

Hydrogen Ion Mobility in Normal and
Heavy Water Solutions of Electrolytes

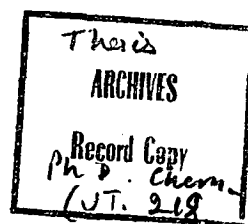
by

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Declaration

I, *H. R. Hanchey* declare that except as stated herein, this thesis contains no material which has been accepted for the award of any other degree or diploma in any university, and that, to the best of my knowledge and belief, it contains no copy or paraphrase of material previously published or written by another person, except when due reference is made in the text of the thesis.

To my dear mother
and the memory of my father

Abstract

Proton and deuteron mobility in normal and heavy water solutions of some alkali halides and tetraalkylammonium bromides has been measured polarographically, and the diffusion coefficients of the proton and deuteron calculated using a corrected form of the Ilkovic equation. The value of the constant in the correction factor of the equation was found to be 17, in agreement with other experimental and theoretical work.

In all cases, proton and deuteron diffusion was retarded as concentration of supporting electrolyte increased. This was also found to occur when cadmium ion diffusion was measured in some nitrate solutions. The main difference was the rapid decrease for hydrogen and deuterium ion diffusion in the 0 - 1 m concentration range. The similarity of both diffusion current and half-wave potential vs. concentration plots for hydrogen and cadmium ions at higher concentrations seemed to point to a complete reduction of any abnormal diffusion mechanism for the hydrogen ion, in agreement with the conclusions drawn by some other workers.

When, however, results were analysed in terms of the effect of electrolyte concentration on the excess or Grotthuss mobility of the hydrogen and deuterium ions, it was found that some of the Grotthuss component was present even up to concentrations of supporting electrolyte of about 4 m. These results also raise some questions about the accepted mechanism for the transport of normal and heavy hydrogen ions in electrolyte solutions. It appears that it is the field-induced orientation of water molecules or hydrogen ions that is the rate-determining step in proton and deuteron transport. This exceeds the

rate of thermal orientation, is slower than proton or deuteron tunnelling and has been justified theoretically. The thermal orientation of water molecules appears to be no guide to the field-induced orientation in the presence of electrolytes.

The lower diffusion currents in heavy water solutions are attributed to the more extensive deuterium bonding as compared with the hydrogen bonding in normal water. The greater reduction of proton and deuteron diffusion in solutions of electrolytes considered to be structure-makers is, therefore, in agreement with this.

Energy of activation measurements support generally the above conclusions.

When hydrogen ion diffusion coefficients obtained in this study were compared with literature values there appeared some discrepancies, but some values agreed with present ones. It is thought that diffusion through a glass diaphragm cell may not give reliable results for the hydrogen ion because water structure becomes modified when water moves through very fine glass capillaries or pores, and this would affect the abnormal Grotthuss component of mobility.

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List of Principal Symbols

A	Constant in correction term in the modified Ilkovic equation.
C	Concentration of the depolariser in millimoles per litre.
c	Concentration of supporting electrolyte in mole per litre.
D	Diffusion coefficient in $\text{cm}^2 \text{sec}^{-1}$.
E	Standard electrode potential.
$E_{1/2}$	Half-wave potential vs. S.C.E. in volt.
F	Faraday.
i_d	Diffusion current in microamperes.
m	Rate of flow of mercury in milligram per second <u>or</u> molal concentration of supporting electrolyte.
n	Number of faradays per mole of electrode reaction.
R	Gas constant.
T	Temperature in K.
t	Drop time in seconds.
temp.	Temperature in $^{\circ}\text{C}$.
λ	Limiting ionic conductivity.
ν	Vibrational mode or frequency.
τ	Relaxation time for motion of water molecules.

Appendix

Papers published by N.K. Roberts and H.L. Northey during this study.

1. Proton Mobility in Aqueous Solutions of some Alkali Halides.
J. Chem. Soc. A, 2573, (1971).
2. Polarography of the Hydrogen Ion in Aqueous Solutions of some Tetraalkylammonium Bromides.
J. Chem. Soc. A, 2640, (1971).
3. Proton Mobility in Water in Glass Pores of 15 μ m Diameter.
Nature, Physical Science, 237, 144, (1972).
4. Hydrogen Ion Mobility in Aqueous Electrolyte Solutions.
Comparison of Polarographic and Diaphragm Cell Methods.
J.C.S. Faraday I., 68, 1528 (1972).
5. Proton and Deuteron Mobility in Normal and Heavy Water Solutions of Electrolytes.
J.C.S. Faraday I., 253 (1974).
6. "Structure of Water in Porous Glass" - a discussion between Dr. N.K. Roberts (Tasmania) and Dr. G. Belfort (Israel),
Nature, Physical Science, in the press 1974.

Chapter 1

Theoretical Introduction

1.1. Introduction

Hydrogen ions move through aqueous solutions at a greater rate than other ions. This is due to a mechanism whereby the effective transfer of charge is greater than the bodily transfer of an ion. The rate-determining step of this abnormal mechanism is the field induced rotation of water molecules or hydrated hydrogen ions. The freedom of these entities to rotate is affected by the degree and extent of hydrogen bonding in solutions.

In the present study the diffusion of normal and heavy hydrogen ions in aqueous solutions of some electrolytes at various concentrations has been followed polarographically, and an attempt has been made to separate the excess mobility effect, the Grotthus component, from the total diffusion measurements.

This Chapter sets out current views on the structure of water and proton mobility, and also a brief account of the polarographic method.

1.2. The Structure of Liquid Water

1.2.1. Introduction

The study of aqueous solutions, so important in biological, geophysical and other natural systems, has made it clear that water is not merely a medium in which solute particles are dispersed, but that there is interaction between water and these particles. This interaction affects the spatial relationships between particles and thus can be said to affect, and be affected by, the structure of water. Structure in water is to be understood in terms of the relative positions of two particles at close range and over a very short period of time, and is

therefore an inherently different concept from that of structure in crystals where angular and spatial relationships are fixed¹. It is only possible to specify the probability of finding certain distributions of molecules in specified volumes of liquid².

Theories of water structure should account for observed properties of water and, ideally, be amenable to mathematical treatment so that predictions can be made and the theory tested further.

1.2.2. Brief Historical Survey

The first to speak of the possibility of "solid particles" in liquid water was Whiting³ in 1884, and others followed his lead in offering explanations of the temperature of maximum density, the anomalous temperature variation of viscosity, and other properties which differed markedly from those of other liquids, in terms of water structure.

Bernal and Fowler⁴ in 1933 proposed an irregular, four-coordinated structure for water, based upon spectral and X-ray data. Although they considered that there were three chief forms of the arrangement of H_2O in water, viz. tridymite ice-like, quartz-like and an ammonia-like ideal liquid, there was no question of a mixture of volumes with different structures; at all temperatures the liquid was considered to be homogeneous.

A "flickering cluster" model was proposed by Frank and Wen⁵. They considered hydrogen-bond making and breaking in water to be cooperative phenomena since, chemically, hydrogen-bond formation is an acid-base interaction which renders one molecule more acidic and the other more basic than an unbonded molecule, and consequently there would result a stronger bond when the acidic or basic molecule became bonded to another, and so on. This model was treated by statistical thermodynamical analysis by Némethy and Scherager⁶ who showed that it was able to account

for the thermodynamic and volume properties of liquid water from 0° to 70°C. The calculated results also agreed well with the radial distribution curve derived from X-ray diffraction.

On the basis of radial distribution curves and Raman spectroscopy Davis and Litovitz⁷ proposed a two-state model in which the water molecules are arranged in puckered hexagonal rings similar to those found in ice crystals. Some of these rings are joined in an open-packed structure while others are in a more closely packed structure.

Other mixture models include interstitial models, the first one postulated by Samoilov⁸, and clathrate models. The latter assume water to resemble some hydrates in which groups of hydrogen bonded molecules form open, tetragonal dodecahedra in which non-hydrogen-bonded molecules reside⁹. In other interstitial models one species of water molecule forms an ice-like hydrogen-bonded framework containing cavities in which single, non-hydrogen-bonded water molecules reside. Danford and Levy¹⁰, showed by calculating radial distribution functions that a model similar to Samoilov's was theoretically tenable but that Pauling's clathrate model was inconsistent with the observed radial distribution for water.

All mixture models assume the hydrogen bond to be covalent and so highly directional. Pople¹¹ proposed a model in which hydrogen-bonds were distorted rather than broken. Lennard-Jones and Pople¹² showed that hydrogen-bonds can be explained by the electrostatic attraction of the lone-pair electrons of one molecule for a proton of another. Such electrostatic attraction allows for the distortion of the hydrogen-bonds so that all four hydrogen bonds from one molecule can bend independently giving rise to a flexible network of water molecules in the liquid. Pople¹¹ was able to show that his theory gave results in agreement with the radial distribution functions of Katzoff¹³ and Morgan and Warren¹⁴.

Reviews by Conway¹⁵ and Eisenberg and Kauzmann¹⁶ gave details of the

main theories up to 1968, and of the techniques used to substantiate these.

1.2.3. Three Meanings of Water Structure

It is of interest to note that Eisenberg and Kauzmann¹⁶ draw attention to three different kinds of structure in water when time scales are considered. Molecular motions of water may be divided into rapid oscillations and slower diffusional motions. The former are found from spectroscopic studies to have an average period, τ_V , of about 2×10^{-13} sec. Relaxation techniques show that there is diffusion of the equilibrium positions and orientations of the water molecules. The dielectric relaxation time of water indicates that a molecule experiences a displacement on the average about once every 10^{-11} sec. near the melting-point, so $\tau_D \sim 10^{-11}$ sec.

There can thus be three meanings of the term "structure" by considering what could be seen if it were possible to take snapshots with exposure times less than τ_V , greater than τ_V but less than τ_D and greater than τ_D . Eisenberg and Kauzmann¹⁶ call the "pictures" thus obtained those of the instantaneous (I), vibrationally-averaged (V) and diffusionally-averaged (D) structures. Spectroscopic measurements give information on the V-structure, and thermodynamic measurements probe the D-structure but there is at present no way to investigate the I-structure.

1.2.4. Experimental Evidence

After considering evidence from such techniques as X-ray diffraction, static dielectric constants and n.m.r. chemical shift and also optical and thermodynamic properties, Eisenberg and Kauzmann¹⁶ conclude that most results obtained can be explained by both mixture and continuum

theories though they favour the latter. Frank¹⁷ has noted that one of the principal problems in the discussion of water structure is the difficulty in finding experimental evidence which requires either the acceptance or rejection of any given model. To find a model with which one set of new data is consistent, or which it suggests, is relatively easy, but uniqueness of interpretation is another matter.

Those who support a continuum model see liquid water as a homogeneous network of hydrogen-bonded molecules, a "heap" rather than a "pile" as Bernal has said¹⁸, without long-range order. Mixture and interstitial models require the presence of a small number of distinguishable species in liquid water. Kell¹⁹ suggests that the distinction between continuum and mixture theories may depend on the time scale, since a process taking, say, 3×10^{-12} sec. is slow compared to the O-H stretching vibration near 3500 cm^{-1} , (10^{-14} sec.) but fast compared to dielectric relaxation, (10^{-11} sec.).

There seems to be most controversy over the interpretation of infra-red and Raman spectra in favour of one or other model. Interpretation of these spectra is difficult and must be done after comparison with the spectra of ice and water vapour.

The O-H stretching band (maximum near 3490 cm^{-1} in the infra-red spectrum and 3440 cm^{-1} in the Raman spectrum) has been studied more thoroughly than other bands. To clarify the study it is usual to prepare dilute solutions of HDO in either H_2O or D_2O , by adding a small quantity of D_2O or H_2O to H_2O or D_2O respectively. These solutions give rise to almost pure O-H and O-D stretching motions in an HDO molecule whereas in pure H_2O or D_2O the O-H or O-D stretching vibrations are coupled to the stretching vibrations of neighbouring molecules. The shape of the HDO band can give information on the V-structure of liquid water.

Wall and Hornig²⁰ and Walrafen²¹ have studied the uncoupled stretching bands in the Raman spectrum of water. These bands show slight asymmetry, and they are much broader than the corresponding bands in ice. Walrafen used a laser Raman source and a narrower slit than Wall and Hornig and his bands show a shoulder on the high frequency side. Wall and Hornig attributed the breadth of the bands to structural disorder in liquid water, and suggested that the slight asymmetry could be attributed to the lower energy of stronger hydrogen bonds. Falk and Ford²² and Franck and Roth²³ interpreted the uncoupled stretching bands in the infra-red spectra they obtained as being due to a continuous distribution of intensities. They thus supported a continuum model for water, since they argued that if there were a small number of distinct species present in water then there would appear a similar number of separate peaks, as occur in the uncoupled O-D stretching band for Ice-II, since the molecular environment is different.

Walrafen²¹ proposed an alternative explanation for the shape of the uncoupled stretching band. By means of an analogue computer he analysed his curves according to Gaussian components and inferred the presence of at least two such components. Spectra obtained at two temperatures, or with the perchlorate ion in solution²⁴ show that the intensity of the high frequency component increases in comparison to the low frequency component as temperature increases. Walrafen attributed this to the increase in the fraction of the non-hydrogen-bonded species with temperature rise. He also pointed to the isosbestic point he noted, as evidence for two species in equilibrium. This is a likely but not unique interpretation of this phenomenon^{25,26}.

Eisenberg and Kauzmann¹⁶ question this interpretation both because of the assumption of the Gaussian shape of the separate bands and also because of the width of the band obtained for the non-hydrogen-bonded water. They suggest that there may be two broad classes of environments

corresponding to Walrafen's²¹ two-state model, but this does not conflict with the continuum model preferred by the other authors^{20,22,23}. Further work by Walrafen²⁷, however, is interpreted clearly in favour of a two-state model since he claims that the presence of narrow overlapping components in liquid water has not been demonstrated experimentally whereas several workers have recently been successful in resolving spectral bands in the fundamental as well as overtone and combination bands into Gaussian components^{28,29}.

There is a broad band appearing in infra-red, Raman and inelastic neutron spectra¹⁶. This has its maximum near 700 cm^{-1} in the infra-red spectrum of H_2O , and near 500 cm^{-1} in D_2O . The position of this band and its isotopic dependence suggest that it is the counterpart of the librational band in ice. There appears as a shoulder on this band another band having its maximum near 193 cm^{-1} for H_2O and 187 cm^{-1} for D_2O and this is attributed to hindered translations. A third band is also attributed to hindered translations. This has its maximum near 60 cm^{-1} in the Raman spectra of both H_2O and D_2O . The maxima of the first two bands are lower than those for ice and they shift to lower frequencies with rise in temperature. This may be interpreted as signifying more distorted hydrogen-bonds or less hydrogen-bonding.

Walrafen³⁰ has undertaken the study of these bands, a difficult task because of their low intensities. On evidence from X-ray diffraction he has assumed tetrahedrally coordinated water. He found three Gaussian components for the 700 cm^{-1} band and assigned these to librations about the three molecular moments of inertia of the model. The other bands were assigned to hydrogen-bond stretching and bending, and shifts due to temperature change were attributed to changes in the equilibrium between bonded and unbonded molecules resulting from the breakdown of the tetrahedral grouping with increasing temperature.

Buijs and Choppin³¹ studied bands in the 8,000 to 9,000 cm^{-1} region asserting that these were due to the sum of the fundamental vibration bands, ν_1 , ν_2 and ν_3 , (due respectively to symmetric stretching, bending and antisymmetric stretching of the molecule). They resolved the band into three components and ascribed these to three species of water with zero, one and two hydrogen-bonds respectively. Hornig³² questioned the assignment of the band to a combination band, arguing that it was more likely to be due to overlap of ν_1 and ν_3 , and the overtone of ν_2 , and that the observed intensity variations were due to Fermi resonance between $2\nu_2$ and ν_1 . If there were three species present then there should also be evidence of them in the O-H and O-D vibrations of HOD. It has already been stated that Walrafen^{21,24,27,30} claims that there is such evidence while others^{22,23} deny this.

Further work by McCabe et al²⁸ and Choppin and Violante²⁹ near the 7,000 cm^{-1} region supports a mixture model for water. McCabe et al²⁸ studied the temperature variation of the 6,900 cm^{-1} band. The appearance of a shoulder indicates the presence of a second species whose concentration increases with temperature rise. Fermi resonance does not explain the spectral change. They resolve their spectrum into two Gaussian curves, but find that there may need to be a third component, which would correspond to non-hydrogen-bonded water. McCabe et al²⁸ agree with the general interpretation of Walrafen but believe that the two main species are not bonded and unbonded species but singly-bonded and "ice-like" species.

Choppin and Violante²⁹ ascribe the band near 7000 cm^{-1} to the ν_1 and ν_3 combination band and discount the possibility of explaining this band by Fermi resonance. As well as pure water they studied solutions of acetone and dioxane in water. They were able to resolve the band into three Gaussian components and ascribed these to species S_0 , S_1 , and

S_2 with zero, one and two hydrogen-bonds respectively, in accordance with the previous work of Buijs and Choppin³¹, and supported by the observed increase in S_0 concentration with rise in temperature, and decreases in S_1 and S_2 concentration.

These authors conclude that their results show the presence of three spectroscopically distinct species of water and therefore support a mixture model for water, and that the large half-widths of their component bands agree with a band model such as that proposed by Vand and Senior³³.

1.2.5. Conclusion from Experimental Work

It thus appears that the most recent infra-red and Raman spectra are interpreted in favour of some kind of mixture model. Davis and Jarzynski³⁴ have reviewed evidence supporting mixture models and concluded that a mixture model with two molecular environments where percentages change with temperature is the most likely model for liquid water. It is interesting to note, however, that they state that the "continuum" properties suggested by X-ray spectra appear to be entirely consistent with the "mixture" properties suggested by structural relaxation and Raman spectra. In the terminology of Eisenberg and Kauzmann¹⁶ this means that while studies of D-structure support a continuum model, vibrational spectroscopy "sees" distinct components in the shorter time-scale of the V-structure, and, therefore, supports a mixture model.

Frank³⁵ makes the point that in order to solve the water problem it is necessary to draw on information obtainable from several fields at once. He supports the interpretations of vibrational spectra given by Walrafen²¹ and Senior and Verrall²⁵, then calls upon evidence from the X-ray scattering work of Narten and Levy³⁶ to conclude that an

interstitial model, such as that proposed by Samoilov⁸ and supported by Danford and Levy¹⁰ and Narten et al³⁷ is the mixture model compatible with known facts about liquid water.

Direct experimental evidence for continuum models is at present lacking, especially if the resolution of peaks in i-r and Raman spectra into two or more separate peaks is correct. It has already been stated that much experimental work can be explained by a continuum model but that such interpretation is not actually compelling. Recent work of O'Neil and Adami³⁸ on the oxygen isotope partition function ratio for water may support a continuum model but an interstitial model would also be compatible with their data, provided that the concentration of monomer is small or remains fairly constant with temperature change.

It is seen, then, that much recent experimental work can be used to support a mixture model, especially an interstitial model but that a continuum model is not entirely ruled out.

1.2.6. Recent Theoretical Work

During the last few years several statistical mechanical theories have been advanced. Some authors have applied their calculations to mixture models only³⁹, as these are more amenable to mathematical treatment than continuum models^{39,40,41}, although Levine and Perram⁴⁰ have stated that the two kinds of model are not conflicting since a single hydrogen bond energy state can be replaced by a set of states which describe the bending of hydrogen-bonds in terms of a partition function.

Watts⁴¹ notes that the complexities involved in using statistical mechanics to predict the properties of real liquids are great but shows how recent calculations using integral equation methods, perturbation theory and direct machine simulation methods e.g. Monte-Carlo and

molecular dynamics, have been useful for monatomic liquids and, with some approximations, for liquid water. He prefers continuum to mixture theories since the latter are based upon the idea that hydrogen-bonds are essentially covalent and can therefore be broken, an idea which, he says, is not supported by experimental evidence.

O'Ferrall et al³⁹ on the other hand, show that calculations for frequencies for intramolecular bending and stretching modes as well as for intermolecular stretching and bending of hydrogen bonds agree with those determined experimentally by Walrafen^{21,24,27,30} and thus support mixture models.

There is, however, debate upon whether the best mixture model is a two- or many-state model. The simplicity of a two-state model appeals to Arakawa and Sasaki⁴² whose calculated thermodynamic quantities agree with those obtained experimentally. Nomoto and Endo⁴³ show that sound absorption in water is compatible with the interstitial model proposed by Narten et al³⁷ provided a cluster-structure of finite size is assumed. Narten and Levy³⁶, on the basis of radial distribution functions, find only an interstitial model based on ice-I to be tenable. They point out that most proposed models for liquid water cannot be tested against diffraction data because they are not sufficiently defined at the molecular level.

Gurikov's⁴⁴ calculations for a mixture model based on a regularly expanded framework in which all the distances of the ice lattice are increased by the same factor, reproduce the characteristic features of the radial distribution curve, molal volume and coordination number of water.

Perram⁴⁵ suggests that most models for the structure of water do not predict the density maximum observed in liquid water, so he proposes one which does. This is a three-dimensional lattice with large interstices

and is related to a two-dimensional array proposed by Bell and Lavis⁴⁶, by a simple transformation. Perram's⁴⁵ theory is independent of the bent or straight nature of the hydrogen-bond although the retaining of ice-I lattice in the short-range requires strong, highly directional hydrogen bonds formed between water molecules. He claims that arguments about discrete or continuum models, flickering clusters and bent or straight H-bonds, on a qualitative level, are irrelevant. In an earlier paper, Perram and Levine⁴⁷ examined the statistical consequences of cooperative hydrogen bonding and showed that such bonding leads to an extensive bond network, interrupted by regions containing relatively few bonds. This is in agreement with Del Bene and Pople's⁴⁸ MO calculations which showed that the strength of bonding increases with the number of units in a chain and that ring polymers are more stable than chains. It has also been shown⁴⁷ that the formation of flickering clusters is not a necessary consequence of cooperative hydrogen bonding.

Levine and Perram⁴⁰ have indicated that the concentration of monomer in liquid water is very small. This conclusion has also been reached by Glew et al⁴⁹ and Lenzi⁵⁰. Glew et al also make the claim that the statistically and semantically different mixture and continuum theories are physically similar. Once the number of species in a mixture model is increased it gradually becomes a continuum model, but most statistical evidence for mixture models favours a two-state model at present. Stillinger and Rahman⁵¹, however, state that molecular dynamics calculations conflict with two-state theories which divide molecules dichotomously into "bonded" vs "unbonded". They declare that separate molecular energies should be calculated for molecules engaging in different numbers of H-bonds.

A "two-state" thermodynamic model has been postulated by Angell⁵² by assuming a random tetrahedral structure as the configurational ground-

state and obtaining a "bond lattice" by considering the whole region of space between neighbouring oxygen atoms along the lone pair-to-proton axis as a bond lattice point. Thus the set of strongly interacting matter points of the water lattice is replaced by a new set of twice the number of weakly interacting energy points. Hydrogen-bonds can be broken and this results in the "turning off" of the interaction between adjacent molecules, and an accompanying configurational excitation producing an instability which is reduced when a near-neighbour oxygen "snaps" out of line along the O-H --- O axis and the various neighbours readjust positions to reduce local strain to a minimum. There are thus two states of the lattice, "off" (broken bond) and "on" (intact bond), but no molecular species are postulated as in the usual mixture models. This is a distinct advantage when it is considered that other authors are not agreed on whether there are non-H-bonded water molecules present, and if there are, then what fraction of all molecules is unbonded. Falk & Ford²² compiled a list of values estimated for 0°C and found variation from 2 to 72%.

Angell's model⁵² leads to reasonable agreement with such properties as the temperature dependence of chemical proton shift and the more contentious two-species Raman and infrared spectra. The broad band aspects of these spectra are indeed expected from the distribution of bond energies characteristic of the random network.

In addition, various transport properties can be predicted by this model. These include the temperature dependence of viscosity and dielectric relaxation times.

So it is seen that recent theoretical work generally supports a mixture model but as most authors applied their calculations only to mixture models their work does not rule out the possibility of continuum models and Watts⁴¹, does, in fact, support such a model.

Ben-Naim's⁵³ work is, then, of particular interest and importance. He discusses the problem of splitting a one-component fluid into a mixture of various species differing in their local environments. This is done by following a certain molecule and introducing the probability of observing this molecule in a well-prescribed environment. The distribution function thus defined may be reinterpreted as comprising the mole fractions of the various quasicomponents. He describes two quasicomponent distribution functions, one representing a discrete type, the other a continuous type, then links the two. It is concluded that whenever an exact classification into quasicomponents is carried out, the "uniform" or the "mixture" point of view should be equivalent. He believes this discussion is useful to the understanding of liquid water.

1.2.7. Conclusion

It is thus seen that both experimental and theoretical work may lead to the conclusion that, from the formal point of view, the so-called "continuum" and "mixture model" approaches to the theory of water are equivalent⁵³. This then allows one to choose the more satisfactory alternative to aid interpretation of phenomena observed when water structure may be disturbed by the introduction of solutes.

1.3. Proton Mobility

1.3.1. Introduction

The mobility of a proton in water and also in ice is much greater than that of other ions, even when hydrated ions of similar radius to H_3O^+ are considered. In water the mobility of most ions is in the $4 \text{ to } 8 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1} \text{ V}^{-1}$ range whereas the proton's mobility is $36 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1} \text{ V}^{-1}$ ⁵⁴. Furthermore, protons have a higher mobility in ice than in water, in contrast to other ions. These great disparities

suggest that the proton moves by a different mechanism from that of other ions.

The overall hydration energy of the proton ($266 \text{ kcal mol}^{-1}$) is larger than its energy of interaction with one water molecule⁵⁵, indicating interaction between H_3O^+ and other water molecules, and H_9O_4^+ groups of tetrahedral structure most probably exist.

Any theory of proton mobility must be able to account for the following experimental findings⁵⁶:

- (1) an increase of mobility with pressure,
- (2) a low apparent energy of activation,
- (3) a decrease in activation energy with increase of temperature,
- (4) an isotope ratio of 1.4 for hydrogen ions,
- (5) a decrease in mobility when water is partially replaced by alcohols.

1.3.2. Mechanism of Proton Transport

The reaction $\text{H}_3\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{H}_3\text{O}^+$ takes place readily when a proton is directed towards a vacant orbital of an adjacent water molecule, since the configurations are of equal energy. This very fast proton transfer enhances the normal method by which ions, with their solvation sheaths, are translated bodily through the medium, for although a proton moves only about 0.8 \AA , there is a charge transport over about 3 \AA .

Proton tunnelling is most probably the way the proton moves but no transfer can take place unless the receiving water molecule is correctly oriented to receive the proton. Rotation of water molecules will be occurring continually by normal thermal motions but these alone are too slow to account for the measured proton mobility⁵⁵. There is, however, attraction between a proton and a water dipole so that water molecules are more readily rotated, bringing an empty orbital in line with a proton. Conway, Bockris and Linton⁵⁶ have calculated that at

least 90% of the protons (and deuterons) are transported in this way, (Lown and Thirsk⁵⁷ say 79%), and they have shown that in liquid water, orientation of the water molecule is the rate-determining step in proton transfer.

Eigen and de Maeyer⁵⁴ postulate what is essentially a similar mechanism, viz. the proton oscillates rapidly within the H_9O_4^+ complex until hydrogen bond rupture and formation occur at the periphery with a water molecule appropriately oriented. There is thus structural diffusion⁵⁸ since an originally secondary hydration H_2O becomes the centre of a new complex.

It is to be noted that Mandel⁵⁹ pointed out that proton transfer as described must be initiated as well as propagated and most authors consider only the latter. Hills et al⁶⁰ replied that in the case of water there is no difficulty, as the symmetry of the water molecule, the rapid intra-molecular charge transfer and the nature of inter-molecular bonding readily enable both steps to proceed.

The mechanism described above is entirely in accord with the fact that protons exist in water as H_3O^+ , since the jumping protons have no independent existence except during the actual transfer which occurs very rapidly.

1.3.3. Isotope Effect

The ratio of the mobilities of the proton and deuteron in water viz. 1.4, is higher than the size difference would be expected to account for. Gierer and Wirtz⁶¹ have, however, shown that the mobilities of hydrogen and hydroxyl ions depend upon a frequency factor which in turn is proportional to the square root of the reciprocal mass, and so have provided an explanation for the large mobility difference of protons and deuterons.

1.3.4. The Effect of Temperature and Pressure

The energy of activation of most ionic mobilities is constant over an appreciable temperature range, but that for proton mobility decreases with increase of temperature. Increase of pressure also increases proton mobility. The models of Conway et al⁵⁶ and of Eigen and de Maeyer⁵⁴ can explain this anomalous behaviour since the reduction in the degree of hydrogen bonding in water with rising temperature or pressure means that fewer hydrogen bonds have to be disrupted or distorted when a water molecule re-orientates. Experimental work of Conway et al⁵⁶ supports their theory that proton transfer is not the rate-determining step in proton mobility.

Further evidence for a different mechanism for proton transport from that of other ions comes from Horne et al⁶² who studied the pressure dependence of the conductance of some electrolytes and found that the activation energy of conductance curve for KCl resembled that for the viscosity of water, even though the minima occurred at slightly different pressure values, while the curve for HCl bore little relation to either the KCl curve or the viscosity curve. Ions such as K^+ and Cl^- move, with their hydration sheaths, bodily through the medium and their conductance should be expected to depend upon the viscosity of the medium. That the HCl curve is so different may be taken as evidence for an entirely different mechanism from normal ionic transport for the proton, since it is the proton's contribution that dominates HCl conductance.

1.3.5. Proton Mobility in Ice

Confirmation for the model described above comes from a consideration of the very high proton mobility in ice, as compared with water. Eigen and de Maeyer⁵⁴ invoke the imperfection of hydrogen bonding in

water as compared with ice to account for the lower mobility of the proton in water, while Conway et al⁵⁶ argue that proton-tunnelling must be the rate-determining step in ice. Conway⁶³ notes that re-orientation has a different meaning in ice and water, since in ice it is only by librational oscillations that molecules are moved from the "right" position for proton transfer. Thus, in agreement with Eigen and de Maeyer⁵⁴, this shows that lattice order plays a major part in the excess proton mobility in ice. Horne and Axelrod⁶⁴ question this, quoting results of Bradley⁶⁵ and Heinmets⁶⁶ who claim that proton mobility in water and ice is comparable. Conway and Bockris⁶⁷ had previously answered Bradley⁶⁵, though, by pointing out that although conductivity may be similar in water and ice this required a much greater proton mobility in ice to counter the low proton concentration in ice. It is possible that the use of impure ice gave incorrect values for proton mobility measured by Heinmets⁶⁶.

Bockris and Reddy⁵⁵ assert that with the low concentration of protons in ice, normal re-orientation times would be sufficient not to hold up proton transfer from H_3O^+ to H_2O . The actual number of protons crossing a given surface will be less than in water, but the protons will travel faster in ice - at a speed concordant with quantum mechanical tunnelling which thus becomes the rate-determining step in proton transfer. Forslind, however, in 1963, in a private communication to Kavanau⁶⁸, warns against unreserved acceptance of tunnelling as a working hypothesis to explain proton exchange in aqueous systems.

Nevertheless the model of Eigen and de Maeyer and Conway et al can explain satisfactorily the excess mobility of protons, its anomalous variation with temperature and pressure, its low energy of activation and its high isotope ratio and will therefore be accepted here.

1.3.6. The Effect of Electrolytes

Another factor affecting proton diffusion is the presence of electrolytes in the solution. When their concentration becomes so high that nearly all water molecules are under their influence then proton mobility is lowered to a value more like that of other ions. This is pertinent to the question of the forces between water molecules in the bulk solution. Hills et al⁶⁹ argue that free rotation of water molecules requires free water molecules, and that aggregates, as proposed by Frank and Wen⁵, for example, would be a hindrance to water rotations. They acknowledge the occurrence of chain transport of protons, particularly at low temperatures, but suggest that high proton mobility occurs in spite of hydrogen bonding rather than because of it, and also that the same interactions which result in cluster formation will also hinder the rotation of water molecules and so reduce proton mobility. Horne and Johnson⁷⁰ believe that proton transfer requires "free" rotatable water molecules, though they also say⁷¹ that the "free" water molecules are aware of each other by virtue of weaker bonding forces. Conway⁷² claims that no molecules are free, and upholds the possibility of bent hydrogen bonds throughout the solution rather than the existence of some free and some bound water molecules. He doubts if water molecules in the condensed structure of water can ever be regarded as free in the sense of being steam-like, and re-affirms his theory of field-induced orientations within the structural "lattice" of liquid water.

Lown and Thirsk⁵⁷ discuss the effect of pressure on conductance of alkali metal hydroxide solutions and find that as concentration of electrolyte increases the conductivity-pressure relationship changes until it begins to resemble that for ions other than hydrogen and hydroxyl as concentration exceeds about 3.5M. They suggest that

this is due to the decrease in the number of "bulk" water molecules in the solution, as a consequence of which proton transfer is hindered and its contribution to total conductance thereby reduced. In a 1m solution of 1:1 electrolyte which dissociates completely there are 56 moles of water to each two moles of ions; in a 3.5m solution there are 16 moles of water to each two moles of ions. At even higher concentrations ion-pairing may occur.

Table 1.3.1 shows estimates of the average separation of ions in a solution, assuming that the ions are arranged on a cubic lattice, at least as a time-average.

Table 1.3.1⁷³ Average Separation of Ions in a Solution of a 1:1 Electrolyte

c (mole ℓ^{-1}):	0.001	0.01	0.1	1.0	10.0
Separation (\AA):	94	44	20	9.4	4.4

It is seen that even at a concentration of 1m there are few molecules that are not influenced by an ion which inhibits their ability to re-orientate and thus impedes the proton transfer mechanism, while it is reasonable to talk of successive layers of water molecules round one particular ion only below about 0.1m⁷³. At high concentrations of electrolyte, therefore, proton conductance most probably occurs by the "normal" hydrodynamic mechanism.

The temperature dependence⁵⁷ of conductance in aqueous alkali metal hydroxide solutions also corroborates Low and Thirsk's view⁵⁷ that the mechanism of conductance in very concentrated solutions is of the hydrodynamic type rather than the proton transfer type.

1.3.7. Conclusion

The model of proton transport suggested by Conway et al⁵⁶ and Eigen and de Maeyer⁵⁴ is considered satisfactory to account for high proton mobility in dilute solutions. As the concentration of electrolyte increases, though, the number of water molecules able to re-orientate freely is so reduced that proton transfer may take place in the same way as that of other ions.

1.4. Polarography

1.4.1. Diffusion Current and Diffusion Coefficient

In the early 1920's Jaroslav Heyrovsky made a study of the current-voltage relationships obtained in electrolysing solutions using mercury electrodes, one of which was easily polarised while the other remained unpolarised. To a dilute solution of the electroreducible (or oxidisable) substance, A, another electrolyte was added. This added electrolyte, whose concentration should be about a hundred times that of A, must not participate in any way in the electrode reaction or react with A, so it is termed an indifferent electrolyte. Its presence is required to carry the migration current so that transport of species A occurs by diffusion only in the concentration gradient set up as the electrode reaction takes place. It can be shown that the limiting value of this diffusion current is proportional to the concentration of the substance being reduced or oxidised. The theory and techniques of polarography have been well described by several authors including Milner⁷⁴ and Kolthoff and Lingane⁷⁵, so only main points are mentioned here.

In the present study the easily polarised electrode was a dropping mercury electrode i.e. it consisted of a piece of glass capillary tubing from which mercury dropped at the rate of a drop every few seconds.

Such an electrode is continually renewed by the formation of small droplets of reproducible size. The high hydrogen over-potential on mercury enables this electrode to be used in acid solutions.

As the potential difference across the cell is gradually changed, there is at first a small current flowing, the residual current. After a certain potential has been reached - the decomposition potential - the ions are discharged at the dropping mercury electrode, thus reducing their concentration near the drop-solution interface. Diffusion takes place to compensate. As the pd is changed further there comes a time when the ions are reduced so rapidly that their concentration at the interface is virtually zero, so that the rate of diffusion becomes steady. Thus there is a steady diffusion current which is practically unaffected by further changes of applied potential.

In 1934 Ilkovic⁷⁶ published a derivation of the relationship between the diffusion current and the concentration of an electro-reducible or -oxidisable species, for the case of the dropping mercury electrode, using the fundamental equation of linear diffusion. This was followed three years later by another derivation by MacGillavry and Rideal⁷⁷ based on the equation of spherically symmetrical diffusion, but using certain approximations. For the average current, the Ilkovic equation is, at 25°C:

$$i_d = 607 n D^{1/2} C m^{2/3} t^{1/6}$$

where i_d = diffusion current in microamperes,

n = number of faradays per mole of electrode reaction,

D = diffusion coefficient of the depolariser in $\text{cm}^2 \text{sec}^{-1}$,

C = concentration of the depolariser in millimoles per litre,

m = rate of flow of mercury in mg sec^{-1} ,

t = drop time in seconds.

In later years, modified forms of the Ilkovic equation were derived. These are of the form:

$$i_d = 607 n D^{1/2} C_m^{2/3} t^{1/6} (1 + A D_m^{-1/3} t^{1/6}) \quad \text{at } 25^\circ\text{C.}$$

In 1950 Strehlow and von Stackelberg⁷⁸ published a derivation of the Ilkovic equation which gave A the value 17 after retaining mathematical operations previously neglected by Ilkovic⁷⁶ and MacGillavry and Rideal⁷⁷, and which allow for the curvature of the mercury electrode surface.

In the same year Lingane and Loveridge⁷⁹ obtained a value of 39 for A in their derivation of the Ilkovic equation, making allowance for the difference between the equations for linear and spherical diffusion. In 1953, Matsuda⁸⁰ took account of the screening influence of the capillary tip and arrived at 24 for the value of A. Each value is claimed to be supported by experimental results, the various authors generally finding a weakness in the method of others. As will be demonstrated in Chapter 3 of this thesis, the present experimental work supports Strehlow and von Stackelberg's⁷⁸ results. While the correction factor may not be very great for most ions, it is sufficiently large in the case of the hydrogen ion to show that the best of the suggested values of A is 17.

After this work had been completed, it was found that work of Turnham⁸¹ had been overlooked. He studied the value of A in the modified form of the Ilkovic equation using several reducible ions in a number of supporting electrolytes. He measured the rate of change of current towards the end of a non-first drop of lifetime about 16 seconds and, using the differentiated form of the equation, found that the value of A is dependent on the individual ion and supporting electrolyte. Hans and Jensch⁸² obtained a value of 18.4 ± 1.7 in their

hydrogen ion studies. This supports the conclusion drawn from the present studies.

It is to be noted that the diffusion coefficient, D , measured polarographically is actually the coefficient of "inter-diffusion" of the ion under study and the electrolyte solution in which it diffuses. Thus the extrapolated value of D at zero concentration of indifferent electrolyte is not quite the same as the value, D° , obtained for infinite dilution of the ion studied, a value related to the limiting ionic conductivity, λ° , through the Nernst expression, $D^{\circ} = \frac{RT}{F^2} \lambda^{\circ}$, where R , T and F have their usual significance.

Stokes et al⁸³ have shown, however, that for the iodide ion in dilute electrolyte solutions there is little change in the value of the diffusion coefficient as concentration of iodide is reduced. Kolny and Zembura⁸⁴ measured the diffusion coefficient of the hydrogen ion in a 0.1M solution of sodium chloride and found that this was independent of the concentration of hydrogen ion present. It is assumed, then that the values of D determined for the low concentrations of reducible ion in the present study are very close to the values at infinite dilution.

1.4.2. The Half-wave Potential

The half-wave potential is defined as the value of the emf at the mid-point of the polarographic wave where $i = i_d/2$. The most important characteristic of the half-wave potential is that, in a given supporting electrolyte, it is, for a reversible wave, constant and independent of concentration of the reducible ion, provided that the supporting electrolyte concentration and the temperature are kept constant⁷⁵.

In the case of the irreversible reduction of hydrogen, the potential at which hydrogen gas is liberated is much more negative than the ordinary standard $\text{H}-\text{H}^+$ ion potential. This difference in potential is called the overvoltage of hydrogen.

Herasymenko⁸⁵ and Herasymenko and Slendyk⁸⁶ showed that the overvoltage is shifted to more negative values with increasing concentrations of neutral salts in the solution.

Novak⁸⁷ has found that the half-wave potential of deuterium from DCl in D_2O at 20°C was 0.087 more negative than that of hydrogen from the same concentration of HCl in H_2O .

Chapter 2

Experimental Work

2.1. Introduction

Over the years a number of different techniques has been used to probe the water structure problem and to study the effects of solutes on this structure. If hydrogen ion mobility in water could be studied under varying conditions of solute concentration and temperature then this should give new information which, together with that obtained by other means, may help to elucidate the problem.

Polarography enables the diffusion of the hydrogen ion to be studied in the presence of electrolytes. An electrolyte is dissolved in a very dilute solution of a strong acid and the polarographic wave of the solution is recorded⁸⁸. The mobility of the hydrogen ion is affected by the degree and strength of hydrogen bonding in the solvent and this mobility is reflected in the height of the polarographic wave.

Furthermore, the half-wave potential gives information about the over-voltage of hydrogen on mercury and hence changes in the ease with which reduction takes place at the dropping mercury electrode. This in turn is related to the structure of water.

Preliminary work in this laboratory⁸⁸ indicated that polarography could be used profitably to study hydrogen ion mobility since results obtained by this method for the hydrogen ion in lithium chloride solutions, were compatible with those obtained from n.m.r. spectroscopy⁸⁹.

In this Chapter will be found discussions of the purification and analysis of salts, the preparation of solutions, and the various techniques associated with the polarographic analysis carried out in this study.

2.2. Preparation of Acid Solutions

Preliminary work showed that solutions with hydrogen ion concentrations of ca 2×10^{-3} M gave a reasonable range of values of the limiting current when polarograms were run with sodium chloride of concentrations 0.1 - 5m as supporting electrolyte. This agrees with similar findings of Kolny and Zembura⁸⁴ who noticed bubbles of hydrogen on the electrode when the pH of the solution was less than 2.3 and failed to obtain clear-cut polarographic waves above a pH of 4.4.

A stock solution of dilute hydrochloric acid was prepared by adding a calculated amount of AnalaR HCl to deionized water. This was de-oxygenated as far as possible by bubbling through high purity nitrogen which was first passed through two solutions of hypo-vanadous chloride⁹⁰ and then washed in water. The solution was then stored under nitrogen. A check on its concentration was made at frequent intervals by measuring the pH of the solution. The actual concentration was measured by potentiometric titration with sodium tetraborate, and found to be 1.849×10^{-3} M.

