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Influence of magnetic field on microstructural and dynamic properties of sodium, magnesium and calcium ions

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Abstract: Molecular dynamics (MD) simulation was performed to investigate the effects of magnetic field on sodium, magnesium and calcium ions in chloride solutions. According to the research on pair correlation function $g_{ij}(r)$, mean square displacement L_{MSD} and diffusion coefficient D, the changes of microstructural and dynamic properties were studied. The results show that with the effect of magnetic field, the interaction between ions and water weakens, the contact ion pairs increase and the solvent separated pairs decrease. Magnetic treatment leads to an increase of diffusion coefficients of cations and a decrease of anions. The separation efficiency of brine from seawater may be improved by magnetic treatment.

Key words: magnetic field; microstructural property; dynamic property; molecular dynamics simulation

1 Introduction

Seawater reserves are vast on the earth and there are averagely 35.7×10^6 t/km^3 of minerals in seawater. More than 80% of the chemical elements can be found in seawater [1]. Therefore, it is an effective way to extract minerals and metal elements from brine which are the by-products of seawater desalination. This method can not only reduce cost significantly but also improve utilization ratio and protect the environment [2]. In view of the fact that magnetic fields have been successfully used in water treatment [3−5], the magnetic field was tried to apply to the separation process. The purpose is to investigate whether it can enhance the separation of brine from seawater and then extract the required minerals and metal elements.

Various numerical studies associated with the influence of magnetic field on the physicochemical properties of water and aqueous solutions have been performed under different conditions. MURAD [6] performed MD simulations to show that magnetic fields could make water clusters weaker and increase the transport rate of water molecules across membranes significantly. TOLEDO et al [7] used ab initio calculations to study the effects of magnetic field on the hydrogen bond and revealed that the intercluster hydrogen bonds were weakened, while the intracluster hydrogen bonds were enhanced, and the competition gave rise to smaller water clusters. However, CHANG and WENG [8−9] investigated the influence of magnetic fields with intensity of 1−10 T on liquid water and NaCl solutions at different concentrations, and showed that the magnetic fields enhanced the mobility of the Na^+ and Cl^- ions and the hydrogen bond was enhanced by the application of magnetic fields in pure water and aqueous NaCl solutions at low concentrations. In this work, molecular dynamic (MD) simulation was used to study the effect of magnetic field on the sodium, magnesium and calcium ions which are the three most cations in seawater.

2 MD simulation

In all simulations, the SPC/E intermolecular potential was used for water. Intermolecular interaction for water and ions is expressed as a sum of Columbic and Lennard-Jones pair potentials given by:

$$U_{ij}=\frac{q_iq_j}{r_{ij}}+4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12}-\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \quad (1)$$

where q_i, q_j and r_{ij} are the charges of atoms i, j and

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the distance between them, and ε_{ij}, σ_{ij} are obtained by using the Lorentz-Berthelot rules. The values of the potential parameters q_i, ε_j, and σ_j are summarized in Table 1.

Table 1 Interaction parameters for potential models [10−12]

Atom/ion	Charge/e	ε/(J·mol^{-1})	σ/Å
O	−0.847 6	0.650 6	3.165 5
H	+0.423 8	0	0
Cl^-	−1.0	0.419 1	4.400 0
Na^+	+1.0	0.544 3	2.350
Mg^{2+}	+2.0	5.942 2	1.397 6
Ca^{2+}	+2.0	1.882 8	2.360 9

The force on atom i is expressed as:

$$\boldsymbol{F}_i = \boldsymbol{F}_i^{\text{pot}} + \boldsymbol{F}_i^{\text{mag}} \tag{2}$$

where $\boldsymbol{F}_i^{\text{pot}}$ and $\boldsymbol{F}_i^{\text{mag}}$ represent the force from the potential force field and external magnetic field, respectively. The force from the potential force field is

$$\boldsymbol{F}_i^{\text{pot}} = -\nabla_i U_{ij} \tag{3}$$

The magnetic field is treated in most common physical way [6] and the force from the magnetic field $\boldsymbol{B}$, i.e, Lorentz force is

$$\boldsymbol{F}_i^{\text{mag}} = q_i \cdot \boldsymbol{v}_i \times \boldsymbol{B} \tag{4}$$

where $\boldsymbol{v}_i$ is the velocity of atom i, and × represents the outer product of vectors. In this work, $\boldsymbol{B}$ is 0.2 T. The systems were made up of 1431 water molecules and 16 $NaCl/MgCl_2/CaCl_2$ respectively in cubic boxes, to which the lengths are chosen to match the density of 0.62 mol/L. The NTP ensemble was sampled with the Nose thermostat. Periodic boundary condition and minimum image convention were adopted. Long-range force was truncated at the half of box length and the Ewald summation technique was employed to treat the long-range coulomb interaction. The equations of motion were integrated using the Gear5 predictor-corrector algorithm and the SHAKE technique of constraints was applied for the water model. In the initial configuration, the particles were randomly distributed in the cubic volume. The simulations use 1fs integration time step and extend 1ns to calculate the equilibrium quantities.

