

# Dynamics of Aqueous Solutions of Ions and Neutral Solutes at Infinite Dilution at a Supercritical Temperature of 683 K

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Received June 5, 2000. Revised Manuscript Received September 13, 2000

**Abstract:** We discuss the results of a molecular dynamics (MD) study of the residence times of water in the primary hydration shells of ions and uncharged solutes at infinite dilution in supercritical water at 683 K, as well as the solvation dynamics and diffusion coefficients of these species. The SPC/E model is used to represent water in this paper and its companion, where structural aspects of the same systems are discussed. The residence times at 683 K are found to be lower than those under ambient conditions and only weakly dependent on the size and sign of the charge on the ions. In contrast to earlier studies at room temperature (298 K at a solvent density of 0.997 g cm<sup>-3</sup>), the solvation dynamics of sodium and chloride ions at 683 K and a solvent density of 0.35 g cm<sup>-3</sup> are very similar to each other and indicate a solvent relaxation time of 0.8 ps. The ion diffusion coefficients are larger in magnitude at 683 K and less differentiated by size and charge sign at low solvent density ( $\leq 0.35$  g cm<sup>-3</sup>) than they are at room temperature. In the low-density range, an uncharged solute of the same size as an ion diffuses 2–9 times faster than the corresponding charged species, with the smaller solutes moving much faster than the larger ones. Increasing the solvent density to 0.997 g cm<sup>-3</sup> at 683 K decreases the diffusion coefficients of ions and uncharged solutes. At this density, the diffusion coefficients pass through distinct maxima as a function of size at both 298 and 683 K. An explanation of the diffusion coefficients of charged and uncharged species at low solvent density is sought in terms of a semicontinuum theory. The importance of the time scale of the solvent density fluctuations in controlling diffusion as distinct from the spatial extent of these fluctuations (determined by the correlation length) is emphasized. These observations suggest that the mechanisms of solute diffusion at supercritical conditions and at room temperature may be fundamentally different.

## 1. Introduction

Studies of aqueous solutions of ions and uncharged solutes at room temperature (298 K) and a water density of 0.997 g cm<sup>-3</sup> support the view that the structure and the dynamics of ions in solution require explicit consideration of the charge asymmetry of the water molecule.<sup>1,2</sup> One of the main goals of this study is to see how these properties are affected by extreme changes in temperature and solvent density. We investigate this by comparing the behavior of the same solutes in aqueous solution under widely different conditions. Specifically, we want to know whether supercritical conditions enhance or reduce the differences in the equilibrium and transport properties of solutes of different size and charge observed at room temperature. In the preceding paper,<sup>3</sup> we have already discussed the structures of these systems at 683 K at solvent densities of 0.35, 0.997, and 0.2 g cm<sup>-3</sup>, respectively. Here we investigate the diffusion coefficients of the ions and uncharged solutes as well as the solvation dynamics and residence times of water in the first hydration shells at 683 K. Previous studies of ion transport under supercritical temperatures have been reported by Balbuena et

al.,<sup>4,5</sup> who discussed mobilities of ionic solutions in terms of a semicontinuum model incorporating local and bulk viscosities.

At room temperature, negative and positive ions in infinitely dilute aqueous solution show quantitatively different behavior, exemplified by distinct plots of the diffusion coefficients or mobility as a function of ion size that pass through a maximum for each charge type. The distinction between negative and positive ions in these solutions is much deeper than just the reversal of charge sign. Its roots lie in the different orientation of water in the solvation shell around the ion, due to the charge asymmetry of the water molecule. This results in either hydrophilic (e.g., Li<sup>+</sup>, I<sup>-</sup>) or hydrophobic (e.g., I<sup>0</sup>) solvation within the first solvation shell that influences ion mobility in unexpected ways,<sup>2,3</sup> determined by the solvent density and temperature. The differences in the diffusion coefficients of ions and uncharged solutes are most striking and remarkable for charged iodine I<sup>-</sup> ion, and the fictitious I<sup>0</sup> and I<sup>+</sup> discussed in this paper. The characteristic behavior of the diffusion coefficients of ions at room temperature is absent at 683 K at a solvent density of 0.35 g cm<sup>-3</sup>, but reappears when the solvent density is increased to 0.997 g cm<sup>-3</sup>. The presence of fluctuating voids and solvent clusters in supercritical aqueous solutions influences the mechanism of ion and uncharged solute transport. The diffusion coefficients are also correlated with the thermo-

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**Table 1.** Coordination Numbers and Residence Times of Water in First Hydration Shells of Solutes under Ambient and Supercritical Conditions<sup>a</sup>

| solute          | hydration number         |                          |                         |                         | residence time $\tau_{\text{res}}$ (ps) |                          |                         |                         |
|-----------------|--------------------------|--------------------------|-------------------------|-------------------------|---|--------------------------|-------------------------|-------------------------|
|                 | 298 K                    |                          | 683 K                   |                         | 298 K                                   |                          | 683 K                   |                         |
|                 | 0.997 g cm <sup>-3</sup> | 0.997 g cm <sup>-3</sup> | 0.35 g cm <sup>-3</sup> | 0.20 g cm <sup>-3</sup> | 0.997 g cm <sup>-3</sup>                | 0.997 g cm <sup>-3</sup> | 0.35 g cm <sup>-3</sup> | 0.20 g cm <sup>-3</sup> |
| F <sup>-</sup>  | 6                        | 7                        | 6                       | —                       | 24                                      | 3.1 ± 0.7                | 2.6 ± 0.0               | —                       |
| Cl <sup>-</sup> | 7                        | 10                       | 8                       | 7                       | 13                                      | 3.1 ± 0.5                | 2.0 ± 0.1               | 2.3 ± 0.1               |
| I <sup>-</sup>  | 8                        | 17                       | 9                       | —                       | 9                                       | 3.0 ± 0.4                | 2.2 ± 0.0               | —                       |
| Li <sup>o</sup> | 11                       | 8                        | none                    | —                       | 4                                       | —                        | none                    | —                       |
| Na <sup>o</sup> | 13                       | 12                       | none                    | none                    | 9                                       | 2.8 ± 0.6                | none                    | none                    |
| F <sup>o</sup>  | 17                       | 15                       | none                    | —                       | 16                                      | —                        | none                    | —                       |
| Cl <sup>o</sup> | 23                       | 19                       | none                    | none                    | 18                                      | 2.9 ± 0.1                | none                    | none                    |
| I <sup>o</sup>  | 27                       | 22                       | none                    | —                       | 24                                      | 3.8 ± 0.4                | none                    | —                       |
| Li <sup>+</sup> | 4                        | 5                        | 4                       | —                       | 55                                      | 3.2 ± 0.                 | 6.1 ± 0.6               | —                       |
| Na <sup>+</sup> | 6                        | 6                        | 5                       | 5                       | 20                                      | 2.3 ± 0.1                | 2.7 ± 0.1               | 2.8 ± 0.2               |
| Rb <sup>+</sup> | 8                        | —                        | 6                       | —                       | 10                                      | —                        | 2.0 ± 0.1               | —                       |
| Cs <sup>+</sup> | 8                        | 11                       | 7                       | —                       | 10                                      | 2.0 ± 0.3                | 1.9 ± 0.0               | —                       |
| I <sup>+</sup>  | 25                       | 17                       | 9                       | —                       | 19                                      | 3.8 ± 0.4                | 2.2 ± 0.0               | —                       |

<sup>a</sup> The absence of an entry, denoted by (—), implies that no simulations were performed at this state point.

dynamics of solvation in ways that have yet to be addressed theoretically.

