Friction Coefficients of Ions in Aqueous Solution at 25 °C

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Abstract: The diffusion coefficients of ions and of uncharged solutes in aqueous solution at 25 °C and at infinite dilution are studied by computer simulation using the SPC/E model for water and solute−water potentials employed in previous work (Koneshan, S.; et al. *J. Phys. Chem.* **1998,** *102,* 4193−4204). The mobilities of the ions calculated from the diffusion coefficients pass through a maximum as a function of ion size, with distinct curves and maximums for positive and negative ions in qualitative agreement with experiment. We aim to understand this at a microscopic level in terms of theoretical studies of the friction coefficient ζ, which is related to diffusion coefficient by the Stokes−Einstein relation. This provides one method of calculating ζ, but it can also be obtained in principle from the random force autocorrelation function which is the starting point of molecular theories of the friction. Molecular and continuum theories divide the friction into hydrodynamic and dielectric components calculated in different ways on the basis of certain approximations that are tested in this paper. The two methods of determining ζ give consistent results in simulations of large ions or uncharged solutes but differ by a factor of nearly 1.5 for smaller ions. This is attributed to the assumption, in our simulations and in some molecular theories, that the random force autocorrelation function of a moving ion can be approximated by the total force autocorrelation function of a fixed ion but the observed trends in ζ with ion size are unchanged. Three different separations of the force autocorrelation function are studied; namely, partitioning this into (a) electrostatic and Lennard-Jones forces (b) hard and soft forces, and (c) forces arising from the first shell and more distant forces. The cross-terms are found to be significant in all cases, and the contributions of the sum of the soft term and the cross-terms, which are of opposite sign, to the total friction in the hard−soft separation, is small for all the ions (large and small). This suggests that dielectric friction calculated using this separation, with the neglect of cross-terms, is less accurate than previously supposed and the success of these theories is due to a cancellation of errors in the approximations. This is supported by recent a theoretical study of Chong and Hirata (Chong, C.; Hirata, F. *J. Chem. Phys.* **1998,** *108,* 739) which evaluates the cross-terms. A phenomenological theory due to Chen and Adelman (Chen, J. H.; Adelman, S. A. *J. Chem. Phys.* **1980,** *72,* 2819) calculates the friction in terms of effective hydrodynamic and dielectric radii for the ions (cf. solventberg picture) and predicts low dielectric friction for large ions and small strongly solvated ions. This also agrees qualitatively with our simulations but a complete molecular theory, applicable to positive and negative ions in hydrogen-bonded solvents such as water, has yet to be developed.

1. Introduction

The mobilities of ions in polar solvents in the bulk phase and in channels have been studied extensively over the past several years.[1−3] The size and charge dependence of ion mobility at infinite dilution in aqueous solutions at room temperature is anomalous, with small ions such as lithium and sodium diffusing more slowly than larger ones such as rubidium and cesium. These studies indicate that Stokes' law breaks down for small ions in highly polar solvents. One reason for this is explained by the solventberg picture which assumes that the solvent molecules immediately next to a small ion are tightly bound and travel with the ion, making it act more like a large ion. This provides a plausible explanation for the mobility of the lithium ion in water at 25 °C for which there is evidence

that the water of hydration in the first shell is firmly held with a residence time of ∼50 ps but must be modified to account for the mobility of Cl^{−} which has a much lower residence time of nearly 13 ps, indicating that the water in the primary hydration shell is not so firmly held as in Li^{+}. An alternative explanation is that dielectric friction must be considered in addition to the normal viscous resistance embodied in Stokes' law and recent theoretical studies have emphasized this.

Experimental investigations of the mobilities of ions in water at room temperature also show two separate curves for cation and anion mobilities as a function of size with each passing through a distinct maximum. This behavior was also reported for ions in methanol, ethanol, and propanol and in non-hydrogen-bonded solvents such as pyridine and acetonitrile at room temperature. Again it is dielectric friction that is usually invoked in explaining the maximum although there is no theory that describes the different maximums for positive and negative ions in molecular solvents such as water. It has been suggested[1−3] that the explanation for this lies in the asymmetric charge distribution of the solvent molecule and this effect would be

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absent in a simple dipolar solvent. This paper describes a computer simulation study of the different contributions of particular interest in solution chemistry to the frictional force on ions in aqueous solution at 25 °C and at infinite dilution.

The mobility $u = v/E$ is the drift velocity v per unit electric field E. It is also related to the diffusion coefficient in the absence of a field via the fluctuation dissipation theorem and may be determined from the slope of the mean square displacement at large times

$$D = {}^1\!/_6 \lim_{t \to \infty} \mathrm{d}(|\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2)/\mathrm{d}t \qquad (1.0)$$

or from the integral of the velocity autocorrelation function:

$$D = 1/(3kT) \int_0^\infty \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle \, \mathrm{d}t \qquad (1.1)$$

Theoretical discussions of ion mobility are usually couched in terms of the friction coefficient ζ on the ion which, in the linear regime, is related to the diffusion coefficient in the absence of an electric field by the Stokes−Einstein relation:

$$D = k_\mathrm{B}T/\zeta \qquad (1.2)$$

The friction coefficient ζ of a charged Brownian particle is usually divided into hydrodynamic ζ_v and dielectric ζ_D components. It is related to the integral of the random force autocorrelation function, which is the starting point of molecular theories of ion mobility that predict the total friction and the relative contributions of each component.[4,5]

The motion of an ion in a solvent can be discussed in terms of the generalized Langevin equation for the total force $\mathbf{F}(t) = m\dot{\mathbf{v}}$ acting on the ion, which is the sum of three terms:[5,6]

$$m\dot{\mathbf{v}}(t) = \mathbf{F}^\mathrm{ext} - \int_0^\infty \kappa(\tau)\mathbf{v}(t - \tau) \, \mathrm{d}\tau + \mathbf{f}(t) \qquad (1.3)$$

Here the first term $\mathbf{F}^\mathrm{ext}$ is the external force such as, for example, the force $q\mathbf{E}$ on an ion of charge q in an external electric field $\mathbf{E}$, the second term is the frictional force in which $\kappa(\tau)$ is called the memory function, and the third term is the random force whose ensemble average $\langle \mathbf{f}(t) \rangle = 0$. The memory function can be related to the friction coefficient and also to the random force autocorrelation function.

