Flotation and molecular dynamics simulation of muscovite with mixed anionic/cationic collectors

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Abstract: In this study, three kinds of anionic collectors (sodium oleate (NaOl), sodium dodecyl sulfonate (SDS) and naphthenic acid (NA)) were used in combination with dodecylamine (DDA) to investigate the flotation behavior of muscovite under the action of different mixed anionic/cationic collectors, and their mechanisms for adsorption on the muscovite (001) surface were clarified using molecular dynamics simulations. The flotation results indicated that different mixed anionic/cationic collectors could improve the recovery of muscovite to varying degrees, but the optimum molar ratio of anionic collectors to DDA and the optimum mixed collector dosage were different. Molecular dynamics simulations showed that the mixed anionic/cationic collectors could significantly increase the hydrophobicity of the muscovite, as evidenced by the decrease in the calculated water molecule density on the muscovite surface and the diffusion coefficient of water molecules at the solid/liquid interface. The interaction between the amino group and the polar group of anionic collectors reduced the electrostatic repulsion between DDA cations and theoretically increased the adsorption capacity of the mixed anionic/cationic collectors on the muscovite surface. Moreover, DDA/NA and DDA/NaOl could improve the calculated carbon atom density on the muscovite surface, which enhanced the hydrophobic association between nonpolar carbon chains, thus further achieving an enhanced flotation performance.

Keywords: muscovite, mixed anionic/cationic collectors, flotation, molecular dynamics simulation

1. Introduction

Because muscovite has good electrical insulation, transparency, chemical stability and can maintain the above excellent physical and chemical properties at high temperatures (Wang et al., 2015), it has been widely used in electronics, communications, metallurgy, building materials, national defense and other advanced industrial fields (Li, 2011; Wang et al., 2014). However, muscovite is often symbiotic with other silicate minerals and is difficult to separate from mixed minerals by gravity separation, so flotation has gradually become the main means to obtain fine muscovite (Hu and Feng, 2006). Many investigations on muscovite flotation have indicated that the use of cationic surfactants as collectors, including the use of primary amines, quaternary ammonium salts and Gemini cationic compounds (Pugh et al., 1996; Sekulić et al., 2004), yields a good collection performance and is influenced by metal ions slightly. However, the strong acid pulp in the flotation process is likely to cause environmental pollution and strong corrosion of flotation equipment (Bayraktar et al., 1997). Moreover, amines exhibit a high sensitivity and poor selectivity for slimes, which are prone to produce abundant foam in the flotation, resulting in the decrease of the muscovite grade (Al-Thyabat, 2012).

Compared with a single collector, the mixed anionic/cationic collectors show a good performance in the flotation of muscovite due to synergistic effects in solid/liquid systems. Wang et al. (2014) used dodecylamine (DDA) and sodium oleate (NaOl) as mixed surfactants for the flotation separation of

muscovite from quartz. The results revealed that neither muscovite nor quartz is floated with NaOl alone, and while using DDA alone, the minerals can be separated only under strongly acidic conditions (pH < 3). However, mixed NaOl/DDA collectors exhibit an excellent performance in the flotation separation of muscovite from quartz at pH 10. Rao et al. (1990) successfully separated muscovite from original ore containing 15.4% muscovite, 13% biotite, 1.8% pyrite and 69% siliceous gangue (mainly quartz and feldspar) by using a mixture of oleate and amine. In recent years, many studies have been conducted on the adsorption mechanism of mixed anionic/cationic surfactants on muscovite. The results show that mixed anionic/cationic collectors can effectively reduce the surface tension of a solution (Rosen and Gu, 1987), and the critical micelle concentration (CMC) of mixed collectors can be effectively reduced due to the formation of ion-pair associations and the electrostatic attraction between polar groups with different charges (Paria and Khilar, 2004). There are also views that the interaction between hydrophobic chains (Wang et al., 2014) and the reduction in electrostatic repulsion (Vidyadhar et al., 2012) between mixed anionic/cationic collectors make the collector adsorption on mineral surfaces more stable, thus, resulting in better hydrophobic effects. However, most of the above mechanisms were obtained by traditional experiments, and there remains a lack of the microcosmic understanding of the adsorption behavior at the interface.

Molecular dynamics (MD) simulations, as an advanced tool, can be used to explore the microphenomena of solid/liquid interfaces and provide useful information for understanding surface potential, collector adsorption and mineral floatability, which are beyond the reach of traditional experimental methods. Xu et al. (2013) found that amine ions have thermodynamic advantages to sufficiently break through the hydration layer for effective flotation. The length of the carbon chain has little influence on the adsorption energy of amine ions on the muscovite (001) surface, and the hydrogen atoms in polar groups determine the adsorption energy. Wang et al. (2015) studied the adsorption of a mixed DDA/NaOl collector on the muscovite (001) surface by MD simulation. The results showed that under the action of a mixed DDA/NaOl collector, DDA adsorbs on the muscovite surface to form a positive charge center, and NaOl fills in to reduce the electrostatic repulsion force between the polar groups of DDA. Unfortunately, these studies are limited to the synergistic mechanism between DDA and NaOl, and whether they are applicable to DDA with other anionic collectors is still unclear.

