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TITLE: COMPUTER SIMULATION OF AQUEOUS NA-CL ELECTROLYTES

AUTHOR(S): G. HUMMER
D.M. SOUMPASIS
M. NEUMANN

Los Alamos

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Computer simulation of aqueous Na-Cl electrolytes

G Hummer[1], D M Soumpasis[2], and M Neumann[3]

[1]Theoretical Biology and Biophysics, Group T-10, MS K710,

Los Alamos National Laboratory, Los Alamos, NM 87545, U.S.A.

[2]Abteilung Molekulare Biologie, Max-Planck-Institut für Biophysikalische Chemie,

Postfach 2841, D-38017 Göttingen, Germany

[3]Institut für Experimentalphysik der Universität Wien, Strudlhofgasse 4,

A-1090 Wien

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Abstract

The equilibrium structure of aqueous Na-Cl electrolytes in the concentration regime between 1 and 5 mol/l is studied by means of molecular dynamics computer simulation using interaction site descriptions of water and the ionic components. The electrostatic interactions are treated both with the newly developed charged-clouds scheme and with Ewald summation. In the case of a 5 mol/l electrolyte. the results for pair correlations obtained by the two methods are in excellent agreement. However. the charged-clouds technique is much faster than Ewald summation and makes simulations at lower salt concentrations feasible. It is found that both ion-water and ion-ion correlation functions depend only weakly on the ionic concentration. Sodium and chloride ions exhibit only a negligible tendency to form contact pairs. In particular, no chloride ion pairs in contact are observed.

1. Introduction

A detailed understanding of the physical properties of aqueous electrolytes at an atomic level is of considerable importance in various scientific fields, ranging from physical chemistry to biology and medicine. Advanced experimental techniques like the isotopic differential neutron scattering method have significantly contributed to our understanding of the structure of aqueous electrolytes [1]. On the theoretical modeling side, it has been found that integral equation methods such as extended RISM [2–5] face considerable difficulties owing to the molecular nature of water as a solvent and the presence of strong interactions (charge, hydrogen bond, *etc.*). Computer simulations of electrolytic systems employing molecular water models can provide some insight, but up to date have been severely limited by their resource requirements. In order to study the whole ionic concentration regime it is essential to develop fast and accurate methods to describe the Coulomb interactions in electrolytes. In this work we present a strongly screened, only distance-dependent, effective Coulomb interaction. It is compared with Ewald summation in the case of a 5 mol/l Na-Cl electrolyte and then applied to studying the concentration dependence of the structure of 1, 3, and 5 mol/l aqueous Na-Cl solutions.

2. The charged-clouds Coulomb interaction

In the computer simulation of homogeneous charged fluids, usually systems containing a few hundred or thousand particles are studied under periodic boundary conditions. It is well established that this can cause serious problems, if the Coulomb interactions are not treated carefully. An elegant way to do this is of Ewald summation [6]. Charges do not only interact with all other charges in the simulation cell, but also with the images of the charges obtained by periodic replication of the cell. This gives rise to an effective modified Coulomb interaction, which can be expressed in terms of a real space and a Fourier space contribution. Ewald summation gives excellent results for various types of Coulombic systems. However, it is comparably difficult to implement and the evaluation is more time consuming than for a simple, only distance-dependent, short-range interaction.

The reaction field method for polar systems tries to mimic the response of particles beyond the cutoff as that of a dielectric continuum. This method can be generalized to systems containing ions and polar molecules, resulting in a screened Coulomb interaction, which is the electric field of a point charge surrounded by a sphere of radius r_c homogeneously filled with a compensating background charge. Despite its simplicity, this method gives good results for a wide class of polar and ionic systems [7].

We now try to eliminate an asymmetry present in the reaction field model,

where only single charges are surrounded by compensating backgrounds. If pairs of particles are surrounded by compensating background charges and all interactions (charge-charge, charge-background, and background-background) are counted, the effective interaction obtained is no longer monotone and therefore has no practical value. However, if we change the sign of one of the background charges and make it additive, we obtain an effective interaction we call the *charged-clouds* model, namely

$$\phi(r) = \frac{1}{r} \left(1 - \frac{r}{r_c} \right)^4 \left(1 + \frac{8r}{5r_c} + \frac{2r^2}{5r_c^2} \right) \Theta(r_c - r) . \tag{1}$$

Here, r_c is the diameter of the spheres surrounding the two point charges. $\Theta(x)$ is the Heaviside unit step function. $\phi(r)$ and all its derivatives are monotone and of alternating sign, exactly like $1/r$. $\phi(r)$ and its derivatives up to third order vanish at the cutoff r_c. Therefore, $\phi(r)$ has very nice properties. For instance, if used in molecular dynamics simulations, it leads to energy conservation.

