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SELF-DIFFUSION COEFFICIENT OF WATER IN THE PRESENCE OF ALKALI HALIDE IONS

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The self-diffusion coefficient of water in aqueous solutions of alkali halides at different concentrations was studied using the polarizable BK3 model of water [1]. As ion potentials, initially the alkali halide force field fitted to this water potential by the solvation free energy, ion-water clusters as well as, for the purpose of crosschecking, to the ambient crystal energy and density was investigated. It was found that the strength of attraction between the central ion and the water molecules in the hydration shell is stronger than in reality, which manifests itself in the reduced mobility of water. For small ions, this discrepancy is small. By omitting the dipolar polarization of larger ions, the estimates could be improved. Similarly, increasing the size of the anions within reasonable limits also enhances the results but the structural breaking effect is insufficient. If the relative permittivity of water is smaller than that measured experimentally, typically ionic charges in non-polarizable water models can be decreased to recover the correct semi-macroscopic Coulomb energy. Since our polarizable water model reasonably estimates the relative permittivity, smaller ionic charges were used to quantify the differences in the strengths of ion-water attraction. Our estimates of self-diffusion in aqueous solutions by varying the concentration of ions are presented and discussed for LiCl, NaCl, NaBr, NaI, RbF and RbI.

Keywords: aqueous solution, polarizable BK3 model, simulation

1. Introduction

The strict tetrahedral structure of hexagonal ice breaks down in liquid water. In ambient water, depending on the calculation method, the average number of hydrogen bonds in a molecule is 3.2-3.6. The bonds break and reform but maintain this imperfect network. Since a relatively dilute liquid is maintained by this arrangement, external pressure destroys the network to some extent, leading to extreme conditions during transport processes. At low temperatures, an external pressure of several hundred kilobars breaks the bonds resulting in faster transport, while under even larger pressures, the compressive force decreases the rate of transport again as is the case with normal liquids. This behavior is reproduced qualitatively by the BK3 and TIP4P/2005 models of water [1]-[3].

Charged solutes in water also formally increase the pressure because the energy density in the dielectric dimensionally is pressure. Therefore, it should be straightforward to determine the degree of self-diffusion of water by calculating the pressure caused by the ions and connecting this to the appropriate value in a diagram by plotting the pressure against the degree of self-diffusion. An essential part of this procedure is the relative permittivity of water. In a strong electric field, the dielectric constant exhibits nonlinear behavior which in the case of an electrolyte equates to a function dependent on the distance from the ion. Near to the ion, the dielectric constant decreases as a result of two phenomena, namely the break-down of the structure of the liquid and dielectric saturation. The initial value is the internal index of refraction, which originates from the atomic and electronic polarization of the particle as well as corresponds to the high frequency limit of this parameter. The experimental optical dielectric constant of water under ambient conditions is $n^2 = \varepsilon_\infty = 1.78$, which increases with distance until the frequency, ε_0, falls to zero and the static dielectric constant is reached. For water under ambient conditions, $\varepsilon_0 = 78.4$. The nonlinear dielectric behavior was studied in detail by Ruff, Liszi and Mészáros for several solvents and solutes, who even drew up a function of the distance-dependent dielectric constant which, beyond 0.4-0.8 nm, depending on the solvent, asymptotically approached the corresponding ε_0 [4]-[7]. They also tested it in terms of the solvation free energy which yielded good results. The size of the ion, that is, the radius of the ionosphere, determined the values of the function that should be used. For small ions, this interaction was stronger.

Since small ions strongly attract water molecules, the energy density corresponds to a high-pressure state where the self-diffusion and viscosity exhibit the behavior of a normal compressed liquid with a lower degree of transport. For large ions, given that the

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attraction is weaker, the resulting energy density in the first hydration shell corresponds to a moderate pressure as the transport of momentum or particles increases [8]. Although this semi-macroscopic and semi-empirical idea qualitatively describes the phenomena, it does not reveal any information about the microscopic nature of a granulated liquid.

