The current state of our understanding of ionic mobilities

Robert L. Kay

Chemistry Department, Carnegie Mellon University, 4400 Fifth Ave., Pittsburgh, PA 15213, USA

Abstract - As a result of extensive development of experimental techniques and equipment, highly precise limiting ionic conductances with their temperature and pressure dependences have been available for some time. This has resulted in several attempts to provide a theoretical basis to account for the deviations reported from Stokes' behavior. These deviations in the conductance-visocsity product include a maximum in the ion size dependence, positive and negative temperature dependencies and different size dependencies for cations and anions as well as for large and small ions. Furthermore, specific solvent effects must be accounted for. In this article an attempt is made to evaluate several theories as to their ability to account for these deviations.

INTRODUCTION

During the first sixty years of this century little progress was made in explaining the magnitude of limiting conductances. Some of the more important factors affecting their magnitude had not been recognized but discussions generally were limited to a consideration of Stokes' law and to various solvation schemes. Although the data available were voluminous, few systematic precise studies, with some notable exceptions,[1] had been carried out in any solvent except water and temperature and pressure dependencies were for the most part unknown. Inspite of the fact that some early workers had developed the experimental techniques required for precise work[2,3] the methods were time consuming, tedious and required considerable skill. Furthermore, the general lack of transference data required a consideration of the salt conductances which are dependent on the properties of two entirely different ions.

In the past thirty years the situation has changed dramatically. Modern equipment and techniques[4,5] have produced a wealth of highly precise ionic conductance data for a broad cross section of solvents.[6] Temperature and pressure coefficients have been established for several systems. Advances in conductance theory[7] produced a reliable extrapolation procedure when coupled with least squares computer programs.[8] Transference data, including temperature and pressure dependencies, are available for several of the more common solvents. The net effect has been a clear picture of how ionic mobilities were affected by the more important variables and the response from the theorists was considerable.

In this review an attempt will be made to illustrate how well the various theoretical models actually reflect the experimental facts. It is not possible to document even a small portion of the experimental data. The actual data can be traced in the references given. Several systems such as surfactants, protonic conductance and ionic melts are not included. The temperature range considered is that in which the mobilities are not affected by small changes in solvent density. For the most part computer simulations are a separate subject and only special cases are considered here.

STOKE'S LAW

Most discussions of limiting ionic conductances λ_o commence with a discussion of Stokes' law

$$\lambda_o \eta = \frac{Fez_i}{f\pi R_i} \tag{1}$$

which assumes non interacting spherical ions of radius R_i (generally set equal to the crystallographic radius r_x) and charge $z_i e$ in a solvent continuum of viscosity η. The boundary factor f varies between 6 for perfect stick conditions and 4 for perfect slip. A comparison of the predictions of Eq. (1) with experimental data[9] at 25°C can be found in the Walden product plot in Fig. 1. It is clear that Stokes' law does not reproduce the size dependence of typical ions except for large ions for which there is the uncertainty as to whether the $f = 4$ or 6 condition holds. An appeal to solvation to form a large moving entity qualitatively could explain the values of $\lambda_o \eta$ below either of the Stokes' lines but not those points above. Perhaps the most serious problem for theories that treat the solvent as a continuum is the fact that cations and anions lie on two distinct curves. Also, for the higher alcohols (1-PrOH and 2-BuOH) it is not possible to join the large R_4N^+ and alkali-metal ions by a simple curve without introducing maxima and minima. Such behavior suggests either a serious restriction of Stokes' law or a different mechanism of conductance for small and large ions in these solvents.

Stokes's law also predicts that the Walden product should be independent of temperature and pressure. Although the temperature coefficient of $\lambda_o \eta$ is small, amounting to less than 1%, for ions in most organic solvents, its magnitude is considerable for aqueous solutions[10] as shown in Fig. 2 where both positive and negative temperature coefficients of $\lambda_o \eta$ are evident. The pressure coefficients[11] of $\lambda_o \eta$ on the other hand are substantial in all solvents and show complicated behaviour. Data for aqueous solutions are shown in Fig. 3a, and for methanol solutions in Fig. 3b.