Clearly, the applicability of the charged-clouds interaction $\phi(r)$ in computer simulations has to be tested. In the following we will compare it with Ewald summation for a 5 mol/l Na-Cl electrolyte. In our calculations we use the same pair-potential model to describe the interactions between ions and water as in our previous studies [3-5] with SPC water [8] and the parameters of Pettitt and Rossky for ion-water and ion-ion interactions [2].

A standard Verlet algorithm is used in the molecular dynamics simulations

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combined with a constraint algorithm for the rigid water molecules. Heavy water along with a time step of 5 fs is used. All simulations are carried out in the NVE ensemble, at an average temperature of approximately 298 K. In the Ewald simulation, the system comprises 416 water molecules and 42 ion pairs. Data are averaged for 350 ps (after extensive equilibration). For the Ewald summation, a real space damping factor of $5.6/L$ and 2×510 vectors in k-space are used.

The Ewald results are compared to data obtained for two systems analysed with the charged-clouds method. One contains 208 water molecules and 21 ion pairs, the other 832 water molecules and 84 ion pairs. For both systems a cutoff of 0.9 nm is employed. For the small system, averaging extends over 1 ns. For the large system, 300 ps are used for data collection. A rhombic dodecahedron is used as simulation cell in the case of the charged-clouds calculations, whereas a cubic cell is used in the Ewald simulation.

In figure 1(a), the water site correlation functions obtained with Ewald summation and the charged-clouds method are compared. They are practically indistinguishable. In particular, the charged clouds method does not induce any artificial oszillations at the cutoff. The same is also true for the ion-water correlations shown in figure 1(b) and 1(c). Again hardly any differences between Ewald and charged-clouds results are observed. Only in the case of the ion-ion pair correlation functions shown in figure 1(d), minor differences appear, some of which can be attributed to the greater statistical uncertainty.

But still the agreement is very good.

3. Salt concentration dependent structure

We next analyse Na-Cl solutions at 1, 3, and 5 mol/l concentration. The systems comprise 1000 particles each. The number of ion pairs ranges from 18 to 84. The charged-clouds interaction is used along with a cutoff of 0.9 nm. In the case of the 5 molar solution, 300 ps are used for averaging. The 1 and 3 molar electrolyte data are averaged for 550 ps, always after extensive equilibration.

The water-water correlations shown in figure 2(a) dependend considerably on the ionic concentration. The first peak of the O-O correlation decreases and shows a shoulder at high ionic concentrations. The *ice* peak at 0.45 nm reflecting the tetrahedral ordering in water also decreases. The ions clearly distort the water structure characterized by a distinct hydrogen bond pattern. At 5 mol/l concentration the ratio of the numbers of water molecules and ions is approximately 5. This means roughly speaking that every water molecule is part of the first hydration shell of an ion.

The concentration dependence of the ion-water correlation functions shown in figure 2(b) and 2(c), is small, in agreement with the neutron scattering experiments. The Cl-water correlations show some differences beyond 0.4 nm distance. Interestingly, the first peak height of the ion water correlations increases with increasing concentrations.

The Na-O correlations show a very distinct first peak followed by a deep and broad minimum. The negatively charged Cl^- is not able to form such a stable first hydration shell. The peak positions of the Cl-H and Cl-O correlation indicate that the Cl^- ion, H. and O are by and large lying on a straight line.

Unlike the water-water and water-ion correlations, the ion-ion correlations shown in figure 2(d) are subject to somewhat larger statistical uncertainties, particularly in the case of the 1 molar solution. In the case of the Na-Cl correlation function the contact peak at 0.27 nm is consistently small. The solvent-separated peak at 0.5 nm distance with one water molecule between the ions is dominating. The Cl-Cl correlations show the first maxima at about 0.55 nm. No contact anion pairs are observed. The Na-Na correlations show more structure with peaks at 0.37 and 0.6 nm. As expected, with decreasing concentration. like charged ions tend to stay further apart.

4. Conclusions

The screened Coulomb interaction model we have introduced yields results for a 5 molar Na-Cl electrolyte that agree very well with Ewald summation data, but is computationally more efficient. This model enables us to study fairly large electrolytic systems with reasonable CPU time requirements. We have analysed aqueous Na-Cl solutions at 1, 3, and 5 molar concentration. The water-water correlations reveal a distorting influence of the ions on the water structure. The ion-water correlations depend only weakly on the ionic concen-

tration. The main features of the ion-ion correlations are also concentration independent. In particular, no like charged Cl^- pairs in contact are observed; and in agreement with the Arrhenius' picture of fully dissociated electrolytes, Na^+ and Cl^- remain well solvated and rarely approach each other closer than a distance corresponding to one water molecule.

