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# Atomic insights into flotation separation of KCl and NaCl from a new viewpoint of hydration layer: A molecular dynamic study

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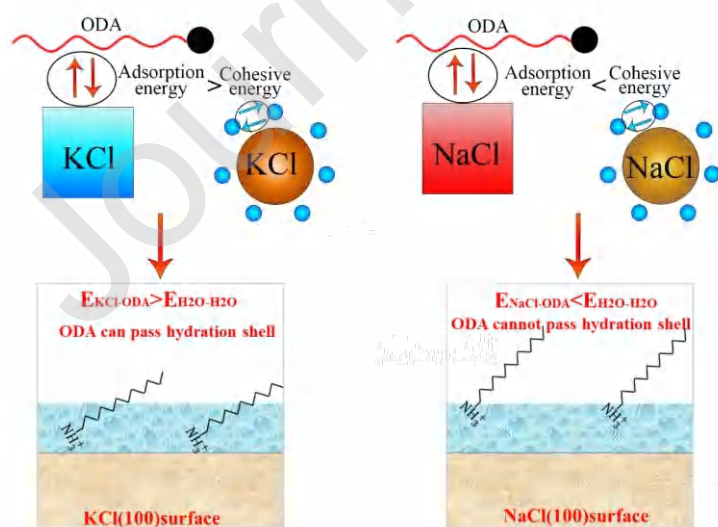
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## Graphical abstract



**Abstract:** The flotation separation of sylvite (KCl) and halite (NaCl) had drawn much attention, but the mechanism is still controversial. In this work, the atomic insights into the flotation separation of KCl and NaCl was conducted using molecular dynamics simulation (MDs). A novel concept that the hydration layer on minerals surface has been introduced. The molecular dynamic calculation shows that the adsorption energy between the octadecylamine (ODA, the most common collector for KCl flotation) and NaCl is smaller than the cohesive energy in the hydration layers on NaCl surface. However, the adsorption energy of ODA/KCl is much larger than the cohesive energy of the hydration layers on KCl surface. Hence, the collector ODA can pass through the hydration layers and then be adsorbed onto the KCl surface, but that cannot do occur on the NaCl surface, which perfectly explains the mechanism of the separation of KCl and NaCl by ODA. Notably, the new viewpoint of hydration layer may open up a new path to explain the behavior of flotation separation. The flotation experiment results also show the KCl is easily floated while the NaCl hardly floated by ODA, which agrees well with the calculation results.

**Keywords:** Flotation separation; KCl; NaCl; Molecular dynamic simulations; Hydration layers; Cohesive energy

## 1. Introduction

Currently, the population of world is 7.6 billion, which is expected to reach 8.6 billion in 2030[1]. With population explosively increasing, the requirement of crops tends to sharply accelerating. Potassium fertilizer is an efficient manure for enhancing and improving the output of crops to meet the huge food demands. Potassium fertilizer was normally produced by sylvite (KCl) which principally comes from potash ores containing KCl and halite (NaCl). Now, over 80% of the world's KCl is produced by flotation which is the most popular and efficient way to separate KCl and NaCl[2]. Hence, the research about flotation of KCl from saturated brines has been attracted many interests[3–6]. It has been found that octadecylamine (ODA) can successfully realize the flotation separation of KCl and NaCl[7]. Despite the successful application of flotation technology in the potash industry, the flotation mechanism of separating KCl and NaCl by ODA is still the subject of much debate due to complex solution environment and high ions concentration in the soluble salt flotation system[8,9]. The mechanism studies on selective separation of KCl and NaCl by flotation aiming at a better cognition of the flotation process are still on the way in past few decades, which is expected to provide a theoretical guidance for practical production and exploiting novel collectors.

