$C_2H_4{}^{2+}$ results from strong hyperconjugation.

What experiments are possible to test our theoretical predictions? Table I shows the calculated ionization energies I_2 for the adiabatic removal of two electrons from substituted ethylenes. The data may serve to give an estimate if stable dications can be expected in a condensed phase. The ionization energies of C_2H_4 (**1**) and C_2F_4 (**4**) are very high (27.5 eV for **1** and 26.2 eV for **4**), too high to expect that salt compounds may be formed. The lowest I_2 value is found for $C_2(NH_2)_4$ (**10**; 15.2 eV). The I_2 values of $C_2(OH)_4$ (**7**; 19.4 eV), $C_2H_2(NH_2)_2$ (**13–15**; 18.2–21.4 eV), $C_2(OH)_2(NH_2)_2$ (**21–23**; 17.1–17.5 eV), and $C_2(SH)_4$ (**29**; 19.1 eV) are intermediate. However, since salt compounds of tetra-thiofulvalen are known,[16] it seems feasible that dications of these molecules may be prepared and the geometries be measured. Our calculations indicate that $C_2(OR)_2(NR_2)_2$ may be the best candidates. In case of the ethylene diamines $C_2H_2(NR_2)_2$, the 1,2-substituted isomers should be much easier to prepare than the 1,1 isomers.

Ion Solvation in Polarizable Water: Molecular Dynamics Simulations

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Abstract: We present the results of molecular dynamics simulations on gas-phase ion water clusters and ion solvation in liquid water using nonadditive many-body potential models. To our knowledge, this is the first simulation model that has led to very good agreement with experiment for the energies of water, ion clusters, and ionic solutions as well the coordination numbers for the aqueous solutions of Na^+ and Cl^-. We have studied the Na^+ ion gas-phase complexes with one to six water molecules. In addition to obtaining good agreement with the experimental enthalpies, the calculated Na^+–oxygen radial distribution function (RDF) for the $Na^+(H_2O)_6$ cluster displays two distinguishable zones; integrating over the first zone yields four water molecules, and the remaining two water molecules belong the second zone. In contrast to the structure of the Na^+ complex with four water molecules, the four water molecules around the Cl^- ion in $Cl^-(H_2O)_4$ are found clustered together in one hemisphere of the ion. These waters form weak hydrogen bonds with each other, resulting in an average water–water binding energy of −4.6 kcal/mol. These results indicate that the stability of the $Cl^-(H_2O)_4$ complex arises in part from water–water binding. The coordination number of the Na^+ and Cl^- ions obtained from ionic solution simulations is approximately 6, in good agreement with experimental results. We have also calculated the water–water interactions in the first hydration shell of Na^+ and Cl^- solutions to examine the effect of these ions on the water–water interactions. We found the water–water interactions in this region of the Cl^- solution are positive and ∼4 kcal/mol less repulsive than the corresponding water–water interactions for the Na^+ solution. Thus, the structure in the first hydration shell of full ionic solution simulation of the anion appears to have significantly different character from that of the gas-phase anion–water cluster. In addition, we found the water molecules between the first and second hydration shells are strongly mobile. Finally, we find it to be essential to include the three-body potential (ion–water–water) in the simulation of the ionic solution to obtain quantitative agreement with the experimental solvation enthalpies and coordination numbers.

I. Introduction

The study of the thermodynamic and structural properties of ions in water by statistical mechanics or computer simulation techniques has made a significant contribution to the understanding of the chemistry and physics of solvation. To date, there have been numerous studies on this important subject.[1-11] With few exceptions,[4,5,7] however, almost all of these water–water and water–ion potential models used in these studies are pairwise additive. Consequently, these studies often overestimate the coordination numbers and the solvation enthalpies of the ions. It is now recognized that many-body or nonadditive interactions are important if one wishes to describe ionic interactions in clusters and in solution quantitatively.[4,7,11,12]

Recently, we have developed a polarizable water potential model that explicitly includes the electronic polarization energy.[13] We have carried out a molecular dynamics simulation on liquid water using this model. We have obtained good agreement with experimental results for the water dimer and the structural and the thermodynamic properties of liquid water. We have also examined complexes of Na^+ and Cl^- with one to six water molecules using the molecular mechanics method.[13] In addition to the good agreement with gas-phase experimental enthalpies, the study of