## 2. Model and Method

We used the extended simple point charge (SPC/E) model for water<sup>6</sup> and the ion–water parameters developed by Dang et al.<sup>7</sup> and employed by us<sup>1</sup> in previous studies of ion and neutral solute diffusion coefficients at room and supercritical temperatures. The details of our simulations under supercritical conditions are also described fully in our previous papers.<sup>1,3</sup>

The solutes used in this work fall into three categories: anions, cations, and uncharged particles, which we call “drones”. The primary system in this study, at 683 K and a solvent density of 0.35 g cm<sup>-3</sup>, consisted of the anions F<sup>-</sup>, Cl<sup>-</sup>, and I<sup>-</sup>, the cations Li<sup>+</sup>, Na<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>, and the fictitious ion I<sup>+</sup>. The latter was identical to I<sup>-</sup>, except for the reversed charge sign. Following previous work,<sup>1,2</sup> we also studied the uncharged solutes, Li<sup>o</sup>, Na<sup>o</sup>, F<sup>o</sup>, Cl<sup>o</sup>, and I<sup>o</sup> by assigning zero charge to the corresponding ions. To investigate the effect of solvent density, additional systems with solvent densities of 0.20 and 0.997 g cm<sup>-3</sup> at 683 K were also studied. These included F<sup>-</sup>, Cl<sup>-</sup>, I<sup>-</sup>, Li<sup>+</sup>, Na<sup>+</sup>, Cs<sup>+</sup>, the fictitious ion I<sup>+</sup>, as well as the uncharged Li<sup>o</sup>, Na<sup>o</sup>, F<sup>o</sup>, Cl<sup>o</sup>, and I<sup>o</sup>.

## 3. Lifetime and Population of Solvent around the Solute

The hydration number  $N_h$  of the ions was calculated in the preceding paper<sup>3</sup> as an integral of ion–oxygen pair distribution function  $g_{io}(r)$ :

$$N_h = \rho_w \int_0^{R_h} g_{io}(r) 4\pi r^2 dr \quad (3.1)$$

where  $R_h$  is the position of the first minimum in  $g_{io}(r)$  and  $\rho_w$  is the bulk density of water. The results are compared with those obtained under ambient conditions<sup>1</sup> in Table 1. Similar calculations of the hydration numbers of the uncharged solutes at 298 K from the solute–oxygen distribution functions  $g_{so}(r)$  are also presented in Table 1 and are discussed in the preceding paper.<sup>3</sup> The hydration numbers of uncharged solutes or “drones” reflect the extent and size of the hydrogen-bonded cages around the solutes. The cages tend to break down in the supercritical region studied (~683 K and  $\rho_w = 0.35$  g cm<sup>-3</sup>) but can be restored by applying pressure to increase the solvent density. The hydration

numbers of small cations and anions are essentially the same at 298 and 683 K. Exceptions are the large anion I<sup>-</sup> and the fictitious ion I<sup>+</sup>, for which the hydration numbers of ions at 683 K depend on the solvent density.

To get a better understanding of the dynamics of hydration at high temperature, we need to consider the residence times of water in the hydration shells. This property also helps us characterize the moving entity in solution as a bare ion or uncharged solute, or a strongly solvated species as in the case of Li<sup>+</sup>, or something in between. The size and charge of the solute and the solvent relaxation in its vicinity determine the frictional drag to diffusion in solution.

We determined the residence time ( $\tau$ ) in the standard way from the residence time correlation function,

$$R(t) = \frac{1}{N_h(t)} \sum_{i=1}^{N_h(t)} \langle \theta_i(t) \theta_i(0) \rangle \quad (3.2)$$

Here,  $\theta_i(t)$  is the Heaviside unit step function, which is 1 if a water molecule  $i$  is in the coordination shell of the ion at time  $t$  and 0 otherwise, and  $N_h(t)$  is the hydration number of this shell at time  $t$ . The residence time is given by

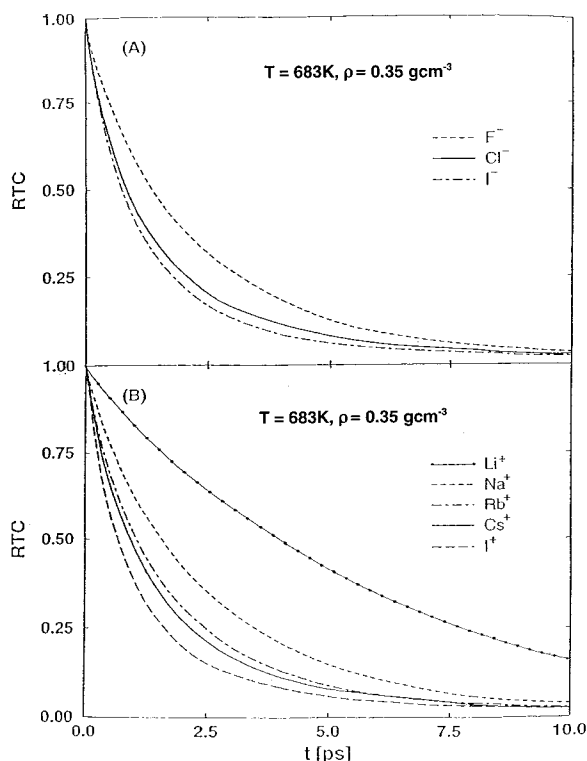
$$\tau_{\text{res}} = \int_0^{\infty} R(t) dt \quad (3.3)$$

As in the previous work,<sup>1</sup> the integration of the correlation function  $R(t)$  was carried out numerically from 0 to 10 ps, and the remainder was determined analytically by fitting the tail end to an exponential function. In our definition of  $R(t)$ , we do not allow for “excursions”<sup>8</sup> of water—i.e., even the shortest absence in the solvation shell is excluded from the residence time. Figure 1 shows the time dependence of the function  $R(t)$  for several ions at 683 K. Figure 2 displays the residence time  $\tau_{\text{res}}$  at 298 and 683 K as a function of ion size. The residence times at 298 K and a solvent density of 0.997 g cm<sup>-3</sup> are taken from previous work.<sup>1</sup> The minimum that exists for cations at room temperature disappears under supercritical conditions at a solvent density of 0.35 g cm<sup>-3</sup>. The change is most visible on the side toward larger ions, exemplified by a largely reduced residence time for the cation of iodine. In the preceding study

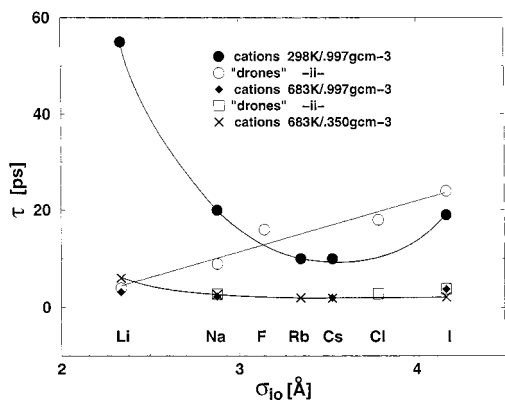
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**Figure 1.** Residence time correlation functions of water in the first hydration shells of anions (A) and cations (B) as a function of time at 683 K and solvent density of  $0.35 \text{ g cm}^{-3}$ .



**Figure 2.** Residence times of water in the first hydration shells of "drones" and cations as a function of their size at 683 and 298 K.

of the structure of ions and uncharged solutes at 298 K, the abnormally high residence time for  $\text{I}^+$  was associated with cage formation around the solute. The hydrophobic nature of that cage was explained as due to the hydrogen bonding. This is in agreement with the analysis of solvation entropy.<sup>2</sup> It is not surprising that, at high temperatures, these effects would show up much less, due to the reduction in hydrogen bonding. For the anions, the difference between 298 and 683 K is mostly in the magnitude of the residence time, and as with the hydration number, there are indications that the charge sign is of lesser importance at 683 K than it is at 298 K.