Obviously, the dielectric behavior of the liquid in an ionic solution is a crucial factor. The dielectric constant is a difficult property to determine by computer simulation because it is time-consuming to calculate. The dielectric constant is a function of the dipole moment as well as the dipole moment distribution and structure in polarizable models. Regarding the BK3 model [1], the average dipole moment in ambient water is ≈ 2.65D which is much larger than in non-polarizable models which severely underestimate this parameter because their fixed dipole moment is most commonly fitted to the ambient internal energy, density and the pair correlation function or even self-diffusion. The moderate dipole moments prevent these models from reproducing the experimental ε_0. Kann and Skinner wanted to reproduce the self-diffusion of water in the presence of alkali halide ions using computer simulations by considering possibilities and surveying the literature on interaction models [9]. As a result, Kann and Skinner introduced a scale based on the following equality [9]:

$$q^2 \,/\, \varepsilon_0 r = q_{eff}^2 \,/\, \varepsilon_{sim} r \qquad (1)$$

They used the new q_{eff} in their calculations, carried out a comprehensive number of simulations of different models and managed to improve the self-diffusion of water in the presence of alkali halides.

Our aim is to study polarizable water and ion models. The BK3 model with its Gaussian charges, charge-on-spring polarization and exponential repulsion covers the entire phase diagram from high-pressure solids to vapors with an acceptable degree of accuracy [1]. For ambient liquids, the estimates are correct even numerically. Most importantly, the temperature-dependent dielectric constant within the margin of error is accurate [1]. A further advantage is that the model qualitatively reproduces the pressure-dependent extremes of self-diffusion and viscosity [2]. As models of ions, polarizable force fields parametrized to the BK3 model were used and the fitted properties were the hydration free energy, energy and geometry of the ion-water cluster as well as the ambient crystal energy and structure [10].

Granulated water is quite different from a semi-macroscopic model. There are two effects which sometimes compete with each other that need to be taken into account: the strength of attachment of the water molecule to the ion and the breakage of the hydrogen-bond network by the ion. A water molecule, depending on the ion attached to it, spends approximately 10 picoseconds [11] before leaving the hydration shell, allowing other molecules to hydrate. During this time, the ion joins the attached water molecules and creates a larger but less mobile entity. Even though the strength of this attachment is obviously large for smaller ions like Li^+ and Na^+, because of their size they can only be surrounded by 4 or 5 molecules, respectively [10]. The degrees of coordination of the oxygen in water to K^+, Rb^+ and Cs^+ using this model are 6.99, 8.18 and 9.55, respectively. For anions, the hydration shell is less definite, mainly as a result of the smaller degree of attraction and the imperfect structural fit of the ion [10], thereby increasing the presence of large anions close to the free surface of water [12]. The degrees of coordination of water molecules to F^-, Cl^-, Br^- and I^- are 5.40, 5.85, 6.18 and 6.37, respectively [10]. These values were obtained from evaluating the partial pair correlation functions. It was concluded that no water molecule is bonded by both of its hydrogen atoms [10]. Interestingly, although the repulsive parameters of chloride closely resemble those of water (see *Tables 1 and 2*), its coordination number is 5.85.

In this paper, the impact of three parameters on the self-diffusion of water is studied. In certain cases, the polarization is omitted and, within reasonable limits, the size of anions is increased. A relatively free approach is adopted and the charges of ions varied to quantify the "apparent" connection strength between the ion and its solvation shell. This approach creates a slightly unrealistic system because the smaller charge not only interacts with its adjacent neighbors. However, other charges in the system, including the relatively large partial charges of water, screen these interactions. While an error is introduced with regard to the energy of the system, it will only have a moderate impact on the long-distance structure. Experimental results for several typical ion pairings reported by Müller and Hertz are taken into consideration [13].

