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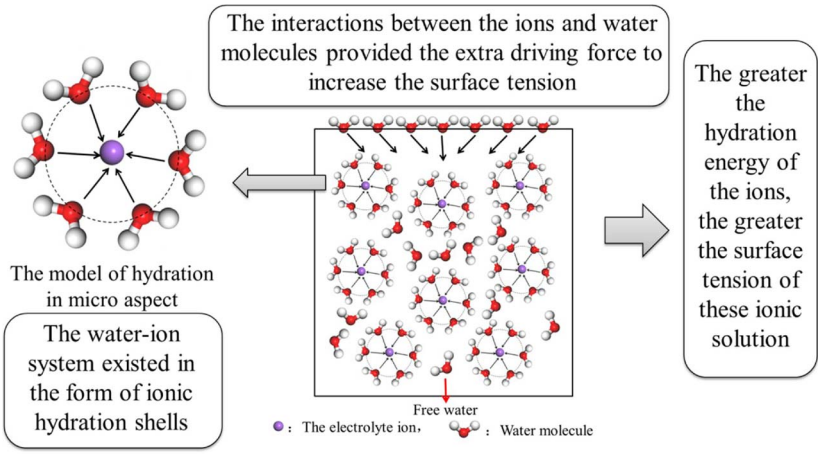
Molecular dynamics simulations study for the effect of cations hydration on the surface tension of the electrolyte solutions

Yuan Yuan[a], Weiquan Zhan[a], Hao Yi[a], Yunliang Zhao[a,b,*], Shaoxian Song[a,c,*]

[a] School of Resources and Environmental Engineering, Wuhan University of Technology, Luoshi Road 122, Wuhan, Hubei, 430070, China
[b] Hubei Key Laboratory of Mineral Resources Processing and Environment, Wuhan University of Technology, Luoshi Road 122, Wuhan, Hubei, 430070, China
[c] Hubei Provincial Collaborative Innovation Cente for High Efficient Utilization of Vanadium Resources, Wuhan University of Technology, Luoshi Road 122, Wuhan, Hubei, 430070, China

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the influence of different cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) on the surface tension of electrolyte solution was investigated using molecular dynamics simulations (MDs). The structure of the water-ion system was discussed in terms of ion-oxygen, ion-hydrogen radial distribution function (RDF) and hydration numbers of different electrolyte ions. It was found that the water-ion system existed in the form of ionic hydration shells. Besides, the interactions between the ions and water molecules were illustrated by the hydration energy, which provided the extra driving force to enlarge the surface tension of the ionic solution compare to the water. These results commendably explained the phenomenon that the greater the hydration energy of the ions, the greater the surface tension of these ionic solution.

1. Introduction

It's well known that the surface tension is important in the analysis of distillation in salt solution [1], absorption refrigeration, desalination [2], and especially in flotation [3–5] which is a common way in mineral processing. It is significant to study the theoretical research of the surface tension of electrolyte solutions. However, due to the long-range interaction and solvent effect, it is much more difficult to study electrolyte

* Corresponding authors at: School of Resources and Environmental Engineering, Wuhan University of Technology, Luoshi Road 122, Wuhan, Hubei, 430070, China.
E-mail addresses: zyl286@whut.edu.cn, yunliang286@163.com (Y. Zhao), ssx851215@whut.edu.cn (S. Song).

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solution than non-electrolyte solution. Many researchers focused on studying the electrolyte solutions in microscopic structure. The hydration theory is one of the theories that reveal the entity of the electrolyte solution. The first hydration model was put forward by Stokes and Robinson [6,7]. Nesbitt [8] found that the parameter of hydration number might be related to the ionic radius. Moreover, experimental studies showed that the ionic hydration is one of the basic characters of electrolyte solution.