Preparation of a deuterium chloride solution of similar concentration presented some difficulty as the molarity of the concentrated DCl solution from Stohler Isotope Chemicals was not known. An approximate calculation of the quantity to add to the heavy water, 99.75% by weight, obtained from the Australian Institute of Nuclear Science and Engineering, was made. The resulting solution was found by potentiometric titration with sodium tetraborate to be 1.17×10^{-3} M. Back titration after adding excess sodium tetraborate and titrating the excess with hydrochloric acid gave the same result.

This solution was also de-aerated and stored under high purity nitrogen, though no attempt to purify the nitrogen further was made. This was considered justified because oxidation of the hypovanadous

chloride used with the HCl solution took place so slowly that the nitrogen seemed truly oxygen-free. A specially designed tap system on the DCl storage vessel enabled the DCl to be obtained from it with very little chance of exchange with H_2O .

2.3. Purification and Analysis of Salts

Where obtainable, AnalaR salts were used, and for the nine alkali halides - chlorides, bromides and iodides of lithium, sodium and potassium - no purification was carried out before the preliminary investigations of the diffusion current were made, though it was found necessary to dry the salts overnight, at reduced pressure at $110^\circ C$.

Tetramethyl-, tetraethyl-, tetrapropyl- and tetrabutylammonium bromides from Eastman Kodak were also used without purification. These bromides were chosen as they are quite soluble in water and are not hygroscopic⁹¹.

When quite different values of the diffusion current were obtained using different samples of AnalaR potassium chloride, it was thought that the variation may be due to a slight excess of acid or alkali in the samples, since pH measurements on several solutions covered quite a wide range. Thus purification of all salts was deemed necessary to enable valid quantitative comparisons of the diffusion currents and coefficients to be made.

Pre-distilled, de-ionised water was used for the recrystallisation of alkali halides and tetramethylammonium bromide. Ethanol was used to precipitate sodium and potassium chlorides and to increase the yield. Unnecessary contact with light and heat was avoided for the iodides as there was a tendency for oxidation to occur when a solution containing dissolved oxygen was heated. After two recrystallisations for the alkali halides and three for tetramethylammonium bromide the salts were dried

under reduced pressure at 110°C for at least a week.

Tetraethylammonium bromide and tetrapropylammonium bromide were recrystallised three times from super-dry ethanol and methanol respectively, and dried under reduced pressure at 110°C . Tetrabutylammonium bromide was recrystallised five times from dry acetone, and dried under reduced pressure at 80°C .

The drying of hydrated salts proved difficult unless phosphorus pentoxide was used for preliminary dehydration of the crystals before they were heated in the oven.

All salts were analysed by titration with silver nitrate previously standardized against sodium chloride, using fluorescein as indicator for chlorides and eosin for bromides and iodides⁹⁰. Knowing the amount of halide present, and assuming the purity of the sample, calculation of the number of moles of water of crystallisation was possible. Allowance for this water was made in calculations of the molalities of these salts and the concentration of the acid.

The melting-point of tetrabutylammonium bromide was used as the criterion for purity. Accascina et al⁹² reported that there is a metastable form of tetrabutylammonium bromide which melts at $101 - 102^{\circ}\text{C}$, while the normal melting-point is $116 - 117^{\circ}\text{C}$. This sample melted at $101 - 102^{\circ}\text{C}$ but when, after solidifying, it was again heated, the melting-point was usually 116°C . No test was made of the purity of tetramethylammonium bromide used in measurement of proton mobility.

As only anhydrous salts could be used in the study of deuteron mobility, sodium chloride, the three potassium halides and four tetraalkylammonium bromides were chosen. The purity of the tetraalkylammonium bromides was calculated after titration of their solutions with standardised silver nitrate solution using the Mohr method, to give the following

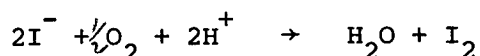
results: Me_4NBr 100.00%, Et_4NBr 100.00%, Pr_4NBr 99.88% and Bu_4NBr 99.69%.

2.4. Preparation of Solutions

Solutions used in measuring proton mobility were prepared by adding a measured volume of HCl solution to a known weight of salt. For deuteron mobility both salt and DCl were weighed and all transfers of solid and liquid to the weighing tube were made inside a glove-bag filled with dry nitrogen.

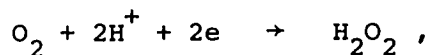
Concentrations of supporting electrolytes were measured on the molal scale for proton mobility measurements, and on the aquamolal scale i.e. mole of salt per 55.5 mole of heavy water, for deuteron mobility measurements.

Experience showed that it was best to prepare solutions immediately before use. This was most essential in the case of iodides which were readily oxidized in the acid solution at the expense of the hydrogen ion concentration.

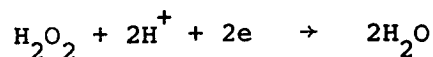


2.5. De-oxygenation of Solutions

Oxygen is reduced in two steps at the dropping mercury electrode. In acidic solutions the first wave is caused by the reduction of oxygen to hydrogen peroxide:



and the second wave is due to the reduction of the hydrogen peroxide to water:



Since this double wave interferes with the reduction of hydrogen, all oxygen must be removed from the test solution.

This was done by bubbling high-purity nitrogen through test solutions for ten minutes. In the proton mobility study the nitrogen was passed through a train of two solutions of hypovanadous chloride to remove any oxygen which may have been present, and then through distilled water which washed the gas. In this way the nitrogen was also saturated with water vapour to prevent evaporation into or condensation from the gas stream. As there was no evidence for the presence of oxygen this purification was omitted in the deuteron mobility studies.

When a pool of mercury was used as anode, it was found that this deoxygenation must be done in the absence of mercury, for when mercury is in contact with a halide solution there is formed HgX_2^{93} which is markedly covalent.



Since
$$E = E_{\text{Hg}/\text{Hg}^{2+}}^{\circ} + \frac{0.059}{n} \log [\text{Hg}^{2+}]$$

the lowering of Hg^{2+} concentration in the presence of Cl^- makes E more negative, e.g. if $[\text{Hg}^{2+}]$ is lowered from 1 to 10^{-1}M , then

$$\begin{aligned} E &= 0.79 + \frac{0.059}{2} \log 10^{-1} \\ &= 0.79 - 0.03 \\ &= 0.76 \end{aligned}$$

If $[\text{Hg}^{2+}]$ is 10^{-3}M then

$$\begin{aligned} E &= 0.79 - 0.09 \\ &= 0.70 \end{aligned}$$

Now in the solutions used, $[\text{H}^+] \approx 2 \times 10^{-3}\text{M}$

so E for $\text{O}_2/\text{H}_2\text{O}_2$, H^+ is not 0.68

$$\text{but } E = E_{\text{O}_2/\text{H}_2\text{O}_2, \text{H}^+}^{\circ} + \frac{0.059}{2} \log \frac{[\text{H}_2\text{O}_2]}{[\text{H}^+]^2 [\text{O}_2]^2}$$

Then if $[\text{H}_2\text{O}_2] = [\text{O}_2] = 1\text{M}$, and $[\text{H}^+] = 2 \times 10^{-3}\text{M}$,

$$\begin{aligned}
 E &= 0.68 + 0.03 \log (4 \times 10^{-6}) \\
 &= 0.68 + 22 \\
 &= 0.90
 \end{aligned}$$

i.e. the potential of Hg/Hg^{2+} in the presence of a halide ion is less than the potential of $\text{O}_2/\text{H}_2\text{O}_2, \text{H}^+$ and so oxygen is reduced to OH^- .

2.6. Constant Temperature Bath

The water bath was maintained at the required temperature with a variation of $\pm 0.1^\circ\text{C}$. For deuteron mobility studies the water was replaced with a light oil to minimise the possibility of isotope exchange.

2.7. Polarograph

A Yanagimoto A.C. - D.C. Polarograph model P.A. 102 was used. This is a pen-recording instrument with an electronic self-balancing recorder, including the potential measuring, residual current compensating, damping and initial voltage applying circuits and the zero adjuster.

The span voltage may be adjusted to cover values from 0 to 3V. In this work span voltages of either 2 or 2.5V. were used, corresponding to 0.1 or 0.125 volt per cm of chart paper. A parallel capacitance circuit enables the oscillations to be adjusted.

2.8. Reference Electrode

A saturated calomel electrode was used in obtaining the first series of polarograms. This enabled the half-wave potentials to be measured. When measurements were made at temperatures above 25°C the limiting current was not always reproducible. As this could be due to exchange of electrolyte between salt bridge and test solution, a possibility considered more probable when the salt bridge was distinctly

reddened after use with tetrabutylammonium nitrate, it was decided to eliminate the salt bridge and substitute a pool of mercury as the anode.

2.9. Polarographic Maxima

Some polarograms for the reduction of H^+ in electrolyte solutions showed slight maxima. Attempts to suppress these with gelatine or methyl red were unsuccessful.

2.10. Measurement of i_d and $E_{1/2}$

Most polarograms showed a sufficiently clear plateau for measurement of the wave-height to be standardized quite simply. Preliminary measurements of the residual current of aqueous solutions of supporting electrolytes and comparison with the curves obtained in the acid solutions indicated that allowance for the residual current could effectively be made by extending the base line obtained before the decomposition potential was reached. The most general allowance, of the order of 1%, compared favourably with the precision with which the limiting current could be measured. Three measurements of i_d were made generally.

In the case of deuteron reduction, the upper parts of some polarograms were not exactly parallel to the lower parts, so the method suggested by Meites⁹⁴ was used.

Lines A A' and B B' were drawn through the mid-points of the lower and upper sections of the polarographic wave, as shown in Figure 2.10.1, making these two lines as near to parallel as the curve permitted. C C' was also drawn through mid-points of the steep section of the curve. The vertical height D F, drawn so that D E = E F, then gave the required current.

The half-wave potential is the value of the e.m.f. at the mid-point

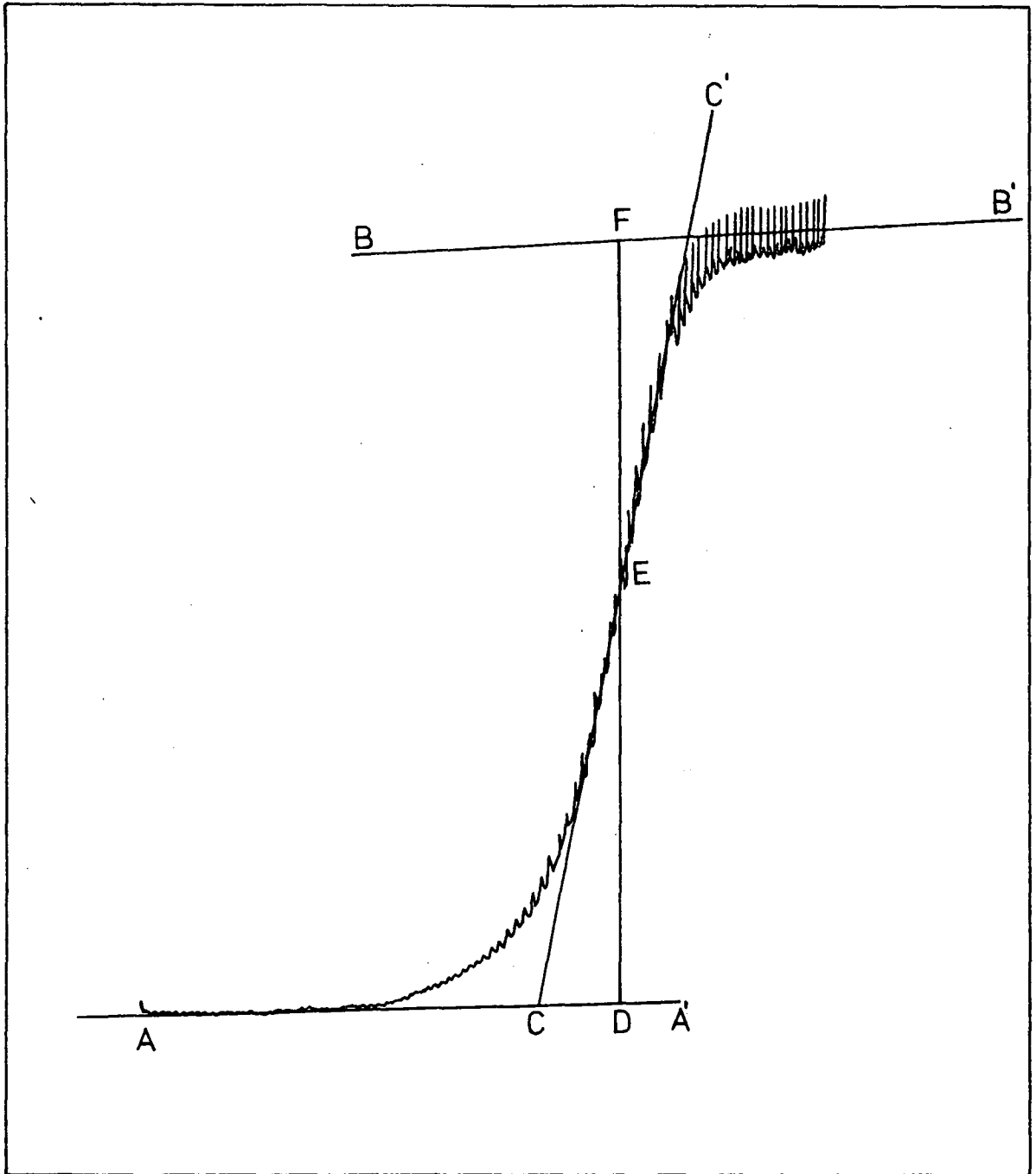


Figure 2.10.1 Method of measuring i_d

of the polarographic wave, where $i = \frac{1}{2}i_d$, i.e. the voltage at D in Figure 2.10.1. This is only of significance when a standard reference electrode is used, as in the first set of measurements on alkali and tetraalkylammonium halides at 25°C.

2.11. Measurement of m

The rate of flow of mercury, m , was measured by counting, weighing and timing drops of mercury falling into a small glass cup in the test solution while the pd at which the limiting current was measured was applied to the cell. The upper portion of the cell was widened as shown in figure 2.11.1 in order to contain both dropping mercury electrode and cup, but the dimensions of the lower part were the same as those of the ordinary cells so that the surface area of the anode was sensibly the same at all times. Mercury was always allowed to drop freely for several seconds before the collecting and timing began. An automatic device described by Lingane⁹⁵ unfortunately proved unreliable.

2.12. Measurement of t

As it was desirable to measure t , the drop time, while each polarogram was being obtained, values of t were calculated from the chart which turned through 1 cm in 35.92 seconds, by counting the number of drops which fell in a given time, while the applied potential was near that at which the limiting current was measured. The three values obtained sometimes showed a 2% difference but values of $i_d/t^{1/6}$ usually fell within 1% of each other.

2.13. Polarography of the Cadmium Ion

It was suggested by Franks⁹⁶ that the mobility of hydrogen ions and

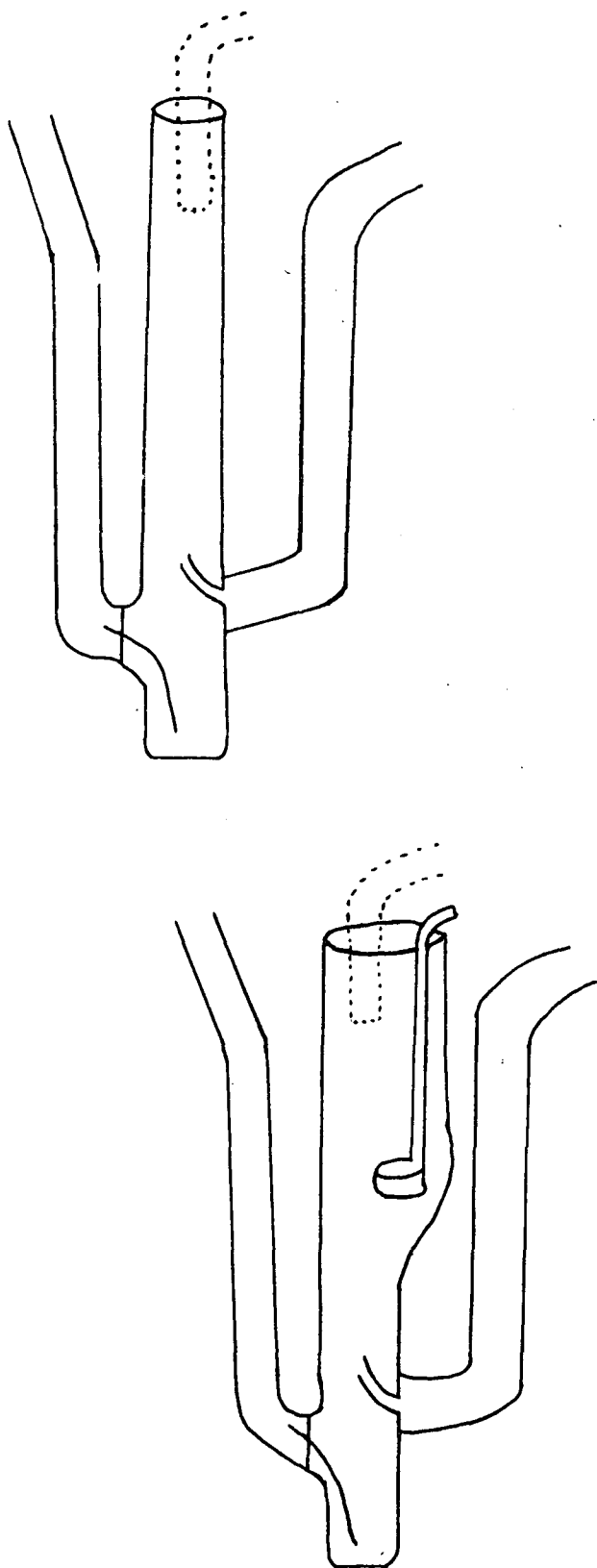


Figure 2.11.1 Comparison of cells used (a) in normal measurement of i_d and (b) in the measurement of m

alkali metal ions would be affected differently by modifications of water structure, since the ratio of their mobilities in ice and water is 10^3 for the hydrogen ion and $<10^{-4}$ for the lithium ion. The reduction potentials of the alkali metal ions were considered too negative to enable their ionic diffusion currents to be studied in the same way as those of the hydrogen ion, but it seemed that another metallic ion could be substituted and the cadmium ion was chosen, since the use of this ion for periodic checks of the polarograph showed that its wave is well-defined and reproducible. When alkali chlorides were used as supporting electrolytes the anomalous shape of the current vs concentration curves was realised to be due to complex formation. Alkali nitrates were then used instead of chlorides. This was considered reasonable as the structure-modifying effect of the nitrate ion has been found by several authors⁹⁷ to lie between that of the chloride and bromide ions.

2.14. The Use of Oxy-ions as Supporting Electrolytes

The nitrates of sodium and potassium, and potassium chlorate were used as supporting electrolytes. No clear plateau was obtained with the nitrates. The low solubility of potassium chlorate allowed only very few measurements to be made, so no useful information could be obtained from this study.

2.15. Measurement of pH

A Pye Potentiometric pH meter was used for all pH measurements that were made.

2.16. Measurement of Viscosity

Some relative viscosities were calculated from data compiled by Stokes and Mills⁹⁸. Others were determined using an Ostwald viscometer.

2.17. Energy of Activation

The temperature of the water (or oil) bath was adjusted to enable diffusion current measurements to be made at various temperatures. Care was taken to allow solutions to come to the required temperature before diffusion currents were measured.

2.18. Stability of Tetraalkylammonium Ions in Heavy Water Solutions

The n.m.r. spectra of the DCl solution and of tetrabutylammonium bromide solution in DCl freshly-prepared, and again after 24 hours, were taken. These showed (a) that there was a very small number of protons present and (b) that there was no exchange of tetrabutylammonium bromide hydrogen atoms with deuterium atoms.

Chapter 3

Results

3.1. Introduction

In this Chapter, data obtained experimentally and results derived from these are presented.

Section 3.2 gives data obtained in preliminary work on proton diffusion in a number of halide solutions and enables general trends in the relationships between concentration of supporting electrolyte and (a) diffusion current and (b) half-wave potential to be seen. Similar data for cadmium ion diffusion are reported in Section 3.3.

The validity of the polarographic method is tested using results presented in Section 3.4. Values of the diffusion coefficient were calculated by computer.

In Section 3.5, data obtained for deuterium diffusion in selected supporting electrolytes are reported, together with calculations made from these.

Finally, in Section 3.6 are found data for proton and deuterium diffusion at various temperatures and the corresponding diffusion coefficients. These values are used later in calculating the energies of activation of the diffusion processes.

All data refer to measurements made at 25°C unless otherwise stated.

Throughout this work some quantities are mentioned frequently by symbol without any statement of their units. These quantities are listed below:

D = diffusion coefficient in $\text{cm}^2 \text{sec}^{-1}$

$E_{1/2}$ = half-wave potential in volts vs S.C.E.

i_d = diffusion current in microamperes

T = temperature in K

temp. = temperature in $^{\circ}\text{C}$.

m = rate of flow of mercury (mg sec⁻¹) or mobility

3.2. Proton Diffusion in Solutions of Halides - Preliminary Investigation

At first no attempt was made to purify the salts used in the measurement of the hydrogen ion diffusion current and half-wave potentials in electrolyte solutions, although after a few measurements had been made it was decided to dry the salts.

This preliminary work on nine alkali halides and four tetraalkylammonium bromides gave results summarised in Tables 3.2.1 - 3.2.13, and plotted, for some cases, in Figures 3.2.1 - 3.2.4.

3.3. Diffusion of the Cadmium Ion

The reasons for studying diffusion of the cadmium ion are stated in Chapter 2. Results obtained are reported in Tables 3.3.1 - 3.3.3, while Figure 3.3.1 shows how the diffusion current varies with concentration of the supporting electrolyte for hydrogen and cadmium ions in potassium chloride and nitrate solutions respectively.

3.4. Proton Diffusion in Solutions of Purified Salts

Preliminary work indicated that polarography could be used to study differences in proton mobility in solutions of various electrolytes. It also gave information which can be used to compare proton diffusion with that of the cadmium ion. It was then necessary to test the validity of the method by calculations of the diffusion coefficients using the Ilkovic equation. Well dried, purified salts were used in these determinations.

Table 3.2.1.

Data for proton diffusion in lithium chloride

molality	i_d	$-E_{1/2}$
0.15	18.74	1.56
0.31	17.22	1.56
0.45	16.71	1.56
0.76	14.74	1.56
0.95	14.33	1.56
1.139	13.29	1.56
1.898	12.27	1.525
2.368	11.76	1.53
2.864	10.80	1.52
3.413	9.62	1.50
3.942	8.88	1.48
4.491	7.90	1.475
4.985	7.83	1.375

Table 3.2.2.

Data for proton diffusion in lithium bromide

molality	i_d	$-E_d$
0.169	16.46	1.56
0.348	15.20	1.55
0.515	13.70	1.55
0.081	12.60	1.54
0.808	12.65	1.55
1.211	11.19	1.53
1.600	9.82	1.52
1.984	8.35	1.52
2.361	7.82	1.51
2.733	7.09	1.51
3.099	6.47	1.51
3.460	6.14	1.50
3.818	5.62	1.49

Table 3.2.3.

Data for proton diffusion in lithium iodide

molality	i_d	$-E_{\frac{1}{2}}$
0.14	14.97	1.545
0.29	12.44	1.54
0.42	10.61	1.54
0.55	8.82	1.54
0.69	7.87	1.535
1.01	5.11	1.525
1.33	2.54	1.52

Table 3.2.4.

Data for proton diffusion in sodium chloride

molality	i_d	$-E_{1/2}$
0.2	18.58	1.58
0.4	17.70	1.58
0.59	17.06	1.58
0.8	15.36	1.58
1.0	15.78	1.57
1.5	14.93	1.56
2.0	14.44	1.56
2.5	13.40	1.55
3.0	12.76	1.55
3.5	12.22	1.53
4.0	11.87	1.53
4.5	11.44	1.52
5.0	10.48	1.50

Table 3.2.5.

Data for proton diffusion in sodium bromide

molality	i_d	$-E_{1/2}$
0.2	18.78	1.57
0.4	17.36	1.56
0.6	15.82	1.56
0.8	15.44	1.55
1.0	15.39	1.55
1.5	13.88	1.54
2.0	12.89	1.53
2.5	12.74	1.525
3.0	12.09	1.52
3.5	11.36	1.51
4.0	10.89	1.50
4.5	9.65	1.50
5.0	9.94	1.48

Table 3.2.6.

Data for proton diffusion in sodium iodide

molality	i_d	$-E_{1/2}$
0.199	14.60	1.575
0.394	11.43	1.575
0.587	10.03	1.57
0.767	7.42	1.565
0.954	5.92	1.56
1.41	2.62	1.56
1.85	1.64	1.57
2.27	1.27	1.575

Table 3.2.7.

Data for proton diffusion in potassium chloride

molality	i_d	$-E_{1/2}$
0.2	18.78	1.56
0.4	18.20	1.56
0.6	17.14	1.56
0.8	15.92	1.56
1.0	15.65	1.56
1.5	14.93	1.55
2.0	14.75	1.55
2.5	14.54	1.545
3.0	13.62	1.545
3.5	13.22	1.54
4.0	12.72	1.54
4.5	12.55	1.54

Table 3.2.8.

Data for proton diffusion in potassium bromide

molality	i_d	$-E_{1/2}$
0.2	17.60	1.53
0.4	15.72	1.53
0.6	14.13	1.51
0.8	12.11	1.48
1.0	11.68	1.48
1.5	10.30	1.47
2.0	8.30	1.47
2.5	7.99	1.48
3.0	7.11	1.48
3.5	7.02	1.50
4.0	7.11	1.51
4.5	6.24	1.50

Table 3.2.9.

Data for proton diffusion in potassium iodide

molality	i_d	$-E_{1/2}$
0.2	15.33	1.57
0.4	11.42	1.57
0.6	9.38	1.55
0.8	7.85	1.56
1.0	6.60	1.57
2.0	3.89	1.55
2.5	2.67	1.555
3.0	1.55	1.555
3.5	0.64	1.54
4.5	0.07	

Table 3.2.10.

Data for proton diffusion in tetramethylammonium bromide

molality	i_d	$-E_{\frac{1}{2}}$
0.5	11.72	1.50
1.0	8.35	1.43
1.5	6.00	1.45
2.0	4.11	1.44
2.5	2.46	1.44
3.0	1.41	1.44
3.5	0.65	1.38
4.0	0.47	1.37

Table 3.2.1.

Data for proton diffusion in tetraethylammonium bromide

molality	i_d	$-E_{1/2}$
0.1	14.78	1.52
0.2	13.57	1.50
0.4	11.87	1.49
0.6	9.80	1.48
0.8	7.56	1.48
1.0	6.70	1.49
1.5	3.56	1.51
1.8	2.04	1.53
2.5	0.75	1.45
3.0	0.86	1.51
3.5	0.92	1.53
4.0	0.86	1.53
4.5	0.83	1.54
5.0	0.89	1.51

Table 3.2.12.

Data for proton diffusion in tetrapropylammonium bromide

molality	i_d	$-E_{1/2}$
1.0	10.50	1.55
1.5	8.60	1.56
2.0	7.39	1.56
2.5	6.13	1.61
3.0	4.96	1.675
3.5	4.26	1.67
4.0	3.51	1.69

Table 3.2.13.

Data for proton diffusion in tetrabutylammonium bromide

molality	i_d	$-E_{\frac{1}{2}}$
0.2	15.01	1.57
0.4	13.64	1.57
0.6	11.26	1.60
0.8	10.03	1.60
1.0	8.71	1.64
1.5	6.77	1.68
2.0	4.77	1.67
2.5	3.59	1.64
3.0	3.33	1.69
3.5	2.53	1.69
4.0	2.05	1.69

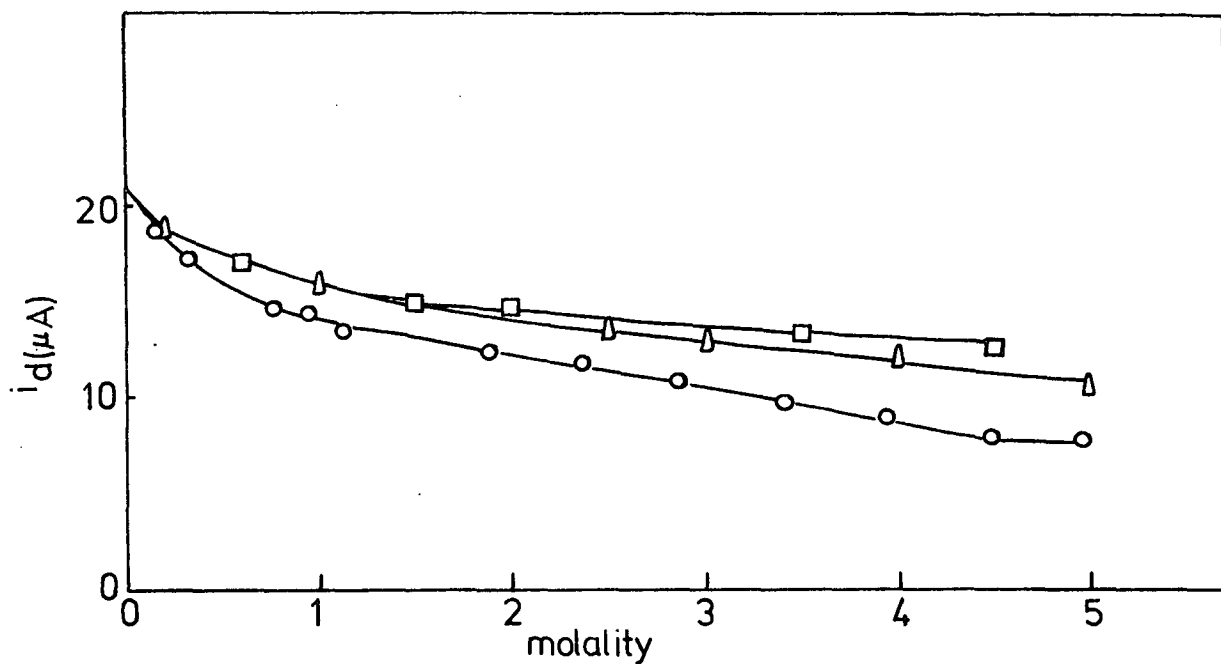


Figure 3.2.1 The effect of concentration of alkali chlorides on the diffusion current of the proton.
 \circ LiCl, Δ NaCl, \square KCl.

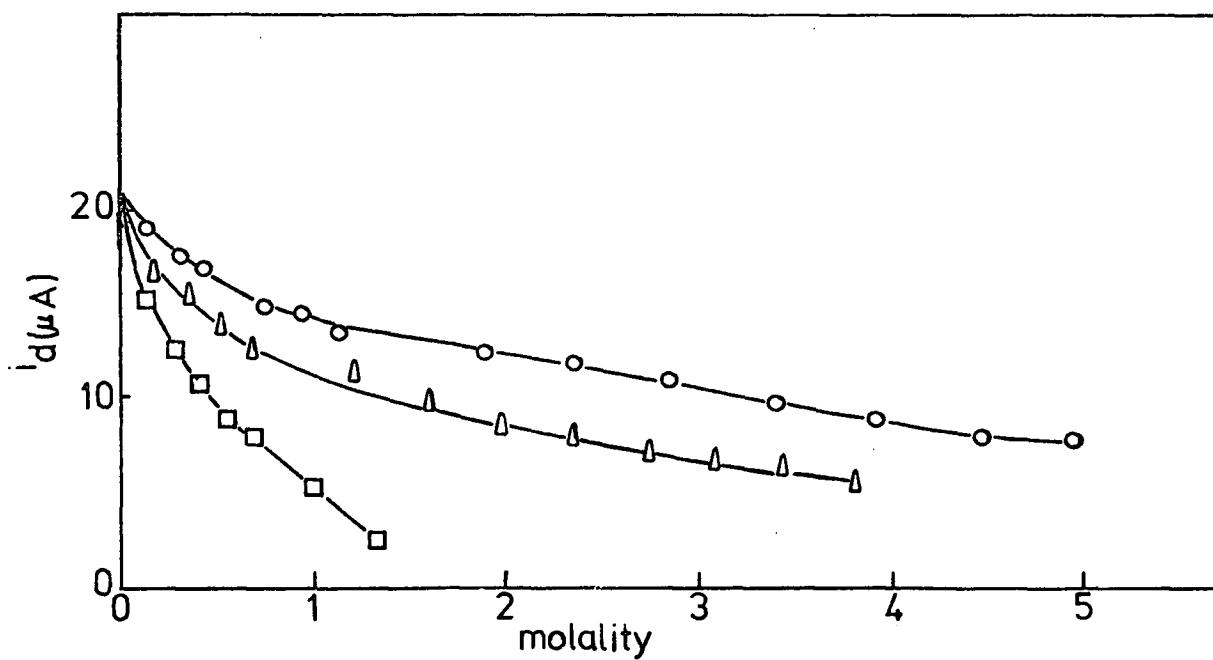


Figure 3.2.2. The effect of concentration of lithium halides on the diffusion current of the proton
 \circ LiCl, Δ LiBr, \square LiI.

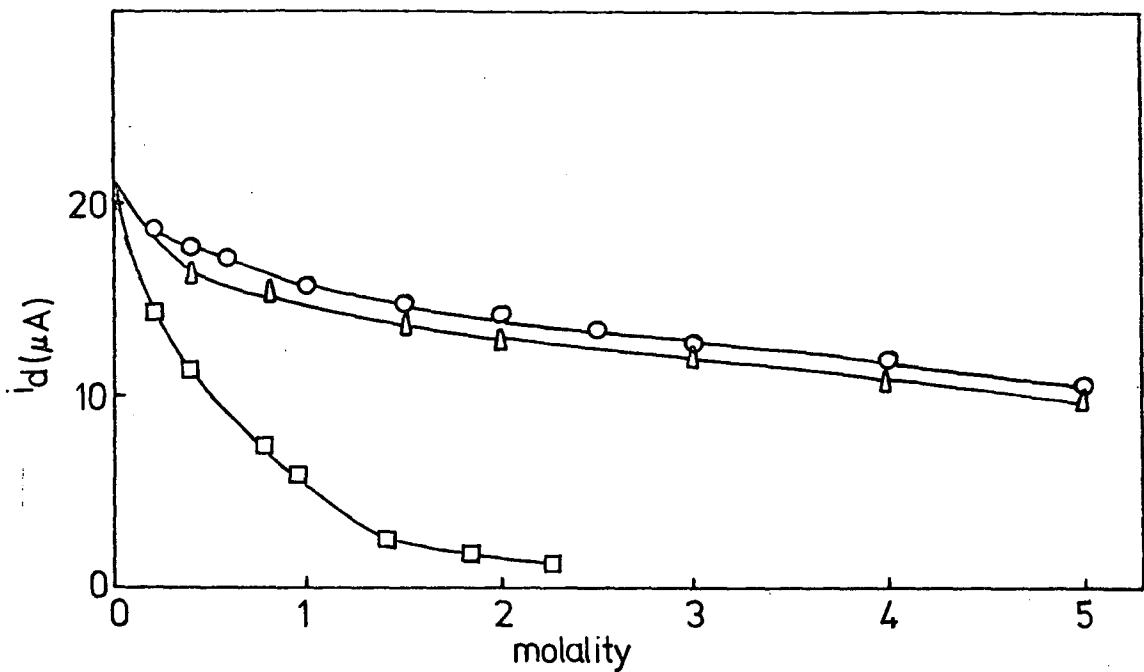


Figure 3.2.3 The effect of concentration of sodium halides on the diffusion current of the proton.
 ○ NaCl, Δ NaBr □ NaI

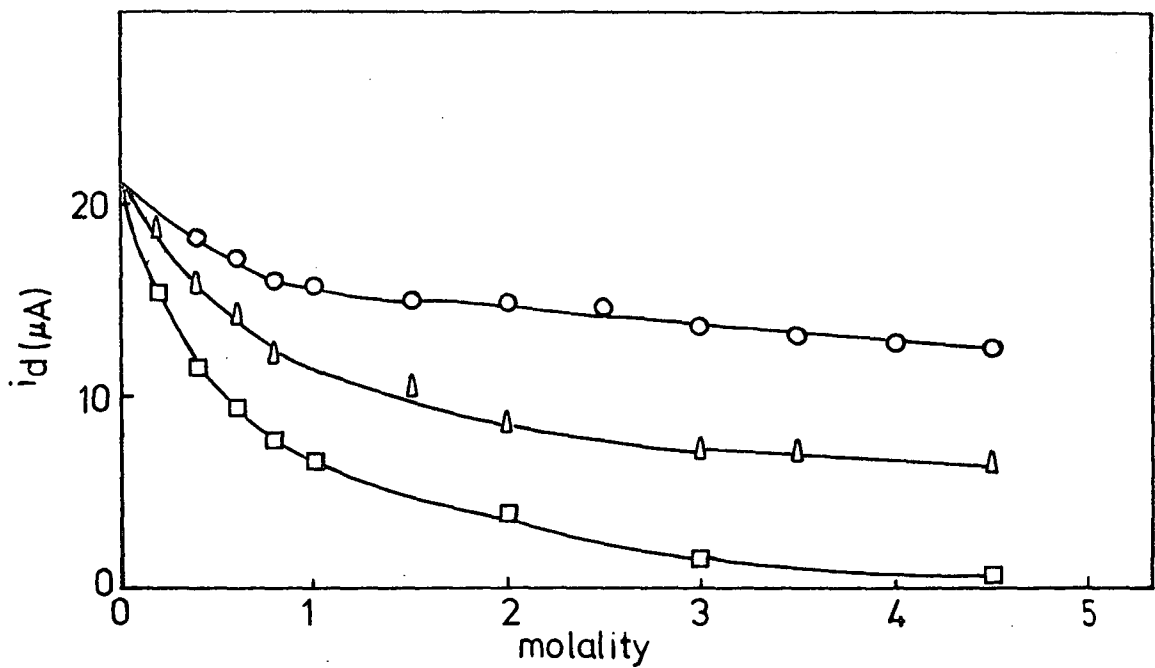


Figure 3.2.4 The effect of concentration of potassium halides on the diffusion current of the proton.
 ○ KCl, Δ KBr, □ KI.

Table 3.3.1.

Data for cadmium ion diffusion in lithium nitrate

molality	i_d	$-E_{1/2}$
0.398	14.49	0.59
0.779	14.37	0.58
1.144	14.26	0.575
1.665	13.58	0.57
1.800	12.91	0.575
2.285	11.93	0.575
2.785	11.38	0.57
3.127	10.98	0.57
3.564	10.77	0.57
4.144	9.925	0.56

Table 3.3.2.

Data for cadmium ion diffusion in sodium nitrate

molality	i_d	$-E_{1/2}$
0.4	14.82	0.59
0.6	14.46	0.58
0.97	14.54	0.59
1.6	14.08	0.58
2.0	13.84	0.58
2.5	13.14	0.58
3.1	12.53	0.58
3.5	12.15	0.575
4.0	11.59	0.575
4.7	10.61	0.57
5.3	10.50	0.57
5.9	9.84	0.57
6.4	9.52	0.57
7.0	8.92	0.55
7.6	8.03	0.56
8.0	8.25	0.555
8.4	8.03	0.545
8.9	7.69	0.55
9.4	7.24	0.54
10.0	7.07	0.535

Table 3.3.3.

Data for cadmium ion diffusion in potassium nitrate

molality	i_d	$-E_{1/2}$
0.34	14.40	0.59
0.55	14.25	0.592
0.82	14.28	0.59
1.23	13.91	0.592
1.64	13.55	0.59
1.97	13.3	0.598
2.47	13.06	0.588
2.96	12.65	0.585
3.3	12.46	0.58
3.7	12.2	0.582

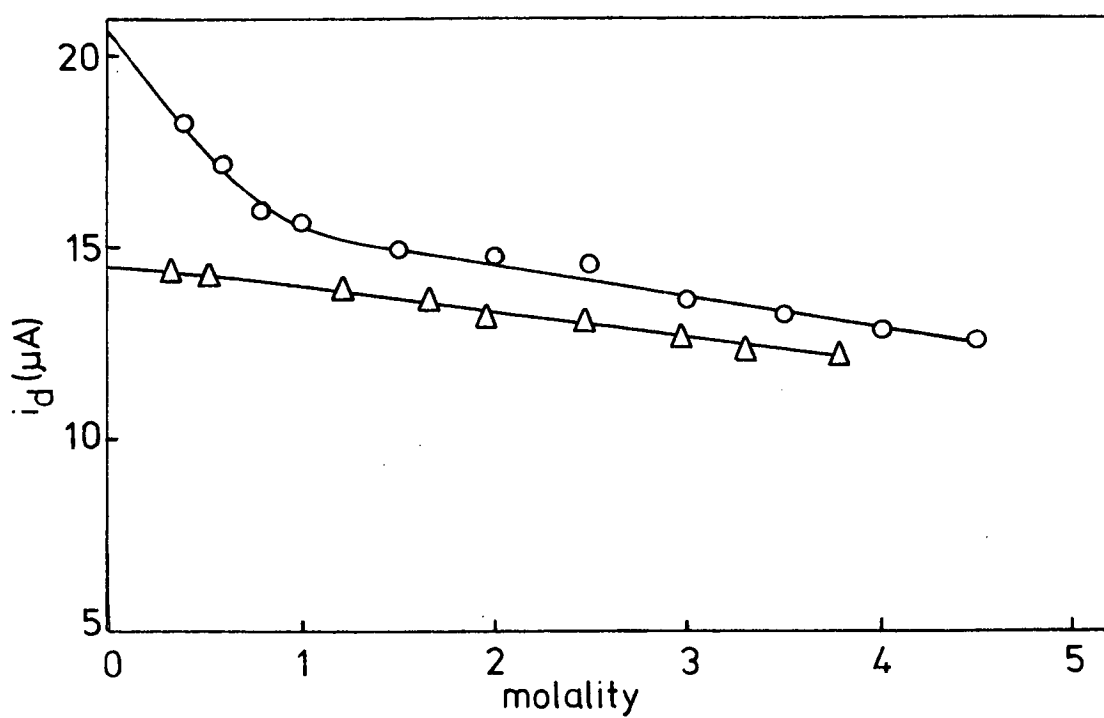


Figure 3.3.1 The effect of concentration of potassium salts on the diffusion current of hydrogen and cadmium ions.
 ○ H^+ in KCl Δ Cd^{2+} in KNO_3

Polarograms were run for a variety of halides at concentrations ranging from ca 0.1 to 5m, and the diffusion currents and drop times were obtained in the manner indicated earlier. These results are reported in Tables 3.4.1 - 3.4.8.

