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MD simulation and evaluation of the self-diffusion coefficients in aqueous NaCl solutions at different temperatures and concentrations

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ABSTRACT

Aqueous NaCl solutions are the most common electrolyte with a wide range of applications. One of the most important transport properties of aqueous electrolytes are the self-diffusion coefficients. In this study, molecular dynamics (MD) simulations of aqueous NaCl solution are carried out to study the effect of temperature, which is not often reported in the literature, and also of salt concentration on the self-diffusion coefficients. The self-diffusion coefficients of water, Na^+ and Cl^- are calculated from the long-time limit of the mean square displacements (MSD) and the results are validated with experimental results from the literature. The simulation results show that the self-diffusion coefficients of water, Na^+ and Cl^- increase with increasing temperature, whereas they decrease with increasing salt concentration. The temperature effect on the self-diffusion coefficient is more obvious at low concentrations. The radial distribution functions for all atom pairs in the NaCl electrolyte are plotted and the effect of temperature on these functions is investigated. The effects of temperature and concentration on the ion hydration numbers and the Na^+–Cl^- coordination numbers are also studied. Furthermore the self-diffusion coefficient of the NaCl salt is calculated in two ways, directly from the simulation, and also from the Cussler equation, which has been proposed to evaluate the average value of electrolyte diffusion coefficient from the diffusion coefficients of the constituent ions. A good consistency was observed between the obtained results with the two methods.

1. Introduction

The solvation of ions in liquid water is a fundamental problem encountered in a wide range of biological and chemical systems. Thermodynamic and transport properties of electrolyte solutions are very important for a variety of applications in many industrial processes, such as extractive distillation, solution crystallization, ion exchange, membrane separation, wastewater treatment, etc. NaCl is one of the most common solutes in aqueous fluids in a wide variety of geological setting [1]. Moreover, the description of ions, in particular Na^+ and Cl^-, is essential for biophysical systems. As an example the physiological liquid in the human body containing about 0.8 mol of salt, i.e. one ion pair per 100 water molecules [2]. Furthermore, studies of aqueous NaCl are needed due to its important role in various industrial applications such as water desalination [3], food industry [4] and medicine. Therefore the properties of NaCl solution have been investigated both theoretically and experimentally by many authors. Numerous studies have been carried out about the thermodynamic properties of salt–water system [5,6], the transport properties of salt water system have also been investigated by many authors [7–10]. The modeling of thermodynamic and transport properties of electrolyte solutions is reviewed in [11].

Nowadays computer simulations have become an important tool for the understanding and modeling of natural systems at the molecular level. Different simulation techniques have been applied to investigate the dynamics of aqueous electrolyte solutions, including Langevin dynamics (LD), Brownian dynamics (BD), and molecular dynamics (MD) simulations [12]. In some of these cases, the water molecules are not considered explicitly. The solvent phase is rather considered as a continuum medium and the ions interact through solvent averaged potentials. These techniques have been employed to study diffusion and conductivity of concentrated electrolyte solutions [13,14]. In these techniques, due to their only implicit consideration of the solvent, it is not possible to study certain dynamical aspects such as the dependence of solvent dynamical properties on ion concentration and the dynamical coupling between ion motion and solvent motion [15]. On the other hand molecular dynamics simulations have been very successful in predicting the properties of pure water and aqueous solutions. In MD methods both solvent molecules and ions are considered explicitly and therefore it is possible to study the dynamics of ions and water molecules. The high computation cost of MD for electrolyte solutions is considered as a disadvantage of this method. In spite of developments in computing machines there are still limitations in the number of ions and solvent molecules that can be simulated. However, the MD method is increasingly being applied to simulate and study the properties of electrolytes due to the general good agreement that can be achieved with experimental studies. For instance Carleo et al. [16] have used the MD method

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to analyze transport properties of concentrated electrolytes containing KCl, $MgCl_2$ and a mixture of both. Crozier et al. [17] have simulated NaCl ion currents in water solution with applied electric field by using the molecular dynamics method. Also, Okada et al. [18] studied the crystal growth from a supersaturated NaCl aqueous solution by MD simulation.

One of the most important transport properties of aqueous electrolytes is the translational self-diffusion coefficient. Self-diffusivity is a measure of the mobility of the molecules or ions in the absence of a driving force, e.g. a concentration or chemical potential gradient [19]. More precisely, according to the IUPAC definition, self-diffusion is the diffusion coefficient of species *i* when the chemical potential gradient is zero [20]. A more comprehensive discussion on the theory of self-diffusion can be found in [21]. Knowing the self-diffusion coefficients is necessary when studying mass transfer in many industrial applications, especially in electrochemical systems, Theoretical models have been developed to predict self-diffusion coefficients in electrolyte solutions [22,23]. However, for many systems the theories are limited or there are no theories or correlations that can accurately predict the self-diffusivity. Frequently, the best, and sometimes the only, recourse is to turn to laboratory experiments and computer simulations [19]. As discussed above, nowadays the MD simulations have become a powerful and relatively inexpensive tool to evaluate self-diffusion coefficients and they have been employed by numerous authors to predict transport properties and especially self-diffusion coefficients in electrolyte solutions [2,15,16,24].