GURNEY–FRANK–WEN MODEL

Gurney[12] was the first to offer a model that provided a reasonable explanation for the size and temperature dependence of ionic mobilities in aqueous solutions. He introduced the concept of an ionic cosphere, that part of the solvent surrounding an ion whose physical properties differ from the bulk solvent properties due to the presence of the ion. His ideas can best be demonstrated by what has become known as the Frank-Wen model[13] which is shown in Fig. 4.
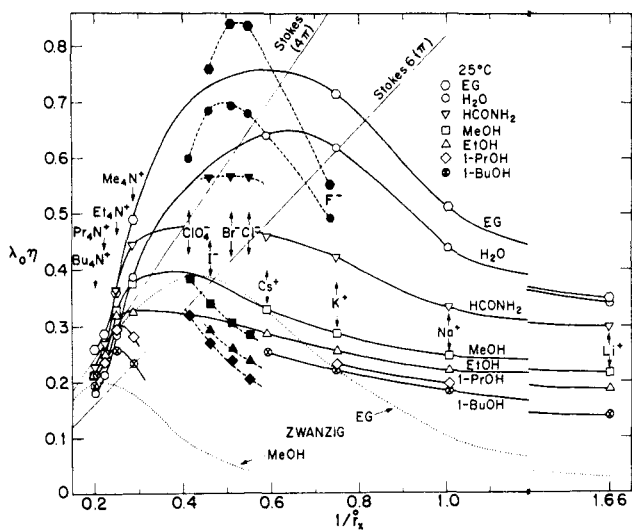
Fig. 1. Limiting conductance-viscosity products for the alkali metal, halide, perchlorate and tetralkyl- ammonium ions in ethylene glycol, water, formamide, methanol, ethanol, 1-propanol and 1-butanol as a function of the reciprocal crystallographic radii at 25°C. Cations are depicted by open symbols and anions by closed symbols. Equation (1) is shown for the two extreme conditions. The Zwanzig theory [Eqs. (2, 3)] is shown as broken curves for methanol and ethylene glycol.
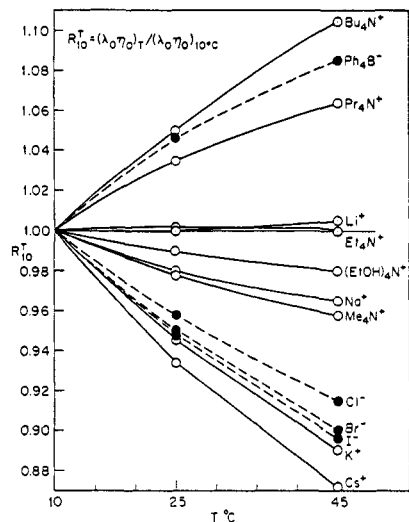
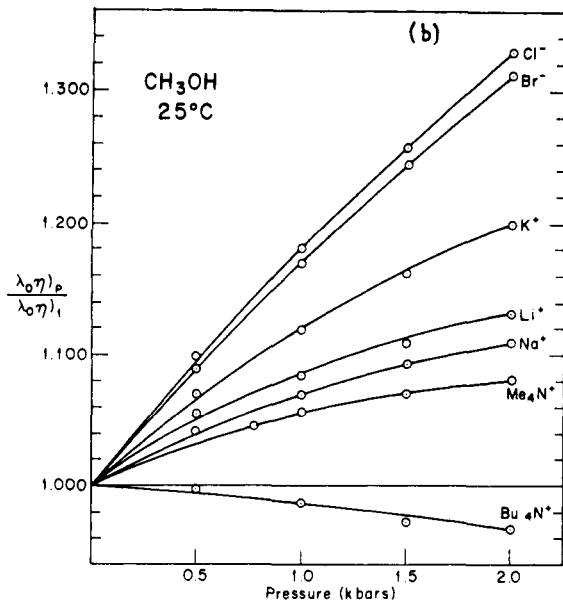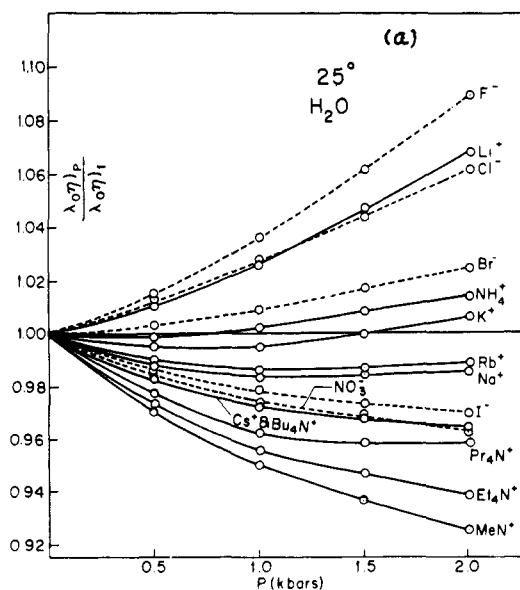Fig. 2. Temperature dependence of the Walden product for aqueous solutions.

Fig. 3a and 3b. Conductance-viscosity products at 25°C for (a) aqueous and (b) methanol solutions as a function of pressure.