It was thought that the initial slopes of $i_d/t^{1/6}$ vs concentration curves may provide some information about the separate contributions of the ions to proton diffusion, but mobility was so enhanced that all values of $i_d/t^{1/6}$ for concentrations below 0.5m fell on or about a single line.

When values of m , the rate of flow of mercury, had also been measured, data for the calculation of D , the diffusion coefficient were compiled, and values of D were calculated by computer using the modified form of the Ilkovic equation viz. $i_d = 607n C D^{1/2} m^{2/3} t^{1/6} (1 + A m^{-1/3} t^{1/6})$. A was given values of 17, 24 and 39, these being three of the values derived theoretically by various workers^{78,79,80}.

Figure 3.4.1 shows the curves obtained when values of D/D^0 (where D is as calculated as indicated above and D^0 is the theoretical value of the diffusion coefficient calculated from the Nernst equation, $D^0 = \frac{RT}{F^2} \lambda^0$), were plotted against concentration of sodium chloride solutions. As the curve obtained when $A = 17$ extrapolates to 1 and the others do not, it appears that 17 is the value to use, in agreement with the findings of Hans and Jensch⁸². Similar calculations using diffusion currents measured for the cadmium ion in alkali nitrate solutions again indicated that the correct value for A is 17 (see Figure 3.4.2).

Values of D at zero concentration of supporting electrolyte were calculated using extrapolated values of i_d and $i_d/t^{1/6}$ to obtain $t^{1/6}$, and the limiting value of m , measured as concentration of supporting

Table 3.4.1.

Data for proton diffusion in sodium chloride

molality	i_d	$t^{1/6}$	$i_d/t^{1/6}$
0.099	20.70	1.147	18.05
0.160	19.81	1.148	17.26
0.203	19.39	1.148	16.89
0.299	19.10	1.149	16.63
0.394	18.43	1.149	16.04
1.98	15.16	1.159	13.08
2.32	14.68	1.159	12.67
2.81	13.98	1.159	12.06
3.91	12.39	1.154	10.74
4.87	10.96	1.150	9.53

Table 3.4.2.

Data for proton diffusion in sodium bromide

molality	i_d	$t^{1/6}$	$i_d/t^{1/6}$
0.121	20.38	1.143	17.830
0.133	20.10	1.140	17.631
0.213	19.14	1.141	16.775
0.220	19.20	1.135	16.916
0.237	18.96	1.137	16.675
0.265	18.64	1.140	16.351
0.291	18.70	1.142	16.375
0.333	18.24	1.143	15.958
2.635	13.107	1.155	11.348
3.384	12.155	1.153	10.542
3.674	11.795	1.159	10.177
4.391	10.757	1.166	9.225
4.667	10.763	1.167	9.223

Table 3.4.3.

Data for proton diffusion in sodium iodide

molality	i_d	$t^{1/6}$	$i_d/t^{1/6}$
0.096	20.46	1.139	17.963
0.152	19.85	1.140	17.412
0.221	19.22	1.148	16.742
0.233	19.11	1.144	16.705
0.323	18.50	1.144	16.171
0.399	17.64	1.141	15.460
1.948	12.611	1.172	10.760
2.934	10.192	1.182	8.623
3.624	8.845	1.177	7.515
4.377	8.960	1.189	7.536
5.047	6.701	1.199	5.589

Table 3.4.4.

Data for proton diffusion in potassium chloride

molality	i_d	$t^{1/6}$	$i_d/t^{1/6}$
0.081	20.22	1.131	17.878
0.100	19.84	1.149	17.267
0.201	19.00	1.146	16.579
0.203	19.00	1.142	16.637
0.286	18.70	1.137	16.447
0.303	18.70	1.144	16.346
0.355	18.27	1.142	15.998
2.077	16.52	1.141	14.479
2.775	16.09	1.135	14.176
3.67	15.39	1.142	13.476
4.14	15.38	1.136	13.539
4.34	15.08	1.135	13.286

Table 3.4.5.

Data for proton diffusion in potassium bromide

molality	i_d	$t^{1/6}$	$i_d/t^{1/6}$
0.112	19.93	1.128	17.668
0.128	19.46	1.113	17.484
0.129	19.42	1.123	17.293
0.200	19.02	1.127	16.877
0.217	19.31	1.132	17.058
0.268	18.98	1.135	16.722
0.287	18.98	1.133	16.752
0.365	18.44	1.118	16.494
0.380	18.70	1.132	16.519
0.402	18.70	1.143	16.360
2.07	13.57	1.186	11.442
2.78	2.91	1.196	10.794
2.85	12.78	1.185	10.785
3.78	11.24	1.190	9.445
4.88	10.12	1.191	8.497

Table 3.4.6.

Data for proton diffusion in potassium iodide

molality	i_d	$t^{1/6}$	$i_d/t^{1/6}$
0.089	20.54	1.133	18.129
0.100	20.26	1.127	17.969
0.137	19.97	1.128	17.704
0.162	19.79	1.128	17.544
0.187	19.52	1.128	17.305
0.212	19.42	1.134	17.125
0.250	18.90	1.121	16.860
0.289	18.51	1.123	16.483
1.953	13.128	1.160	11.317
2.414	12.792	1.153	11.095
3.170	11.448	1.162	9.852
3.933	10.480	1.169	8.965
4.392	10.288	1.161	8.861

Table 3.4.7.

Data for proton diffusion in tetramethylammonium bromide

molality	i_d	$t^{1/6}$	$i_d/t^{1/6}$
1.842	11.76	1.106	10.46
2.412	9.70	1.105	8.78
2.969	8.62	1.108	7.78
3.313	8.30	1.096	7.57
3.505	7.99	1.105	7.23

Table 3.4.8.

Data for proton diffusion in tetrabutylammonium bromide

molality	i_d	$t^{1/6}$	$i_d/t^{1/6}$
0.432	13.46	1.136	11.85
0.54	12.544	1.161	10.80
1.095	9.204	1.143	8.05
1.74	6.748	1.136	5.94
2.19	5.536	1.133	4.89
2.256	5.232	1.139	4.59
2.52	4.95	1.133	4.37
2.894	4.284	1.144	3.74

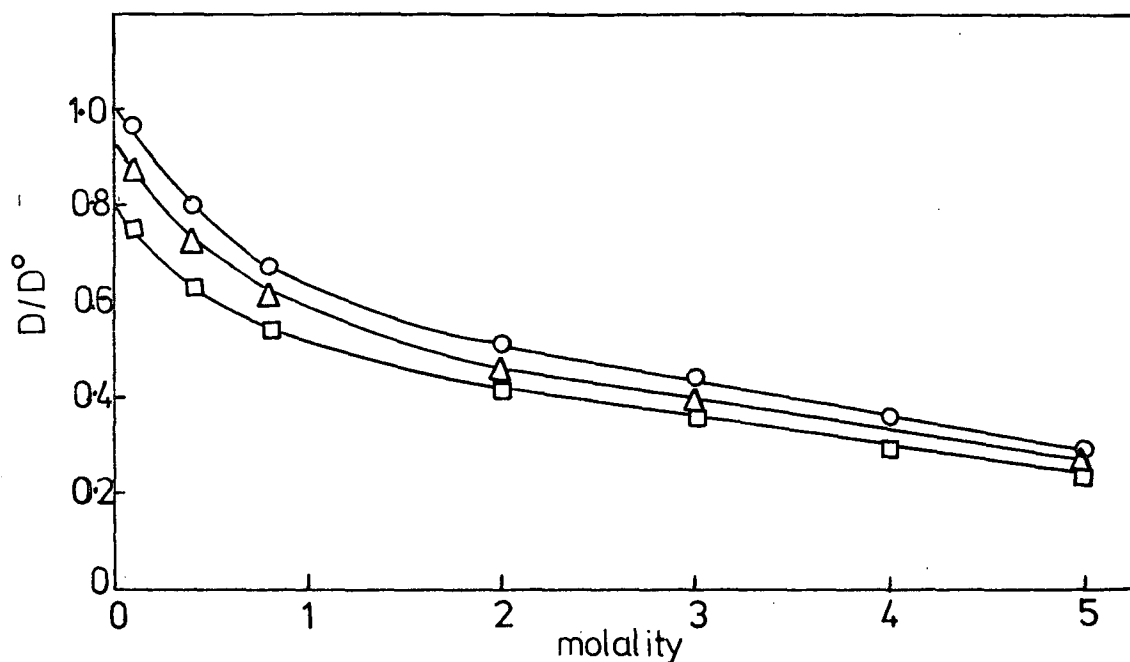


Figure 3.4.1 The effect of the term A in the modified Ilkovic Equation, on diffusion coefficients for the proton in sodium chloride solution

- A = 17
 △ A = 24
 □ A = 39

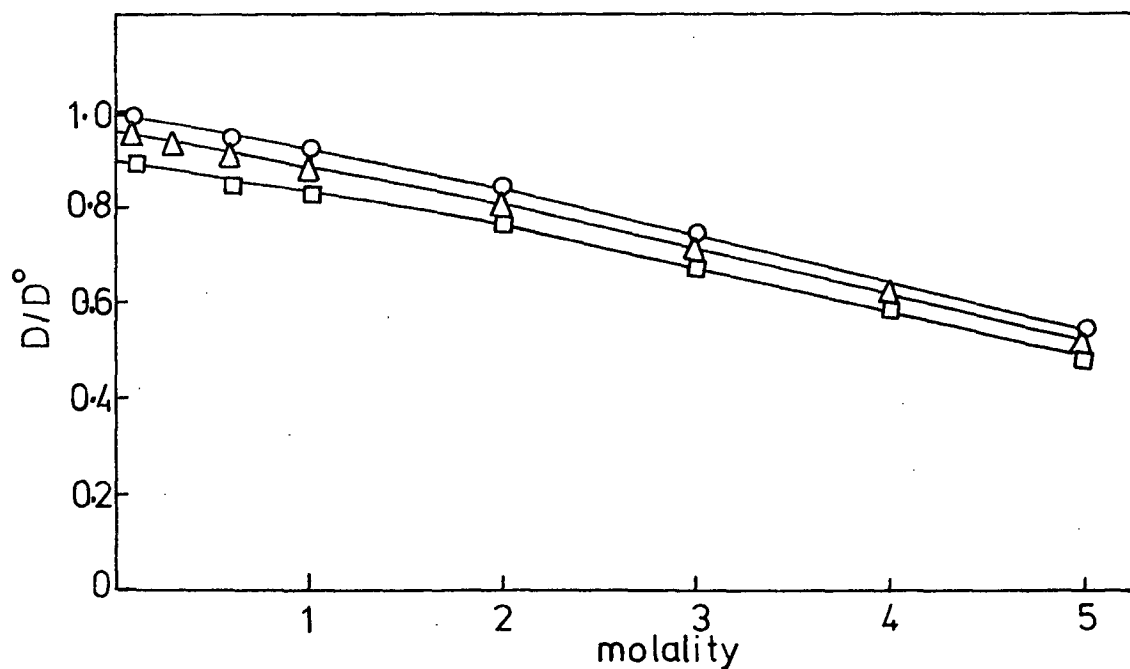


Figure 3.4.2 The effect of the term A in the modified Ilkovic Equation on diffusion coefficients for the cadmium ion in sodium nitrate solution

- A = 17 △ A = 24 □ A = 39

electrolyte approached zero. These were substituted in the modified form of the Ilkovic equation giving the results reported in Table 3.4.9.

Table 3.4.9. Values of diffusion coefficients in zero concentration of supporting electrolyte

Ion	Molar concentration	$D \times 10^5 \text{ cm}^2 \text{ sec}^{-1}$		
		A = 17	A = 24	A = 39
H_3O^+	1.849×10^{-3}	9.40	8.65	7.28
Cd^{2+}	1.66×10^{-3}	0.712	0.690	0.641

The accepted values of D^0 (at infinite dilution) are $9.31 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ for the proton and $0.72 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ for the cadmium ion. Allowing for a possible 2% error in D , it is seen at once that values calculated using $A = 17$ agree with these theoretical values in contrast to those using $A = 24$ or 39 . It seems clear, then, that the polarographic method gives a reliable measure of D for hydrogen ion diffusion when the value of 17 is used for A in the correction term in the Ilkovic equation. This value was used in subsequent calculations where results are reported in Table 3.4.10.

Further confirmation for this method is found when results obtained in the present work are compared with others from the literature for the diffusion coefficient of the hydrogen ion in electrolyte solutions.

Table 3.4.11 lists values which have been reported in 0.1M solutions together with results from the present study. Only in this study and that of Woolf^{118,124} has hydrogen ion diffusion in more concentrated solutions been reported.

Table 3.4.10.

Diffusion coefficients for proton diffusion in various

electrolyte solutions

(D^0 is the theoretical value of the diffusion coefficient
of the proton)

electrolyte	molality	t_d	m	t	$D \times 10^5$	D/D^0
NaCl	0.1	20.5	1.76	2.27	8.98	0.965
	0.299	19.1	1.76	2.29	7.93	0.853
	0.4	18.5	1.76	2.30	7.44	0.799
	0.8	17.1	1.80	2.40	6.24	0.671
	2.0	15.1	1.86	2.42	4.80	0.515
	3.0	13.8	1.83	2.42	4.11	0.442
	4.0	12.3	1.83	2.36	3.38	0.363
	5.0	10.8	1.83	2.32	2.68	0.288
	0.1	20.5	1.76	2.20	9.10	0.978
	0.330	18.8	1.76	2.17	7.79	0.836
NaBr	0.4	18.0	1.76	2.15	7.28	0.781
	0.8	16.4	1.76	2.20	6.10	0.655
	2.0	14.1	1.754	2.35	4.54	0.487
	3.0	12.6	1.755	2.35	3.70	0.398
	4.0	11.4	1.756	2.44	3.02	0.325
	5.0	10.3	1.75	2.50	2.49	0.267
	0.1	20.5	1.76	2.23	9.03	0.969
	0.152	19.9	1.76	2.23	8.58	0.921
	0.4	18.2	1.76	2.204	7.35	0.790
	0.8	16.4	1.76	2.30	6.03	0.648
NaI	2.0	12.5	1.754	2.60	3.55	0.382
	3.0	10.1	1.755	2.73	2.33	0.250
	4.0	8.4	1.756	2.70	1.67	0.180
	4.4	8.2	1.750	2.97	1.54	0.165

Table 3.4.10 cont.

electrolyte	molality	i_d	m	t	$D \times 10^5$	D/D^0
KCl	0.1	19.7	1.76	2.03	8.73	0.938
	0.201	18.7	1.76	2.08	7.88	0.847
	0.4	18.3	1.76	2.125	7.54	0.810
	0.8	17.7	1.80	2.150	6.86	0.737
	2.0	16.5	1.836	2.181	5.93	0.636
	3.0	15.8	1.821	2.247	5.45	0.585
	4.0	15.3	1.861	2.284	5.00	0.537
	4.4	15.3	1.853	2.359	4.96	0.532
KBr	0.1	20.3	1.76	2.03	9.13	0.981
	0.217	19.3	1.76	2.08	8.29	0.891
	0.4	18.3	1.76	2.14	7.46	0.801
	0.8	16.6	1.77	2.50	5.94	0.638
	2.0	13.8	1.789	2.92	4.01	0.430
	3.0	12.3	1.764	2.76	3.35	0.360
	4.0	11.0	1.787	2.82	2.65	0.285
	5.0	10.0	1.777	2.88	2.22	0.239
KI	0.1	20.2	1.76	2.05	9.08	0.975
	0.187	19.5	1.76	2.05	8.51	0.914
	0.4	18.1	1.76	2.05	7.47	0.802
	0.8	16.4	1.78	2.12	6.07	0.652
	2.0	13.5	1.82	2.42	3.97	0.427
	2.5	12.5	1.76	2.46	3.58	0.384
	3.0	11.6	1.79	2.55	3.04	0.327
	3.9	10.4	1.77	2.41	2.56	0.275
Me ₄ NBr	1.8	11.9	1.68	1.85	3.82	0.410
	2.0	11.0	1.68	1.83	3.30	0.355
	2.5	9.5	1.68	1.82	2.51	0.270
	3.0	8.6	1.68	1.82	2.10	0.225
	3.5	8.0	1.68	1.82	1.85	0.198

Table 3.4.10 cont.

electrolyte	molality	i_d	m	t	$D \times 10^5$	D/D^0
Bu_4NBr	0.5	12.7	1.75	2.15	3.90	0.419
	1.0	9.0	1.77	2.12	2.05	0.221
	1.5	7.3	1.76	2.15	1.38	0.149
	2.0	6.0	1.76	2.18	9.46	0.102
	2.5	4.9	1.76	2.20	6.44	0.069
	2.9	2.9	1.75	2.24	4.93	0.053

Table 3.4.11.

Diffusion coefficients of H^+ in 0.1M solutions of
sodium and potassium chlorides

Electrolyte	$D_{H^+} \times 10^5 \text{ cm}^2 \text{ sec}^{-1}$	Method	Reference
0.1M NaCl	7.8 ± 0.4	Rotating disc electrode (amalgamated copper)	Kolny & Zembura ⁸⁴
0.1M NaCl	8.01	Diaphragm cell	Woolf ^{118,124}
0.1M NaCl	8.5 ± 0.4	Rotating disc electrode (platinum)	Jahna ¹³⁷
0.1M NaCl	8.8 ± 0.1	Polarography	Roberts & Northey ¹¹⁷
0.1M KCl	8.5 ± 0.2	Polarography	Hans & Jenssch ⁶
0.1M KCl	8.01	Diaphragm cell	Woolf ^{118,124}
0.1M KCl	8.7 ± 0.1	Polarography	Roberts & Northey ¹¹⁷

It is clear from Table 3.4.11 that values obtained from polarography are consistently higher than those from the diaphragm cell, and that the rotating disc electrode gives both high and low values depending on the disc material. That the higher figures are not peculiar to the polarographic method lends support to the claim that results from the present study are likely to be correct.

3.5. Deuteron Diffusion in Solutions of Purified Salts

Polarograms for deuteron diffusion in heavy water solutions of sodium chloride, and potassium chloride, bromide and iodide, were obtained, these anhydrous, AnalaR salts being considered to be a repres-

entative selection of those alkali halides used in the study of proton mobility. Four tetraalkylammonium bromides were also used as supporting electrolytes. As in the previous study, t was measured from the chart, and m by timing and weighing drops of mercury caught in a glass cup. Results of these experiments are reported in Table 3.5.1. Figures 3.5.1 - 3.5.3 show the variation of D with concentration of supporting electrolyte.

3.6. Energy of Activation

Measurements were made to enable the diffusion coefficient for proton diffusion in sodium and potassium chlorides, bromides and iodides, tetramethyl- and tetrabutyl-ammonium bromides, and deuteron diffusion in potassium chloride and bromide solutions to be calculated. These are recorded in Tables 3.6.1 and 3.6.2. Then, when $-\ln D$ was plotted against $1/T$, as shown in Figures 3.6.1 - 3.6.10, activation energies for these processes could be calculated. These values are tabulated in Table 4.12.1.

Table 3.5.1.

Diffusion coefficients for deutron diffusion in various electrolyte solutions

(D⁰ is the extrapolated value of the diffusion coefficient of the deutron)

electrolyte	molality	aquamolality	i_d	$t^{1/6}$	$i_d/t^{1/6}$	m	$D \times 10^5$	D/D^0
NaCl	0.267	0.296	4.648	1.255	3.704	0.528	4.623	0.726
	0.354	0.393	4.440	1.255	3.538	0.528	4.220	0.681
	0.735	0.816	3.968	1.252	3.169	0.548	3.124	0.504
	1.436	1.594	3.264	1.248	2.620	0.547	2.390	0.385
	2.822	3.132	2.704	1.253	2.144	0.547	1.664	0.268
	4.419	4.905	2.110	1.261	1.673	0.542	1.077	0.174
KCl	0.188	0.209	4.832	1.255	3.850	0.538	4.809	0.776
	0.333	0.370	4.488	1.252	3.585	0.542	4.269	0.689
	0.938	1.041	3.832	1.246	3.075	0.547	3.240	0.523
	1.110	1.232	3.676	1.255	2.929	0.548	2.866	0.462
	2.657	2.949	3.000	1.226	2.447	0.537	2.181	.352
	3.586	3.980	2.956	1.246	2.372	0.532	2.143	.346

Table 3.5.1 cont.

electrolyte	molality	aquamolality	i_d	$t^{1/6}$	$i_{d/t}^{1/6}$	m	$D \times 10^5$	D/D^0
KBr	0.083	0.092	5.044	1.248	4.042	0.542	5.206	0.840
	0.218	0.242	4.680	1.255	3.729	0.532	4.581	0.739
	0.573	0.636	4.056	1.248	3.250	0.537	3.638	0.587
	0.702	0.779	3.920	1.244	3.151	0.549	3.302	0.533
	1.572	1.745	3.196	1.248	2.561	0.544	2.350	0.379
	2.468	2.739	2.640	1.252	2.109	0.543	1.627	0.262
	3.287	3.649	2.236	1.250	1.817	0.537	1.256	0.203
	3.958	4.393	1.880	1.250	1.504	0.544	0.792	0.128
KC	0.091	0.101	4.876	1.240	3.932	0.544	4.720	0.761
	0.485	0.538	4.132	1.233	3.351	0.547	3.758	0.606
	0.660	0.735	3.760	1.245	3.020	0.530	3.142	0.507
	0.811	0.900	3.596	1.248	2.881	0.538	2.775	0.448
	0.990	1.099	3.464	1.255	2.760	0.548	2.654	0.428
	4.260	4.729	1.298	1.253	1.036	0.549	0.418	0.067

Table 3.5.1 cont.

electrolyte	molality	aquamolality	i_d	$t^{1/6}$	$i_d/t^{1/6}$	m	$D \times 10^5$	D/D^0
Me_4NBr	0.096	0.107	4.988	1.222	4.082	0.537	5.426	0.875
	0.407	0.452	4.464	1.198	3.726	0.547	4.516	0.728
	0.669	0.743	4.040	1.177	3.432	0.545	3.875	0.625
	0.856	0.950	3.874	1.196	3.239	0.544	3.643	0.588
	1.149	1.275	3.756	1.206	3.114	0.530	3.424	0.552
	2.316	2.571	2.842	1.194	2.380	0.534	2.114	0.341
	3.787	4.204	2.296	1.196	1.920	0.548	1.356	0.219
Et_4NBr	0.097	0.108	4.804	1.196	4.017	0.554	4.909	0.792
	0.336	0.373	4.348	1.211	3.590	0.546	4.240	0.684
	0.673	0.747	3.680	1.207	3.049	0.520	3.345	0.540
	0.910	1.010	3.456	1.202	2.875	0.540	2.894	0.467
	1.346	1.494	2.844	1.204	2.362	0.536	2.017	0.325
	2.013	2.234	2.320	1.213	1.913	0.539	1.391	0.224
	3.000	3.330	1.639	1.170	1.401	0.530	0.772	0.125
	3.086	3.425	1.638	1.170	1.400	0.547	0.768	0.124

Table 3.5.1 cont.

electrolyte	molality	aquamolality	i_d	$t^{1/6}$	$i_d/t^{1/6}$	m	$D \times 10^5$	D/D^0
Pr_4NBr	0.056	0.063	4.736	1.240	3.819	0.536	4.756	0.767
	0.138	0.153	4.672	1.238	3.774	0.530	4.709	0.760
	0.441	0.490	3.756	1.235	3.041	0.519	3.395	0.548
	1.493	1.657	2.150	1.235	1.741	0.532	1.195	0.193
	1.741	1.933	1.657	1.220	1.348	0.534	0.715	0.115
Bu_4NBr	0.040	0.045	5.048	1.250	4.038	0.526	5.355	0.864
	0.174	0.193	4.312	1.238	3.483	0.521	4.235	0.683
	0.330	0.366	3.824	1.229	3.111	0.532	3.315	0.535
	0.512	0.568	3.224	1.238	2.604	0.527	2.579	0.416
	0.722	0.801	2.628	1.229	2.138	0.521	1.736	0.280
	0.875	0.971	2.324	1.238	1.877	0.515	1.453	0.234
	1.568	1.740	1.236	1.233	1.002	0.526	0.458	0.074
	1.712	1.900	0.597	1.244	0.480	0.524	0.095	0.015

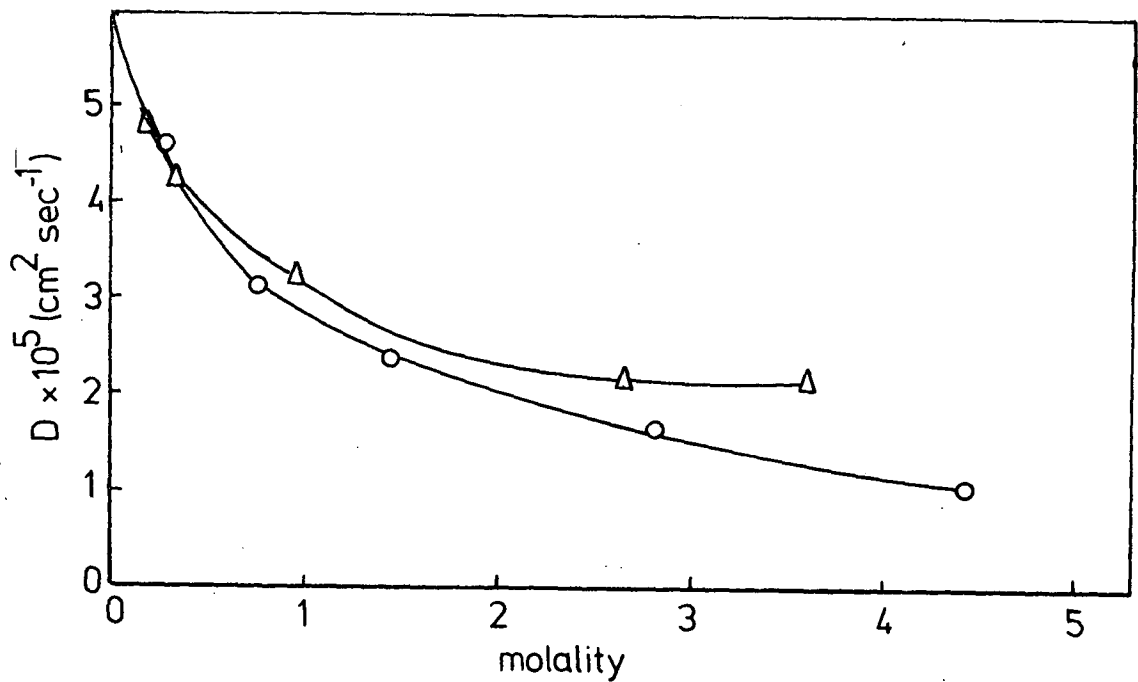


Figure 3.5.1 Tracer diffusion coefficients of the deuteron in two alkali chloride solutions
 ○ NaCl Δ KCl

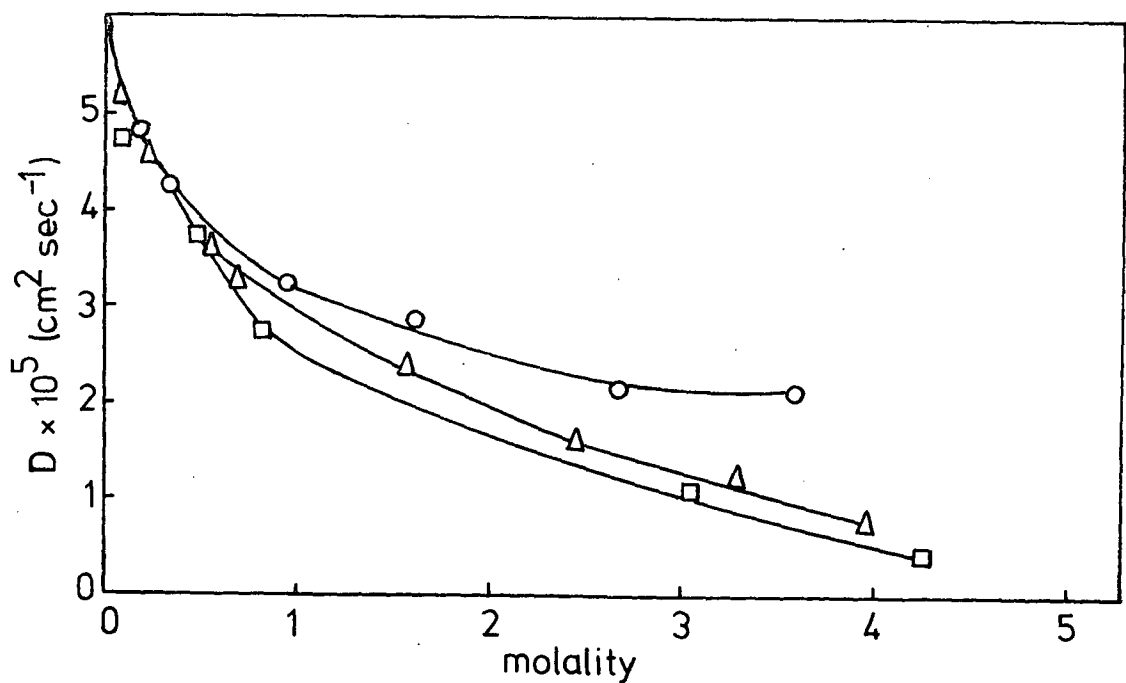


Figure 3.5.2 Tracer diffusion coefficients of the deuteron in potassium halide solutions
 ○ KCl Δ KBr □ KI

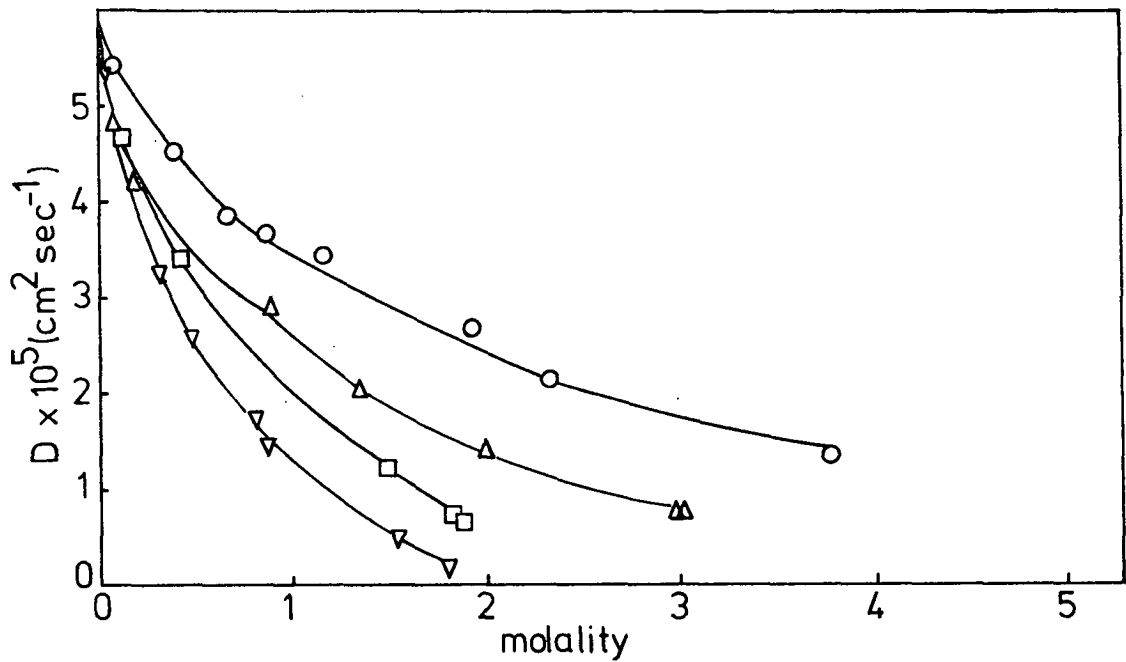


Figure 3.5.3 Tracer diffusion coefficients of the deuterium in tetraalkylammonium bromides
 $\circ \text{Me}_4\text{NBr}$ $\Delta \text{Et}_4\text{NBr}$ $\square \text{Pr}_4\text{NBr}$ $\nabla \text{Bu}_4\text{NBr}$

Table 3.6.1.

Data for calculation of Energy of Activation for proton
diffusion in various electrolyte solutions

Electrolyte	Molality	- ln D	temp.	$\frac{1}{T} \times 10^3$
NaCl	2.0	10.167	25	3.35
	3.0	10.457	25	3.35
	4.0	10.742	25	3.35
	5.0	10.953	25	3.35
	2.0	10.007	35	3.25
	3.0	10.297	35	3.25
	4.0	10.620	35	3.25
	5.0	10.846	35	3.25
	2.0	9.946	40	3.19
	3.0	10.269	40	3.19
	4.0	10.459	40	3.19
	5.0	10.633	40	3.19
	2.0	9.853	45	3.14
	3.0	10.197	45	3.14
	4.0	10.414	45	3.14
	5.0	10.673	45	3.14
NaBr	2.0	10.164	17	3.45
	3.0	10.284	17	3.45
	4.0	10.485	17	3.45
	5.0	10.716	17	3.45
	2.0	10.000	25	3.35
	3.0	10.204	25	3.35
	4.0	10.407	25	3.35
	5.0	10.601	25	3.35
	2.0	9.957	30	3.30
	3.0	10.075	30	3.30
	4.0	10.284	30	3.30
	5.0	10.455	30	3.30
	2.0	9.801	35	3.25
	3.0	9.987	35	3.25
	4.0	10.194	35	3.25
	5.0	10.407	35	3.25

Table 3.6.1 cont.

Electrolyte	Molality	- ln D	temp.	$\frac{1}{T} \times 10^3$
NaI	2.0	10.384	17	3.45
	2.5	10.536	17	3.45
	3.0	10.699	17	3.45
	3.5	10.875	17	3.45
	4.0	11.064	17	3.45
	4.5	11.272	17	3.45
	2.0	10.162	25	3.35
	2.5	10.385	25	3.35
	3.0	10.619	25	3.35
	3.5	10.778	25	3.35
	4.0	10.924	25	3.35
	4.5	11.017	25	3.35
	2.0	10.097	30	3.30
	2.5	10.267	30	3.30
	3.0	10.453	30	3.30
	3.5	10.625	30	3.30
	4.0	10.796	30	3.30
	4.5	10.955	30	3.30
	2.0	10.069	35	3.25
	2.5	10.213	35	3.25
	3.0	10.367	35	3.25
	3.5	10.542	35	3.25
	4.0	10.710	35	3.25
	4.5	10.829	35	3.25
KCl	2.0	9.823	17	3.45
	3.0	9.980	17	3.45
	4.0	10.093	17	3.45
	2.0	9.731	25	3.35
	3.0	9.822	25	3.35
	4.0	9.904	25	3.35
	2.0	9.583	35	3.25
	3.0	9.687	35	3.25
	4.0	9.796	35	3.25
	2.0	9.553	40	3.19
	3.0	9.632	40	3.19
	4.0	9.712	40	3.19

Table 3.6.1 cont.

Electrolyte	Molality	- ln D	temp.	$\frac{1}{T} \times 10^3$
KBr	2.0	10.257	17	3.45
	3.0	10.507	17	3.45
	4.0	10.785	17	3.45
	5.0	11.111	17	3.45
	2.0	10.199	25	3.35
	3.0	10.397	25	3.35
	4.0	10.637	25	3.35
	5.0	10.902	25	3.35
	2.0	9.913	30	3.30
	3.0	10.212	30	3.30
	4.0	10.526	30	3.30
	5.0	10.784	30	3.30
	2.0	9.891	35	3.25
	3.0	10.077	35	3.25
	4.0	10.276	35	3.25
	5.0	10.507	35	3.25
KI	2.0	10.404	17	3.45
	3.0	10.518	17	3.45
	4.0	10.661	17	3.45
	4.5	10.779	17	3.45
	2.0	10.154	25	3.35
	3.0	10.425	25	3.35
	4.0	10.725	25	3.35
	4.5	10.887	25	3.35
	2.0	10.138	30	3.30
	3.0	10.284	30	3.30
	4.0	10.349	30	3.30
	4.5	10.694	30	3.30
	2.0	10.031	35	3.25
	3.0	10.185	35	3.25
	4.0	10.430	35	3.25
	4.5	10.598	35	3.25

Table 3.6.1 cont.

Electrolyte	Molality	- ln D	temp.	$\frac{1}{T} \times 10^3$
Me ₄ NBr	2.2	10.555	17	3.45
	2.5	10.704	17	3.45
	3.0	10.913	17	3.45
	3.5	11.073	17	3.45
	4.0	11.181	17	3.45
	2.2	10.460	25	3.35
	2.5	10.592	25	3.35
	3.0	10.772	25	3.35
	3.5	10.899	25	3.35
	4.0	10.987	25	3.35
	2.2	10.372	30	3.30
	2.5	10.488	30	3.30
	3.0	10.682	30	3.30
	3.5	10.861	30	3.30
	4.0	11.040	30	3.30
	2.2	10.345	35	3.25
	2.5	10.461	35	3.25
	3.0	10.647	35	3.25
	3.5	10.832	35	3.25
	4.0	10.997	35	3.25

Table 3.6.1 cont.

Electrolyte	Molality	- ln D	temp.	$\frac{1}{T} \times 10^3$
Bu ₄ NBr	0.5	10.225	17	3.45
	1.0	10.876	17	3.45
	1.5	11.365	17	3.45
	2.0	11.797	17	3.45
	2.5	12.232	17	3.45
	3.0	12.667	17	3.45
	0.5	10.145	25	3.35
	1.0	10.793	25	3.35
	1.5	11.188	25	3.35
	2.0	11.569	25	3.35
	2.5	11.953	25	3.35
	3.0	12.298	25	3.35
	0.5	9.960	30	3.30
	1.0	10.459	30	3.30
	1.5	10.932	30	3.30
	2.0	11.454	30	3.30
	2.5	11.853	30	3.30
	3.0	12.306	30	3.30
	0.5	9.834	35	3.25
	1.0	10.351	35	3.25
	1.5	10.851	35	3.25
	2.0	11.301	35	3.25
	2.5	11.750	35	3.25
	3.0	12.078	35	3.25

Table 3.6.2.

Data for the calculation of Energy of Activation for
deuteron diffusion in two electrolyte solutions

Electrolyte	Molality	- ln D	temp.	$\frac{1}{T} \times 10^3$
KCl	0.5	10.457	20	3.41
	1.0	10.732	20	3.41
	2.0	10.897	20	3.41
	3.0	10.958	20	3.41
	4.0	11.001	20	3.41
	0.5	10.119	25	3.35
	1.0	10.375	25	3.35
	2.0	10.616	25	3.35
	3.0	10.740	25	3.35
	4.0	10.803	25	3.35
	0.5	10.018	30	3.30
	1.0	10.187	30	3.30
	2.0	10.373	30	3.30
	3.0	10.553	30	3.30
	4.0	10.627	30	3.30
	0.5	9.862	35	3.25
	1.0	10.019	35	3.25
	2.0	10.284	35	3.25
	3.0	10.398	35	3.25
	4.0	10.452	35	3.25

Table 3.6.2. cont.

Electrolyte	Molality	$-\ln D$	temp.	$\frac{1}{T} \times 10^3$
KBr	0.5	10.219	20	3.41
	1.0	10.483	20	3.41
	2.0	11.000	20	3.41
	3.0	11.567	20	3.41
	4.0	12.224	20	3.41
	0.5	10.203	25	3.35
	1.0	10.412	25	3.35
	2.0	10.797	25	3.35
	3.0	11.212	25	3.35
	4.0	11.720	25	3.35
	0.5	9.907	30	3.30
	1.0	10.124	30	3.30
	2.0	10.457	30	3.30
	3.0	10.634	30	3.30
	4.0	10.850	30	3.30
	0.5	9.892	35	3.25
	1.0	10.064	35	3.25
	2.0	10.397	35	3.25
	3.0	10.596	35	3.25
	4.0	10.686	35	3.25

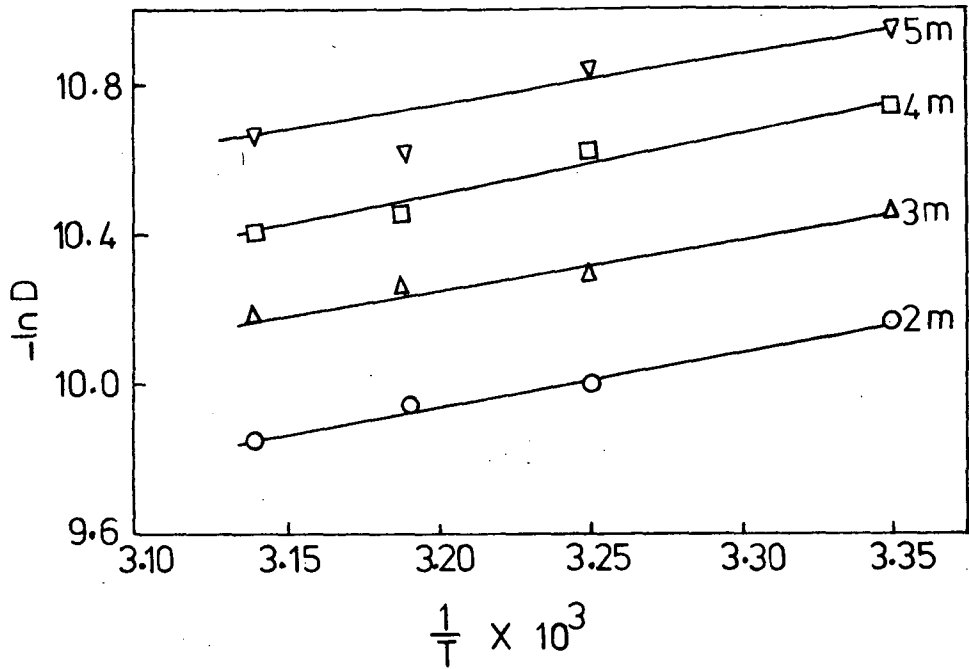


Figure 3.6.1 Curves for activation energy calculations for proton diffusion in sodium chloride solutions.