In previous reports, several theories have been put forward to explain the separation mechanism of KCl and NaCl. Fuerstenau[10–12] has proposed that the collector was adsorbed onto the KCl surface through the way of ion exchange because the size of  $K^+$  and amine ion are similar. However, some phenomenon that sulfoacid

group with the size larger than that of  $\text{Cl}^-$  can also be adsorbed onto the KCl surface, which cannot be explained by the ion exchange theory. Besides, the amine collector was supposed to be adsorbed onto the KCl surface through electrostatic interaction on account of the opposite surface charge of KCl and collector. However, it is found that KCl with negative surface charge can also be collected by the anionic collector sodium dodecyl sulfate [13–16]. Recently, interfacial water structure theory has been developed and widely studied[17–19]. Some ions are considered to facilitate the hydrogen bonds between the water molecules on the salt surface (water structure maker) while others are expected to disrupt the hydrogen bond (water structure breaker)[20]. As a result, the water structure maker salts (such as NaCl) can be fully wetted and showed a completely hydrophilic surface while the water structure breaker salts (like KCl) showed the opposite behaviors, and the different surface wettability leads to the successful separation of KCl and NaCl. However, many researches have shown that  $\text{K}^+$  and  $\text{Na}^+$  have very strong hydration strength, both of which have the ability to influence the arrangement of water molecules around them[21–23]. Besides, many previous studies have shown that there is little difference in surface wettability between KCl and NaCl[20,24]. Therefore, it is believed that the interfacial water structure theory is still not perfect yet.

It is still a challenge to reveal the separation mechanism between KCl and NaCl. According to previous study, the formation of hydration layers on the surface of various kinds of minerals is widely accepted, which has huge adverse effect on the flotation of minerals[15,25,26]. In addition, the electrolyte ions in the flotation pulp

also influence the hydration layers. It was found that electrolyte ions would promote the hydration of minerals and formation of stronger hydration layers on the minerals surface[22,23,27–29]. In this study, the different interactions among the collectors, hydration layers and KCl/NaCl surface are believed to be closely related to the different flotation behaviors between KCl and NaCl. The  $\text{Na}^+$  and  $\text{K}^+$  in the flotation solution are expected to promote the strength of hydration layers on the KCl/NaCl surface, and the KCl can be floated only on condition that collectors can pass through the hydration layers and interact with KCl surface. In order to explain the flotation mechanism, a novel atomic insight into the flotation separation of the KCl and NaCl using molecular dynamic simulations (MDs) has been proposed in this work.

The interactions between water molecules in the hydration layer, also called cohesive energy[30], have been calculated to investigate the strength of hydration layers. Besides, the adsorption energy between collectors and soluble salt surface has also been calculated for the purpose of investigating the interaction between collectors and KCl/NaCl surface. By comparing the cohesive energy among water molecules in hydration layers and adsorption energy between ODA and KCl/NaCl, it is easy to find out that whether the ODA can pass through the hydration layers on the KCl/NaCl surface. Only the surface interacted with ODA that passed through the hydration layers can be collected by flotation, which finally determines the flotation behaviors of KCl and NaCl. The objective of this study is to correlate the adsorption energy of salt surface/ODA and the cohesive energy of water molecules among the hydration layers, thus to obtain an atomic understanding of the separation mechanism of KCl

and NaCl.

## **2. Experimental materials and methods**

### **2.1. Materials**

Potassium chloride (KCl), sodium chloride (NaCl), terpenic oil and octadecylamine (ODA) with analytical grade were obtained from the Sinopharm Chemical Reagent Co. Ltd., China.

### **2.2. Flotation tests**

The micro-flotation tests were carried out by floatation machine (XFGII, China) with a volume of 100 mL and an impeller speed of 1900 rpm at 25~27 °C at natural pH. The flotation tests were performed in saturated KCl/NaCl solution with or without 85g/t ODA. Each time, 90 g saturated brine solution and 35 g minerals sample were added into the cell with a conditioning time of 2 min. Collectors (ODA) and frothers (terpineol) were orderly added to the solution with a stirring for 2 min each one. Thereafter, the flotation was carried out for 3 min. Then, both the concentrates and tailings were collected, dried by vacuum filtration, and recovery was productivity.