In the Frank-Wen model for aqueous solutions, ions are separated into three catagories: type (a) are small ions with large surface charge densities whose cospheres contain a completely oriented, strongly bound layer of water molecules (electrostriction). Since for those ions the moving entity is larger than the crystallographic size their conductance-viscosity product should be lower than that given by Stokes' law and, since the solvent binding is strong, should show little temperature dependence at ordinary temperatures; type (b) are larger ions of lower surface charge density which is insufficient to orient most of the water molecules completely but which can interfere with the normal three-dimensional hydrogen bonded structure of water. Thus, the ions in a cosphere of type (b) ions are moving in a region whose viscosity is less than the bulk solvent viscosity. Such ions have been described as structure-breakers and appear to have an excess mobility that is more pronounced as the solvent structure increases at lower temperatures. The third type (c) are large ions with hydrophobic surfaces which are postulated to be surrounded by a cosphere containing water molecules which are more highly hydrogen bonded than in bulk water. These ions should have a lower than expected Walden product at lower temperatures but the effect should be highly temperature dependent since hydrogen bonding effects rapidly diminish at higher temperatures. Thus, ions of type (c) should have Walden products that increase with temperature.
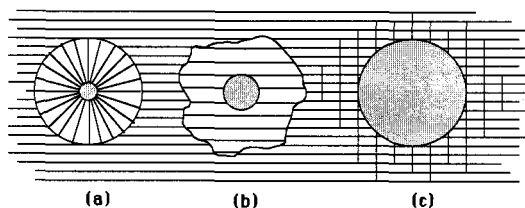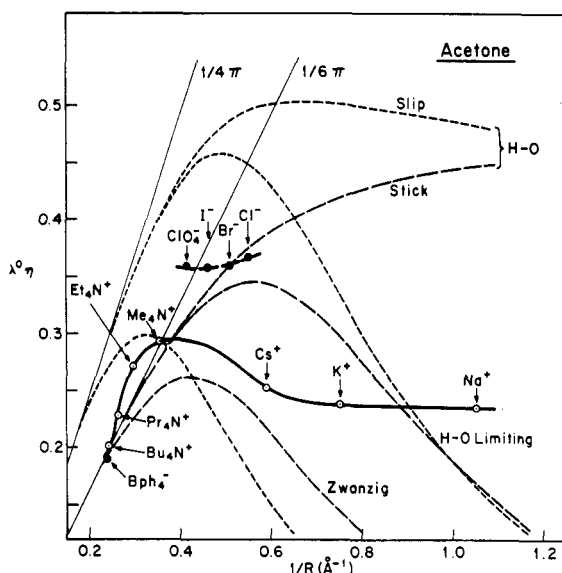
Fig. 4. Gurney-Frank-Wen Model.

Fig. 5. A comparison of experimental and predicted Walden products as a function of the reciprocal crystallographic radii for acetone solutions at 25°C. The predictions of the Zwanzig, (Eqs. 2, 4), limiting Hubbard-Onsager (H-O Limiting) Eqs. (2, 5) and extended Hubbard-Onsager (H-O), Eqs. (7-9)are included. [Reproduced with permission from D. F. Evans, T. Tominaga, J. B. Hubbard, and P. G. Wolynes, Ref. 19.]

The peculiar behavior of aqueous conductance-viscosity products has, for the most part, been explained qualitatively by this model.[14] The small Li^+ ion is a highly hydrated ion [type (a)] with a small temperature coefficient for $\lambda_o\eta$ (Fig. 2). The large inorganic ions (including ClO_4^- shown later in Fig. 6) are structure-breakers with negative temperature coefficients of $\lambda_o\eta$[type (b)]. It is also of interest to note that Reddy and Berkowitz[15] were able to show from molecular dynamics computer simulation that the temperature dependence of the Walden products for the K^+ Cl^- and Cs^+ ions are related to the difference in the reorientation times of water molecules in the ion cosphere and in the bulk solvent.

Although Me_4N^+ is a structure-breaker and Et_4N^+ shows a zero temperature coefficient of $\lambda_o\eta$, as the size of the tetraalkylammonium ions increase the temperature coefficient becomes positive [type (c)]. It is interesting to note that the $(EtOH)_4N^+$ ion, possibly an analog of the Pr_4N^+ ion, is not a hydrophobic ion is such a large ion that its charge has little effect on its cosphere, *i.e.*, only a small negative temperature coefficient is evident in Fig. 2 compared to the large positive temperature coefficient of its analog the hydrophobic Pr_4N^+ ion.

