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# Ion Solvation in Water from Molecular Dynamics Simulation with the ABEEM/MM Force Field

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A systematic study on monovalent ions in water clusters and in aqueous solution is presented for providing insight into their solvation structures, charge distributions, binding energies, as well as dynamic and thermodynamic properties in terms of the atom-bond electronegativity equalization method fused into molecular mechanics (ABEEM/MM) that is to take ABEEM charges into the Coulomb term in MM. For hydrated systems of $M^+(H_2O)_n$, $M^+$ being $Li^+$, $Na^+$, and $K^+$, as well as $X^-(H_2O)_n$, $X^-$ being $F^-$, $Cl^-$, and $Br^-$, with $n = 1-6$, parameters for the effective interaction between the ion and the water molecules were determined, so as to reproduce the experimental or ab initio results. The corresponding parameters were tested with molecular dynamics (MD) simulations of these ions in liquid water and with solvation free energy calculations using the perturbation technique. The results of aqueous ionic solution simulations with the ABEEM/MM force field provide a reasonable description of many important properties, which are in good agreement with the experimental measurements. This work demonstrates that the combination of ABEEM/MM-MD provides a powerful tool in analyzing solvation processes of monovalent ions in water.

## 1. Introduction

A detailed investigation of ionic clusters and aqueous ionic solutions is important in chemistry and biochemistry. The alkali metal cations and halide anions play various roles in nature, and the solvation of these monovalent ions has lately been an active subject for an increasing amount of experimental and theoretical studies.[1−6] Molecular dynamics simulation is a powerful tool in analysis of the properties of ions in water. An accurate description of molecular interactions is a key point in simulations. Though ab initio MD study has high accuracy, it is still limited in both system size and systematic investigation. In practice, elaborated empirical potentials have provided a fair description of condensed-phase properties.[6a] Recently, these potentials have included the polarization explicitly in the form of multipoles or fluctuating charges.[6b,7−11] Particularly, a number of fluctuating charge force fields are based on the electronegativity equalization method originally developed in the context of the density functional theory.[12] Very recently, the atom-bond electronegativity equalization method fused into molecular mechanics (ABEEM/MM) for obtaining parameters of the effective interactions has been proposed by Yang et al., aiming at a correct description of the properties of water and ion/water systems.[11] The main feature is that the results from ABEEM/MM agree quite well with both the experimental data and ab initio calculation results for those systems.

For the solvation of alkali metal cations and halide anions in water, much work has been done toward understanding ion hydration using empirical potentials with fixed charges that are unable to describe the conformational dependence of electrostatic properties, and less study has been done by employing the fluctuating charge models. Our goal is to employ the fluctuating charge model for ion/water systems. The ABEEM/MM-based potential can be used in molecular dynamics simulations to obtain radial distribution functions, coordination numbers, diffusion coefficients, mean residence times, OH stretching spectra, water exchanges, solvation energies, solvation free energies, and so on. This work is to present a systematic investigation on the monovalent ions in water using the fluctuating charge model.

## 2. Methodology

For a single ion surrounded by water molecules, two types of potential functions are needed: one for the water−water interaction and the other for the ion−water interaction. The recently developed seven-site flexible ABEEM-7P water model with fluctuating charges[11a,b] can reproduce bulk water properties and so it has been employed here. The effective ion−water interaction potential has been developed to reproduce the experimental or ab initio binding energies and the measured structures for the ionic clusters. The model takes account of all Lennard-Jones interactions between ion and atoms of water molecules and incorporates electrostatic interactions between ion and all charge sites of water molecules where the partial charges are calculated by ABEEM. First, we utilize ABEEM to compute the charge distribution of the system. Then, we use the ABEEM charges to calculate Coulomb interactions of ion−water and water−water. Finally, the total potential energy for an ion in water can be calculated as a sum of intramolecular and intermolecular interactions. When there is a configurational change, we recalculate the charges by ABEEM from time to time, and then recalculate the total potential energy of the system. Therefore, the consistent combination of ABEEM and MM can picture well each ion in water with fluctuating charges and predict the interaction energy quite precisely.