To study the effects of magnetic field on the structural and dynamic properties, $g_{ij}(r)$ was generally used to study the microstructure of solutions, and it is defined as:

$$g_{ij}(r) = \frac{V}{N_i \cdot N_j} \sum_k^{N_i} \frac{z_{ik}(r-\Delta r/2, r+\Delta r/2)}{4\pi r^2 \Delta r} \tag{5}$$

where N_i, N_j is the total number of atoms i and j, and z_{ik} is the number of atoms k included in a spherical shell of thickness Δr located at a distance r, for atoms of the same species, N_j=N_i−1. L_{MSD} is a very important dynamic property of particles which indicates the average displacement of a particle during a fixed time T. It is calculated as follows:

$$L_{\text{MSD}} = \left\langle |\, r(T) - r(0)\,|^2 \right\rangle = \frac{1}{NM} \sum_i^N \sum_k^M |\, r_i(t_k + T) - r_i(t_k)\,|^2 \tag{6}$$

where M is the number of time series data, and t_k is the starting time of k-th time series data. The self-diffusion coefficient D can be calculated from the slope of L_{MSD}.

3 Simulation results and discussion

3.1 Pair correlation function

The influence of magnetic field on the microstructures of sodium, magnesium and calcium ions in chloride solutions is studied. Figure 1 presents the effects of magnetic field on $g_{\text{cation-water}}(r)$, $g_{\text{anion-water}}(r)$ and $g_{\text{cation-anion}}(r)$ of sodium, magnesium and calcium ions in chloride solutions. For clarification, the first peaks are enlarged in the small figures.

The behavior of ion–water interaction as deduced from MD simulations was analyzed. A distinguished feature of $g_{\text{cation-water}}(r)$ is the sharp first peak and the low first valley, which is null in a large interval. Therefore, the first hydration shell of cations is well defined and separated from the second one. With the effect of magnetic field, it is observed that the first peaks decrease in both $g_{\text{cation-water}}(r)$ and $g_{\text{anion-water}}(r)$. The interaction between solute and solvent weakens. The reason is that the increased mobility of the ions under Lorentz force destroys the balance of ion clusters.

The cation–anion interaction is expressed by the pair correlation functions between cations and anions. $g_{\text{cation-anion}}(r)$ are less smooth than the others. This is because the number of ions is less than that of water molecules in chloride solutions. The first valley is also null in a rather large interval due to the well defined contact pairs which are separated from the solvent separated ones. The first peaks decrease as the order Na^+, Mg^{2+}, Ca^{2+} and even disappear in $g_{\text{Ca-Cl}}(r)$. This indicates that the interaction between cations and anions weakens in sequence. With the effect of magnetic field, the first peaks increase, and the second ones decrease. Therefore, the contact ion pairs increase, and the solvent separated pairs decrease. The reason is that the Lorentz force disturbs the system by accelerating the movement of the charged particles, and it is more likely for ions to contact with each other. While, the solvent separated pairs decrease for the weakness of interaction between solute and solvent with the effect of magnetic field.