The surface tension of an electrolyte solution is larger [9,10] in comparision with pure water. To explain this phenomenon, amounts of researchers have done many works. Onuki et al. [11] took into account the solvation and image interactions between ions and solvent. And the result showed that the resultant surface tension change Δg is proportional to the square root of ion density in the dilute limit [12]. Manciu et al. [13] got the conclusion that the surface tension increasesd when simple salts (NaCl, KCl) were added, which might due to that cations cannot approach the interface, the asymmetry of the ion distributions generates a potential, which repels the anions from the interface, and the total adsorption becomes negative. Many researchers [14,15] derived a simple analytic formulation for calculating the surface tension of general electrolyte solutions, which could account the reason that the surface tension increases with increased electrolyte concentration. Therefore, surface tension is related to ion concentration. However, the mechanisms that different changing laws of surface tension were seldom investigated.

The interactions between the ions and water molecules could cause an increase in surface tension to varying degrees, which might be affected by the ionic radius and charge. It is difficult to analyze atoms and the relationship between the structures of molecules and the properties of the bulk system in micro aspect by traditional methods. Molecular dynamics simulations (MDs) can generate the atomic trajectories of a particle system by numerical integration of Newton's equation of motion and provide a molecular level picture of structure. It can export the average microscopic characteristics on a few nanoseconds time scale. This method also allows the direct prediction of the static and dynamic properties of molecules from the interactions between the molecules [16]. Thus, the movement of electrolyte solution molecules can be observed and the atomic insights into the hydration shell can be provided. Besides, MDs also provides an atomistic picture on how solute solvent interactions significantly affect the initial association between solute molecules and determine the polymorphic outcome of the crystallization [17].

In the work, MDs was applied to study several kinds of salt solution in order to get their micro behavior. Radial distribution function and the hydration number were aimed at investigating the microstructure of the arrangement of ions and water molecules. Hydration energy was used to compare the effect of different hydrated ions on surrounding water molecules. By calculating and comparing their hydration numbers and hydration energy, reasonable explanation could be provided for the increased surface tension at micro level. Then the conclusion can provide a theoretical basis for the mineral flotation.

2. Experimental

2.1. Materials

The sodium chloride, potassium chloride, calcium chloride and magnesium chloride of analytical pure grade used in this work were all obtained from Sinopharm Chemical Reagent Co., Ltd, China. The surface tension was measured by the Force Tensionmeter (Kruss K100, Germany) using the Wilhelmy plate method. Ultrapure Milli-Q water used in this work is with electrical resistivity of 18.2 MΩ·cm and the total organic carbon (TOC) contents of 3 ppb, which minimized the effects of impurities on the measurement of surface tension.

2.2. Method

The electrolyte concentrations were 0 mol/L, 0.1 mol/L, 0.2 mol/L, 0.3 mol/L, 0.4 mol/L, 0.5 mol/L. All the experiments in this work were repeated three times and the arithmetic mean value of the results was taken as the final surface tension. The radial distribution function of each ion was integrated through the MATLAB software, and then, the hydration number of each ion was obtained.

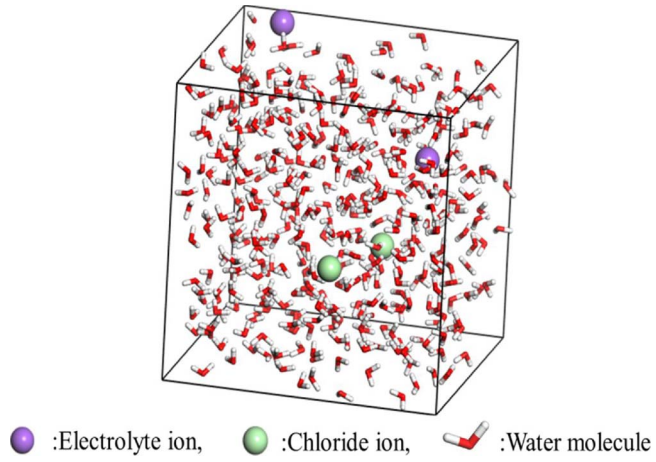

Fig. 1. The electrolyte solution model.

