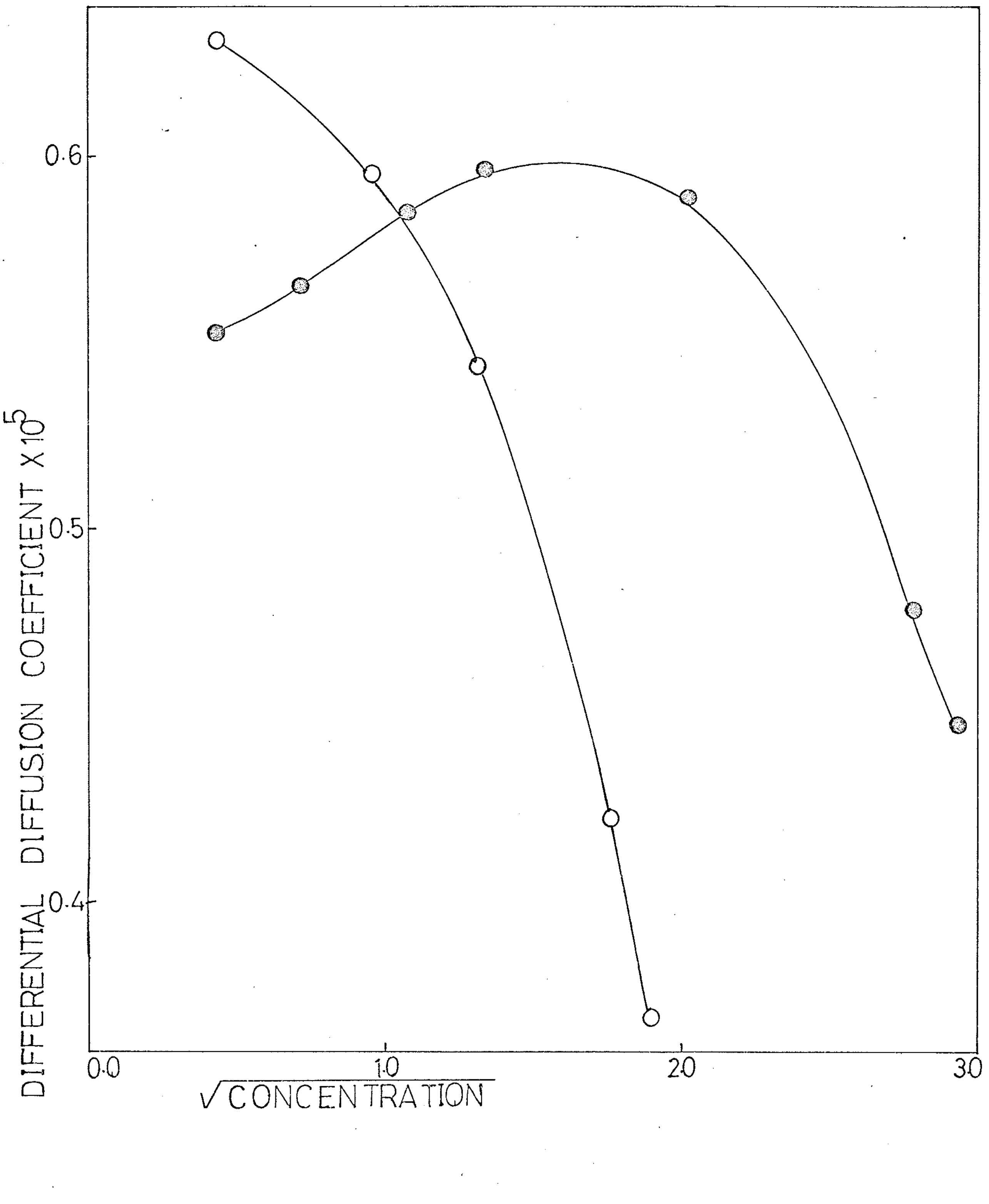