In this paper, the adsorption behaviors of DDA and three kinds of anionic collectors (NaOl, sodium dodecyl sulfonate (SDS) and naphthenic acid (NA)) as well as their mixtures at different molar ratios and dosages were investigated by MD simulations. Through the changes in the atom density before and after adsorption, as well as the changes in the adsorption morphology of the collector at the solid/liquid interface, the synergistic mechanisms of different mixed anionic/cationic collectors were investigated at the atomic level. Additionally, by analyzing the arrangement of water molecules at the solid/liquid interface, the hydrophobicity changes of the muscovite surface were studied, and the results provide a useful basis for the selection of anionic collectors in mixed ionic collectors.

2.   Materials and methods

2.1. Materials

The pure muscovite samples used in these experiments were obtained from Lingshou, Hebei Province, China. The samples were crushed, hand-selected, and ground with a wet agitating ball mill. In order to better compare the flotation performance of muscovite under the action of different mixed anionic/cationic collectors, the ground sample was screened for the -45 μm fraction and repeatedly cleaned with distilled water for the flotation experiments.

The cationic collector DDA and anionic collectors NaOl, SDS and NA, with analytical purity, were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China and Macklin Biochemical Co., Ltd., Shanghai, China. HCl and NaOH of analytical purity were from Shenyang Xinxing Reagents Factory, Liaoning, China and used to adjust the pH of the flotation system.

2.2. Flotation experiments

The mineral flotation experiments were conducted in an XFD 0.5 dm³ laboratory flotation machine (XFD, Jilin Exploration Machinery Corp., Changchun, China). The spindle speed, pulp density,

aeration amount, rotor speed and bubble blowing time were kept constant at 1650 rpm, 100 g/L, 0.1 $m^3/(m^2$ min), 24 r/min and 240 s, respectively. The procedure used in the mineral flotation experiments was as follows: (1) Mineral and distilled water were added to the cell and agitated for 30 s to obtain a mineral suspension. (2) The pulp pH was adjusted by adding regulators and agitating for 60 s. (3) The mixed anionic/cationic collectors were sequentially added to the slurry. The cationic collector and anionic collector conditioning periods were 60 s. (4) The floated products were collected. (5) The concentrate products and tailings were dried at 105°C and weighed to calculate the recovery.

2.3. Zeta potential measurement

Zeta potential measurements were conducted at 20°C using a JS94J micro electrophoresis instrument (JS94J, Zhongchen Digital Technic Apparatus Corp., Shanghai, China). A dilute mineral suspension was prepared by adding 0.02 g of mineral sample to 40 mL KCl (0.01 mol/L) solution. Then, the reagents were added in the same order as in the flotation experiment, and the pH was adjusted and measured. The suspension was magnetically stirred for 10 min. After 10 min of settling, the supernatant liquor was obtained for the zeta-potential measurement. In this paper, the zeta-potential of each sample was measured three times, and the average was reported as the final value.

2.4. Computational details

2.4.1. Models

Muscovite is a typical layered silicate that consists of two [SiO$_4$] tetrahedral sheets and one [AlO$_6$] octahedral sheet. A quarter of silicon atoms in the [SiO$_4$] tetrahedron are replaced by Al atoms and interlaminar potassium ions are used to balance the resulting charge loss. The crystal structure of muscovite was derived from the research of Radoslovich (Radoslovich, 1960), and the lattice parameters were optimized by the PCFF-INTERFACE forcefield. This forcefield has been proven to be accurate in the simulations of phyllosilicates and organic molecules (Heinz et al., 2013), which have performed well in computing the structure of hydroxyapatite, kaolinite, montmorillonite and muscovite in previous studies (Heinz and Ramezani-Dakhel, 2016; Lin and Heinz, 2016). Based on the literature, the muscovite (001) surface, which is the perfect cleavage plane of muscovite, was chosen as the cleavage plane for the interaction model construction. The supercell model of the muscovite (001) surface was chosen for the subsequent simulation study.

The reagent solution layer was constructed with 800 water molecules and different numbers of collector molecules (for different flotation systems) with a length and width identical to those of the supercell model of the muscovite (001) surface. The chloride and sodium ions were added to ensure electric neutrality. The muscovite-collector model was obtained by combining the supercell model of the muscovite (001) surface with the reagent solution layer, and a 60 Å vacuum slab was added to prevent periodic effects. The size of all systems was approximately 26.13 Å×26.13 Å×147.89 Å. Considering the computational efficiency, the polar groups of the collectors were directed toward the muscovite (001) surface, and the carbon chains were directed toward the bulk solution, artificially.

Because the flotation experiment was conducted in a neutral solution, the collector molecules DDA, NaOl, SDS and NA mainly existed in an ionic state based on the solution chemistry calculations. The ionic structure of the collectors was established by the visualizer module, and its Mulliken populations were derived from density functional theory calculations (Fig. 1). The numbers of DDA and anionic collectors for the different flotation systems are listed in Table 1.

