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Low temperature molecular dynamic simulation of water structure at sylvite crystal surface in saturated solution

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ABSTRACT

The low flotation recovery of sylvite from salt lakes at low temperatures has dogged the cryogenic producer for many years. Interfacial water structure at sylvite crystal surfaces has been considered as one noticeable aspect on interpreting the selected KCl collection during flotation, and so the microscopic structure of the water membrane over KCl crystal surfaces at low temperatures was modeled through the use of molecular dynamics methods. In our simulation, the properties of the water membrane adjacent to KCl crystal surface, such as molecular mobility, water structure and preferred molecular orientation, were compared to the results for an otherwise identical system at higher temperatures or in saturated KCl solutions in the absence of a KCl crystal. In our simulation, hydrogen atoms approached the KCl crystal surface more closely, and the mobility of water molecules was more restricted compared to results for saturated KCl solutions. When the temperature decreased, the mobility of water molecules decreased, the number of hydrogen bonds made by the water molecules in the membranes was reduced and the molecules exhibited greater order than in other systems we studied. It was proposed that the property of KCl salt may change from water 'structure breaker' to 'structure maker' when temperature decreases. These results may provide complementary information which cannot be obtained from experiments on the research of flotation at low temperature directly.

1. Introduction

As froth flotation provides an efficient means of separating heterogeneous mixtures of finely subdivided solids; it is therefore used frequently within the primary mineral and chemical industries (Rao, 2004). Potash is currently widely used as an agricultural fertilizer and over 80% of the world's potash is produced by selective flotation, which is especially effective at separating sylvite from complex solid mixtures (Du and Miller, 2007; Ozdemir et al., 2011). Recovery of sylvite by floatation falls precipitately when the temperature decreased, however: recovery is lower than 10% at 278 K (Cheng et al., 2012). The winter temperature of northern part of China, especially Qaidam basin (China) salt lake group area, is always below 273 K, and the sylvite industries have to stop production for about four months every year. Therefore, flotation of sylvite from salt lakes at low temperature remains challenging.

In general, during the process of flotation, the hydrophilic head groups of collectors become adsorbed upon the crystal surface while the hydrophobic tails are recruited to bubbles; crystals then float to the surface with the bubbles. In order to understand the mechanism of soluble salt flotation, considerable effort has been invested into the study of collector adsorption upon soluble salts and several different models have been proposed. These models include the ion substitution model (Fuerstenau and Fuerstenau, 1956), the heat of solution model (Rogers, 1957), the surface charge model (Roman et al., 1968) and the interfacial water structure model (Hancer et al., 2001; Hancer and Miller, 2000; Ozdemir et al., 2011). Unlike other models, the interfacial water structure theory suggests that the basic halides can be conveniently classified as either water 'structure makers' or 'structure breakers', which facilitate or disrupt hydrogen bonding between water molecules, respectively. KCl, for example, is a "structure-breaking" salt, which would disrupt the water membrane, allowing both anionic and cationic collectors access to adsorb to the crystal surfaces (Cao et al., 2010). In contrast, collectors would be excluded from the surface of structure-making salt crystal, such as NaCl, due to their strong ion/water interactions (Hancer et al., 2001).

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Soluble salt flotation is, in fact, a very complicated process, especially from salt lakes containing complex mixtures of salts. Furthermore, information provided by instrumental analysis remains of limited use. Molecular dynamics (MD) simulations provide an effective method for the generation of complementary information at the atomic level, which is difficult to obtain experimentally (Li et al., 2013a,b). Interfacial water structure and surface charge of selected basic chloride, LiCl, NaCl, KCl and RbCl, in saturated brine solutions have previously been investigated by Miller and colleagues (Du and Miller, 2007) using molecular dynamics simulations. Their results suggested that Li^+ and Na^+ lattice cations could interact strongly with interfacial water molecules due to their smaller radii and larger local electrostatic fields, resulting in stable water layers on the corresponding crystal surfaces with distinct orientations. The opposite phenomenon was observed in simulations of KCl and RbCl salts, for which the interaction between interfacial water and surface cations was weaker, allowing collector molecules to substitute for interfacial water. These results were obtained at 300 K, whereas the interfacial water structure at salt crystal surfaces at lower temperatures was not considered. Therefore, interfacial water structure at sylvite crystal surfaces during flotation process at low temperatures is still not clearly understood.

In order to extend and improve our understanding of these processes, we modeled the water structure surrounding KCl salt crystal surfaces at lower temperatures using molecular dynamics simulations in this study. The molecular mobility, distribution of hydrogen bonds and molecular orientation of water membranes adjacent to KCl crystal surfaces at low temperatures was compared to the same system modeled at higher temperatures and in saturated KCl solutions without KCl crystals. This work will allow a better understanding of the structure of interfacial water at KCl crystal surface at low temperatures, and might therefore provide new insights into froth flotation of KCl and help improve flotation recovery at low temperatures.