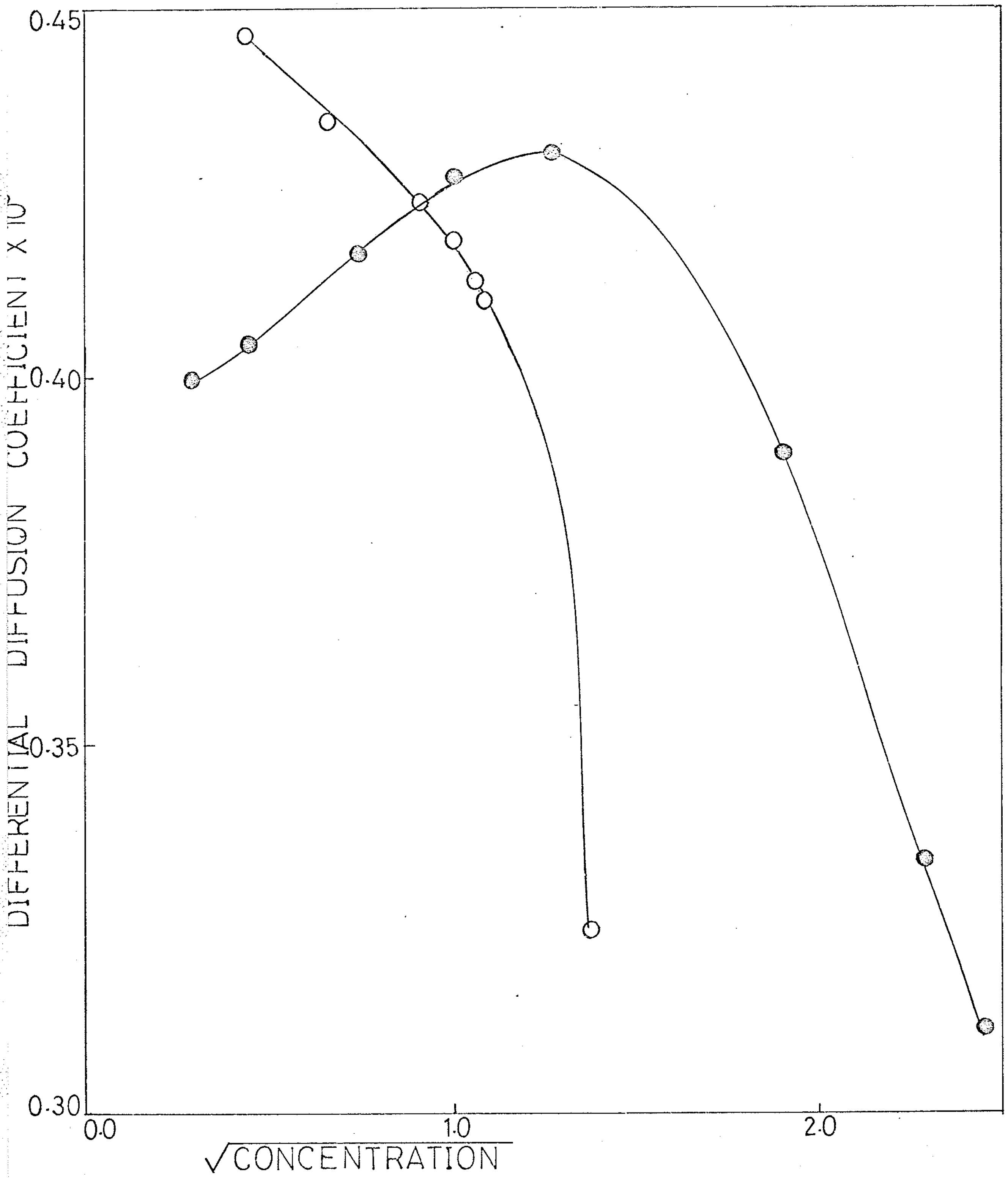