The pressure data for the three types of ion are more complicated than the temperature data because two additional effects must be considered.[16] At lower temperatures the viscosity of water has a negative pressure coefficient due to the fact that pressure breaks the water structure. Water is one of the few liquids that become less viscous with increased pressure. Therefore, at fixed temperature, as the pressure increases the amount of structure in water decreases and the large structure breaking ions should show an initial decrease of $\lambda_o\eta$. This is verified in Fig. 3a particularly for the large structure breaking Cs^+, Rb^+, K^+ and I^- ions whereas this negative contribution is missing in the methanol data (Fig 3b) since methanol has a positive pressure coefficient of the viscosity at all temperatures. Increased pressure can also increase ion-solvent interaction because electrostriction causes a large negative volume change. Such an electrostriction effect should produce a decrease in the Walden product that is more pronounced in methanol than in water because methanol is about three times as compressible as water. However, the opposite is true. For example, the increase in $\lambda_o\eta$ for the Cl^- ion is almost five times its value in water at a pressure of 2 kbars. A more probable explanation for the large positive pressure coefficient of the Walden product for small ions is that the physical properties of the cosphere are dictated more by the ionic charge of small ions than by the small force we impose on the solvent in our pressure experiments. Thus, a small increase in pressure has a large effect on the bulk viscosity of the highly compressible methanol but less effect on the viscosity of the less compressible cosphere.

ZWANZIG THEORY

The ionic cosphere model, although capable of explaining many of the unique properties of ionic aqueous solutions, is restricted by a number of limitations. It is not a quantitative theory and suffers from the assumptions inherent to Stokes' law as applied to charge particles moving in a molecular environment rather than hard spheres in a continuum. Also there are clear indications that the magnitude of ionic conductances decreases as the solvent dielectric constant decreases (Fig. 1). A dielectric frictional effect was first identified very early by Born[17] who postulated the following model for solvation. As an ion moves it orients solvent dipoles in its vicinity. After passage of the ion these dipoles must reorient to their random distribution, but owing to the finite solvent relaxation time, a retarding force is imposed on the moving ion.

Zwanzig[18] was the first to provide a numerical expression for the effect and in his earlier publication reported

$$\lambda_0 \eta = \frac{F e z_i}{f \pi R_i + B'/R_i^3} \tag{2}$$

where

$$B' = (2/3)(z_i e)^2 (\tau/\eta)[(\varepsilon_0 - \varepsilon_\infty)/\varepsilon_0^2] \tag{3}$$

Here τ, ε_0 and ε_∞ are the solvent dielectric relaxation time and the low and high frequency dielectric constants, respectively. The calculated $\lambda_0 \eta$ using this expression were much too small compared to experimental data. Although they did have the same general shape of the $\lambda_0 \eta$ curve as a function of $1/R_i$ the maxima were not nearly at the correct value of the crystallographic radii. A latter revision produced

$$B' = Z(z_i e)^2 (\tau/\eta)[(\varepsilon_0 - \varepsilon_\infty)/\varepsilon_0(2\varepsilon_0 + 1)] \tag{4}$$

which is plotted in Fig. 1 for methanol and ethylene glycol and in Fig. 5 for acetontrile.[19] In Eqs. (2, 4) the constant f and Z have the values 4 and 3/4 for the slip condition and 6 and 3/8 for the stick condition, respectively.

The most distinctive feature of the Zwanzig equation is the fact that it predicts a maximum that is common to all Walden products vs. $1/R$ curves. However, in acetone (Fig. 5) the magnitude of $\lambda_0 \eta$ at the maximum is close only in the case of the slip condition for cations. For smaller cations and all anions in acetone and all ions in methanol and ethylene glycol the predictions of the Zwanzig equations are substantially too low as a result of too high a predicted value of B in Eq. (4). The shift of the experimental maximum in $\lambda_0 \eta$ to lower values of $1/R$ for ions of higher charge is verified by the Zwanzig equation but the absolute values predicted as still too low.[19, 21] For all ions a negative temperature coefficient of the Walden product can be calculated from Eqs. (2, 4) but for most ions in aqueous solutions the experimental values[20] are an order of magnitude more negative and the positive temperature coefficient of the R_4N^+ ions are not predicted. The Zwanzig theory predicts a positive pressure coefficient for all ions in water at 25°C whereas the measured coefficient for many ions is negative.[11,19,20]

HUBBARD–ONSAGER THEORY

A second continuum theory using the Born model was published by Hubbard and Onsager.[22] The result for their limiting equation has the same general form as Eq. (2) but with

$$B = H(z_i e)^2 (\tau/\eta)[(\varepsilon_0 - \varepsilon_\infty)/\varepsilon_0^2] \tag{5}$$

where H has the value 1/15 for the slip and 1/16.5 for the stick condition. Thus, the constants of the limiting HO equation are over two times larger than the Zwanzig equation. Consequently, as seen in Fig. 5 this H-O limiting equation predicts much higher Walden products but otherwise suffers from the same limitations of the earlier Zwanzig equation.

