

# Ionic Mobility and Ultrafast Solvation: Control of a Slow Phenomenon by Fast Dynamics

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## Introduction

What determines the ionic conductivity of an electrolyte solution has remained a problem of great interest to chemists for more than a century.<sup>1–3</sup> Such long-standing interest stems not only from its relevance in many chemical and biological applications, but also from the many fascinating, often anomalous, behaviors that ionic conductivity exhibits in a large number of solvents. Most often discussed of these properties are the concentration and the nonmonotonic ion size dependencies. However, even after century-old debates and discussions, neither of the above two problems has been satisfactorily resolved. The mobility of an ion in a polar solvent is determined by its complex interactions with the surrounding polar molecules; these interactions are long-ranged and anisotropic. In addition, the dynamics of polar liquids were very poorly understood until recently.

There have been several significant developments in the recent past in understanding the dynamics of dense liquids that make the study of this fundamental problem now even more interesting. Perhaps the most important development is the discovery that the polar solvation dynamics in most common solvents is *strongly biphasic with an initial ultrafast component which is in the femtosecond regime* and which often contributes 60–80% to the total energy relaxation.<sup>4–9</sup> The discovery of this ultrafast component raises several interesting questions. For example, what can be the role of this component in determining the mobility of the ions? Both the solvation dynamics of an ion and the dielectric friction on it are expected to be intimately related. The second notable

development has been in the microscopic understanding of the relation between diffusion and viscosity in dense liquids.<sup>10–11</sup> In the study of ionic conductivity, one usually assumes that diffusion of ions is related to the solvent viscosity by the Stokes law, which is *unsatisfactory* for such small ions as Li<sup>+</sup> and Na<sup>+</sup>. Recent theoretical developments<sup>10–11</sup> can now provide microscopic description of diffusion of *small* solutes in dense liquids.

The starting point of most discussions on ionic conductivity is Kohlrausch's law which is expressed as<sup>2</sup>

$$\Lambda_m = \Lambda_0 - \kappa\sqrt{c} \quad (1)$$

where  $\Lambda_m$  represents the equivalent molar conductivity and  $\Lambda_0$  its limiting value at *infinite* dilution.  $\kappa$  is a coefficient that is found to depend more on the nature of the electrolyte (that is, whether it is uni-univalent or bi-univalent, etc.) than on its specific identity.  $\Lambda_0$  is generally obtained by extrapolating experimental  $\Lambda_m$  at zero ionic concentration and is one of the most easily accessible transport quantities. The limiting ionic conductivity ( $\Lambda_0$ ) can be determined by applying Walden's rule which states that, for a particular ion, the product of  $\Lambda_0$  with solvent viscosity ( $\eta_0$ ) should be constant:<sup>2</sup>

$$\Lambda_0\eta_0 = \text{constant} \quad (2)$$

Even though approximate, expressions 1 and 2 are the two most important statements on ionic conductivity of an electrolyte solution. The first one has been explained in terms of the Debye–Hückel–Onsager theory<sup>12–13</sup> which also provides an expression for the prefactor  $\kappa$ ; it is found to depend, among other things, on the limiting ionic conductivity,  $\Lambda_0$ . Equation 1 has been confirmed for very low concentration. Equation 2 can be rationalized in terms of the well-known Stokes law<sup>2</sup> which predicts that the friction on the ion is proportional directly to the viscosity ( $\eta_0$ ) and inversely to the crystallographic radius of the ion ( $r_{\text{ion}}$ ). The use of Einstein's relation between the friction and the diffusion coefficient (which is essentially  $\Lambda_0$ ) then produces eq 2. Experimental results,<sup>14–15</sup> however, indicate that the ionic mobilities in polar solvents do not always decrease monotonically with increasing radius. Instead, there is often a maximum as  $\Lambda_0\eta_0$  is plotted against  $r_{\text{ion}}^{-1}$ , as shown in Figure 1 for both protic and aprotic solvents. In fact, the breakdown of Walden's rule (and of Stokes's law) has been observed for all the solvents studied and can be regarded as *universal*.