DIFFERENTIAL DIFFUSION COEFFICIENT X10^5
0.6
0.5
0.4
0.0
1.0
2.0
3.0
√CONCENTRATION

Figure 22

Differential Diffusion Coefficient Versus the Square Root of Concentration for Sodium Chlorate and Lithium Chlorate in 64.5% Dioxane - 35.5% Water at 25°C.

○ Sodium Chlorate

● Lithium Chlorate


DIFFERENTIAL DIFFUSION COEFFICIENT X 10⁵
0·45
0·40
0·35
0·30
0.0
1.0
2.0
√CONCENTRATION

diffusion coefficients are not available, it can be seen that the curves have the same shapes as those for aqueous solutions over the concentration range observed. But, the absolute values of the diffusion coefficient are reduced on changing the solvent from water to 44.5% dioxane - 55.5% water and to 64.5% dioxane - 35.5% water. This is probably due to the decrease in dielectric constant along with the increase in viscosity in the mixed solvents.

Attempts to obtain a theoretical expression for the diffusion coefficients of these solutions and thus hydration numbers, by the method of Wishaw and Stokes[68], failed. But, it was evident from the increase in dioxane content in the upper compartment, that the solvation sheath of both sodium and lithium chlorate contained more dioxane than the mixed solvent.

Thus, although the derivation of solvation numbers in the mixed solvents was not possible, it has been conclusively proved, from both diffusion and vapour pressure experiments, that dioxane does play a major role in the solvation of sodium and lithium chlorates in the dioxane-water mixtures studied.

Although the theories used in this thesis were useful in predicting the behavior of the activity and diffusion coefficients and in giving a fair approximation to the degree of hydration, it can be seen from Tables 38,39,40,41,49, and 50 that the numerical values of the hydration numbers obtained depended on the equation used to calculate them. This, in itself, is not surprising because each theory ascribes different importance to solvation. Also, in some cases many important effects such as dielectric constant, viscosity, etc. have been completely omitted. Indeed, until a theory has been developed that can predict the effect of dielectric constant, viscosity, ion - ion interaction, ion - solvent interaction, etc. on activity and diffusion, the concept of solvation number will remain vague.

To date, most theoreticians have attempted to solve the problem of electrolyte solutions by extending the dilute solution theory to higher concentrations by the addition of extra terms. This approach leaves much to be desired since many of the approximations used in the dilute region certainly cannot be expected to hold in the more concentrated regions. Clearly a new approach is necessary.

Recently, new approaches to the problem have been made by Angell[69] and by Braunstein[70]. Angell has approached the problem from the concentrated solution while Braunstein has approached the problem from the molten salt, both with promising results. I believe that approaching the problem from these directions will prove more fruitful than attempts to extend the dilute solution theory have proved.

SUMMARY

SUMMARY

The vapour pressures of solutions of sodium chlorate and of lithium chlorate in water and in solvents consisting of 44.5% dioxane - 55.5% water and of 64.5% dioxane - 35.5% water, at 25°C, were determined using a differential manometer. The vapour compositions of the dioxane-water solutions were determined by the air-saturation method.

From the vapour pressures and compositions the mean molal activity coefficients were calculated. The activity coefficients of the aqueous solutions were fitted to the theoretical equations of Stokes and Robinson and of Gleuckauf, yielding hydration numbers for the salts.

The minimum dioxanation numbers of sodium and lithium chlorate in the dioxane-water mixtures were calculated from the experimental activity coefficients by the method of Grunwald.

The diffusion coefficients of sodium chlorate and of lithium chlorate in water and in solvents consisting of 44.5% dioxane - 55.5% water and of 64.5% dioxane - 35.5% water were determined using the Stokes' diaphragm technique.

The diffusion coefficients of the aqueous solutions were treated by the extended Hartley-Crank analysis to obtain hydration numbers for the electrolytes.

Results from both the vapour pressure and diffusion experiments proved conclusively that dioxane plays a major role in the solvation of both sodium and lithium chlorate in the dioxane-water mixtures.

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