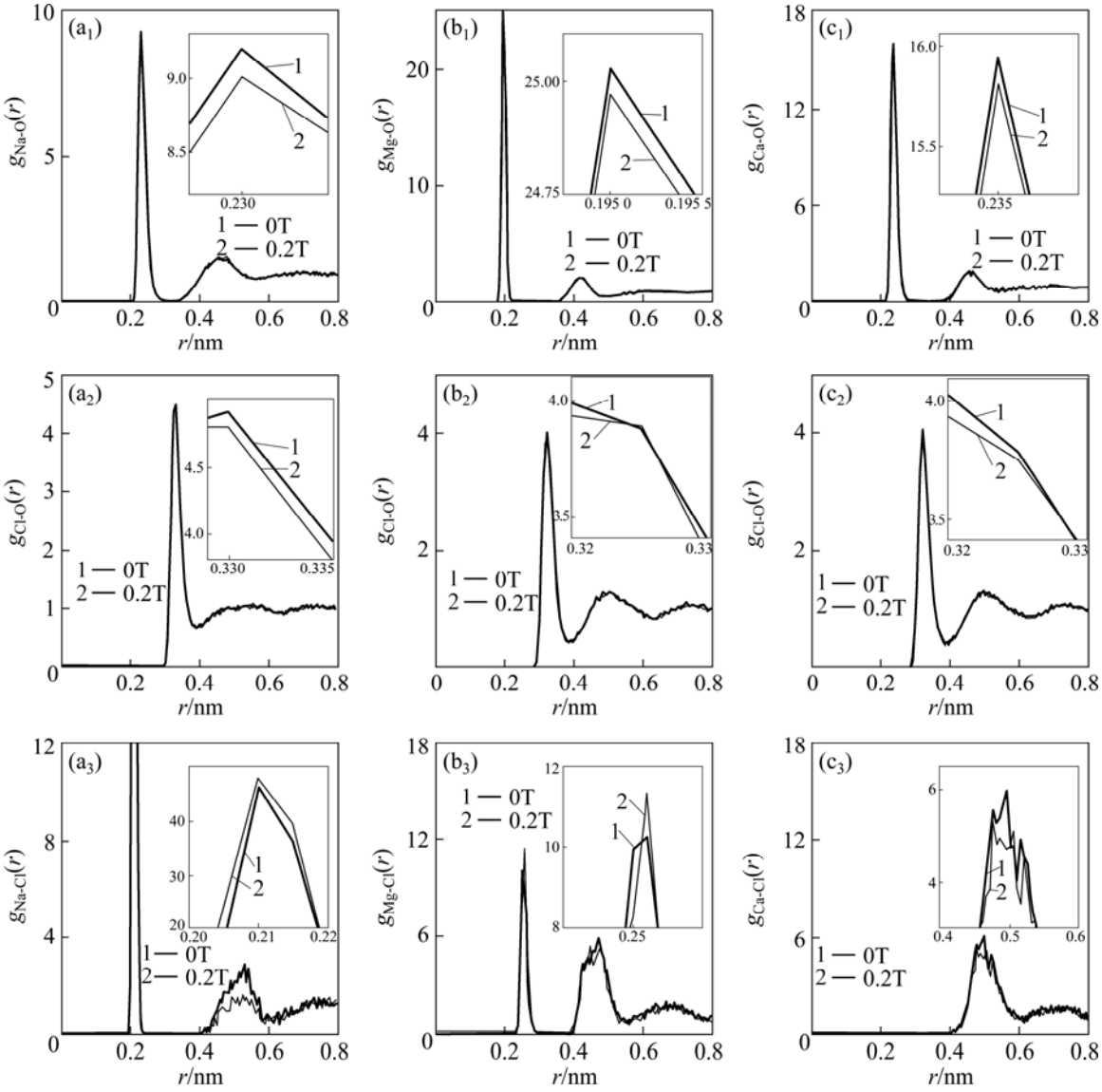

Fig. 1 Effects of magnetic field on $g(r)$ of ion-water and ion-ion in chloride solutions: (a_1), (a_2), (a_3) Sodium ion; (b_1), (b_2), (b_3) Magnesium ion; (c_1), (c_2), (c_3) Calcium ion in chloride solutions

3.2 MSD and diffusion coefficient

The influence of magnetic field on the mean square displacement (MSD) of sodium, magnesium, calcium ions and anions in chloride solutions is shown in Fig. 2. Only the first 600 ps out of 1ns is plotted [13]. With the effect of magnetic field, the MSD of cations increase, while the MSD of anions decrease.

From the slope changes of the MSD, it is clear that the diffusion coefficients of cations and anions increase and decrease, respectively. Moreover, the decrease of anions is more evident compared with the increase of cations. KOTELYANSKII et al [14] stated that anions other than cations limit the salt transport in the FT-30 membranes. The weakened mobility of anions may slow the salt transport in the membranes and then lead to higher brine concentrations. This is certified by the researches of Al-Qahtani [15]. It is found that the separated brine concentrations of the magnetic treated solutions are usually higher than those of the untreated one. Therefore, the separation efficiency of brine from seawater may be improved by magnetic treatment.

4 Conclusions

1) For sodium, magnesium and calcium ions in chloride solutions, magnetic field results in weaker interaction between ions and water, an increase of the contact ion pairs and a decrease of the solvent separated pairs.