Table 1. The numbers of mixed anionic/cationic collectors in the simulations for different flotation systems

Species	DDA cation	NaOl anion	SDS anion	NA anion	Sodium ion	Chloride ion
System A	20	0	0	0	0	20
System B	10	10	0	0	10	10
System C	10	0	10	0	10	10
System D	10	0	0	10	10	10
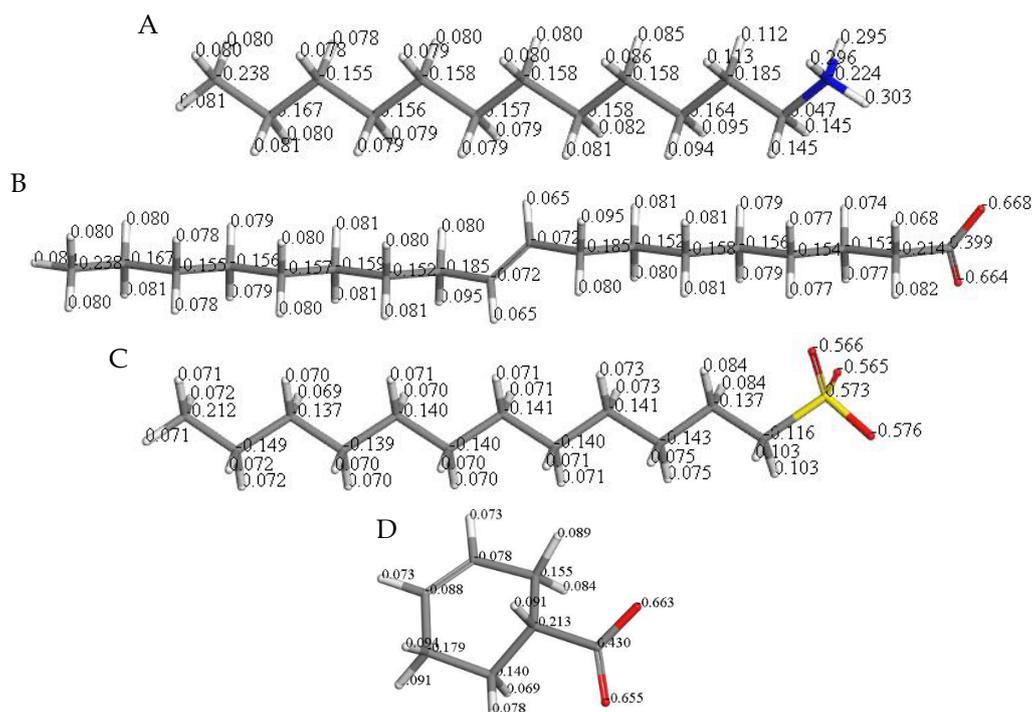
Fig. 1. The Mulliken populations of the optimized collector molecules (A: DDA cation, B: NaOl anion, C: SDS anion and D: NA anion) in an aqueous solution (the white, gray, blue, yellow and red sticks represent hydrogen, carbon, nitrogen, sulfur and oxygen, respectively)

2.4.2. Simulation method

All simulations were carried out by the MD method using the PCFF-INTERFACE forcefield implemented in the Forcite module of Materials Studio 7.0 (Accelrys Inc., San Diego, CA, USA) on a workstation. The parameters of the interaction energy between atoms were derived from the PCFF-INTERFACE forcefield. First, all models were optimized by the smart minimizer method with 50000 steps to reduce the irrational contact between atoms. Then, the MD simulations were performed for a constant mole number, volume, and temperature assembly (NVT ensemble), and the temperature was controlled at 298 k using a Nosé-Hoover-Langevin (NHL) thermostat. The van der Waals and electrostatic interactions were calculated via the Ewald method with a cutoff of 12.5 Å (the accuracy was 4.18×10^{-5} kJ/mol.). The MD processes of all systems proceeded for 1.5 ns, in which the first 1 ns was used for relaxation, and the latter 0.5 ns output 1 frame per 10 fs for analysis of the relevant properties.

2.4.3. Simulation method

Driven by a concentration gradient, stress gradient, etc., the directional migration of substances in a system is called diffusion and is due to the thermal movement of molecules or atoms. The diffusion coefficient is an important physical index of a substance, in which related kinetic properties can be understood by analyzing the diffusion behavior. In this paper, the diffusion coefficient of water molecules in different flotation systems was calculated by the Einstein method (Hervé and Doros, 2001). The diffusion coefficient was derived using the following formula:

$$D = \frac{1}{6N} \times \lim_{t \to \infty} \sum_{i=1}^{N} \left(\left| r_i(t) - r_i(0) \right|^2 \right) \tag{1}$$

where D is the diffusion coefficient, N is the number of diffusive atoms in the simulation cell, $r_i(0)$ and $r_i(t)$ are the mass center positions of the solute at the initial time and time t, respectively.

The radial distribution function (RDF) is the probability of finding another atom at distance r centered on one atom, that is, the probability of two particles occupying each other's space. Therefore,

the RDF can be used to analyze the interaction between two substances. The RDF can be calculated as follows:

$$g_{AB}(r) = \frac{1}{x_A x_B \rho N}\left\langle \sum_{i=1}^{N_A}\sum_{i=1}^{N_B}\delta(r - r_i + r_i)\right\rangle \tag{2}$$

where x_A and x_B are the molar ratios of A and B, N_A and N_B are the atom numbers of A and B, N is the total atom number, ρ is the number density, and $\delta(x)$ is a function of the position.