Once $\mathbf{v}(t)$ reaches a steady state formally at $t = \infty$, $m\langle \dot{\mathbf{v}} \rangle$ is also zero and

$$\mathbf{F}^\mathrm{ext} = \langle \mathbf{v} \rangle \int_0^\infty \kappa(\tau) \, \mathrm{d}\tau \qquad (1.4)$$

from which it follows that the friction coefficient

$$\zeta = \int_0^\infty \kappa(\tau) \, \mathrm{d}\tau \qquad (1.5)$$

If the external force is turned off

$$m\langle \dot{\mathbf{v}}(t) \rangle = -\int_0^t \kappa(\tau)\langle \mathbf{v}(t - \tau) \rangle \, \mathrm{d}\tau \qquad (1.6)$$

from which it is easily shown[6] that the memory function is related to the autocorrelation function of the random force by

$$\kappa(t) = \frac{\langle \mathbf{f}(0) \cdot \mathbf{f}(t) \rangle}{3kT} \qquad (1.7)$$

Combining eqs 1.5 and 1.7, one finds that the friction coefficient is related to the time integral of the random force autocorrelation function (see eq 2.9 below). Note that eqs 1.7 and 1.5 refer to the random force autocorrelation function; the integral of the total force autocorrelation function of a moving ion tends to zero at long times.

The advantage of this formulation, which has been exploited in many theoretical discussions,[7,8] is that it can be split into different contributions; the difficulty with it is that it is the random force and not the total force that is involved. The random force is that part of the force that is orthogonal to the solute dynamics, and formal expressions for its time evolution involve propagations with a projected Hamiltonian.[6] It is difficult to characterize and measure this in a simulation, but an approximation which is often made is to assume that, in the Brownian limit of a stationary ion, the random force autocorrelation function is approximated by the corresponding total force autocorrelation function, which can be calculated directly in a molecular dynamics simulation of a fixed ion. However, any error in this assumption or errors in calculating the time integral (see eq 2.9) that provides the friction coefficient will lead to an inconsistency with the friction coefficient determined from the diffusion coefficient via the Stokes−Einstein relation.

We present a molecular dynamics study of the friction coefficient of several positive and negative ions including a hypothetical ion I^+ and corresponding uncharged species in the SPC/E point charge model for 215 water molecules. The I^+ ion has the same size as I^- except that it is positively charged while the I has zero charge. In this way, we extend the sizes of the simplest positively charged ions beyond the usual range to study their behavior when they are large.[3] The uncharged species are just the same as the corresponding charged ions except that they have zero charge. In previous work,[1−3] we have shown that a simple model of ions dissolved in rigid nonpolarizable water does show mobility maximums as a function of size for both cations and anions. In this work, we analyze the behavior in terms of several theoretical treatments of this problem.

The purpose of our study is (a) to test the accuracy of the fixed ion approximation for the friction coefficient, (b) to investigate the assumptions made about separation of the different contributions to the friction coefficient in molecular theories of ion mobility and determine their limitations, and (c) to identify some of the factors affecting the contributions to the hydrodynamic and dielectric friction of ions in aqueous solution and to assess the relative importance of these contributions for different ions.

It must be recognized that our model with a nonpolarizable water and a small system size has limitations. The neglect of polarizability could change the dielectric response of the water, thereby affecting the calculated dielectric friction. The system may also be too small to fully include the collective dynamics of the solvent and its influence on the ion. Nevertheless, as

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the calculated mobilities and their functional dependence on ion size agree with experiment, we believe that the model and the system size capture the essential physics of ionic mobility in water.

2. The Friction on an Ion

A. Continuum Picture. In the continuum approach, the ion is treated as a charged sphere moving in a viscous dielectric medium. The friction coefficient is divided into two parts, a viscous drag ζ_v given by Stokes' law and a dielectric friction drag ζ_D. It follows that the total friction

$$\zeta = \zeta_v + \zeta_D \tag{2.1}$$

Assuming slip boundary conditions, the viscous drag,

$$\zeta_v = 4\pi\eta R_i \tag{2.2}$$

where η is the solvent bulk viscosity and R_i is the ion or solute radius. The electric field due to the ion polarizes the surrounding dielectric medium, which relaxes relatively slowly as the ion moves causing a retarding force on the ion. The friction arising from this is the dielectric friction (ζ_D), which was first studied by Born[9] and subsequently by Fuoss,[10] Boyd,[11] Zwanzig,[12] and by Hubbard and Onsager.[13] In Zwanzig's revised theory,[12] which contains the essential physics in a simple form, the dielectric friction

$$\zeta_D = C \frac{q^2(\epsilon - \epsilon_\infty)}{R_i^3 \epsilon(1 + 2\epsilon)} \tau_d \tag{2.3}$$

where $C = {}^3/_4$, τ_d is the Debye relaxation time, ϵ and ϵ_∞ are the static and high-frequency dielectric constants of the solvent, respectively, and q is the charge on the ion. We note that the solvent relaxation is described by a single relaxation time and the dielectric friction is symmetrical in the charge since it varies as the square of the charge. Consequently, the dielectric friction in this theory is the same for positive and negative ions of the same radius R_i. This is contradicted by the experimental data for ion mobility in aqueous solution at room temperature.[1,3]

One might expect the above continuum approach to be reasonably satisfactory for the mobility of an ion in a Stockmayer fluid in which the dipolar interactions are approximated by point dipoles, which interact symmetrically with positive and negative ions. However, water is a more subtle substance where the molecular structure and its associated asymmetric charge distribution have a strong effect on the solvation properties.[2,3] The molecular structure of the solvent is particularly important in determining ion mobility as both the viscous resistance and the dielectric friction are local in origin. For dielectric friction, this can also be seen from eq 2.3, which shows that it falls off as R_i^{-3}, which implies that contributions to this frictional component from the solvent outside large ions or beyond the first hydration shell of small ions decreases rapidly with the distance.

Chen and Adelman[14] extended the continuum model of Hubbard and Onsager to include the effects of local solvent structure and dynamics. A coupled set of equations for the

density, flow, and polarization fields induced by the moving ion are derived using projection operators, and an approximation is employed to decouple them into electrostatic and hydrodynamic parts. The equations are then solved by assuming a local density, viscosity, and dielectric constant for the solvent in a solvation sphere of radius R_{is} centered on the ion which is approximately the size of the first solvation shell given by the position of the first minimum in the ion−water radial distribution functions $g_{io}(r)$. This leads to analytic solutions for the viscous ζ_v and dielectric ζ_D friction coefficients which are determined by the ratio of the solvated ion radius R_{is} to the radius R_i of the bare ion, i.e., R_{is}/R_i, and a desolvation function

$$\Delta = \eta \rho_{loc}/\eta_{eff}\rho \tag{2.4}$$

that lies between 0 and 1 ($0 < \Delta \leq 1$) corresponding to the limits of rigid solvation and no solvation, respectively. The desolvation function Δ depends on the local structure (i.e., local density ρ_{loc} and viscosity η_{loc}), and the local solvent dynamics through the effective local viscosity

$$\eta_{eff} = \eta_{loc} + (\tau\rho/6m)[(\rho_{loc}/\rho)^2 - 1][R_{is}/R_i - 1] \times$$
$$[(R_{is}\, dU(r)/dr]_{r=R_{is}} \tag{2.5}$$

where m is the mass of the solvent molecule, τ is local solvent translational relaxation time, and $U(r)$ is the ion−solvent potential averaged over solvent orientations in the gas phase. The function Δ, which measures the degree of desolvation, reachs a limit of 1 for a completely desolvated ion. For rigidly solvated ions, η_{eff} is infinite and $\Delta \rightarrow 0$.