For  $\text{Li}^+$ , the relative change in residence time with temperature matches that of  $\text{I}^+$ , but the trend resembles those for all small ions. In the case of lithium, the very high residence time at room temperature is due to a completely different type of hydration than that for iodine. The hydrophilic solvation of  $\text{Li}^+$  is due to strong electrostatic ion-solvent interactions that characterize the well-known "solventberg" model. In contrast to this, the solvation of  $\text{I}^+$  at room temperature is predominantly

hydrophobic, since the ion lies in a cage of water molecules held by hydrogen bonds. The cage tends to break down at 683 K at a solvent density of  $0.35 \text{ g cm}^{-3}$ , and the residual hydration of  $\text{I}^+$  at this high temperature must be partly hydrophilic. The residence time for lithium at 683 K and a solvent density of  $0.35 \text{ g cm}^{-3}$  is still larger than those of all other ions, despite a very large decrease from the room-temperature value. This suggests that hydrophilic solvation is less affected by the change of temperature, whereas hydrophobic solvation is strongly temperature dependent and, as we will see later, to a certain extent density dependent. Consequently, the hydration numbers of small ions characterized by hydrophilic solvation are insensitive to changes in temperature from 298 to 683 K.

Cage formation around uncharged solutes ("drones") and large cations is restored at 683 K by increasing the solvent density.<sup>3</sup> This is reflected in the increase in hydration numbers with increase in solvent density to  $0.997 \text{ g cm}^{-3}$  at 683 K, as can be seen in Table 1. However, the residence time of water in these cages is only about 2–4 ps, in contrast to much higher values of 20–25 ps under ambient conditions. This shows that, although the cages exist even at supercritical temperatures under appropriate conditions of high solvent density, the exchange of water with the surroundings is an order of magnitude faster than that at room temperature.

#### 4. Solvation Dynamics

We have already studied<sup>1</sup> the details of the solvent response  $S(t)$  of SPC/E water at room temperature to charging up simple cations and anions; see Figures 10 and 11 of ref 1b. The response  $S(t)$  at room temperature can be divided into two or more phases: a rapid drop on a time scale of 20–30 fs followed by the slow, oscillatory long-term relaxation over 1–5 ps. This is in accord with recent time-delayed fluorescence shift experimental studies by Fleming and his group using larger fluorescence probes.<sup>9</sup> It also agrees with several earlier simulations of the solvent response to switching on charges and dipoles of solutes in water and nonaqueous solvents pioneered by Maroncelli et al.<sup>10</sup> The initial phase in the solvent response  $S(t)$  is attributed to fast librational motion accompanied by small-amplitude oscillations of the solvent. This is followed by translational and diffusive motion at longer times that account for the final relaxation on a picosecond time scale. The solvent response can be related to the equilibrium fluctuations in the solvent by way of linear response theory.<sup>10</sup> The effect of solvation on several classes of fast chemical processes has also been studied extensively.<sup>11</sup>

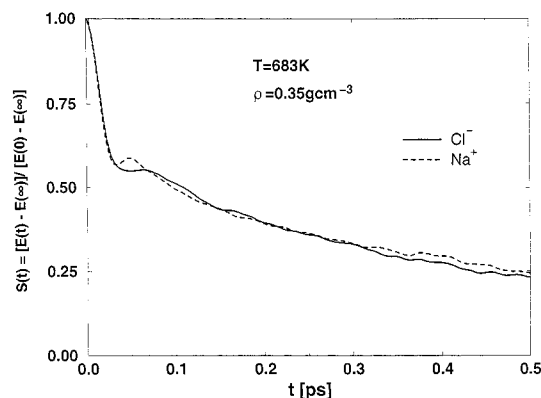
Here we extend our earlier studies<sup>1b</sup> of solvation dynamics to two simple ions,  $\text{Na}^+$  and  $\text{Cl}^-$ , at 683 K at a solvent density of  $0.35 \text{ g cm}^{-3}$ . Similar calculations for the  $\text{Cl}^-$  ion in SPC water at 645 K and three solvent densities ranging from 0.3 to  $0.9 \text{ g cm}^{-3}$  were described earlier by Re and Laria.<sup>12</sup> Their studies are for a smaller system (124 water molecules), with the intermolecular potentials truncated at half the simulation box length and tapering off smoothly to zero at the ends over a short interval. Calculations of the solvent response of a Stockmayer fluid at supercritical temperatures were reported

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(12) Re, M.; Laria, D. *J. Phys. Chem. B* **1997**, 101, 10494.



**Figure 3.** Solvation dynamics  $S(t)$  of ions at 683 K and a solvent density of  $0.35 \text{ g cm}^{-3}$  calculated from eq 4.1, which measures the linear response.

recently by Graf and Nitzan.<sup>13</sup> They found that the nonequilibrium solvent response is sensitive to the solvent density and solute charge, and that its description in terms of the equilibrium fluctuations using linear response theory breaks down in the extreme cases of low solvent density and high solute charge.

We recall the definition of the solvent response function,

$$S(t) = \frac{\langle E(t) \rangle - \langle E(\infty) \rangle}{\langle E(0) \rangle - \langle E(\infty) \rangle} \quad (4.1)$$

Here,  $\langle E(t) \rangle$  is the ensemble-averaged energy of ion–solvent interaction at time  $t$  after switching on the charge of a neutral solute. The initial states in the calculation of  $S(t)$  were generated from an equilibrium trajectory of the uncharged solute separated by intervals of 5 ps. Switching on the charge at  $t = 0$  creates a nonequilibrium initial state, so that  $S(t)$  given in eq 4.1, which follows the relaxation of the nonequilibrium system to equilibrium, is sampled from a distribution of nonequilibrium states. The details of our calculations are similar to those used in our previous discussion of  $S(t)$  for ions in SPC/E water at 298 K.<sup>1b</sup>

Figure 3 shows  $S(t)$  for two ions of similar size but opposite charge, namely  $\text{Na}^+$  and  $\text{Cl}^-$ , at the supercritical conditions of 683 K and a solvent density of  $0.35 \text{ g cm}^{-3}$ . The results for  $\text{Cl}^-$  are similar to those obtained by Re and Laria<sup>12</sup> at nearly the same solvent density. The most striking difference from the results obtained previously at room temperature<sup>1b</sup> is the absence of oscillations associated with the combination of librational and rotational reorientation of water molecules around the solute and vibrational motion in its solvation shell. The initial dramatic change in the structure of the solvation shell takes place a little slower than at lower temperatures (about 0.04 ps, compared to 0.02 ps in the previous work), which can be attributed to the higher kinetic energy under supercritical conditions. Neither the initial first phase nor the subsequent relaxation period substantially differentiates between the oppositely charged ions such as chloride and sodium, in contrast to what was observed at room temperature. The decay at long times is found to be exponential in time i.e.,  $S(t) \approx \exp(-t/\tau_{\text{solv}})$ , with a relaxation time  $\tau_{\text{solv}} \approx 0.8 \text{ ps}$  at a solvent density of  $0.35 \text{ g cm}^{-3}$  at 683 K. The corresponding relaxation time of the solvent at 298 K and a solvent density of  $0.997 \text{ g cm}^{-3}$  is 0.34 ps.