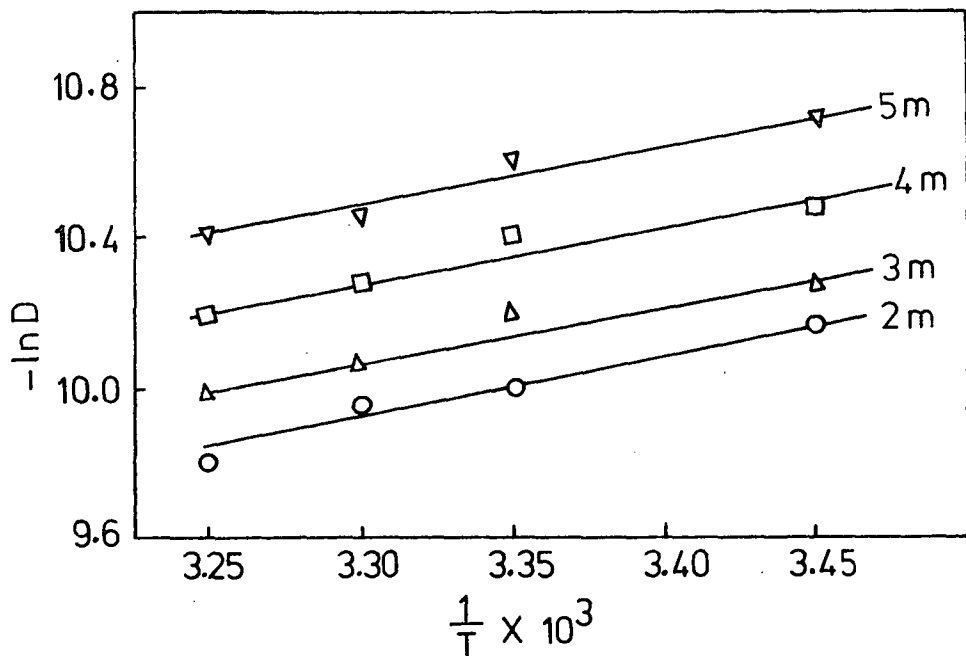


Figure 3.6.2 Curves for activation energy calculations for proton diffusion in sodium bromide solutions.

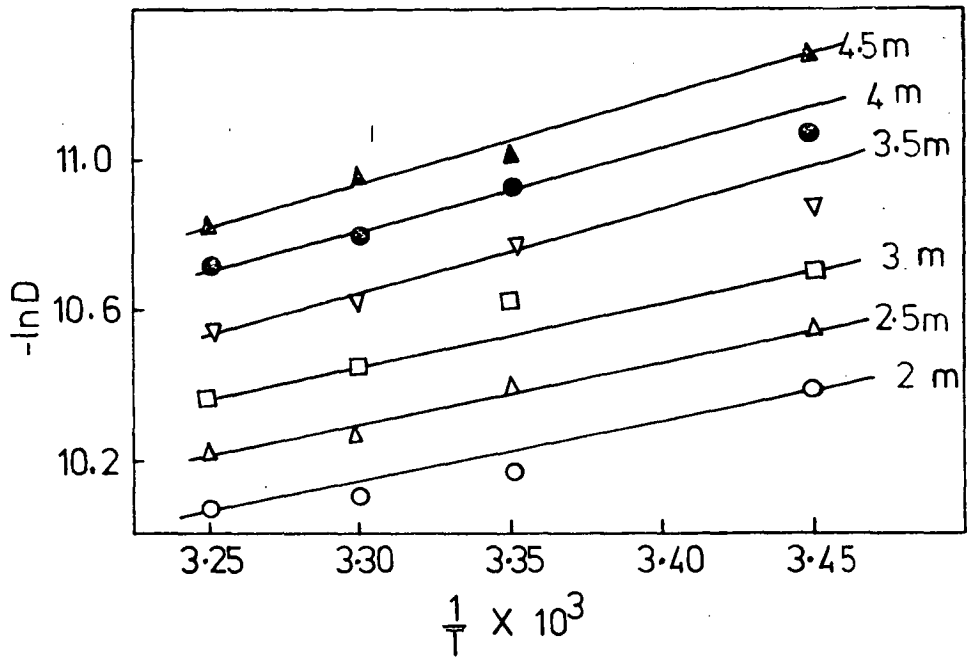


Figure 3.6.3 Curves for activation energy calculations for proton diffusion in sodium iodide solutions.

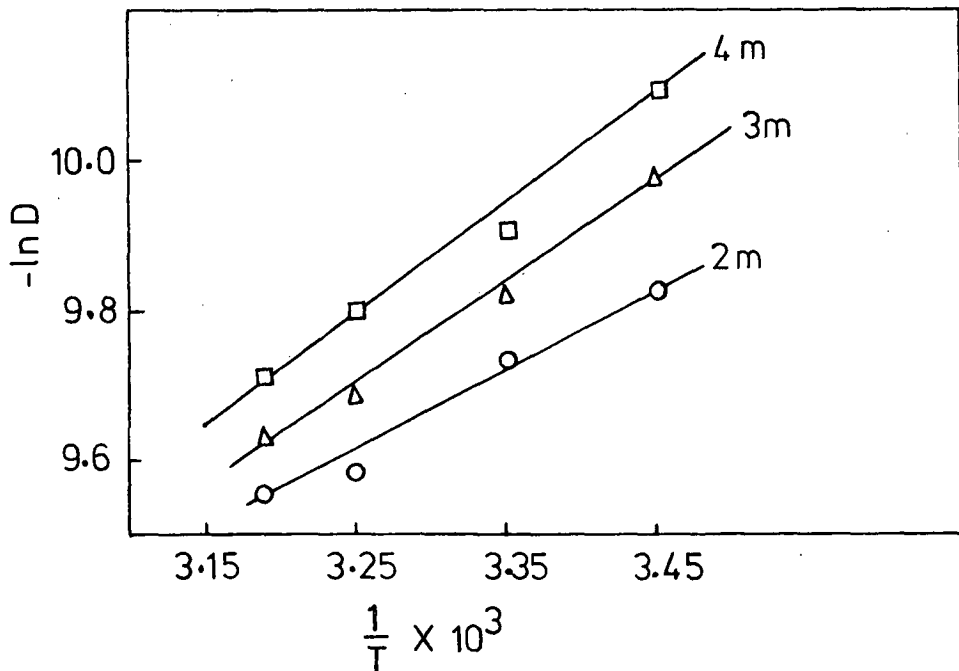


Figure 3.6.4 Curves for activation energy calculations for proton diffusion in potassium chloride solutions.

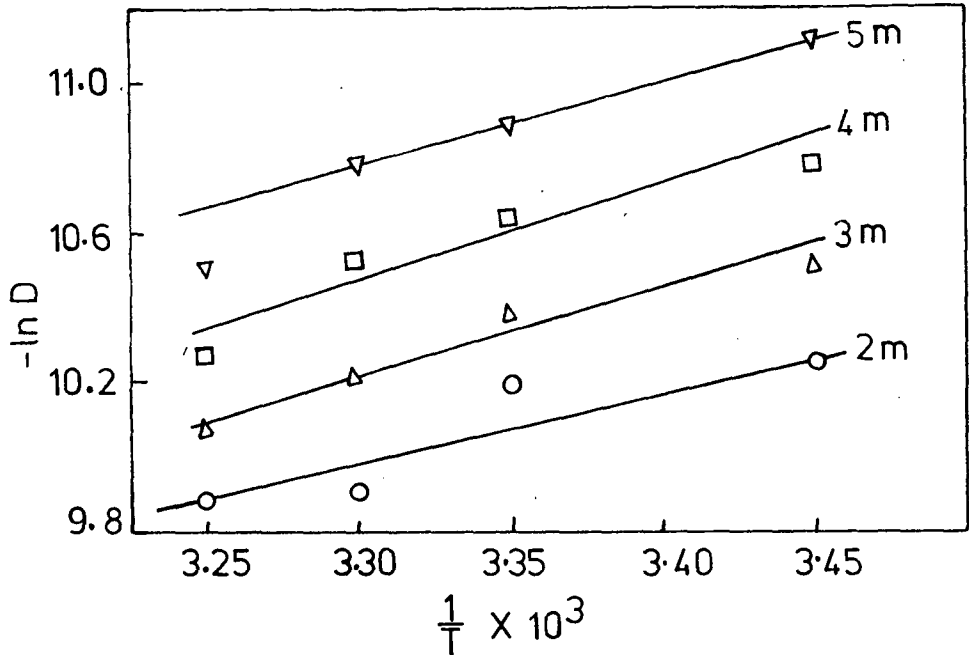


Figure 3.6.5 Curves for activation energy calculations for proton diffusion in potassium bromide solutions.

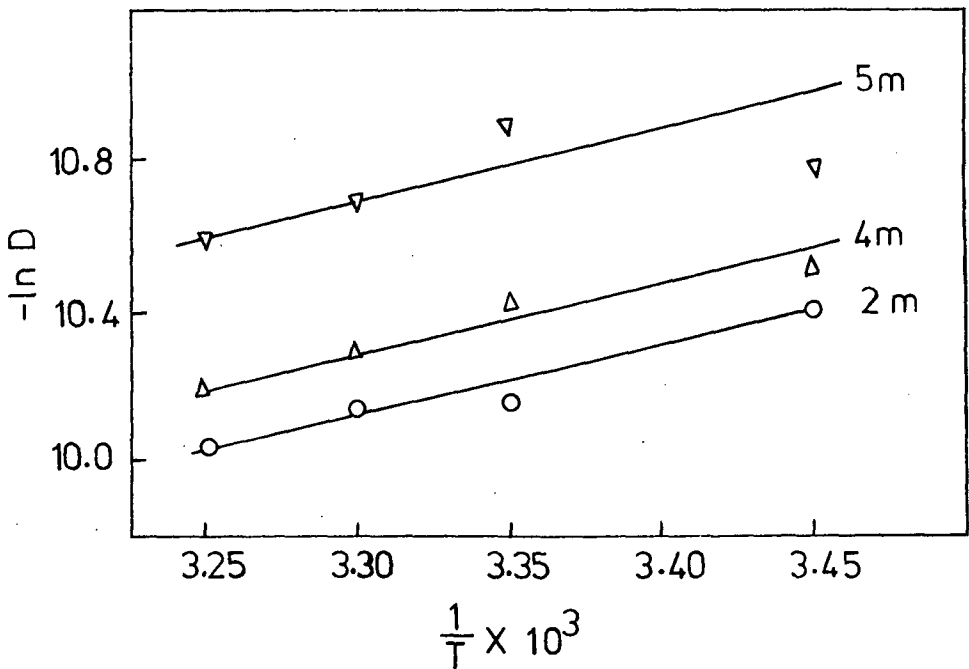


Figure 3.6.6 Curves for activation energy calculations for proton diffusion in potassium iodide solutions.

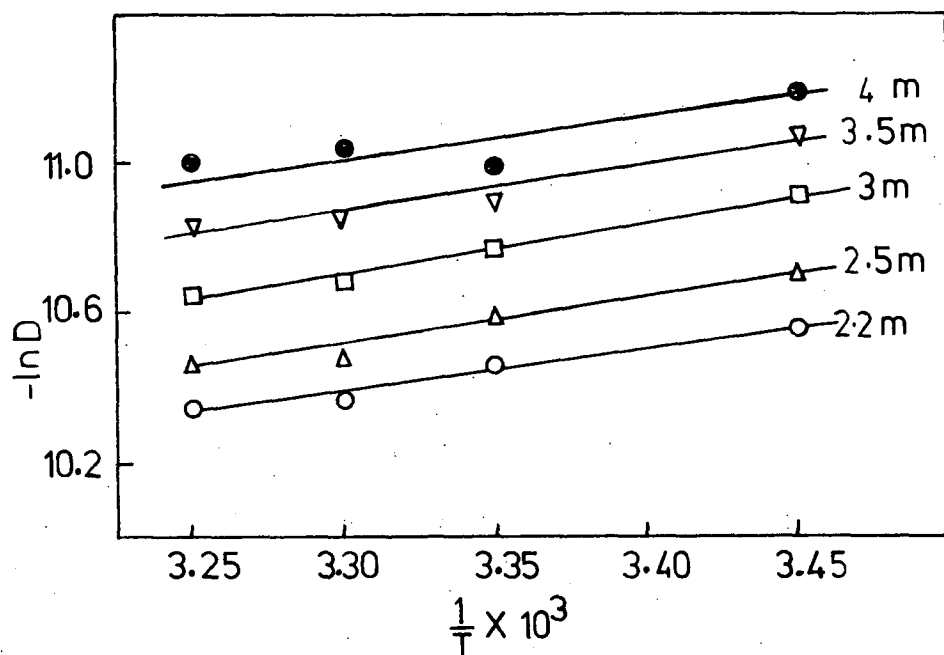


Figure 3.6.7 Curves for activation energy calculations for proton diffusion in tetramethylammonium bromide solutions

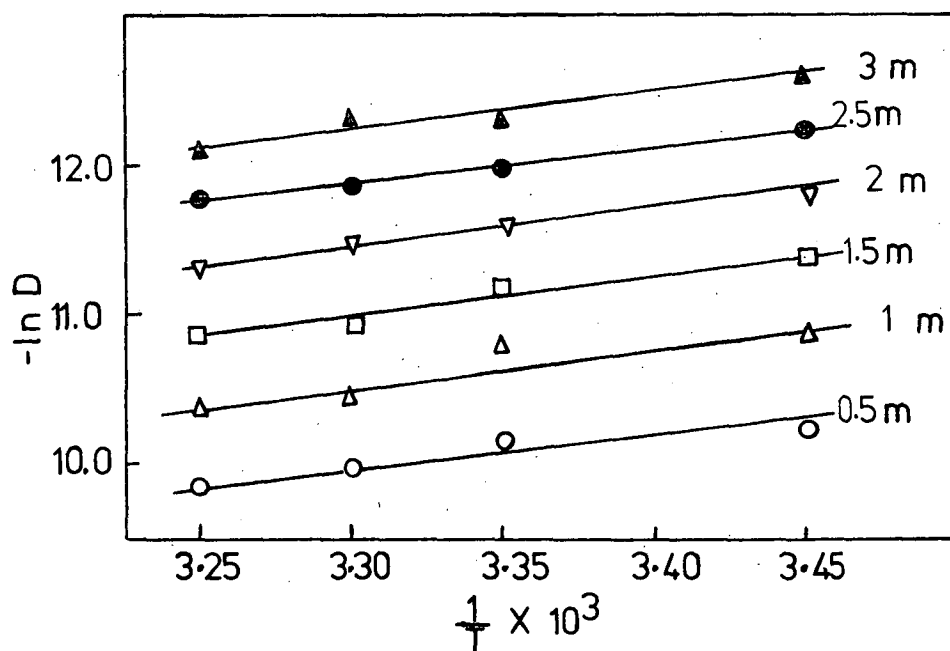


Figure 3.6.8 Curves for activation energy calculations for proton diffusion in tetrabutylammonium bromide solutions

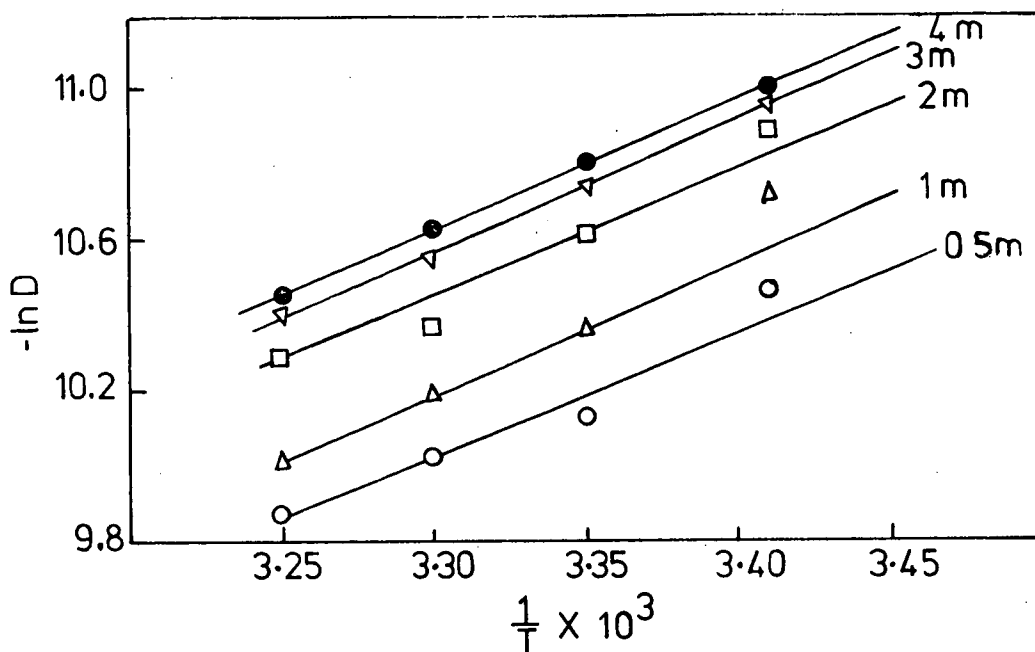


Figure 3.6.9 Curves for activation energy calculations for deuteron diffusion in potassium chloride solutions.

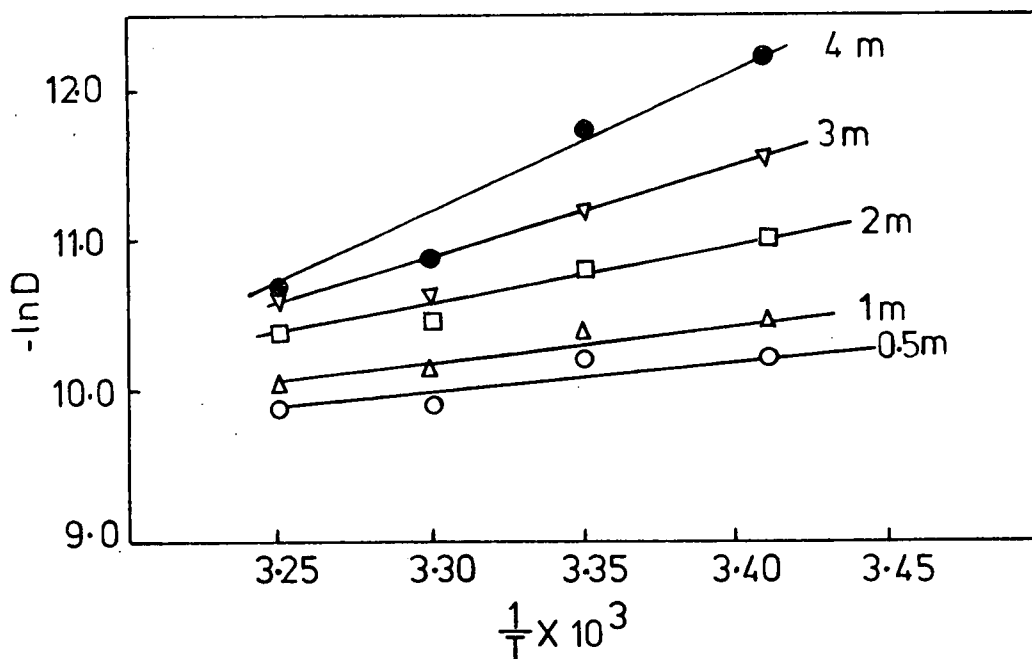


Figure 3.6.10 Curves for activation energy calculations for deuteron diffusion in potassium bromide solutions.

Chapter 4

Discussion

4.1. Proton Diffusion in Solutions of Nine Alkali Halides

Results obtained for the diffusion current of the hydrogen ion as concentration of supporting electrolyte is changed are reported in Tables 3.2.1 - 3.2.9. It is seen from Figure 4.1.1 that:

- (i) Hydrogen ion mobility decreases when a solute is added to water,
- (ii) the initial part of each curve is quite steep, but as the concentration of supporting electrolyte increases beyond 2-3m the curves flatten out considerably,
- (iii) the anion may be more significant than the cation in bringing about variation in the value of the diffusion current.

The first two observations confirm results obtained by Roberts and van der Woude⁸⁸ for the hydrogen ion in lithium chloride solutions. They suggested that the steep initial portion of the curve may be due to a migration current, but subsequent work in this study leads to the conclusion that only when the concentration of supporting electrolyte is below $100 [H^+]$, where $[H^+]$ is the hydrogen ion concentration, is there any likelihood of an abnormally high value for the diffusion current. The fact that all curves extrapolate to a similar value for i_d at zero concentration of supporting electrolyte supports the view that it is truly the diffusion current that has been measured.

When an electrolyte is introduced into water there occurs a re-arrangement of water molecules near the ions. Ion-water interactions are imposed on the former water-water interactions which constituted the "structure" of water. In the dilute hydrochloric acid solutions being considered, proton diffusion may be slowed down because of obstructions¹⁰⁰

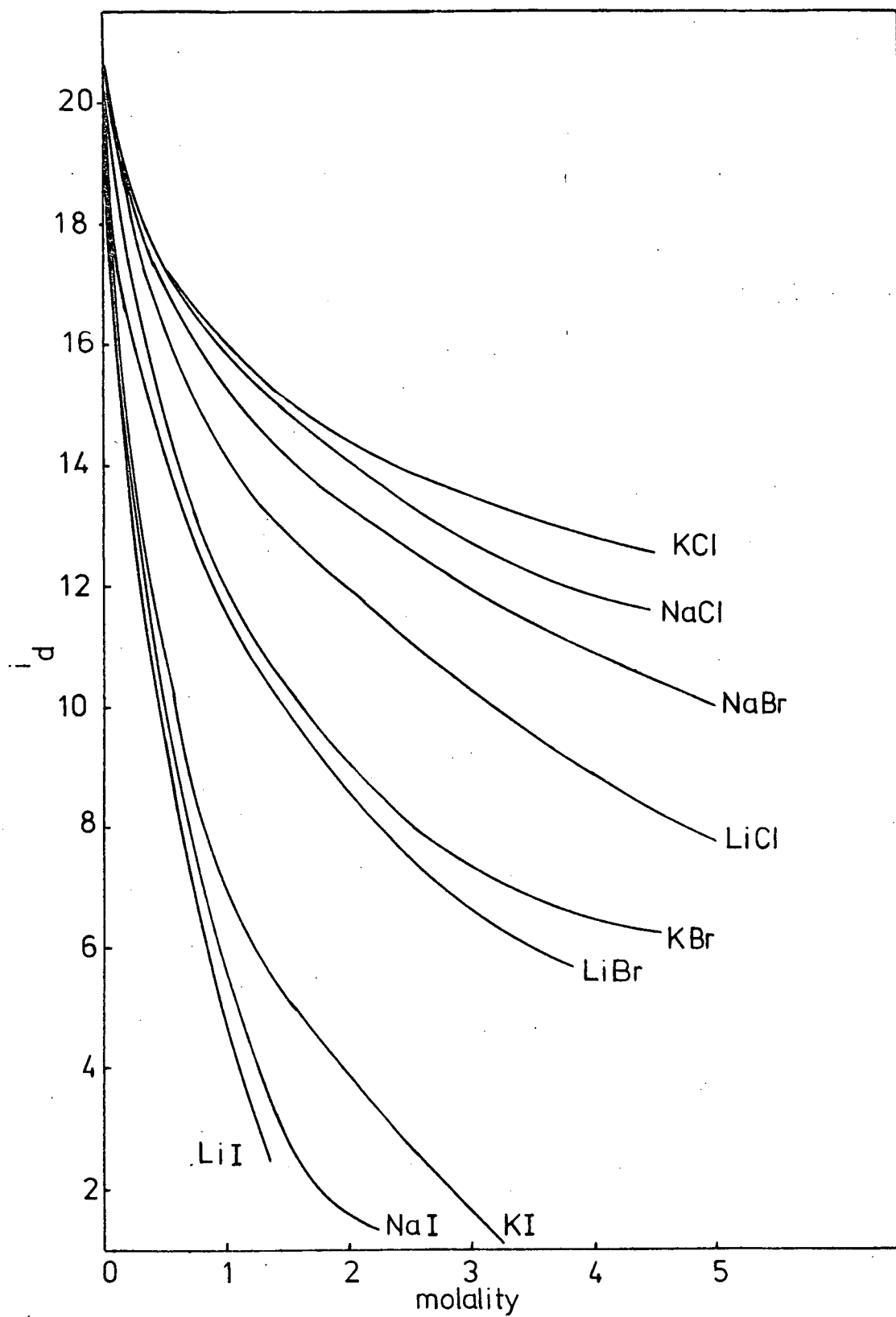


Fig. 4.1.1 The effect of alkali halides on the diffusion current of the proton.

by the added ions and also by a reduction in the number of easily rotatable water molecules brought about by direct hydration of these ions, even though there may be no water molecules rigidly adhering to the ions, as in the kind of hydration envisaged by Samoilov^{8,101}. He suggested that positive hydration occurs when the mobility of water molecules nearest to an ion is smaller than that of bulk water molecules, and negative if the mobility is larger. Which state prevails depends upon the size and charge of the ion¹⁰², since the orienting force on the water molecules near an ion is the sum of the fields acting, so water-water and ion-water forces are competing. If these forces are opposite and almost equal then negative hydration occurs and the water molecules move more easily than in the absence of the ion. For large charge-to-radius ratios of ions, however, the freedom of motion of each water molecule adjacent to an ion is limited.

The change in gradient is considered to be due to a reduction in the number of molecules of water available to produce any abnormal transport of protons. Lown and Thirsk⁵⁷ came to a similar conclusion in their study of the conductance of aqueous alkali hydroxide solutions and Drost-Hansen¹⁰³ refers to several workers who have found that certain properties go through an abrupt change at 1 m in solutions of sodium and potassium chloride. The paucity of available free water molecules in solutions of concentrations above 1-2 m has been drawn attention to in Section 1.3.6, especially in Table 1.3.1. Leung and Safford¹⁰⁴ have noted that the effects of polarisation and of mismatches become more severe at these concentrations. There may be changes in the type of solvent organisation¹⁰³ with perhaps other effects associated with the overlapping of hydration spheres of the ions.

4.2. Anion and Cation Influence

Greyson's¹⁰⁵ work on entropy of transfer of alkali halides between normal and heavy water has shown that the structure-influencing properties of negative ions are more sensitive to ion size than are those of positive ions, a conclusion reached also by Walrafen^{30,106} as a result of studying Raman spectra of electrolyte solutions, and by Yamatera, Fitzpatrick and Gordon¹⁰⁷ studying infra-red spectra of aqueous solutions. This effect is probably related to the polarisability of the ions^{105,106} since this increases with size for the halide ions leading to a water-anion bond less polar than the OH...O of water itself.

Leung and Safford's¹⁰⁴ work on neutron inelastic scattering has shown that interactions between sodium or potassium ions and water are stronger than the average water-water bonds in solution. This results in some immobilisation and electrostriction of nearest neighbour water molecules. This picture does not fit in with the ideas of hydration mentioned above, and Bergqvist and Forslind¹⁰⁸ say that the water is not immobilised but that ions fit into the water lattice and move through it and so have a change of neighbours on which they exert their forces. The net result is the same.

The different effects on water structure of anions and cations of comparable size are due to the opposite signs of their charges. Cations cause water molecules to become oriented with their "hydrophobic" sides¹⁰⁹ (oxygen atoms) inward, and restrict rotation of the water molecules to the dipole axis⁶⁸. Around anions water molecules possibly orient themselves with one of their O-H bonds normal to the surface of the ion. This allows quite free rotation of the water molecules and hydrogen bonding to three other water molecules is possible as compared with two for the cation-bound water molecule.

Both anions and cations, then, may restrict hydrogen ion diffusion

by reducing the ease with which bound water molecules may rotate. On the other hand, the field forces of the ions may facilitate orientation of "free" water molecules and so enhance hydrogen ion diffusion.

Figure 4.1.1 shows how the diffusion current of the hydrogen ion is changed by alkali halide solutions of varying concentrations. The curves for the chlorides show that their effects lie in the order $\text{KCl} < \text{NaCl} < \text{LiCl}$. Those for the iodides are much closer together and the order is the same as for the chlorides. The low values of i_d for higher concentrations of iodides may be due to the fact that H^+ ions are used up to convert I^- to I_2 when the solution is left standing. The lower concentration of hydrogen ions would then reduce i_d . Adsorption of iodide on the mercury would reduce the surface area of the dropping mercury electrode and again reduce i_d .

In the case of the bromides, it is seen that the curve for KBr lies below that for NaBr and very close to the LiBr curve. Subsequent work with purified salts did not alter this order for the bromides.

Frank¹¹⁰ has drawn attention to a "hook" in the order of heats of transport and also the lowering of the temperature of maximum density on the addition of alkali halides to water i.e. the effect of $\text{NaCl} > \text{KCl} > \text{LiCl}$, and he states that such "wrong" order is real and must be accounted for by a reliable theory purporting to account for the interaction of ions with water. It is, however, difficult to understand why, in this study, the order of the influence of the bromides on proton mobility should differ from that of chlorides and iodides, though a similar "wrong" order for Br^- only was obtained by Good¹¹¹ in his measurements of the energy of activation of fluid flow in electrolyte solutions.

Both Greyson¹⁰⁵ and Walrafen¹⁰⁶ assert that for anions and cations of the alkali halides, the greatest effects are produced by the largest

ions. In the present study the iodide ion undoubtedly produces the greatest change in diffusion current but this is in the opposite direction to that found in other studies^{97,105,106,112}. Figure 4.1.1 shows that hydrogen ion diffusion is least in iodide solutions and greatest in those of the chlorides, thus indicating that there is most reduction of proton mobility in iodide solutions. The largest cation, however, brings about the least reduction in i_d . The effects noted here will be discussed later, in section 4.9.

4.3. A Comparison of Hydrogen and Cadmium Diffusion

Franks⁹⁶ has postulated that hydrogen and alkali metal ions would be oppositely affected by structure-modifying ions in solution. He based this on the fact that the ratio of the mobilities in ice to water is 10^3 for the hydrogen ion but less than 10^{-4} for the lithium ion, and on the assumption that the ordered structure of ice was responsible for the enhanced proton mobility.

It has been explained in Section 2.13 that it seemed that another metal could replace lithium and that cadmium was selected. The reason for avoiding halides and using nitrates has also been given, viz. to avoid complex formation. Figures 4.3.1 and 4.3.2 show that in solutions above about 2 molal, both diffusion current and half-wave potential measurements for hydrogen and cadmium ions show similar trends, suggesting that Franks' statement needs to be reconsidered.

The fact that ice is more ordered than water is not likely to be the reason for the greater mobility of protons in ice than in water. As has been explained in Section 1.3, the rate-determining steps differ. Eigen and de Maeyer⁵⁴ have, indeed, likened proton conduction in ice to electron transfer in semi-conductors. It is not certain that structured water resembles the crystalline structure of any of the forms of ice,

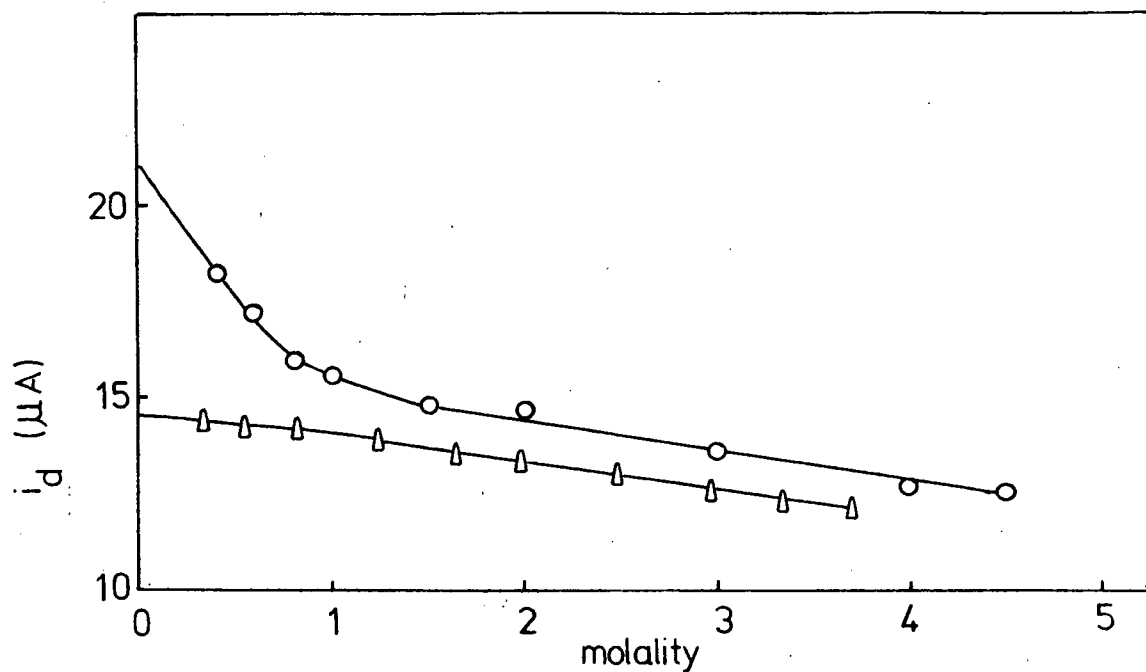


Figure 4.3.1 The effect of concentration of supporting electrolyte on the diffusion current
 ○ H^+ in KCl Δ Cd^{2+} in KNO_3

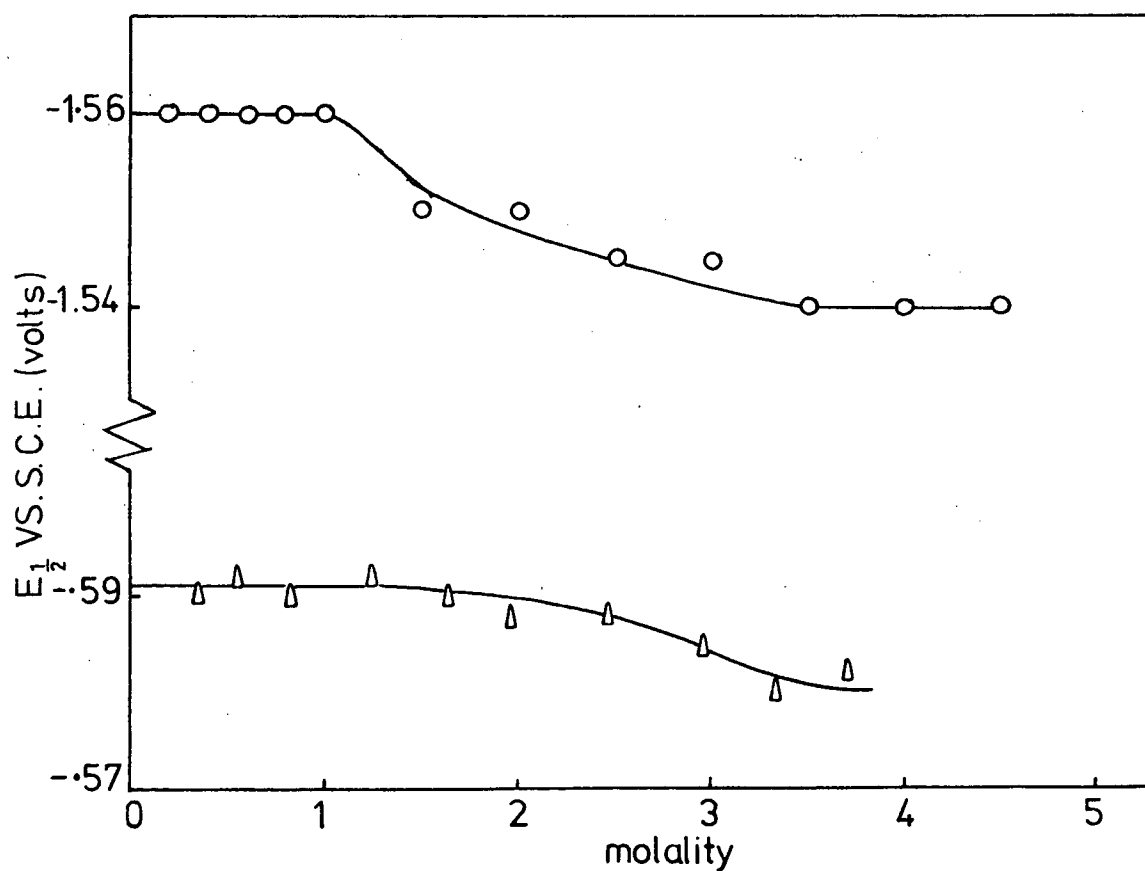


Figure 4.3.2 The effect of concentration of supporting electrolyte on the half-wave potential
 ○ H^+ in KCl Δ Cd^{2+} in KNO_3

but, in any case, Horne et al.⁷¹ have suggested that proton transfer takes place in free, monomeric water and not in the Frank-Wen clusters⁵, and Hills et al.⁶⁹ have shown that increases in temperature and pressure are accompanied by loss of structure and increase in hydrogen ion mobility. So high mobility is not a necessary consequence of much structure.

The similarities in the curves shown for proton and cadmium ions suggest that in concentrated solutions of supporting electrolyte the abnormal component of hydrogen ion diffusion is reduced until both ions diffuse at similar rates. Below about 2 molal, however, proton transfer is greatly enhanced by the proton jump mechanism so that it is much faster than that of other ions, except OH^- . Energies of activation calculated for proton transport support this view, as will be seen in Section 4.12.

4.4. The Half-wave Potential of the Hydrogen Ion

As the half-wave potential of the hydrogen ion reduction would not be affected by any impurities present in the salts used in the preliminary investigations described in Section 3.2, valid comparison of the effects of various supporting electrolytes may be made. All the alkali halides caused the half-wave potential to become less negative as electrolyte concentration was increased. With the tetraalkylammonium salts, however, varying effects were observed. The half-wave potential became less negative when tetramethylammonium bromide was used, showed little variation with tetraethylammonium bromide and became more negative with increasing concentrations of tetrapropyl- and tetrabutyl-ammonium bromides, as shown in Figure 4.4.1.

The increase in the difficulty with which the hydrogen ion could be reduced in the two tetraalkylammonium salts may be due to their adsorption

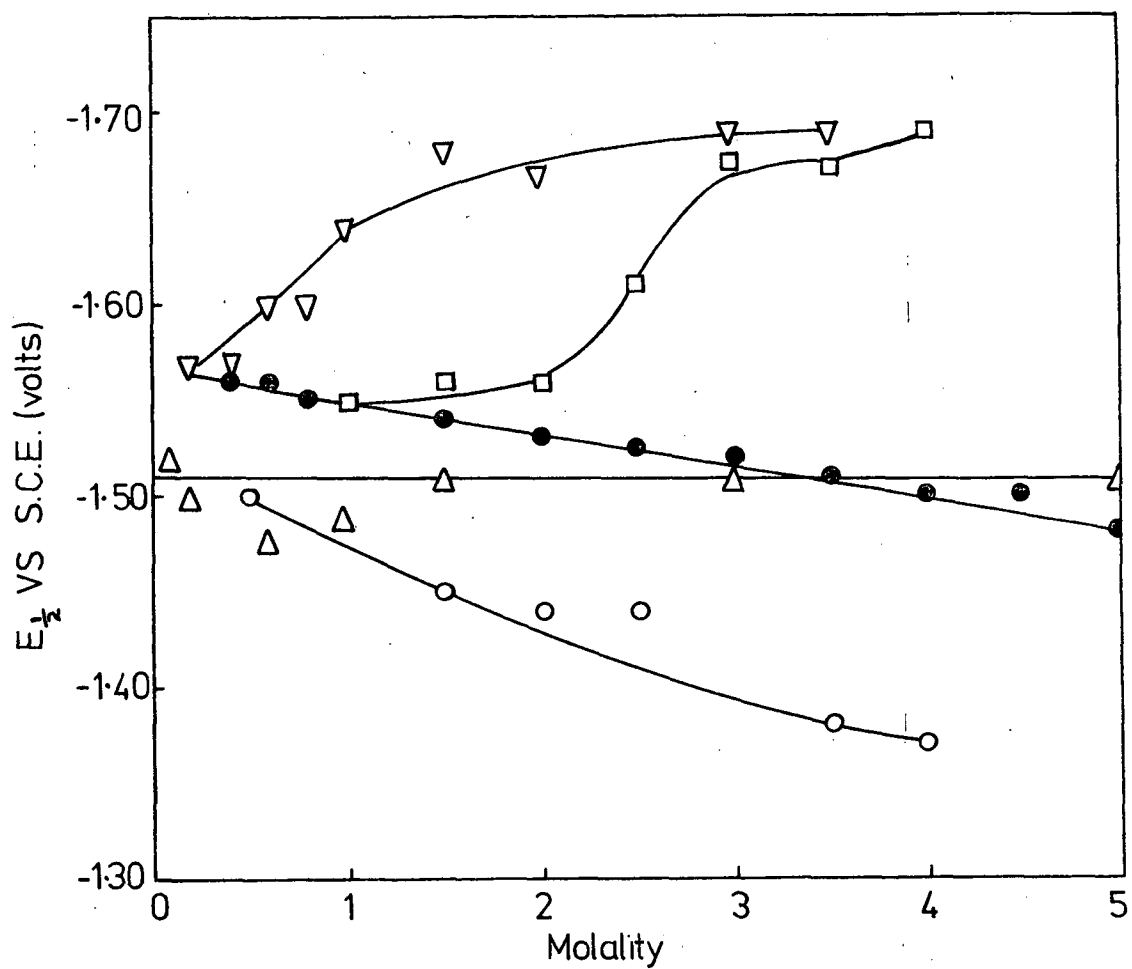


Fig.4.4.1 The effect of concentration of supporting electrolyte on the half-wave potential for the proton.

● NaBr ○ Me₄NBr Δ Et₄NBr □ Pr₄NBr
▽ Bu₄NBr

on to the mercury cathode, since these salts are surface active agents. This would make the half-wave potential more negative, the greater effect being produced by the greater ion.

The trends noted above indicate that tetramethylammonium bromide influences water structure in the same direction as the alkali halides. Other authors have studied apparent molal volumes¹¹³ and conductance and viscosity B-coefficients¹¹⁴ and concluded that the Me_4N^+ ion is a slight electrostrictive structure-breaker, that with the Et_4N^+ ion electrostriction and hydrophobic enhancement of structure are more or less balanced, and that the larger ions enhance water structure. It appears, then, that a structure-breaking influence can be associated with the reduction of the hydrogen ion at a more positive potential, and vice-versa.

It may be noted in passing that Novak⁸⁷ found the half-wave potential for deuterium reduction in dilute DCl at 20°C was 0.087 V more negative than hydrogen reduction in the same concentration of HCl. This more negative value of $E_{1/2}$ in the more structured DCl solution is in agreement with the values measured for $E_{1/2}$ in the HCl solutions with structure modified by the various electrolytes.

Roberts and Northey¹¹⁵ have argued, albeit cautiously, (since the over-voltage of hydrogen on mercury is a complicating factor), that the difference between the most negative potential they measured, -1.69V in 4m solutions of tetrapropyl- and tetrabutylammonium salts, and the most positive, -1.09V in 13m lithium chloride⁸⁸, represents an energy difference of 13.9 kcal, which corresponds closely to the rupture of three hydrogen bonds, since hydrogen-bonding in ice is 4.5 kcal per mole of bonds. This suggests that the hydrogen ion is present as H_9O_4^+ in concentrated solutions of the tetraalkylammonium salts (i.e. there are three hydrogen-bonds between H_3O^+ and three water molecules), and as

H_3O^+ in concentrated lithium chloride. The increase in the ease of reduction of the hydrogen ion may mean that it has a greater activity as a result of dehydration of the ion. Critchfield and Johnson¹¹⁶ have observed that the pH of acid solutions is markedly decreased by the addition of strong electrolytes, and have concluded that the activity of the hydrogen ion increases as it loses its water of hydration.