The end result of Chen and Adelman's theory is that the solute radii are renormalized to include solvation dynamics and structure through the desolvation function Δ and the ratio of the radii of the solvated ion to the bare ion, which is R_{is}/R_i. The hydrodynamic friction is

$$\zeta_v = 4\pi\eta R_V \tag{2.6}$$

where the effective hydrodynamic radius is given by

$$1/R_V = (1 - \Delta)/R_{is} + \Delta/R_i \tag{2.7}$$

The corresponding dielectric friction in the Chen−Adelman theory contains a modified radius R_D that replaces R_i in eq 2.3 with $C = {}^1/_2$ where

$$R_D^{-3} = R_{is}/R_s^4 f(\Delta, R_{is}/R_s, \epsilon_{loc}) \tag{2.8}$$

and ϵ_{loc} is the local dielectric constant of the solvation shell. The function $f(\Delta, R_{is}/R_s, \epsilon_{loc})$ interpolates smoothly between the extremes of a rigidly solvated and completely unsolvated ion. It follows that the recalculated hydrodynamic and dielectric friction also interpolate smoothly between these limits. Note that, even if there is complete desolvation in the sense that $\Delta = 1$, the dielectric radius may be close to R_{is} if there is dielectric saturation in the first shell.

One consequence of the Chen−Adelman theory is that the contribution formally associated with dielectric friction is sharply reduced by solvation to an extent related to the tightness of binding of solvent to ion. Since their expression for dielectric friction is also inversely proportional to the cube of the effective ionic radius, it is small for large ions that are poorly solvated and for small ions that are strongly solvated, but it may be

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significant for ions of intermediate size such as the loosely solvated Cl^- or Br^- in water.[15]

The mobilities of positive and negative ions of the same size in the Chen−Adelman theory could differ due to differences in the local solvent viscosity, density, dielectric constant, or relaxation of the solvent in the vicinity of these ions. This shifts the problem to the calculation of these quantities. Many years earlier, Frank[16] fitted the mobilities of the halides in water at room temperature to Zwanzig's continuum theory by using a local viscosity for the solvent.

The usual explanation of the mobility maximum as a function of ion size is that dielectric friction, which decreases with solute size, dominates for small ions while the viscous resistance, which increases with ion size, dominates for large ions. An alternative view is presented in the Chen−Adelman theory in which the maximum in mobility may occur even when dielectric friction is negligible. They showed that as the ion size increases and Δ changes from 0 to 1, the effective ionic radius for their viscous term (see eq 2.7) goes through a minimum value in certain solvents. They estimated that their dielectric friction term was negligible in non-hydrogen-bonding solvents[14] and that the maximum mobility was entirely due to desolvation. In a later paper, Nguyen and Adelman[15] estimated the maximum contribution of the dielectric friction to be less than 50% for ions in water.[15]

It should be emphasized however that the Chen−Adelman theory is essentially phenomenological. Also, the separation between hydrodynamic and dielectric friction is not as clearly defined as in the continuum model from which it is derived. For instance, the desolvation function Δ, determined by the local viscosity η_{loc} and solvent relaxation time τ, also contibutes to both the hydrodynamic and dielectric friction and influences their relative magnitude.

B. Molecular Picture. In the molecular picture, the focus is on the solvent molecules which change their positions and orientations as the ion moves changing its interaction with the ionic solute. The friction coefficient is given by

$$\zeta = \frac{1}{3k_{B}T}\int_{0}^{\infty} dt \langle \mathbf{f}(0) \cdot \mathbf{f}(t) \rangle \tag{2.9}$$

where $\mathbf{f}$ is the random force exerted on an ion by the solvent molecules and $k_{B}T$ is the thermal energy. The corresponding integral of the total ion solvent force autocorrelation function of an unconstrained moving ion is zero.[17,18]

Equation 2.9 is the usual starting point of molecular theories of ion mobility.[7,8] The first major assumption is to replace the random force on a moving ion by the total force on a fixed ion. By splitting the potential of this force into soft and hard parts, the friction constant can be further divided into four contributions.

$$\zeta = \zeta_{HH} + \zeta_{HS} + \zeta_{SH} + \zeta_{SS} \tag{2.10}$$

The first term is the hard−hard contribution due to the binary and repeated repulsive collisions of the solvent molecules with

the ion. The last term ζ_{SS} is the soft−soft term that depends on the structural rearrangements of the solvent molecules due to attractive forces. Wolynes[7] argued that the time scales associated the hard and soft parts are widely different and the cross-terms $\zeta_{HS} = \zeta_{SH}$, which depend on both time scales, can be ignored. The hard part ζ_{HH} is treated as the hydrodynamic viscous resistance ζ_{v}, while the soft part is associated with the dielectric friction term ζ_{D}. The molecular theory treats the solvent as an overdamped Debye fluid characterized by a single relaxation time. The friction coefficient reduces to the continuum limit in the case of weak long-range interaction potentials and to the solventberg limit, in which the ion moves with its shell, in the case of strong ion solvent interactions.

The molecular theory was further extended and developed for ions in a dipolar fluid by Biswas et al.,[8] who also assumed that the cross-terms are negligible. Their analysis takes account of the ultrafast dynamics of the solvent and the intermolecular correlations that characterize the solvation dynamics of a newly created ion. The short-range repulsive nonpolar interactions contribute to the hydrodynamic friction which they calculated using a mode coupling theory with results similar to the predictions of Stokes' law. The long-range ion−dipole interactions determine the dielectric friction. This depends on the dynamic structure factors of the pure solvent and the ion and on the equilibrium ion−dipole direct correlation function for which they use the mean spherical approximation. The theory was tested against the experimental ion mobilities in water by treating water as a dipole. It gives good agreement for ions of a given charge type (cations) showing that the theory is self-consistent. However, the treatment of water as a simple dipole does not distinguish between the mobilities of positive and negative ions of the same size.[3]

The validity of the approximation of neglecting the cross-terms has been a longstanding problem. This was investigated by Berkowitz and Wan[19] in a molecular dynamics study of Na^+ and Cl^- using TIPS4 model for water. They found that the cross-terms are not zero. Later studies carried out by Sridhar et al.[20] using a different water potential came to similar conclusions. Recently, Chong and Hirata[21] have considered a further extension of the theory of ion mobility in a dipolar solvent in which the cross-terms are not neglected.