### **2.3. Contact angle measurements**

The contact angle measurements were conducted based on Sessile drop method. The sample was frozen dried at -60 °C using freeze dryer (LGJ-10N, China), then it was ground equably and transformed to a mould to be pressed into a hyaline sheet under pressure of 75 Mpa by a hydraulic press (HY-12, China). Subsequently, making the hyaline sheet lie on the plane of machine. Saturated solution dripped on sample



surface using microbubble injector and the contact angle was recorded until the liquid droplet is steady. Finally, each test was repeated three times to get the average value.

#### **2.4 Molecular dynamic simulations**

MDs was performed through the Materials Studio 2017 package. The model of KCl and NaCl was built referred to the American Mineralogist Crystal Structure Database[31,32]. KCl (100) and NaCl (100) surface with  $3\times 3\times 2$  unit cell was cleaved to study the interactions among salt surface, collectors and water molecules in the hydration layers. The type of water molecular models was the SPC model. When study the interaction between KCl/NaCl surface and water molecules, a H<sub>2</sub>O-KCl/NaCl system model consisting of one water molecule and a supercell of KCl/NaCl (100) surface has been built. When research the adsorption energy of ODA and KCl/NaCl, the model contained a ODA molecule and a KCl /NaCl (100) surface has been built. When investigates whether the ODA can pass through the hydration layers, 100 water molecules which were constructed by amorphous cell with a density of 1 g/cm<sup>3</sup> and one ODA molecule were placed on the KCl/NaCl (100) surface. These ODA-hydration layers-KCl/NaCl (100) surface system models were shown in Fig. 1.

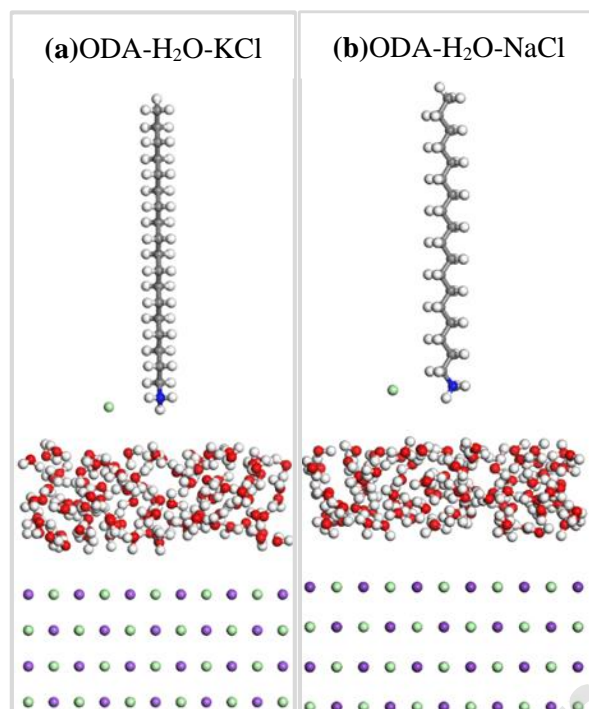


Fig. 1. The model of ODA-H<sub>2</sub>O-KCl (a) and ODA-H<sub>2</sub>O-NaCl (b).

In all the MDs, the Focite module has been used to calculate interaction among soluble salt surface, ODA and water molecules and run the molecular dynamics. Periodic boundary conditions were applied in the x, y, and z directions. Compass force field has been used for describing the interactions between halides, water molecules, ions, and organic reagent molecules in this paper. Cutoff distance of Atom-based summation was 15.5 Å, which is used to describe Van der Waals force and the Ewald summation method was used to calculate the long-range Coulombic interactions. MDs was carried out in NVT ensemble at 298 K. the Nose thermostat method was used to regulate the temperature in MDs. The time to arrive equilibrate was 10 ns with the time step of 1 fs.