The average solvation time is defined by

$$\tau_s = \int_0^\infty S(t) dt \quad (4.2)$$

The values of  $\tau_{\text{solv}}$  quoted above and  $\tau_s$  would be identical if

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**Table 2.** Diffusion Coefficients  $D$  of Solutes at Infinite Dilution in Water at 25 °C and 683 K, Calculated from the Mean-Square Displacement<sup>a</sup>

| solute            | $\sigma_{\text{io}}$<br>(Å) | $D$ ( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ ) |                           |                          |                          |
|-------------------|-----------------------------|--|---------------------------|--------------------------|--------------------------|
|                   |                             | 298 K  |                           | 683 K                    |                          |
|                   |                             | $0.997 \text{ g cm}^{-3}$                    | $0.997 \text{ g cm}^{-3}$ | $0.35 \text{ g cm}^{-3}$ | $0.20 \text{ g cm}^{-3}$ |
| $\text{F}^-$      | 3.143                       | 1.04   | $21 \pm 3$                | $35 \pm 2$               | —                        |
| $\text{Cl}^-$     | 3.785                       | 1.77   | $23 \pm 2$                | $34 \pm 9$               | $40 \pm 5$               |
| $\text{I}^-$      | 4.168                       | 1.60   | $16 \pm 2$                | $32 \pm 1$               | —                        |
| $\text{Li}^\circ$ | 2.337                       | 14.4   | $60 \pm 14$               | $303 \pm 35$             | —                        |
| $\text{Na}^\circ$ | 2.876                       | 5.42   | $26 \pm 5$                | $159 \pm 16$             | —                        |
| $\text{F}^\circ$  | 3.143                       | 3.31   | $21 \pm 1$                | $132 \pm 25$             | —                        |
| $\text{Cl}^\circ$ | 3.785                       | 1.51   | $13 \pm 2$                | $92 \pm 1$               | —                        |
| $\text{I}^\circ$  | 4.168                       | 0.98   | $11 \pm 1$                | $56 \pm 1$               | —                        |
| $\text{Li}^+$     | 2.337                       | 1.22   | $13 \pm 2$                | $37 \pm 6$               | —                        |
| $\text{Na}^+$     | 2.876                       | 1.28   | $15 \pm 2$                | $35 \pm 7$               | $34 \pm 4$               |
| $\text{Rb}^+$     | 3.348                       | 1.98   | —                         | $34 \pm 2$               | —                        |
| $\text{Cs}^+$     | 3.526                       | 1.88   | $18 \pm 3$                | $29 \pm 2$               | —                        |
| $\text{I}^+$      | 4.168                       | 1.28   | $11 \pm 2$                | $26 \pm 5$               | —                        |

<sup>a</sup> The absence of an entry, denoted by (—), implies that no simulations were performed at this state point.

$S(t)$  was a purely exponential time decay, but Figure 3 shows that this assumption is an approximation. Re and Laria<sup>12</sup> find  $\tau_s$  to be equal to 0.57 and 0.41 ps, respectively, at 645 and 298 K at solvent densities of 0.3 and  $1.0 \text{ g cm}^{-3}$ , respectively. They find that  $\tau$  drops to 0.05 ps at  $0.9 \text{ g cm}^{-3}$  and 645 K, which is an order of magnitude different from its value at 298 K.

## 5. Ion and Uncharged Solute Diffusion

The diffusion coefficients of ions are obtained from the mean-square displacement (MSD),

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} |\mathbf{r}_i(t) - \mathbf{r}(0)|^2 \quad (5.1)$$

or from the integral of the velocity autocorrelation function,

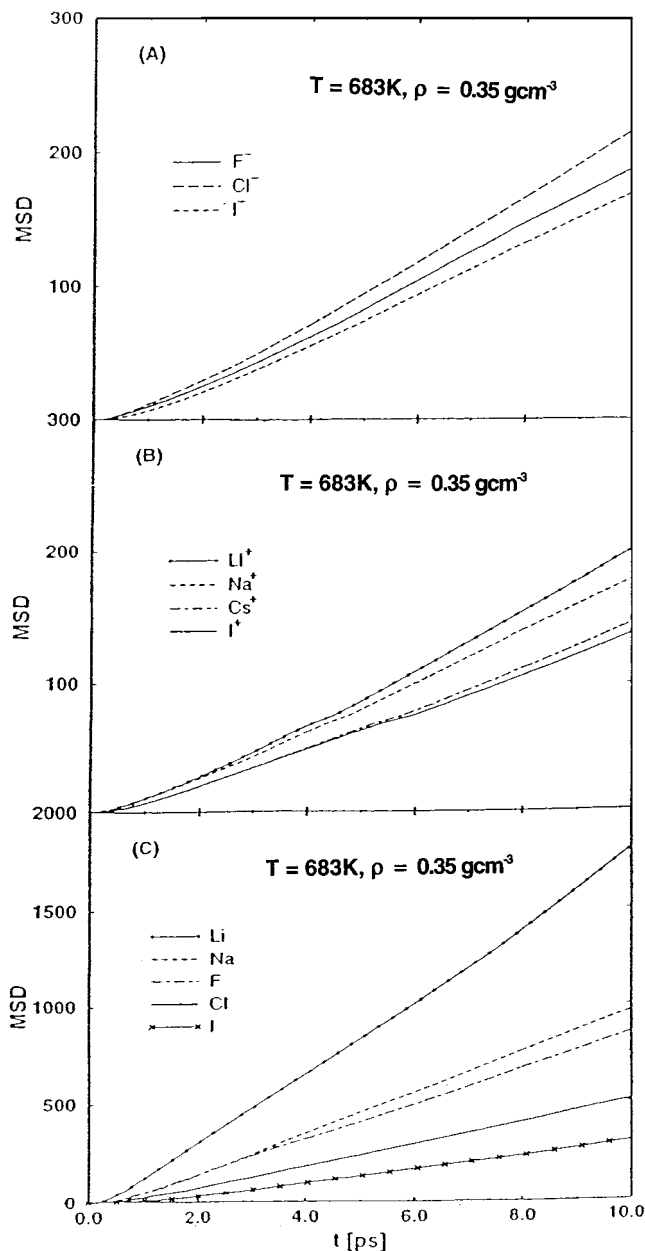
$$D = \frac{1}{3} \int_0^\infty \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle dt \quad (5.2)$$

The mean-square displacement (MSD) is shown as a function of time for anions and cations at 683 K at a solvent density of  $0.35 \text{ g cm}^{-3}$  in Figure 4A and B.

The diffusion coefficients calculated from the MSD at this solvent density and temperature are compared in Table 2, with the values for selected ions and uncharged species at solvent densities of 0.20 and  $0.997 \text{ g cm}^{-3}$ . The same table also contains the diffusion coefficients of all of the solutes at 298 K and a solvent density of  $0.997 \text{ g cm}^{-3}$ , which were reported previously.<sup>1</sup> The values of the diffusion coefficients obtained from the velocity autocorrelation (VAC) function by integration over long enough times agree with those obtained from the MSD within the error bounds. We will first discuss our results at 683 K and low solvent densities ( $<0.35 \text{ g cm}^{-3}$ ) and then consider the diffusion coefficients under extreme conditions of high temperature (683 K) and high solvent density ( $0.997 \text{ g cm}^{-3}$ ). Recall that the critical density of water is approximately  $0.32 \text{ g cm}^{-3}$  and the density at room temperature is  $0.997 \text{ g cm}^{-3}$ .

The velocity autocorrelation functions (VAC) for a number of anions and cations at 683 K and solvent density of  $0.35 \text{ g cm}^{-3}$  are compared in Figure 5A and B. The integral in eq 5.2 requires a larger integration upper limit to reach a plateau at 683 K than at 298 K.