2) With the effect of magnetic field, the diffusion coefficients of sodium, magnesium and calcium ions increase, while, the diffusion coefficients of anions decrease. Magnetic field is beneficial to the separation process of brine from seawater.

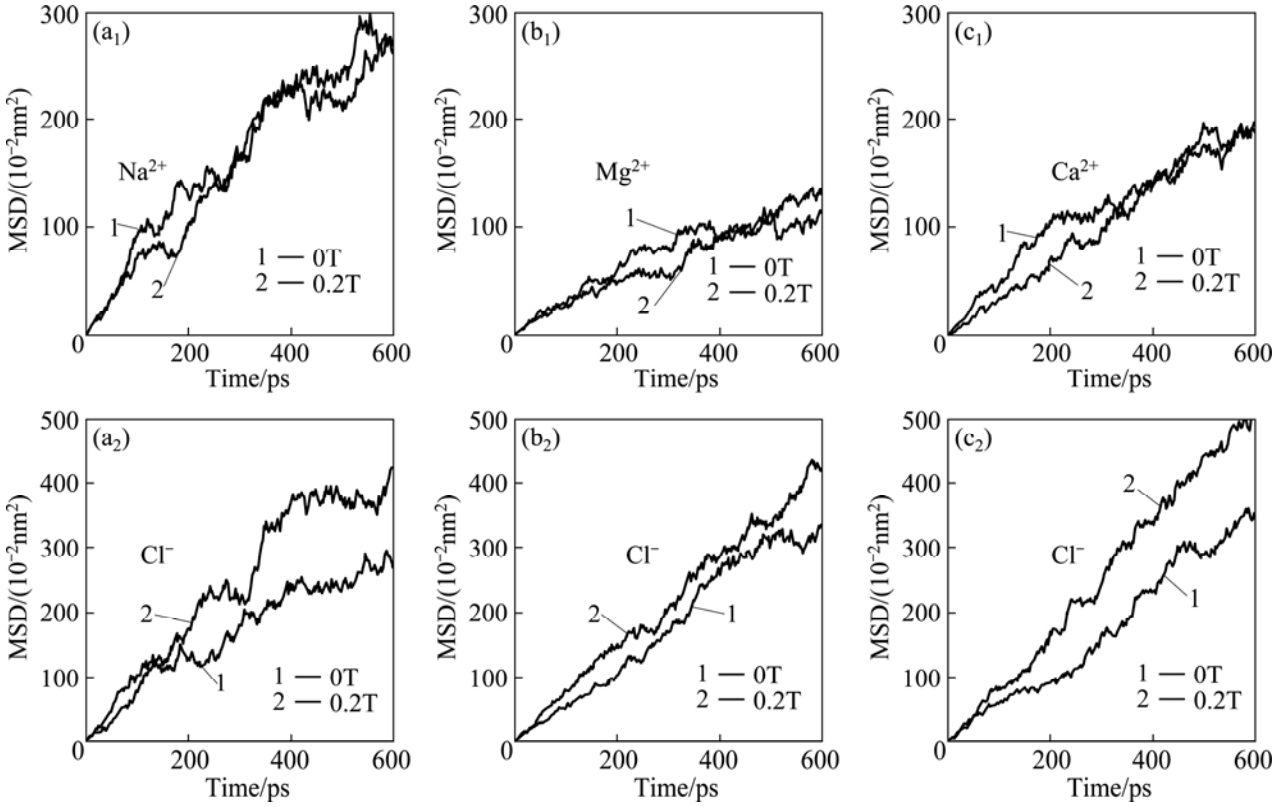

Fig. 2 Effects of magnetic field on MSD of cations and anions in chloride solutions: (a_1), (a_2) Sodium ion; (b_1), (b_2) Magnesium ion; (c_1), (c_2) Calcium ion in chloride solutions

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磁场对钠、镁和钙离子微观结构和动力学性质的影响

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摘 要：采用分子动力学模拟(MD)的方法研究磁场对氯溶液中钠、镁和钙离子的影响。通过对相关函数 $g_{ij}(r)$、均方位移 L_{MSD} 和扩散系数 D 的分析，研究磁场对微观结构和动力学性质的影响。结果表明：离子和水之间的作用力减弱，接触离子对增加，溶剂分离离子对减少。磁处理导致阳离子扩散系数增加，阴离子扩散系数减少。磁处理能够改善从海水中分离出浓盐水的效率。

关键词：磁场；微观结构性质；动力学性质；分子动力学模拟

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