Flotation and adsorption of mixed cationic/anionic collectors on muscovite mica

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The adsorption of dodecylamine acetate (DAA), sodium oleate (NaOL) and DAA–NaOL mixtures on muscovite mica were investigated through flotation tests, zeta potential measurements, and pyrene fluorescence tests. The results show that the muscovite mica has a negative charge over the pH range 2–12. The muscovite mica did not float in the presence of NaOL alone. However, the recovery of muscovite mica ranged from ca. 80% (at pH 2) to 50% (at pH 11) using DDA alone. In the presence of mixed DAA–NaOL, the recovery ranged from 90% (at pH 2) to 90% (at pH 11). The individual cationic collectors DAA can be adsorbed strongly onto the muscovite mica, but no significant adsorption of anionic collectors NaOL can be detected by zeta potential measurements. In the mixed systems, the adsorption of both the cationic and anionic collectors are enhanced due to co-adsorption. The presence of NaOL in the mixture decreases the electrostatic head–head repulsion between the surface and ammonium ions and increases the lateral tail–tail hydrophobic bonds. Molecular dynamics (MD) simulations were conducted to further investigate the adsorption of DDA, NaOL, and DAA–NaOL on the (001) basal planes of muscovite using Materials Studio 5.0 program. The conclusions drawn from theoretical computations are in good agreement with experimental results.

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1. Introduction

Muscovite mica has the general composition KAl₂(AlSi₃O₁₀)(OH)₂, and its theoretical composition is 11.8%K₂O, 45.2%SiO₂, 38.5%Al₂O₃, and 4.5%H₂O. Micas have a layered lattice type structure composed of two silica tetrahedral sheets with a central octahedral sheet. In the case of muscovite mica, this central layer is dioctahedral, with only two-thirds of the possible octahedral positions being filled (Bailey, 1984). Aluminium substitution for one in every four silicon sites in the siloxane sheets leads to a negative layer charge. The charge balance of the siloxane plane is provided by interlayer cations which, in the case of muscovite, are potassium. Muscovite mica exhibits perfect cleavage along the (001) (siloxane) plane, which exposes interlayer potassium ions. In aqueous suspensions, the potassium ions readily enter into solution, leading to the development of a net negative charge on the siloxane plane. Thus, the surface of the muscovite mica is negatively charged at all pH > 1 (Nishimura et al., 1992).

Due to the negative charge surface over the whole pH range of 2–12, the muscovite mica would not be expected to respond to anionic collectors in the absence of an activator. Conversely, the mineral is readily recovered using cationic collectors, such as amines. At pH values greater than 5, many silicates are negatively charged. This means that selective separation of muscovite mica from these minerals, using a cationic collector, may not be possible (Nakazawa et al., 1988).

There are a number of processes where the mixtures of dissimilar surfactants have shown better properties than the individual components and there is strong interest in the behavior of mixed surfactant systems in recent years. The interactions between two surfactants in solution and at the air/liquid interface have been studied (Hanumantha Rao and Forsberg, 1997; Vidyadhar and Hanumantha Rao, 2007; Zhang and Somasundaran, 2006). In general, the physicochemical properties of a mixed monolayer does not obey the additive rule. Such a non-additive behavior is designated as synergism (Hua and Rosen, 1982; Von Rybinski et al., 1987). Although the adsorption of a single surfactant at the solid–liquid interface has been studied thoroughly, few studies exist for the case of adsorption in mixed surfactant solutions. The use of mixed cationic/anionic collectors for enhanced flotation and selectivity has only recently been recognized (Hosseini and Forssberg, 2007; Vidyadhar and Hanumantha Rao, 2007; Vidyadhar et al., 2012). However, the adsorption mechanism of mixed cationic/anionic collectors in flotation processes is still largely unidentified.

The objective of this work is to understand the underlying adsorption mechanism of the mixture of cationic DAA and anionic NaOL collectors in muscovite mica flotation. Flotation tests,
zeta-potential measurements, and fluorescence spectroscopic tests were undertaken. Results are discussed using molecular dynamics (MD) simulation to verify experimental results using theoretical computations. This study focused on elucidating the role of mixed cationic/anionic collectors systems in muscovite mica flotation.

2. Materials and methods

2.1. Materials

Muscovite mica, obtained from Lingshou of Hebei province (China), were crushed by a hammer and ground in a procelain mill. And –0.074 mm fractions were used in the experiments. X-ray fluorescence spectrometer (XRF) (Table 1) and X-ray diffraction (XRD) (Fig. 1) were used to study chemical and mineral compositions. The results showed the purity of the muscovite to be roughly 90%.