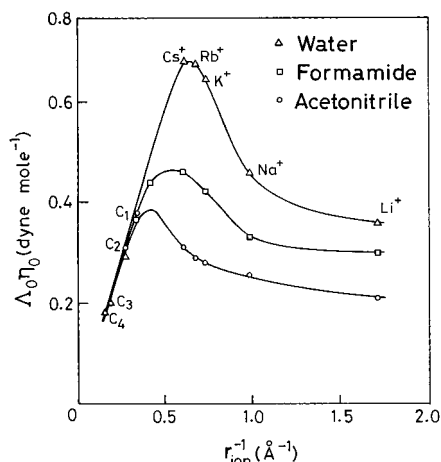
What makes the experimental results deviate so strongly from Walden's rule? Two completely different explanations have been put forward to understand this problem. The first and the oldest one is the *solvent-berg* model.<sup>2</sup> In this picture it is postulated that the solvent molecules immediately adjacent to the ion are rigidly bound to it. The translational movement of the ion is, therefore, the

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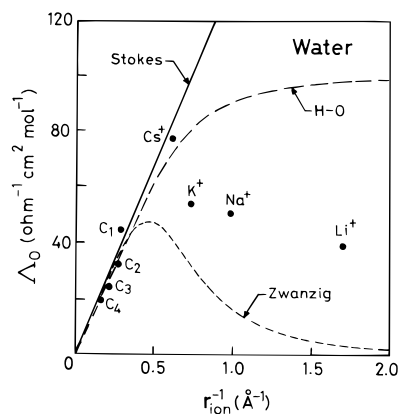
**FIGURE 1.** Experimental<sup>14–15</sup> values of the Walden product ( $\Lambda_0\eta_0$ ) of rigid, monpositive ions in water (open triangles), acetonitrile (open circles), and formamide (open squares) at 298 K plotted as a function of the inverse of the crystallographic ionic radius,  $r_{\text{ion}}^{-1}$ . The solid line in each case is simply an aid to the eye. The crystallographic radii of the ions are taken from Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr. B* **1969**, *25*, 925–946. Here, the tetraalkylammonium ions are represented by  $C_1$ – $C_4$  where  $C_n = (C_nH_{2n+1})_4N^+$ ,  $n$  being 1, 2, 3, or 4.

movement of this kinetic unit termed as *solvent-berg*. The effective size of the solvent-berg is larger than that of the ion, and therefore, its mobility is much reduced from that of the bare ion. However, it has proved very difficult to quantify this model.

The second, more successful, model is based on a *continuum description* of the solvent. Because of the long-range nature of the ion–dipole interaction potential, it was originally believed that this interaction can be replaced by the interaction of the ion with a continuum solvent and the molecularity of interaction might not be important. This model was originally introduced by Born who modified the usual Stokes–Einstein hydrodynamic model of diffusion by coupling the ionic field of the solute with the bulk polarization mode of the solvent.<sup>3</sup> According to his picture, the ionic motion disturbs the equilibrium polarization of the solvent, and the relaxation of the ensuing nonequilibrium polarization dissipates energy, thereby enhancing the friction on the ion. He coined the term *dielectric friction* to describe this extra dissipative mechanism and expressed the total friction ( $\zeta_{\text{total}}$ ) experienced by the ion moving through the viscous continuum as follows:

$$\zeta_{\text{total}} = \zeta_{\text{bare}} + \zeta_{\text{DF}} \quad (3)$$

where  $\zeta_{\text{DF}}$  is the dielectric friction and  $\zeta_{\text{bare}}$  is the friction arising from the Stokes law due to the shear viscosity ( $\eta_0$ ) of the solvent. This model was further developed by Fuoss,<sup>16</sup> Boyd,<sup>17</sup> and Zwanzig.<sup>18</sup> The final expression (due to Zwanzig) for dielectric friction leads to an overestimation of friction for small ions. In an attempt to rectify this lacuna, Hubbard and Onsager (H–O) studied the ionic mobility problem in great detail<sup>19</sup> within the framework of the continuum picture. They proposed a theory which can be regarded (in the language of Wolynes)<sup>20</sup> as the



**FIGURE 2.** Comparison between the experimental results on  $\Lambda_0$  and those from continuum theories. The experimental values of the limiting ionic mobility ( $\Lambda_0$ ) of rigid, monpositive ions in water at 298 K are plotted as a function of the inverse of the crystallographic ionic radius,  $r_{\text{ion}}^{-1}$ . The experimental results are denoted by the solid circles. The solid line represents the predictions of Stokes's law (with the slip boundary condition), the large-dashed line the Hubbard–Onsager theory, and the small-dashed line the theory of Zwanzig (with the slip boundary condition). Note that the Stokes law is valid for tetraalkylammonium ions.

“ultimate achievement in a purely continuum theory of ionic mobility”.