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the structure of small clusters of water around ions revealed some interesting characteristics. For example, the Na^+ complex with six water molecules prefers to have a 4 + 2 structure rather than an octahedral structure. The water molecules of the Cl^-–water complex are clustered on the same side of the Cl^- ion so that they can contribute to the stability of the Cl^-–water cluster. These results are consistent with previous Monte Carlo simulations on the same systems.[4]

In the molecular dynamics studies reported here, we have studied Na^+ and Cl^- gas-phase water clusters and ionic solution using the polarizable water model (POL1).[13] We have studied ion–water gas-phase cluster formation by examining the radial distribution functions (RDF) and the structural changes during the dynamics simulations. We have extended the simulation to study ion solvation in a periodic box of water. We have determined the thermodynamics and structural properties for these systems. In each case, we obtain good agreement with the experimental data, including the enthalpies and coordination numbers. We have also examined the role of an exchange repulsion three-body potential (ion–water–water) on the structure and thermodynamic quantities of ionic solutions. We have found that it is necessary to include the ion–water–water interactions in the total potential function in order to obtain good agreement with experimental measurements. In section II, we describe the potential models and methodology. The results and discussion are presented in section III. The conclusions are given in section IV.

II. Potential Models and Methodology

The following equations describe the interaction energy of the system by use of a rigid three-point-charges water model with an internal geometry of $109.47°$ and 1 Å for the HOH angle and OH distance, respectively. The interaction energy consists of the Lennard-Jones and electrostatic interactions between water–water and waters–ion pairs, a nonadditive polarization energy, and a term that includes explicit exchange repulsion nonadditivity for ion–water–water interactions. Thus, the total potential is given as

$$U_{tot} = U_{pair} + U_{pol} + U_{3-body} \qquad (1)$$

where the pair additive potential is

$$U_{pair} = \sum_i \sum_j A_{ij}/r_{ij}^{12} - C_{ij}/r_{ij}^6 + q_i q_j/r_{ij} \qquad (2)$$

and the polarization energy is

$$U_{pol} = -\tfrac{1}{2} \sum_i \mu_i E_i^0 \qquad (3)$$

Finally, the three-body exchange repulsion potential is written as follows:

$$U_{3-body} = A \exp(-\beta r_{12}) \exp(-\beta r_{13}) \exp(-\gamma r_{23}) \qquad (4)$$

Here, μ_i is the induced dipole moment and E_i is the electric field at atom i and E_i^0 and T_{ij} are the electrostatic fields from the charges and the dipole tensor, respectively, where α_i is the polarizability of atom i, r_{ij} is the vector from atom j to atom i, q_j is the charge at atom j, r_{12} and r_{13} are ion–oxygen distances for the ion–water trimer, r_{23} is the oxygen–oxygen distance for the two water molecules involved in the ion–water trimer, and A, β, and γ are empirical parameters.

$$\mu_i = \alpha_i E_i \qquad E_i = E_i^0 + \sum_{j=1, j \neq i} T_{ij} \mu_j \qquad (5)$$

$$E_i^0 = \sum_{j=1, j \neq i} q_j \frac{\mathbf{r}_{ij}}{r_{ij}^3} \qquad T_{ij} = \frac{1}{r_{ij}^3} \left(3 r_{ij} \frac{\mathbf{r}_{ij}}{r_{ij}^2} - 1 \right) \qquad (6)$$

The analytical derivative of the three-body potential was calculated by use of the chain rule. The analytical derivative of the polarization energy including the dipole–monopole and dipole–dipole forces is an extension of the work of Vesely on a system of dipolar molecules[14] and is identical with that used in ref 15.

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Table I. Van der Waals Parameters, Charges, and Polarizabilities for Atoms

atom type	σ^a (Å)	ϵ^a (kcal/mol)	q^a	α (Å^3)
Q	3.169	0.155	0.730	0.465[b]
H	0.000	0.000	0.365	0.135[b]
Na^+	2.156	0.130	1.000	0.240[c]
Cl^-	4.321	0.100	−1.000	3.250[c]

[a] Reference 13. [b] Reference 17. [c] Reference 18.