The HO theory[22] in its extended form has been presented by Nakahara[23, 24] by defining a residual friction coefficient $\Delta\zeta$

$$\Delta\zeta = z_i e F/\lambda_0 - 4\pi\eta R \tag{6}$$

for the slip condition. The Walden product as expressed by Eq. (2) then becomes

$$\lambda_0 \eta = \frac{F e z_i}{4\pi R + \Delta\zeta/\eta} \tag{7}$$

From the original HO theory Nakahara has obtained an analytical expression for $\Delta\zeta$ given by

$$\Delta\zeta = \eta R_{HO} \Sigma a_j (R_{HO}/R)^j \tag{8}$$

$$R_{HO} = \left[\frac{z_i^2 e^2}{16\pi} \frac{(\varepsilon_0 - \varepsilon_\infty)}{\varepsilon_0^2} \left(\frac{\tau}{\eta}\right) \right]^{1/4} \tag{9}$$

where a_j are numerical constants which have been tabulated by Nakahara for various ratios of R/R_{HO}.

Evans et al.[17] have evaluated this theory by comparing the experimental values of $\lambda_0 \eta$ with those predicted by Eqs. (6-9) for the systems shown in Figs. 5 and 6. For each system the extended HO theory predictions approach a finite limit as R approaches zero rather than showing a definite maximum. For all the curves in Figs. 5 and 6 it is clear that the HO theory cannot account for the alkali metal and halide ion data.

There are a number of important features evident for the hydrogen bonded solvents in the top right hand plot of Fig. 6. The HO theory does predict a decrease in $\lambda_0 \eta$ as the dielectric constant of the solvents decrease. Also, the shift in the $\lambda_0 \eta$ maxima to higher values of R_i as the dielectric constant of the solvent decreases is correctly predicted. Consequently, one must assume that dielectric friction as outlined by the H-O theory makes a contribution to the magnitude of $\lambda_0 \eta$ but it is by
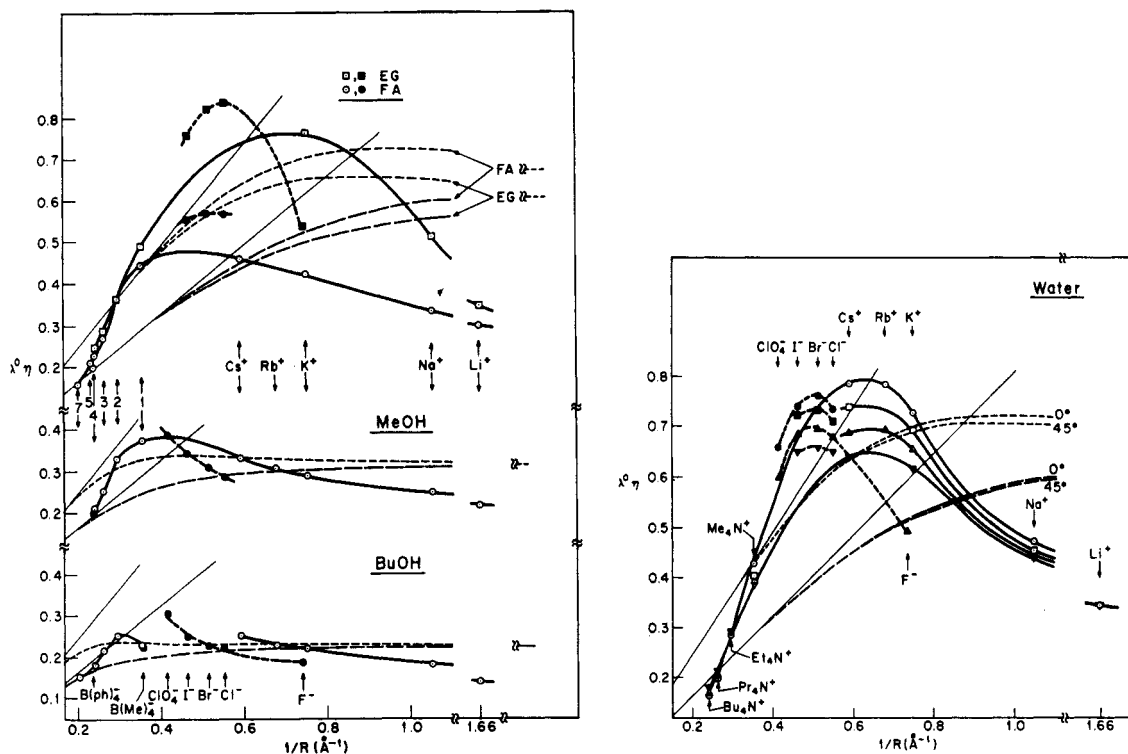
Fig. 6. Comparisons of the extended Hubbard-Onsager theoretical values of $\lambda_o \eta_o$ with the experimental values for ethylene glycol (EG), formamide (FA), methanol (MeOH), 1-butanol (BuOH) and water, O, 0°C; □, 10°C; and △, 45°C. [Reported with permission of the authors of Ref. 19.].