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Figure Legends

Figure 1: Comparison of correlation functions in a 5 mol/l Na-Cl-H_2O electrolyte obtained with charged-clouds interaction and Ewald summation. (—·), Ewald summation with 500 particles; (– – –), charged-clouds interaction with 250 particles; (- - - -), charged-clouds interaction with 1000 particles. (a) water-water correlations (g_{O-H} and g_{H-H} are shifted vertically by 0.75 and 1.5, respectively); (b) Cl-water correlations (g_{Cl-H} is shifted vertically by 0.5); (c) Na-water correlations (g_{Na-H} is shifted vertically by 2); (d) ion-ion correlations (g_{Cl-Cl} and g_{Na-Na} are shifted vertically by 1 and 2, respectively).

Figure 2: Concentration dependence of the correlation functions in Na-Cl-H_2O electrolytes. (——), 5 mol/l; (– – –), 3 mol/l; (- - - -), 1 mol/l; (······), pure SPC water data from a Monte Carlo simulation with the charged-clouds model. For vertical shifts see figure 1.
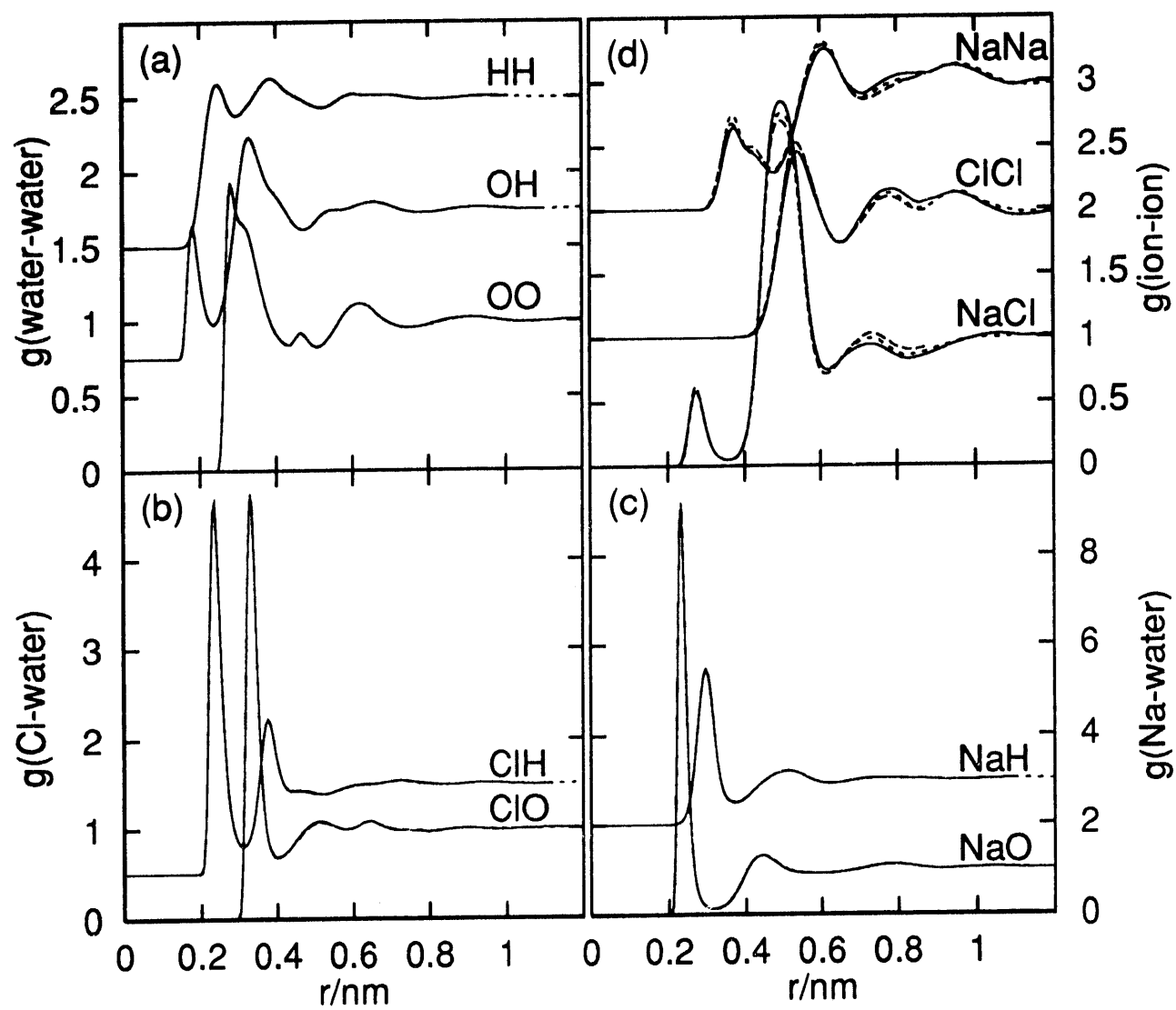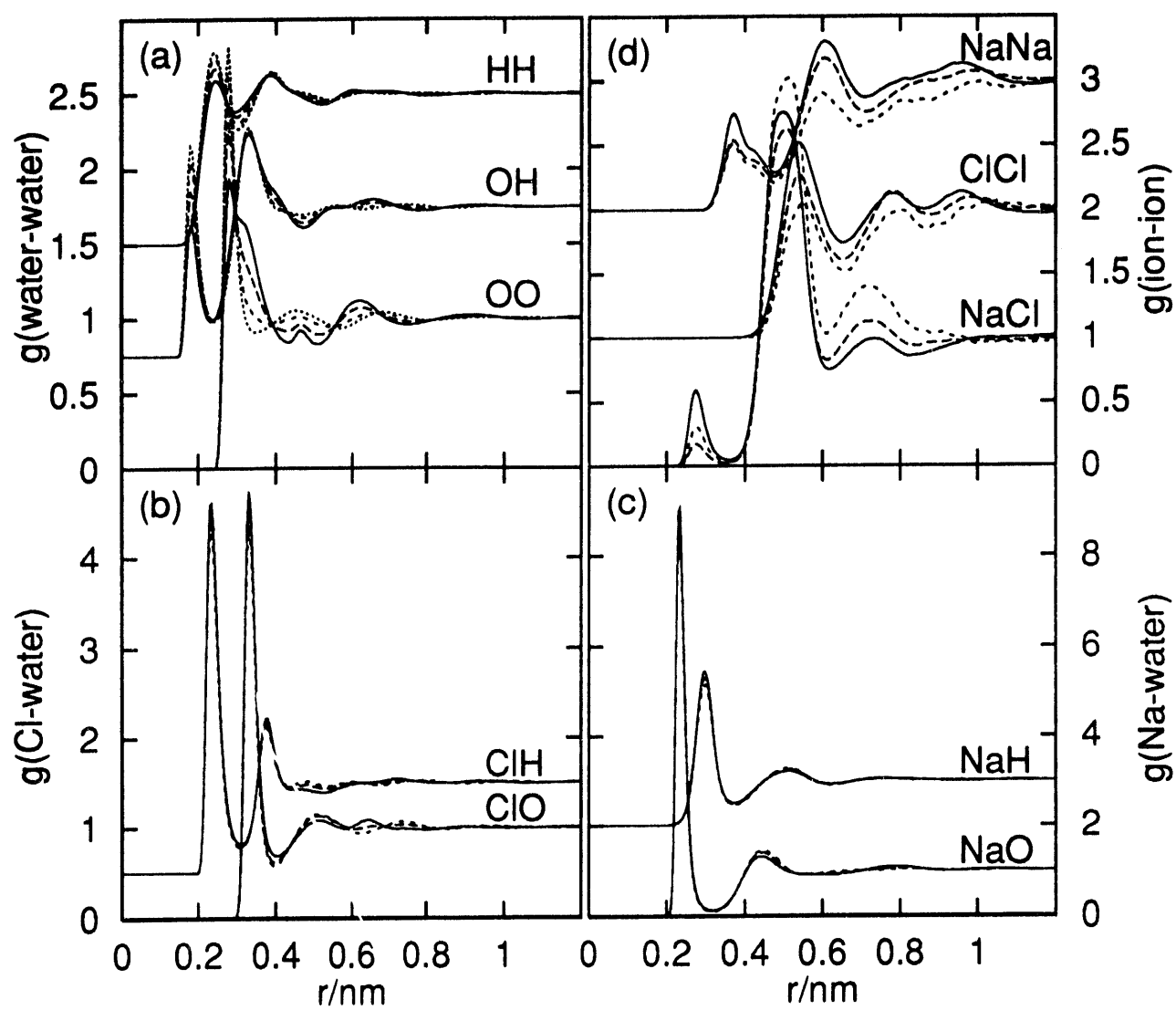
Figure 1

Figure 2

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