We test the validity of replacing the random force of a moving ion by the total force on a fixed ion in the expression for the autocorrelation function by comparing the friction coefficient obtained from this approximation with the friction coefficient calculated from the Stokes−Einstein relation. We also report on a comprehensive study of the cross-terms associated with this separation and with other possible separations of the ion−solvent force in SPC/E water for several ions of different sizes. We critically examine some of the important predictions of different theories by comparing them with the results of our computer simulation.

3. Molecular Dynamics Simulations

Molecular dynamics computer simulations provide a unique way to investigate ion mobility at a molecular level. In earlier studies, it was shown that the SPC/E model water (charged Lennard-Jones spheres plus simple point charges on the atoms in rigid water) shows distinct maximums in the mobility of cations and anions as a function of ion size.[1,3] Thus, despite

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Table 1. Potential Parameters for Ion−Water and Water−Water Interactions (SPC/E Model)[a]

ion−water	σ_{io} (Å)	ϵ_{io} (kJ mol^{-1})	charge (e)
Li$^+$	2.337	0.6700	+1
Na$^+$	2.876	0.5216	+1
I$^-$	4.168	0.5216	−1
O(H$_2$O)	3.169	0.6502	−0.8476
H(H$_2$O)		0.0	+0.4238

[a] In the SPC/E model for water, the charges on H are at 1.000 Å from the Lennard-Jones center at O. The negative charge is at the O site and the HOH angle is 109.47°.

any shortcomings due to simplicity and neglect of polarizability, we believe that the model contains the essential physics of this phenomenon. Here we report attempts to test the various assumptions made in theoretical descriptions and also the accuracy of the friction coefficient calculated directly from the time integral of the force autocorrelation function of a stationary ion in a computer simulation.

While the total force can be measured during an ion's trajectory, it is less easy to obtain the random force associated with the generalized Langevin equation. We note that the memory function $\kappa(\tau)$ is independent of the mass of the ion and the total force autocorrelation function $<\mathbf{F}(0)\cdot\mathbf{F}(t)>$ can be written as

$$\langle \mathbf{F}(0)\cdot\mathbf{F}(t)\rangle = \langle \mathbf{f}(0)\cdot\mathbf{f}(t)\rangle - \int_0^t \kappa(\tau)\langle \mathbf{F}(0)\cdot\mathbf{v}(\tau)\rangle\,d\tau \quad (3.1)$$

If the mass of the solute is increased, the amplitude of the cross-correlation $\langle \mathbf{F}(0)\cdot\mathbf{v}(t)\rangle$ decreases (as $|v|$ decreases as m^{-1}) and although the integral of this cross-correlation is invariant to mass changes, the values over the time in which $\kappa(\tau - \tau)$ is significant tend to zero. Thus, $\langle \mathbf{F}(0)\cdot\mathbf{F}(t)\rangle$ will become closer and closer to the random force autocorrelation function for longer and longer times as $m \rightarrow \infty$. This means that we can get a good approximation of the random force autocorrelation function by fixing the particle with zero velocity relative to the solvent and measuring the actual force autocorrelation function. This allows us to split the force in various ways in order to probe the assumptions made in theoretical approaches.

We have calculated the diffusion coefficients independently from the mean square displacements and the velocity autocorrelation functions, respectively, in the usual way for several solutes (Li$^+$, Na$^+$, I$^+$, F$^-$, Cl$^-$, I$^-$, and the corresponding uncharged species) in 215 SPC/E water molecules at 298 K. Each simulation was carried out in the NVT ensemble in a cube box of length 18.64 Å at a density of 0.997 g/cm^3. The total interaction potential of the system is given by

$$U_{\text{total}} = \sum_i \sum_j \left\{ 4\epsilon\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right\} \quad (3.2)$$

where r_{ij} is the distance between atom site i and j, σ and ϵ are the Lennard-Jones parameters, and q is the atomic charge. The ion water parameters are given in Table 1 and their origin is described elsewhere.[1−3] Standard periodic boundary conditions were used along with minimum image criterion. A spherical cutoff of 9.0 Å was employed with a long-range correction for water−water and ion−water interactions using a reaction field. The equations of motion were integrated over time with a step of 1 fs. A Gaussian isokinetic thermostat was used. Following equilibration, the motion of the mobile ion/uncharged species was followed over 500 ps and its mean square displacement and velocity autocorrelation functions were calculated. Then

Table 2[a]

ion	τ	friction coeff (10^{-12} kg/s)			
		MSD	vac	fac	fac/MSD
Li$^+$	51	3.4	3.5	4.7 ± 0.2	1.4 ± 0.2
Na$^+$	22	3.2	3.2	5.2 ± 0.1	1.6 ± 0.2
Rb$^+$	12	2.1	2.1	3.2 ± 0.1	1.5 ± 0.2
I$^+$	21	3.2	3.4	3.7 ± 0.2	1.1 ± 0.1
Li	8	0.29	0.26		
Na	13	0.76	0.72		
I	28	4.2	4.1	4.5 ± 0.5	1.1 ± 0.2
F$^-$	25	4.0	4.1	6.1 ± 0.4	1.5 ± 0.2
Cl$^-$	17	2.3	2.5	4.1 ± 0.2	1.8 ± 0.1
I$^-$	14	2.6	2.6	3.6 ± 0.2	1.4 ± 0.

[a] MSD, mean square displacement; vac, velocity autocorrelation function; fac, force autocorrelation function.

Table 3. Electrostatic Lennard-Jones Separation

ion	friction coeff (10^{-12} kg/s)				
	ζ_{EE}	ζ_{LL}	ζ_{CROSS}	sum[a]	ζ
Li$^+$	20.3	15.4	−15.6	4.6	4.7
Na$^+$	23.3	18.1	−17.9	5.5	5.2
I$^+$	4.0	6.5	−3.5	3.6	3.7
F$^-$	25.9	22.1	−20.9	6.2	6.1
Cl$^-$	16.9	14.7	−13.8	4.0	4.1
I$^-$	11.1	12.1	−9.9	3.4	3.6

[a] Sum = $\zeta_{EE} + \zeta_{LL} + 2\zeta_{CROSS}$.