The potential energy of KCl/NaCl, water molecules, ODA is carried out to analyze the interaction between the surface of salt crystal. The potential energy is calculated when the equilibrium trajectories of absorption between reagent and

minerals surface were got. The adsorption energy between ODA and KCl/NaCl, H<sub>2</sub>O and KCl/NaCl, and cohesive energy is calculated by follow equation:

$$\Delta E_{Ads-H_2O} = E_{Sur-H_2O} - E_{Sur} - E_{H_2O} \quad (1)$$

$$\Delta E_{Ads-ODA} = E_{Sur-ODA} - E_{Sur} - E_{ODA} \quad (2)$$

$$E_{coh} = \frac{1}{n} (E_{nH_2O} - nE_{H_2O}) \quad (3)$$

where the  $\Delta E_{Ads-H_2O}$   $\Delta E_{Ads-ODA}$  were the adsorption energy between KCl/NaCl and a water molecule, KCl/NaCl and an ODA molecule, respectively.  $E_{Sur-ODA}$ ,  $E_{Sur-H_2O}$  mean the total energy of KCl/NaCl surface and water molecule/ODA.  $E_{Sur}$ ,  $E_{H_2O}$  and  $E_{ODA}$  represent the energy of KCl/NaCl, H<sub>2</sub>O, ODA[29,33].  $E_{coh}$  is the cohesive energy of the hydration shell on the surface of KCl/NaCl. where the  $E_{nH_2O}$  is the energy of water molecules on KCl/NaCl surface, and  $E_{H_2O}$  is the energy of a water molecule. The  $n$  is the number of water molecules[30].

### 3. Results and discussion

#### 3.1. Assessment of surface wettability and floatability

Wettability is a crucial factor affecting the floatability of minerals[34]. In order to verify the wettability of minerals surface, the contact angle measurements for the surface of KCl and NaCl at saturated brines were carried out. As shown in Fig. 2, the contact angle of KCl and NaCl was 28° and 23°, respectively, indicating that little differences for the surface wettability of KCl and NaCl have been observed. The result is different with the previous interfacial water structure theory that NaCl can be fully wetted while KCl showed a relatively hydrophobic surface[8]. Some new

insights into the flotation separation mechanism need to be studied.

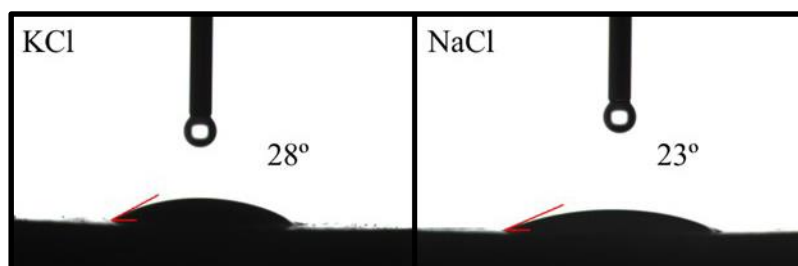


Fig. 2. Contact angle of KCl and NaCl.

Notably, the surface wettability usually is influenced by contamination and roughness[35]. MDs as a novel method was performed to investigate the interactions between KCl/NaCl surface and water molecule[36]. As can be seen from Fig. 3, The adsorption energy of KCl/H<sub>2</sub>O and NaCl/H<sub>2</sub>O were -8.11 kcal/mol and -7.53 kcal/mol, respectively. Since the interaction between surface and water molecules can be used to qualitatively analyze the surface wettability, the very little differences of the adsorption energy between salt surface and water molecules demonstrate that the KCl and NaCl surface has almost the same affinity for water molecules. Therefore, similar surface wettability of NaCl and KCl surface has been proved by the MDs, in agreement with the experimental results.