Table II. Parameters for Three-Body Ion–$(H_2O)_2$ Interactions

ion	A (kcal/mol)	β (Å^{-1})	γ (Å^{-1})
Na^+	4.5d6	3.20	0.10
Cl^-	8.0d5	2.25	0.25

We have used the traditional iterative approach to solve eq 5 with the iteration continuing until the root mean square rms of the difference in the induced dipole between successive iterations is less than 0.01 D/atom. We find that self-consistency is usually achieved within five iterative steps. These changes have been incorporated in a modified version of AMBER 3.0.[16]

The atomic polarizabilities for water and for the ions are taken from the work of Applequist et al.[17] and of Sangster and Atwood,[18] respectively. In constructing the nonadditive potential for ion–water clusters, we started out with a molecular dynamics simulation at 300 K using the ion–$(H_2O)_1$ complex. The Lennard-Jones parameters of the ion were adjusted so that the experimental enthalpy of the complex formation was reproduced. Then, a second molecular dynamics simulation was carried out with the previous potential parameters for the three-body exchange repulsion[13] to calibrate the data to experimental results for the ion–$(H_2O)_2$ cluster.[19] The final parameters have also been chosen so that the analytic three-body potential functions approaches zero beyond the first hydration shell. Without further adjustment, these ion parameters are used in subsequent molecular dynamics simulations for the larger clusters (three to six water molecules) and ionic solutions. For the ionic solution simulations, the sample consisted of one single ion and 215 waters in a cubic cell of 18.6 Å. The equations of motion were solved by use of the standard Verlet algorithm[20] with an average temperature of 300 K with a coupling constant of 0.2 ps for temperature[21] and a time step of 1 fs. The SHAKE[21] procedure was adapted to constrain all the bond lengths to their equilibrium values, and the nonbonded interactions were cut off at a molecular separation of 8 Å. Each simulation consisted of 20 ps of equilibration following 40 ps of data collection for later analysis. Each full ionic solution simulation required approximately 100 CPU h on the IBM 3090E. The parameters for these simulations including the potential parameters are given in Tables I and II.

III. Results and Discussion

We begin in this section by examining the energetic and structural properties of the ion–water clusters. We study the Na^+ ion complexes with one to six water molecules and the Cl^- ion complexes with one to four water molecules. In particular, we focus on the results of the $Na^+(H_2O)_4$, $Na^+(H_2O)_6$, and $Cl^-(H_2O)_4$ clusters since these structures exhibited some interesting characteristics. We then proceed to discuss the structures of water

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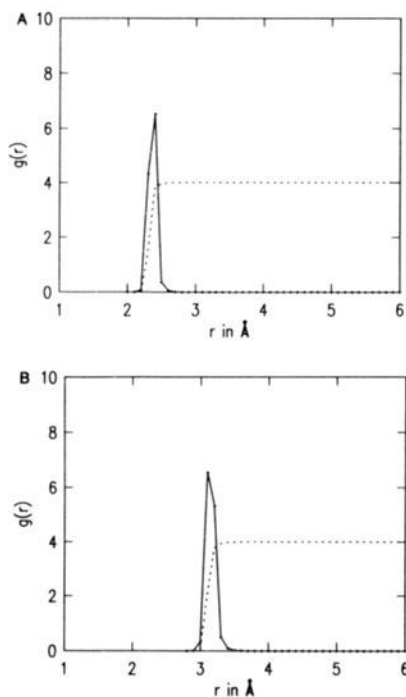
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Table III. Calculated and Experimental Enthalpies of Binding (Kilocalories per Mole) of ion–$(H_2O)_n$ Clusters at 300 K

ion	n	molecular dynamics	exptl[a]
Na^+	1	-24.2 ± 0.5	-24.0
	2	-44.2 ± 0.5	-42.8
	3	-61.4 ± 0.6	-59.6
	4	-74.4 ± 0.6	-73.4
	5	-85.0 ± 0.7	-85.7
	6	-97.6 ± 0.9	-96.4
Cl^-	1	-12.8 ± 0.4	-13.1
	2	-25.9 ± 0.5	-25.8
	3	-38.6 ± 0.6	-37.5
	4	-49.4 ± 0.8	-48.6

[a] Reference 19.

Figure 2. The structure of water around the ions at the end of a 100-ps molecular dynamics simulation: (A) $Na^+(H_2O)_4$, (B) $Cl^-(H_2O)_4$.