DAA and NaOL of analytical grade from Tianjin Damao Chemical Reagent Factory were used as collectors. DAA–NaOL were prepared by the mixing DAA with NaOL together, and the mixture were freshly prepared just before using with needs in order to avoid precipitation. Pyrene was from Sigma–Aldrich (Shanghai) Trading Co., Ltd., China. Pyrene was recrystallized twice using anhydrous ethanol. KCl of analytical purity was used as background electrolyte solution. Solutions of HCl and NaOH were used to adjust the pH of the system. Double distilled water was used in all tests. All reagents are listed in Table 2.

2.2. Flotation

Micro flotation tests were carried out in a 40 ml hitch groove flotation cell (Fig.2) (Liu et al., 2010). Mineral particles prepared (2 g) were placed in a plexiglass cell, and then filled with distilled water. HCl or NaOH were added for adjustment pH. After adding the desired amount of reagents, the suspension was agitated for 3 min. Flotation was conducted for 4 min. The froth products and tails were weighed respectively after filtration and drying, and the recovery was calculated based on the weight of the products.

2.3. Zeta-potential measurements

A suspension containing 0.1 wt.% mineral particles grounded to –5 μm in an agate mortar was prepared in the 1 × 10⁻⁵ mol/L KCl solution, and conditioned by magnetic stirring for 5 min. After settling for 10 min, the supernatant of dilute fine particle suspension was taken for zeta potential measurement.

The zeta-potentials were measured using a Malvern Zetasizer Nano ZS90 (England) equipped with a rectangular electrophoresis cell. The conductivity and pH of the suspension were monitored continuously during the measurement and the environmental temperature was maintained at 22 °C.

2.4. Pyrene fluorescence tests

Samples for fluorescence measurements were prepared by mixing pyrene stock solution with surfactant and mineral pulp, and allowed to stand for 2 h to equilibrate. The pyrene steady-state emission spectra in the suspension was obtained using a hitachi F-4500 fluorescence spectrophotometer. The excitation wave length of pyrene was 335 nm. The pyrene stock solution was prepared by dissolving pyrene in hot water until saturation, then cooling to 25 °C, and filtering. The concentration of pyrene in the solution was determined to be 6.53 × 10⁻⁷ mol/L (Mathias et al., 2001).

2.5. Molecular dynamics (MD) simulations

All calculations were performed in the framework of the MD, using the Material Studio 5.0 (MS) package. Firstly, CASTEP module included in MS software was adopted to optimize the crystal structure of muscovite mica. By comparing different parameters to be optimized, the best optimization parameters are as follows: a function was GGA + PBESOL, F-point set was 3 × 3 × 4, SCF tolerance was 1.0 × 10⁻⁶ eV/atom, use custom energy cutoff was 340 eV. Other parameters were default settings. The lattice optimization results are a = 5.202, b = 9.037, c = 20.160, α = 90°, β = 95.417°, γ = 90°. Then, a 2D periodic surface cell is created from the unit cell of the mineral at the cleavage plane (001) and then optimized in this same way.

Secondly, the DAA, NaOL, DAA–NaOL molecule was optimized using DMol3 module. The optimization parameters are as follows: Quality was medium, Functional was LDA + PWC. A symmetry calculation was opened. According to molecule charged situation, charge was chosen, DAA was +1, NaOL was –1, DAA–NaOL was 0.

Finally, Discover module was employed to calculate adsorption energies. DAA, NaOL and DAA–NaOL are as adsorbate, muscovite mica is as adsorbent. First of all, the geometry optimization of the system of reagent–muscovite mica was conducted using Smart Minimizer in pcpp force field. MD simulations were run using a canonical ensemble (NVT) at 298 K with the time step of 1 fs. Total run length was 10 ps. Ewald summation method corrected was employed for calculating both electrostatic and van der Waals forces (Pradip et al., 2002; Rai et al., 2011):

\[ \Delta E = E_{\text{complex}} - (E_{\text{surface}} + E_{\text{reagent}}) \]  

where \( E_{\text{complex}} \) is the total energy of the optimized reagent–muscovite mica complex, \( E_{\text{reagent}}, E_{\text{surface}} \) is the summation of single point energies of the free reagent and muscovite surface. The more
negative the magnitude of interaction energy ($\Delta E$) shows, the more favorable the interactions between the muscovite surface and the collectors are. However, the adsorption of collectors on muscovite surface is less favorable if the magnitude of interaction energy ($\Delta E$) is positive. The magnitude of $\Delta E$ is thus an excellent measure of the relative efficiency of interaction of different collectors with minerals.