To quantitatively describe the ability of anionic collectors to reduce the repulsion between DDA cations in aqueous solutions, the calculation method of the interface formation energy (IFE) was used for reference. The value of the IFE is a measure of the average intermolecular interaction per anionic collector molecule arising from the insertion of one anionic collector molecule at the DDA/water interface. The more negative the IFE is, the stronger the ability of an anionic collector to reduce the repulsion between DDA cations and the higher the recovery of muscovite from the macroscopic point of view. The IFE was obtained by the following formula (Zhen et al., 2015):

$$IFE = \frac{E_{Total} - \left(n \times E_{Anionic\ collector} + E_{DDA-water}\right)}{n} \tag{3}$$

where IFE is the interface formation energy, and E_{Total}, $E_{Anionic\ collector}$ and $E_{DDA-water}$ denote the energies of the whole system, the single anionic collector molecule, and a bare DDA-water system, respectively. The variable n is the number of anionic collector molecules.

3.   Results and Discussion

3.1. Flotation results

When DDA was used alone, the recovery of muscovite decreased gradually with increasing pH, and the decrease was significant under strongly acidic and alkaline conditions (Fig. 2(a)). When the pH was 2, DDA mainly existed in the form of RNH^{3+} or $(RNH_3)^{2+}$, and its concentration reached a maximum. Because of the permanent negative charge on the muscovite (001) surface, DDA exhibited an excellent collection performance in a strongly acidic environment, and the recovery of muscovite was 80%. Over the whole pH range, the performances of the three anionic collectors in muscovite flotation remained the same, that is, the recovery of muscovite increased with the pH, but the growth slowed down gradually. When the pH was 12, the collection performances of three anionic collectors NaOl, SDS and NA on muscovite were optimal, and the recoveries were 50.26%, 67.08% and 52.76%, respectively.

(a) Single collector　　　　　　　　　(b) Mixed anionic/cationic collector
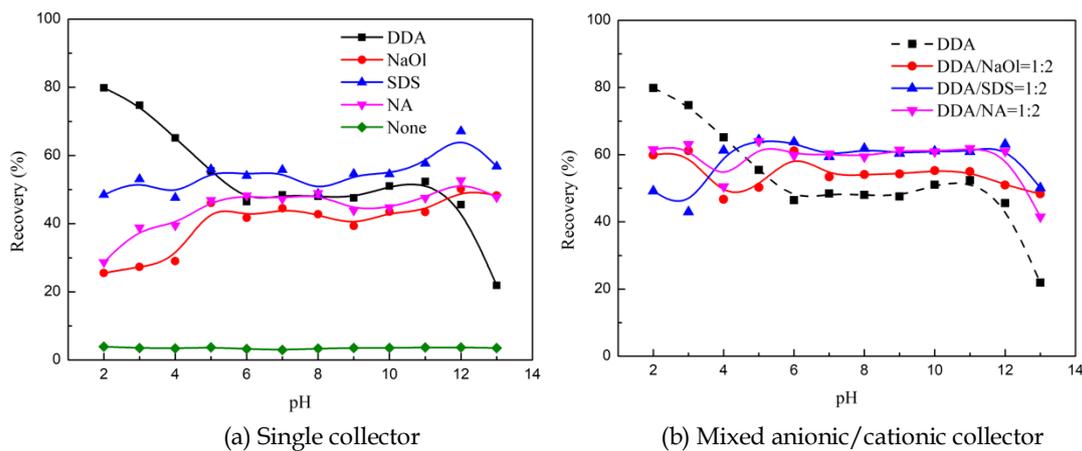
Fig. 2. The effect of pH on the recovery of muscovite under the condition of a collector concentration of 2.0×10^{-4} mol/L

Compared with using DDA alone, the three kinds of anionic collectors were used in combination with DDA, and all pairings could improve the recovery of muscovite in the range of pH=5-13 at the same collector dosage. The ability to improve the recovery was as follows: DDA/SDS ≥ DDA/NA > DDA/NaOl (Fig. 2(b)). Under the action of mixed anionic/cationic collectors, the recovery of muscovite

showed a trend of declining-rising-declining with increasing pH. This observation was because DDA mainly existed in the form of a cation under strongly acidic conditions, while anionic collectors mainly existed in the form of molecules that presented a poor ability to collect muscovite. Therefore, the recoveries of muscovite floated by these three kinds of mixed anionic/cationic collectors were essentially the same. With the gradually increasing pH (pH=3-4), some anionic collectors began to ionize, and the ionized anions reacted with DDA cations, resulting in a failure of the mixed collectors, thus, reducing the recovery of muscovite. In the range of pH=5-13, the mixed anionic/cationic collectors produced a positive synergistic effect, and the recovery of muscovite increased significantly over that obtained using DDA alone. When the pH exceeded 12, the recovery of muscovite began to decrease, but it remained higher than that using DDA alone.