Table 4. Hard−Soft Separation

ion	sep (Å)	friction coeff (10^{-12} kg/s)				
		ζ_{HH}	ζ_{SS}	ζ_{CROSS}	sum[a]	ζ
Li$^+$	1.95	4.4	10.4	−5.0	4.9	4.7
Na$^+$	2.45	4.6	10.8	−5.1	5.3	5.2
I$^+$	3.83	6.0	5.9	−4.4	3.1	3.7
Na	2.97	1.7	0.02	0.02	1.7	1.8
I	4.25	4.0	0.04	0.02	4.1	4.5
F$^-$	2.60	5.4	9.8	−5.2	4.8	6.1
Cl$^-$	3.2	5.9	5.0	−3.6	3.7	4.1
I$^-$	3.60	3.5	4.8	−2.3	3.6	3.6

[α] Sum = $\zeta_{HH} + \zeta_{SS} + 2\zeta_{CROSS}$.

the ion/uncharged species and the center of mass of the water molecules were fixed and the system was equilibrated again followed by a further 500-ps run, during which the desired quantities such as the force on the ion were saved for further analysis. As there is only one solute particle in the system, long runs (0.5 ns or more) are necessary to gain good statistics. The force autocorrelation functions and its different contributions discussed in the next section were calculated as averages from the saved data. A fair idea of the accuracy is obtained by comparing x, y, and z autocorrelation functions for either the velocities or the forces and by comparing the results from different runs. The integrals of the random force autocorrelation functions reached constant values after ~2.5 ps with errors of ~5%. More difficulty was found in determining the integrals for some of the divisions of the random force which decayed more slowly. The results are summarized in Tables 1−5. We previously determined the residence times of water in the first hydration shells of the species studied.[3] They are included in Table 2 for easy reference in connection with the discussion that follows.

Figure 1 shows the mean square displacement (MSD) of a Li$^+$ ion, the MSD of the center of mass of the first solvation shell of the Li$^+$ ion, and the MSD of the center of mass of the Li$^+$ ion and its first solvation shell. The corresponding curves

Table 5.   First Shell-Outside Separation

ion	sep (Å)	friction coeff (10^{-12} kg/s)				
		ζ_{II}	ζ_{OO}	ζ_{CROSS}	sum[a]	ζ
Li$^+$	2.65	46	51	-46	5	4.7
Na$^+$	3.25	69	83	-73	6	5.2
I$^+$	5.85	25	20	-21	3	3.7
F$^-$	3.20	38	42	-38	4	6.1
Cl$^-$	3.80	33	31	-30	4	4.1
I$^-$	4.30	19	18	-17	3	3.6
Na	4.76	2	0	-0	2	1.8
I	6.03	4	0	-0.03	4	4.5

[a] Sum $= \zeta_{II} + \zeta_{OO} + 2\zeta_{CROSS}$.
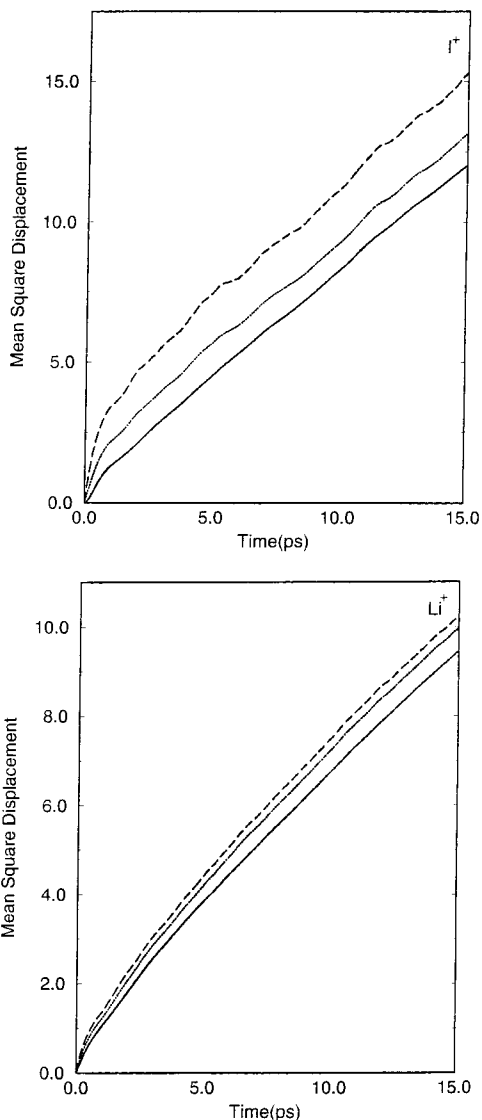
Figure 1. Mean square displacements of Li$^+$ and I$^+$ ions (—), the center of mass of the first solvation shell of each ion (- - -), and the center of mass of each ion and its first solvation shell ($\cdots$) as a function of time in SPC/E water at 25 °C. The I$^+$ ion is a hypothetical ion of the same size as I$^-$. After a short time, the mean square displacements for each species become parallel, showing that each ion moves with its solvent shell over at a time period of at least 15 ps.

for I$^+$ are in the same figure. Examining these one finds that, for Li$^+$ and I$^+$, the slopes of the mean square displacements are nearly coincident and essentially identical at long times, showing that the first solvation shell travels with the ion for at least 15 ps. This is the classical solventberg picture and is in
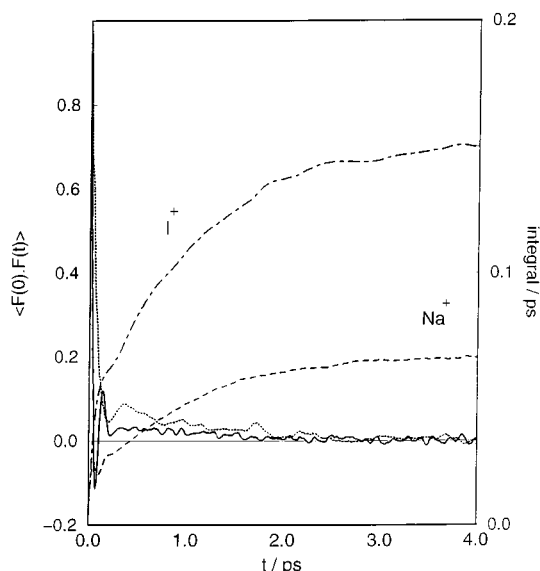

Figure 2. Force autocorrelation function of fixed Na$^+$ (—) and hypothetical I$^+$ ($\cdots$) as a function of time in SPC/E water at 298 K together with their integrals Na$^+$ ($\bullet\bullet\bullet$) and I$^+$ ($-\cdot-$). This shows that the integrals reach a plateau and for small ions there are oscillations in the fixed force autocorrelation function at short times.

accord with the large residence times of water in the primary hydration shells around these ions,[3] which are 51 ps for Li$^+$ and 21 ps for I$^+$. The differences in the MSDs arise from short time effects due to the different amplitudes of relative motion of the ion and its first solvation cage.