### 3. Results and discussion

#### 3.1. Flotation

Fig. 3 shows the flotation responses of muscovite mica as a function of pH with cationic collectors DAA, anionic collectors NaOL and mixed collectors DAA–NaOL. With anionic collectors NaOL ($2 \times 10^{-4}$ mol/L), no muscovite mica is floated in the pH range studied. With cationic collectors DAA ($1 \times 10^{-4}$ mol/L), the flotation recovery of muscovite mica decreases with increasing in pH. The recovery of muscovite mica with DAA changed in the range of 80–50%. The flotation behavior of muscovite mica is different from the other oxides and silicates (Fuerstenau and Pradip, 2005). Similarly to kaolinite, muscovite mica belongs to phyllosilicate mineral. It seems that the anomalous behavior is relate to the mineral crystal structure (Hu et al., 2005; Jiang et al., 2011). The recovery of muscovite mica increased using mixed DAA–NaOL, improved up to 90%.

#### 3.2. Zeta potential

In general, the basal planes of muscovite mica are permanent negatively charged, which is attributable to isomorphous substitution of lattice elements. Si$^{4+}$ can be replaced by Al$^{3+}$. This permanent negative charge is pH-independent. In the case of the edges,
the charge is pH-dependent, arising from hydrolysis reactions of broken Al–O and Si–O bands (Steele et al., 2000). It is evidenced that muscovite mica have anisotropic surface charge, which complicates the electrophoretic analysis. The electrophoretic measurement does not take into consideration the structural anisotropic particle (Gupta and Miller, 2010). In recent years, Vishal Gupta and Hongying Zhao reveal the anisotropic surface charge by AFM colloidal probe technique (Gupta and Miller, 2010; Zhao et al., 2008). However, the anisotropic surface charge of muscovite mica is not the focus of this research. It should be emphasized that the electrophoretic properties of muscovite mica is described only by electrophoretic technique in this study.

Zeta-potential of muscovite mica in the absence and in the presence of DAA, NaOL and DAA–NaOL as a function of pH are illustrated in Fig. 5. The results showed that the PZC of muscovite mica in aqueous solution is at pH 1.3 above which the negative zeta potential increases in magnitude. In the presence of DAA and DAA–NaOL, the zeta potential is positive. It indicates that the cationic collector has adsorbed onto the negatively charged muscovite mica surface by electrostatic force. NaOL has little effect on the cationic collector has adsorbed onto the negatively charged muscovite mica in the presence of NaOL alone but more negative when compared to DAA alone.

### 3.3. Fluorescence spectroscopy

The fluorescence measurements are generally carried out by a steady state fluorescence spectrofluorometer and time resolved fluorescence lifetime instruments. Many researchers have adopted this technique to investigate the nano-structures of adsorbed layers at solid surfaces and to obtain information on the polarity and viscosity of the interior of the adsorbed layer as well as the aggregation number of the surfactant soloids at the solid/solution interface (Atkin et al., 2003; Zhang and Somasundaran, 2006).

A typical emission spectrum has five peaks at 373, 379, 384, 390, and 397 nm, respectively. The ratio of relative intensities of the third peak to the first peak $I_3/I_1$ is sensitive to the local environment of pyrene. In steady state fluorescence spectroscopy, $I_3/I_1$ in a pyrene emission spectrum shows the greatest solvent dependency. This ratio increases as the polarity decreases and hence can be used to estimate the solvent polarity of an unknown nanoenvironment in which the pyrene probe is located. In hydrophobic environments, the value of $I_3/I_1$ is higher than that when the pyrene is in a hydrophilic environment. The values of $I_3/I_1$ are 0.5–0.6 in water, 0.8–0.9 in surfactant micelles, and >1 in nonpolar solvents, respectively (Misra and Somasundaran, 2008).