4.5. Proton Mobility in Solutions of Purified Electrolytes

The chlorides, bromides and iodides of sodium and potassium were purified for use as supporting electrolytes. Pure samples of tetramethyl- and tetrabutyl-ammonium bromides were also used. Tetraalkyl-ammonium cations combine large size and symmetrical shape with low charge and it seemed useful to compare their effect on hydrogen ion mobility with that of other 1:1 electrolytes, especially as some of them have been found to be hydrophobic structure-makers. The bromides were chosen for study because they are quite soluble and not hygroscopic.

Tables 3.4.1 - 3.4.8 show the values of the diffusion current measured in solutions of the eight purified salts together with $t^{1/6}$, where t is the drop-time in seconds. Curves (see Figure 4.5.1) drawn from these data, which were more reproducible than those obtained with the samples that were merely dried, showed the same general trends as those noted previously for alkali metal and halide ions, viz. hydrogen ion mobility is reduced most by the smallest alkali metal ion and the largest halide ion, and they also showed that tetrabutylammonium bromide reduced mobility more than tetramethylammonium bromide. Again the position of potassium bromide seemed anomalous. It may be noted here that this behaviour also appears in energy of activation values.

From the smoothed curves obtained from these data, values of $i_d/t^{1/6}$

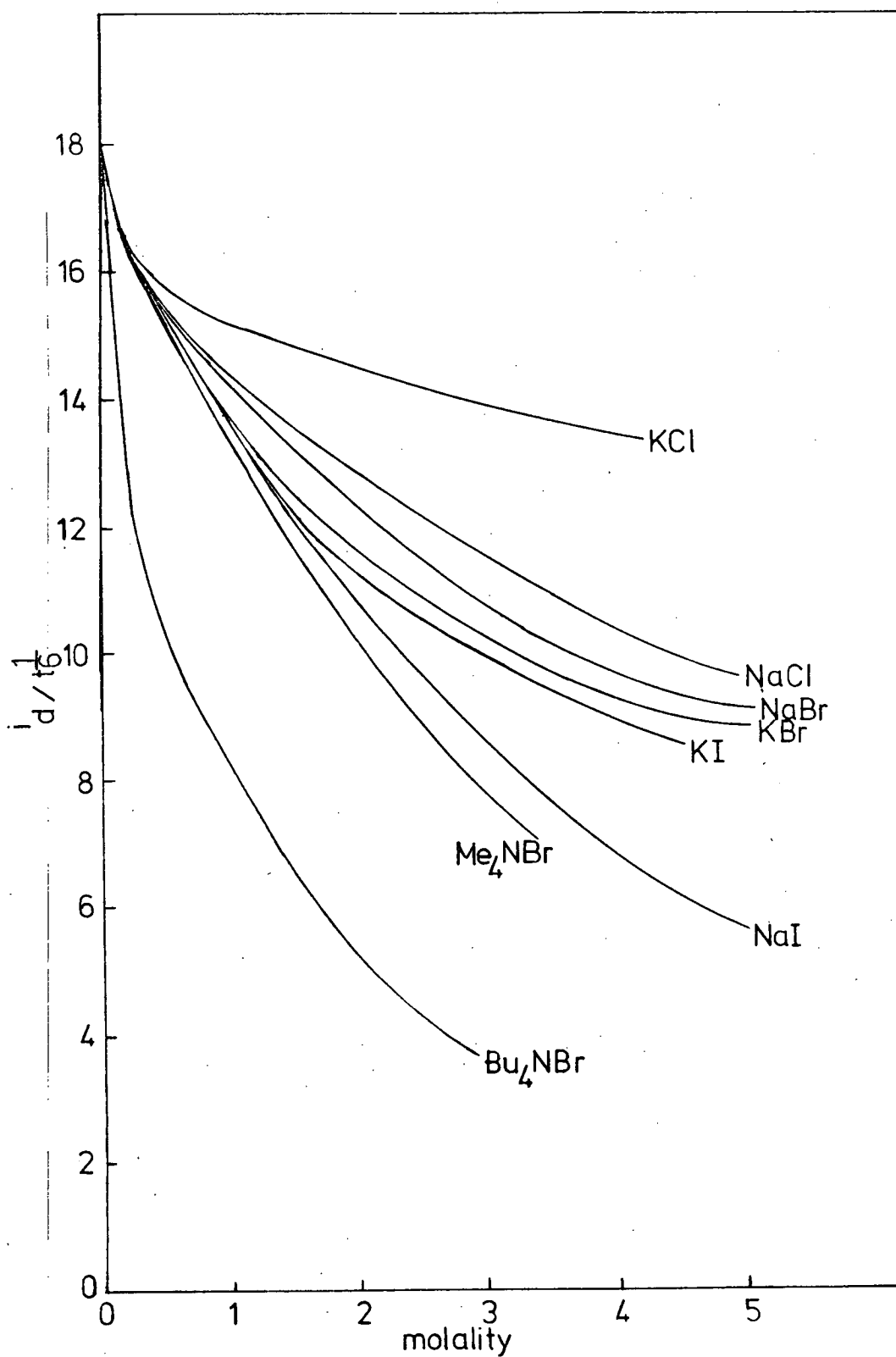


Figure 4.5.1 The effect of electrolyte concentration on the diffusion current of the proton.

were obtained for use with a computer programme to calculate the diffusion coefficient, D , for the hydrogen ion in the various electrolyte solutions.

4.6. Diffusion Coefficients of the Hydrogen Ion

Table 3.4.10 records values of D/D^0 (where D is the diffusion coefficient calculated from the diffusion current, i_d , measured polarographically, using the modified form of the Ilkovic equation viz.

$$i_d = 607 n D^{1/2} C m^{2/3} t^{1/6} (1 + 17 D^{1/2} m^{-1/3} t^{1/6}),$$

and D^0 is the theoretical value of the diffusion coefficient for the hydrogen ion at infinite dilution) for the proton in eight electrolyte solutions.

This form of the Ilkovic equation has been shown in Section 3.4 to give reliable values of D . It is interesting, therefore, to compare D/D^0 values obtained in this study and shown in Figures 4.6.1 and 4.6.2 with others previously reported, as has been done by Roberts and Northey¹¹⁷. The data of Woolf¹¹⁸ for hydrogen ion diffusion in aqueous solutions of sodium and potassium chlorides are compared with values obtained in the present study in Figure 4.6.3. Not only do the actual values differ, but it is clearly seen that only the polarographically obtained D/D^0 values extrapolate to 1 at zero concentration of supporting electrolyte. When D/D^0 values for other cations are plotted against concentration of supporting electrolyte as in Figure 4.6.4, it is seen that the curves for

- i) cadmium ion diffusion in sodium nitrate studied polarographically,
- ii) sodium ion diffusion in potassium chloride studied by the porous diaphragm cell method¹¹⁹, and
- iii) thallium ion diffusion in potassium chloride studied polarographically¹²⁰

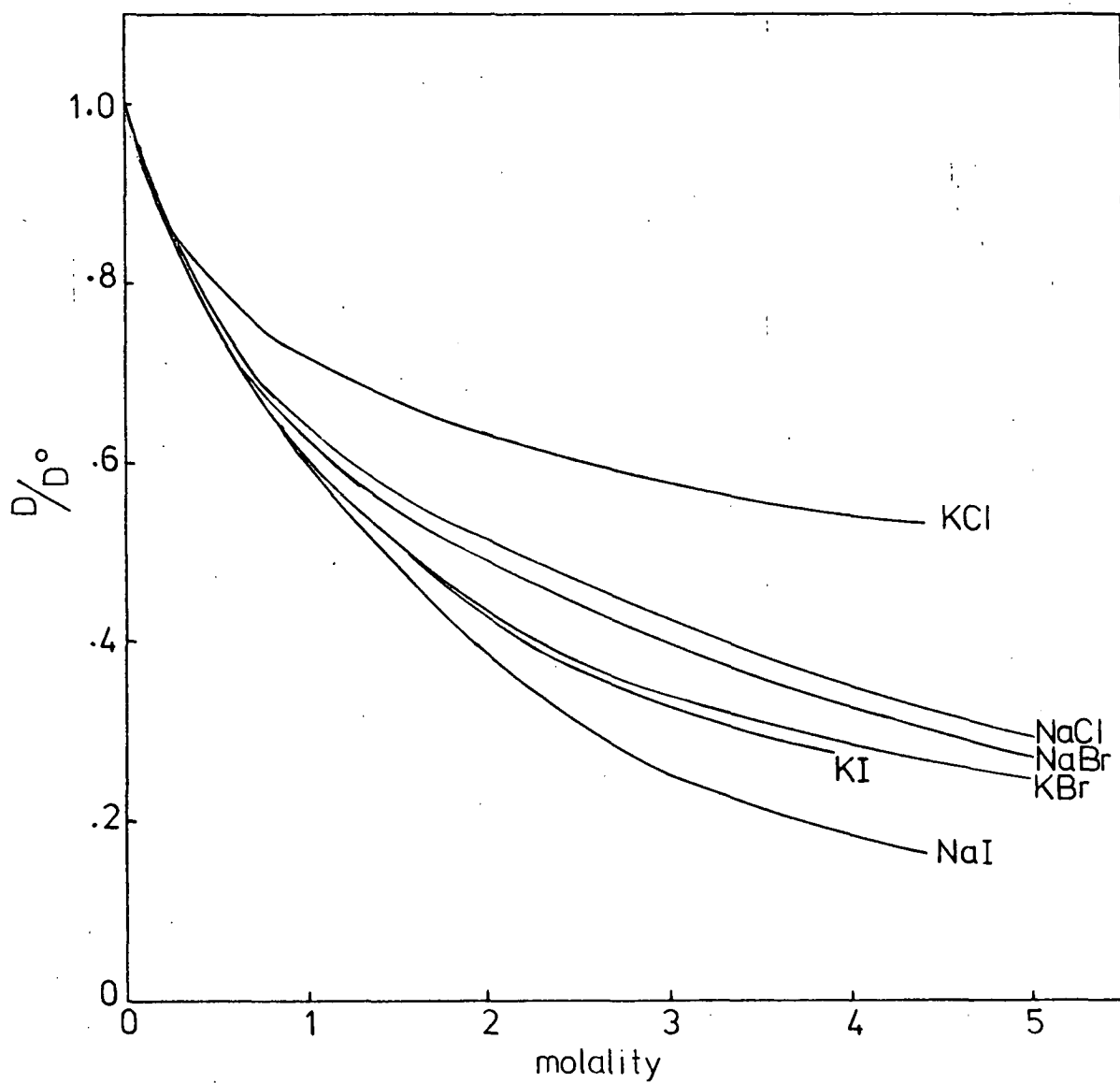


Figure 4.6.1 The effect of alkali halide concentration on the diffusion coefficient of the proton.

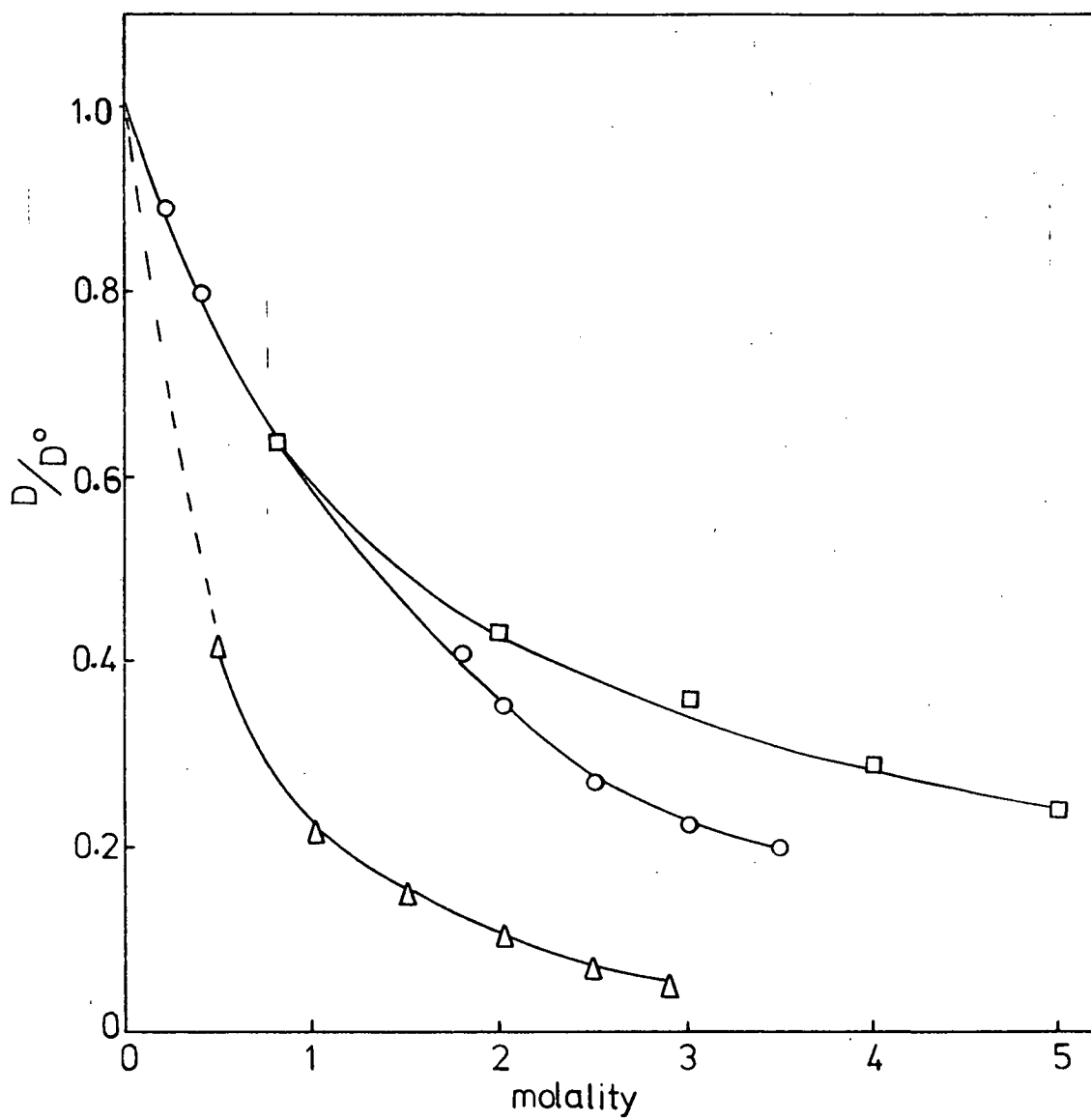


Figure 4.6.2 The effect of three bromides on the diffusion coefficient of the proton
 ○ Me₄NBr △ Bu₄NBr □ KBr

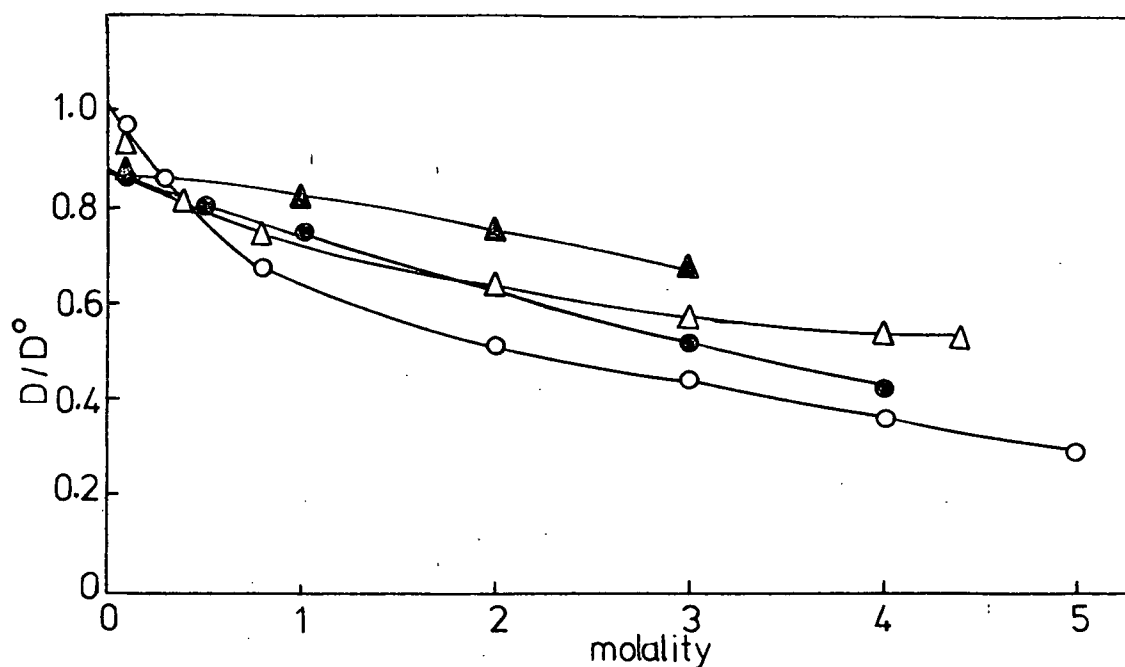


Figure 4.6.3 Tracer diffusion coefficients of the proton in electrolyte solutions

- NaCl present work
- NaCl Woolf¹¹⁸
- △ KCl present work
- ▲ KCl Woolf¹¹⁸

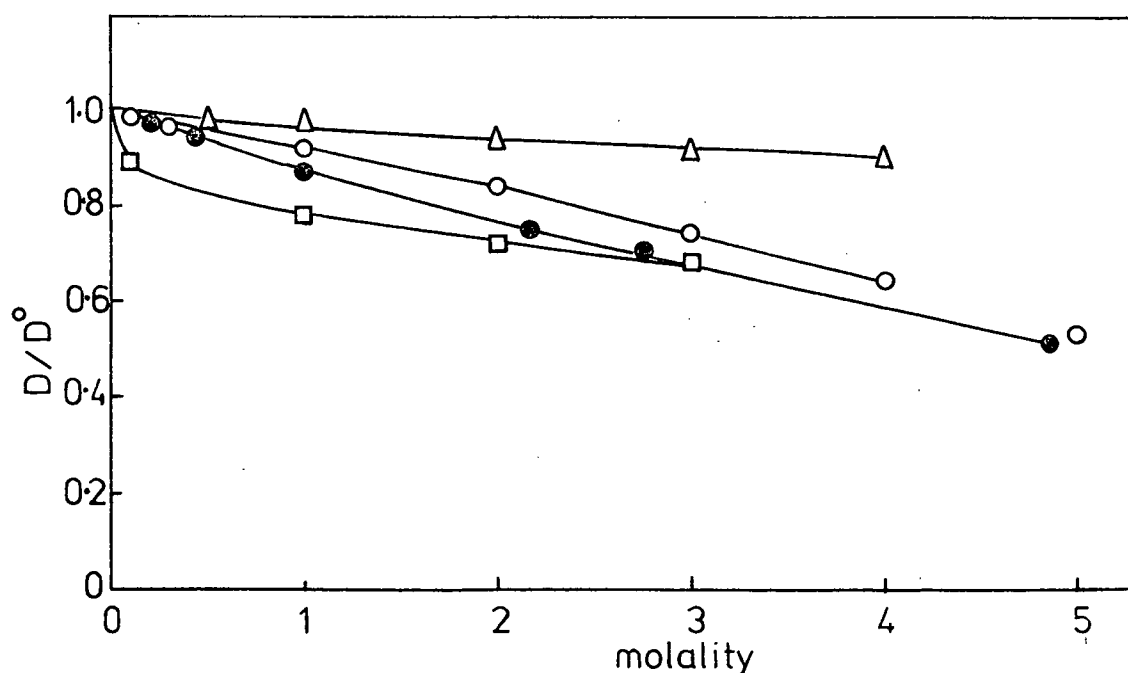


Figure 4.6.4 Tracer diffusion coefficients of metallic cations in electrolyte solutions

- $1.66 \times 10^{-3} \text{ M Cd}^{2+}$ in NaNO_3 , present work
- $0.83 \times 10^{-3} \text{ M Cd}^{2+}$ in NaNO_3 , present work
- △ Na^+ in KCl, Mills¹¹⁹
- Tl^+ in KCl,¹²⁰

also extrapolate to 1 at zero concentration of supporting electrolyte. This suggests that the present values of D are likely to be correct and that one must look for a possible source of error in Woolf's data for hydrogen ion diffusion.

In the porous diaphragm cell method the cells were calibrated by diffusion of potassium chloride solutions into water, and then used to measure the diffusion coefficients of other ions. Mysels and McBain¹²¹ have shown that when water is drawn through a disc of fritted Pyrex glass, resistance to hydrodynamic flow develops, as thick, rigid layers of water form in the pores of the disc. This does not affect the diffusion of other ions, but hydrogen ion diffusion is so sensitive to the structure of water, because of its particular mechanism, that it will be hindered by this phenomenon. This view is supported by recent articles by Drost-Hansen¹²² and Schufle and Yu¹²³.

It is possible, therefore, that the very fine capillaries (pore size $\sim 5\text{--}15\ \mu\text{m}$) used in the porous diaphragm cell method of determining diffusion coefficients, may hinder proton transport even though the mobilities of other ions are unaffected, and that this may explain differences in values and relationships obtained by the two methods discussed for proton diffusion in electrolyte solutions. In Chapter 5 the question of the anomalous behaviour of water near interfaces, as compared with that of bulk water, will be discussed further.

4.7. The Effect of Viscosity

Stokes, Mills et al^{83,98,125} have suggested that viscosity effects should be considered in conjunction with diffusion coefficients. Now viscosity is a property arising primarily from the movement of solvent molecules and gives ideas of solvent structure¹²⁶. Proton mobility in electrolyte solutions depends as well on the nature, number and movement

of solute particles present. Mills and Kennedy¹²⁵ have measured the self-diffusion coefficients of I^- , K^+ and Rb^+ in a series of aqueous metal iodide solutions. When the diffusion-viscosity product, $D\eta/\eta^0$, for the iodide ion was plotted against supporting electrolyte concentration a straight line was obtained, showing that, although the product was not constant, as predicted by the Walden relation, $\lambda^0\eta^0 = \text{constant}$, there existed a simple relation between diffusion of the iodide ion and the viscosity of the solution. This was not the case, though, for the cations studied. Neither did Stokes et al¹²⁴ obtain a straight line for the diffusion-viscosity vs. concentration graph for tracer diffusion of the iodide ion in three alkali chlorides. They did suggest, however, that the viscosity "correction" had some significance since it brought the curves closer together, even though, in their study, it caused over-correction, in that the order of the curves was reversed from that obtained when the diffusion coefficient alone was plotted against \sqrt{c} .

In the present study relationships between some variable and concentration (not \sqrt{c}) are shown. This is reasonable since the Onsager-Fuoss and Debye-Hückel linear relationships between, say, conductivity and the square root of concentration hold only up to concentrations lower than those considered here, so there is no compelling theoretical justification for plotting \sqrt{c} values as abscissae. As Blandamer¹²⁷ has pointed out, it is reasonable to note the trend shown when values of a certain variable change with concentration, and it has been shown that, as far as can be ascertained by extrapolation of a non-linear curve, values of D/D_0 , obtained polarographically, extrapolate to unity for the proton and the cadmium ion in the supporting electrolytes considered.

Figure 4.7.1 shows the diffusion-viscosity vs. concentration curves for three bromides. When these are compared with diffusion vs. concen-

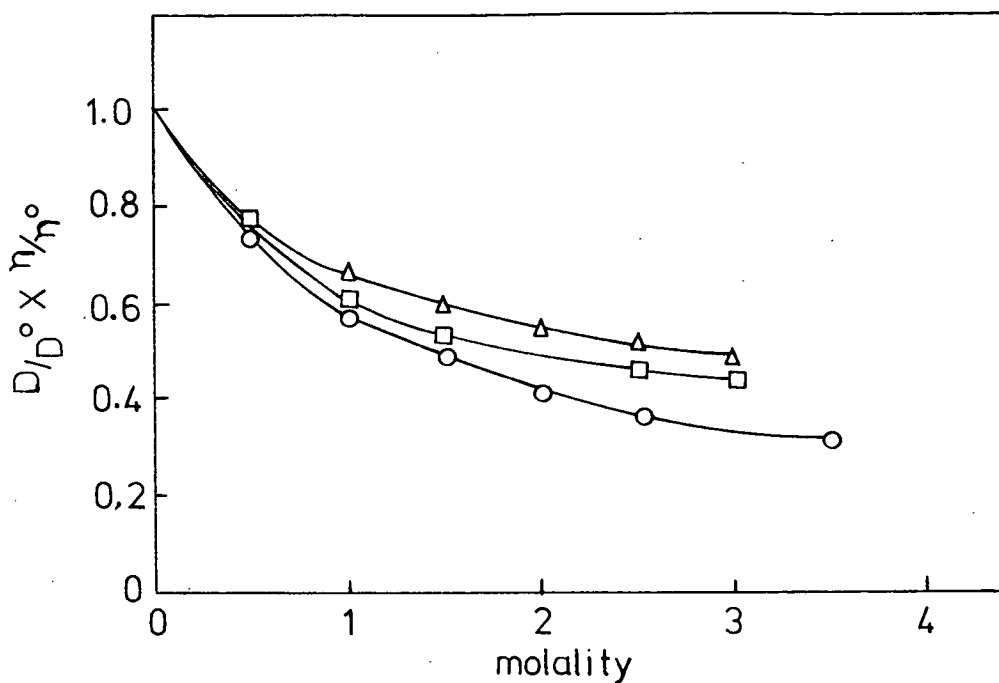


Figure 4.7.1 The effect of concentration of supporting electrolyte on the diffusion - viscosity product for proton diffusion.

\circ KBr Δ NaBr \square Bu₄NBr

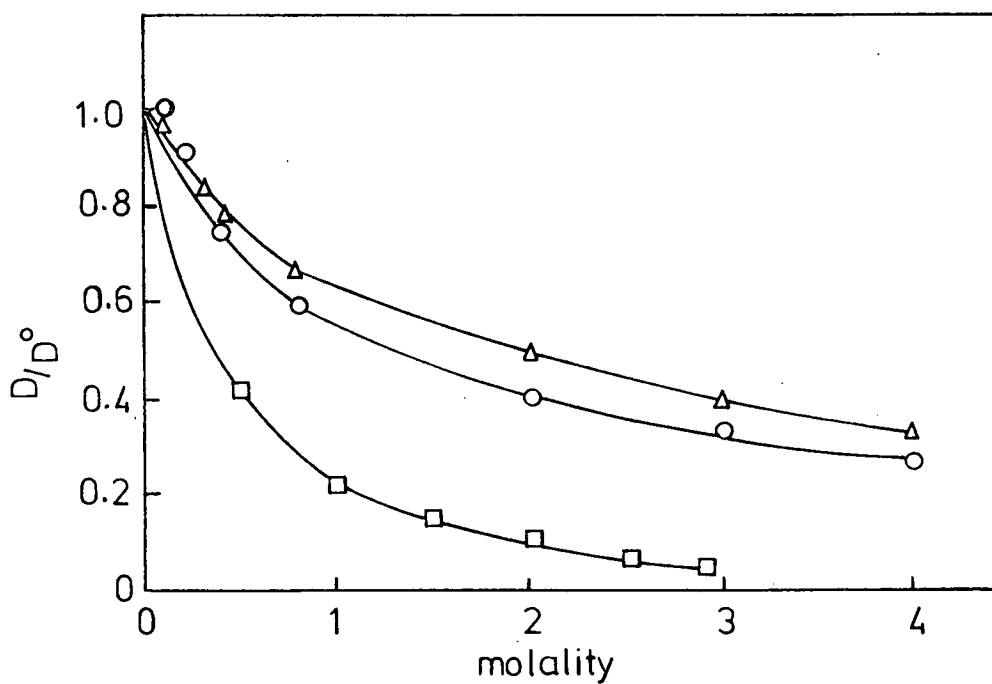


Figure 4.7.2 The effect of concentration of supporting electrolyte on the diffusion coefficient ratio for proton diffusion

\circ KBr Δ NaBr \square Bu₄NBr

tration curves, Figure 4.7.2, it is seen that the Bu_4NBr curve is most affected, but that in no case is a straight line obtained. For KBr , little difference is noted since $\eta/\eta^0 \approx 1$.

Increase in viscosity is thus not the chief cause of the reduction of proton mobility in electrolyte solutions. This will be discussed again later, (Section 4.9).

4.8. Deuteron Diffusion in Some Electrolyte Solutions

D_2O is generally considered to be more structured than H_2O since its higher viscosity, melting point, temperature of maximum density and heat capacity indicate more structural order. It was, therefore, decided to study deuteron mobility in heavy water solutions of some electrolytes. No hydrated salts could be used. Sodium chloride, three potassium halides and four tetraalkylammonium bromides were chosen and solutions were prepared as described in Section 2.4.

Deuteron mobility in heavy water solutions showed the same trends as proton diffusion in normal water solutions, viz. deuteron mobility was higher in potassium chloride than in sodium chloride solutions, among the potassium salts the order was $\text{Cl}^- > \text{Br}^- > \text{I}^-$, and among the tetraalkylammonium bromides it was $\text{Me}_4\text{N}^+ > \text{Et}_4\text{N}^+ > \text{Pr}_4\text{N}^+ > \text{Bu}_4\text{N}^+$. The curves are shown in Figures 4.8.1 and 4.8.2. Concentration is given as aquamolality which is the number of moles of solute per 55.5 mole of water. This scale is used to enable comparisons with normal water solutions to be made.

That the largest alkali metal cation causes the least reduction in mobility whereas the smallest tetraalkylammonium ion does likewise, indicates that the two kinds of ion affect water differently¹¹⁵.

It has already been pointed out in Section 4.4 that Me_4N^+ is an electrostrictive structure breaker and the larger ions in the series

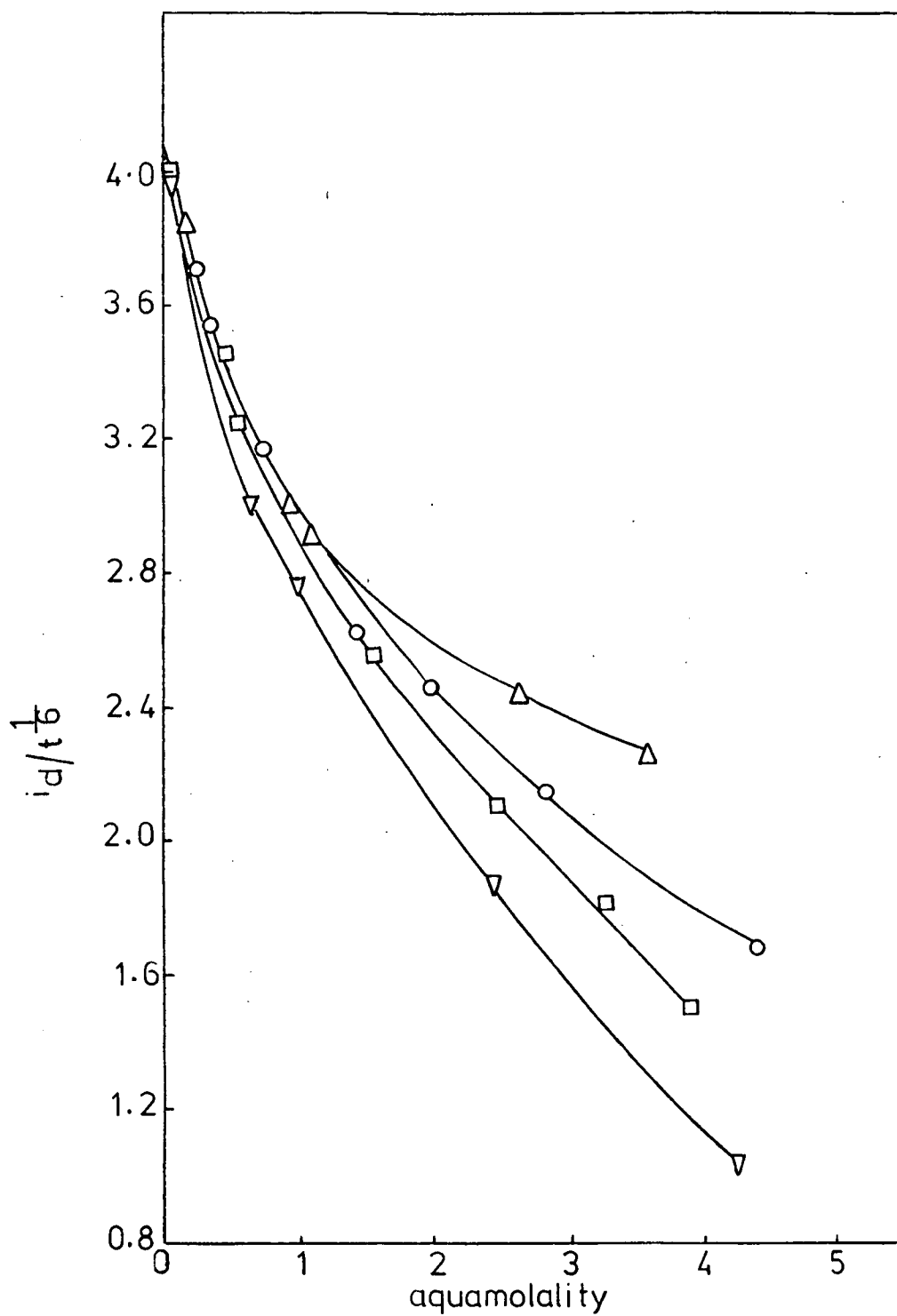


Figure 4.8.1 The effect of concentration of some alkali halides on the diffusion current of the deuteron
 \circ NaCl Δ KCl \square KBr ∇ KI

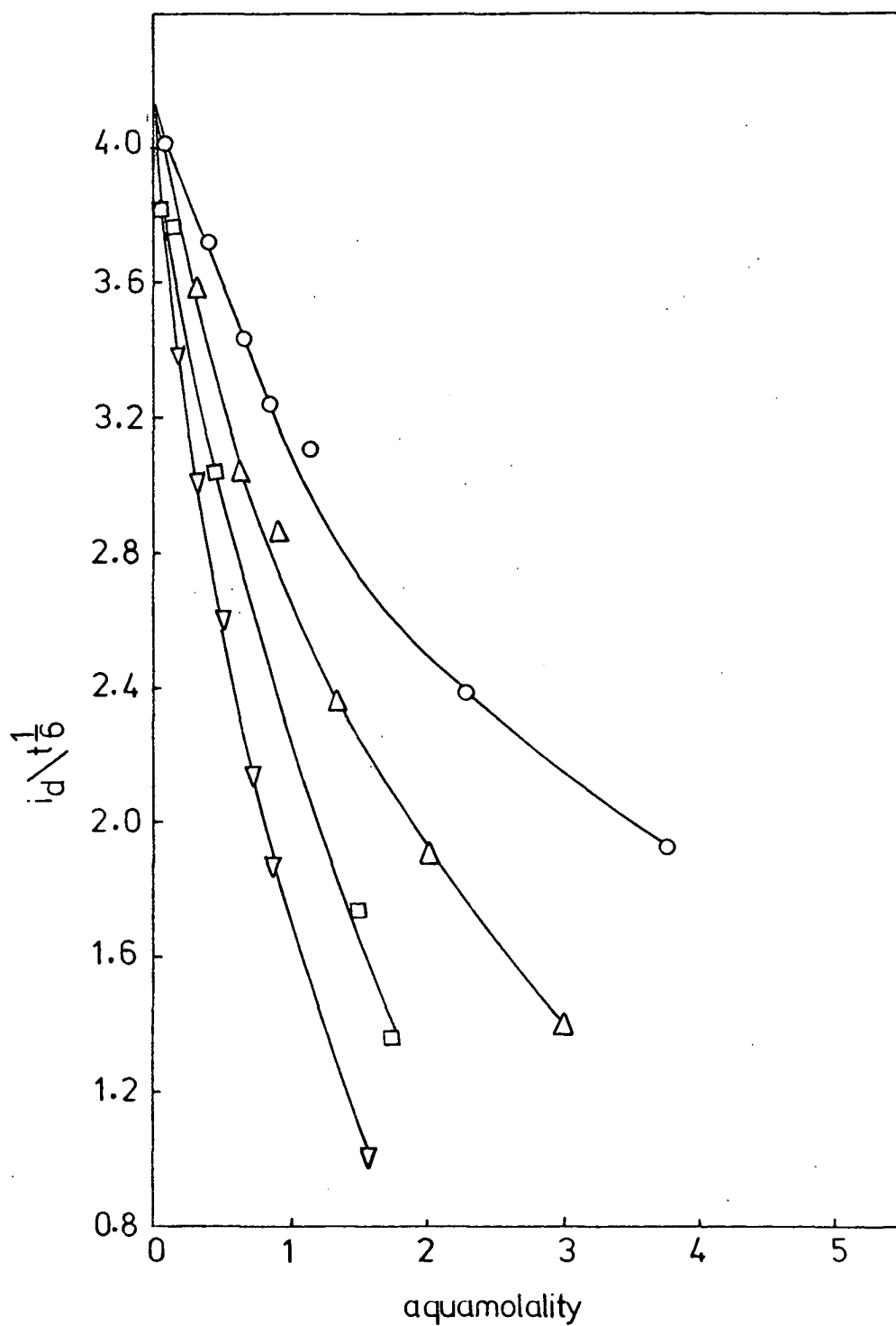


Figure 4.8.2 The effect of concentration of tetraalkylammonium bromide solutions on the diffusion current of the deuteron

○ Me₄NBr Δ Et₄NBr □ Pr₄NBr
 ▽ Bu₄NBr

are hydrophobic structure makers. This means that solvent-solvent interactions become stronger near the non-polar tetraalkylammonium ions¹²⁸. The charge is screened and its density is greatly decreased¹²⁶ but the strongly hydrophobic hydrocarbon groups perturb nearby water molecules. At the same time these ions tend to stabilise each other's tendencies to be surrounded by cages of water molecules¹²⁹, as cation-cation pairing seems to occur. The length of the alkyl chain, not the charge density, seems to be the dominant factor affecting proton mobility in solutions of tetraalkylammonium ions, whereas in solutions of alkali metal ions proton mobility is reduced more as the surface charge density increases and water molecules become more tightly bound to the ions.

The relative structure-modifying effects of the tetraalkylammonium ions indicated above are in agreement with conclusions based on viscosity^{114,130,131}, heats of mixing of ionic solutions¹³² and infrared spectroscopy¹³³. Although a cage type of structure is suggested above, the exact kind of water-structure modification brought about by these large ions is not known.

In Figures 4.8.3 and 4.8.4 the diffusion coefficients calculated from experimental data are plotted against concentration of supporting electrolyte. It is seen that these curves extrapolate to a value ca $6.2 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$. This compares quite favourably with the value of $6.5 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ calculated from ionic mobility data.