In Figure 2, the predictions of the continuum theories have been compared with the experimental results on ionic mobility in water. It is clear from this figure that although the simple expression of Zwanzig<sup>18</sup> can explain the observed nonmonotonic dependence of  $\Lambda_0$  on  $r_{\text{ion}}^{-1}$ , it fails to reproduce the experimentally observed ionic mobilities as it overestimates the dielectric friction. The Hubbard–Onsager theory<sup>19</sup> is satisfactory up to intermediate-sized ions, but fails to describe the sharp decrease for small ions.

Clearly, the above continuum model based theories fail to describe the ion transport in polar solvents. There are many reasons for this failure, which have been extensively discussed in the literature.<sup>20–21</sup> The most important is the representation of the real solvent by a viscous dielectric continuum. No molecularity of the solvent was considered. In addition, the description of solvent dynamics was vastly inadequate.

## Development of Microscopic Theories

To overcome the limitations of the continuum theories, Wolynes<sup>20–21</sup> pioneered a microscopic approach which was applied later by Colonomos and Wolynes<sup>21</sup> in an attempt to explain the experimentally observed anomalous ionic mobility at zero ionic strength. Their theory was based on Kirkwood's formula for dielectric friction on a solute molecule<sup>22</sup>

$$\zeta_{\text{DF}} = \frac{1}{3k_B T} \int_0^\infty dt \langle \mathbf{F}_{\text{id}}(0) \mathbf{F}_{\text{id}}(t) \rangle \quad (4)$$

where  $\mathbf{F}_{\text{id}}(t)$  is the force acting on the ion due to the ion–dipole interaction only,  $k_B$  is Boltzmann's constant,  $T$  is the temperature (K), and  $\langle \dots \rangle$  stands for the ensemble

averaging. The total friction is obtained by adding this friction to the bare friction (see eq 3).

The results obtained were far superior to any previous approach and suggested that molecularity of solute–solvent interactions is certainly important and needs to be properly included for successful descriptions of ionic mobility of small solutes. The limitations of Wolynes's approach<sup>20–21</sup> were that the solvent was treated as an overdamped Debye liquid characterized by a single relaxation time,  $\tau_D$ , and that the self-motion of the ion was neglected. Nevertheless, Wolynes's work<sup>20–21</sup> is a landmark and has served as the starting point of many subsequent discussions in this field.

Recently, the above microscopic approach has been generalized<sup>23–26</sup> to include the ultrafast dynamics of dipolar solvents,<sup>4–9</sup> a proper description of the intermolecular orientational correlations present in a dense polar liquid and the self-motion of the ion. The microscopic theory is based on a simple physical picture. Consider a tagged, singly charged ion in a dipolar liquid. For spherical solute ions, the interaction between the ion and the dipolar liquid molecules can be separated into two parts,<sup>20–21,23</sup> as envisaged in eq 3. The first, *nonpolar* part (referred to as  $\zeta_{\text{bare}}$ ) can be calculated by using the recently developed mode coupling theory (MCT).<sup>10–11</sup> The latter assumes that, in a *dense* liquid, the primary source of fluctuation in the force acting on a molecule originates from the latter's coupling to the fluctuations of the microscopic solvent density. There are several ways to obtain the time correlation function of this nonpolar force, all leading to the same final expression. However, it is found that the theoretical<sup>11</sup> values of  $\zeta_{\text{bare}}$  are surprisingly close to the ones given by Stokes's law. The second part originates from the long-range ion–dipole interaction and, as already mentioned, is referred to as the dielectric friction,  $\zeta_{\text{DF}}$ . The latter is dominated by the long-wavelength solvent polarization fluctuations. Here, it is particularly important to note that these long-wavelength polarization fluctuations are the ones primarily responsible<sup>7–9</sup> for the ultrafast polar solvation dynamics observed in experiments. As the size of the ion decreases,  $\zeta_{\text{bare}}$  decreases, but  $\zeta_{\text{DF}}$  increases rapidly. The diffusion coefficient of the ion is given by the Einstein relation  $D_T^{\text{ion}} = k_B T / \zeta_{\text{total}}$ , where  $\zeta_{\text{total}}$  is given by eq 3.