We next consider our calculations of the random force autocorrelation functions on the fixed ions. Figure 2 depicts the total force autocorrelation functions calculated for the fixed Na$^+$ and I$^+$, respectively. The area under the total force autocorrelation function reaches a plateau in each case after ~2.5 ps. Using these values, it is possible to check the consistency of the friction coefficients calculated from the MSD or VAC via the Einstein relation and the friction coefficient determined from the force autocorrelation functions of the fixed ion using eq 2.9 or 1.5. This tests the approximation. The values are given in Table 2. For most ions, the friction coefficient calculated from the fixed ion simulations is ~50% larger than that calculated from the diffusion constants measured in the moving ion simulations, but in the case of I$^+$ and I, the methods agree. This is consistent with the earlier simulations of Wilson et al.,[22] who found that the friction coefficient of Na$^+$ in water calculated from the fixed ion simulations is ~60% larger than that calculated from the diffusion constants determined from the VAC. A correction of the same magnitude was found by Alder and Alley for hard-sphere solutes of the same size and mass as the solvent.[23] This seems to suggest that the friction coefficients of large solutes (I$^+$) calculated from the Einstein relation are consistent with those determined from the force autocorrelation function of a fixed ion, but this is not so for small ionic solutes. To check whether this is a system size effect, we carried out simulations of Na$^+$ in a larger system of 511 water molecules which is twice the number of water molecules used in the other cases. The discrepancies in the friction coefficients of small ions still remain even for the larger system. This shows that the approximation of using a fixed

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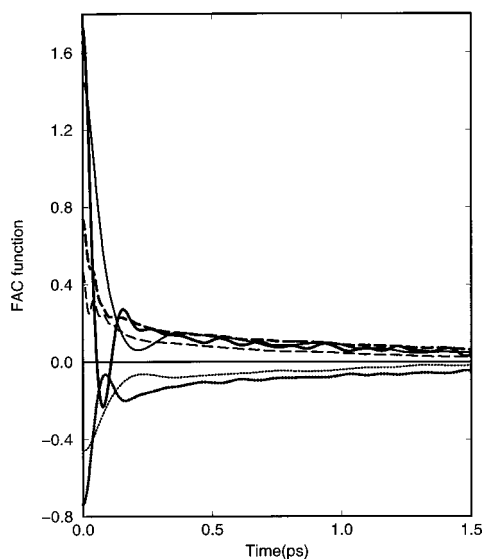
Figure 3. Electrostatic (- - -), Lennard-Jones (—), and their cross-terms (···) for fixed Na$^+$ (dark curves) and I$^+$ (light curves). The cross-correlation is comparable in magnitude to the pure electrostatic term.

Figure 4. Hard−soft separation of force autocorrelation function for fixed Na$^+$ (dark curves) and for I$^+$ (light curves). Cross-term (···), soft correlation (—), and hard correlation (- - -). After ∼0.3 ps, the cross-term is similar in magnitude to the hard term, and all terms decay slowly.

ion to determine the random force autocorrelation function for a moving ion is not very accurate and that the self-correction are not negligible. However, this discrepancy should not invalidate any qualitative conclusions that we may make from analyzing different parts of the random force.

4. Resolution of the Force Autocorrelation Function

We next turn to examining a number of separations of the random force in an attempt to throw light on the question of the importance of dielectric friction. We compare an ion Na$^+$, which is smaller than the ions with maximum mobility, with the hypothetical large ion I$^+$, which is larger. In the standard explanation of the mobility maximum, one would say that dielectric friction slows the Na$^+$ ion but is not important for the I$^+$ ion.

(A) Electrostatic Lennard-Jones Separation. The traditional separation of the friction coefficient into dielectric and hydrodynamic friction terms also suggests a division of the random force into electrostatic and Lennard-Jones components. Figure 3 shows the results of this division of the force autocorrelation function for Na$^+$ and I$^+$, respectively. There is no qualitative difference between the time correlation functions for the electrostatic forces on these two ions. In both cases, the cross-correlation is negative and similar in magnitude to the electrostatic term. In Table 3, we show the contributions from the respective terms to the total friction coefficient (proportional to the product of the integrals under the curves in Figure 3 and the mean square forces). Examining this table, we see (as expected from the figure) the contribution of the cross-correlation to the friction coefficient is very important, so that it may not be valid to consider the pure electrostatic term. We can, however, point to the fact that the pure electrostatic term is larger for the smaller ions where a contribution from dielectric friction is possible. We conclude that this separation is not very informative.

(B) Hard−Soft Separation. This is the separation suggested in Wolynes' theory and also used by Biswas et al. We implemented this in our simulations by splitting the total force into the sum of hard and soft parts, where the hard terms arise from interactions with water molecules whose oxygen atom is closer than the first maximum of the ion−oxygen radial
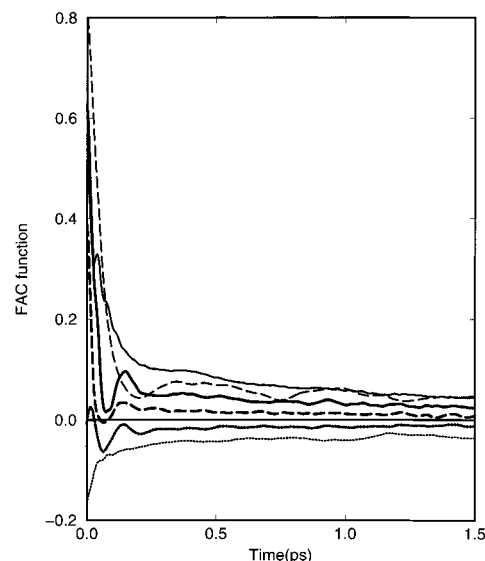
distribution function,[1] and the soft part arises from all other interactions. Table 4 gives the position of the cut and the values of the various contributions to the total friction coefficient. Once again we see that the cross-term is the same order of magnitude as the individual correlations and it is still difficult to make any definite statement about the contribution of dielectric friction. One argument which suggests that the dielectric friction is small for the small ions is that the contribution of the hard forces, which is certainly a viscous term, is approximately equal to the total friction for the smaller ions. The problem with this argument is that for some of the larger ions the hard term is greater than the total, so that one needs to argue that the contribution of the dielectric friction and other long-range effects is negative, reducing the friction. Figure 4 shows time correlation functions for the random force components based on this division for two ions. For Na$^+$, the cross-contribution from the hard and soft components is zero at time zero and at longer times tends to cancel the hard and soft self-correlations. In the case of I$^+$, the cross-component is negative even at short times.