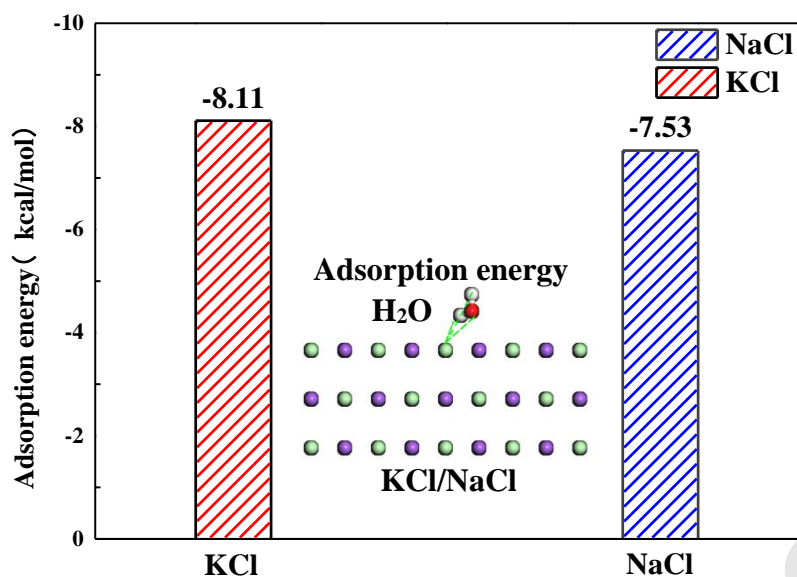


Fig. 3. Adsorption configurations of H<sub>2</sub>O on KCl/NaCl and adsorption energy between one water molecule and KC/NaCl.

Flotation is an approach to separate valuable minerals according to the different surface property of minerals. In order to explore the flotation mechanism, the single minerals flotation tests of KCl and NaCl with and without addition of ODA were conducted. As shown in Fig. 4, the recovery of KCl and NaCl without the addition of ODA was 2.1% and 0.5%, respectively, which is consistent with the contact angle measurements that both KCl and NaCl were hydrophilic. In order to analyze the flotation process, the surfactant-ODA which has excellent flotation effect for KCl according to previous report was chosen to be used as collectors. Fig.4 shows that the recovery of KCl is 97.1 % and NaCl is 0.7 %, respectively. This result suggested that ODA has strongly collecting ability for KCl and brilliant selectivity against NaCl. However, previous theories cannot explain the flotation mechanism of separation KCl and NaCl by ODA perfectly. Subsequently, MDs was carried out to calculate the interaction among water molecule, ODA, KCl/NaCl to explore the flotation

mechanism.

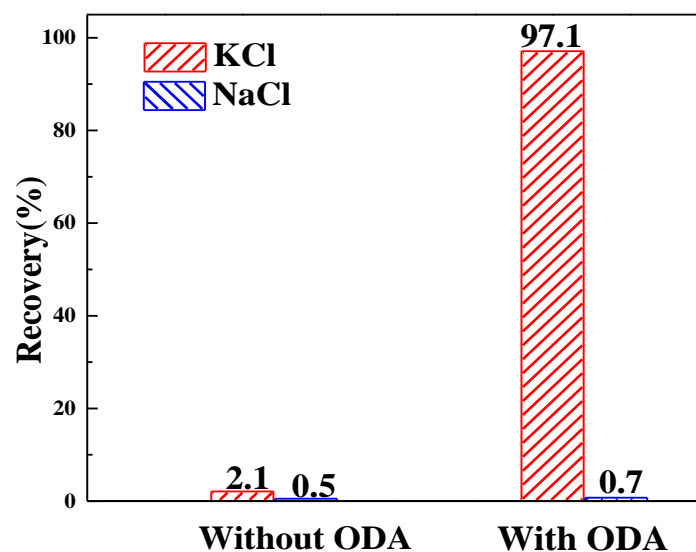


Fig. 4. Flotation experiments of KCl/NaCl with and without ODA.

### 3.2 Cohesive energy of water molecules in hydration layers

It is well known that hydration layer played a vital role in flotation process. And in the previous interfacial water structure theory, some ions are considered to facilitate the hydrogen bonds between the water molecules on the salt surface while others are expected to disrupt the hydrogen bond. If so, the strength of hydration layers on KCl surface are much stronger than that on NaCl surface. In the present study, cohesive energy, which stands for interaction among water molecules in hydration layers, has been calculated to determine the affinity between adjacent water molecules on the hydration shell. As shown in Fig. 5, the cohesive energy on the hydration layer of KCl and NaCl surface were  $-9.50$  kcal/mol and  $-8.79$  kcal/mol, respectively, and more negative adsorption energy means more strong affinity. Different from previous reports that KCl can serve as water breaking disrupting the hydrogen bond between