Figure 3. Calculated RDF for the Na^+–O of the $Na^+(H_2O)_6$. Dashed line is the running coordination number.

Figure 1. Calculated RDFs for Na^+–O and Cl^-–O for the ion–water cluster: (A) $Na^+(H_2O)_4$, (B) $Cl^-(H_2O)_4$. Dashed line is the running coordination number.
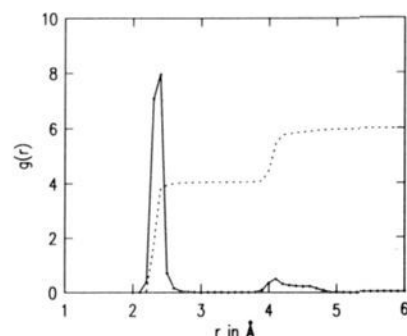
around the ions in the aqueous ionic simulations by calculating the RDFs and the coordination numbers. We also determine the solvation enthalpies by taking the difference in energies of the aqueous ionic simulation compared to the simulation of liquid water.

The enthalpies of the cluster were calculated from the time average of the molecular dynamics simulation as follows

$$\Delta H = \Delta U + p\Delta V = \Delta U - \Delta nRT \qquad (7)$$

where ΔU is the total energy of the cluster and n is the number of water molecules in the cluster. In Table III, the enthalpies of the clusters and the corresponding experimental enthalpies are presented. In all cases, we have obtained good agreement with the experimental results.[18] Of particular interest are the results for the ion complexes with three or more water molecules, since for these we did not make any further adjustment of the ion–water potential parameters.

In Figure 1, the RDFs for the $Na^+(H_2O)_4$ and $Cl^-(H_2O)_4$ clusters are displayed together with the coordination numbers obtained from molecular dynamics simulations at 300 K. Both complexes are very stable at 300 K, but the structures of the water molecules around these ions are different in detail. Snapshots of water molecules around the Na^+ and Cl^- ions are shown in Figure 2. The water molecules cluster in the same hemisphere of the Cl^- ion and form hydrogen bonds with each other. These results indicate that the stability of the anion–water complexes

arises in part from water–water binding. On the other hand, the four water molecules bind directly to the Na^+ ion in the $Na^+(H_2O)_4$ cluster and do not interact favorably with one another. We computed the water–water energies for both ion clusters; they are -4.6 and 15 kcal/mol for the Cl^- and Na^+ clusters, respectively. Thus, the contribution of the water–water binding to the stability of the cation–water cluster is less important than in the case of the anion–water complex. This result is related to the results obtained from the calculations of the water–water interactions within the first hydration shell of the ion in the aqueous ionic simulations of Na^+ and Cl^- discussed in the following text.

In previous molecular mechanics studies of the $Na^+(H_2O)_6$ complex, we found the 4 + 2 structure to be more stable than the octahedral structure.[4,13] To investigate these results further, we carried out two molecular dynamics simulations using the octahedral and 4 + 2 structures as starting coordinates. In both simulations, the calculated RDFs display two distinguishable shells. Integrating over these RDFs, we found that the first shell contains four water molecules and the remaining two water molecules belong to the second shell. These results agree with previous molecular mechanics studies, and they are summarized in Figure 3. In Figure 4, we present the snapshots of the molecular dynamics simulations of the $Na^+(H_2O)_6$ cluster. Although the transition from the octahedral structure to the 4 + 2 structure occurs within the first 10 ps of the simulation, we found that the time to achieve the stable 4 + 2 structure is $\sim$30 ps. We have also carried out similar simulations with the three-body exchange repulsion forces turned off; we obtained the same characteristics for the RDFs, but the calculated enthalpies are $\sim$−8 kcal/mol too exothermic compared with the corresponding experimental measurements.