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The ABEEM/MM-MD simulations were performed for the systems consisted of 215 water molecules and an ion in a cubic simulation cell with a linear dimension equal to 18.625 Å per side. Periodic boundary condition was applied in all three dimensions. The simulations were carried out in a canonical ensemble at 298 K, with the minimum image convention. Temperature was kept constant by the Berendsen algorithm.[13b] The equations of motion were solved using the velocity Verlet algorithm with a time step of 1.0 fs. The nonbonded interactions were truncated at a molecular separation of 9.0 Å for all simulations using the force shifting.[14] A simulation was carried out 300 ps to equilibrate the system, followed by at least 500 ps of data collection for analysis. The solvation free energy for $Na^+$ and $Cl^-$ was calculated using the free energy perturbation and molecular dynamics. The calculation was carried out in two stages (growth and charging) according to the method reported by Ponder et al.[9b] The solvation free energy for $Li^+$ and $K^+$ was calculated starting from the final structure of the sodium charging calculation, and the van der Waals parameters were changed linearly from sodium to lithium and potassium values. $F^-$ and $Br^-$ perturbation simulations were performed with $Cl^-$-water as a starting point. In these simulations, 150 ps trajectories were analyzed after 50 ps equilibration for each $\lambda$ value ($\lambda$ increases in a number of steps from 0 to 1). The Helmholtz solvation free energy was then calculated from these trajectories using the free energy perturbation method.[13a,15]

## 3. Results and Discussion

We first calculated the properties of ionic clusters $M^+(H_2O)_{1-6}$ ($M^+ = Li^+$, $Na^+$, and $K^+$) as well as $X^-(H_2O)_{1-6}$ ($X^- = F^-$, $Cl^-$, and $Br^-$). For the cation−water clusters, the average $M^+$−O distances are found to be within 0.04 Å of those distances determined by the accurate ab initio calculations.[16,17] In the investigated anion−water clusters, our model also reproduces the ab initio results. In addition, we found the agreement between the observed data[18−20] and the computed binding energies to be quite reasonable in all these cases. Then we investigated the static, dynamic, and thermodynamic properties of aqueous ionic solutions based on ABEEM/MM-MD simulations. The structural feature of the waters surrounding an ion is described by the ion−oxygen and ion−hydrogen radial distribution functions $g_{IO}(r)$ and $g_{IH}(r)$, which are shown in Figures 1 and 2. For $Li^+$, $Na^+$, and $K^+$ ions in aqueous solution, the first maximum peaks in $g_{IO}(r)$ obtained from the simulations locate at 1.95, 2.31, and 2.77 Å, respectively. The position of the first peak for $Na^+$ is comparable to that obtained from Monte Carlo simulations with TIP4P−FQ intermolecular potential.[8b] For the halide anions in aqueous solution, the first peak in $g_{IH}(r)$ is closer to the anion than in $g_{IO}(r)$, which indicates the formation of a first hydration shell of hydrogen atoms, and two separated peaks in $g_{IH}(r)$ correspond to two nonequivalent hydrogen atoms of the same water molecule, one of which is closer to the anion than the other one. Clearly, there is a significant difference between $g_{IH}(r)$ of anions and cations: only one peak per hydration shell for cations, but two peaks for anions. The calculated average coordination numbers for these ions increase with increasing ionic radii. According to angular distributions, we found that the most favorable orientation of a water dipole in the first hydration shell of a cation is not parallel to the cation−oxygen vector but shifts an angle and there is a consistent maximum position around 52° for the angle between the water dipole and the oxygen−anion vector consisting of a nearly linear hydrogen bond. In addition, the effect exerted by an ion on its adjacent water molecules results in increased OH length and smaller HOH angle, and this effect is the strongest in the case of $Li^+$ and $F^-$.

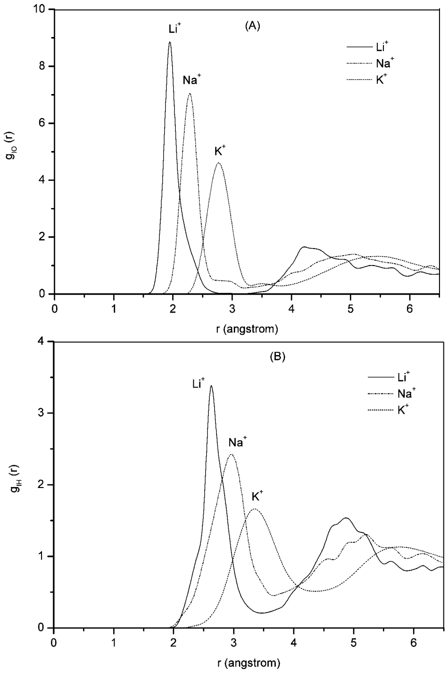

**Figure 1.** Ion−oxygen $g_{IO}(r)$ (A) and ion−hydrogen $g_{IH}(r)$ (B) distribution functions for cations $Li^+$, $Na^+$, and $K^+$.