water molecules and NaCl was classified as water making to facilitating the hydrogen bond between water molecules[26], this calculation show that the relative strength of hydration layer on the KCl is slightly stronger than that of NaCl. Hence, it suggested that the interfacial water theory still cannot explain the relative strength of hydration on KCl and NaCl surface. However, in flotation tests, KCl shown excellent floatability with addition of ODA. Hence, it can be inferred that the adsorption of ODA on KCl surface played a vital role in flotation process. In order to investigate the flotation mechanism of separation KCl and NaCl, the interaction between ODA and KCl/NaCl was calculated next.

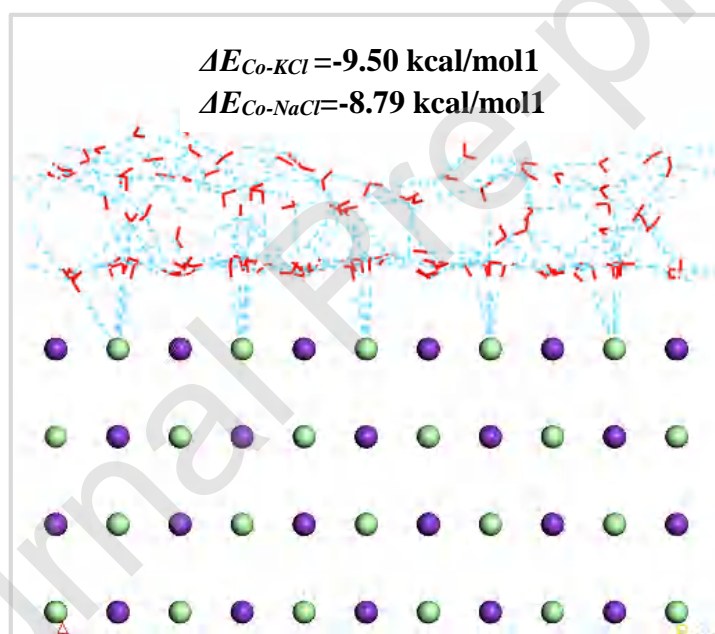


Fig. 5. Cohesive energy of water molecules in the hydration layers on KCl/NaCl surface.

### 3.3 Adsorption energy of ODA on the KCl/NaCl (100) surface

In general, collectors are surfactants which can modify the surface property of

minerals to realize the aim of flotation separation. Adsorption as a universal phenomenon is frequently used to describe the interaction between reagents and minerals in flotation[37–40]. To further study the flotation mechanism between KCl/NaCl and ODA, the MDs is used to simulate the adsorption configurations of ODA on KCl/NaCl surface in Fig.6. The adsorption energy of ODA on KCl and NaCl surface are -20.26 kcal/mol and -8.47 kcal/mol, respectively. It can be inferred that the adsorption between KCl/NaCl and ODA was physical adsorption because of the small adsorption energy. The calculation revealed that the adsorption energy of ODA on KCl (100) surface was higher than that on NaCl (100) surface, indicating that ODA tends to be adsorbed on KCl surface.

However, flotation is normally performed in the ore pulp, thus it is essential to introduce the hydration layers. In Fig.5, the cohesive energy was calculated to characterize the strength of hydration layers. Combine with Fig. 5 and Fig. 6, it is obvious that the adsorption energy of ODA on KCl surface (-20.26 kcal/mol) was larger than the cohesive energy of hydration layer on KCl surface (-9.50 kcal/mol), suggesting that the ODA has the potential to pass through the hydration layer on KCl surface. As for the NaCl, it has a weak adsorption energy of ODA (-8.47 kcal/mol) which is smaller than the cohesive energy of hydration layer on NaCl surface (-8.79 kcal/mol). This result indicated that ODA has a strong tendency to pass the hydration shell on KCl surface instead of NaCl surface. It can be inferred that ODA tends to be adsorbed on the KCl surface rather than NaCl surface, leading to the flotation separation of KCl and NaCl. As a result, it is the huge difference of adsorption energy



instead of similar relative strength of hydration, resulting in the efficient separation of KCl and NaCl with ODA as collectors. In a conclusion, only when collectors pass the hydration shell can minerals be floated.