In this study, we have employed molecular dynamics simulations to estimate the self-diffusivities of NaCl–water system at atmospheric pressure. The self-diffusion coefficients of the water molecules and of the constituent ions in aqueous NaCl solutions at different concentrations and constant temperatures have been investigated by other authors, for instance [2,15]. But the effect of temperature on the self-diffusion coefficients of such a system has been less often reported. The main objective of this work is to investigate the dependency of the self-diffusion coefficient of the water molecule, Na^+ and Cl^- ions on the salt concentration and temperature. Furthermore in this study the self-diffusion coefficient of NaCl salt is calculated in two ways, directly from the simulations and also from Cussler equation, proposed to evaluate the average value of electrolyte diffusion coefficient from the diffusion coefficients of the constituent ions.

2. Simulation method

2.1. Simulation details

MD simulations were carried out for 5 values of temperatures (10, 25, 40, 60 and 80 °C) at 9 different ion concentrations (from dilute to almost saturate at the lowest temperature) in the NVT ensemble (NVT: constant number, volume, and temperature). At each concentration, the system is made up of 1000 water molecules plus the appropriate numbers of ions in a cubic box. The length of cubic box, L, is chosen so that to match the experimental density. The experimental densities at different temperatures and concentrations are taken from Perry's handbook [25] and these values are presented in Table 1. The simulation parameters and experimental densities are listed in Table 1.

The initial configurations were obtained by a random displacement of the cubic lattices of water molecules in the box. Then the ions were distributed randomly in the volume. The LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) program [26] was used to run all simulations on a parallel Linux cluster. VMD [27] software was used to visualize the results.

In all simulations, the water molecules are characterized by the flexible SPC potential model and the ions are modeled as charged Lennard–Jones particles. The SPC model was chosen due to its simplicity and also by the fact that the diffusion coefficient constants of the flexible SPC model are sometimes very close to the experimental values [2,15]. In these models, the interactions between atomic sites (or ions) are expressed as:

$$u\left(r_i, r_j\right) = 4\varepsilon_{ij}\left(\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right) + \frac{q_i q_j}{r_{ij}}.C \tag{1}$$

where q_i is the charge of the *i* th atom (or ion) and *C* is a constant. The Lennard–Jones parameters σ_{ij} and ε_{ij} are obtained by using the combination rules $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$. The values of the potential parameters q_i, σ_{ij} and ε_{ij} for water and Na^+ and Cl^- ions are available in Ref. [2,15] and are summarized in Table 2.

Short-range forces were truncated at the half of the box length and the particle–particle particle–mesh (PPPM) solver [28] was employed to treat the long range columbic interactions. The integration time step was set to 0.5 fs although the value of 1 fs was enough for most of simulations but in some cases, especially low concentrated cases, instability in results was observed. So in order to compare results under the same conditions the smaller time step (0.5 fs) was chosen for all simulations. In all the simulations, the stability of the total energies was better than 0.01%. MD runs of 500 ps were used to equilibrate each system and then the self-diffusion coefficient for water molecules and each type of ions were calculated over a period of at least 10 ns for solutions at specified concentrations. This relative long period of time was chosen for simulation in order to obtain accurately the radial distribution functions for each pairs of particles, especially in the case of the ion–ion functions at law salt concentrations.

2.2. Self-diffusion coefficients

A major objective of the present simulations is to study the effects of temperature and ion concentration on the self-diffusion in aqueous

Table 1
Simulation parameters at different temperatures and concentrations.

	System	1	2	3	4	5	6	7	8	9
	Number of H_2O molecules	1000	1000	1000	1000	1000	1000	1000	1000	1000
	Number of Na^+ ions	3	9	18	36	50	64	72	90	100
	Number of Cl^- ions	3	9	18	36	50	64	72	90	100
	Salt concentration (m)	0.167	0.500	1.000	2.000	2.778	3.556	4.000	5.000	5.556
T = 10	Exp density (gr/cm^3)	1.007	1.021	1.040	1.077	1.104	1.130	1.144	1.174	1.190
	Box length (A)	31.061	31.120	31.212	31.407	31.566	31.730	31.826	32.044	32.164
T = 25	Exp density (gr/cm^3)	1.007	1.017	1.036	1.072	1.098	1.123	1.137	1.166	1.182
	Box length (A)	31.061	31.157	31.255	31.460	31.625	31.794	31.891	32.113	32.235
T = 40	Exp density (gr/cm^3)	0.999	1.012	1.030	1.066	1.091	1.116	1.129	1.158	1.174
	Box length (A)	31.144	31.211	31.314	31.523	31.692	31.863	31.961	32.186	32.309
T = 60	Exp density (gr/cm^3)	0.990	1.002	1.021	1.055	1.081	1.105	1.118	1.147	1.162
	Box length (A)	31.238	31.308	31.412	31.624	31.794	31.966	32.065	32.290	32.414
T = 80	Exp density (gr/cm^3)	0.960	0.991	1.009	1.044	1.069	1.093	1.106	1.135	1.150
	Box length (A)	31.260	31.428	31.531	31.742	31.911	32.083	32.181	32.405	32.527