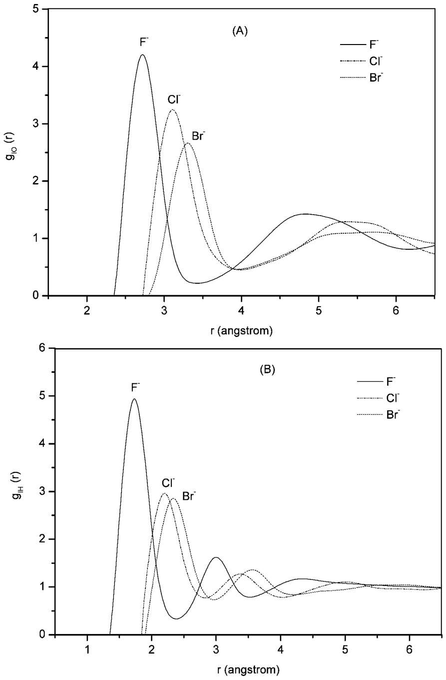

**Figure 2.** Ion−oxygen $g_{IO}(r)$ (A) and ion−hydrogen $g_{IH}(r)$ (B) distribution functions for anions $F^-$, $Cl^-$, and $Br^-$.

The simulations allow the charges on the interacting sites to fluctuate as a function of time. Table 1 gives the average charges of each ion and every charge site of water molecules for $Li^+$, $Na^+$, and $K^+$ ions in aqueous solution. The absolute values of average charges of O atom, H atom, OH bond, and lone pair in the first hydration shell are higher than those in the external hydration shells, reflecting that the ionic effect on the first-shell water structure is very strong. The charge transfer is very obvious for the cations in water due to the stronger cation−water interaction. For instance, 0.068 e has been transferred to $Li^+$ (with a small fluctuation) in $Li^+$(aq). A small amount of

**TABLE 1: Average ABEEM Charges for Different Aqueous Ionic Solutions**[a]

| solution | ion | O atom | H atom | OH bond | lone pair |
|---|---|---|---|---|---|
| $Li^+$(aq) (inner) | 0.932 ± 0.017 | 0.107 ± 0.066 | 0.418 ± 0.242 | −0.147 ± 0.036 | −0.297 ± 0.174 |
| $Li^+$(aq) (outer) | | 0.102 ± 0.009 | 0.338 ± 0.072 | −0.147 ± 0.005 | −0.242 ± 0.037 |
| $Na^+$(aq) (inner) | 0.959 ± 0.010 | 0.106 ± 0.042 | 0.369 ± 0.182 | −0.148 ± 0.024 | −0.272 ± 0.099 |
| $Na^+$(aq) (outer) | | 0.102 ± 0.007 | 0.337 ± 0.068 | −0.147 ± 0.004 | −0.240 ± 0.036 |
| $K^+$(aq) (inner) | 0.971 ± 0.007 | 0.101 ± 0.021 | 0.350 ± 0.123 | −0.147 ± 0.012 | −0.248 ± 0.052 |
| $K^+$(aq) (outer) | | 0.103 ± 0.005 | 0.343 ± 0.071 | −0.147 ± 0.004 | −0.247 ± 0.036 |

[a] “Inner” denotes the first hydration shell and “outer” denotes the external hydration shells.

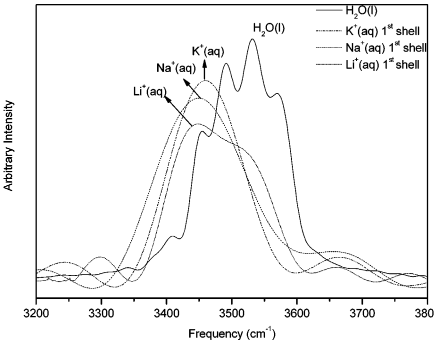

**Figure 3.** OH stretching spectra for the first-shell water molecules of cations and liquid water.

charge transfer is seen for $Na^+$(aq) and $K^+$(aq). Our model also shows that the hydrogen atoms bound directly to an anion have larger positive charges than others, and the charges of hydrogen atoms in the first hydration shell can demonstrate that the bifurcated hydrogen bonds, where the two hydrogen atoms of a water molecule are bridged by the anion, are seldom found.