While only the zero frequency dielectric friction,  $\zeta_{\text{DF}}(\omega \rightarrow 0)$ , is required to find the limiting ionic conductivity in solution, the frequency (or time) dependent dielectric friction,  $\zeta_{\text{DF}}(\omega)$  (or  $\zeta_{\text{DF}}(t)$ ), is often required in theoretical studies of other problems. For example, in the study of the intramolecular proton ( $\text{H}^+$ ) transfer reaction<sup>28a</sup> and in vibrational relaxation<sup>28b</sup> in dipolar liquids, the frequency, dependence of dielectric friction plays a crucial role. The microscopic expression for  $\zeta_{\text{DF}}(\omega)$  is given by<sup>24–27</sup>

$$\zeta_{\text{DF}}(\omega) = \frac{2k_B T \rho_0}{3(2\pi)^2} \int_0^\infty dt e^{-i\omega t} \times \int_0^\infty dk k^4 S_{\text{ion}}(k, t) |c_{\text{id}}^{\text{L}}(k)|^2 S_{\text{solvent}}^{\text{L}}(k, t) \quad (5)$$

where  $c_{\text{id}}^{\text{L}}(k)$  and  $S_{\text{solvent}}^{\text{L}}(k, t)$  are the longitudinal compo-

nents of the ion–dipole direct correlation functions and the *orientational* dynamic structure factor of the pure solvent, respectively. The former describes the *effective coupling* between the ion and the solvent molecules while the latter contains the relevant solvent static and dynamic orientational correlations, as probed by the ion's electric field.  $\rho_0$  is the average number density of the solvent.  $S_{\text{ion}}(k, t)$  denotes the self-dynamic structure factor of the ion. The  $\omega = 0$  limit of eq 5 provides the macroscopic friction which is related to the limiting ionic conductivity,  $\Lambda_0$ .

The above microscopic expression has a very simple physical interpretation: It couples the motion of the ion (described by  $S_{\text{ion}}(k, t)$ ) with that of the solvent (described by  $S_{\text{solvent}}^{\text{L}}(k, t)$ ) via the effective, length dependent, coupling constant,  $c_{\text{id}}^{\text{L}}(k)$ . The coupling is present on all length scales; hence, the integration is over all wavenumbers ( $k$ ).

The limiting ionic conductivity,  $\Lambda_0$  is calculated by using the well-known *Nernst–Einstein* relation<sup>2</sup>

$$\Lambda_0 = \frac{(zF)^2 k_B T}{RT \zeta_{\text{total}}} \quad (6)$$

where  $z$  is the valency on the ion,  $F$  the amount of electricity carried by 1 gram-equivalent of the conducting ion, and  $R$  the universal gas constant.

**Relation of Dielectric Friction with Ultrafast Solvation Dynamics.** The solvation energy time correlation function (STCF) is defined by<sup>4–6</sup>

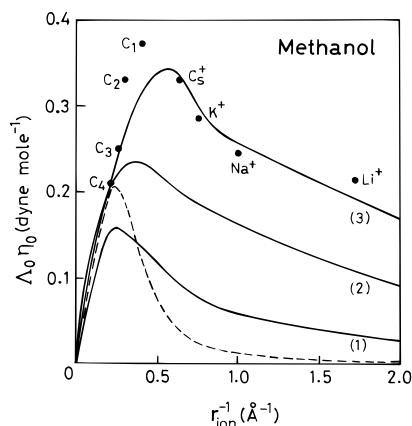
$$S(t) = \frac{\langle \Delta E_{\text{solv}}(0) \Delta E_{\text{solv}}(t) \rangle}{\langle |\Delta E_{\text{solv}}(0)|^2 \rangle} \quad (7)$$

where  $\Delta E_{\text{solv}}(t)$  is the time dependent fluctuation in the solvation energy of the polar solute. The molecular theory described above has been used to derive a microscopic expression for the solvation energy time correlation function (STCF) which is given by<sup>7,9</sup>

$$S(t) = A \int_0^\infty dk k^2 S_{\text{ion}}(k, t) |c_{\text{id}}^{\text{L}}(k)|^2 S_{\text{solvent}}^{\text{L}}(k, t) \quad (8)$$

where  $A$  is the normalization constant determined by the equilibrium value of STCF,  $S(t=0)$ . Comparison of eqs 5 and 8 shows that the dynamics that determine both the dielectric friction and the ion solvation dynamics are essentially the *same*, with one significant difference: the friction is more sensitive to the local structure and dynamics than the solvation. Another important point to note is that the dielectric friction (hence the ionic mobility) is determined by the integration over all time. Therefore, the presence of a slow component in the dynamics can make a significant contribution to the friction, which was the logic for the use of an overdamped description in the earlier works.