no means the only contributing factor. One serious problem is evident in the data for 1-butanol in this figure. The data for the Me_4N^+ ion is less than that for the Cs^+ ion and that for Me_4B^- ion is less than that for the ClO_4^- ion. Thus, there are definite discontinuities evident in both the cation and anion curves. It would appear that the mechanism of ionic transport is different for small and large ions in long chain hydrogen bonded solvents although it is not clear whether this is a dielectric effect or even if it is common to all types of solvents.

The results shown in Fig. 6 for water at three temperatures indicated the problems encountered in trying to account for the unique properties of $\lambda_o \eta$ in aqueous solutions by an appeal to only one effect, the dielectric friction effect. Neither the ion size dependence, the large negative temperature dependence of $\lambda_o \eta$ for the alkali metal and halide ions nor the positive temperature dependence of the R_4N^+ ions are predicted by the HO theory. In an attempt to explain the temperature coefficient for the Cs^+ ion, Nakahara and coworkers[23] were forced to postulate a special mechanism which they refer to as "passing through cavities" but Reddy and Berkowitz[15] were unable to detect such a mechanism in a computer simulation. It should be noted that in the cosphere model no special mechanism is required for the Cs^+ ion. In general the extended Hubbard-Onsager theory predicts almost zero temperature dependence of the Walden product for aqueous solutions and consequently is correct only for the Li^+ ion.

The temperature dependencies predicted by the Eqs. (6-9) is small for all solvents. This is easily seen in Eq. (9). Since both τ and η have about the same temperature dependence, R_{HO} varies approximately as the one fourth power of $1/\varepsilon_o$ and the temperature dependence of $\lambda_o \eta$ is small for all ions in most nonaqueous solvents.

For the pressure data shown in Fig. 3a, this theory again predicts a positive pressure coefficient of $\lambda_o \eta$ for the Li^+ ion in water but not the initial negative coefficient for most of the other ions. In methanol and other nonaqueous solvent τ as a function of pressure have not been reported so that an unambiguous evaluation of the theory is not possible.

Evans et al.[19] have also studied the effect of high charge and found the HO theory accounts roughly for the maximum magnitude but not for the size dependence of $\lambda_o \eta$.

MOLECULAR APPROACH

Ideally the mechanism of ionic transport would be described in terms of ion-solvent interactions and molecular motions of the solvent molecules rather than relying on a continuum model. A start in the direction has been made[25] with the result that the use of a hard sphere distribution function and molecular dynamics radial distribution functions for water give increasingly better fits to the experimental data. However, in a recent monograph dedicated to ionic solvation[26] it was pointed out that "the continuum model predictions of ionic mobility, although they are in qualitative agreement with experiment, are too far off the mark to claim that all important physical mechanisms have been accounted for. On the other
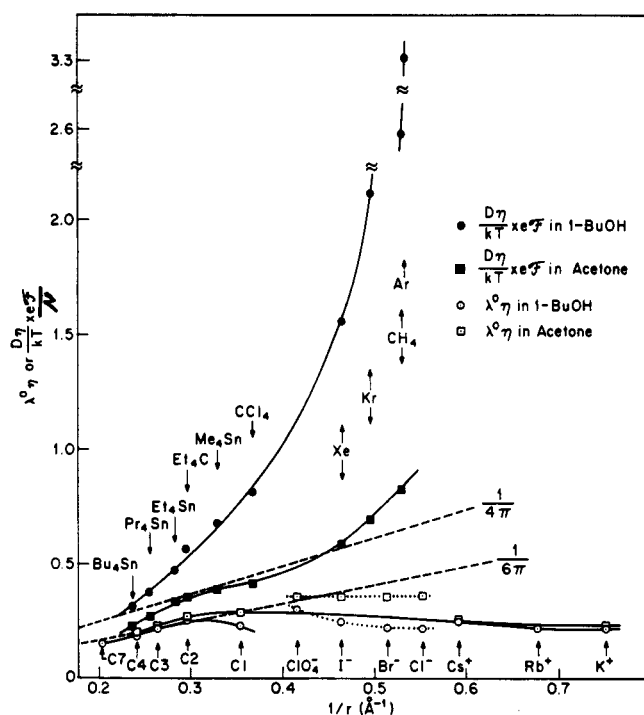
Fig. 7. Comparison of the conductance-viscosity product and diffusion-viscosity
products in 1-butanol and acetone at 25°C.