2. Details of the simulations

The Gaussian charges of a molecule or ion in general are represented by a spherical charge distribution as follows:

$$\rho_{ia}(\mathbf{r}) = \frac{q_{ia}}{(2\pi\sigma_{ia}^2)^{3/2}} exp\left(\frac{-|\mathbf{r}-\mathbf{r}_{ia}|^2}{2\sigma_{ia}^2}\right) \qquad (2)$$

where ρ_{ia} denotes the charge density of site a on molecule i centered at r_{ia}, whose charge is represented by q_{ia} and its distribution width by σ_{ia}. The corresponding Coulomb interaction energy, U_{qq}, between Gaussian charges then becomes:

$$U_{qq} = \frac{1}{2}\sum_{i,j\neq i}^{N}\sum_{a,b}\frac{q_{ia}q_{jb}}{4\pi\varepsilon_0|\mathbf{r}_{ia}-\mathbf{r}_{jb}|} erf\left(\frac{|\mathbf{r}_{ia}-\mathbf{r}_{jb}|}{\sqrt{2(\sigma_{ia}^2+\sigma_{jb}^2)}}\right) \qquad (3)$$

where *erf* denotes the error function. It can be seen from *Eq. (3)* that as the distribution width approaches zero, i.e. $\sigma \to 0$, the usual formula for the Coulomb interaction energy between point charges is recovered. This energy is a function of the σ -s, namely the wider the distribution is, the higher the energy will be between two opposite point charges positioned the same distance from each other. *Eq. (3)* can be estimated by using the Ewald method previously described in detail [14]. A non-electrostatic form is added to the charge-charge interactions:

$$U(r) = A\exp(-Br) - C/r^6 \qquad (4)$$

Kong suggested a combined rule [15] based on the following approximation:

$$U_{ij}(R) = \frac{1}{2}\left[U_{ii}(2r_1) + U_{jj}(2r_2)\right] \qquad (5)$$

where

$$r_1 + r_2 = R \quad \text{and} \quad \left.\frac{dU_{ii}(r)}{dr}\right|_{r=2r_1} = \left.\frac{dU_{jj}(r)}{dr}\right|_{r=2r_2}$$

By applying it in terms of exponential repulsion leads to:

$$A_{ij} = \frac{1}{2}\left[A_{ii}\left(\frac{A_{ii}B_{ii}}{A_{jj}B_{jj}}\right)^{\frac{B_{ii}}{B_{ii}+B_{jj}}} + A_{jj}\left(\frac{A_{jj}B_{jj}}{A_{ii}B_{ii}}\right)^{\frac{B_{jj}}{B_{ii}+B_{jj}}}\right] \qquad (6a)$$

$$B_{ij} = \frac{2B_{ii}B_{jj}}{B_{ii} + B_{jj}} \qquad (6b)$$

It is used not just for ion-ion but for ion-water interactions as well. The advantage of this formula if the sizes are additive was presented earlier [10]. The *C* parameters are combined according to the typical formula below:

$$C_{ij} = \sqrt{C_{ii}C_{jj}}$$

In *Table 1*, the parameters of repulsion are presented [10]. The simulations were conducted using our own code in a cubic simulation box and under periodic boundary conditions. The integrator was an isothermal-isobaric implementation of the Velocity Verlet algorithm [16], while the rotational degrees of freedom for water were handled by quaternions along with an algorithm [17]. The iteration of the three charge-on-spring (COS) charges for water and the ion have previously been described [1,10,14,18]. Typically, a predictor-corrector scheme was used to decrease the number of iterations before the minimum energy of the actual atomic configuration was reached. The pressure and temperature were fixed at 1 bar and 298 K, respectively.

The parameters of the BK3 model are presented in *Table 2*. Point *M* denotes the base of the negative charge on the bisector of the HOH angle.