(a) Molar ratio of mixed anionic/cationic collector   (b) Mixed anionic/cationic collector dosage
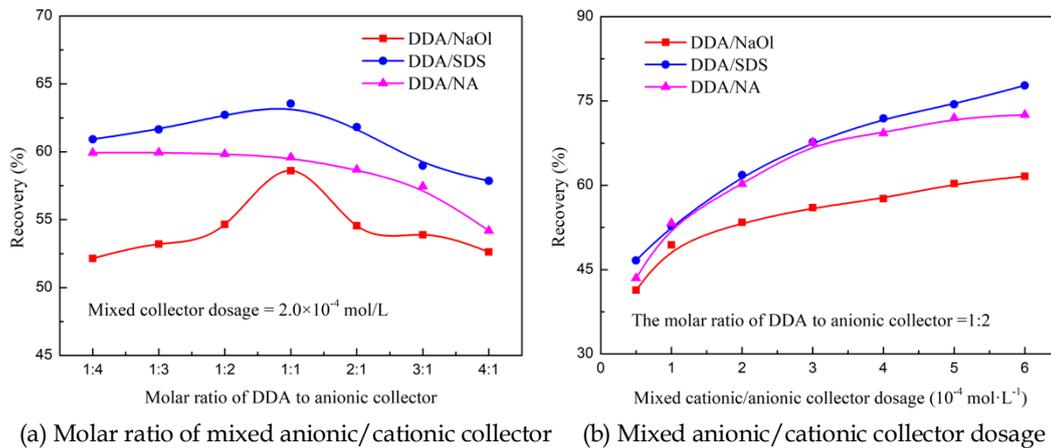
Fig. 3. The relationship between the recovery of muscovite and the mixed anionic/cationic collector at pH=7

Fig. 3(a) shows the recovery of muscovite for different molar ratios of DDA to anionic collector. As analyzed from the results, the flotation performance of muscovite was clearly different under the action of mixed anionic/cationic collectors with different molar ratios. When using DDA/NaOl, the recovery of muscovite first increased and then decreased, reaching a maximum at a molar ratio of DDA/NaOl of 1:1. The flotation behavior of muscovite was similar to that of DDA/NaOl when using DDA/SDS, and the maximum recovery of muscovite was 63.55%. For DDA/NA, the recovery of muscovite decreased with increasing DDA molar ratio, and the maximum recovery was 59.95% at a molar ratio of 1:3. Fig. 3(b) shows the relationship between the mixed anionic/cationic collector dosage and the recovery of muscovite. The recovery of muscovite increased with the mixed collector dosage, but for different mixed anionic/cationic collectors, the recovery growth trend was not consistent. In summary, the different mixed anionic/cationic collectors could all improve the recovery of muscovite to varying degrees, but the optimum molar ratios of DDA to the anionic collector and the optimum mixed collector dosages were different.

3.2. Zeta potential

The zeta potential of muscovite as a function of pH in the absence and presence of DDA (1×10^{-4} mol/L), anionic collectors (2×10^{-4} mol/L) and mixed DDA/anionic collectors ($1\times10^{-4}/2\times10^{-4}$ mol/L) are depicted in Fig. 4. It can be seen from Fig. 4(a) that the zeta potential of muscovite shifted to a more positive value with increasing pH in the presence of DDA alone, which showed that DDA presented a good adsorption effect on the muscovite surface. Under acidic conditions, DDA cations were adsorbed on the negatively charged muscovite (001) surface in the form of electrostatic adsorption, resulting in the increase in the zeta potential of muscovite. With the rise in pH value, the adsorption capacity of DDA cations on the muscovite surface decreased apparently, which could be proven by the decrease in the recovery of muscovite. However, the zeta potential of muscovite continued to rise under alkaline conditions, which may have been due to the adsorption of multilayer DDA on the muscovite surface. The multilayer DDA drastically reduced the hydrophobicity of the muscovite surface (Wang et al., 2014). Anionic collectors provided little effect on the zeta potential of muscovite at all pH values; only a little negative shift

occurred under alkaline conditions, which indicated that almost no significant amount of the anionic collectors was adsorbed on muscovite.

(a) Single collector (b) Mixed anionic/cationic collector
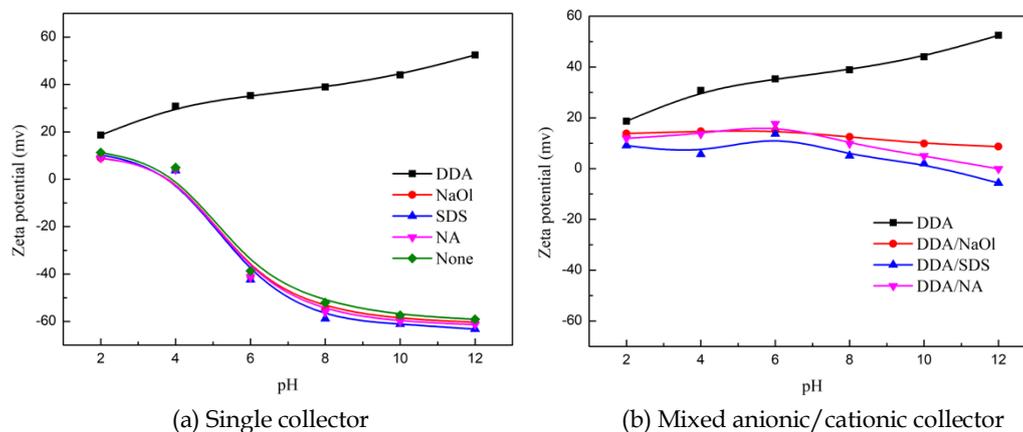
Fig. 4. The relationship between pH and the zeta potential of muscovite

A comparison of the results in Fig. 4(a) and Fig. 4(b) reveals that, under the action of the mixed anionic/cationic collectors, the zeta potential of muscovite was between that of DDA and anionic collectors used alone, which indicated that there was a synergistic effect on the adsorption. The addition of anionic collectors neutralized the positive charge of DDA cations, which showed a decrease in the zeta potential of muscovite. Under the same pH condition, the ability of different anionic collectors to neutralize the positive charge of DDA cations was different, and the order of their abilities was as follows: SDS > NA> NaOl. Combined with the recovery of muscovite under the action of different mixed anionic/cationic collectors, it could be seen that the stronger this ability was, the higher the recovery of muscovite.