The ABEEM/MM-MD simulations can well reproduce the experimental diffusion coefficient and mobility of ions.[21] The simulations also give the reasonable residence times that are 47.0, 28.5, 16.6, 27.3, 17.2, and 12.8 ps for the water molecules around $Li^+$, $Na^+$, $K^+$, $F^-$, $Cl^-$, and $Br^-$, respectively. The average jump angles between the velocity vectors computed at two subsequent simulation steps have been worked out, and they are 5.26, 2.07, and 1.54° for $Li^+$, $Na^+$, and $K^+$, as well as 4.19, 2.51, and 1.63° for $F^-$, $Cl^-$, and $Br^-$, respectively, decreasing with the increase of ionic size. By taking the Fourier transform of the velocity autocorrelation (VAC) function over all atoms, we can obtain the water spectrum. The difference between the spectra of these solutions can be seen by studying the influence of an ion on the OH stretching band for the water molecules around the ion. In aqueous ionic solutions, because the structure change involves the breakdown of the basic tetrahedral water structure and the re-formation of new local structure around the dissolved ions, the water molecules in the first hydration shell of each ion are obviously different from liquid water and the shift of OH stretching frequency happens accordingly. Just as shown in Figure 3, the OH stretching spectra for the water molecules around $Li^+$, $Na^+$, and $K^+$ give bands around 3448, 3449, and 3460 $cm^{-1}$, respectively, corresponding to a certain downshift with respect to the calculated band for pure liquid water at 3523 $cm^{-1}$. The spectra for the water molecules around $F^-$, $Cl^-$, and $Br^-$ also have certain shifts. Moreover, because our model can timely recalculate the charge distribution of the system according to the changed configurational environment, it correctly indicates water exchanges and hydration shell fluctuations.

We can obtain the average solvation energies for these ions in water by the total potential energy of aqueous ionic solution subtracting the energy of 215 bulk water molecules. The calculated solvation energies for $Li^+$, $Na^+$, $K^+$, $F^-$, $Cl^-$, and $Br^-$ ions in water are −133.1, −107.3, −91.6, −115.4, −93.1, and −76.9 kcal/mol, respectively, in fair agreement with the experimental solvation enthalpies.[22,23] Another measurable thermodynamic property is the solvation free energy calculated from the free energy simulations, and the computed ion solvation free energies are −119.0, −91.4, −74.2, −114.3, −85.1, and −76.8 kcal/mol, respectively, which agree well with the results obtained from the experiments[22,23] and simulations with the polarizable force field.[9b] Note that some important results of ionic clusters and aqueous ionic solutions in terms of ABEEM/MM calculations and simulations are given in the Supporting Information.

## 4. Conclusion

The good results of this systematic study on monovalent ions in water show that the model has significantly improved to predict the static, dynamic, and thermodynamic properties of these ions in aqueous solution. More importantly, the interaction potential proves successfully that the good effective parameters can be obtained by studying small enough systems and can be naturally transferred to aqueous ionic solutions without further modification and the results are generally satisfactory in comparison with the results of existing high-level ab initio calculations and experiments. Thus ABEEM/MM calculations and simulations can with fair accuracy describe the properties of ionic clusters as well as solutions and will be further applied to a wide range of systems.

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**Supporting Information Available:** Discussion, tables, and figures giving important results of ionic clusters and aqueous ionic solutions based on ABEEM/MM calculations and simulations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) Doyle, D. A.; Cabral, J. M.; Pfuetzner, R. A.; Kuo, A. L.; Gulbis, J. M.; Cohen, S. L.; Chait, B. T.; MacKinnon, R. *Science* **1998**, *280*, 69.

(2) Ayotte, P.; Weddle, G. H.; Kim, J.; Johnson, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 12361.

(3) Guidoni, L.; Torre, V.; Carloni, P. *Biochemistry* **1999**, *38*, 8599.

(4) Kropman, M. F.; Bakker, H. J. *Science* **2001**, *291*, 2118.

(5) (a) Raugei, S.; Klein, M. L. *J. Am. Chem. Soc.* **2001**, *123*, 9484. (b) Klein, M. L. *Science* **2001**, *291*, 2106.

(6) (a) Rasaiah, J. C.; Noworyta, J. P.; Koneshan, S. *J. Am. Chem. Soc.* **2000**, *122*, 11182. (b) Koneshan, S.; Rasaiah, J. C.; Dang, L. X. *J. Chem. Phys.* **2001**, *114*, 7544.