In Figures 5 and 6, the RDFs of Na^+–O, Na^+–H, Cl^-–O, and Cl^-–H for the molecular dynamics simulations of the aqueous solutions of Na^+ and Cl^- are presented. The ion–oxygen RDFs display two well-defined peaks for both simulations. For the Na^+ ion–oxygen RDF, the position for the first maximum and minimum are located at 2.35 and 3.4 Å; whereas for the Cl^- ion–oxygen RDF, they are at 3.2 and 3.9 Å. We obtained similar results for

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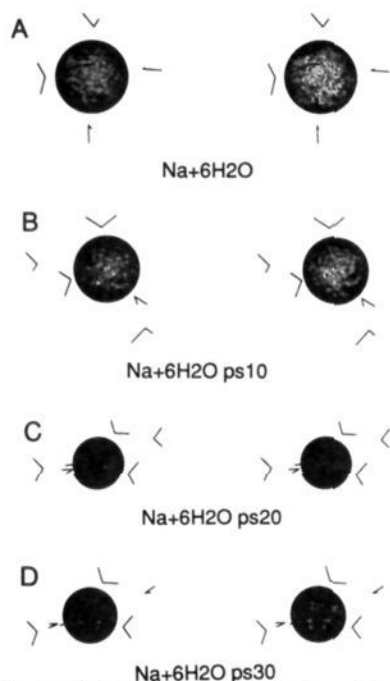
Figure 4. The snapshot of water around the ions of the $Na^+(H_2O)_6$ complex during the dynamics simulations: (A) 1 ps, (B) 10 ps, (C) 20 ps, (D) 30 ps.
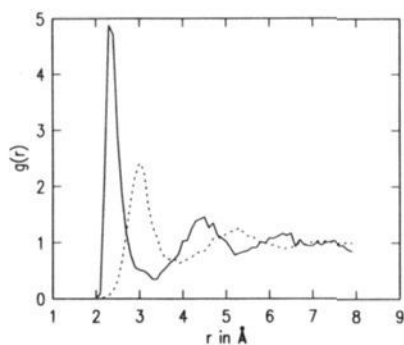
Figure 5. Calculated RDFs for Na^+–O (solid line) and the Na^+–H (dashed line) obtained from molecular dynamics simulation of aqueous solutions of Na^+.
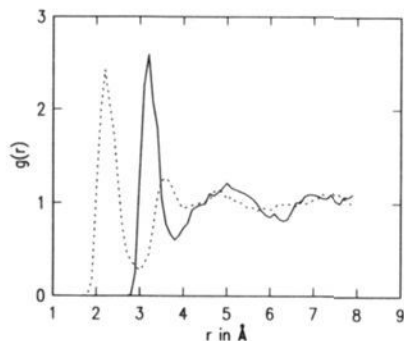
Figure 6. Calculated RDFs for Cl^-–O (solid line) and the Cl^-–H (dashed line) obtained from molecular dynamics simulation of aqueous solutions of Cl^-.

Table IV. Structural and Thermodynamic Properties of Ion in Water at 300 K Obtained from Molecular Dynamics Simulations

	Na^+	Cl^-
Ion–Oxygen Distance (Å)		
this work	2.35	3.20
Jorgensen MC[a]	2.33	3.21
Beveridge MC[b]	2.35	3.25
Clementi MC[c]	2.33	3.40–3.50
Impey MD[d]	2.29	3.29
X-ray[e]	2.38, 2.4	3.10, 3.5
neutron diffraction[f]		3.20–3.34
Ion–Hydrogen Distance (Å)		
this work	2.90	2.20
Jorgensen MC[a]	2.90	2.25
Beveridge MC[b]	2.90	2.30
Clementi MC[c]	3.00	2.55
Impey MD[d]	2.95	2.35
neutron diffraction[f]		2.22–2.26
Coordination Number		
this work	5.7 (5.8)[h]	6.1 (7.1)[h]
Jorgensen MC[a]	6.0	7.4
Beveridge MC[b]	5.96	8.36
Clementi MC[c]	5.4	5.6
Impey MD[d]	6.0	7.2
X-ray[e]	4.6	
neutron diffraction[f]		5.3–6.2
ΔH_{sol} (kcal/mol)		
this work	-105^j (-84.3 ± 1.2)[i]	-80^j (-59.3 ± 1.3)[i]
this work	-112^k	-87^k
experiment[g]	-106	-82

[a] Reference 6. [b] Reference 9. [c] Reference 10. [d] Reference 8. [e] Reference 22. [f] Reference 23. [g] Reference 25. [h] Value without inclusion of three-body exhange repulsion term. [i] Value before Born correction. [j] Value after Born correction. [k] Value after Born correction without inclusion of three-body exchange repulsion term.