(C) First Shell. Outside Separation. In this case, the separation was made by splitting the force on the ion between the first shell and the rest of the solvent, that is at the first minimum of the ion−oxygen radial distribution function which lies at 3.25 Å for Na$^+$ and at 5.85 Å for I$^+$.[1,3] The results for these ions are shown in Figure 5. The most remarkable feature of this plot is the very slow decay in the different components of the forces which does not show up in the total shown in Figure 2. The decay rate (∼0.2 ps^{-1}) is similar for all ions, and we attribute it to a structural relaxation of the water which does not affect the ion mobility directly. This results in large values for the components of the friction coefficient, which are canceled by a large cross-term, as shown in Table 5. This demonstrates the unsuitability of this separation for the discussion of the friction coefficient. We note that the slow component can be removed by writing $F = F_I + F_O = (F_I + \lambda F_O) + F_O(1 - \lambda)$, where λ is chosen to minimize the cross-correlation between a renormalized outside force $F_O(1 - \lambda)$ and a first shell force $(F_I + \lambda F_O)$ from which the part that is correlated with the outside force has been projected out. When
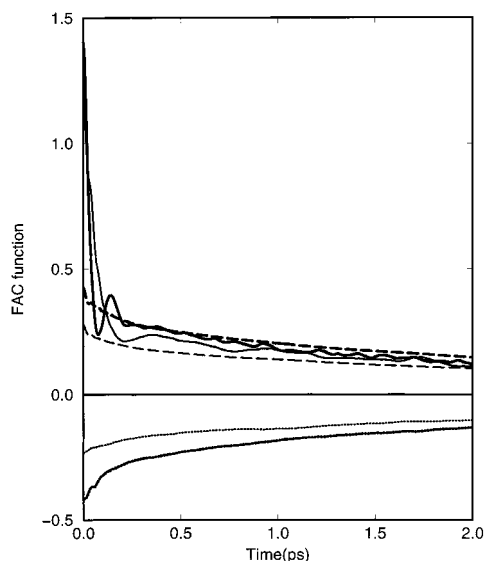
Figure 5. First shell-outside separation of force autocorrelation function for fixed Na^+ (broad curves) and I^+ (thin curves). Cross-term (···), outside term (- - -), and first shell term (—). The cross-term and the first shell contribution almost cancel at all times. Note that there is a slow relaxation of each of the parts of the force on the fixed ion when divided in this way which does not show up in the total force correlation function shown in Figure 3.

this is done, the random force autocorrelation function is found to be almost entirely due to the latter, that is the part of the first shell force which is uncorrelated with the outside. We deduce that the direct contribution of long-range terms to the friction is small.

5. Can the Friction Be Entirely Due to Viscous Resistance?

In the Chen−Adelman theory described earlier, the viscous resistance is proportional to the effective hydrodynamic radius, which is equal to that of the solvated ions for small ions and equal to that of the bare ions for large ions—see eq 2.7. If we make the hypothesis that the friction coefficient is entirely due to viscous resistance with no contribution from dielectric friction, we can determine an effective radius of each ion by comparison with the friction coefficients of uncharged species. If the resulting radii are unreasonably large, then the hypothesis is refuted.

The diffusion coefficients for uncharged particles in SPC/E water was determined in our earlier work.[3] Converting these values to friction coefficients (eq 1.2) one finds the relationship

$$\zeta = -1.86 + 2.18 R_i \qquad (5.1)$$

where R_i is the particle radius defined in terms of the Lennard-Jones diameters for ion−water and water−water interactions

$$R_i = \sigma_{io} - \sigma_{oo}/2 \qquad (5.2)$$

Figure 6 shows the effective radii for the simulated ions obtained from their diffusion constants and eq 4.1. Also shown are the positions of the first minimum in the ion−water distribution functions which we identify as the radii of the ions plus their first shells, R_{is}. The straight line shows $R_{eff} = R_i$. The effective radii of the positive ions (solid circles) lie between this line and the graph of R_{is} (open circles), while the effective radii of the larger negative ions are even slightly less than R_i, which is consistent with the shorter distance to the nearest water
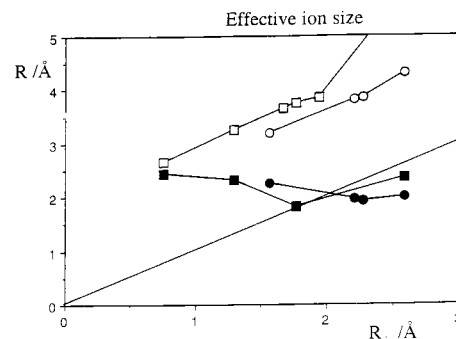

Figure 6. Ionic radii. Squares and circles refer to positive and negative ions, respectively. Filled symbols: effective ionic radii, R_{eff} calculated from the ion diffusion coefficients by assuming that the friction is entirely due to viscous resistance. Open symbols: radii of ions plus first solvation shells, R_{is} (first minima in the radial distribution functions). Straight line: bare ion radii, R_i. Note that the effective ionic radii approach the bare ionic radii as the ions get larger and are never greater than R_{is}, showing that the hypothesis that the friction is mainly hydrodynamic cannot be refuted.

atom for negative ions (a proton) than for positive ions (an oxygen). These results are consistent with the hypothesis that dielectric friction is negligible, but do not prove it. We can, however, argue that dielectric friction is unlikely to be significant for the ions whose effective radii are nearly equal to R_i, as any dielectric friction would raise the calculated value of R_{eff} above the hydrodynamic radius, R_v, and it is unlikely that the value of R_v is significantly lower than R_i. Thus, the only candidates for significant dielectric friction are Li^+, Na^+, and F^-. We note that the effective radius of Li^+ is close to that of the ion plus its first shell, so that if there is no significant dielectric friction, this ion is moving with its first shell as a solventberg. Dielectric friction may be significant for Na^+ and possibly F^- as well.

It should be noted that the arguments of this section are based on the diffusion coefficients of the moving ion and are unaffected by the validity or otherwise of the friction coefficient calculation.

6. Conclusion

We have presented a detailed study of the friction coefficient at infinite dilution as a function of size for positive and negative univalent ions and for the corresponding uncharged solutes. Our aim has been to examine some of the assumptions currently used in theories of ion mobility at infinite dilution.

An important question is the role of dielectric and viscous friction in continuum and molecular theories. This division is not entirely unambiguous since it depends on how the forces on an ion are divided. We examined the hypothesis that the friction coefficient could be completely explained by a local viscous term and a changing effective ionic radius as suggested by Chen and Adelman.[14] We found no evidence from the diffusion constants and sizes of ions with their first solvation shells measured in our simulations to contradict this hypothesis, but could not prove it.

To investigate this point further, we turned our attention to measuring the friction coefficient from the correlation functions of different parts of the random force. We used simulations in which the ion and the center of mass of the water molecules are fixed to get an approximation to the random force. According to the Zwanzig−Mori theory of relaxation in thermodynamic systems the time dependence of the random force should be followed in a system in which the slow degrees of freedom (here the ion motion) have been projected out.

Although one would expect that fixing the ion relative to the solvent should achieve this projection, we find a discrepancy of up to 50% between the friction coefficients calculated for the same systems by the direct measurement of the diffusion constant and the integral of the forces on the fixed ion. We have checked these results and their errors carefully and note that Berkowitz and Wan[19] and Wilson et al.[22] also found the same difference.