2.3. Molecular dynamics simulations (MDs)

All the simulation works including building models and running MDs were carried out by Materials Studio 8.0. To begin with, the simulation model was built. The model was comprised of 400 water molecules, electrolyte ions and chloride ions which were added to make the charge balanced. The types of water molecular models were the SPC model. The water solution was composed of NaCl, KCl, $MgCl_2$ or $CaCl_2$. The 400 water molecules were initially filled in the amorphous cell with a density of 1 g/cm^3. Fig. 1. shows the electrolyte solutions model.

Forcefield is vital in the molecular simulation, which is a rather important factor because the forcefield describes the interactions between atoms, which decides the microstructure, physical and chemical properties of the system. The COMPASS forcefield is always used to describe interatomic potentials for the ions and water components. It stands for Condensed-phase Optimizes Molecular Potentials for Atomistic Simulation Studies. It's a powerful forcefield that supports atomistic simulations of condensed phase materials [18].

After the model of water and salt molecules system were built, the solution system was firstly optimized. Then MDs were run to simulate the trajectories of the solution. The MDs was run under NVT ensemble (the particle number (N), volume (V), and temperature (T) were constant, thus the total momentum were also constant) conditions for 500 ps to make the solution system get equilibrated. During this simulation, the original velocities of the molecules were assigned according to the Boltzmann distribution; the time step was set to 0.001 ps and they were saved for every 500 steps. The temperature was controlled at 298 K according to the Nosé-Hoover scheme. The Atom-based method was used in Van der waals forces and Eward method in electrostatic interaction. At the end of such simulations, the trajectories of all molecules were recorded; it was possible to calculate the Radial Distribution Function (RDF) and the hydration energy of cation according to this trajectories. Moreover, a further analysis to the calculation results allowed for a better understanding on surface tension.

3. Results and discussion

3.1. Surface tension

Surface tension is pulling force interaction between the two adjacent parts of the liquid surface perpendicular to their unit length. Fig. 2 presented the surface tension for sodium chloride solution,

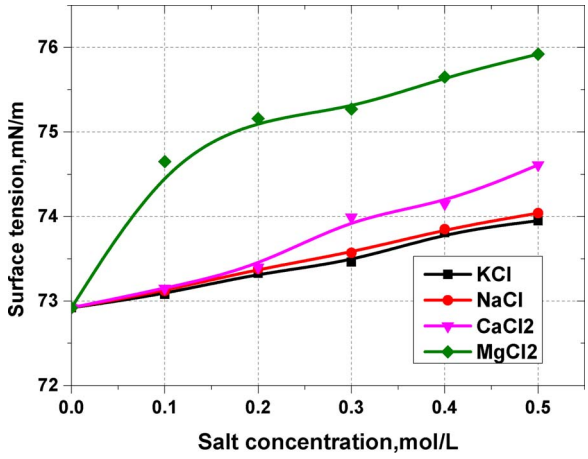

Fig. 2. Surface tension of electrolyte solution (NaCl, KCl, $CaCl_2$, $MgCl_2$) with concentration of 0 mol/L, 0.1 mol/L, 0.2 mol/L, 0.3 mol/L, 0.4 mol/L, 0.5 mol/L, respectively.

potassium chloride solution, calcium chloride solution and magnesium chloride solution at a series of concentration. It was visualized that the value of surface tension increased as the concentration increased. Under the same concentration, the surface tension of the different aqueous solutions was in the descending order of magnesium chloride solution, calcium chloride solution, sodium chloride solution and potassium chloride solution. The results are consistent with previous study [19], in which Philippe Leroy provided the analysis in terms of the energy of ionic bond and found that the smaller the ionic radius would lead to the greater the energy of the ion bond and the stronger the surface tension.

3.2. Radial distribution function (RDF)

The calculation formula of RDF is [20]:

$$\rho g(r) 4\pi r^3 = dN \tag{1}$$

Where ρ is the density of system. When the number of molecules in the system is N, we can get this:

$$\int_0^{\infty} \rho g(r) 4\pi r^3 = \int_0^N dN = N \tag{2}$$

RDF can be understood as the ratio of area density and the average density of the system. And the density around the target electrolyte molecule is different from the average density of system, while it's the same in place away from it. Hence, the RDF is close to 1 when *r* increases. Using the RDF, the hydration of molecules in the solutions can be studied.