The effects of ultrafast inertial solvation dynamics on ionic mobility are shown in Figure 3, where the effects of sequential addition of the fast modes are plotted for liquid methanol. The mobility decreases drastically when all the ultrafast modes are absent. It is interesting to note that,



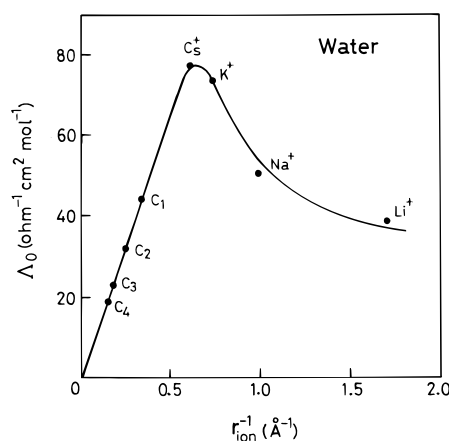
**FIGURE 3.** Effect of the *sequential addition* of the ultrafast component of the solvent orientational motion on the *limiting* ionic mobility in methanol at 298 K. The values of the Walden product ( $\Lambda_0\eta_0$ ) are plotted as a function of the inverse ionic radius. The curves labeled 1, 2, and 3 are the predictions of the present molecular theory including the first (slowest) one, the first two, and all three Debye relaxations of the experimentally obtained dielectric relaxation data by Kindt and Schmuttenmaer [Kindt, J. T.; Schmuttenmaer, C. A. *J. Phys. Chem.* **1996**, *100*, 10373–10379]. The experimental results of the Walden product for different ions are denoted by the solid circles. The dashed line represents the predictions of the theory of Zwanzig.<sup>18</sup>

in the complete absence of the fast modes, the molecular theory predicts ionic mobility comparable to the continuum model of Zwanzig.<sup>18</sup> It is also interesting to note that the viscosity plays no role in this dependence of  $\Lambda_0$  on the ultrafast modes. The same behavior has been found for ionic mobilities in water.

The physical origin of this large effect of ultrafast solvation on limiting ionic conductivity is easy to understand. The presence of a sizable ultrafast component allows a rapid decay of the polarization disturbance created by the ion's motion. This dramatically reduces the dissipation of the total energy involved. In the earlier studies, the decay of this disturbance was assumed to proceed *only through the slowest channel!*

## Analysis of Experimental Results

The above theory has been applied to understand ionic mobility in several common solvents. The calculations of the wavenumber ( $k$ ) dependent ion–dipole direct correlation function,  $c_{id}^L(k)$ , and the solvent orientational dynamic structure factor,  $S_{\text{solvent}}^L(k, t)$ , have been described elsewhere;<sup>7,24–27</sup> here we mention only the bare essentials. The pure solvent property,  $S_{\text{solvent}}^L(k, t)$ , is obtained by using an inversion procedure<sup>7</sup> which uses experimental results on dielectric and Kerr relaxations. The static, orientational, solvent pair correlation functions have been obtained from the calculations of Raineri et al.<sup>8</sup> The ion–solvent coupling function  $c_{id}(k)$ , on the other hand, has been obtained from an analytic theory,<sup>29</sup> called the mean-spherical approximation, which assumes that both solute and solvent molecules are spheres, with a point ion and a point dipole at their respective centers. While this treatment provides an accurate description of



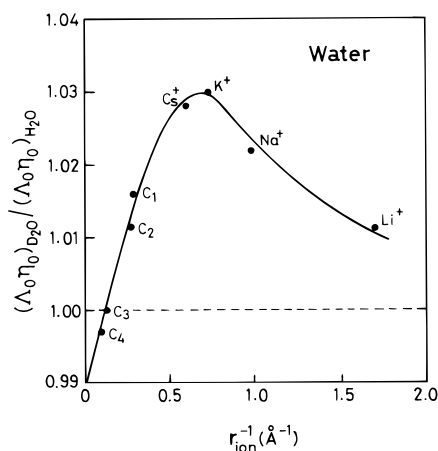
**FIGURE 4.** Values of the limiting ionic conductivity ( $\Lambda_0$ ) of rigid, monovalent ions plotted as a function of the inverse ionic radius  $r_{\text{ion}}^{-1}$  in water at 298 K. The solid line represents the predictions of the present microscopic theory. The solid circles denote the experimental results.

the long-range correlations, its description of the short-range correlations is only approximate. This is partly justified in the present case because we are studying primarily the effects of long-range polar interactions.