The change in intensity ratio, $I_3/I_1$, of pyrene in different collectors solutions of varying concentrations is given in Fig. 6a. The $I_3/I_1$ values increase gradually with collectors concentrations. $I_3/I_1$ change sharply from a value of 0.6, corresponding to pyrene in water, to about 1.0, corresponding to pyrene solubilized in collectors micelles. When the concentration is up to the CMC, a flat horizontal is presented and $I_3/I_1$ reach to the maximum value. The critical micelle concentration (CMC) for NaOL, DAA, DAA–NaOL are $2.0 \times 10^{-3}$ mol L$^{-1}$, $1.05 \times 10^{-2}$ mol L$^{-1}$, and $8.0 \times 10^{-4}$ mol L$^{-1}$, respectively. It is also showed that compared with the corresponding individual components DAA and NaOL, the mixed collector DAA–NaOL has slightly greater $I_3/I_1$ value and also has a much lower value of CMC. The CMC of adsorbed surfactants is in the order of DAA–NaOL < NaOL < DAA. These properties result in a much better collecting property of DAA–NaOL than the corresponding individual components at the solid/solution interface. It is explained that the presence of NaOL in the mixture decreases

![Graph](image_url)

**Fig. 6.** (a) $I_3/I_1$, fluorescence parameter of pyrene in collectors solutions and (b) fluorescence parameter of pyrene in NaOL/muscovite mica slurries, DAA/muscovite mica slurries, DAA–NaOL/muscovite mica slurries, respectively.
the electrostatic head–head repulsion between the surface and ammonium ions and increases the lateral tail–tail hydrophobic bonds.

Fig. 6b shows the behavior of pyrene in different collectors-muscovite mica slurries as a function of the varying concentrations. Interestingly, when the surfactants concentrations are over the CMC, no pyrene was detected in the supernatants of the slurries, which suggests that pyrene is completely solubilized in the adsorbed layer (Chandar et al., 1987). The data in Fig. 4b show an abrupt change in the local polarity of the probe from aqueous environment to a relatively nonpolar, micelle-type environment. This change occurs in a region that is well below the CMC (where no micelles are present). The results suggest the existence of solubilization sites for pyrene on the surface that are formed by micelle-like association of hydrocarbon chains (Chandar et al., 1987). Clearly, such aggregation takes place only when the surfactants concentration is below or near CMC.

### 3.4. Computation of interaction energy by MD simulations

MD simulations are able to describe the crystal structure specificity of collector molecules with the different minerals as well as its interactions with different crystallographic planes of the same minerals. The computed interaction energies of NaOL, DAA, DAA–NaOL molecules with muscovite mica (001) surfaces are compared in Table 1. The magnitude of adsorption energies are in the order DAA–NaOL > DAA > NaOL, which is consistent with the flotation result. It is demonstrated that MD simulations results match well with those observed experimentally. The adsorption energy sum of individual components NaOL and DAA is −72.86 kJ/mol, but the co-adsorption energy of mixtures of DAA–NaOL is −203.82 kJ/mol. The adsorption energy reduces by 130.96 kJ/mol, which is attributable to synergies between NaOL and DAA molecule.

As illustrated in Table 3, it is expected that the NaOL molecule adsorption is considerably less on muscovite surfaces. There are no Al atoms with broken bonds on the muscovite (001) surfaces (Rai et al., 2011), and the surface consists of Si and O atoms only. The Al atoms are present below the surface atomic layer and are in octahedral coordination, thereby making it least favorable for adsorption of NaOL.

### 4. Conclusions

The zeta potential measurements and pyrene fluorescence tests show that the presence of NaOL increases the adsorption of DAA attributed to its co-adsorption. Meanwhile, the incorporation of NaOL in between the DAA decreases the electrostatic head–head repulsion and thereby increases the DAA adsorption by increasing the hydrophobic tail–tail bonds. The results of MD simulations show that the adsorption energy sum of individual components NaOL Molecules and DAA molecules is −72.86 kJ/mol, but the co-adsorption energy of mixtures of DAA–NaOL is −203.82 kJ/mol. The adsorption energy reduces by 130.96 kJ/mol, which is attributable to synergies between NaOL and DAA molecule. The conclusions drawn from purely theoretical computations are in good agreement with flotation, zeta potential and fluorescence results.

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Table 3

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Surfactant molecules</th>
<th>NaOL (kJ/mol)</th>
<th>DAA (kJ/mol)</th>
<th>DAA–NaOL (kJ/mol)</th>
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<tbody>
<tr>
<td>Muscovite mica</td>
<td></td>
<td>43.43</td>
<td>−116.29</td>
<td>−203.82</td>
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</table>