Table V. Average Water–Water Energies (Kilocalories per Mole) for the $Na^+(H_2O)_4$ and $Cl^-(H_2O)_4$ Clusters and the Water–Water Energies within the First Hydration Shell for the Aqueous Solutions of Na^+ and Cl^- Obtained from Molecular Dynamics Simulations at 300 K

	Na^+	Cl^-
cluster	15.0 ± 0.8	−4.6 ± 0.3
solution	10.4 ± 0.3	6.1 ± 0.2

the Na^+–H RDF, but the positions of the peaks move outward with respect to the Na^+ ion–oxygen RDF since the hydrogens point away from the ion. On the other hand, the Cl^-–H RDF displays a second peak due to the other hydrogen in the first shell of the Cl^- ion. The results are qualitatively similar to those of Chandrasekhar et al.,[6] Impey et al.,[8] and Mezei et al.[9] In Table IV, we compare the calculated ion–oxygen and ion–hydrogen distances in the first hydration shell with available experimental data ob-

tained by X-ray[22] or neutron diffraction[23] methods and with the simulations using different potential models. The results for the positions of the first ion–oxygen and ion–hydrogen peaks are in good agreement with the experimental data and are very similar to those obtained with Monte Carlo and other molecular dynamics simulations.[4,13] Since there are only a few water molecules interacting directly with the ion, the structural properties of water such as the g_{OO}, g_{OH}, and g_{HH} RDFs derived from the ionic solutions simulations are nearly identical with those obtained for pure water reported in ref 13.

In previous Monte Carlo simulations,[5,6] the first minimum of the calculated g_{Na-O} is very near zero, suggesting that the water molecules in the first hydration shell are held tightly by the sodium ion and that there is little water exchange between solvation shells. On the other hand, our calculated g_{Na-O} shows that the first minimum has a magnitude of ~0.35. These results strongly indicate that, in this model, there is significant transfer of water molecules between the first and second hydration shells. These *results arise in part from the inclusion of the three-body and the polarization forces in the total energy since it is well-known that the waters in the first hydration shell are strongly polarized.* We obtained similar results for the calculated g_{Cl-O} RDF. We have

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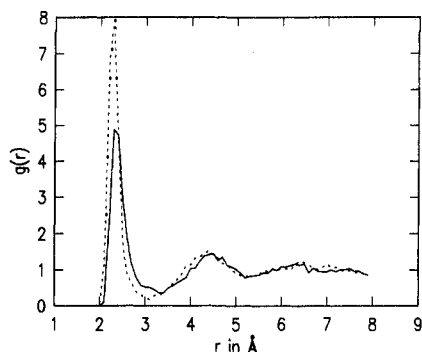(23) Neilson, G. W.; Enderby, J. E. *Annu. Rep. Prog. Chem., Sect. C* **1979**, *76*, 185.

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Figure 7. Calculated RDFs for the Na^+-O obtained from molecular dynamics simulation of aqueous solutions of Na^+: solid line is the simulation including the three-body forces; dashed line is simulation without the three-body exchange repulsion forces.
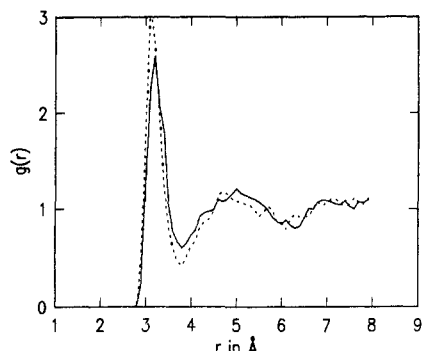

Figure 8. Same as Figure 7 for the aqueous solution of Cl^-.

also examined the properties of the water molecules in the first hydration shell by calculating the water–water interactions for this region. We obtained a value of 6.1 kcal/mol for the Cl^- ion solution, whereas the simulation of the Na^+ ion in water gave a value of 10.4 kcal/mol. In Table V, these results are summarized together with the water–water energies for the $Na^+(H_2O)_4$ and $Cl^-(H_2O)_4$ clusters. Thus, the water–water binding in the first hydration shell of full ionic solutions of Cl^- is less important than the water–water binding in the Cl^-–water cluster. The water structure in the first hydration shell on the Cl^- ion solution appears to have different character to that in the Cl^-–water cluster.