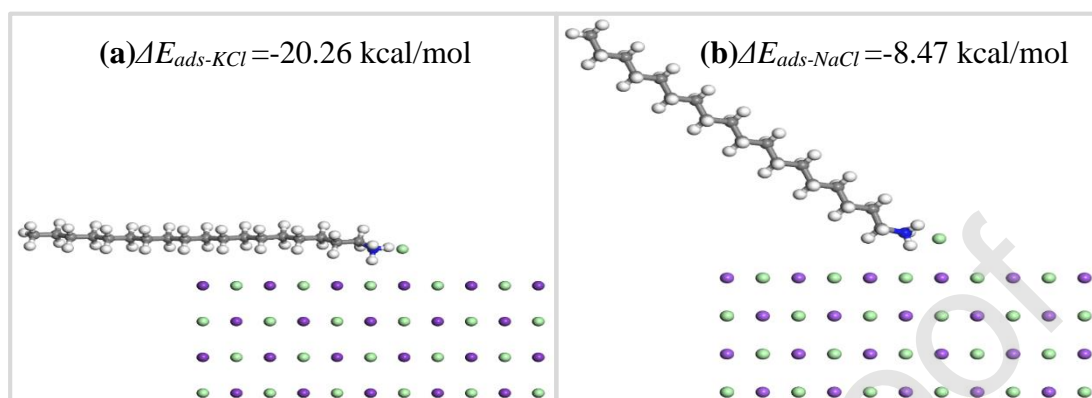


Fig. 6. Adsorption configurations of ODA on KCl surface (a) and NaCl surface(b).

### 3.4 Flotation separation mechanism of KCl and NaCl

According to preceding calculation of adsorption between ODA and KCl/NaCl, cohesive energy of hydration layer on KCl and NaCl surface, it appeared that ODA can permeate hydration shell of KCl, but cannot do that to NaCl. Fig. 7 showed the final equilibrium configurations of ODA-hydration layers-KCl/NaCl surface models. It is obvious that DOA was blocked by hydration shell and cannot pass through the hydration shell on NaCl surface. However, the head group of ODA has permeated the hydration shell on the KCl surface and passed the hydration layers, even almost touched the KCl surface, which indicated that ODA can pass the hydration shell successfully and be adsorbed on the KCl surface. The calculation result demonstrated that ODA can pass the hydration shell on KCl surface but not the NaCl surface, leading to successful flotation separation of KCl and NaCl.

Base on the above calculation, the flotation mechanism of separating KCl and NaCl was shown schematically in Fig. 8. The adsorption energy of ODA/KCl is larger than that of the cohesive energy among the water molecules in the hydration layers, indicating that the collector ODA can pass through the hydration layers and then be adsorbed onto the KCl surface but not the NaCl surface, which is the flotation mechanism of separation of KCl and NaCl.