As Fig. 3(a–d) shows, the RDF of different electrolyte ions in water is given respectively. Compared with other simulation results [20], there

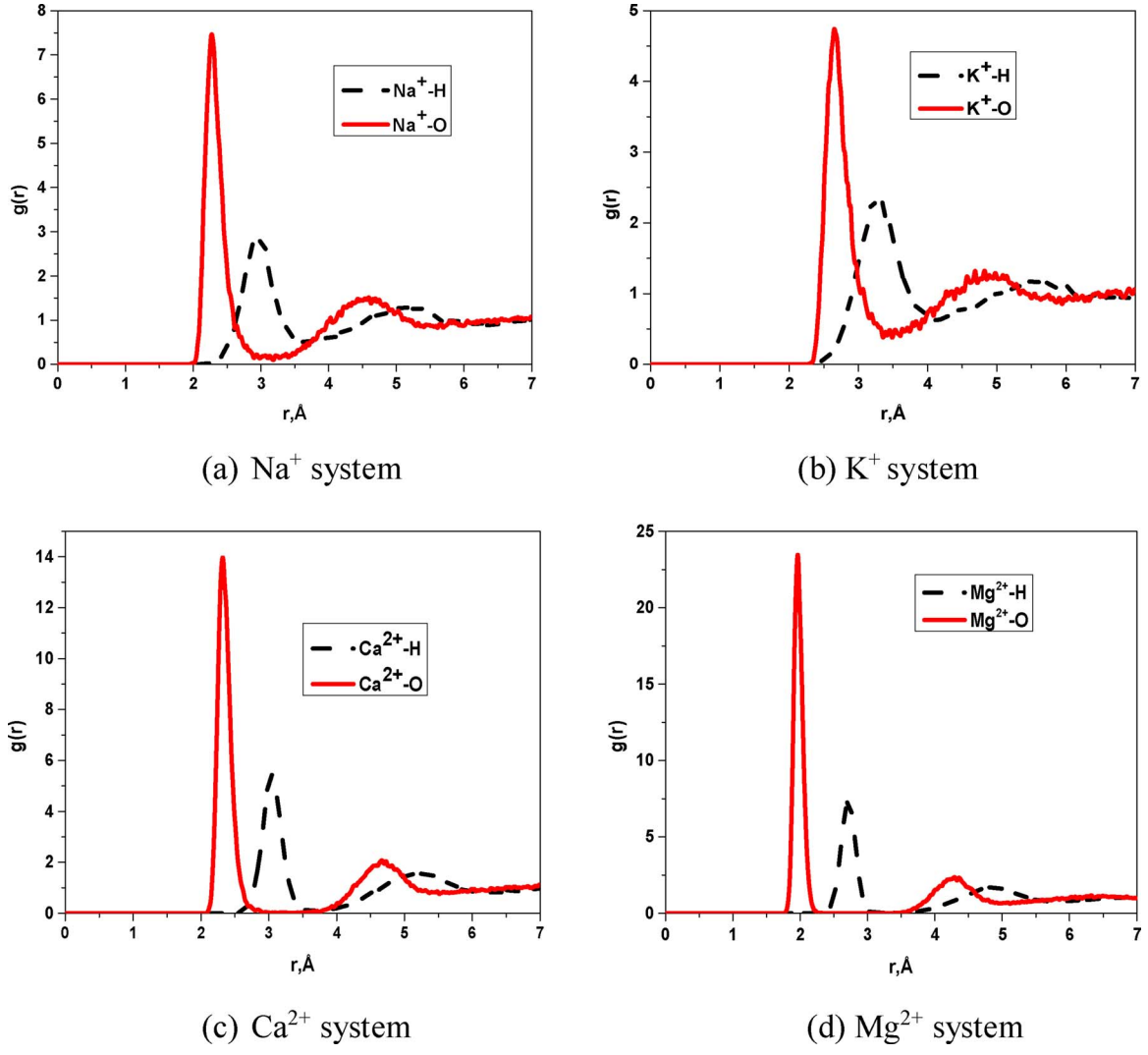

Fig. 3. Radial distribution function of electrolyte ions systems at 298 K.