4.9. Proton and Deuteron Diffusion Compared

Figure 4.9.1 shows plots of $i_d/t^{1/6}$ vs. aquamolality for the proton and deuteron in sodium chloride and tetrabutylammonium bromide solutions. Only qualitative comparison can be made, as the concentrations of H^+ and D^+ differ. It is seen, however, that the initial steep

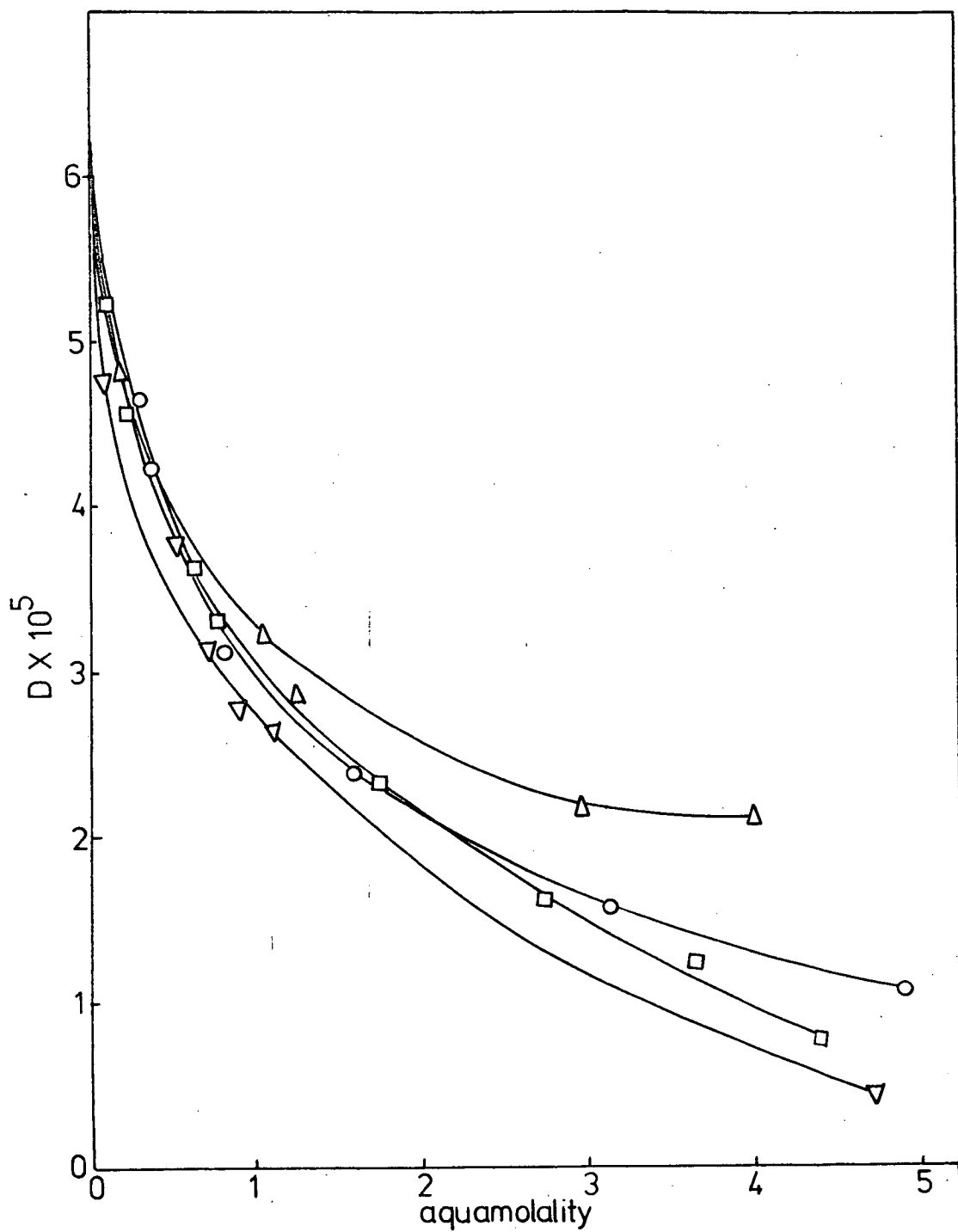


Figure 4.8.3 Tracer diffusion coefficients of the deuterium in alkali halide solutions
 ○ NaCl △ KCl □ KBr ▽ KI

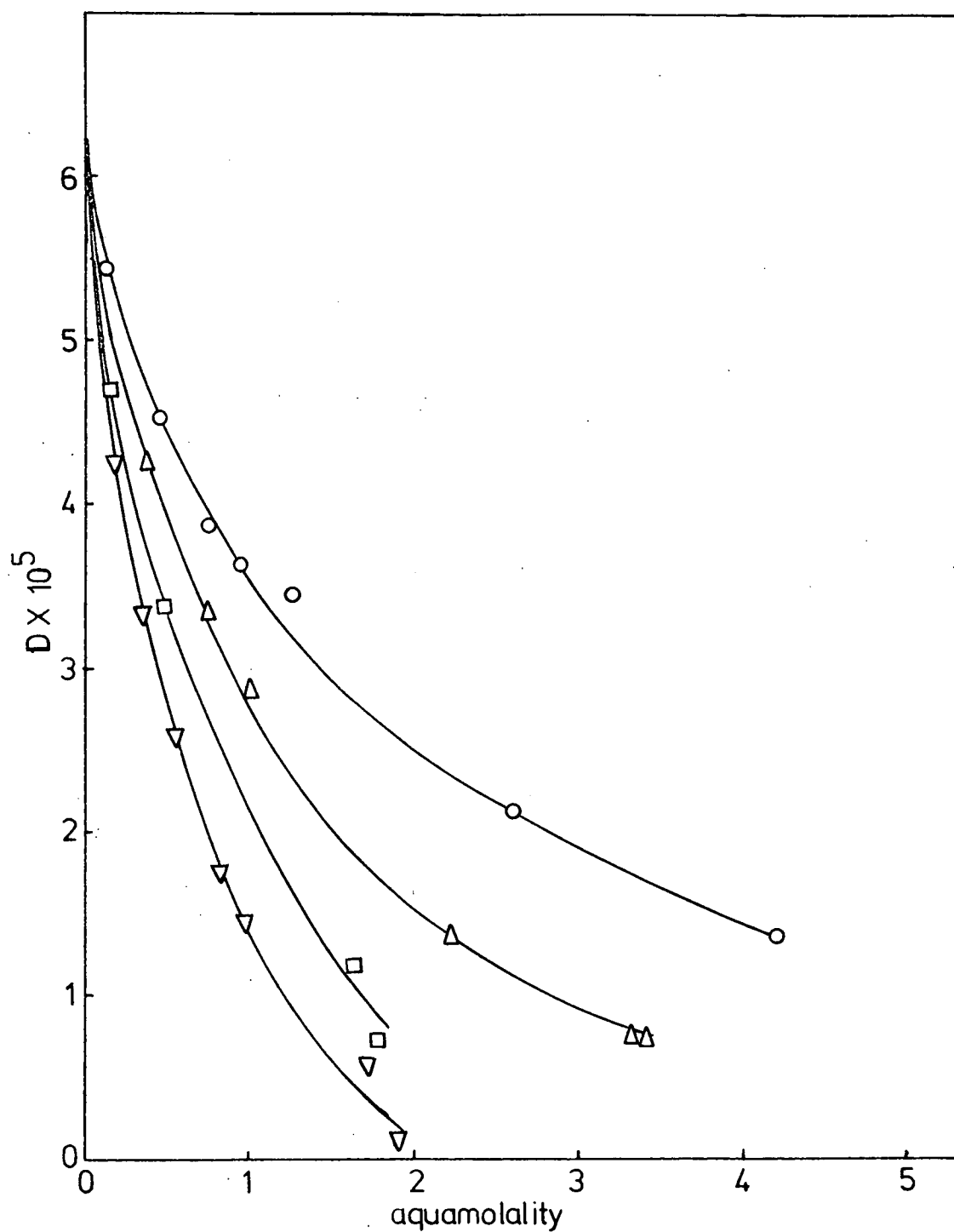


Figure 4.8.4 Tracer diffusion coefficients of the deuteron in tetraalkylammonium bromide solutions
 \circ Me_4NBr Δ Et_4NBr \square Pr_4NBr ∇ Bu_4NBr

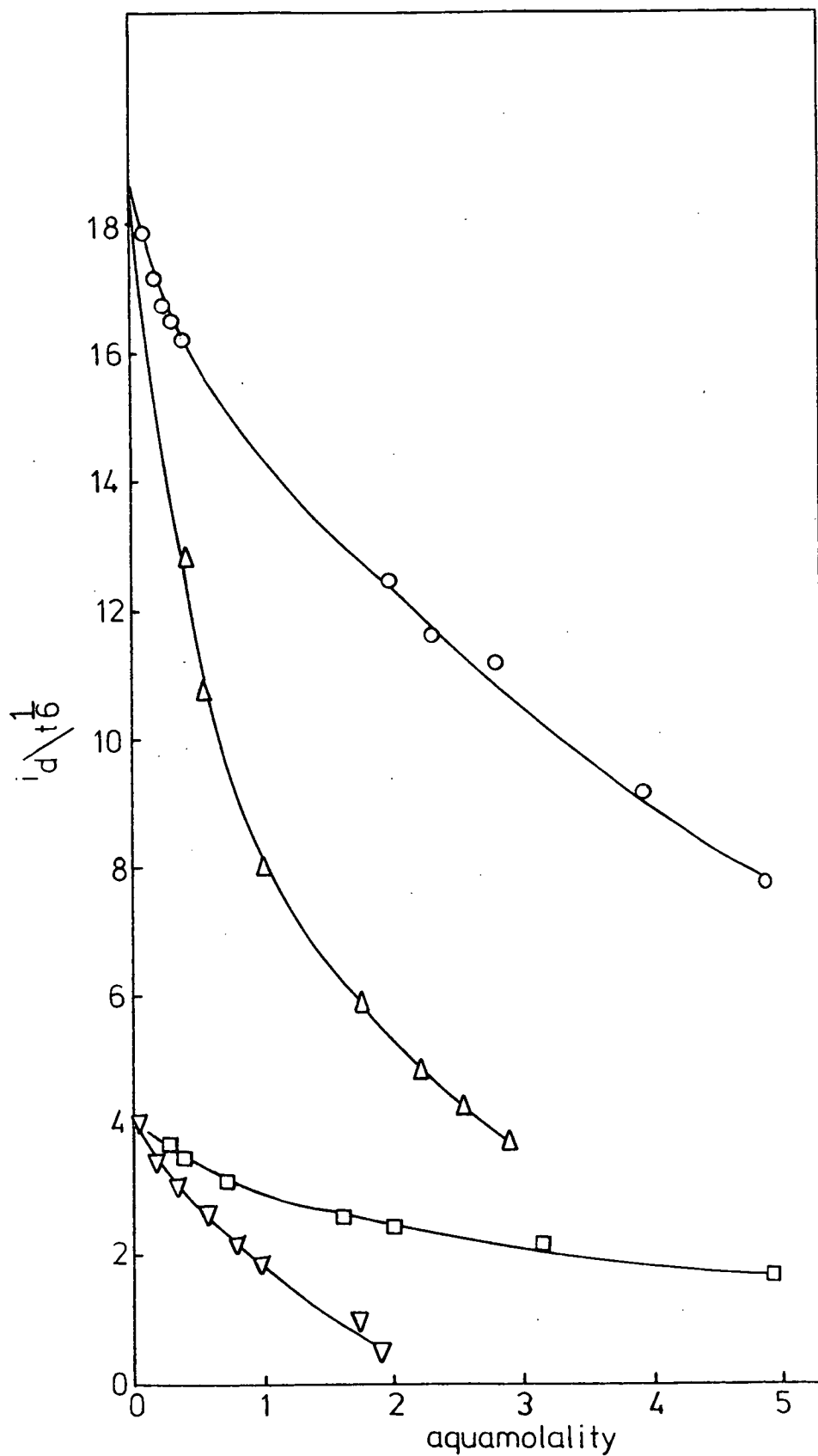


Figure 4.9.1 Proton and deuteron diffusion compared.
 Proton in \circ NaCl Δ Bu_4NBr
 Deuteron in \square NaCl ∇ Bu_4NBr

portions of all curves give way to flatter portions at about the same concentration of supporting electrolyte.

The changes brought about by the supporting electrolyte in the diffusion coefficients of the proton and deuteron may be compared by plotting D/D^0 values against the concentration of supporting electrolyte. These plots are shown in Figures 4.9.2 - 4.9.7 which also include, for comparison where available, data^{100,134,135} for the self-diffusion of water in the presence of some electrolytes. The D/D^0 vs. concentration curves for the four alkali halides show that deuteron mobility in D_2O is affected to a greater extent than proton mobility in H_2O ; the effect is the same, however, for the two tetraalkylammonium bromides up to 1m, though the curves diverge after this. This difference in behaviour may arise from the different modes of interaction of the solvent with alkali halides and the tetraalkylammonium bromides, and the consequent effects on hydrogen ion mobility.

If the latter portions of the curves represent maximum hydration of the hydrogen ion, as was suggested in Section 4.4 concerning the values of half wave potentials, and if they also represent the regions where water molecules are shared between ions, then the initial portions show where the Grotthuss mechanism most affects hydrogen ion mobility. This is reduced more readily in the more highly structured heavy water than in normal water. Above 1 aquamolal concentration of alkali halides (except KI), the rate of change of D/D^0 for D^+ and H^+ does not vary greatly, indicating that changes in structure are not of paramount importance above this concentration, where the Grotthuss contribution to hydrogen ion transport has decreased considerably so that diffusion by the usual mechanism is more significant.

It is to be noted that D/D^0 values for the deuteron in Me_4NBr solution of concentration above 1 molal exceed those for the proton, in

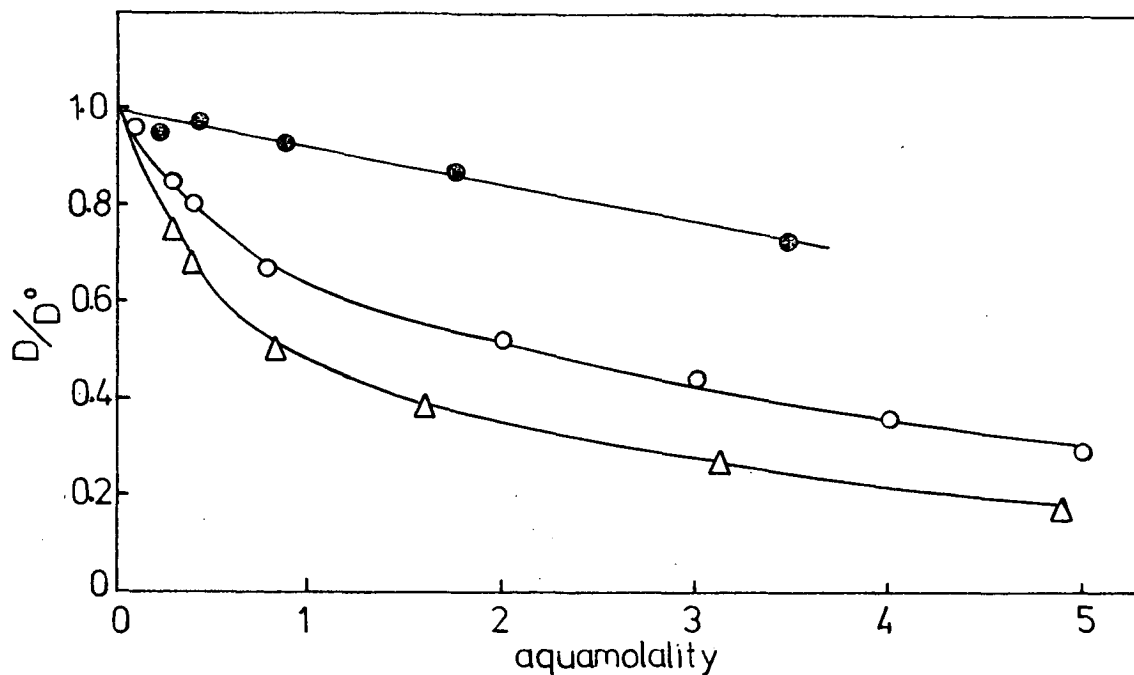


Figure 4.9.2 Tracer diffusion coefficients of the proton and deuteron in sodium chloride solutions at 25°C
 \circ H^+ Δ D^+ \bullet The self-diffusion ratio for normal water at 23°C

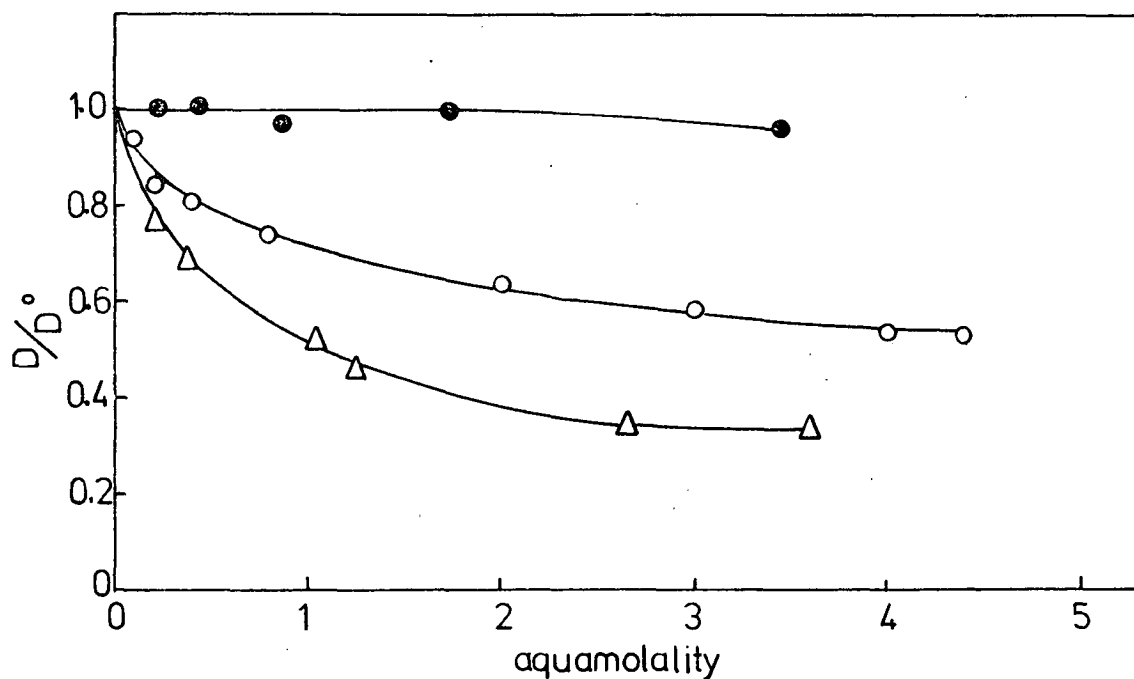


Figure 4.9.3 Tracer diffusion coefficients of the proton and deuteron in potassium chloride solutions
 \circ H^+ Δ D^+ \bullet The self-diffusion ratio for normal water at 23°C

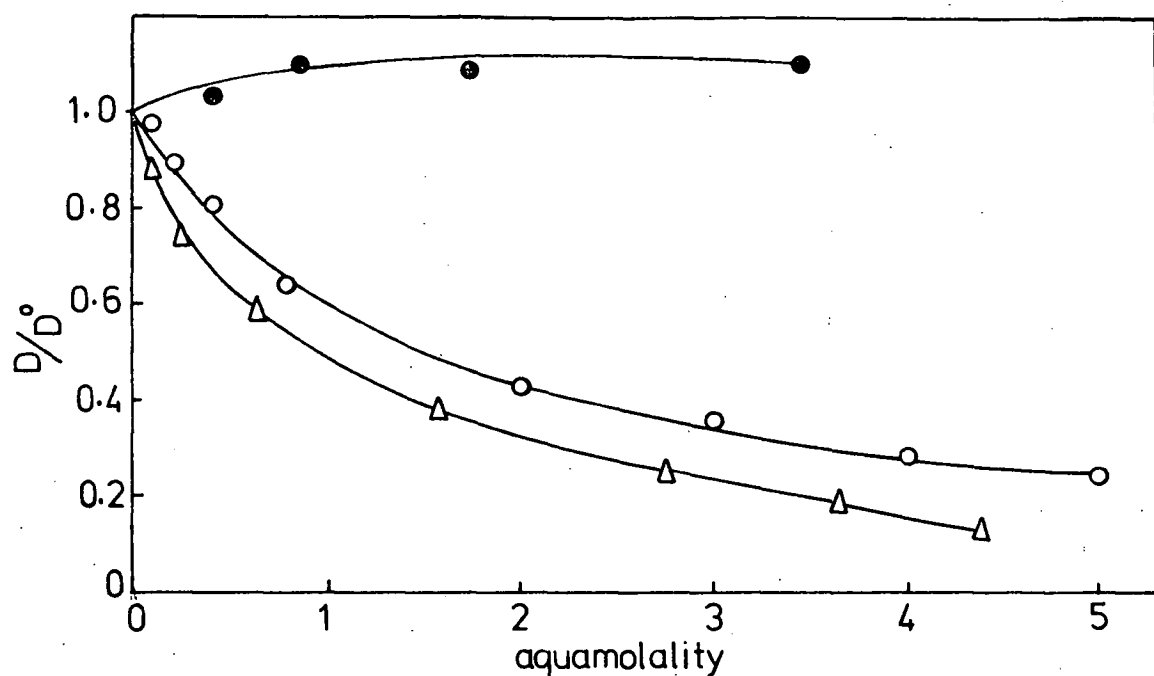


Figure 4-9-4 Tracer diffusion coefficients of the proton and deuteron in potassium bromide solutions at 25°C
 ○ H^+ △ D^+ ● The self-diffusion ratio for normal water at 23°C

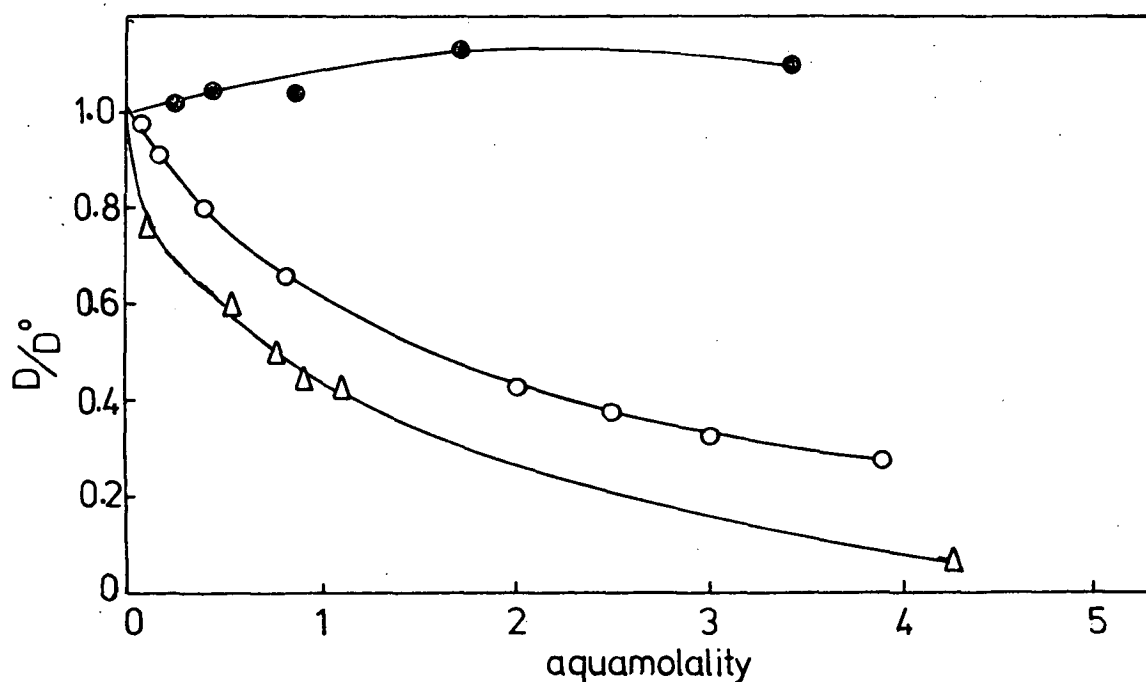


Figure 4-9-5 Tracer diffusion coefficients of the proton and deuteron in potassium iodide solutions at 25°C
 ○ H^+ △ D^+ ● The self-diffusion ratio for normal water at 23°C

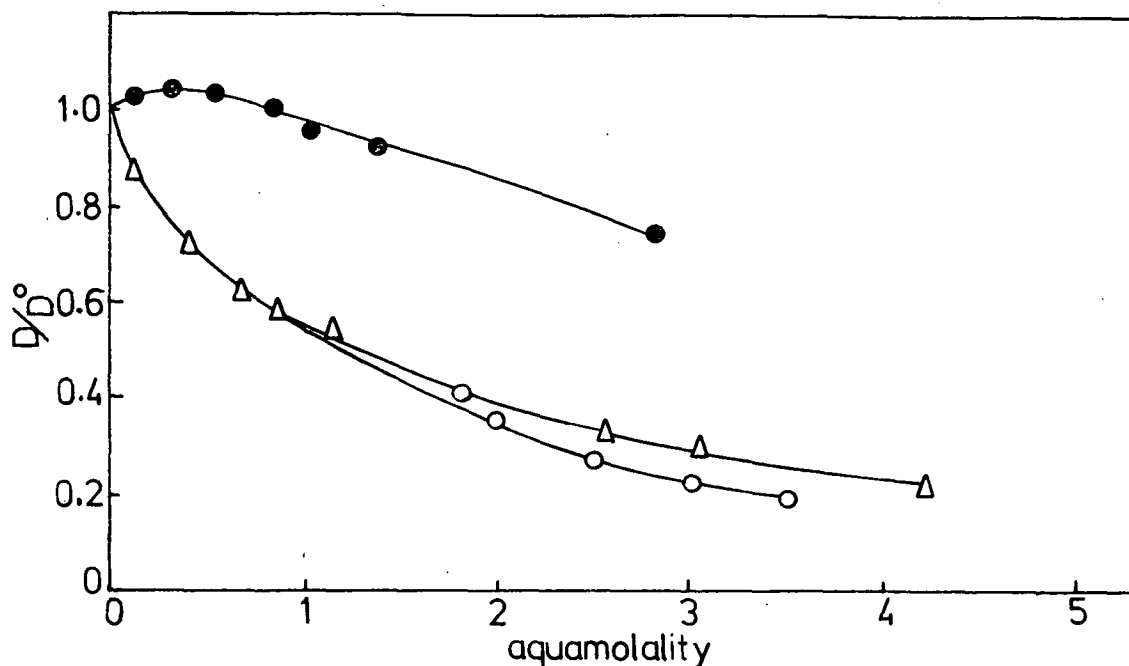


Figure 4.9.6 Tracer diffusion coefficients of the proton and deuteron in tetramethylammonium bromide solutions 25°C
 $\circ H^+$ ΔD^+ \bullet The self-diffusion ratio for normal water at 23°C

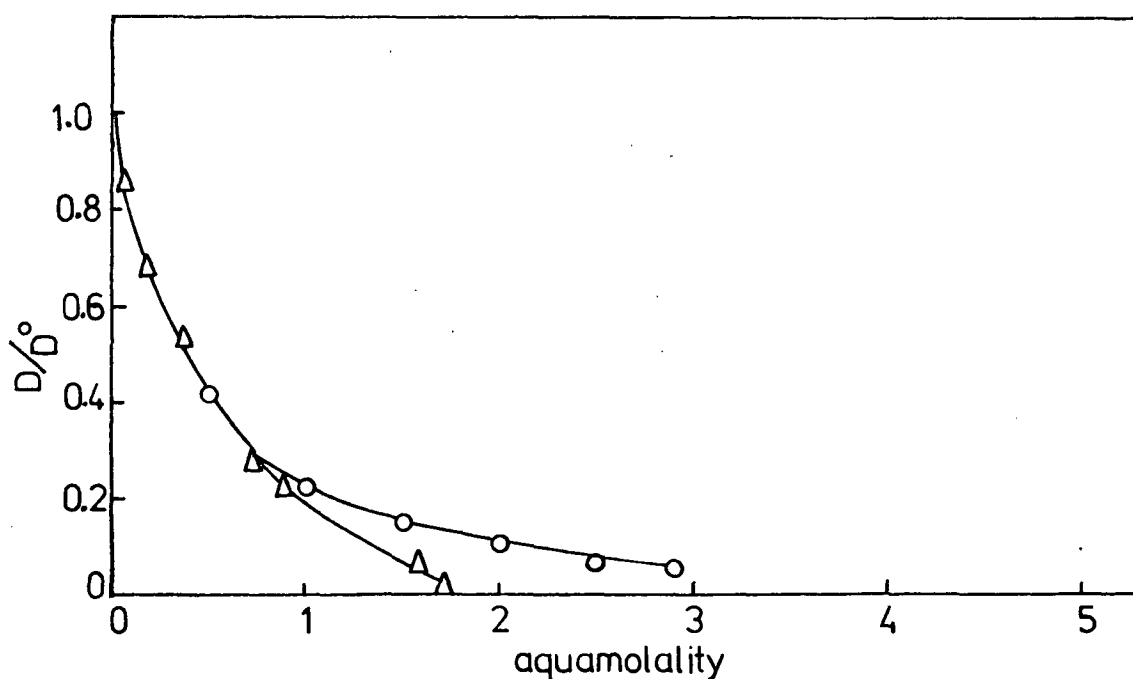


Figure 4.9.7 Tracer diffusion coefficients of the proton and deuteron in tetrabutylammonium bromide solutions
 $\circ H^+$ ΔD^+

contrast to the other cases, including Bu_4NBr where proton values lie above those for the deuterion. This may be related to relative viscosities since Kay and Evans^{114,130} found that the Walden product ratio in normal and heavy water is below 1 for Me_4N^+ and above 1 for Bu_4N^+ salts. Otherwise it is difficult to account for the unusual trend of the ratios above in tetramethylammonium bromide solutions.

In Table 4.9.1 is shown the effect of concentration of supporting electrolyte on the diffusion coefficient of the hydrogen ion relative to that of the deuterium ion.

Sodium chloride, and potassium chloride and bromide show much the same trend in the ratio $\frac{D_{\text{H}^+}}{D_{\text{D}^+}}$, whereas potassium iodide shows a much more rapid increase as a result of the relatively lower diffusion coefficient of the deuterium ion. The difference may arise as a result of some specific interaction between the iodide ion and D_2O . In this connection it is worthy of note that Greyson¹⁰⁵ and Walrafen³⁰ have shown that in the case of water, structure-influencing properties are more sensitive to ion size for negative than for positive ions since the protons in water may polarise anions to an extent increasing with increasing anion size thus producing between the water and anion a bond which is less polar than the OH-O bond of water itself and which therefore tends to destroy structure in the surrounding water.

From the values of the ratios for H^+ and D^+ in alkali halides and acknowledgement of greater structure in D_2O , one may conclude that more rapid reduction of proton mobility is due to greater structure in the electrolyte solutions being considered.

Table 4.9.1.

Values of the ratio of the diffusion coefficients in
normal and heavy water solutions of electrolytes

Supporting Electrolyte	Concentration (aquamolal)	$D_{H^+} \times 10^5$ $\text{cm}^2 \text{ sec}^{-1}$	$D_{D^+} \times 10^5$ $\text{cm}^2 \text{ sec}^{-1}$	D_{H^+}/D_{D^+}
NaCl	0	9.3	6.5	1.43
	0.5	7.1	3.8	1.9
	1	6.0	2.9	2.1
	2	4.9	2.1	2.3
	3	4.1	1.7	2.4
	4	3.4	1.3	2.6
KCl	0.5	7.3	4.1	1.8
	1	6.7	3.2	2.1
	2	5.9	2.4	2.5
	3	5.5	2.2	2.5
	4	5.1	2.0	2.6
KBr	0.5	7.1	3.9	1.8
	1	5.6	3.0	1.9
	2	4.0	2.0	2.0
	3	3.2	1.4	2.3
	4	2.6	0.98	2.7
KI	0.5	7.1	3.7	1.9
	1	5.7	2.7	2.1
	2	4.0	1.7	2.4
	3	3.1	1.0	3.1
	4	2.5	0.5	5.0
Me_4NBr	1.8	3.8	2.6	1.5
	2.0	3.3	2.4	1.5
	2.5	2.5	2.0	1.3
	3.0	2.1	1.7	1.2
	3.5	1.9	1.4	1.4
Bu_4NBr	0.5	3.9	2.5	1.6
	1.0	2.1	1.2	1.8
	1.5	1.4	0.5	2.8
	2.0	0.95	—	—
	2.5	0.64	—	—
	2.9	0.49	—	—

4.10. The Grotthuss Component of Hydrogen Ion Diffusion

The discussion so far, while acknowledging the abnormal mobility of hydrogen ion diffusion, has made no attempt to separate the excess Grotthuss contribution from the total measures of the diffusion coefficients. The work on proton conductance of Conway, Bockris and Linton⁵⁶ suggests that the Grotthuss component may be obtained by subtracting the component due to normal ionic diffusion from the values measured for the proton and deuteron diffusion coefficients. The potassium ion is of comparable radius to the hydrogen ion, so for proton diffusion in normal water solutions at various electrolyte concentrations, it is reasonable to say:

$$\text{Grotthuss contribution} = (D_{\text{H}^+} - D_{\text{K}^+})_{\text{H}_2\text{O}}$$

There are, however, no values available for the diffusion coefficient of K^+ in various electrolyte solutions, but such values are available for Cl^- in sodium and potassium chloride solutions⁷¹, and since the diffusion coefficients at infinite dilution for K^+ and Cl^- are little different (being 1.98×10^{-5} and $2.03 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ respectively), it is reasonable to substitute the Cl^- values for those of K^+ . Then:

$$\text{Grotthuss contribution} = (D_{\text{H}^+} - D_{\text{Cl}^-})_{\text{H}_2\text{O}}$$

Similarly for deuteron diffusion in heavy water solutions:

$$\text{Grotthuss contribution} = (D_{\text{D}^+} - D_{\text{Cl}^-})_{\text{D}_2\text{O}}$$

Now the diffusion coefficient of the chloride ion in heavy water is not known, but it may be estimated using the Einstein equation:

$$D = RT/6\pi \eta r N.$$

which indicates that $D \propto \frac{1}{\eta r}$, where η is the viscosity of the electrolyte

solution and r is the radius of the ion. The chloride ion is only slightly hydrated so there will be little error in assuming that its ionic radius is the same in D_2O as in H_2O . Then $(D_{Cl^-})_{D_2O}$ in various electrolytes may be put equal to:

$$(D_{Cl^-})_{H_2O} \times \frac{\eta_{H_2O}}{\eta_{D_2O}}$$

where η_{H_2O}/η_{D_2O} is known for various electrolyte solutions. Stokes and Mills⁹⁸ give values of the viscosity of potassium chloride solutions in normal water, and those for heavy water solutions were obtained from Selecki et al¹³⁶. All viscosities were calculated for an aquamolality basis. The results of these calculations are shown in Table 4.10.1 which shows also the ratio of the Grotthuss component of the proton in normal water solutions to that of the deuteron in heavy water solutions of potassium chloride. This Table also contains similar values for sodium chloride solutions, though another approximation was necessary to calculate these as viscosity data for heavy water solutions of sodium chloride were not available. Thus the ratio η_{H_2O}/η_{D_2O} for the pure solvents was multiplied by $(D_{Cl^-})_{H_2O}$ values at the various concentrations to obtain $(D_{Cl^-})_{D_2O}$ values.

When the ratio of the Grotthuss component for H^+ in H_2O solutions of electrolyte to this component for D^+ in D_2O solutions was plotted against aquamolal concentration of supporting electrolyte straight lines were obtained (see Figure 4.10.1). These extrapolated to the accepted value of the ratio of the diffusion coefficient at infinite dilution. They may be contrasted with the non-linear curves obtained when the total diffusion coefficient ratios were plotted against concentration (Figure 4.10.2). The straight lines indicate some regularity in the reduction of the Grotthuss component in both normal

Table 4.10.1.

Total diffusion coefficients and Grotthuss components
for hydrogen ion diffusion in electrolyte solutions

NaCl

Conc. (aquamolal)	$D_{H^+} \times 10^5$	$D_{Cl^-} \times 10^5$	$(D_{H^+} - D_{Cl^-})_{H_2O} \times 10^5$
0	9.31	2.03	7.28
0.5	7.10	1.84	5.26
1.0	5.98	1.77	4.21
2.0	4.92	1.60	3.32
3.0	4.11	1.45	2.66
4.0	3.38	1.26	2.12

Conc. (aquamolal)	$D_{D^+} \times 10^5$	$(D_{Cl^-})_{D_2O} \times 10^5$	$(D_{D^+} - D_{Cl^-})_{D_2O} \times 10^5$
0	6.50	1.64	4.86
0.5	3.81	1.48	2.33
1.0	2.92	1.43	1.49
2.0	2.10	1.29	0.81
3.0	1.66	1.17	0.49
4.0	1.34	1.02	0.32

Conc. (aquamolal)	$(D_{H^+} - D_{Cl^-})_{H_2O} / (D_{D^+} - D_{Cl^-})_{D_2O}$
0	1.50
0.5	2.26
1.0	2.83
2.0	4.10
3.0	5.43
4.0	6.63

Table 4.10.1 cont.

KCl

Conc. (aquamolal)	$D_{H^+} \times 10^5$	$D_{Cl^-} \times 10^5$	$(D_{H^+} - D_{Cl^-})_{H_2O} \times 10^5$
0	9.31	2.03	7.28
0.5	7.34	1.96	5.38
1.0	6.68	1.95	4.73
2.0	5.94	1.90	4.04
3.0	5.45	1.85	3.60
4.5	5.10	1.77	3.33

Conc. (aquamolal)	η_{H_2O}	η_{H_2O} corrected to aquamolality	η_{H_2O}/η_{D_2O}
0	0.8903	1.103	0.8072
0.5	0.8882	1.083	0.8201
1.0	1.8878	1.076	0.8251
2.0	0.8960	1.086	0.8250
3.0	0.9200	1.096	0.8394
4.0	0.9575	1.102	0.86

Conc. (aquamolal)	$D_{D^+} \times 10^5$	$(D_{Cl^-})_{D_2O} \times 10^5$	$(D_{D^+} - D_{Cl^-})_{D_2O} \times 10^5$
0	6.50	1.64	4.86
0.5	4.06	1.60	2.46
1.0	3.18	1.61	1.57
2.0	2.39	1.57	0.93
3.0	2.17	1.55	0.62
4.0	2.00	1.54	0.46

Conc. (aquamolal)	$(D_{H^+} - D_{Cl^-})_{H_2O} / (D_{D^+} - D_{Cl^-})_{D_2O}$
0	1.50
0.5	2.19
1.0	3.01
2.0	4.34
3.0	5.81
4.0	7.24

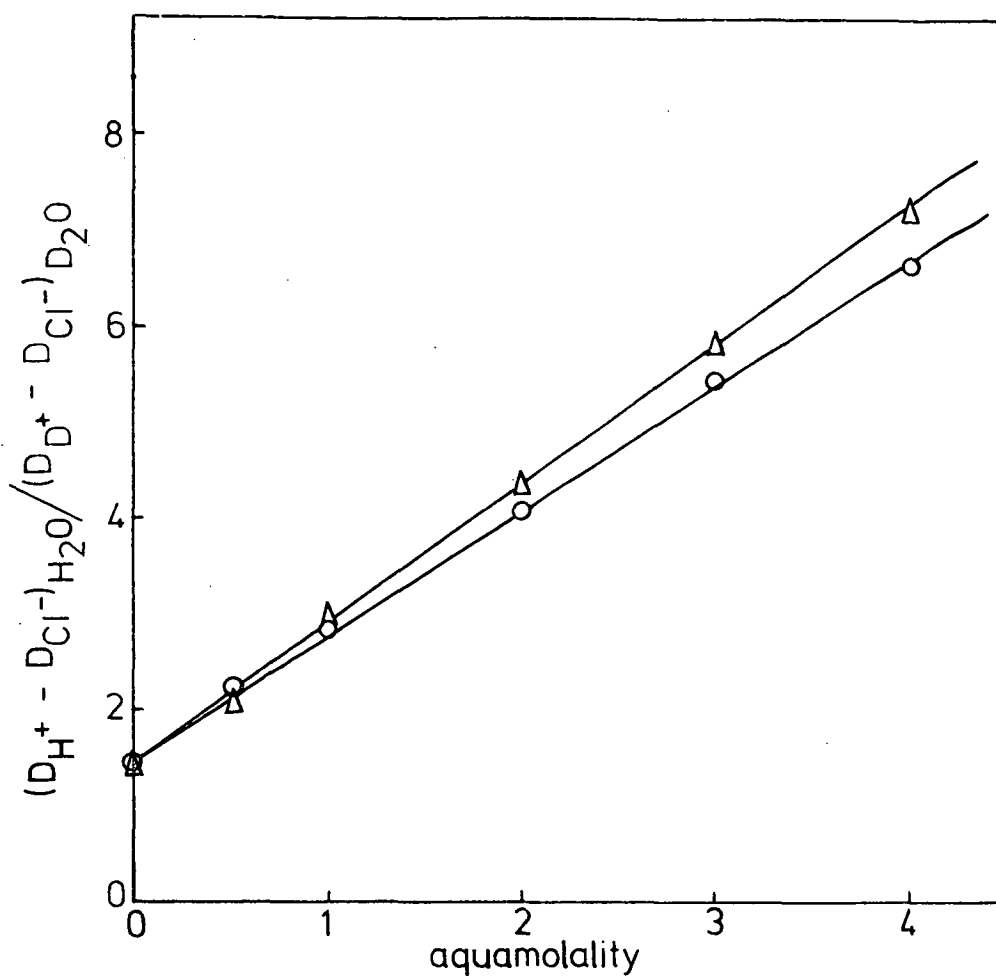


Figure 4.10.1 The effect of electrolyte concentration on the ratio of the Grotthuss components of the diffusion coefficients in normal and heavy water solutions.

○ NaCl Δ KCl

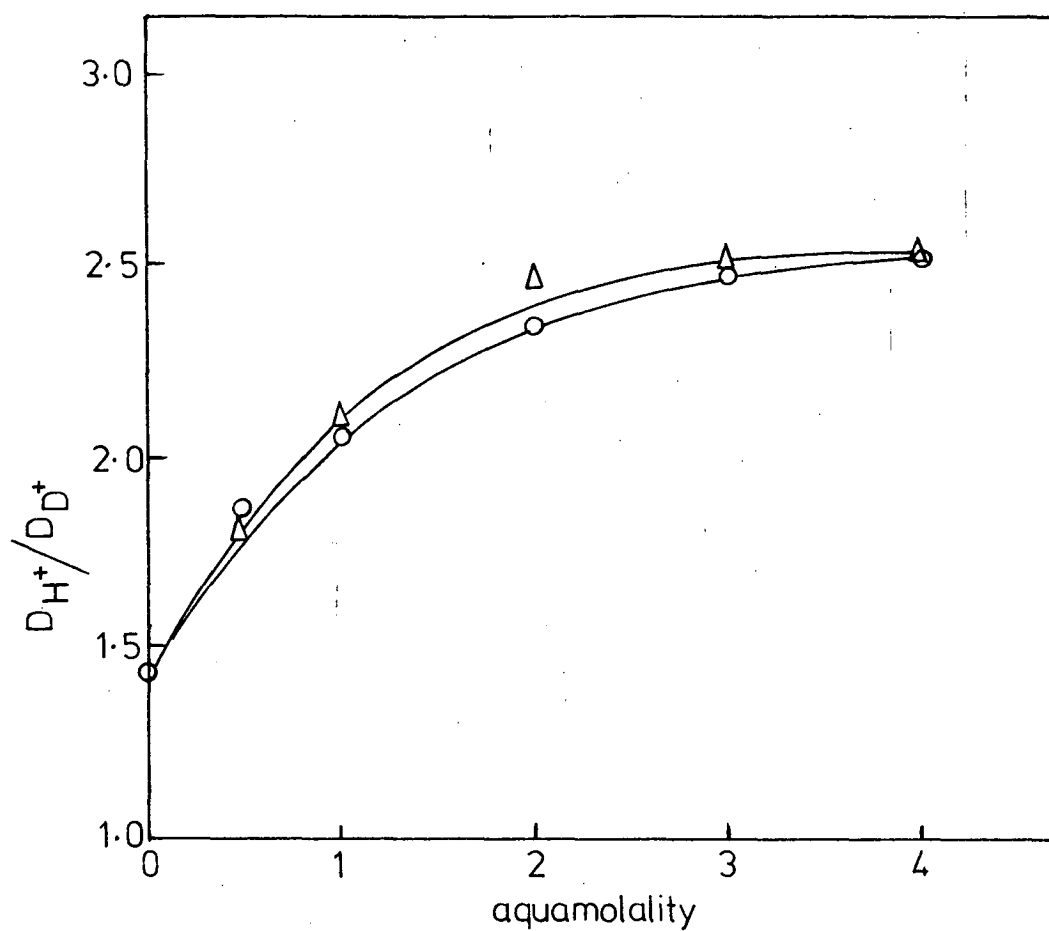


Figure 4.10.2 The effect of electrolyte concentration on the ratio of the diffusion coefficients in normal and heavy water solutions

○ NaCl Δ KCl

and heavy water by both electrolytes.

When the Grotthuss contributions alone are plotted against concentration, Figure 4.10.3, it is seen that the curves for deuterium diffusion are extremely close. This may indicate, once again, the importance of the anion in the reduction of deuteron mobility, though, with only two curves available, it is difficult to draw a definite conclusion. These curves also indicate that the Grotthuss contribution to the diffusion coefficient is very much greater for the proton than the deuteron and also that the Grotthuss contribution does not cut out at concentrations of supporting electrolyte above 2 molar, but is simply reduced less rapidly than at the low concentrations, where the Grotthuss component is 3-4 times that of normal ionic diffusion and at 3-4m still approximately twice the normal ionic component in H_2O . In contrast with the conclusions drawn by Lown and Thirsk⁵⁷ in their work on aqueous solutions of KOH, NaOH and LiOH, the Grotthuss contribution in 4m NaCl and KCl is significant. In D_2O solutions the Grotthuss component falls below the normal component near 1 m.