Table I. Hydrodynamic Frictional Coefficients ($f = kT/D\eta\pi r$) for Symmetrical Solutes

Solvent	Temperature, °C	CCl$_4$ ($r = 2.73$ Å)	Et$_4$C ($r = 3.40$ Å)	Me$_4$Sn ($r = 3.06$ Å)	Et$_4$Sn ($r = 3.55$ Å)	Pr$_4$Sn ($r = 3.94$ Å)	Bu$_4$Sn ($r = 4.26$ Å)
Hexane	25	4.15	—	4.00	4.26	4.68	5.07
Decane	25	3.29	3.30	3.18	3.52	4.05	4.47
Tetradecane	25	2.54	2.80	2.51	2.89	3.33	3.77
	40	2.65	—	2.60	3.02	3.39	3.98
Acetonitrile	25	4.24	—	4.11	4.47	4.85	—
Acetone	10	4.54	4.05	4.17	4.16	4.58	5.18
	25	4.36	4.09	4.18	4.17	4.65	5.08
Methanol	10	3.75	3.74	3.64	4.00	4.36	4.76
	25	3.87	3.74	3.77	4.03	4.37	4.73
	40	3.95	3.81	3.86	4.06	4.48	4.71
Ethanol	25	2.96	—	3.16	3.59	—	4.70
2-Propanol	10	2.23	2.71	2.38	2.91	3.35	3.65
	25	2.51	2.91	2.61	3.13	3.55	3.82
1-Butanol	10	2.01	2.37	2.18	2.75	3.17	3.60
	25	2.21	2.56	2.38	2.93	3.31	3.69
1-Octanol	10	1.49	—	1.52	1.74	2.31	2.70
	25	1.67	—	1.72	2.04	2.51	2.98
	40	1.90	—	1.88	2.27	2.75	3.16

hand, the numerical success of the molecular theory may well be fortuitous in view of the nature of the approximations made and it would be most desirable to perform more rigorous computations with a more realistic model for the dynamic interactions." One could add to this the fact that the cosphere model works well in cases where structural effects in the ionic cosphere are large. This suggests that a molecular theory is needed that takes into account the actual physical properties of the cosphere. At present our experimental knowledge of this domain is almost nonexistent but the recent precise dielectric relaxation studies of Barthel and coworkers are most promising in this regard.

DIRECT EVALUATION OF THE f FACTOR

The theories outlined above are concerned with accounting for the effect of the ionic charge on the motion of ions and attribute all deviation from Stokes' law to that effect while the other limitations of Stokes' law are mainly ignored. In this regard it has been demonstrated by Monte Carlo[27] evaluation of self diffusion that Stokes' law holds for hard spheres in a solvent continuum for the perfect slip condition. From this result Evans and coworkers[28, 29] concluded that the Walden product for uncharged particles in real liquids, if measurable, could be compared to the Walden product for charged particles of the same size and any differences could be attributed to the effect of the ionic charge.

Proceeding along these lines Evans and coworkers measured the diffusion coefficient of a considerable number of spherical nonelectrolytes of varying size in many of the solvents used by the solution chemist. They were able to show that for any given uncharged spherical molecule the quantity $D_0\eta^P$ was a constant in all solvents studied. Furthermore, the quantity P which is a constant for any given solute was found to be a known linear function of the radius of the solute molecule. Thus, it is possible to calculate diffusion coefficients with reasonable precision without any approximations.

Since Stokes' law for limiting diffusion coefficients is similar to Eq. (1) and is given by

$$D_0\eta = kT/f\pi R \qquad (10)$$

where k is the Boltzmann constant and T the Kelvin temperature. From Eq. (10) and the experimental values of D_0 a value of the factor f can be calculated for each solvent system as a function of R.

$$f = kT/D_0\eta\pi R \qquad (11)$$

Using the procedure Evans obtained the values of f shown in Table I for three temperatures. It is clear that most entries are less than 4, the perfect slip condition. As a matter of fact f reaches quite low values as the carbon chain of the alcohols increase. It is also clear that f increases with increasing temperature.