Table 1. Interaction parameters of ions taken from [10] (Polarizability (α), Gaussian distribution width (σ) as well as the parameters of repulsion (A, B and C))

	α (Å^3)	σ (Å)	A (kJ/mol)	B (Å^{-1})	C (kJÅ^6/mol)
Li$^+$	0.032	0.37	1.8x10^{12}	20	150
Na$^+$	0.157	0.65	8.5x10^{12}	15	550
K$^+$	0.830	0.70	1.7x10^{15}	13	1900
Rb$^+$	1.37	0.75	1.95x10^{13}	10	4500
Cs$^+$	2.36	0.85	1.22x10^{12}	8	9000
F$^-$	1.30	0.78	1.2x10^4	2.4	1000
Cl$^-$	3.50	0.96	9.4x10^5	3.1	8000
Br$^-$	4.60	1.01	4.4x10^8	4.5	11000
I$^-$	7.50	1.14	1.25x10^{13}	6.5	20000

Table 2. Interaction parameters for the water model as taken from [1]

Geometry	Electrostatics	Polarization	Nonelectrostatic
$d_{OH} = 0.975$ Å	$q_H = 0.584\ esu$	$\propto = 1.44$ Å^3	$A = 322000\ kJ/mol$
$\theta_{HOH} = 104.52°$	$q_M = -1.168\ esu$	$\propto_H = 0.25 \propto = 0.36$ Å^3	$B = 3.56/$Å
$d_{OM} = 2.661$ Å	$\sigma_H = 0.4$ Å^{-1}	$\propto_M = 0.5 \propto = 0.72$ Å^3	$C = 3320\ kJ$Å$^6/mol$
	$\sigma_M = 0.71$ Å^{-1}		

250 water molecules were examined and the ions implanted by replacing water molecules with 4, 10, 14, 18, 22, 30 and 50 ions corresponding to 0.45, 1.57, 1.65, 2.16, 2.68, 3.79 and 6.94 mol/kg of solvent, respectively. These solutions were equilibrated with a general ion pair. The time step was 2fs and for each ion pair studied, the system was equilibrated further for 200-600 thousand time steps and diffusion data collected according to the expression:

$$D = \lim_{t\to\infty}\frac{1}{6t}\left\langle\frac{1}{N}\sum_{i=1}^{N}[\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2\right\rangle \qquad (7)$$

for 800 thousand time steps. The results were tested over longer time ranges as well. The results remained practically identical and any irregularities originated from the small size of the system which sometimes can stabilize special local configurations. The lines were fitted to the last 2,500 time steps of the 4,000-time-step-long dataset of *Eq. (7)*. Since the self-diffusion coefficients calculated under periodic boundary conditions depend strongly on the size of the system, the following correction factor to eliminate the finite-size effect was applied [19]:

$$D_0 = D_{PBC} + 2.837297\frac{k_B T}{6\pi\eta L} \qquad (8)$$

where D_0 denotes the self-diffusion coefficients of the infinite system, D_{PBC} stands for the value calculated under periodic boundary conditions, η represents the viscosity and L refers to the length of the cubic simulation box. The viscosity of the BK3 model under ambient conditions is η = 951.0 ± 007.0 mPs, slightly larger than the experimental value of 0.896. The self-diffusion coefficient, D_w $(10^{-9}\text{m}^2\text{s}^{-1})$ = 2.28 ± 0.04, closely resembles the experimental value of 2.30 [1]. These quantities were not used to fit the parameters for the BK3 model.

3. Results and Discussion

Measurements of water self-diffusion [13] can be separated into two groups of aqueous solutions of alkali halides. Although the list is not comprehensive for the 20 possible combinations, the trends are quite clear. Small cations like Li^+ and Na^+ decrease the self-diffusion of water as the ion concentration increases monotonically (LiCl, LiBr, NaCl, NaBr, NaI) as do fluorides (KF, RbF, CsF) because the anion is very small. This trend can be observed less rapidly for KCl as both ions are of medium size. For larger combinations of cations and anions, local maxima were observed for KBr, RbCl, RbBr, RbI, CsCl, CsBr and CsI in this order of the size of the maxima, however, the data for the last two ion pairs is not so comprehensive.