is mild difference in the peak position and height, which is caused by different potential models. For the four ions systems, the existed two peaks in RDF mean that there are two hydration layers around ions. In all solution system, no matter on the first peak position or the second peak position of RDF, the distance between oxygen atom and electrolyte ion is greater than the distance between hydrogen atom and electrolyte ion. This phenomenon indicates that water molecules are around the cations, it is the oxygen atom rather than hydrogen atoms that is close to the cation. Thus, the water molecules around electrolyte ions in micro aspect were shown in Fig. 4. In Fig. 4, r_1 is the distance between the electrolyte ion and the first hydration layer, which corresponds to the abscissa value of the first peak in the RDF. Also, r_2 is the distance between the electrolyte ion and the second hydration layer, which corresponds to the abscissa value of the second peak in the RDF.

3.3. Hydration number

The calculation formula of hydration number is:

$$n_{ij}(r) = 4\pi h\rho_j \int_0^r r^2 g_{ij}(r)dr \tag{3}$$

Where $g_{ij}(r)$ means RDF, and ρ_j means the number density, h means the hydration factor of ions, the hydration factors of sodium, potassium, calcium and magnesium ions are 0.69, 0.40, 1.00 and 1.00, respectively [20]. The hydration factor was added to calculate the hydration number in the first hydration layer. The corresponding hydration numbers were obtained through the MATLAB software, which are presented in Table 1. The results showed that the hydration number of electrolyte ions was in descending order of Mg^{2+}, Ca^{2+}, Na^+ and K^+.

3.4. Hydration energy

In order to compare the effect of different ions on attracting the surrounding water molecules by hydration, the hydration energy between the liquid droplet and the corresponding ions is analyzed by following formula:

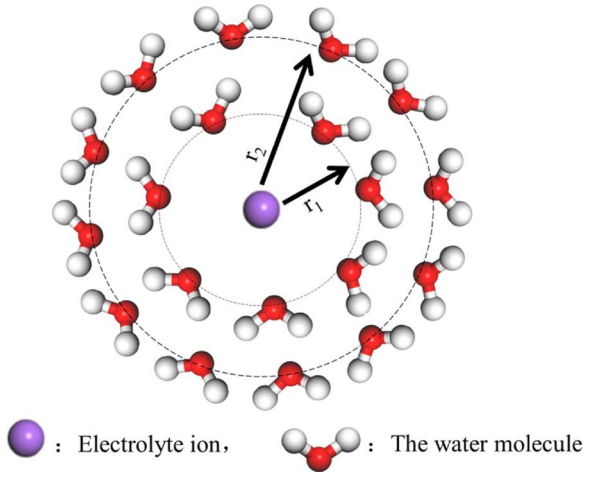

Fig. 4. Model of the water molecules around electrolyte ions in micro aspect.

Table 1
Hydration number of the electrolyte ions.

Electrolyte ions	Na^+	K^+	Ca^{2+}	Mg^{2+}
Hydration number of the first hydration layer	3.8469	2.9352	7.4377	8.6937
Hydration number of the second hydration layer	23.4057	22.3895	26.6903	28.2549

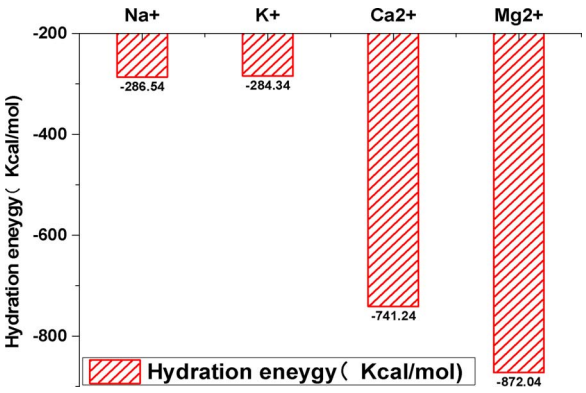

Fig. 5. Hydration energy of the electrolyte ions.