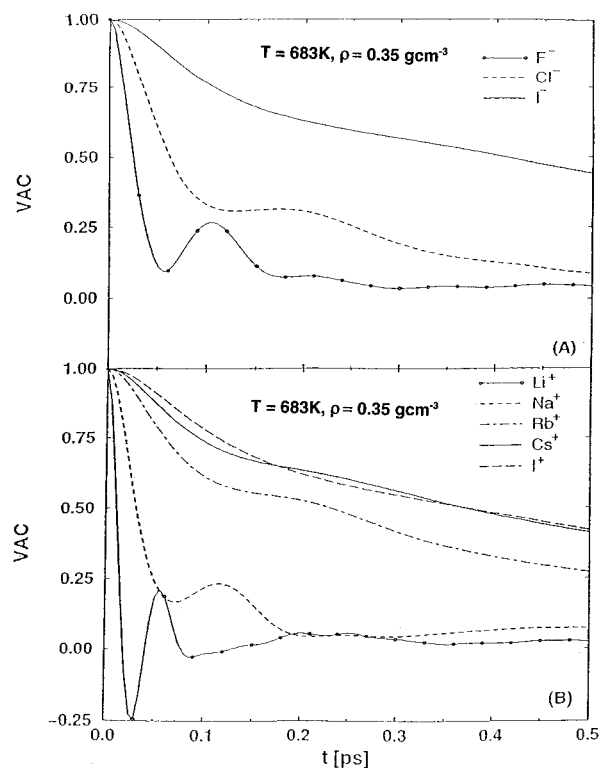
Examination of the corresponding plots of the VAC for ions in our earlier work (Figure 3 in ref 1b) at 298 K shows that a small central ion like  $\text{Li}^+$ ,  $\text{Na}^+$ , or  $\text{F}^-$  under ambient conditions



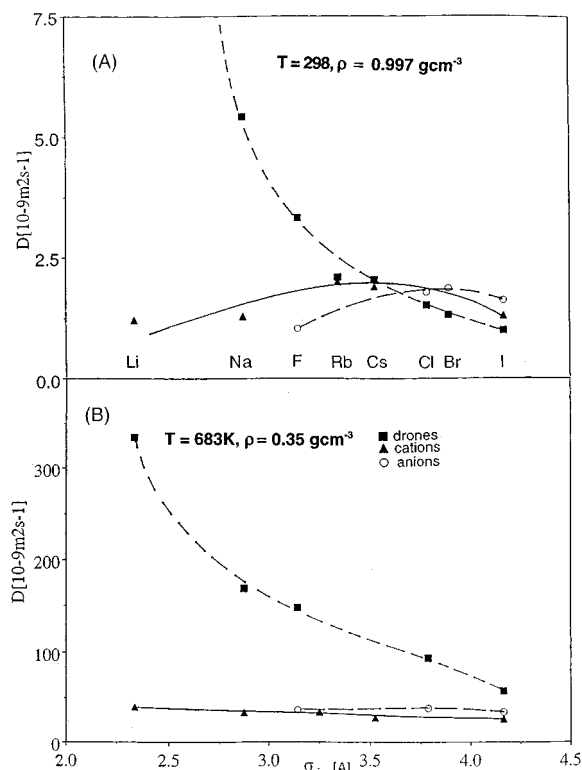
**Figure 4.** Mean-square displacements of anions (A) and cations (B) as a function of time at 683 K and solvent density of 0.35 g cm<sup>-3</sup>.

undergoes oscillatory motion within its first hydration shell. The oscillations for larger ions are much weaker. When the temperature is increased to 683 K, the velocity autocorrelation functions of all but the smallest ions show a monotonic decay modulated by weak oscillations, similar to the behavior of large ions at room temperature. This implies that the water molecules in the first solvation shell are held more loosely around the central particle than at room temperature. The oscillations in the velocity autocorrelation functions of all of the ions in solution at 683 K except Li<sup>+</sup> are of low amplitude, and the functions are never negative, in contrast to the behavior of small ions such as Na<sup>+</sup> and F<sup>-</sup> at room temperature. This indicates that, except for Li<sup>+</sup>, the interaction between an ion and its solvation shell at 683 K slows the ion but rarely reverses its relative direction of motion within its hydration shell during its lifetime; see Table 1 for the relevant residence times.

The diffusion coefficients of the charged and uncharged species at 683 K and at a solvent density of 0.35 g cm<sup>-3</sup> are plotted as a function of the size parameter  $\sigma_{io}$  in Figure 6B.



**Figure 5.** Velocity autocorrelation functions of anions (A) and cations (B) as a function of time at 683 K and solvent density of 0.35 g cm<sup>-3</sup>.



**Figure 6.** Diffusion coefficients of ions and uncharged solutes as a function of their size at 298 K and a solvent density of 0.997 g cm<sup>-3</sup> (A) and at 683 K and a solvent density of 0.35 g cm<sup>-3</sup> (B).

For comparison, the diffusion coefficients of the same species at 298 K and at a solvent density of 0.997 g cm<sup>-3</sup> are plotted in Figure 6A. The diffusion coefficients of cations and anions at 683 K as a function of ion size fall on nearly the same curve, unlike the corresponding values at 298 K.

The mobility of an ion is, of course, much larger above the critical point of the solvent than at room temperature. However, the relative differences between various solutes at 683 K and at a solvent density of  $0.35 \text{ g cm}^{-3}$  are much less pronounced than those at lower temperature (298 K) and higher solvent density ( $0.997 \text{ g cm}^{-3}$ ). For the anions there is still a slight maximum in the plot of diffusion coefficient versus solute size, which is not noticeable on the scale of Figure 6B, but the differences are of comparable magnitude with the statistical error. The differences are even less significant for cations. An obvious conclusion is that cations at this temperature and solvent density have slightly higher mobilities than anions, in contrast to the observation made for the ambient conditions where the order changes with the size. The change in the behavior of large solutes above the critical point shows up here as well. At 683 K, large positive and negative ions are more alike in their behavior than the same ions at room temperature. The order of the diffusion coefficients of  $\text{I}^-$  and the fictitious  $\text{I}^+$  and  $\text{I}^\circ$  at each of the two temperatures and densities is as follows:

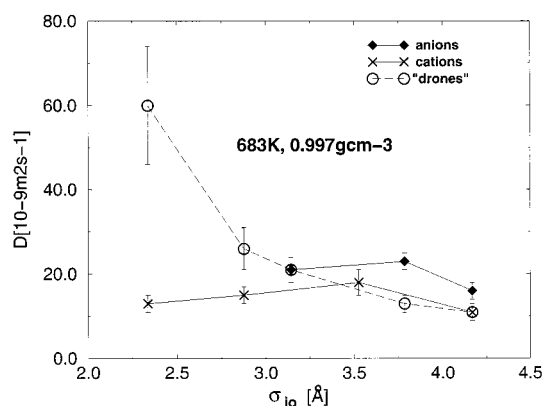
$$D(\text{I}^-) > D(\text{I}^+) > D(\text{I}^\circ) \quad \text{at } 298 \text{ K, } \rho_{\text{solv}} = 0.997 \text{ g cm}^{-3}$$

$$D(\text{I}^\circ) > D(\text{I}^-) \geq D(\text{I}^+) \quad \text{at } 683 \text{ K, } \rho_{\text{solv}} = 0.35 \text{ g cm}^{-3}$$

The increase in the diffusion coefficient on charging  $\text{I}^\circ$  to  $\text{I}^+$  or  $\text{I}^-$  at 298 K is a consequence of the destabilization of the hydrophobic cage around the uncharged  $\text{I}^\circ$  when it is charged. Studies of the entropy of solvation<sup>2</sup> have shown that this destabilization is greater for  $\text{I}^-$  than it is for  $\text{I}^+$ . This correlates with the faster diffusion  $\text{I}^-$  ion compared to the diffusion of the  $\text{I}^+$  ion of the same size at 298 K. The hydrophobic cage effect is absent at 683 K and at a solvent density  $\rho_{\text{solv}} = 0.35 \text{ g cm}^{-3}$ , and the order of the diffusion coefficients of the charged and uncharged iodine species is different.

For the “drones”, i.e., the uncharged solutes, the diffusion coefficients follow Stokes’s law, as discussed in section 6. One exception is uncharged lithium,  $\text{Li}^\circ$ , for which the diffusion coefficient is higher than expected from this law. Charging the neutral solutes decreases the diffusion coefficients at 683 K and at a solvent density of  $0.35 \text{ g cm}^{-3}$ , in contrast to the behavior at 298 K and a solvent density of  $0.997 \text{ g cm}^{-3}$ . Comparing the behavior of the solutes at the two temperatures (683 and 298 K) and corresponding densities ( $0.35$  and  $0.997 \text{ g cm}^{-3}$ ), the diffusion coefficients of the ions above the critical temperature lie between the values for the uncharged species at 683 and 298 K, as can be seen in Figure 6.