3.3. MD simulations

Fig. 5 shows the stable configuration of different collectors adsorbed on the muscovite (001) surface. Regardless of which collector was used, the distance between nitrogen atoms and the muscovite (001) surface was almost the same, which was in the range of 1.7-1.8 Å (Fig. 6). Combined with the adsorption morphology of the collectors, it can be concluded that the DDA cations were stably adsorbed on the [(Si, Al)O$_4$] tetrahedral sheet, showing good adsorption behavior on the muscovite (001) surface. In the system of mixed anionic/cationic collectors, the anionic collectors were spontaneously inserted in between the DDA cations, and the position of the oxygen atoms in the anionic collector was higher than that of the nitrogen atoms along the Z-axis, which meant that the anionic collector was relatively farther from the muscovite (001) surface. According to the calculated RDF between the hydrogen atoms in the amino groups and the oxygen atoms in the anionic collectors in Fig. 7, there were mainly two peaks: the first peak at approximately 1.65 Å and the second peak at approximately 2.19 Å (System B and System D) or 2.67 Å (System C), which indicated that the interaction between the two components was hydrogen bonding and van der Waals forces (Lee et al., 2011). It can be inferred that the DDA cations were first adsorbed on the muscovite surface, and then, the anionic collectors were indirectly inserted into the adsorption layer of DDA cations through electrostatic interactions and hydrogen bonding interactions, which was consistent with the XPS (X-ray photoelectron spectroscopy) results that NaOl is adsorbed on the muscovite surface through co-adsorption with DDA (Wang et al., 2014). Based on the research with fluorescence spectroscopy, the CMC of a mixed DDA/NaOl surfactant is substantially lower than that of DDA or NaOl alone (Xu et al., 2013). Therefore, the mixed anionic/cationic collectors are more likely to form a micelle-like spherical structure, which proves that the hydrophobic association between nonpolar carbon chains also plays an important role in the adsorption process (Wang et al., 2015).

The calculated distribution of oxygen atoms (O$_{water}$) in the water molecules can well reflect the change of hydrophobicity under the action of different collectors. The higher the calculated density of O$_{water}$ is, the stronger the hydrophilicity of the muscovite (001) surface (Wang et al., 2015). Fig. 8 investi-
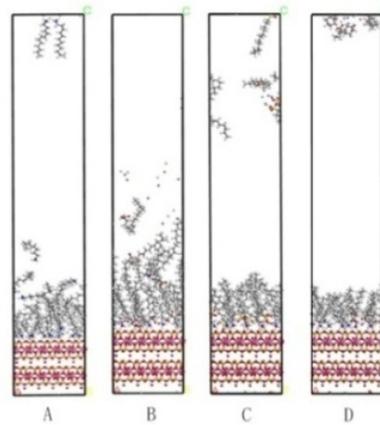
Fig. 5. The stable configuration of different collectors adsorbed on the muscovite (001) surface (the blue, red and yellow spheres represent nitrogen, oxygen and silicon respectively; the water molecule have been hidden)
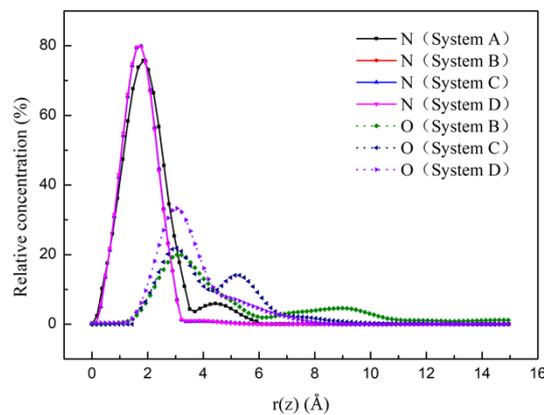
Fig. 6. The calculated distribution function of nitrogen atoms in DDA cations and hydroxyl oxygen atoms in anionic collectors along the Z-axis in different flotation systems
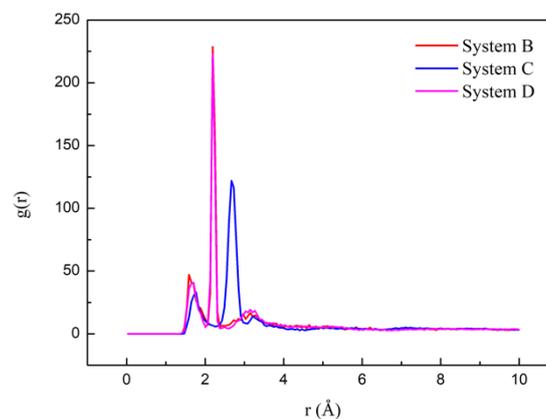
Fig. 7. The calculated RDF for the hydrogen atoms in the amino groups and the oxygen atoms in the anionic collectors in different flotation systems

gated the calculated density distribution function of O_{water} on the muscovite surface after adsorbing different collectors. As shown in the figure, although the calculated density of O_{water} varied under the action of different collectors, the curve shapes and the peak positions were similar. The peaks were located at 1.74, 3.98, 6.77, and 9.90 Å, which mean that at least four distinct water molecule layers were formed at the interface (Xu et al., 2014). This result was similar to that of the adsorption of amine collectors on the muscovite surface using the PCFF-phyllosilicates force field (Xu et al., 2014), but the positions of the peaks were slightly different, which may have been related to the different force field