4.11. Mechanism for Transfer of H^+ and D^+ in the Presence of Electrolytes

The results above call into question the accepted mechanism for the transport of H^+ and D^+ in H_2O and D_2O respectively. Currently proton mobility is considered to proceed via three steps⁵⁵:

1. Rotation of H_2O (or H_3O^+)
2. Proton flip or tunnelling
3. Randomisation of H_2O .

At one atmosphere pressure the slow step is considered to be the rotation of the water molecule or H_3O^+ . Prima facie one would expect,

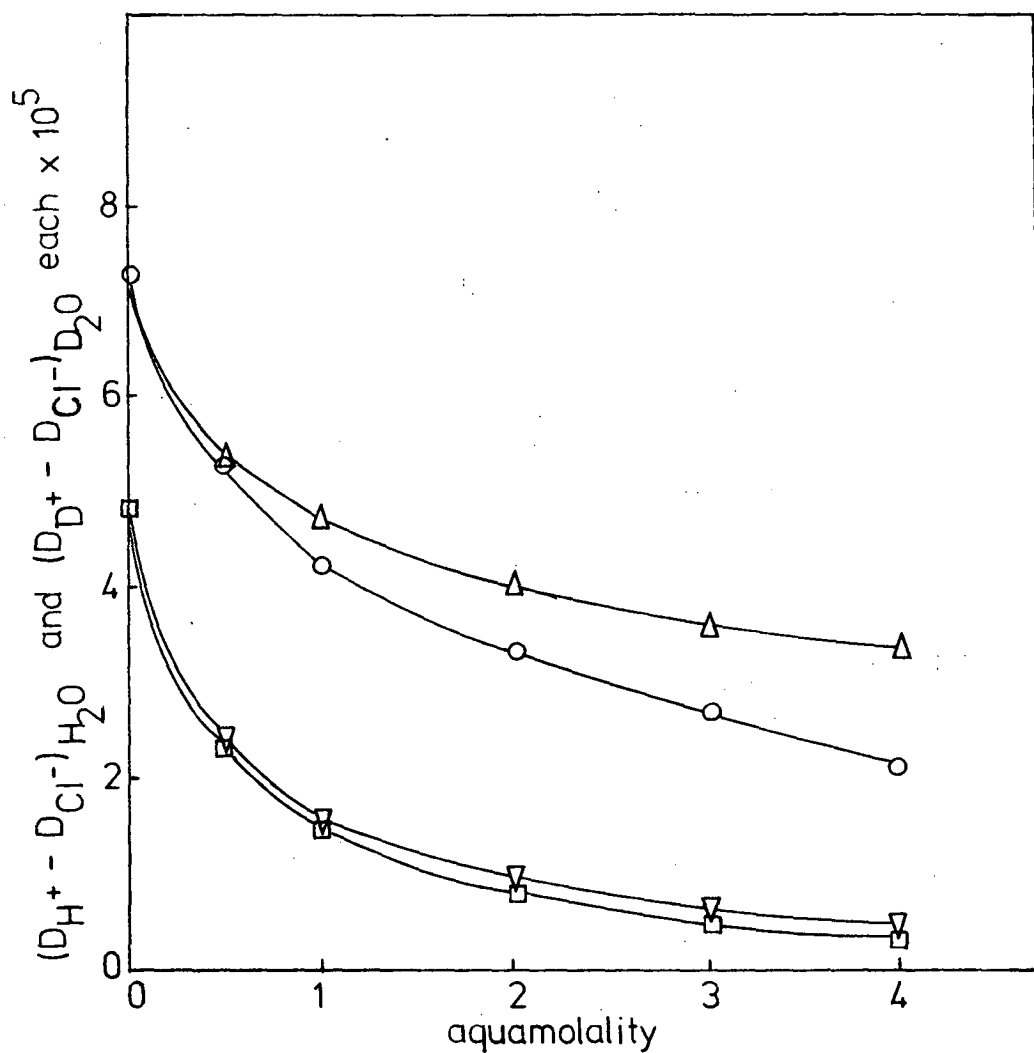


Figure 4.10.3 The effect of electrolyte concentration on the Grotthuss component of the diffusion coefficient in normal and heavy water.

○ NaCl Δ KCl/ H_2O

□ NaCl ▽ KCl/ D_2O

therefore, that electrolytes which cause water to become more fluid (i.e. reduce viscosity) and to increase the self-diffusion of water e.g. KCl, KBr and KI, would make the rotational step easier and promote proton mobility.

McCall and Douglass¹³⁴, Devell¹⁰⁰ and Brun et al¹³⁵ have measured the self-diffusion coefficients for water in a number of electrolyte solutions, and these have been compared with the fluidity of the solutions as electrolyte concentration increased. The two quantities correlate well. As can be seen in Figures 4.9.2 - 4.9.6, the self-diffusion ratios for NaCl decrease steadily, those for KCl are constant up to 2M, those for KBr and KI go through a maximum at about 2M and those for Me₄NBr decrease steadily after passing through a maximum at about 0.5M.

Proton mobility is reduced in all these electrolytes, though K⁺ halides reduce it less than Na⁺ or Li⁺ halides. Thus even in the case of the cations the rate of change of proton mobility does not agree with that of self-diffusion, e.g. the self-diffusion of water is almost constant in that region (0-1 molal) where proton mobility is changing most rapidly. The anions present a problem, already noted in Section 4.2, because they not only fail to enhance proton mobility, they decrease it in the wrong order i.e. I⁻ which produces the most fluid water and increases the self-diffusion of water decreases proton mobility to a greater extent than Br⁻ and Cl⁻. Thus the order for the decrease in proton and deuteron mobility is I⁻ > Br⁻ > Cl⁻ whereas the order of increasing viscosity is Cl⁻ > Br⁻ > I⁻. It is generally agreed that anions move by a different mechanism from cations¹¹⁰ and the explanation may lie here.

It has, however, been shown by O¹⁷ n.m.r. measurements¹³⁸ that proton exchange of the water molecule is slower in solutions than in pure

water, and that the degree of slowing down of this proton exchange increases as the strength of structure breaking becomes greater. As I^- is a stronger structure breaker than Br^- and Cl^- , then the excess Grotthuss mobility would be reduced more by I^- than Br^- or Cl^- , and so the resultant proton diffusion rate would be less. Hertz and Klute¹³⁸ also point out that at least for KI and NaI, cation influence is very small.

The tetraalkylammonium bromides decrease proton and deuteron mobility in the order one might expect i.e. in the direction of increasing viscosity, so that proton and deuteron mobility are greatest in solutions of Me_4NBr and least in Bu_4NBr . That both R_4N^+ ions show the same behaviour, which differs from that of the alkali halides, is, no doubt, due to the different kind of hydration these ions bring about. Horne and Young¹³⁹ have shown that the viscosity B-coefficients of R_4N^+ ions lie on quite a different curve from those of the alkali metal ions, with the NH_4^+ ion situated on a point common to the two curves. The influence of four alkyl groups for each bromide ion must also be appreciated as well as the possibility of cation-cation contact¹⁴⁰ with the tetraalkylammonium ions. So R_4N^+ ions, as well as changing the number of hydrogen bonds, also, by their size, may alter the geometrical arrangement of solvent water molecules.

It can be argued that the viscosity of a solution reflects both the translational and rotational movement of the water molecules and in the present discussion it is the rotational movement of the water molecule which is of importance. Fortunately it is not necessary to attempt to separate the two components in the work of McCall and Douglass¹³⁴ and Devell¹⁰⁰, as Hertz and Zeidler¹⁴⁶ from an n.m.r. study of the longitudinal relaxation time of the proton and deuteron have estimated the orientation time of H_2O and D_2O in the pure liquids and

also in many diamagnetic salt solutions. A selection of their results is given in Table 4.11.1.

The lower rotational times of H_2O and D_2O in KBr and KI solutions compared with pure water support the previous argument based on the viscosities of the electrolyte solutions and the self-diffusion of water in these solutions.

Strictly speaking the rate determining step in proton and deuteron mobility is not the rotation of H_2O or D_2O but the field-induced orientation of H_2O or D_2O ⁵⁶ and this may not coincide with the thermally induced orientation of water in the presence of electrolytes. In the presence of electrolytes, too, the coulombic fields of these ions may restrict field-induced orientation of some water molecules by the proton or deuteron with a consequent lowering of the hydrogen ion mobility. The present work suggests that a measure of the thermally induced orientation of water, i.e. viscosity, self-diffusion of water or rotational orientation times may give little or no indication of the field-induced rotation of H_2O or D_2O in the presence of electrolytes.

4.12. Energy of Activation

Treating hydrogen ion diffusion as a rate process, its energy of activation can be calculated from the Arrhenius equation,

$$D = A \exp (-E/RT)$$

where D = diffusion coefficient, A = a constant, E = energy of activation, R = the gas constant and T = absolute temperature by plotting $\ln D$ vs. $1/T$ and measuring gradients. Values of E so obtained for proton and deuteron diffusion in selected electrolyte solutions are listed in Tables 4.12.1 and 4.12.2. It is useful to compare this with values found in the literature, Table 4.12.3. With the exception of the value

Table 4.11.1.

Thermally Induced Orientation Times of the H_2O and D_2O
Molecule in the Primary Hydration Layer of Various
Diamagnetic Ions

Ion	τ_{\pm}/τ	
	(1)	(2)
Na^+	2.1	1.4
K^+	1.0	1.0
$(\text{CH}_3)_4\text{N}^+$	1.6	1.6
$(\text{C}_2\text{H}_5)_4\text{N}^+$	-	2.1
$(\text{C}_3\text{H}_7)_4\text{N}^+$	-	3.1
$(\text{C}_4\text{H}_9)_4\text{N}^+$	-	2.9
Cl^-	1.0	1.0
Br^-	0.6	0.8
I^-	0.35	0.6

where τ_{\pm} = orientation time of a H_2O or D_2O molecule
in the primary hydration sphere

τ = orientation time of a H_2O or D_2O molecule
in pure H_2O and D_2O respectively ($\sim 10^{-11}$ sec)

(1) = results for water solutions

(2) = results for heavy water solutions

Note that:

(a) $\tau_{\pm}(\text{K}^+)/\tau$ is placed = $\tau_{\pm}(\text{Cl}^-)/\tau$ because the
longitudinal relaxation time of KCl solutions up
to ~ 4 molal equals that for pure water.

(b) The ratio τ_{\pm}/τ depends on the value assumed for the
hydration number of the ion.

Table 4.12.1.

Energy of Activation for proton diffusion in
electrolyte solutions

Electrolyte	Molality	E_a
NaCl	2	3.0
	3	2.8
	4	3.2
	5	2.7
NaBr	2	3.2
	3	3.0
	4	3.1
	5	3.1
NaI	2	3.1
	3	3.3
	4	4.2
	4.5	4.4
KCl	2	2.1
	3	2.7
	4	3.0
KBr	2	3.7
	3	4.8
	4	5.2
	5	4.4
KI	2	3.7
	3	3.8
	4.5	3.8

Table 4.12.1 cont.

Electrolyte	Molality	E _a
Me ₄ NBr	2.2	2.1
	2.5	2.4
	3	2.5
	3.5	2.4
	4	2.4
Bu ₄ NBr	0.5	4.8
	1	5.2
	2	5.4
	3	5.5

Table 4.12.2.

Energy of Activation for deuteron diffusion in
electrolyte solutions

Electrolyte	Molality	E _a
KCl	0.5	6.6
	1	7.1
	2	6.7
	3	7.1
	4	7.0
KBr	0.5	4.0
	1	4.8
	2	7.5
	3	11.9
	4	18.7

Table 4.12.3.

Energy of activation for hydrogen ion transport

Author	Energy of Activation	Temperature range
Eigen and de Maeyer ^{54,a}	2.1	25-50°C
	2.4	0-25°C
Kolny and Zembura ^{84,b}	2.66	5-75°C
Luz and Meiboom ^{142,c}	2.4	15-75°C
Loewenstein and Szöke ^{148,d}	2.6 ± 0.3	20-80°C

- a. Calculated from conductivity measurements of Johnston¹⁴⁴.
- b. Polarography with rotating copper disc electrode; hydrogen ion in 0.2m NaCl.
- c. Proton transfer reactions measured by n.m.r., and extrapolated to zero buffer concentration.
- d. Proton transfer reactions measured by n.m.r., regulating buffer concentration until further dilution had no effect.

obtained by Kolny and Zembura⁸⁴, all these literature values refer to the hydrogen ion at infinite dilution in water, while the present experimental values refer to the hydrogen ion at a concentration of $1-2 \times 10^{-3} \text{ M}$ in varying concentrations of electrolyte solutions. It is seen that values obtained in the present study generally exceed the literature values.

Although there is some irregularity in the present values due to the possible 2% error in each diffusion coefficient value and also the difficulty of choosing the best straight line through only four points, it is seen that:

- (a) for alkali halides (except KBr) and for the Me_4NBr , proton transfer takes place by a mechanism requiring less energy than normal ionic diffusion (cf. Table 4.12.4),
- (b) for the sodium salts the anion effect is greatest for the iodide and least for the chloride,
- (c) potassium bromide results seem anomalous,
- (d) the larger tetraalkylammonium ion has the greater effect,
- (e) values for the hydrogen ion in potassium chloride and tetramethylammonium bromide are similar, and
- (f) the energies of activation for deuterium diffusion exceed those for proton diffusion.

These observations support conclusions drawn from diffusion current measurements at 25°C concerning the hampering of the abnormal Grotthuss mobility by the presence of electrolytes in solution, even though many of these electrolytes increase the fluidity of water. The higher values of the energy of activation for proton diffusion in tetrabutylammonium bromide solutions may be due to the hydrophobic hydration of the cations. It has already been noted, in Section 4.4, that half-wave potential

values for proton mobility in solutions of this electrolyte suggest maximum hydration of the proton. The increased energy of activation may be due to this. The comparable values for potassium chloride and tetramethylammonium bromide suggest that the net result of their modification of water structure is similar even though there may be a difference in the mechanism.

The greater degree of hydrogen bonding or the stronger bonds formed in heavy water than in normal water gives rise to the increased energy of activation for the deuteron in the solutions studied. The very high values of energy of activation for diffusion in potassium bromide solutions are noted but not explained.

Good¹¹ has studied the energy of activation for fluid flow in alkali halide solutions at 20°C and found that this energy of activation is reduced as the concentration of potassium halides increased. Values in sodium halide solutions go through a minimum in the 2-3 M range and then slowly increase, but up to 4 M the energy of activation is still less than at infinite dilution. MacDonald¹⁴⁷ has likewise calculated the activation energy for fluid flow in heavy water solutions of various electrolytes at 30°C. For KCl, KBr and KI this energy of activation decreases as the concentration of electrolyte increases. Below 2 M the KBr curve lies above that for KCl, but after this $KCl > KBr > KI$. These two studies show that fluid flow is easier in these electrolyte solutions than in pure normal or heavy water.

The energy of activation for hydrogen ion diffusion becomes larger as electrolyte concentration is increased, despite the fact that fluid flow becomes easier. The energy of activation cannot directly give information about the mechanism of hydrogen ion diffusion since it is a measure only of the energy barrier to be overcome before diffusion by whatever mechanism can proceed. Nevertheless the above information leads

to the conclusion that hydrogen ion diffusion is limited, not enhanced, by the presence of electrolytes in solution.

So, while the lack of precision in the present energy of activation measurements renders them not, by themselves, conclusive, their direction supports conclusions drawn from diffusion current measurements regarding the general trends brought about by the various electrolytes, and also that thermal orientation does not alone account for the whole of the abnormal Grotthuss mobility of hydrogen ions.

When the values for the energy of activation for other ions, at infinite dilution, are compared with those given above for hydrogen, see Table 4.12.4, it is seen that those for hydrogen are lower than the others.

That the energies of activation of hydrogen ion diffusion as electrolyte concentration increases do approach, and even exceed, in some cases, those for normal ionic diffusion is, however, further evidence to support the view that as the concentration of supporting electrolyte increases, the abnormal Grotthuss mobility is reduced until proton diffusion proceeds in the same manner as that of other ions.

4.13. Conclusion

Although this work has not drawn on the various theories of water structure, except to suggest that there are monomers present in electrolyte solutions to facilitate orientation of water molecules or hydrogen ions, it has highlighted some of the factors which must be considered in postulating a theory of water structure, and which have not been predicted by present theories.

Chief among these is the failure of certain electrolytes which lower the viscosity of water, increase the self-diffusion of water and lower the orientation time of water molecules, to enhance proton mobility in

Table 4.12.4.

Activation Energies for Diffusion for Infinitely
Dilute Aqueous Solution¹⁴⁵

Ion	E
K^{+}	3.99
Na^{+}	4.39
Cl^{-}	4.17
Br^{-}	4.07
I^{-}	4.05

normal and heavy water solutions. This expectation is, of course, based on the assumption that Bockris et al's theory of proton transfer is correct.

An acceptable theory of water structure would also have to explain why the Grotthuss contribution in heavy water solutions at moderate concentrations of electrolyte is so much lower than in normal water solutions. Attention has been drawn to the fact that the greater reduction of deuteron mobility in the more structured D_2O agrees with the lowering of proton mobility in solutions of electrolytes held to be structure-makers.

Chapter 5

Water in Glass Pores

5.1. Introduction

It has been shown in Section 4.6 that values of the diffusion coefficient of the hydrogen ion are different when obtained by polarography, rotating disc electrodes and porous diaphragm cells. It was suggested that this could be due to the formation of partially immobilised layers of water within the pores of diaphragms, since these would reduce diffusion to the normal mechanism whereby other ions diffuse. Drost-Hansen¹²², also, has drawn attention to variations in measurements of the self-diffusion coefficients of water and has suggested that "classical" diffusion experiments using single capillaries or porous fritted discs may be affected by the presence of changed surface layers.

It was thought that n.m.r. spectra could show whether water molecules were bound within the pores of a sintered glass disc.

5.2. Experimental

Sintered glass discs of pore size 5-15 μm were cut into slithers which could be fitted tightly into polythene tubing. De-ionised water was drawn through the sintered glass for about 30 hours, then the slithers were removed from the tubing, blotted and securely fastened, by means of teflon plugs, in n.m.r. tubes. Their spectrum was recorded with a JEOL, Model JNM-4H-100 analytical spectrometer using tetramethylsilane (TMS) as an external reference, and compared with the spectrum of free water, recorded under identical conditions.

Further spectra were recorded after the sintered glass had simply been soaked in water for long periods, for sintered glass of different pore sizes soaked in water, for some (of pore size 5-15 μm) which had

been soaked in $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures of various proportions and also for dry sintered glass slithers.

5.3. Results and Discussion

There were two features of the spectra that required further investigation, viz. the differing widths of the bands and the presence of side bands.

When this was done it was found:

- 1) that side bands were due to modulation of the field by the glass in the spinning tube. This is shown in Figure 5.3.1 in which the splitting of the TMS signal is the same as that for the water signal. The TMS was contained in a fine capillary tube inserted next to the sintered glass in the n.m.r. tube. As the tube rotated, therefore, the external magnetic field was modulated, giving rise to a split signal.
- 2) that the separation of the peaks was related to the spinning rate in such a way that signals were closer together when the spinning rate was lowered, and
- 3) that side bands were obtained with sintered glass slithers soaked in both chloroform and dioxane.

Thus the presence of side bands was not indicative of modification of the water.

It was, however, noted that only with pore size 5-15 μm did the background indicate a broad band upon which sharper bands were superimposed. This agrees with the findings of Mills¹⁴⁸ who has used glass diaphragms in diffusion cells to measure the self-diffusion of tritiated water and has obtained anomalous results, even reduction by a factor of 2, with certain diaphragms where the pore diameter is 5 μm .

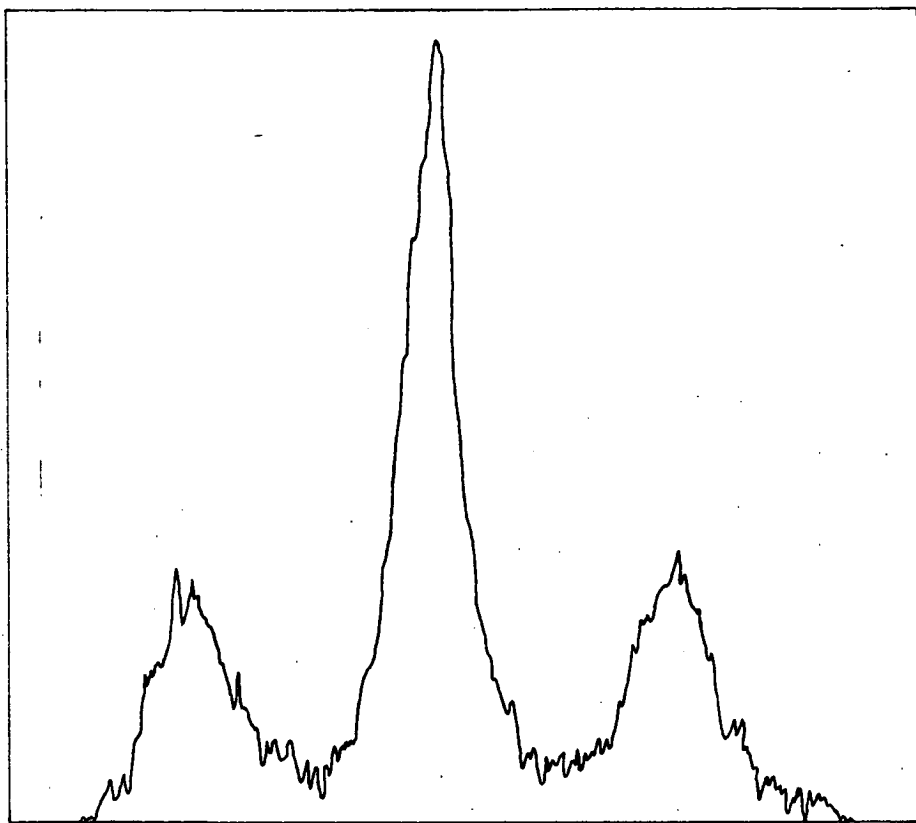
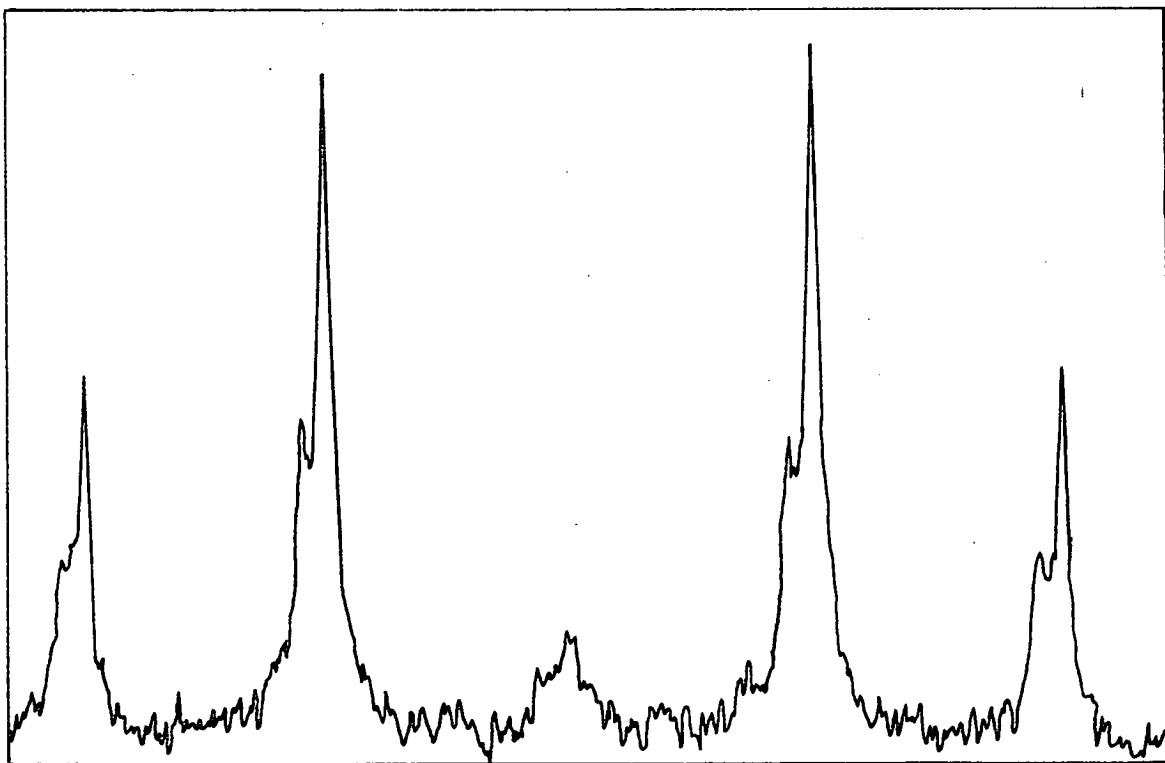


Figure 5.3.1 n.m.r. spectra showing the splitting of the water signal (above) and tetramethylsilane signal (below) at the same spinning rate.



The markedly different widths of the n.m.r. spectra of water in sintered glass and free water shown in Figure 5.3.2. have been interpreted¹⁴⁹ as signifying changed environments for some of the water molecules. This interpretation finds support in the conclusions of Hechter et al¹⁵⁰ who conducted a series of experiments on water in an agar gel system and concluded that the broadening of the water signal in the n.m.r. spectrum they obtained for this system could best be interpreted as indicating a modification of water structure. The more recent work of Schufle and Yu¹²³ on conduction of dilute HCl solutions in glass capillaries from 5 μm to 2,000 μm diameter also suggests water structure becomes modified in capillaries whose diameter is less than 100 μm . Everett, Haynes and McElroy¹⁵¹, however, have investigated the behaviour on freezing and subsequent melting of anomalous water in capillary tubes as large as 25 μm in diameter. They noted the formation of a gel in the capillary and attributed this to a surface chemical reaction between water and silica, possibly combined with an enhanced reactivity of water in a multimolecular film.

So with the 5-15 μm pore diameter used in this study the band broadening can be taken to have resulted from modification of the water structure as water moved through the sintered glass slithers.

Belfort¹⁵² has challenged the validity of this interpretation but his argument deals with instantaneous adsorption of water on glass surfaces rather than the effect that prolonged movement of water in the glass pores may produce. He suggests that the broadening is more likely to be due to field inhomogeneities produced by the glass matrix. Mysels and McBain¹²¹ have reported the development of hydrodynamic resistance in sintered glass discs in contact with water over an extended period, and Wentworth¹⁵³, too, has drawn attention to water's becoming rigid after prolonged movement through an orifice.

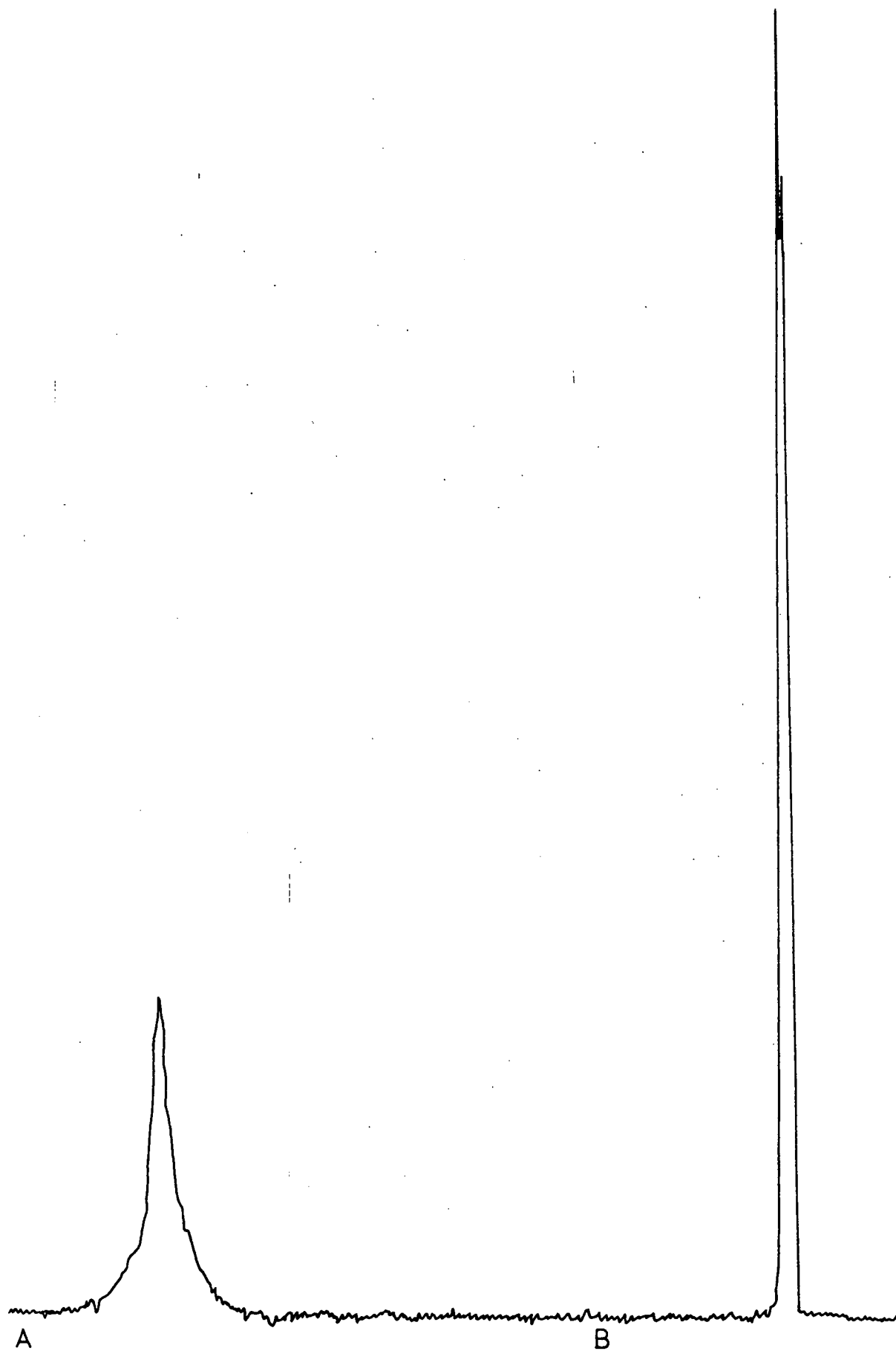


Figure 5.3.2. The n.m.r spectra of water in sintered glass (A) and free water (B) recorded under the same conditions.

Furthermore, the n.m.r. signal of occluded water was broader after prolonged movement of water through the glass disc than it was after brief contact, the extra broadening being 8 Hz at half height, Figure 5.3.4. It is, therefore, the prolonged movement and not the instantaneous contact of water with glass that is significant, and Mysels and McBain's¹²¹ observation that the conductivity of ions other than H^+ (and probably OH^-) were not affected while hydrodynamic resistance developed points to the exceptional behaviour of the hydrogen ion in prolonged diffusion through glass capillaries. Drost-Hansen¹²², too, has compiled evidence for the modification of water structure at or near interfaces.

That the broad signal was not due to the glass was confirmed by studying the spectra of dry sintered glass and also slithers soaked for some hours in various H_2O/D_2O mixtures. The dry glass gave no signal, while the spectra obtained from the H_2O/D_2O mixtures showed a reduced signal as the proportion of D_2O increased, until no signal was obtained for glass soaked in pure D_2O , as shown in Figure 5.3.3.

Thus the glass contributed nothing to the signals obtained. They were due solely to H_2O .

5.4. Conclusion

These experimental results lead to the conclusion that water becomes partially immobilised when it moves in very fine capillaries (ca 5 μm diameter) for a prolonged period. This is offered as an explanation for the difference in diffusion current values for the proton obtained by polarography and the porous diaphragm cell method. As has been shown in Section 3.4, values of the diffusion coefficient obtained using a rotating disc electrode support the polarographic method.

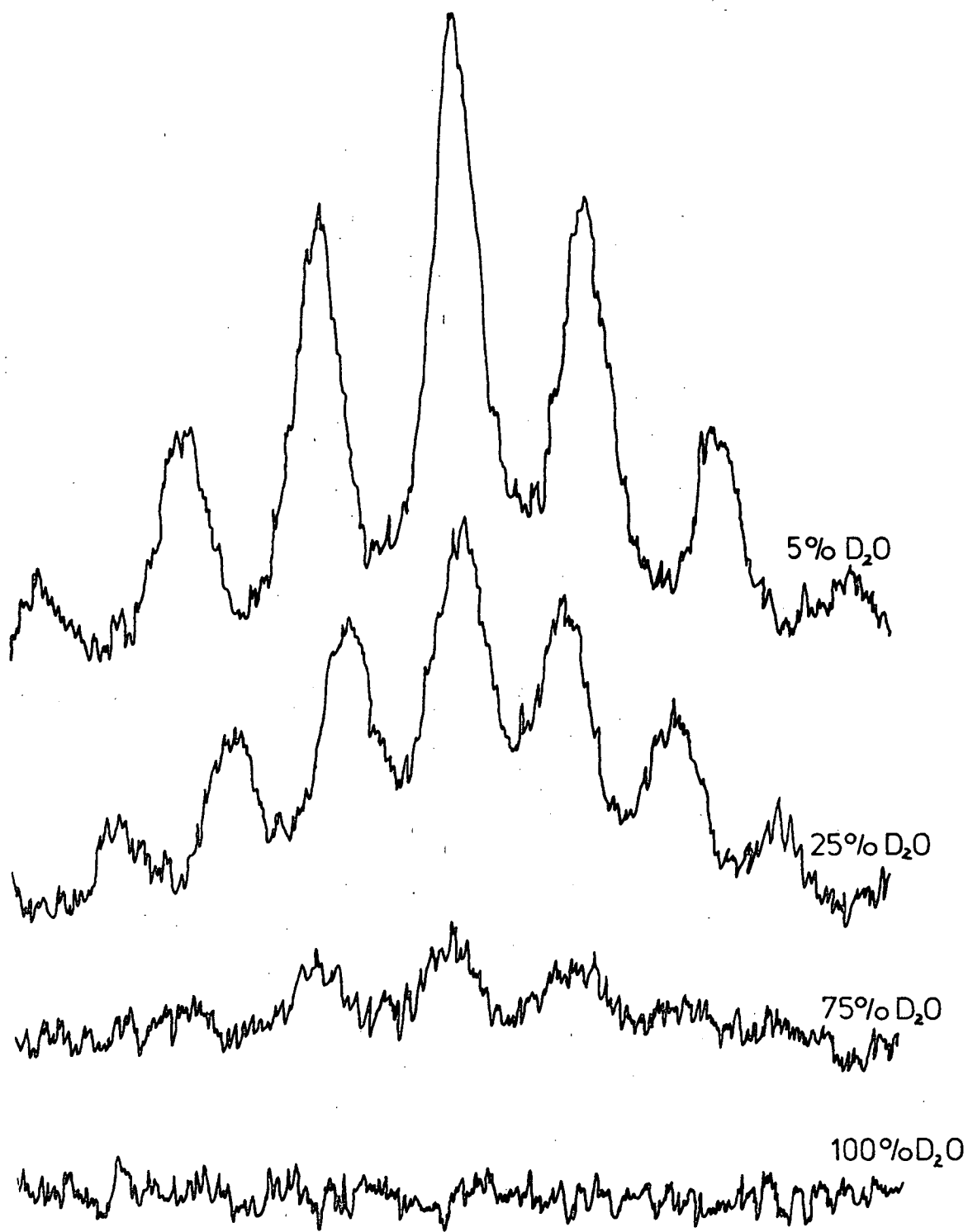


Figure 5.3.3. The n.m.r. spectra of normal and heavy water in sintered glass.

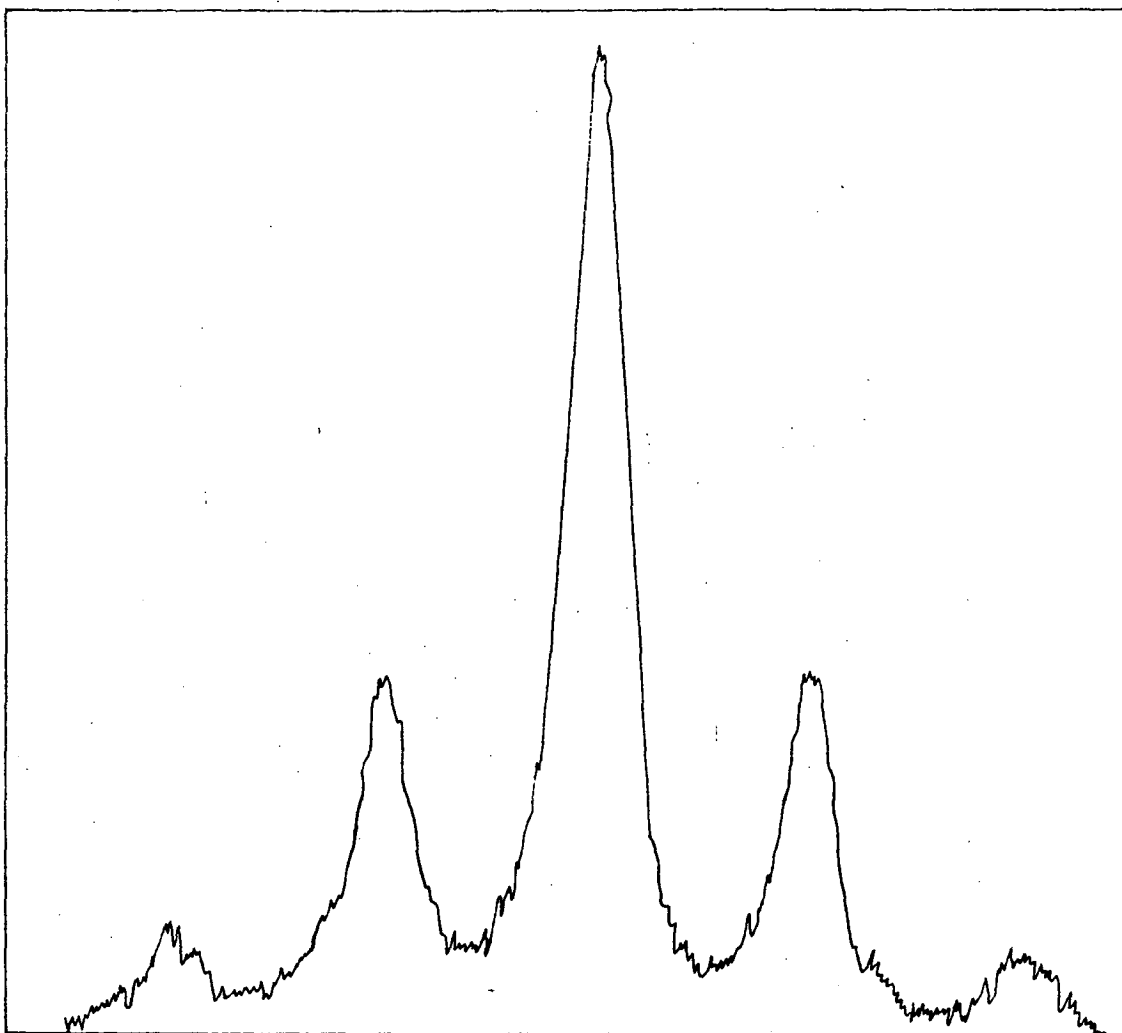
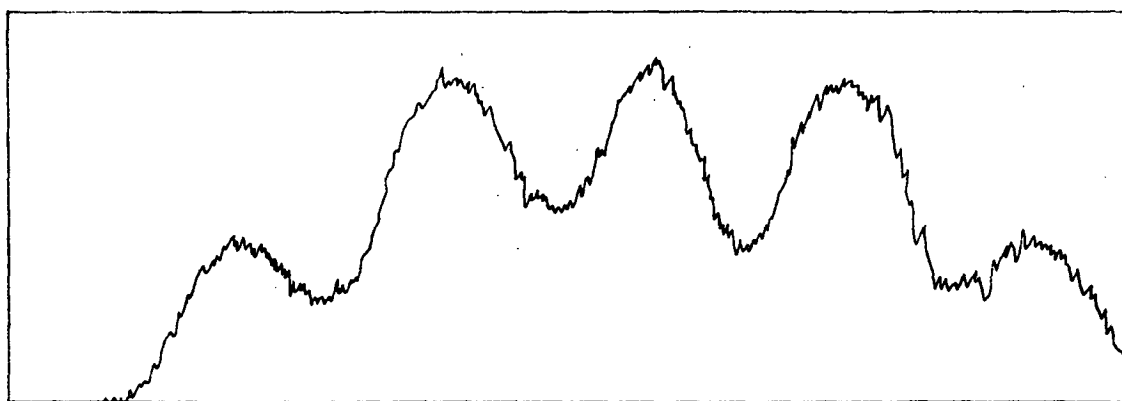


Figure 5.3.4 n.m.r. of water after brief contact with sintered glass of pore size 5-15 μ m (above) and after prolonged movement through the pores (below)



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It has been shown (J. Chem. Phys. 24, 1282, 1956) that the Nernst-Einstein equation relating the conductance of an ion to its diffusion coefficient i.e.

$$D_i = \frac{RT}{F^2} \cdot \frac{\lambda_i}{z}$$

(where D_i is the diffusion coefficient and λ_i the equivalent ionic conductance of a z -valent ion i)

is only applicable if the modes of transport under thermal and electric fields are the same. Consequently any method relying on this relationship, e.g. conductance measurements, to calculate D_i is unreliable perhaps to the extent of 10% or more. In this thesis the polarographic method was used to estimate the diffusion coefficient D_i of the hydrogen and deuterium ions. It should be noted that polarography is not open to this objection because it measures a current not a conductance and consequently the diffusion current is a true measure of the total flux of the electro-active ion to the electrode, including those which do and do not contribute to conductance. Hence the corrected Ilkovic equation gives a correct measure of the diffusion coefficient of the electro-active ion.

Only at infinite dilution has the Nernst-Einstein equation been used to compare polarographic diffusion coefficients with those calculated from conductance data. And at infinite dilution it has been shown by B.E. Conway, J. O'M. Bockris and H. Linton, J. Chem. Phys. 24, 834 (1956) that the error in the Nernst-Einstein equation is negligible.

Consequently it is clear that the diffusion coefficients of the hydrogen and deuterium ions calculated in this thesis are not in error.