Despite this problem, we believe that it is possible to learn something about the mechanisms involved in determining ionic mobilities from divisions of the random force. It is not entirely clear what one means by dielectric friction in aqueous solutions. The structure of water is very different from that of a simple dipolar fluid mainly as a result of electrostatic interactions, which are more complex than dipolar. One result is differences between positive and negative ions. Indeed, the water molecules in the first shell of negative ions tend to align with a bond facing the ion rather than with the dipole moment facing the ion. If we were to label the results of all the electrostatic interactions between the ion and the solvent as "dielectric friction", then the first separation into electrostatic and Lennard-Jones contributions to the force is the one to consider. Here we found a large correlation between the electrostatic and Lennard-Jones contributions, which is hardly surprising as there is a strongly attractive electrostatic force at short range in the region that is probed by collisions. On the other hand, if we were to assign that part of the friction which is not Lennard-Jones as electrostatic we would end up with a negative electrostatic contribution.

The division into "hard" (short range) and "soft" (longer range), first introduced by Rice and Allnatt[24] in their study of transport properties, is a natural separation that projects out the repulsive part of the random force from the attractive part. It is similar to the separation used subsequently by Weeks et al.[25] in developing a perturbation theory of equilibrium fluids. If we use this division of the forces and assume that the viscous friction is essentially the hard−hard repulsive contribution of the random force correlation function, we must necessarily identify the remainder, which includes the cross-terms, as the dielectric friction plus possibly some other longer ranged terms. Since the cross-components are symmetrical ($\zeta_{SH} = \zeta_{HS}$), this gives for the dielectric friction in this case

$$\zeta_D = \zeta_{SS} + 2\zeta_{SH} \qquad (5.3)$$

As expected, ζ_{SS} and ζ_{SH} are zero (or close to it within the simulation error) for uncharged solutes and the total friction in these cases is the hydrodynamic friction ζ_V. Table 3 shows that ζ_{SS} and ζ_{SH} are of opposite sign for the charged species and the total dielectric friction ζ_D calculated in this way is negligible (due to cancellation of ζ_{SS} with the cross-terms) for small ions such as Li$^+$ and Na$^+$ and for the large I$^-$ ion. However, it is negative for the I$^+$ and Cl$^-$, which is difficult to reconcile with the normal concept of dielectric friction. The low dielectric friction of small and large ions agrees with the predictions of the Chen−Adelman theory.[14] We interpret the negative values as due to the breaking of water structure on charging I to I$^+$, which is in accord with calculations of the changes in the entropy of solvation as a continuous function of the charge.[26]

Finally, the separation into first shell and longer ranged forces was undertaken to examine the importance of long-range forces to the friction. Here we found a slow relaxation process which, though it contributed to the individual parts of the friction coefficient, did not contribute to the overall random force autocorrelation function. We found that it could be removed by projecting out the part of the first shell force, which was uncorrelated with the outer force. The result was to leave a negligible contribution of the outer force to the total friction coefficient, and we conclude that the friction coefficient does not have direct contributions from long-range forces of the ion− dipole type. We conclude that if dielectric relaxation is important it is basically local in nature for this model.

However, real water is polarizable and relaxes more slowly[27] than nonpolarizable water modeled in our simulations. The slower relaxation in polarizable water increases the dielectric friction of an ion, and our conclusions about the local nature of this friction may need revision for real water. A larger simulation cell may also be required to capture the collective dynamics of the polarizable solvent.

Although the friction coefficient of most ions calculated from the diffusion coefficient and the Stokes−Einstein relation does not agree with the friction calculated directly from the force autocorrelation function of the stationary ion, there is no such difficulty for I$^+$ within the limits of the error in our calculations. We take the view that the Stokes−Einstein relation is correct in the linear response regime of our calculations. It is of course true that the true random force is only approximately measured by fixing the ion relative to the solvent. It seems that this approximation may be better for larger ions. The true friction differs from the fixed ion approximation and can be calculated from the projected dynamics of the solute, discussed in a different context by Berne et al.,[28] or from the Stokes−Einstein relation, but this would not test the prevailing molecular theories of ionic friction that concern us here.

We have considered three separate divisions of the total force acting on a fixed ion, (a) the electrostatic and Lennard-Jones, (b) the hard−soft, and (c) the first shell and outer components, which may be appropriate in molecular theories of ionic friction. In none of these separations is the cross-term zero or even small, so that a simple division in which the pure random force components (hard−soft, first shell-outside, etc.) are identified with the hydrodynamic and dielectric friction does not appear to be feasible. The success of theories employing one or other of these divisions with the neglect of the cross-terms is partly due to cancellation of errors in the approximations employed. Recently, Chong and Hirata[21] calculated the cross-terms and found them to be significant in the hard−soft separation of the friction of ions in a simple polar fluid.

We have shown that it is possible, in the spirit of the hybrid molecular-continuum theory of Chen and Adelman,[14] to interpret the mobility maximum as a minimum effective hydrodynamic radius. The physical picture is that for small ions the desolvation function Δ (eq 2.4) is zero and the first solvation shell moves rigidly with the ion. As the ion size increases, the molecules in the solvation shell become more mobile with a steadily decreasing local viscosity. When the ion is large enough, the hydrodynamic properties in the first shell become indistinguishable from those of the bulk so that $\Delta = 1$ (desolvation is complete) and the effective hydrodynamic radius becomes equal to the bare ion radius. The contribution of dielectric friction to

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the total friction in this model follows from eq 2.3 with the radius given by eq 2.8. It is largest for ions of intermediate size and smaller for large poorly solvated and small strongly solvated ions—see Table 2 of ref 14.

Although the hybrid molecular-continuum theory of Chen and Adelman[14] is qualitatively correct, it does not fully take into account the molecular nature of the solvent. It is mainly a phenomenological theory with a local viscosity, local dielectric constant, and solvent dynamics described by a single relaxation time.

The hydrodynamic mechanism may not be valid for small solutes[29,30] or ions unless they are strongly hydrated, making them effectively larger. Also, water, in particular, with its hydrogen-bonded network and molecular charge distribution cannot be described adequately as a simple dipolar fluid and shows specific molecular effects. One manifestation of this is the asymmetry between positive and negative ions.[3] Another, which may be relevant to this problem, is the variation of solvent entropy with ion size. Previous work[26] with the same ion models showed that the entropy of solvation goes through maximums for positive ions a bit larger than sodium and for negative ions about the size of chloride. This is close to the maximum mobilities, suggesting that an additional factor in the position of mobility maximum in water as opposed to other solvents may be the structure breaking caused by the corresponding ions.

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(31) **Dedication.** In memory of Professor Brian Green, Chemistry Department, University of Maine, 1956−1998. Distinguished teacher, scholar, advisor, genial host and friend of students and colleagues. A man for all seasons.