2. Simulation details

In order to understand the interfacial water structure affected by basic chloride salt crystals, a saturated potassium chloride solution was seeded within the simulation cell, completely covering the surface of the potassium chloride salt crystal. The composition of each system drew from previous work (Du and Miller, 2007) and is summarized in Table 1. The simulation cell was orthorhombic with the parameters $\alpha = \beta = \gamma = 90°$, $a = b = 24$ Å, and periodic boundary conditions. For comparison, another simulation cell with the same parameters was introduced which contained only saturated sylvine solution located in the middle of the cell. Both configurations are shown in Fig. 1. It is noted that the crystal size for all the systems is $a = b = 24$ Å, $c = 6.29$ Å. Potassium and chloride ions were initially randomly solvated with water. The thickness of potassium chloride solution is 20.3 Å and 21.2 Å for 278 K system and 278 K system, respectively. The temperature listed in the Table 1 is the simulation temperature for each corresponding system; we refer to the systems containing only KCl saturated solution at 278/298 K as ‘solution-278’ and ‘solution-298’ respectively, while those containing KCl saturated solution and a KCl crystal at 278/298 K are ‘crystal-278/crystal-298’. The temperature was maintained using the Berendsen thermostat for simulations (Berendsen et al., 1984; Plazzer et al., 2011).

Table 1
The composition and simulation temperature of each system.

System	KCl crystal	Number of particles			Temperature (K)
		K^+ in solution	Cl^- in solution	Water molecule	
solution-278	No	22	22	300	278
solution-298	No	26	26	300	298
crystal-278	Yes	22	22	300	278
crystal-298	Yes	26	26	300	298

All of MD simulations were performed by software Materials Studio 4.4 which could exactly simulate the properties of liquid–solid interface. After initial configuration, energy minimization was conducted for each system. The minimized system was then pre-equilibrated in the NVT ensemble, which described one closed system with constant particle number, system volume, and temperature. The COMPASS force field (Sigal et al., 1998; Sun, 1998) was used for all MD simulations, and the modified SPC model (Berendsen et al., 1981, 1987; Plazzer et al., 2011) was used to simulate liquid water. In the simulation, the cut-off distance is 8.5 Å. The total energy could be expressed as (Xu et al., 2011):

$$E = E_{bonds} + E_{angles} + E_{dihedrals} + E_{cross} + E_{VDW} + E_{elec} \tag{1}$$

where E_{VDW} and E_{elec} could be calculated as

$$\begin{aligned} E_{nonbond} &= E_{VDW} + E_{elec} \\ &= \sum \varepsilon_{ij}\left[2\left(\frac{\sigma_{ij}}{r_{ij}}\right)^9 - 3\left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right] + \sum \frac{q_i q_j}{r_{ij}} \end{aligned} \tag{2}$$

where r_{ij}, σ, ε, and q_i are the distance between particle i and j, size parameter, energy parameter and the charge of the ith atom/ion, respectively. The charge of each element in all the systems was set and listed in the Table 2.

For all MD simulations, the time step was 1 fs. After 1 ns equilibration, a further 1 ns simulation with 100 fs intervals was performed, from which the last 200 ps was used to obtain MD trajectory data for further analysis.

3. Results and discussions

3.1. The thickness of the water membrane at the crystal surface

In order to study the structure of water near the KCl crystal surfaces, it is necessary to define the thickness of the water membrane closest to crystal surface, which will exhibit the influence of the crystal on the properties of water most strongly. We calculated the particle number density distribution along the z-axis (Fig. 2); from the density profiles, it is apparent that there were two distinguishable peaks for H density and one strong peak for O density in both the crystal-278 and crystal-298 systems. Additionally, the first peak of the H density profile in the crystal-278 system was closer to the crystal surface than was calculated for the crystal-298 system. The shorter distance between H atom and KCl crystal may result in stronger columbic interaction between them in lower temperature.

Therefore, the thickness of the water membrane, expressed as d, ordered on the crystal surface can be defined on the basis of the density profiles. Commonly, the definition of the thickness of a complicated interface is conducted by ‘10–90’ rule, which was defined by the distance along the interfacial normal direction over which the density changes from 10% to 90% of the density of the bulk water (Gao et al., 2014; Jang et al., 2004; Li et al., 2013b). However, this criterion is most appropriate for the system without a clear boundary. In this work, a thickness criterion for water membrane is proposed, as shown in Fig. 2, corresponding to the distance from the start point of the H density profile to the second minimum after the two H density peaks. The calculated thickness