Following some pilot calculations, it became clear that the attraction between the ions and water molecules in the hydration shell is stronger than that implied by the experimental data. Since previous calculations only dealt with static properties, the dynamics of the electrolyte system were not examined [10]. To quantify the discrepancies, the charges of the ions were varied, in some cases the polarization of ions was ignored, and repulsion increased to change the steric effects. Although such a drastic change in the charges seems unphysical, this introduces a more tangible factor about overestimating the strength of forces in the original model [10] than polarization or increased repulsion. Nevertheless, even though the latter two are the most significant, they should be more realistic, that is, more complex than dipolar polarization and repulsion with more appropriate functional forms and parameters not necessarily fixed in different surroundings. Since the change in charge for the hydration shell alone cannot be limited, the system will be somewhat artificial.

As examples, LiCl, NaCl, NaBr, NaI, RbF and RbI were dealt with. The figures for these systems are presented. A previous model is referred to as the original to simplify the explanation [10]. The symbols are the same for all the figures (see explanation under the figures).

The results for LiCl are shown in *Figure 1*. Although the original model underestimates the experimental results, the difference is not that significant. By decreasing the charges, the results are improved since the simulation overestimates the experimental values when 0.50 esu is applied. It is true of all systems that for smaller charges the absence of polarization is less important simply according to the charge-on-spring technique of the method.

The underestimation of the experimental data by the original model of NaCl is larger than that of LiCl. Even though the repulsion of the chloride ion is similar to that of water as has previously been alluded to before, it cannot be involved in hydrogen bonding. By removing the polarization, the calculated results are significantly improved (*Figure 2*). The results of NaBr are similar to those of NaCl but their difference compared to the experimental ones is larger (*Figure 3*).

For NaI (*Figure 4*), again the non-polarizable form of the original is significantly improved, even though the data points are scattered. The scattered values were checked with a long equilibration and data collection but the results remained practically the same. The scattered nature is assumed to be an artifact of the limited size of the system. While the difference between the polarized and non-polarized values with 0.65 esu for the chloride ions was negligible, for iodide this cannot be neglected because it is highly polarizable.

The results for RbF are shown in *Figure 5*. Since the degree of polarization of both ions is moderate, the improvement by removing polarization is also moderate. The charge of 0.50 esu for RbF provides a good estimate of the experimental results. On this figure, the results calculated by the original potential when parameter A for the repulsion of fluoride (green dots) is ten times larger are shown. The impacts of this enhanced repulsion and the removal of polarization are similar.

From our chosen samples, the real challenge is the aqueous solution of RbI (*Figure 6*). The experimental self-diffusion coefficient values of water show a rapid increase and after a moderate maximum remain high even at large concentrations, indicating that these ions destroy the hydrogen-bonded network of the system by only weakly attracting their neighbors. It is shown in *Figure 6* that by removing the dipolar polarization, the results are significantly improved but far worse than the experimental ones. (The data points for the original were so low at the highest concentrations that a linear trend from *Eq.(6)*. was not obtained). Decreasing the charges in itself did not help. The dark blue diamonds denote the results when repulsion of the iodide ions was increased by a factor of 10 for the non-polarizable model with a charge of 0.50 esu. The brown diamonds represent the results when parameter A of the repulsive wing was multiplied by 10 for both ions. Although the plot of these results is scattered, such interactions are necessary to reproduce the experimental results.

The factor of 10 with regard to parameter A of the iodide ions is not as unrealistic as it seems. Ambient crystals of alkali halides provide lattice constants which approximately give the size of the ions. However, the size of one ion should be chosen arbitrarily, otherwise the problem is underestimated, thereby distributing the relative sizes of cations vs. anions. Its size is manifested by a repulsion wing which is a continuous function according to a chosen mathematical form. The height and gradient characterize the function which in classical simulations is constant.