parameters. By comparison, it was found that the position and intensity of the first peak did not change for either with mixed anionic/cationic collectors or DDA alone, indicating that the position of the first peak was only related to the surface properties of muscovite (Xu et al., 2018). Starting from the second peak, the intensity of the peaks changed as DDA > DDA/NaOl > DDA/SDS > DDA/NA, indicating that the density of water molecules on the muscovite (001) surface that adsorbed mixed anionic/cationic collectors was less than that of only the adsorbed DDA. The existence of anionic collectors made the muscovite (001) surface more hydrophobic, and the hydrophobicity was different under the action of different mixed anionic/cationic collectors.
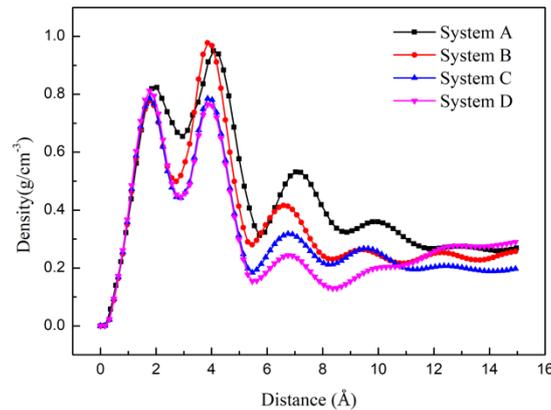
Fig. 8. The calculated density distribution of O_{water} atoms on the muscovite (001) surface in different flotation systems

To describe the movement of water molecules, the calculated mean square displacement (MSD) of water molecules on the muscovite (001) surface for 100 ps under a dynamic equilibrium state was calculated, as shown in Fig. 9. According to the Einstein equation, the diffusion coefficients of water molecules in different flotation systems were $2.15×10^{-3}$ Å/ps (System A), $1.98×10^{-3}$ Å/ps (System B), $1.87×10^{-3}$ Å/ps (System C) and $1.73×10^{-3}$ Å/ps (System D). Compared with the mixed anionic/cationic collectors, the water molecules had the largest diffusion coefficient when the muscovite surface adsorbed DDA alone. At this time, water molecules were the freest and had the lowest degree of motion restriction. When anionic collectors were added, the diffusion coefficient of the water molecules decreased to varying degrees, indicating that the diffusion and migration processes of water molecules became more difficult and that the muscovite surface became more hydrophobic (Wang et al., 2019). Among the three mixed anionic/cationic collectors, the diffusion coefficient of the water molecule decreased most dramatically when DDA/NA was adsorbed on the muscovite surface, which was consistent with the density distribution of water molecules on the muscovite (001) surface.
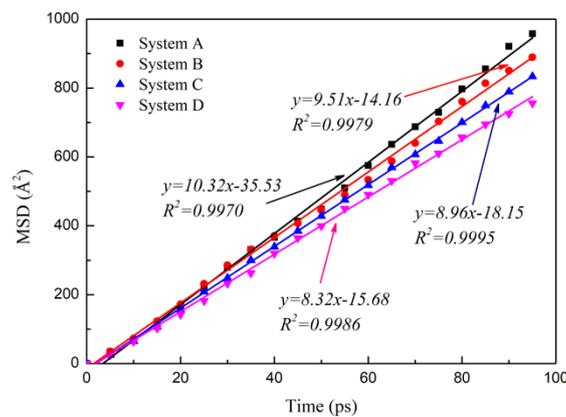
Fig. 9. The calculated MSD curves of water molecules on the muscovite (001) surface for 100 ps after dynamic equilibrium in different flotation systems