$$E_{Interaction} = \frac{1}{m}\left[E_{MCl:nH_2O} - \left(E_{nH_2O} + E_{mMCl}\right)\right] \tag{4}$$

where $E_{MCl.nH2O}$ means the total energy of MCl and water in form of adsorption configuration for liquid droplets; and E_{mMCl} is the energy of MCl in system; E_{nH2O} means the energy of water in system; and n, m are the number of water molecules and MCl; E_{H2O} is the energy of a single water molecule in a vacuum. M is the electrolyte ion. The calculation results are shown in Fig. 5. The hydration energy distribution of the ions in descending order is Mg^{2+}, Ca^{2+}, Na^+ and K^+, respectively. The relation is in line with hydration number. The results showed that the hydration numbers and hydration energy of the cations were in the descending order of Mg^{2+}, Ca^{2+}, Na^+ and K^+. For cations with similar radius, the cation with greater valence would have stronger hydration ability. When cations are in the same valence, cation with smaller radius would have stronger hydration ability.

In the electrolyte solution, the salt exists in the water solution in the form of ions [21]. These hydrated cations attract water molecules and tend to drag them into internal part of solution, resulting in more water molecules aggregating around cations to form a sphere in micro aspect just like Fig. 6. Thus, in macro aspect, the solution is made of myriad structures in micro aspect displayed in Fig. 6. It has been known that the neutralization of internal interaction existed among ions, when the hydration ability gets bigger, more water molecules will be dragged into internal part of solution, which might be the reason for the increased surface tension. Meanwhile, the surface work produced by the increase of unit surface tension must include the consumption work of overcoming electrostatic gravity. The increased hydration ability leads to more adsorption of molecules in liquid surface caused by the cations hydration. Then the molecules on the surface squeeze into the inside liquid, which make the solution surface reduced as far as possible, resulting in the increase of surface tension. All in all, the above findings

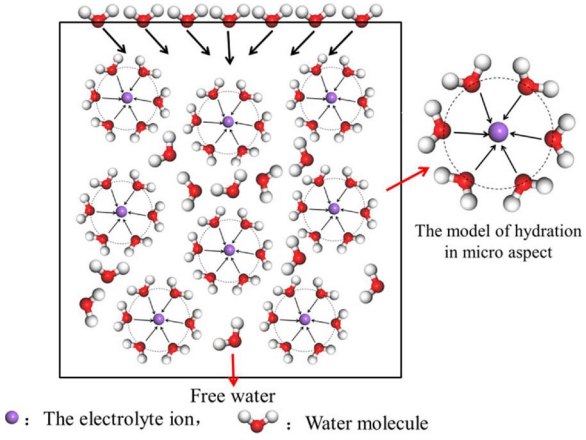

Fig. 6. The model of hydration in macro aspect.

would provide a theoretical basis for the mineral flotation, especially for the flotation using saline water.

4. Conclusions

The surface tension of the four different cations was in the descending order of Mg^{2+}, Ca^{2+}, Na^{+} and K^{+}, respectively. Clear configuration of ions in micro aspect in aqueous solutions was that water molecules surround cations with oxygen atoms approaching them. It was found that the water-ion system presented in the shape of ionic hydration shells. Besides, the hydration strength of the cations were in the descending order of Mg^{2+}, Ca^{2+}, Na^{+} and K^{+}, respectively. These are serviceable information for further establishment of molecular thermodynamic models for electrolyte solutions. The hydration energy leads to molecules in liquid surface more absorbed by the cations, squeeze the liquid inside, which makes the solution surface reduce as far as possible, providing the extra driving force to magnify the surface tension the ionic solution in contrast with the aqueous solution. These consequences well accounted for phenomenon that the greater the hydration energy of the ions, the greater the surface tension of these ionic solution.

Acknowledgements

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