Clearly, this is not the case in reality. While the polarizability of anions is large, especially of iodide, it is reasonable to presume that it is manifested by the rapid redistribution of local charge densities in response to the

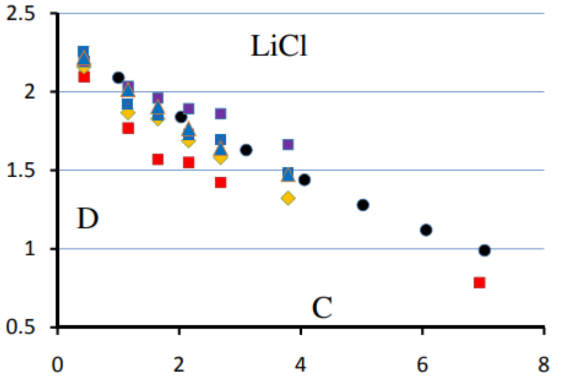

Figure 1. Self-diffusion coefficient of water is shown in terms of LiCl concentration, *C*, in mol/kg of solvent. The self-diffusion coefficient, *D*, is given in $10^{-9}m^2s^{-1}$.

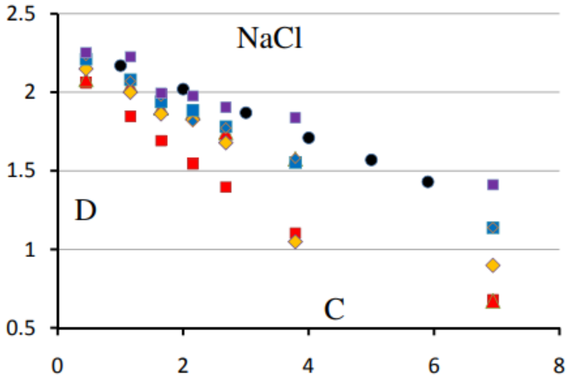

Figure 2. Self-diffusion coefficient of water in terms of NaCl concentration, *C*, in mol/kg of solvent. The self-diffusion coefficient, *D*, is given in $10^{-9}m^2s^{-1}$.

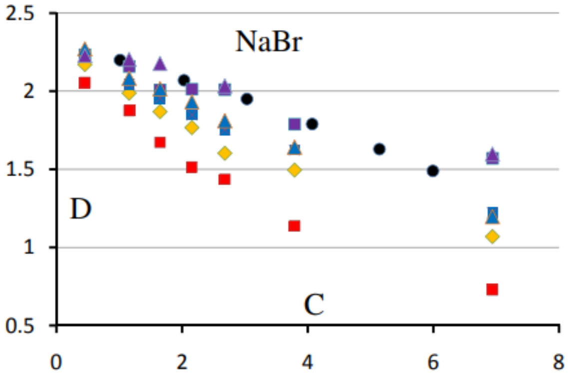

Figure 3. Self-diffusion coefficient of water is shown in terms of NaBr concentration, *C*, in mol/kg of solvent. The self-diffusion coefficient, *D*, is given in $10^{-9}m^2s^{-1}$.

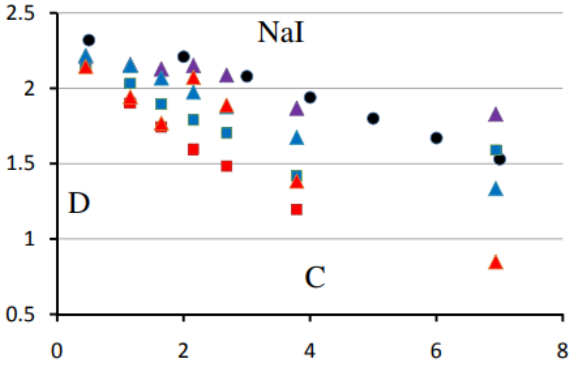

Figure 4. Self-diffusion coefficient of water in terms of NaI concentration, *C*, in mol/kg of solvent. The self-diffusion coefficient, *D*, is given in $10^{-9}m^2s^{-1}$.