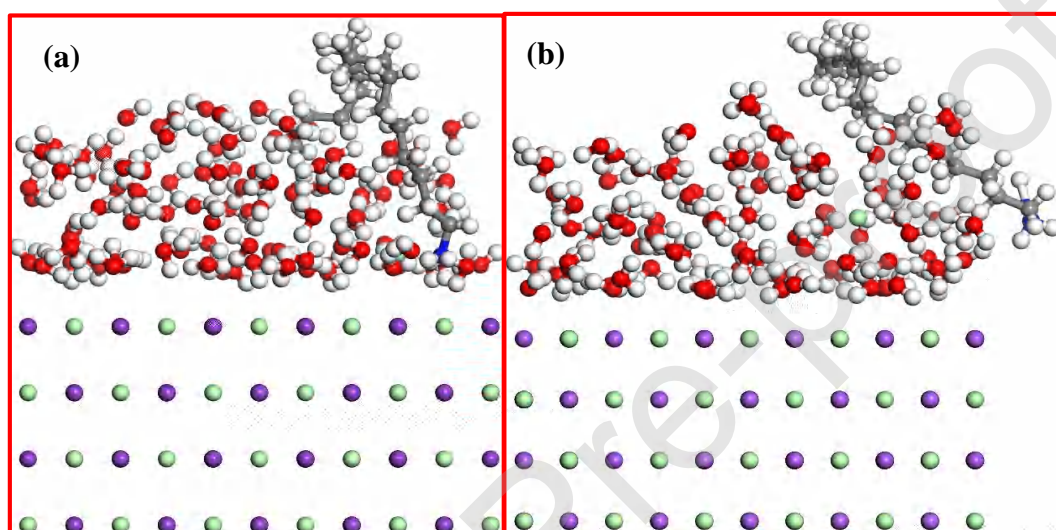


Fig. 7. Equilibrium trajectories of configuration after molecular kinetics in KCl-H<sub>2</sub>O-ODA system (a), NaCl-H<sub>2</sub>O-ODA system (b).

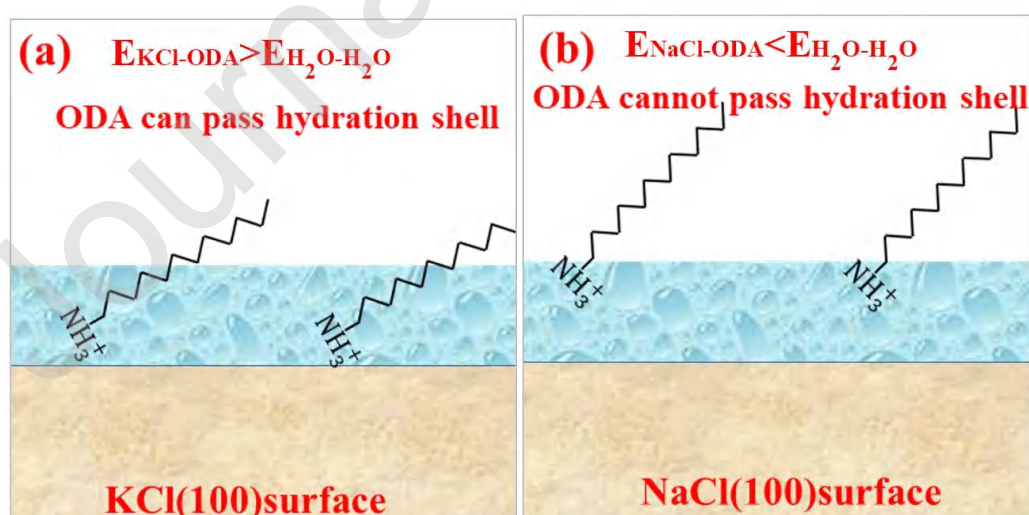


Fig. 8. Schematic diagram of flotation separation of KCl and NaCl.

#### 4. Conclusions

The adsorption energy of ODA/NaCl is smaller than that of the cohesive energy among the water molecules in the hydration layers on NaCl surface. On the contrary, the adsorption energy of ODA/KCl is larger than that of the cohesive energy among the water molecules in the hydration layers on KCl surface. As a result, the collector ODA can pass through the hydration layers and then be adsorbed onto the KCl surface, but cannot do that to the NaCl surface, which determined that only collection of KCl from the potash ores with the addition of ODA as well as the final successful flotation separation of KCl and NaCl. This new atomic insight has provided better understanding of the flotation separation mechanism of KCl and NaCl.

#### Author Contribution Statement

**Zhong Ai:** Writing-Original draft preparation, Conceptualization, Methodology.

**Shoujiang Li:** Visualization, Investigation.

**Yunliang Zhao:** Writing- Reviewing and Editing.

**Hao Yi:** Data curation.

**Peng Chen:** Software.

**Licai Chen:** Investigation.

**Guihua Nie:** Validation.

**Shaoxian Song:** Conceptualization, Supervision.

### Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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