We have also computed the diffusion coefficient data of ions at solvent densities of  $0.20$  and  $0.997 \text{ g cm}^{-3}$  at 683 K. Lowering the solvent density leads to faster ion diffusion, but the effect is relatively less significant than that of changing the temperature of the system. Simulations of the mobility of ions at room temperature carried out by our group showed two separate curves for the diffusion coefficients of cations and anions in an infinitely dilute aqueous solution as a function of size.<sup>1b</sup> Similar trends appear for cations and anions at a solvent density of  $0.997 \text{ g cm}^{-3}$  when the temperature is raised to 683 K, although the absolute magnitudes of the diffusion coefficients are different at the two temperatures, and the anions lie uniformly above the cations, unlike their behavior at 298 K. Figure 7 shows the diffusion coefficients as a function of the size for the system at high solvent density and temperature. Comparing this with Figure 6A, we see that the characteristic behavior of cations and anions at room temperature with respect to ion size appears to be more closely correlated with the solvent density than with the temperature, since analogous behavior is found at high



**Figure 7.** Diffusion coefficients of ions and uncharged solutes in aqueous solution at 683 K as a function of their size. The solvent density is  $0.997 \text{ g cm}^{-3}$ .

density at 683 K. However, such a high density is not typical of the supercritical region unless the system is subjected to high pressure.

In what follows we discuss the diffusion of ions and uncharged solutes at low density in terms of a simple model and its relation to the residence time and the solvent relaxation time. Specifically, we consider our results at 683 K and a solvent density of  $0.35 \text{ g cm}^{-3}$ , which is typical of the supercritical region of water.

## 6. Discussion of the Diffusion Coefficients in the Supercritical Region

Although it is not fully justified to treat the motion of ions as if they were Brownian particles, we assume that this is so. We also assume tentatively that hydrodynamic concepts are applicable at a molecular level. The friction  $\zeta$  and diffusion  $D$  coefficients of a solute are related by the Stokes–Einstein equation,  $D = kT/\zeta$ . The frictional resistance to the motion of an uncharged solute in a continuum solvent is entirely viscous, or hydrodynamic, and is given by Stokes’s law,

$$\zeta_{\text{v}} = B\eta R_i \quad (6.1)$$

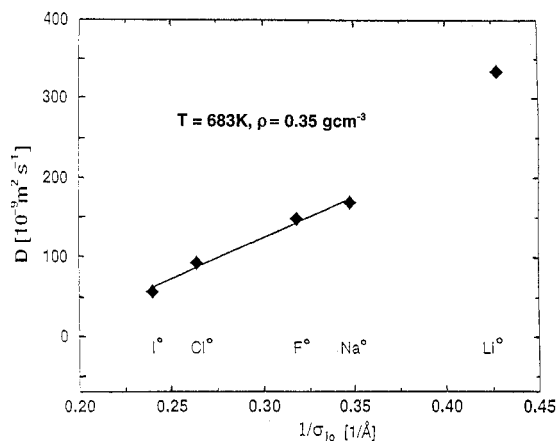
Here,  $\zeta_{\text{v}}$  is the hydrodynamic friction coefficient,  $R_i$  is the radius of the solute,  $\eta$  is the solvent bulk viscosity, and the constant  $B$  is  $6\pi$  or  $4\pi$ , depending on whether stick or slip boundary conditions are used at the solute–solvent surface. Assuming slip boundary conditions and a hydrodynamic radius  $R_i = \sigma_{\text{io}}$ , the diffusion coefficient of the uncharged solute is

$$D_0 = \frac{kT}{4\pi\eta\sigma_{\text{io}}} \quad (6.2)$$

where the subscript 0 refers to the uncharged solutes and  $\sigma_{\text{io}}$  is the Lennard-Jones parameter. We have plotted  $D_0$  versus  $\sigma_{\text{io}}$  for the uncharged species at 683 K in Figure 8. The plot is linear if we exclude  $\text{Li}^\circ$ , which has an anomalously larger diffusion coefficient than the Stokes law prediction. Battacharyya and Bagchi<sup>14</sup> explained this change in hydrodynamic behavior of small solutes dissolved in dense liquids as due to the coupling of the solute motion to density fluctuations. From the slope, we determine the solvent viscosity  $\eta$  to be  $0.8 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$ . The experimental result from compilations of the National Bureau of Standards<sup>15</sup> (now the National Institute

(14) Battacharyya, S.; Bagchi, B. *J. Chem. Phys.* **1997**, *106*, 1757.

(15) Gallagher, J. S.; Haar, L. National Engineering Laboratory, Thermophysics Division, National Bureau of Standards: Gaithersburg, MD, 1985.



**Figure 8.** Stokes' law plots of the diffusion coefficients of uncharged solutes at 683 K (solvent density of 0.35 g cm<sup>-3</sup>).

of Standards and Technology) at this temperature and solvent density is approximately  $3 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$ .

An ion moving in a polar solvent experiences an additional friction  $\zeta_D$  from the relaxation of the solvent polarization, so that the total friction,

$$\zeta = \zeta_V + \zeta_D \quad (6.3)$$

The dielectric friction  $\zeta_D$  has been the focus of recent theoretical and computational studies. The continuum description reported by Zwanzig<sup>16</sup> and Hubbard and Onsager<sup>17</sup> shows that it varies as  $R_i^{-3}$  and is proportional to the square of the charge  $q$ :

$$\zeta_D = C \frac{q^2(\epsilon - \epsilon_{\infty})}{R_i^3 \epsilon(1 + 2\epsilon)} \tau_D \quad (6.4)$$

where  $C = 3/4$ ,  $\tau_D$  is the Debye relaxation time,  $\epsilon$  and  $\epsilon_{\infty}$  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 because the cation and anion mobilities lie on two separate curves as a function of ion size at 298 K but not, as shown here, at supercritical temperatures. The explanation for the qualitative difference in the mobilities of cations and anions at room temperature was traced to the charge asymmetry of the water molecule.<sup>1</sup>

The observed diffusion coefficients of charged and uncharged solutes as a function of temperature can only be understood through a detailed molecular explanation. The effect of charge asymmetry of the water molecule on the mobilities of cations and anions at room temperature is one example of the importance of treating the problem at a molecular level. In a pioneering molecular study of ionic friction, Wolynes<sup>18</sup> assumed Brownian dynamics and split the total friction coefficient into four terms,  $\xi_{HH}$ ,  $\xi_{HS}$ ,  $\xi_{SH}$ , and  $\xi_{SS}$ , where the first and the last are essentially equivalent to the hydrodynamic drag and dielectric friction respectively and the cross-terms were ignored.

(16) Zwanzig, R. *J. Chem. Phys.* **1963**, *38*, 1603; *J. Chem. Phys.* **1970**, *52*, 3625.

(17) (a) Hubbard, J. B.; Onsager, L. *J. Chem. Phys.* **1977**, *67*, 4580. (b) Hubbard, J. B. *J. Chem. Phys.* **1978**, *68*, 1649.

(18) Wolynes, P. *J. Chem. Phys.* **1978**, *68*, 473.