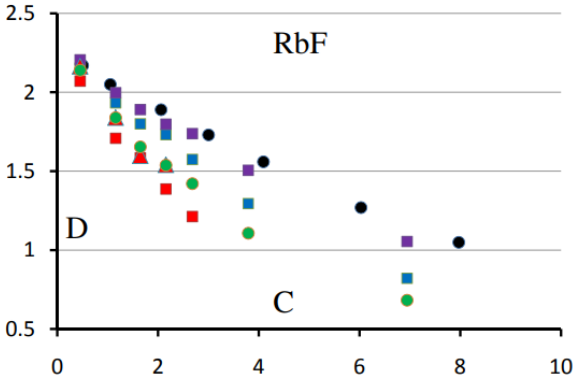

Figure 5. Self-diffusion coefficient of water in terms of RbF concentration, *C*, in mol/kg of solvent. The self-diffusion coefficient, *D*, is given in $10^{-9}m^2s^{-1}$.

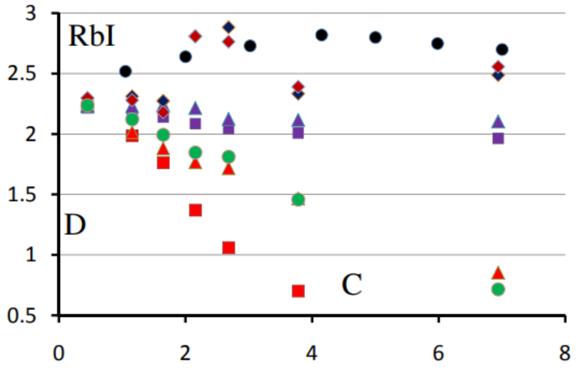

Figure 6. Self-diffusion coefficient of water in terms of RbI concentration, *C*, in mol/kg of solvent. The self-diffusion coefficient, *D*, is given in $10^{-9}m^2s^{-1}$.

- ● (black dots) - experimental
- ■ (red squares) - original
- ▲ (red triangles) - original without polarization
- ♦ (yellow diamonds) - original with a charge of 0.75 esu
- ■ (blue squares) - original with a charge of 0.65 esu
- ▲ (blue triangles) - original with a charge of 0.65 esu without polarization
- ■ (purple squares) - original with a charge of 0.50 esu
- ▲ (purple triangles) - original with a charge of 0.50 esu without polarization
- ● (green dots) - original with $A(I)_{used} = 10xA(I)_{orig}$
- ♦ (dark blue diamonds) - original with a charge of 0.50 esu without polarization and $A(I)_{used} = 10xA(I)_{orig}$
- ♦ (brown diamonds) - original with a charge of 0.50 esu without polarization and $A(I)_{used} = 10xA(I)_{orig}$ and $A(Rb)_{used} = 10xA(Rb)_{orig}$

liberation of neighboring water molecules. Nevertheless, the ion predominantly remains a spherical entity in contrast to the result of dipolar polarization. Therefore, while alkali halides seem to be simple and strongly ionic particles exhibiting spherical symmetry, good results to determine particular properties either in their pure form or in solution are not guaranteed. A good example is the lithium ion with bromide or iodide anions in crystalline form. The lithium ion gets much closer to these anions than any reasonable set of additive ion sizes would predict [10].

It is futile to vary the parameters of water since the performance of the model for pure water is excellent. Regarding ions, other parameters, e.g. parameter B which represents the steepness of repulsion, could obviously have been changed. Furthermore, the energy of the neighboring ion could have been changed by varying σ, but this would have been complicated to examine as a result of varying too many parameters.