**Ionic Mobility in Water: Solvent Isotope Effect.** The extended three-dimensional hydrogen bonding greatly influences both the static and the dynamic properties of liquid water. Recently, Fleming and coworkers<sup>4a</sup> have shown that the dynamical solvent response of water to a laser-induced external perturbation is ultrafast and 70–80% of the total energy relaxation is completed within 55 fs. The rest is carried out by a much slower dynamics with a time constant in the picosecond regime. These observations have been corroborated by several theoretical<sup>7–9</sup> and computer simulation studies.<sup>5</sup> Theoretical studies<sup>7d,30</sup> reveal that the ultrafast solvation could arise from the intermolecular vibration of the O–H···O hydrogen bond which manifests as a collective excitation at 193  $\text{cm}^{-1}$  in the far-infrared (far-IR) line shape studies. It is probably no surprise that even the solvation dynamics of water is determined by its hydrogen bond network! However, early studies on ionic mobility have completely neglected this ultrafast solvent response.

The results of theoretical studies for  $\Lambda_0$  in water at room temperature for monovalent tetraalkylammonium and alkali-metal ions are shown in Figure 4, where  $\Lambda_0$  is plotted as a function of the inverse of the crystallographic ionic radius. The agreement with the experimental results<sup>14</sup> is particularly encouraging since the theory could successfully demonstrate the breakdown of the Stokes law. The present theory also predicts quantitatively the experimental  $\Lambda_0$  of small ions like  $\text{Na}^+$  and  $\text{Li}^+$ .

The complete deuteration of liquid water brings out subtle changes in both static and dynamic properties of water. The isotopic substitution leads to stronger hydrogen bonding and hence more structural order in  $\text{D}_2\text{O}$  compared to that in  $\text{H}_2\text{O}$ . This relatively more stable network increases both the viscosity and the Debye relaxation time ( $\tau_D$ ) by about 25% and reduces  $\Lambda_0$  by about the same.<sup>14–26</sup> However, this variation alone does not

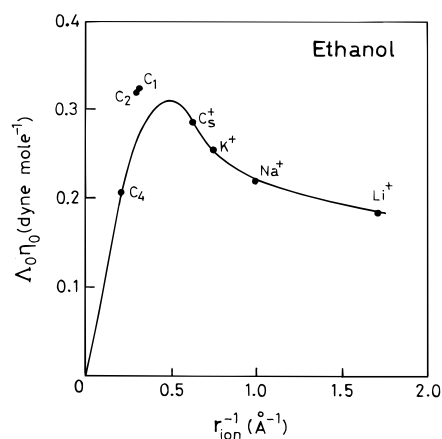


**FIGURE 5.** Solvent isotope effect on limiting ionic conductivity in water at 298 K. The values of the ratio  $(\Lambda_0\eta_0)_{D_2O}/(\Lambda_0\eta_0)_{H_2O}$  for various ions are plotted as a function of the inverse of the crystallographic ionic radius. The viscosity ( $\eta_0$ ) values of normal water ( $H_2O$ ) and heavy water ( $D_2O$ ) used in this calculation are 0.8904 and 1.0970 cP, respectively [CRC Handbook of Chemistry and Physics 57th ed.; Weast, Ed.; CRC Press: Boca Raton, FL, 1976].

reflect the whole picture because the ratio  $(\Lambda_0\eta_0)_{D_2O}/(\Lambda_0\eta_0)_{H_2O}$  varies systematically from unity when plotted as a function of the inverse of the crystallographic ionic radius. The molecular theory can capture this aspect as shown in Figure 5. This indicates the probable participation of the solvent dynamics in determining the  $\Lambda_0$ . Theoretical studies<sup>7d</sup> on solvation dynamics in  $D_2O$  have shown that while the initial ultrafast response remains unchanged both in amplitude and in time constant compared to those in normal water ( $H_2O$ ), the long time part is slowed by about 20%. However, the effects of the deuteration on ionic mobility are rather small, the maximum being only about 3. It does not affect the ultrafast inertial part of the force correlation function but only the slow, diffusive part whose contribution to the whole is small.

**Ionic Mobility in Alcohols.** Ionic mobility of rigid cations has been studied extensively in the lower members of monohydroxy straight-chain alcohol series.<sup>14</sup> Here the mobility is lower than that for water and decreases systematically as one studies the higher alcohols. One of the unique problems here has been the rather large value of  $\Lambda_0$  for small ions like  $Li^+$  or  $Na^+$ . In particular, the reduction in  $\Lambda_0$  after the maximum is rather small in ethanol which is different from that in methanol. Another problem of interest is the validity of the solvent-berg model which has been proposed for alcohols.