The cross-terms, however, are significant<sup>1b</sup> and have been taken into account in a recent molecular theory of ionic friction proposed by Chong and Hirata.<sup>19</sup> Application to ions at supercritical temperatures would require extensive theoretical calculations of the correlation functions that are beyond the scope of this study. We have instead analyzed the mobility of ions using a simple semicontinuum model that goes back to the work of Chen and Adelman,<sup>20</sup> Wolynes,<sup>21</sup> and Impey et al.<sup>8b</sup>

Chen and Adelman extended the continuum model to include the effects of local solvent structure and dynamics by using an effective hydrodynamic radius  $R_V$ , defined by

$$\frac{1}{R_V} = (1 - \Delta) \frac{1}{R_{is}} + \Delta \frac{1}{R_i} = \frac{1}{R_i} \left[ \Delta + (1 - \Delta) \frac{R_i}{R_{is}} \right] \quad (6.5)$$

and an effective dielectric radius  $R_D$ , defined by

$$\frac{1}{R_D^3} = \frac{R_{is}}{R_i^4} f(\Delta, R_i/R_{is}, \epsilon_{loc}) \quad (6.6)$$

instead of the bare radius  $R_i$  appearing in the expressions for the viscous and dielectric friction, respectively. Here,  $R_{is}$  is approximately equal to the size of the first solvation shell of the ion. Within that shell is defined a local density  $\rho_{loc}$ , viscosity  $\eta_{eff}$ , dielectric constant  $\epsilon_{loc}$ , and the solvation function

$$\Delta = \frac{\eta \rho_{loc}}{\eta_{eff} \rho} \quad (6.7)$$

in which  $\eta$  and  $\rho$  are the viscosity and density of the bulk solvent, respectively. This solvation function  $\Delta$  is determined by the extent of solvation of the ion, and its value lies between 0 and 1, corresponding to rigid solvation and no solvation, respectively. The function  $f(\Delta, R_i/R_{is}, \epsilon_{loc})$  interpolates smoothly between the fully solvated and unsolvated limits. It follows that the recalculated hydrodynamic and dielectric friction can be interpolated smoothly between these limits. Note that even if there is complete desolvation in the sense that  $\Delta = 1$ , the dielectric radius may still be close to  $R_{is}$ , as long as there is dielectric saturation in the first shell. The effective hydrodynamic and dielectric radii of an ion are both larger than the bare radius of small ions that are strongly solvated. This leads to the counterintuitive notion that the dielectric friction is relatively weak for both very small and very large ions. It is weak for large ions because of their size, and weak for small ions that are strongly solvated because the moving entity is the large solvated species—this is the classic “solventberg” picture. A recent analysis of the friction coefficients of ions at 298 K supports this view.<sup>1c</sup>

These ideas have given rise to the notion that ionic friction can be treated hydrodynamically by a semicontinuum theory using effective local and bulk viscosities determined by solvent relaxation in different regions around the ion. This is clarified further by a suggestion of Wolynes and Hubbard<sup>21,22</sup> that the friction coefficient can be written as

$$\frac{1}{\zeta} = \int_{R_i}^{\infty} \frac{dr}{4\pi r^2 \eta(r)} \quad (6.8)$$

(19) Chong, C.; Hirata, F. *J. Chem. Phys.* **1998**, *108*, 739.

(20) Chen, J. H.; Adelman, S. *J. Chem. Phys.* **1980**, *72*, 2819.

(21) Wolynes, P. *Annu. Rev. Phys. Chem.* **1980**, *31*, 345.

(22) Hubbard, J.; Wolynes, P. *Theories of Solvated Ion Dynamics*. In *The Chemical Physics of Solvation*, Part C; Dogonadze, R. V., Kalman, E., Koryshev, A. A., Ulstrup, J., Eds.; Elsevier: Amsterdam, 1988.

**Table 3.** Ratio  $D/D_0$  of the Diffusion Coefficients of Charged and Uncharged Solutes in Aqueous Solution at Infinite Dilution at 683 K and Solvent Density of  $0.35 \text{ g cm}^{-3}$  Compared with Theory<sup>a</sup>

| solute                        | $D/D_0$<br>(simulation) | $\tau_{\text{solv}}/\tau_{\text{res}}$ | $\sigma_{\text{io}} (\text{\AA})$ | $R_{\text{h}} (\text{\AA})$ | $R_{\text{i}} (\text{\AA})$ | $F = D/D_0$<br>(theory) |
|-------------------------------|-------------------------|--|-----------------------------------|-----------------------------|-----------------------------|-------------------------|
| $\text{Li}^+/\text{Li}^\circ$ | 0.12                    | 0.13                                   | 2.337                             | 2.9                         | 0.75                        | 0.37                    |
| $\text{Na}^+/\text{Na}^\circ$ | 0.22                    | 0.29                                   | 2.876                             | 3.5                         | 1.29                        | 0.55                    |
| $\text{F}^-/\text{F}^\circ$   | 0.27                    | 0.31                                   | 3.143                             | 3.7                         | 1.56                        | 0.61                    |
| $\text{Cl}^-/\text{Cl}^\circ$ | 0.37                    | 0.40                                   | 3.785                             | 4.7                         | 2.20                        | 0.68                    |
| $\text{I}^+/\text{I}^\circ$   | 0.46                    | 0.36                                   | 4.168                             | 5.3                         | 2.58                        | 0.70                    |
| $\text{I}^-/\text{I}^\circ$   | 0.57                    | 0.36                                   | 4.168                             | 5.1                         | 2.51                        | 0.70                    |

$$^a \sigma_{\text{oo}}/2 = 1.584 \text{ \AA}; F = F(\tau_{\text{solv}}/\tau_{\text{res}}, (\sigma_{\text{io}} - \sigma_{\text{oo}}/2)/R_{\text{h}}).$$

Here,  $R_{\text{i}}$  is the bare ion radius and  $\eta(r)$  is the local viscosity, equal to the bulk value  $\eta$  at  $r = \infty$ . Impey, Madden, and Macdonald<sup>8b</sup> modeled the distance-dependent viscosity as a step function, with

$$\eta(r) = \begin{cases} \eta_{\text{s}} & R_{\text{i}} < r < R_{\text{is}} \\ \eta & r > R_{\text{is}} \end{cases} \quad (6.9)$$

where  $R_{\text{is}}$  is the radius of the coordination shell, within which the viscosity is  $\eta_{\text{s}}$ . Substitution in eq 6.8 leads to

$$\frac{1}{\zeta} = \frac{1}{4\pi R_{\text{i}}} F(\eta/\eta_{\text{s}}, R_{\text{i}}/R_{\text{is}}) \quad (6.10)$$

in which

$$F(\eta/\eta_{\text{s}}, R_{\text{i}}/R_{\text{c}}) = \left\{ \frac{\eta}{\eta_{\text{s}}} + \left( 1 - \frac{\eta}{\eta_{\text{s}}} \right) \frac{R_{\text{i}}}{R_{\text{is}}} \right\} \quad (6.11)$$

This is unity for an unsolvated ion when  $R_{\text{i}} = R_{\text{is}}$  and  $\eta_{\text{s}} = \eta$ . If we neglect electrostriction and identify  $\eta_{\text{s}}$  with  $\eta_{\text{eff}}$ , eq 6.11 is identical to the Chen–Adelman expression for the viscous friction. Impey et al.<sup>8b</sup> applied this model to the friction of ions in aqueous solution at room temperature, and Balbuena et al.<sup>4,5</sup> used the same model to interpret the mobilities of ions at supercritical temperatures. We use the model to discuss our results for the diffusion coefficients of charged and uncharged species at infinite dilution, where the complications of interionic interactions are absent.