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Proton and Deuteron Mobility in Normal and Heavy Water Solutions of Electrolytes

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Proton and deuteron mobility in normal and heavy water solutions of some alkali halides (NaCl, KCl, KBr and KI) and tetra-alkylammonium bromides (where alkyl is Me, Et, Pr or Bu) is measured polarographically and the diffusion coefficients calculated from a corrected Ilkovic equation. The results are analysed in terms of the effect of electrolyte concentration on the excess or Grotthuss mobility of the hydrogen and deuterium ion. The results raise some questions about the accepted mechanism for the transport of the proton and deuteron in solution.

Earlier studies¹⁻⁵ on proton mobility in aqueous electrolyte solutions using polarography gave useful information about the degree of hydration of the proton and the structure of water in the presence of electrolytes. In this paper we give a more detailed analysis as a result of further work on deuteron mobility in heavy water solutions of electrolytes.

EXPERIMENTAL

Apparatus, purification techniques and special procedures are described elsewhere.¹⁻⁵ As was noted previously⁴ it is important to purify all salts thoroughly before use. For example, different samples of A.R. KCl gave different results before purification and the most marked difference was observed in the case of the tetra-alkylammonium salts. After purification the order of the diffusion currents for the hydrogen ion in the presence of the tetra-alkylammonium salts was altered from that reported previously,³ fig. 1(e) and (f). However, the half-wave potentials remained unchanged. Tetramethylammonium bromide (Kodak) was recrystallised three times from distilled de-ionised water and dried under reduced pressure at 110°C for 1 week. Tetraethylammonium bromide (Kodak) and tetrapropylammonium bromide (Kodak) were recrystallised three times from super-dry ethanol and methanol respectively, and dried under reduced pressure at 110°C. Tetra-butylammonium bromide (Kodak) was recrystallised five times from dry acetone, and dried under reduced pressure at 80°C. The purity of the recrystallised tetra-alkylammonium salts was determined by titration against silver nitrate using the Mohr method as percentage bromide and gave the following results, Me₄NBr 100.00 %, Et₄NBr 100.00 %, Pr₄NBr 99.88 %, Bu₄NBr 99.69 %. The alkali halides (A.R.) were recrystallised twice from distilled de-ionised water and dried under reduced pressure at 110°C for at least a week. In two previous publications⁴⁻⁵ and in this work all salts were exhaustively purified as described above and the diffusion coefficients for the proton and deuteron so obtained were reproducible within 1 %.

The D₂O, 99.75 % by weight, was obtained from the Australian Institute of Nuclear Science and Engineering and was made 1.17×10^{-3} mol dm³ in DCl by adding a small quantity of a solution of DCl in D₂O (Stohler Isotope Chemicals). The concentration of DCl was determined by potentiometric titration with sodium tetraborate. The solution of DCl in D₂O was de-aerated with high purity nitrogen and stored in a glass dispensing vessel under nitrogen. To make up the solutions a quantity of DCl+D₂O was dispensed with high purity nitrogen into a weighed glass container to which a known weight of salt had been added in a nitrogen-filled glove bag. The weight of DCl+D₂O was obtained by difference.

A light oil was used in the constant temperature bath and while the polarogram was recorded nitrogen was run over the surface of the solution. All solutions were de-aerated before recording the polarogram of the deuterium ion.

RESULTS AND DISCUSSION

The corrected form of the Ilkovic equation ⁴

$$i_d = 607nD^{1/2}m^{3/2}ct^{1/2}(1 + AD^{1/2}m^{-1/2}t^{1/2})$$

was used to calculate the diffusion coefficient of the deuterium ion and the limiting value for D^+ , D_D^+ , calculated as described for the hydrogen ion ⁴ except that all extrapolations were performed on an aquamolality basis (i.e. moles of electrolyte per 55.51 moles of D_2O). The corrected form of the Ilkovic equation for the hydrogen ion agrees with that obtained previously by Hans and Jensch. We obtained a value of 17 ± 1 for the constant A and Hans and Jensch obtained $A = 18.4 \pm 1.7$.^{6,7} Strictly the value of D_D^+ so obtained refers to the diffusion coefficient of D^+ in the concentration of DCl originally added to the D_2O (i.e. 1.17×10^{-3} mol dm^{-3} DCl). However Kolny and Zembura ⁸ found that the concentration of H^+ has no effect on the value of the diffusion coefficient in 0.1 mol dm^{-3} NaCl between pH 2.3 and 3.3. Also, in the diaphragm cell method the effect of the concentration of the tracer ion appears to have a negligible effect on the value of the diffusion coefficient. Stokes, Woolf and Mills ⁹ reported that for the I^- ion the diffusion coefficient at vanishing concentration of I^- in alkali chloride solutions differed by less than 1 % from that in more concentrated solutions (~ 0.1 mol dm^{-3}). Woolf ¹⁰ observed a similar dependence for H^+ in LiCl, NaCl and KCl, although there is some doubt about the applicability of the diaphragm cell method to the hydrogen ion.⁵ Consequently it appears legitimate to equate the experimentally obtained diffusion coefficients with the true diffusion coefficients of H^+ and D^+ .

TABLE 1

ion	$D^+ \times 10^5 / cm^2 s^{-1}$ ^a	$D^+ \times 10^5 / cm^2 s^{-1}$ ^b
H^+	9.4 ± 0.1	9.3
D^+	6.2 ± 0.1	6.5

^a ref. (4) and ^b present study; ^c ref. (11), (12) and (13).

The value of D_D^+ is shown in table 1 together with D_H^+ obtained previously ⁴ and the values of D_D^+ and D_H^+ calculated from conductance data.

Once again the good agreement between polarography and conductivity measurements validates the method used in this study.

TABLE 2.—DIFFUSION COEFFICIENTS OF H^+ IN 0.1 mol dm^{-3} SOLUTIONS OF KCl AND NaCl

electrolyte conc./mol dm^{-3}	$D_H^+ \times 10^5 / cm^2 s^{-1}$	method	ref.
0.1 KCl	8.5 ± 0.2	polarography	6
0.1 KCl	8.7 ± 0.1	polarography	4
0.1 KCl	8.01	diaphragm cell	10
0.1 NaCl	7.8 ± 0.4	rotating disc electrode (amalgamated copper)	8
0.1 NaCl	8.01	diaphragm cell	10
0.1 NaCl	8.5 ± 0.4	rotating disc electrode (platinum)	14
0.1 NaCl	8.8 ± 0.1	polarography	4

It is also of interest to compare other results for the diffusion coefficient of the hydrogen in electrolyte solutions. Table 2 lists values which have been reported in 0.1 mol dm^{-3} solutions together with results from the present study. Only the present authors¹⁻⁵ and Woolf¹⁰ have studied hydrogen ion diffusion in more concentrated electrolyte solutions.

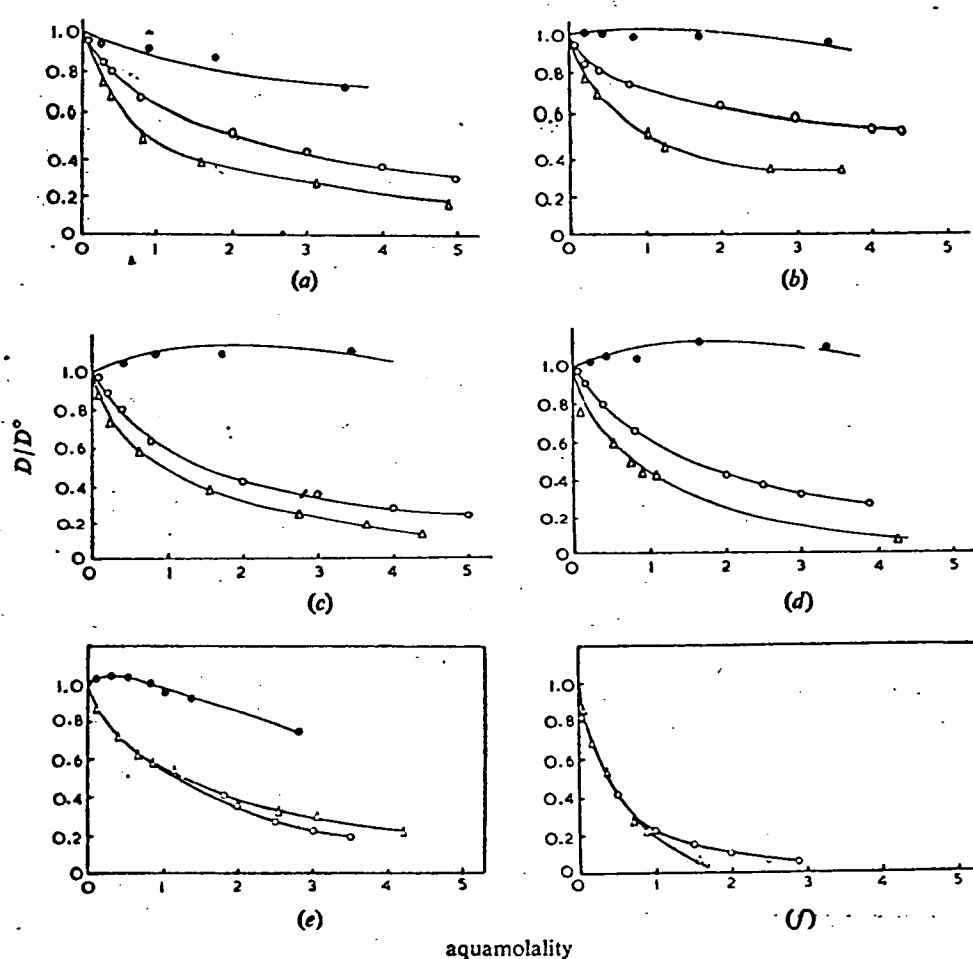


FIG. 1.—Tracer diffusion coefficients of the proton (○) and deuteron (△) at 25°C in solutions of (a) NaCl, (b) KCl, (c) KBr, (d) KI, (e) Me₄NBr, (f) Bu₄NBr. ●, the self diffusion ratio for normal water at 23°C.

It is clear from table 2 that values from polarography are consistently higher than those obtained from the diaphragm cell method, and that the rotating disc electrode gives both high and low values depending on the disc material. It would appear, then, that the higher figures are not peculiar to the polarographic method and this lends support to our earlier claim^{4, 5} that our results are correct.

Plots of D/D° for the hydrogen and deuterium ion against aquamolality of electrolyte were constructed for the following electrolytes, NaCl, KCl, KBr, KI, Me₄NBr and Bu₄NBr, fig. 1. Where available, data for the self-diffusion of water in the presence of these electrolytes were included for comparison from the work of

McCall and Douglas¹⁵ and Brun *et al.*¹⁶ As for the proton in normal water, deuteron mobility was higher in KCl than in NaCl solutions, greatest in KCl and least in KI. With the tetra-alkylammonium salts mobility was greatest in the tetramethyl- and least in the tetrabutyl-ammonium bromide solutions. Fig. 2 shows the results for deuteron mobility in Me₄NBr, Et₄NBr, Pr₄NBr and Bu₄NBr.

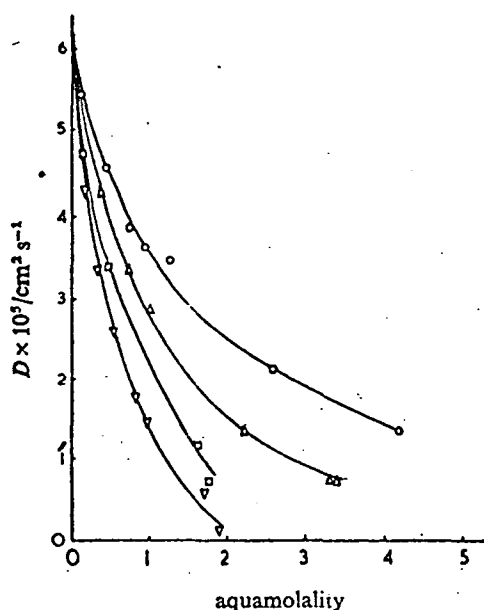


FIG. 2.—Tracer diffusion coefficients of the deuteron in tetra-alkylammonium bromide solutions. O, Me₄NBr; Δ, Et₄NBr; □, Pr₄NBr; ▽, Bu₄NBr.

With the alkali halides it is observed that D/D° for deuteron mobility in D₂O is affected to a greater extent than proton mobility in H₂O, whereas with the tetramethyl and tetrabutylammonium bromide salts the effect is almost the same up to ~1 aquamolal. Above 1 aquamolal D/D° decreases more slowly for D⁺ than for H⁺ with increasing concentration of Me₄NBr while the reverse is true for Bu₄NBr and the alkali halides. The anomalous behaviour of Me₄NBr is evident. Furthermore the alkali halides reduce the mobility of the deuterium ion at a greater rate up to ~1 aquamolal but above this concentration the rate of change of D/D° for H⁺ and D⁺ is almost the same.

In table 3 is shown the effect of concentration of supporting electrolyte on the diffusion coefficient of the hydrogen ion relative to that of the deuterium ion.

Sodium chloride, and potassium chloride and bromide show much the same trend in the ratio D_{H^+}/D_{D^+} , whereas potassium iodide shows a much more rapid increase as a result of the relatively lower diffusion coefficient of the deuterium ion. The difference may arise as a result of some specific interaction between the iodide ion and D₂O. In this connection it is worthy of note that Greyson¹¹ and Walrafen¹² have shown that in the case of water, structure-influencing properties are more sensitive to ion size for negative than for positive ions since the protons in water may polarise anions to an extent increasing with increasing anion size thus producing between the water and anion a bond which is less polar than the OH—O bond of water itself and which therefore tends to destroy structure in the surrounding water.

TABLE 3

supporting electrolyte	aquamolality	$D_{H^+} \times 10^5 / \text{cm}^2 \text{ s}^{-1}$	$D_{D^+} \times 10^5 / \text{cm}^2 \text{ s}^{-1}$	D_{H^+}/D_{D^+}
NaCl	0.0	9.3	6.5	1.43
	0.5	7.1	3.8	1.9
	1.0	6.0	2.9	2.1
	2.0	4.9	2.1	2.3
	3.0	4.1	1.7	2.4
	4.0	3.4	1.3	2.6
KCl	0.5	7.3	4.1	1.8
	1.0	6.7	3.2	2.1
	2.0	5.9	2.4	2.5
	3.0	5.5	2.2	2.5
	4.0	5.1	2.0	2.6
KBr	0.5	7.1	3.9	1.8
	1.0	5.6	3.0	1.9
	2.0	4.0	2.0	2.0
	3.0	3.2	1.4	2.3
	4.0	2.6	0.98	2.7
KI	0.5	7.1	3.7	1.9
	1.0	5.7	2.7	2.1
	2.0	4.0	1.7	2.4
	3.0	3.1	1.0	3.1
	4.0	2.5	0.5	5.0
Me_4NBr	1.8	3.8	2.6	1.5
	2.0	3.3	2.4	1.4
	2.5	2.5	2.0	1.3
	3.0	2.1	1.7	1.2
	3.5	1.9	1.4	1.4
Bu_4NBr	0.5	3.9	2.5	1.6
	1.0	2.1	1.2	1.8
	1.5	1.4	0.5	2.8
	2.0	0.95	—	—
	2.5	0.64	—	—
	2.9	0.49	—	—

THE GROTTTHUSS COMPONENT OF HYDROGEN AND DEUTERIUM ION DIFFUSION

The discussion so far, while acknowledging the abnormal mobility of hydrogen ion diffusion, has made no attempt to separate the excess Grotthuss contribution from the total measures of the diffusion coefficients. The work on proton conductance of Conway, Bockris and Linton¹² suggests that the Grotthuss component may be obtained by subtracting the component due to normal ionic diffusion from the values measured for the proton and deuterium diffusion coefficients. The potassium ion is of comparable radius to the hydrogen ion, so for proton diffusion in normal water solutions at various electrolyte concentrations, it is reasonable to say:

$$\text{Grotthuss contribution} = (D_{H^+} - D_{K^+})_{H_2O}.$$

There are, however, no values available for the diffusion coefficient of K^+ in various electrolyte solutions, but such values are available for Cl^- in sodium and potassium chloride solutions,¹¹ and since the diffusion coefficients at infinite dilution for K^+ and Cl^- are little different (being 1.98×10^5 and $2.03 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$ respectively), it is reasonable to substitute the Cl^- values for those of K^+ . Then:

$$\text{Grotthuss contribution} = (D_{H^+} - D_{Cl^-})_{H_2O}.$$

Similarly for deuteron diffusion in heavy water solutions:

$$\text{Grotthuss contribution} = (D_{D^+} - D_{Cl^-})_{D_2O}.$$

Now the diffusion coefficient of the chloride ion in heavy water is not known, but it may be estimated using the Einstein equation:

$$D = RT/6\pi\eta rN.$$

which indicates that $D \propto 1/\eta r$, where η is the viscosity of the electrolyte solution and r is the radius of the ion. The chloride ion is only slightly hydrated so there will be little error in assuming that its ionic radius is the same in D_2O as in H_2O . Then $(D_{Cl^-})_{D_2O}$ in various electrolytes may be put equal to:

$$(D_{Cl^-})_{H_2O} \times \eta_{H_2O}/\eta_{D_2O}$$

where η_{H_2O}/η_{D_2O} is known for various electrolyte solutions. Stokes and Mills¹⁷ give values of the viscosity of potassium chloride in normal water, and those

TABLE 4.—TOTAL DIFFUSION COEFFICIENTS AND GROTTHUSS COMPONENTS FOR HYDROGEN AND DEUTERIUM ION DIFFUSION IN ELECTROLYTE SOLUTIONS

aquamolality	$D_{H^+} \times 10^5$	$D_{Cl^-} \times 10^5$	$(D_{H^+} - D_{Cl^-})_{H_2O} \times 10^5$	$D_{D^+} \times 10^5$	$(D_{Cl^-})_{D_2O} \times 10^5$ ^a	$(D_{D^+} - D_{Cl^-})_{D_2O} \times 10^5$
NaCl						
0.0	9.31	2.03	7.28	6.50	1.64	4.86
0.5	7.10	1.84	5.26	3.81	1.48	2.33
1.0	5.98	1.77	4.21	2.92	1.43	1.49
2.0	4.92	1.60	3.32	3.10	1.29	0.81
3.0	4.11	1.45	2.66	1.66	1.17	0.49
4.0	3.38	1.26	2.12	1.34	1.02	0.32
KCl						
0.0	9.31	2.03	7.28	6.50	1.64	4.86
0.5	7.34	1.96	5.38	4.06	1.60	2.46
1.0	6.68	1.95	4.73	3.18	1.61	1.57
2.0	5.94	1.90	4.04	2.39	1.57	0.93
3.0	5.45	1.85	3.60	2.17	1.55	0.62
4.0	5.10	1.77	3.33	2.00	1.54	0.46

^a η_{H_2O}/η_{D_2O} is not available for NaCl solutions; relative viscosity for the pure liquids was used for calculations. Thus

$$(D_{Cl^-})_{D_2O} = (D_{Cl^-})_{H_2O} \times \eta_{H_2O}/\eta_{D_2O}, \text{ where } \eta_{H_2O}/\eta_{D_2O} = 0.8072 \text{ at } 25^\circ\text{C.}$$

for heavy water solutions were obtained from Selecki *et al.*¹⁸ All viscosities were calculated for an aquamolality basis. The results of these calculations are shown in table 4 which shows also the ratio of the Grotthuss component of the proton in normal water solutions to that of the deuteron in heavy water solutions of potassium chloride. This table also contains similar values for sodium chloride solutions, though another approximation was necessary to calculate these as viscosity data for heavy water

solutions of sodium chloride were not available. Thus the ratio $\eta_{\text{H}_2\text{O}}/\eta_{\text{D}_2\text{O}}$ for the pure solvents was multiplied by $(D_{\text{Cl}^-})_{\text{H}_2\text{O}}$ values at the various concentrations to obtain $(D_{\text{Cl}^-})_{\text{D}_2\text{O}}$ values. This seems a justifiable assumption as the viscosity ratio for KCl solutions does not vary by more than 5% from that of the pure solvents.

When the ratio of the Grotthuss component for H^+ in H_2O solutions of electrolyte to this component for D^+ in D_2O solutions is plotted against aquamolal concentration of supporting electrolyte straight lines are obtained (fig. 3). These extrapolate to the accepted value of the ratio of the diffusion coefficients at infinite dilution,¹² i.e. 1.42.

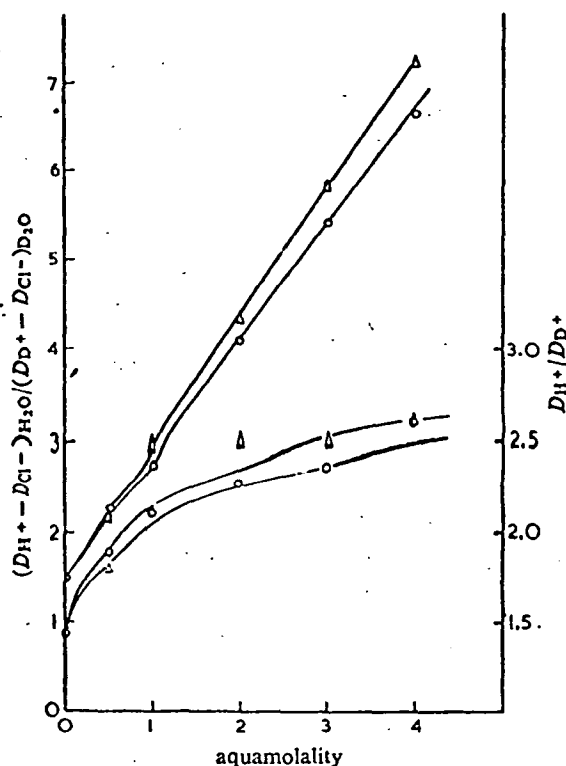


FIG. 3.—The effect of electrolyte concentration on the ratio of the total diffusion coefficients (curves) and the Grotthuss components (straight lines) in normal and heavy water solutions. Δ , KCl; \circ , NaCl.

They may be contrasted with the non-linear curves obtained when the total diffusion coefficient ratios were plotted against concentration. The straight lines indicate some regularity in the reduction of the Grotthuss component in both normal and heavy water by both electrolytes.

When the Grotthuss contributions alone are plotted against concentration, fig. 4, it is seen that the curves for deuterium diffusion are extremely close. This may indicate, once again, the importance of the anion in the reduction of deuterium mobility, though, with only two curves available, it is difficult to draw a definite conclusion. These curves also indicate that the Grotthuss contribution to the diffusion coefficient is very much greater for the proton than the deuterium. Also the Grotthuss contribution to H^+ diffusion does not cut out at concentrations of supporting electrolyte above 2 molal, but is simply reduced less rapidly than at the low concentrations, where the Grotthuss component is 3-4 times that of normal ionic diffusion and at 3-4 mol

kg^{-1} still approximately twice the normal ionic component in H_2O . In contrast with the work of Lown and Thirsk¹⁹ on aqueous solutions of KOH, NaOH and LiOH the Grotthuss contribution in 4 mol kg^{-1} NaCl and KCl is significant. In D_2O solutions the Grotthuss component falls below the normal component near 1 aquamolal.

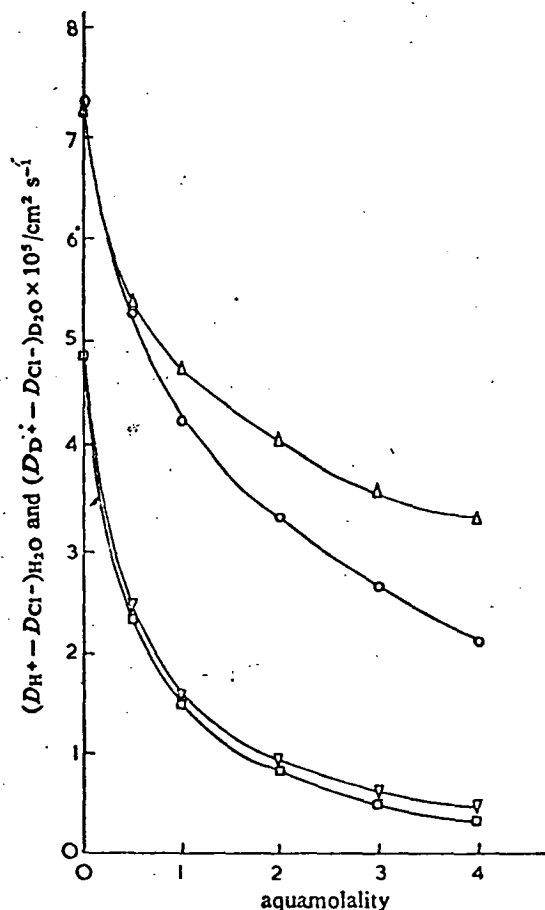


FIG. 4.—The effect of electrolyte concentration on the Grotthuss component of the diffusion coefficient in normal and heavy water. Δ , KCl in H_2O ; \circ , NaCl in H_2O ; ∇ , KCl in D_2O ; \square , NaCl in D_2O .

MECHANISM FOR TRANSFER OF H^+ AND D^+ IN THE PRESENCE OF ELECTROLYTES

The results above call into question the accepted mechanism for the transport of H^+ and D^+ in H_2O and D_2O respectively. Currently proton mobility is considered to proceed via three steps.¹²

1, Rotation of H_2O (or H_3O^+); 2, proton flip or tunnelling; 3, randomisation of H_2O .

At one atmosphere pressure the slow step is considered to be the rotation of the water molecule or H_3O^+ . Prima facie one would expect, therefore, that electrolytes which cause water to become more fluid (i.e. reduce viscosity) and increase the self-diffusion of water e.g. KCl, KBr and KI, would make the rotational step easier and promote proton mobility. None of the electrolytes we have studied increase proton or deuteron mobility though K^+ decreases it less than Na^+ or Li^+ . However,

even in the case of the cations the rate of change is incorrect e.g., the self-diffusion of water is almost constant in that region (0.1 molal) where proton mobility is changing most rapidly. The anions present a problem because they not only fail to enhance proton mobility they decrease it in the wrong order i.e. I^- which produces the most fluid water and increases the self-diffusion of water decreases proton mobility to a greater extent than Br^- and Cl^- . Thus the order for the decrease in proton and deuteron mobility is $I^- > Br^- > Cl^-$ whereas the order of increasing viscosity is $Cl^- > Br^- > I^-$. It is generally agreed that anions move by a different mechanism to cations²⁰ and the explanation may lie here.

The tetra-alkylammonium bromides decrease proton mobility in the order one might expect i.e. in the direction of increasing viscosity so that proton and deuteron mobility are greatest in solutions of Me_4NBr and least in Bu_4NBr .

It can be argued that the viscosity of a solution reflects both the translational and rotational movement of the water molecules and in the present discussion it is the rotational movement of the water molecule which is of importance. Fortunately it is not necessary to attempt to separate the two components in the work of McCall and Douglass¹⁵ as Hertz and Zeidler²¹ from an n.m.r. study of the longitudinal relaxation time of the proton and deuteron have estimated the orientation time of H_2O and D_2O in the pure liquids and also in many diamagnetic salt solutions. A selection of their results is given in table 5.

TABLE 5.—THERMALLY INDUCED ORIENTATION TIMES OF THE H_2O AND D_2O MOLECULE IN THE PRIMARY HYDRATION LAYER OF VARIOUS DIAMAGNETIC IONS

ion	τ_{\pm}/τ	
	(1)	(2)
Na^+	2.1	1.4
K^+	1.0	1.0
Me_4N^+	1.6	1.6
Et_4N^+	—	2.1
Pr_4N^+	—	3.1
Bu_4N^+	—	2.9
Cl^-	1.0	1.0
Br^-	0.6	0.8
I^-	0.35	0.6

τ_{\pm} = orientation time of a H_2O or D_2O molecule in the primary hydration sphere; τ = orientation time of a H_2O or D_2O molecule in pure H_2O and D_2O respectively ($\sim 10^{-11}$ s); (1) = results for water solutions; (2) = results for heavy water solutions.

Note that: (a) $\tau_{\pm}(K^+)/\tau$ is placed equal to $\tau_{\pm}(Cl^-)/\tau$ because the longitudinal relaxation time for KCl solutions up to ~ 4 molal equals that for pure water; (b) the ratio τ_{\pm}/τ depends on the value assumed for the hydration number of the ion.

The lower rotational times of H_2O and D_2O in KBr and KI solutions compared with pure water support the previous argument based on the viscosities of the electrolyte solutions and the self-diffusion of water in these solutions.

Strictly speaking the rate determining step in proton and deuteron mobility is not the rotation of H_2O or D_2O but the field-induced orientation of H_2O or D_2O ¹² and this may not coincide with the thermally induced orientation of water in the presence of electrolytes. The present work suggests that a measure of the thermally induced orientation of water (e.g. viscosity, self-diffusion of water or rotational orientation times) may give little or no indication of the field-induced rotation of H_2O or D_2O in the presence of electrolytes.²²

Further work is in progress on the temperature dependence of proton and deuteron mobility in the presence of electrolytes.

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**HYDROGEN ION MOBILITY IN AQUEOUS ELECTROLYTE SOLUTIONS
COMPARISON OF POLAROGRAPHIC AND DIAPHRAGM CELL METHODS**

Hydrogen Ion Mobility in Aqueous Electrolyte Solutions

Comparison of Polarographic and Diaphragm Cell Methods

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Results for the diffusion coefficient of the hydrogen ion in aqueous solutions of the chlorides, bromides and iodides of sodium and potassium, and tetrabutylammonium bromide obtained from polarography using the modified form of the Ilkovic equation with $A = 17$ are compared with those determined by the porous diaphragm cell.

The different results obtained by Woolf (using the diaphragm cell method) appear to be due to partially immobilized layers of water in the pores of the sintered glass diaphragm.

In earlier communications¹⁻³ the measurement of hydrogen ion mobility in various electrolytes was described. Data tabulated by Robinson and Stokes⁴ were included for comparison, and it was noted that these did not agree with our results. Part of the difference was attributed to streaming of the solution at low ionic strength.¹ We now present results which indicate that our values are likely to be correct.

Diffusion coefficients were calculated from the exact solution of the diffusion problem as derived by Strehlow and von Stackelberg⁵ and tested experimentally by them.⁶ This modified form of the Ilkovic equation is

$$i_d = 607nD^{\frac{1}{2}}Cm^{\frac{3}{2}}t^{\frac{1}{2}}(1 + AD^{\frac{1}{2}}m^{-\frac{1}{2}}t^{\frac{1}{2}})$$

in which i_d = diffusion current in microamperes, C = concentration of depolarizer in millimoles per litre, D = diffusion coefficient of the depolarizer in $\text{cm}^2 \text{s}^{-1}$, m = rate of flow of mercury in mg s^{-1} , n = number of faradays per mole of electrode reaction, t = drop time in seconds, and A is a constant which they evaluated to be 17. Others have deduced a similar equation, differing from the above only in the constant A , which has been calculated to be 24,⁷ 39,⁸ or 45.1.⁹

EXPERIMENTAL

A Yanagimoto a.c.-d.c. polarograph model P.A. 102 was used. A pool of mercury was used as anode and all polarograms were recorded at $25.0 \pm 0.1^\circ\text{C}$. The concentration of H^+ in the HCl solution was determined by potentiometric titration with sodium tetraborate and found to be $1.849 \times 10^{-3} \text{ M}$. The concentration of cadmium ion was measured polarographically to be $1.66 \times 10^{-3} \text{ M}$.

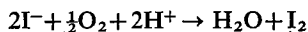
Where they were obtainable A.R. salts were used. All alkali halides were recrystallized twice from conductivity water, and, in the case of sodium and potassium chlorides, ethanol was used to precipitate the salt. Only laboratory reagent sodium bromide was available, but after two recrystallizations its purity, determined by titration with standardized silver nitrate, was found to be 99.7 % (as Br^-). These salts were dried at *ca.* 110°C under reduced pressure for at least 16 h, stored over silica gel and again dried overnight before use.

Tetrabutylammonium bromide from Eastman Kodak was recrystallized four times from

dry acetone and dried overnight at 80°C under reduced pressure. The melting point, 101–102°C, corresponds to that of a metastable form reported by Accascina *et al.*¹⁰ Before use it was again dried overnight.

Solutions were not permitted to come in contact with mercury until all the air had been displaced by high purity nitrogen previously saturated with water. This precaution was found necessary because mercury, in the presence of a large concentration of halide ion, can reduce the dissolved oxygen, with the formation of hydroxyl ions.¹¹

As reported earlier,² ageing has a profound effect on the diffusion current of the hydrogen ion in the presence of iodides. The appearance of a slight yellow coloration and an accompanying increase in the pH of the solution suggest that this is due to a slight oxidation of iodide by atmospheric or dissolved oxygen to produce iodine according to the equation:



As the iodide concentration is much larger than the hydrogen ion concentration it requires only slight oxidation to cause a large change in the hydrogen ion concentration and hence in the diffusion current.

These effects do not occur with chlorides and bromides. Nevertheless solutions were generally prepared immediately before use by adding measured quantities of H_3O^+ or Cd^{2+} solution to a weighed amount of salt. For hygroscopic salts a glove-bag was used when transferring the dried salt to the weighing tube.

The drop-time, t , was measured from the chart. Values of m were determined separately by collecting and weighing drops of mercury which fell from the d.m.e. inserted in the required solution while the p.d. at which i_d was measured was applied. This was usually near -1.7 V against a pool of mercury as anode for chlorides and bromides and about -1.5 V for iodides.

Preliminary measurements of the residual current of aqueous solutions of supporting electrolytes and comparison with the curves obtained with the acid solutions indicated that allowance for the residual current could effectively be made by extending the base line obtained before the decomposition potential was reached. The most general allowance, of the order of 1%, compared favourably with the precision with which the limiting current could be measured.

Some polarograms showed a slight maximum which was not suppressed by small concentrations of gelatine. The plateau was, however, sufficiently well-defined to enable measurements to be standardized. In most cases three measurements of i_d and t were made at each concentration and agreement between the $i_d/t^{1/2}$ values so obtained was within 1%.

RESULTS AND DISCUSSION

Values of the tracer diffusion coefficient, D , were calculated from the Ilkovic equation for H_3O^+ and Cd^{2+} ions in various supporting electrolytes. Values of $t^{1/2}$ were calculated from limiting values at infinite dilution of i_d and $i_d/t^{1/2}$ estimated from curves obtained by plotting values of these against concentration of supporting electrolyte as shown for two cases in fig. 1. The rate of flow of mercury, m , was constant in dilute solutions (below 0.3 m) at a value of 1.76 mg s^{-1} .

The D values so obtained, viz. the tracer diffusion coefficient for H_3O^+ and Cd^{2+} in ca. 2×10^{-3} M aqueous solutions of these ions, are shown in table 1.

These may be compared with the accepted values of D° (at infinite dilution) calculated from limiting conductance measurements, as shown in table 2.

It will be noted that the Ilkovic equation with $A = 17$ gives values of D which compare favourably with calculated values, indicating that the polarographic method is reliable. $A = 17$ is used in subsequent calculations.

It was previously shown^{1,2} that curves for $i_d/t^{1/2}$ against concentration of supporting electrolyte show a distinct numerical decrease in gradient as concentration increases through ca. 1 m. It was earlier suggested¹ that the greater values of the current at low concentrations may be due to streaming so that the diffusion current alone was

not measured. But it is seen that, provided the concentration of supporting electrolyte is at least fifty times that of the depolarizer, such curves extrapolate to a value of $i_d/t^{\frac{1}{2}}$ which gives a satisfactory value of D , so it is unlikely that there is present any

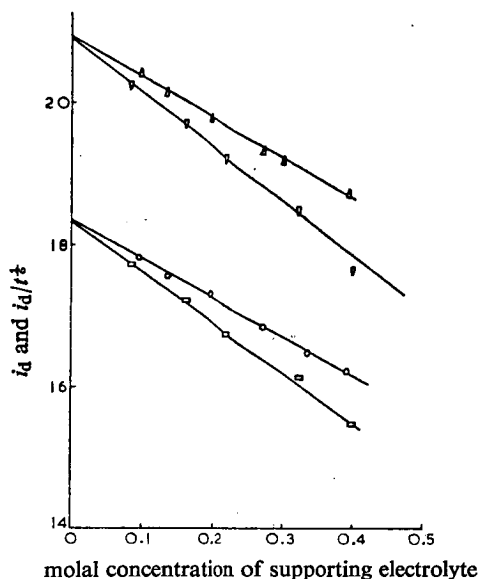


FIG. 1.—Diffusion of the hydrogen ion as a function of electrolyte concentration: Δ , i_d NaCl; ∇ , i_d NaI; \circ , $i_d/t^{\frac{1}{2}}$ NaCl; \square , $i_d/t^{\frac{1}{2}}$ NaI.

TABLE 1.—EXPERIMENTAL VALUES OF DIFFUSION COEFFICIENTS AT 25°C

ion	molar concentration	$D \times 10^5$ (cm ² s ⁻¹)	
		$A = 17$	$A = 39$
H ₃ O ⁺	1.849×10^{-3}	9.40	7.28
Cd ²⁺	1.66×10^{-3}	0.712	0.641

current other than the diffusion current. When the concentration of supporting electrolyte was much less than 0.1 m, however, the measured current was in some cases found to be high.

TABLE 2.—CALCULATED VALUES OF DIFFUSION COEFFICIENTS AT 25°C

ion	$D^\circ \times 10^5$ (cm ² s ⁻¹)
H ₃ O ⁺	9.31
Cd ²⁺	0.720

Values of D/D° (D calculated from polarographic data, D° the diffusion coefficient at infinite dilution) were plotted against the concentration of supporting electrolyte, as shown in fig. 2-4, in which data from other sources are included for reference.

Curves obtained in this study are compared with those drawn from Woolf's⁴ data for the hydrogen ion in sodium and potassium chloride solutions, fig. 2. Our values are generally lower except below about 0.3 m supporting electrolyte, and, whereas the polarographically determined coefficients extrapolate very nearly to 1, those obtained from the diaphragm cell do not.

It will be seen from fig. 3 that the curves for the metallic cations also extrapolate very nearly to 1,

In the diaphragm cell method the cells were calibrated by diffusion of potassium chloride solutions into water¹² and then used to measure the diffusion coefficients of other ions. The results obtained for D/D° for the hydrogen ion and metallic cations are dissimilar, as has been noted.

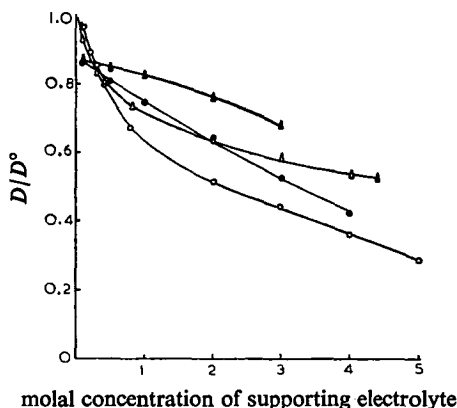


FIG. 2.—Tracer diffusion coefficient of H^+ in alkali-metal chlorides: \circ , NaCl this work; \bullet , NaCl from ref. (4); Δ , KCl this work; \blacktriangle , KCl from ref. (4).

Since the mobility of the hydrogen ion is so very sensitive to the structure of water¹⁻³ the difference in results from the two methods may well be attributable to the use of a porous glass disc (pore size $\sim 15 \mu m$) in the diaphragm cell method to measure the diffusion of hydrogen ion. Mysels and McBain¹³ have shown that a

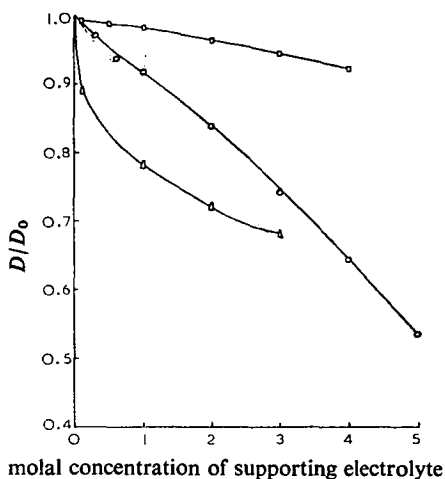


FIG. 3.—Tracer diffusion coefficients in electrolyte solutions: \circ , $1.66 \times 10^{-3} M$ Cd^{2+} in $NaNO_3$ this work; Δ , Tl^+ in KCl from ref. (6); \square , Na^+ in KCl from ref. (4).

disc of fritted Pyrex glass does not affect the diffusion of potassium chloride in concentrated solutions, however with time the hydrodynamic resistance to flow increases by an order of magnitude, which they attribute to thick rigid layers of water in contact with the glass pores of the disc. (A recent article by W. Drost-Hansen supports this view.¹⁴) They argue that the rigid structured water does not impede

the flow of ions. While this appears to be true for potassium chloride there is good reason to believe that this is not true for the hydrogen ion, an ion which diffuses by a mechanism which is extremely sensitive to the structure of water. It should also be

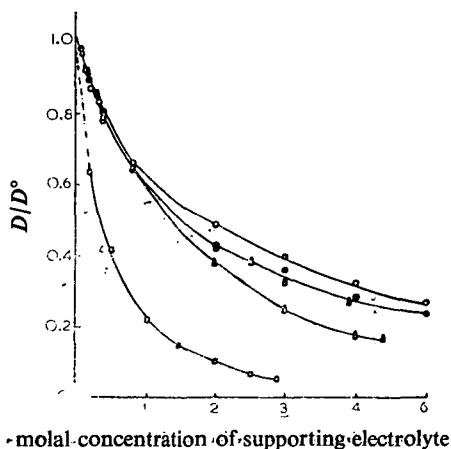


FIG. 4.—Tracer diffusion coefficients of H^+ in some halides: \circ , NaBr; \bullet , KBr; Δ , NaI; \blacktriangle , KI; \square , Bu_4NBr .

noted that Schuffe and Yu¹⁵ observed activation energies of conduction by HCl solutions in capillaries (with pore size corresponding to that used by Woolf, ca. $1.5 \mu m$) which were different from that obtained for the same solutions in the bulk by a factor of as much as 100 %.

Fig. 4 shows D/D° against concentration curves for the hydrogen ion in sodium and potassium bromide and iodide and in tetrabutylammonium bromide. In all cases the curves extrapolate to $D/D^\circ = 1$. There is little difference between the curves for the two potassium salts but, as for sodium bromide the diffusion current is higher than expected as noted previously,² so the diffusion coefficient is likewise higher than that in potassium bromide.

These results show that polarography is a useful method for studying proton mobility in the presence of other ions in aqueous solution when the modified form of the Ilkovic equation is used to calculate diffusion coefficients and that until another absolute method is devised for measuring hydrogen ion diffusion there must remain doubt as to the reliability of the diaphragm cell method as applied to the hydrogen ion.

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