Recent experimental results on solvation dynamics in alcohols have revealed rather diverging results. Except for methanol, Horng *et al.*<sup>4d</sup> found no evidence of an ultrafast component in polar solvation dynamics. Joo *et al.*,<sup>4c</sup> on the other hand, observed a near *universal* ultrafast component in all the monohydroxy alcohols, of the time constant 60–70 fs. The amplitude of this component was found to decrease with increasing chain length. It has been argued recently<sup>9</sup> that the ultrafast component in higher alcohols is due to nonpolar solvation and, therefore, should have no effect on ionic mobility.<sup>31</sup>

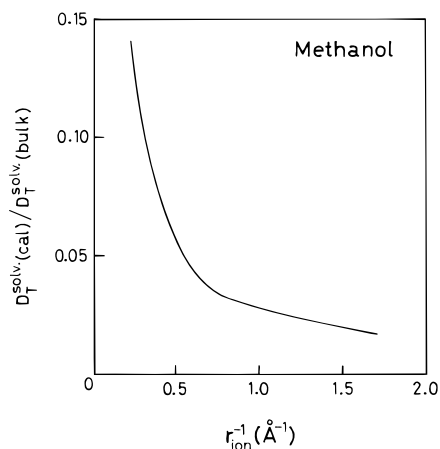


**FIGURE 6.** The values of the Walden product  $(\Lambda_0\eta_0)$  of rigid, monovalent ions plotted as a function of the inverse ionic radius in ethanol at 298 K. The solid line represents the theoretical predictions, and the filled circles denote the experimental results.

The nonmonotonic size dependence of ionic mobilities in methanol is already shown in Figure 3. In Figure 6, the theoretical ionic mobilities at room temperature are shown for ethanol. The experimental results<sup>14</sup> are also presented in the same figure. Here again the agreement between the molecular theory<sup>24–27</sup> and the experiment is excellent.

**Ionic Mobility in Acetonitrile and Formamide.** Among other solvents, ionic mobility has been investigated extensively for acetonitrile and formamide. Acetonitrile is known to exhibit ultrafast solvation dynamics, with an inertial component of about 70 fs. Studies by Horng *et al.*<sup>4d</sup> have shown that formamide also exhibits a fast component of 100 fs, with a smaller amplitude. Note that these two solvents have completely different molecular arrangements. While acetonitrile rotates almost freely, because of its *nearly* spherical shape, formamide is strongly hydrogen-bonded and is known to exist in a two-dimensional sheetlike structure in the liquid state. In both these solvents the theoretical predictions<sup>25,27</sup> are found to be in good agreement with the experimental results.<sup>14–15</sup> This clearly indicates that the dynamics of the solvent plays the dominant role in determining the ionic mobilities in these complex systems.

**Relative Contribution of Rotational and Translational Solvent Modes.** A question of fundamental importance<sup>20–21,23–27</sup> in the microscopic description of ionic mobility is the relative role of rotational and translational motions of the solvent molecules. Theoretical studies<sup>32</sup> have shown that the translational modes are indeed effective in reducing the magnitude of dipolar dielectric friction in slow solvents. In solvents which exhibit ultrafast solvation dynamics (for example, water, acetonitrile, and methanol), the effects of translational modes are found to be unimportant. This is because the ultrafast polar solvation originates from the long-wavelength polarization modes (or bulk response) which make the contribution of the solvent translational modes negligible. For slow liquids (ethanol, propanol, butanol), however, the situation is different. Here the relative contribution between the rotational and the translational modes can



**FIGURE 7.** Quantification of the Franck–Wen model. The ratio of the calculated solvent diffusion coefficient ( $D_T^{\text{soliv}}(\text{cal})$ ) and the bulk solvent diffusion coefficient ( $D_T^{\text{soliv}}(\text{bulk})$ ) of methanol is plotted as a function of the inverse of the crystallographic ionic radius,  $r_{\text{ion}}^{-1}$ . The calculational procedure is described in detail in ref 25.

even determine the validity of the solvent-berg model. This interesting aspect is further discussed below.

**Solvent-Berg versus Dielectric Friction: Quantification of the Franck–Wen Model.** It was Franck and Wen<sup>34</sup> who suggested that there could be a virtually immobile solvent layer around the ion while the natural dynamics of the pure solvent can prevail at a larger distance. The Franck–Wen model<sup>34</sup> provides the textbook explanation of the breakdown of Walden’s rule in terms of the formation of a solvent-berg around the ion. On the other hand, the dielectric friction model largely ignores this solvent-berg picture. However, it is clear that, for a small ion in a slow solvent (characterized by large  $\eta_0$ ), the solvent-berg model should be valid. Recently,<sup>25,26</sup> it has been shown how the solvent-berg model can be recovered from the present microscopic theory, and the following physical picture has emerged. The solvent molecules close to the ion experience a strong electric field from the ion. The decay of this force depends on the mobility of the ion itself and on the motion of the solvent molecules. When the rotational and the translational motions of the solvent molecule in question are slow, then two things could occur synergistically. First, the dielectric friction on the ion increases which slows the ion. This, in turn, increases the friction on the solvent molecule. This is a back-reaction. As the solvent motion itself is slow, this effect gets magnified. This is described in Figure 7, where the reduction in the value of the self-diffusion coefficient of the nearest-neighbor *solvent molecules* is depicted as a function of inverse ion size. When the size of the ion is small, the reduction is large, implying that solvent molecules next to the ion can be essentially immobile.