These results can be seen more clearly in Fig. 7 where $\lambda_0\eta$ or $D_0\eta/Fe$ are plotted as a function of the reciprocal crytallographic radii for several nonelectrolytes and ions in t-BuOH and acetone. It can be seen that at any ionic size $\lambda_0\eta$ is considerably lower than its diffusion counterpart particularly for the smaller inert gases in t-BuOH

By rearrangement of Eq. (2) one can obtain

$$Fe/\lambda_0\eta - f\pi R^3 = B \qquad (12)$$

and the experimental value of f obtained from diffusion coefficients can be used to calculate B', the deviation from Stokes' law attributed to the ionic charge.

It is clear from preliminary calculations that this procedure does not improve the fit of the Zwanzig or Hubbard-Onsager theories to the experimental data. An experimental evaluation of the physical properties of the ionic cospere is still an essential prerequisite for the development of a realistic theory of ionic mobilities

REFERENCES

1. C.A. Kraus and R.M. Fuoss, J. Am. Chem. Soc. 55, 21 (1933).
2. T. Shedlovsky, J. Am. Chem. Soc. 54, 411 (1932).
3. L.G. Longsworth J. Am. Chem. Soc. 54, 2741 (1932).
4. D.F. Evans and M.A. Matesich, in Techniques in Electrochemistry, Vol. 2, Chap. 1 (E. Yeager and A.J. Salkind, eds.), Wiley, New York (1973).
5. R.L. Kay, in Techniques in Electrochemistry, Vol. 2, Chap. 2 (E. Yeager and A.J. Salkind, eds.), Wiley, New York (1973).
6. S.I. Smedley, The Interpretation of Ionic Conductivity in Liquids, Chap. 2, Plenum Press, New York (1980).
7. R.M. Fuoss and K-L. Hsia, Proc. Natl. Acad. Sci. 57, 1550 (1967).
8. R.L. Kay, J. Am. Chem. Soc. 82, 2099 (1960).
9. R.L. Kay, D.F. Evans and M.A. Matesich, in Solute-Solvent Interactions, (J. F. Coetzee and J. F. Ritchie, eds.), Vol. 2, p. 105, Marcel Dekker, New York (1976)
10. R.L. Kay, G.P. Cunnigham and D.F. Evans, in Hydrogen-Bonded Solvent Systems, Taylor and Franes, London (1968).
11. R.L. Kay, in Water, A Comprehensive Treatise (F. Franks, ed.), Vol. 3, p. 173, Plenum Press, New York (1973).
12. R.W. Gurney, Ionic Processes in Solution, McGraw-Hill, New York (1953).
13. H.S. Frank and W-Y Wen, Discussions Faraday Soc. 24, 133-140 (1957).
14. R.L. Kay and D.F. Evans, J. Phys. Chem. 70, 2325-2335 (1966).
15. M.R. Reddy and M. Berkowitz. J. Chem Phys. 88, 7104 (1988); J. Solution Chem. 17, 1183 (1988).
16. K.E. Bett and J.B. Cappi, Nature 207, 620 (1965).
17. R. Zwanzig, J. Chem. Phys. 38, 1603 (1963); 52, 3625-3628 (1970).
18. M. Born, Z. für Physik 1, 221-249 (1920).
19. D.F. Evans, T. Tominaga, J.B. Hubbard and P.G. Wolynes, J. Phys. Chem., 83, 2669 (1979).
20. E. Inada, Rev. Phys. Chem. Jap., 46, 19-30 (1976).
21. T.L. Broadwater, T.J. Murphy and D.F. Evans, J. Phys. Chem., 80, 753-757 (1976).
22. (a) J. Hubbard and L. Onsager, J. Chem. Phys., 67, 4850-4857 (1977); (b) J.B. Hubbard, J. Chem. Phys., 68, 1649-1664 (1978).
23. M. Nakahara, T. Török, N. Takesawa and J. Osugi, J. Chem. Phys., 76, 5145 (1982).
24. K. Ibuki and M. Nakahara, J. Phys. Chem., 91, 1864-1867, 4411-4414, 4414-4416 (1987).
25. P. Colonomos and P.G. Wolynes, J. Chem. Phys., 71, 2644 (1979).
26. J.B. Hubbard and P.G. Wolynes, in The Chemical Physics of Solvation, Part C., Chap. 1, (R.R. Dogonadze, E. Kalman, A.A. Kornyshev and J. Ulstrup, eds.), Elsevier, Amsterdam (1988).
27. B.J. Alder, D.M. Gass and T.E. Wainwright, J. Chem. Phys., 53, 3813 (1970).
28. D.F. Evans, C. Chan and B.C. Lamartine, J. Amer. Chem. Soc., 99, 6492-6496 (1977).
29. D.F. Evans, T. Tominaga and C. Chan, J. Solution Chem., 8, 461 (1979).