We have also determined the coordination numbers in aqueous solution simulations. These are included in Table IV. We obtained a value of 5.7 for Na^+ and 6.1 for Cl^- using the polarizable model with the nonadditive term. These results are in very good agreement with X-ray[22] and neutron diffraction measurements.[23]

We computed the solvation enthalpies for both simulations by substracting the enthalpies of the ionic solution from that of pure water. We have used the simple Born correction for the cutoff distance of 8 Å. The enthalpy correction is given by[24]

$$\Delta H_c = 332 Z^2 \frac{e^2}{2r}\left(\frac{1}{\epsilon} - 1\right) \quad (8)$$

where ϵ is the dielectric constant of the liquid water, Z is the charge of the ion, and r is the cutoff distance. The agreement with the experimental enthalpy is very good.[25]

We also ran two simulations on the aqueous solution of Na^+ and Cl^- in which the three-body repulsion exchange forces were not included. The calculations were carried out to examine the effect of the three-body force on the structural and thermodynamic properties of the ionic solutions. Figures 7 and 8 show the g_{Na-O} and g_{Cl-O} of these simulations together with the previous ion–oxygen RDFs from simulations that include the three-body forces. The removal of the three-body forces has a substantial effect on

Table VI. Calculated and Experimental Enthalpies (Kilocalories per Mole) of Na^+ Complexes with Water Cluster in Gas Phase and in Solutions Using Different Water Models at 300 K

n	model 1[a]	model 2[b]	SPC/E water[c]	exptl
1	-24.2 ± 0.5	-24.2 ± 0.5	-24.0 ± 0.5	-24.0
6	-97.0 ± 0.9	-104.0 ± 1.0	-112.0 ± 1.0	-96.4
solution	-105	-112	-124	-106

[a] Polarizable water with exchange repulsion nonadditivity. [b] Polarizable water without exchange repulsion nonadditivity. [c] The ion Lennard-Jones parameters for the Na^+ are 0.0313 kcal/mol and 2.44 Å for the ϵ and σ, respectively.
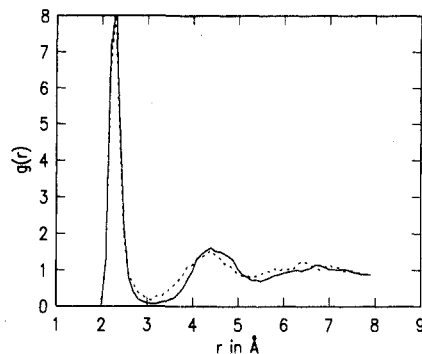

Figure 9. Calculated RDFs for the Na^+-O obtained from molecular dynamics simulation of aqueous solutions of Na^+: solid line is the simulation using the SPC/E water; dashed line is simulation using polarizable water without three-body exchange repulsion.

the structure of water around the ions. In particular, the peak height of the first maximum of the g_{Na-O} is significantly reduced. The peak positions remain the same, however. These observations are similar to the recent Monte Carlo simulation using three-body potentials of the Li^+ ion in water by Corongiu, Migliore, and Clementi.[7] Removal of the three-body forces leaves the coordination number of the aqueous simulation of Na^+ essentially unchanged, but the coordination number for the Cl^- is now 7.1, in poor agreement with experiment. The calculated solvation enthalpy for both the Na^+ and Cl^- solutions decreases by approximately 7 kcal/mol. Thus, it appears to be essential to include the three-body forces in the simulation in order to obtain good agreement with experimental measurements. These results are summarized in Table IV.

To examine further the role of the three-body term, we have carried out molecular dynamics simulations of the $Na^+(H_2O)_1$ and $Na^+(H_2O)_6$ clusters and simulation of a single Na^+ ion dissolved in liquid water using the simple point-charge water model[26] (SPC/E). The results are presented in Table VI together with the results from the simulations using our polarizable water model,[13] with and without the three-body repulsion exchange term. It is clear that the simulations using the nonadditive models give better agreement with the corresponding experimental data.[19] In Figure 9, we see that the Na^+ ion–oxygen RDF for both polarizable and SPC/E water models are similar, with the exception that the first minimum of the g_{Na-O} calculated with use of the SPC/E water model is nearly zero.