### Concentration Dependence of Ionic Mobility: Relaxation of the Ion Atmosphere

The concentration dependence of ionic mobility in strong electrolyte solution exhibits a very rich and complex behavior. The solvent-mediated ion–ion and the ion–solvent Coulombic interactions in concentrated solution

profoundly affect the electrical conductivity of the medium. The square root of concentration ( $\sqrt{c}$ ) dependence of ionic mobility predicted by the Debye–Huckel–Onsager (DHO) theory has only limited validity (valid for  $c \leq 10^{-3}$  mol/L). For moderately concentrated solution ( $c \leq 1$  mol/L), an empirical fit, known as the Shedlovsky equation,<sup>35</sup> was proposed to analyze the conductivity. In addition to the usual  $\sqrt{c}$  term in DHO theory, this equation contains logarithmic and quadratic concentration ( $c^2$ ) dependence. However, the origin of these higher order terms has not yet been fully understood. A microscopic theory which includes the dynamics of the solution and retains the molecularity of the system would be of great help in understanding the molecular origin of the diverse concentration dependence of ionic conductivity in electrolyte solution.

Preliminary investigations<sup>27</sup> have shown that the relative contributions from the rotational and the translational modes can have important consequences in the relaxation of the ion atmosphere in an electrolyte solution. This is an aspect which has not been addressed at all in the Debye–Huckel–Onsager theory of ionic conductivity. Of course, this effect will be important only at moderate to large concentration. The resulting molecular theory has a structure similar to that (eq 5) discussed here.

### Computer Simulation Studies

Recently Lee and Rasaiah<sup>35</sup> have reported detailed computer simulation studies of ionic conductivity of small cations and anions in water. The ion–water intermolecular potentials were obtained by fitting them to the solvation energies of small ion–water clusters. Very good agreement was obtained between simulations and experimental results. These authors also carried out an analysis of the residence times of the nearest-neighbor solvent molecules of the ions. On the basis of these residence times, it was surmised that while a solvent-berg model may be appropriate for  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{F}^-$  ions in water, the dielectric friction model is more appropriate for other ions.

Computer simulation studies have also clarified the origin of the observed difference in the limiting ionic conductivities of the negative ions from those of the positive ones of the same size. The limiting ionic conductance of halide ions in water, when plotted as a function of the inverse of the crystallographic radius, constitutes a curve which is different from that of the alkali-metal ions.<sup>14</sup> This has been explained by Lee and Rasaiah<sup>32</sup> who have shown that this difference could arise from a lack of symmetry between the cation–water and anion–water interactions. The effects of such short-range interactions are yet to be included in a molecular description. Clearly, one requires a microscopic treatment of the bare friction ( $\zeta_{\text{bare}}$  of eq 3).

### Concluding Remarks

It is evident from this Account that considerable progress has been made in recent years in understanding the ion

size and the solvent dependence of ionic mobility. The role of the newly discovered ultrafast polar solvation in enhancing the ionic mobility of small cations is fascinating. It is indeed amusing that such an ultrafast process can profoundly influence the ion diffusion which is inherently a slow phenomenon! Thus, a process which occurs on the time scale of few tens of femtoseconds seems to influence a process taking place on a few tens of picoseconds! The dramatic reduction in the value of the friction on the ion comes from the much enhanced rate of decay of the force correlation function because of the ultrafast component.

There are many problems in this field that remain to be understood. No microscopic understanding of the concentration dependence of the ionic conductivity at intermediate to high concentration has yet evolved. The conductivity of binary mixtures (for example, water and *tert*-butyl alcohol)<sup>36</sup> exhibits an exotic composition dependence which cannot be understood in terms of the continuum models. With the availability of new nonlinear optical techniques, a much better understanding of the details of solvent dynamical response is beginning to emerge. This, in turn, can help in understanding the ionic mobility in many solvents. We can thus look forward to an exciting future of these and related problems of classical physical chemistry, which is currently undergoing a rejuvenation.

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