4. Conclusions

The self-diffusion coefficient of water in alkali halide solutions by molecular dynamics simulations was examined. LiCl, NaCl, NaBr, NaI, RbF and RbI were selected as examples. Our system contained 250 water molecules and the ions were implanted by replacing water molecules with 4, 10, 14, 18, 22, 30 and 50 ions corresponding to 0.45, 1.57, 1.65, 2.16, 2.68, 3.79 and 6.94 mol/kg of solvent, respectively. Our water model was BK3 [1] and our ionic model was taken from the literature [10]. These models were developed consistently by measuring the Gaussian charges, charge-on-spring polarizability and exponential repulsion [1],[10]. The static results for the 20 combinations of ions were given with regard to solvation free energy, ion-water clusters and the structure of the solutions in terms of pair correlation functions. The energy and density of ambient crystals were determined as a crosscheck, the results of which were satisfactory [10].

In this paper, the self-diffusion coefficient of water in solutions was calculated and our results compared to experimental values. The results, which were underestimated in all cases, were small for LiCl but gradually increased as the ions became larger (*Figure 1*). The attraction between the ion and water in the solvation shell was stronger than in reality. To measure the apparent behavior, the charges of the ions were decreased. Gradually smaller charges yielded good estimates as the size and polarizability of the ions increased, namely 0.65 for LiCl and NaCl (*Figure 2*) as well as 0.50 for NaBr (*Figure 3*) and NaI (*Figure 4*). The removal of polarizability from the original model per unit of charge improved the results by enhancing the mobility of the ions, which is shown for NaCl and NaI. By removing the polarization of the chloride, the results very closely resembled the experimental ones, while for NaI, the data points were quite scattered but nevertheless the estimation was obviously substantially improved. For RbF (*Figure 5*), the charge of 0.50 esu yielded a good estimate. It can be seen from the figures that the ions without polarization improve the estimates at mainly small or moderate concentrations. By increasing the repulsion of fluoride by a factor of 10, the results also improve by approximately as much as they improved by removing polarization, indicating that a somewhat better formulation of ionic polarization using the polarized BK3 model can provide accurate results for these systems.

The presence of RbI strongly enhances the water mobility yielding a moderate maximum throughout the concentration range measured (*Figure 6*). Although the results are substantially improved by removing dipolar polarization, to closely resemble the experimental results, the repulsion had to be increased by multiplying factor A in the potential by 10 and the apparent charge of the ions decreased to 0.50 esu. A tenfold enhancement of repulsion can be obtained by defining smaller cations and larger anions. Changing the typical size ratio of cations to anions to a much greater degree can give good results with identical charges, however, this would destroy other properties of the pure alkali halides. The structural breaking effect of iodide is not simply a size-related phenomenon. The response of water to the spherical polarization of iodide can destroy the hydrogen-bond network which enhances the free motion of water molecules.

This study examined whether polarizable models can estimate the experimental values for the self-diffusion coefficient of water in the presence of alkali halides. Since the BK3 potential of water performs excellently in general, especially under ambient conditions, it is unnecessary to change the parameters of water.

Previously, the melting properties of alkali halides were studied [20]-0. First, only the original potential without dipolar polarization was varied, assuming that the symmetric character of the crystals remains approximately valid when melted. Although the results improved [20], they remained unsatisfactory, so an attempt was made to create individual ion potentials by combining the non size-additive rule to predict the correct melting temperature while maintaining the correct internal energy and density of the crystal. While this is straightforward to obtain good results for pairs [21], the possibility to combine individual potentials is limited 0. Melting results in temperature instability which gradually disintegrates the crystal. In this respect, the bottom of the potential well where the ion is positioned and the internal energy is determined as well as the pressure are not the determining factors. Given that the higher parts of the potential well are the barriers that need to be overcome by the ion, the requirements of a potential model are more complex. The present results also indicate that integrated properties like solvation free energy can be obtained with a reasonable degree of accuracy even for semi-macroscopic models, however, the prediction of more subtle properties, either in pure form or in solutions, is far from trivial.

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