IV. Conclusion

We have presented a detailed study of the structure and thermodynamic properties of the ion–water gas-phase clusters and full ionic simulations of Na^+ and Cl^- using molecular dynamics and nonadditive potentials. The simulations of ion–water gas-phase clusters show some interesting features in agreement with the results of previous Monte Carlo, molecular mechanics, and molecular dynamics simulations for the clusters.[4,13] We found that the $Na^+(H_2O)_6$ complex prefers to have a 4 + 2 structure rather than an octahedral one. Also, the water molecules in the $Cl^-(H_2O)_4$ cluster lie on the same side of the Cl^- ion so that their

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interactions can contribute to the stability of the cluster.

The solution simulations using nonadditive many-body potentials have also provided some new interesting observations. In particular, the waters are very mobile between the first and second hydration shells, resulting in a nonzero first minimum in the calculated g_{Na-O}. The calculated enthalpies for both clusters and solution simulations and the coordination numbers in solution are in good agreement with the experimental data.

Thus, a model has been developed that gives energies in ion-water clusters and energies and structural features of ionic solutions in near quantitative agreement with experiment. This lets us suggest with some confidence that both the Na^+ and Cl^- ions have significantly different coordination geometries in ion-water clusters and solution. Our model has included both polarization and exchange repulsion nonadditive effects. We have carried out some simulations without the exchange repulsion nonadditivity, and the agreement with experiment is poorer. One cannot totally rule out that another choice of parameters might allow one to exclude the exchange term, but it appears to be important on the basis of quantum mechanical calculations[4,27] and its inclusion does not cause very large computational demands, the polarization part of the nonadditivity being the most time-consuming part of the model.

There are many directions for further development of this model. What are properties of solutions with more highly charged ions? What role do nonadditive effects play in solvation of nonpolar or neutral solutes? What are the potentials of mean force for the ion-ion and neutral-neutral association including nonadditive effects? Inclusion of the Ewald summation method[28] for the evaluation electrostatic potentials and forces would be worthwhile. Studies on these and related questions are in progress. Nevertheless, the results presented in this report, we feel, have been a significant step toward the understanding of the physics and chemistry of solvation.

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Calculated Heat of Formation of Ammonia

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Abstract: The heat of formation, $\Delta H^\circ_{f,0}$, of NH_3 has been determined using ab initio calculations including extrapolation to the complete basis set (CBS) limit. The extrapolated value for $\Delta H^\circ_{f,0}$ is -8.83 ± 0.5 kcal/mol, which is in good agreement with the best experimental measurement, -9.34 ± 0.01 kcal/mol.

Calculations of the heats of formation of molecules involving multiply bonded or highly polar species are of considerable interest as they offer a more stringent test of theoretical models than simpler systems. An example of one of these more complex systems is the Haber process[1] for the synthesis of ammonia:

$$N_2 + 3H_2 \rightarrow 2NH_3$$
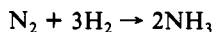
Because of the relatively drastic changes that occur in the bonding characteristics in going from reactants to products, the energy change for this simple reaction is very difficult to calculate accurately. For example, the G1 model chemistry[2] of Pople, Head-Gordon, Fox, Raghavachari, and Curtiss generally gives excellent results for energy changes in chemical reactions. However, the heat of formation of ammonia obtained[2] with the G1 model (-6.52 kcal/mol) is significantly smaller than the experimental value[3] (-9.34 ± 0.01 kcal/mol). We have therefore

subjected this system to a detailed theoretical study including our CBS-QCI model chemistry.[4] The calculated CBS-QCI value of $\Delta H^\circ_{f,0}$ for ammonia, -8.83 ± 0.5 kcal/mol, is in good agreement with the experimental value. The slow convergence of the calculations with both the basis set and the order of perturbation theory illustrates the difficulty one encounters with such systems.

Method and Results

To calculate the heat of formation, $\Delta H^\circ_{f,0}$, of NH_3, we have studied the gas-phase reaction of H_2 with N_2. The standard heats of formation at 0 K of H_2, N_2, and NH_3 are known by definition and experiment[3] to be 0.0, 0.0, and -9.34 kcal/mol, respectively. For our calculations of the total energy, we used the experimental geometries of the reactants and product. The observed internuclear distances for H_2 and N_2 are 0.7414 Å and 1.109 76 Å, respectively.[5] The internuclear distance and H-N-H angle for NH_3 are[6] 1.0124 Å and 106.68°. The determination of $\Delta H^\circ_{f,0}$ requires that the calculated total energy change for the reaction be cor-

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