The bare radius of the solute  $R_{\text{i}}$  in this model is related to the Lennard-Jones parameters. It follows that the ratio of the diffusion coefficients of charged and uncharged species of the same bare radius is given by

$$\frac{D_{\text{i}}}{D_0} = F(\eta/\eta_{\text{s}}, R_{\text{i}}/R_{\text{is}}) \quad (6.12)$$

The results of our simulations and calculations are reported in Table 3. They are compared in the same table with our estimates of the ratio of the bulk to the local viscosity, approximated as the ratio of the bulk solvent relaxation time  $\tau_{\text{solv}}$  to residence time of the water  $\tau_{\text{res}}$  in the first hydration shell of radius  $R_{\text{h}}$ :

$$\frac{\eta}{\eta_{\text{s}}} = \frac{\tau_{\text{solv}}}{\tau_{\text{res}}} \quad (6.13)$$

We take the radius of the bare ion  $R_{\text{i}} = \sigma_{\text{io}} - \sigma_{\text{oo}}/2$ , and  $R_{\text{is}} = R_{\text{h}}$ , which is the radius of the first hydration shell, to determine the function  $F(\eta/\eta_{\text{s}}, R_{\text{i}}/R_{\text{is}})$  for ions. Table 3 shows that our calculation of  $F(\eta/\eta_{\text{s}}, R_{\text{i}}/R_{\text{is}})$  is in qualitative agreement with  $D/D_0$ , despite the approximations involved. The ratio  $D/D_0$ , from  $\text{I}^-/\text{I}^\circ$  to  $\text{Li}^+/\text{Li}^\circ$ , decreases by a factor of 5 in our simulations, while the simple theory gives the correct trend only to within

a factor of 2. The agreement could be improved by assuming  $R_{\text{is}}$  is larger than the radius  $R_{\text{h}}$  of the first hydration sphere. Note, however, that the ratio  $\tau_{\text{solv}}/\tau_{\text{res}}$  is already close to  $D/D_0$ , the ratio of the diffusion coefficients, except for  $\text{I}^+/\text{I}^\circ$  and  $\text{I}^-/\text{I}^\circ$ . This suggests a completely different mechanism for the diffusion of ions at supercritical temperatures, governed largely by fluctuations in the solvent density in the vicinity of an ion, which explains its weak dependence on ion size.

## 7. Conclusions and Summary

Our interest in the structure and dynamics of aqueous ionic solutions at supercritical temperatures has led us to compute the equilibrium and transport properties of a series of ions and uncharged solutes at infinite dilution in this and in the preceding paper. We have carried out MD simulations for an extensive set of positive, negative, and uncharged solutes (“drones”) at infinite dilution under supercritical conditions of 683 K and a solvent density of  $0.35 \text{ g cm}^{-3}$ . We have also carried out simulations of several ions and “drones” at solvent densities of 0.997 and  $0.20 \text{ g cm}^{-3}$  at 683 K. The dynamical properties of solutes at high temperature are compared in this paper with the corresponding properties of the same species at 298 K.

The hydration numbers of small ions are relatively insensitive to changes in either temperature or density. However, the residence times of water in the primary hydration shells of the ions at 683 K are lower by an order of magnitude compared to their values at 298 K and are only weakly dependent on the size and sign of the ionic charge and on the solvent density. We conclude that, although the structures of the hydration shells of small ions associated with hydrophilic solvation are unchanged, the dynamics of these shells are strongly temperature dependent and weakly dependent on the solvent density.

The situation is somewhat different for large ions ( $\text{I}^+$  and  $\text{I}^-$ ) and for uncharged solutes, where there is evidence of cage formation at high density ( $\sim 0.997 \text{ g cm}^{-3}$ ) at both 683 and 298 K. The cages around uncharged solutes collapse at low density, and the solvent is depleted or expelled from the vicinity of uncharged species at 683 K when the solvent density is  $0.35 \text{ g cm}^{-3}$  or less. In this case, there is no discernible hydration shell, which implies the absence of any residence time for the water of hydration. When a cage is formed around a large ion ( $\text{I}^-$  and  $\text{I}^+$ ) or uncharged solute at high solvent density at 683 K, the residence time of water making up the cage is again much smaller than it is at 298 K. We conclude that the exchange dynamics of the cages in hydrophobic hydration are much faster at 683 than at 298 K, although weakly dependent on the solvent density. The high solvent compressibility in the supercritical region can be exploited to change the extent of hydrophobic solvation of uncharged solutes in this region by increasing or decreasing the pressure to produce the required change in the solvent density.

A related property of solvation is the dynamics of solvent reorientation and rearrangement when the charge on an ion is suddenly turned on or off. This has been studied extensively by computer simulation and experimentally using time-delayed fluorescence shift spectroscopy. At room temperature, the solvent response depends on the size of ion being charged up. Our computer simulations show that the solvation dynamics of sodium and chloride ions at 683 K and a solvent density of  $0.35 \text{ g cm}^{-3}$  are very similar to each other, in contrast to their behavior at room temperature 298 K at a solvent density of  $0.997 \text{ g cm}^{-3}$ . In this sense, the details of the solvent structure appear to be less important at high temperature, but there are other factors related to the time scale of the solvent density



fluctuations in the critical region that may affect the response to charging up an ion.

The diffusion coefficients of ions are larger in magnitude at 683 K, and at low solvent density they are less differentiated by size and charge sign than under ambient conditions. This is of particular relevance to the experimental studies of the conductance of the ions under supercritical conditions, obtained by Wood et al.<sup>23</sup> and by Quist and Marshall.<sup>24</sup> An uncharged solute of the same size as an ion diffuses 2–9 times faster than the corresponding charged species, with the smaller solutes moving much faster than the larger ones. The solute viscosity at 683 K and a solvent density of 0.35 g cm<sup>-3</sup> is calculated to within a factor of 4, assuming Stokes's law. Our earlier simulations of uncharged solutes at 298 K and a solvent density of 0.997 g cm<sup>-3</sup> also led to a solvent viscosity in agreement with experimental results to within a factor of 2.<sup>1</sup> The reason Stokes's law applies to such small atomic size solutes in water is not fully understood, although it has been discussed for hard-sphere systems by Cukier et al.<sup>25</sup>

Increasing the solvent density to 0.997 g cm<sup>-3</sup> at 683 K from the critical density of nearly 0.3 g cm<sup>-3</sup> decreases the diffusion coefficients of ions and uncharged solutes. The distinct maxima in the diffusion coefficients of cations and anions as a function of their size found at 298 K are also observed at 683 K and high density (0.997 g cm<sup>-3</sup>) but are absent when the solvent density is lowered to 0.35 g cm<sup>-3</sup>. We conclude that this behavior is correlated with the density of the solvent rather than with the temperature of the system.

We have sought an explanation for the diffusion coefficients of charged and uncharged species at low solvent density typical

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(24) Quist, A. S.; Marshall, W. *J. Phys. Chem.* **1968**, *72*, 684.

(25) Cukier, R. I.; Kapral, R.; Lebenhaft, J. R.; Mahaffey, J. R. *J. Chem. Phys.* **1980**, *73*, 5244.

of the supercritical region in terms of a semicontinuum theory. It shows the right trends, but there are signs that another effect may play a role in controlling diffusion under these conditions. This comes from the observation that at 683 K the ratio of the diffusion coefficients ( $D/D_0$ ) of the otherwise identical charged and uncharged species is nearly equal to the ratio ( $\tau_{\text{solv}}/\tau_{\text{res}}$ ) of the bulk solvent relaxation time  $\tau_{\text{solv}}$  to residence time of the water  $\tau_{\text{res}}$  in the first hydration shell. It suggests that the time scale of the solvent density fluctuations in the vicinity of the ion or solute and in the bulk fluid control ion and neutral solute diffusion in supercritical solutions of low solvent density. These fluctuations could play a role by making the diffusion non-Brownian,<sup>26</sup> with the result that the mobilities of the ions are less dependent on their size. The presence of fluctuating voids and solvent clusters in supercritical solutions adds to the complexity of a theoretical treatment of the dynamics of solutes. A detailed molecular explanation of ion diffusion or mobility at ambient and supercritical temperatures remains to be worked out.

**Acknowledgment.** This study was supported by grants from the National Science Foundation, CHE 99610288 and CHE 9961336, to J.C.R. The assistance of Vice President Dan Dwyer of the University of Maine in providing interim support for J.P.N. is gratefully acknowledged. The hospitality of Drs. J. Hubbard, Anne Plant, R. Mountain, and M. Gilson at the National Institute of Standards and Technology at Gaithersburg, MD, and at the Center for Advanced Research in Biotechnology at Rockville, MD, is most gratefully acknowledged.

JA001979R

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