For ionic surfactants, the CMC in the aqueous solution decreases with the increase in the carbon atoms. Therefore, the higher calculated density of carbon atoms on the muscovite (001) surface indicated the stronger hydrophobic association between nonpolar groups of collectors. Fig. 10 shows the calculated density distribution of carbon atoms on the muscovite (001) surface for different flotation systems. As shown in the figure, when DDA and NaOl were used in combination, the calculated density of carbon atoms was basically the same as that using DDA alone for a height range of 0-15 Å, but above 15 Å, the calculated density of the carbon atoms significantly increased. These results showed that anionic collectors containing longer linear alkyl groups could effectively increase the density of carbon atoms at high regions of the solid/liquid interface, which helped to increase the hydrophobicity of muscovite (Fig. 11). The calculated density of the carbon atoms increased significantly at 6.8 Å when using DDA/NA, which was closely related to the naphthenic structure of NA. Similar to the principle of DDA/NaOl improving the hydrophobicity of the muscovite surface, both the naphthenic and benzene structures could increase the density of carbon atoms, but DDA/NA acted near the solid/liquid interface (Fig. 11). However, DDA/SDS could not increase the calculated density of carbon atoms on the muscovite surface, but the pair still maintained a good synergistic effect due to the sulfonic acid group. According to the research of Vidyadhar et al., the addition of collectors with different charges can reduce the repulsion of the adsorption layer and contribute to the formation of semimicelle adsorption (Vidyadhar and Rao, 2007; Tian et al, 2017). We believe that since the sulfonic acid group has three oxygen atoms, its interaction with the amino group was stronger than that between the carboxyl group and amino group. Under the action of the sulfonic acid group, the electrostatic repulsion force between the DDA cations evidently weakened, and the adsorption capacity of the mixed anionic/cationic collectors on the muscovite (001) surface theoretically increased, thus, improving the recovery of muscovite (Fig. 11). To quantitatively describe the ability of anionic collectors to reduce the repulsion between DDA cations in aqueous solutions, the IFE between anionic collectors and DDA cations was calculated. The results showed that anionic collectors had different abilities to reduce the repulsive interaction between DDA cations in aqueous solution (Table 2), and the order of IFEs was as follows: DDA/SDS > DDA/NaOl > DDA/NA, which indicated that the interaction between SDS anions and DDA cations was the strongest and that the electrostatic repulsion between DDA cations was effectively reduced.
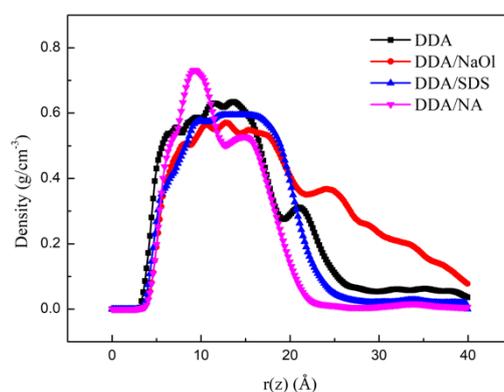
Fig. 10. The calculated density distribution of carbon atoms on the muscovite (001) surface in different flotation systems

Table 2. The interface formation energy (IFE) of different anionic collectors in the DDA-water system

Species	Anionic collector	Energy/(kJ mol⁻¹)			
		E_{Total}	$E_{DDA-water}$*	$E_{Anionic\ collector}$**	IFE
System B	NaOl	-56601.38	-16395.28	-163.54	-1846.77
System C	SDS	-57996.17	-15538.29	-217.89	-1905.00
System D	NA	-54715.02	-16989.59	-76.66	-1809.61

* The DDA-water system contained DDA cations, water molecules and the ions that ensured electrical neutrality

** The $E_{Anionic\ collector}$ is the energy of the anionic collector in an ionic state
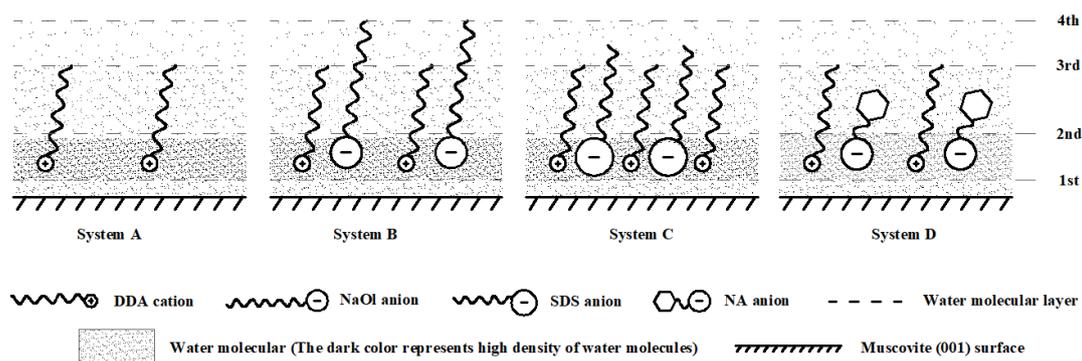
Fig. 11. The adsorption mechanism of different mixed anionic/cationic collectors on the muscovite (001) surface

4. Conclusions

Flotation experiments and MD simulations were used to study the flotation behavior of muscovite when DDA was used in combination with three anionic collectors and the adsorption behavior of mixed anionic/cationic collectors on the muscovite (001) surface. The results of the flotation experiments show that the combination of DDA with NaOl, SDS and NA can produce a positive synergistic effect under the conditions of pulp pH=5-13, and the flotation performance of mixed collectors on muscovite was better than that of a single collector. However, for different kinds of mixed anionic/cationic collectors, the optimum molar ratio of DDA to anionic collector and the optimum mixed collector dosage were different in muscovite flotation. The computational simulations show that DDA cations were first adsorbed on the muscovite surface and the anionic collectors were indirectly inserted into the adsorption layer of DDA cations through electrostatic interactions and hydrogen bond interactions between polar groups. The hydrophobic association between nonpolar carbon chains also played an important role in adsorption. Compared with DDA alone, the mixed anionic/cationic collectors can significantly increase the hydrophobicity of the muscovite surface, as evidenced by the decreases in the calculated water molecule density on the muscovite (001) surface and in the diffusion coefficient of water molecules at the solid/liquid interface. The reason for this phenomenon is that DDA/NA and DDA/NaOl can increase the calculated carbon atom density on the muscovite surface, but they acted on the near and high regions of the solid/liquid interface, respectively. Although DDA/SDS cannot increase the calculated carbon atom density, the interaction between the sulfonic group and amino group can reduce the electrostatic repulsion between DDA cations and theoretically increase the adsorption capacity of the mixed collectors on the muscovite surface, thus achieving a better flotation performance.

Acknowledgments

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