(7) (a) Banks, J. L.; Kaminski, G. A.; Zhou, R.; Mainz, D. T.; Berne, B. J.; Friesner, R. A. *J. Chem. Phys.* **1999**, *110*, 741. (b) Stern, H. A.; Kaminski, G. A.; Banks, J. L.; Zhou, R.; Berne, B. J.; Friesner, R. A. *J. Phys. Chem. B* **1999**, *103*, 4730. (c) Stern, H. A.; Rittner, F.; Berne, B. J.; Friesner, R. A. *J. Chem. Phys.* **2001**, *115*, 2237.

(8) (a) Hribar, B.; Southall, N. T.; Vlachy, V.; Dill, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 12302. (b) Jardn-Valadez, E.; Costas, M. E. *J. Mol. Struct.: THEOCHEM* **2004**, *677*, 227. (c) Lee, S. H. *Mol. Sim.* **2004**, *30*, 669.

(9) (a) Ren, P.; Ponder, J. W. *J. Phys. Chem. B* **2003**, *107*, 5933. (b) Grossfield, A.; Ren, P.; Ponder, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 15671.

(10) (a) MacKerell, A. D., Jr.; Feig, M.; Brooks, C. L., III. *J. Am. Chem. Soc.* **2004**, *126*, 698. (b) Patel, S.; Brooks, C. L., III. *J. Comput. Chem.* **2004**, *25*, 1.

(11) (a) Yang, Z. Z.; Wu, Y.; Zhao, D. X. *J. Chem. Phys.* **2004**, *120*, 2541. (b) Wu, Y.; Yang, Z. Z. *J. Phys. Chem. A* **2004**, *108*, 7563. (c) Li X.; Yang, Z. Z. *J. Phys. Chem. A*, in press. (d) Li X.; Yang, Z. Z. *J. Chem. Phys.* **2005**, *122*, 084514.

(12) (a) Mortier, W. J.; Ghosh, S. K.; Shankar, S. *J. Am. Chem. Soc.* **1986**, *108*, 4315. (b) Rappé, A. K.; Goddard, W. A., III. *J. Phys. Chem.* **1991**, *95*, 3358. (c) York, D. M.; Yang, W. *J. Chem. Phys.* **1996**, *104*, 159. (d) Chelli, R.; Procacci, P. *J. Chem. Phys.* **2002**, *117*, 9175. (e) Geerlings, P.; Proft, F. D.; Langenaeker, W. *Chem. Rev.* **2003**, *103*, 1793.

(13) (a) Postma, J. P. M.; Berendsen, H. J. C.; Haak, J. R. *Faraday Symp. Chem. Soc.* **1982**, *17*, 55. (b) Berendsen, H. J. C.; Postma, J. P. M.; van Gunsteren, W. F.; DiNola, A.; Haak, J. R. *J. Phys. Chem.* **1984**, *81*, 3684.

(14) Steinbach, P. J.; Brooks, B. R. *J. Comput. Chem.* **1994**, *15*, 667.

(15) Torrie, G. M.; Valleau, J. P. *Chem. Phys. Lett.* **1974**, *28*, 578.

(16) (a) Hashimoto, K.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 11436. (b) Hashimoto, K.; Kamimoto, T. *J. Am. Chem. Soc.* **1998**, *120*, 3560.

(17) Merrill, G. N.; Webb, S. P.; Bivin, D. B. *J. Phys. Chem. A* **2003**, *107*, 386.

(18) (a) Searles, S. K.; Kebarle, P. *Can. J. Chem.* **1969**, *47*, 2619. (b) Dzidic, I.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1466. (c) Arshadi, M.; Yamadgni, R.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1475.

(19) Rodgers, M. T.; Armentrout, P. B. *J. Phys. Chem. A* **1997**, *101*, 1238.

(20) (a) Hiraoka, K.; Mizuse, S. *Chem. Phys.* **1987**, *118*, 457. (b) Hiraoka, K.; Mizuse, S.; Yamabe, S. *J. Phys. Chem.* **1988**, *92*, 3943.

(21) Atkins, P. W. *Physical Chemistry*, 4th ed.; Freeman: San Fransico, 1990; p 963.

(22) Schmid, R.; Miah, A. M.; Sapunov, V. N. *Phys. Chem. Chem. Phys.* **2000**, *2*, 97.

(23) Tissandier, M. D.; Cowen, K. A.; Feng, W. Y.; Gundlach, E.; Cohen, M. H.; Earhart, A. D.; Coe, J. V.; Tuttle, T. R., Jr. *J. Phys. Chem. A* **1998**, *102*, 7787.