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## Improving spodumene flotation using a mixed cationic and anionic collector

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**Abstract:** Lithium, a rare-earth element, has been in increasing demand. Spodumene flotation is an important and challenging step for lithium extraction and production from lithium ore. In the present work, flotation tests for three pure minerals (i.e., spodumene, quartz and feldspar) and a real spodumene ore were carried out at laboratory scale. The results showed that YOA, a mixture of oleic acid and dodecylamine with the molar ratio of 10:1, could be used as collector to produce a spodumene concentrate with grade of 5.59% Li<sub>2</sub>O from the feed ore with grade of 1.48% Li<sub>2</sub>O where 85.24% of Li<sub>2</sub>O was recovered to the concentrate. The measured zeta potential, contact angle and adsorption capacity indicated that YOA was preferentially adsorbed on spodumene instead of on quartz or feldspar, with the spodumene surface being more hydrophobic than that of feldspar or quartz. The adsorption energies of YOA on spodumene were calculated and the results provided insights into the superior flotation performance obtained in the present work.

**Keywords:** *spodumene, lithium, silicates, flotation, anionic surfactant, cationic surfactant*

### 1. Introduction

Lithium, one of the rare-earth elements, has been in increasing demand. It is found in battery-powered automobiles, laptops, cell phones, and many other modern electronic devices. The primary source of lithium is lithium-containing minerals such as spodumene. One of the most important methods to separate spodumene from host ore (e.g., pegmatite ore) for lithium extraction is froth flotation. In spodumene flotation, the commonly used collectors include oxidized paraffin soap, naphthenic acid soap, tall oil and oleic acid (de Sousa et al., 2000; Felix and Reiner, 2010; Liu, 2008; Luo et al., 2012; Menéndez et al., 2004; Moon and Fuerstenau, 2003; Yu et al., 2015; Zhu et al., 2015). In addition, an amphoteric collector and hydroxamic acid were applied for the flotation of spodumene (Wang and Yu, 2005; He, 2009).

It has been recognized that collector blends are often more efficient than single collectors in flotation of sulfide and oxide ores (Lotter and Bradshaw, 2010), and the collector blends used in flotation practice can be summarized as follows:

- 1) Mixed collectors of same type. For example, a mixture of sodium isoamyl xanthate and its isomeride (Y89) with mass ratio of 1:2 was successfully used for the flotation of auriferous pyrite (Lu et al., 2016). The flotation rate and recovery of galena was improved by using a mixture of ethyl xanthate and ethyl dithiocarbamate (Mcfadzean et al., 2012). The flotation of phosphate was enhanced by using a mixed collector comprising 54 wt.% oleic acid, 36 wt.% linoleic acid and 10 wt.% linolenic acid (Cao et al., 2015). The flotation of feldspar was improved by using a cationic mixed collector consisting of AERO 3030C, AERO 801 and AERO 825 (Bayat et al., 2006).

- 2) Mixed collectors of different type. For example, a mixed collector of cationic alkyl diamine and anionic sulfonate/oleate was used for the flotation separation of feldspar from quartz, and the presence of sulfonate enhanced the diamine flotation via co-adsorption. A mixture of 12-carbon amine and sulphate/oleate collector was applied in the flotation of hematite (Vidyadhar and Rao, 2007; Vidyadhar et al., 2012). The mixture of n-octyl hydroxamates (AM28) and traditional sulphide collectors was used to simultaneously recover copper sulphides and oxides from a blended ore comprising 70% sulphide ore (bornite and chalcopyrite) and 30% oxide ore (malachite and minor azurite) (Lee et al., 2009). The mixed collector of armac C and potassium amyl xanthate gave promising results for smithsonite flotation (Ejtemaei et al., 2011).
- 3) Mixtures of an ionic collector and neutral oil. For instance, hematite flotation was improved by using a mixture of hydroxamic acid and diesel oil (Lu and Sun, 2007). In the flotation of spodumene using oleic acid as collector, addition of a small amount of diesel oil can also improve the flotation efficiency (Amarante et al., 1999).
- 4) Mixed collectors of different molecular sizes. In quartz flotation with dodecylamine as collector, addition of short chain alcohol can promote the adsorption of collector molecules on quartz (Vidyadhar et al., 2003). A mixture of polyvinyl alcohol and sodium oleate can outperform sodium oleate alone in the flotation of calcite (Labidi and Djebaili, 2008).

The research on anionic and cationic mixed collectors for spodumene flotation is at the early stage (Xu et al., 2016). In the present work, a mixture of oleic acid and dodecylamine, named YOA, was applied in spodumene flotation. The flotation tests were conducted for pure minerals and a real ore. Surface characterization and collector adsorption studies were carried out to fundamentally understand the improved performance of spodumene flotation.

## 2. Materials and methods

### 2.1 Samples and reagents

Bulk samples of spodumene, quartz and feldspar were collected from Koktokay Rare Metals Mine in Xinjiang, China. These samples were hammered and hand-picked to remove a small proportion of impurity minerals, ground in a porcelain mill loaded with agate balls, and sieved with stainless steel screens in deionized water to obtain a sample in the size fraction of  $-0.104+0.038$  mm. The samples were then subjected to high intensity magnetic separation to remove iron impurities, washed by deionized water, filtered and vacuum-dried. Chemical components and XRD results of these samples are shown in Table 1 and Fig. 1, respectively. A pegmatite ore was provided by Ganzi Rongda lithium Co., Ltd. in Sichuan, China. The valuable mineral in this ore is spodumene, and the gangue minerals are quartz, feldspar and mica. The chemical composition and XRD results of this ore are shown in Table 2 and Fig. 2, respectively.

Deionized water (resistivity  $> 18.2$  M $\Omega$ ·cm) was used throughout the experiments. Hydrochloric acid and sodium hydroxide was used as pH regulators in micro-flotation of pure minerals whereas sodium hydroxide, sodium carbonate and calcium chloride were used as modifier in the flotation of the spodumene ore. A mixture of collectors named YOA, which contained oleic acid and dodecylamine (DDA) with molar ratio of 10:1, was adopted as collector after being saponified by sodium hydroxide. The optimal molar ratio of oleic acid and dodecylamine and the optimal dosage of reagents were determined by a series of flotation tests and the detailed results were omitted in the present communication. Note that when YOA was used as collector, further addition of frother was not necessary.

Table 1. Chemical components of single-mineral samples (%)

Minerals	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Li <sub>2</sub> O	K <sub>2</sub> O	Na <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	CaO	MnO	Cr <sub>2</sub> O <sub>3</sub>
Spodumene	61.09	27.43	7.81	0.22	0.32	0.94	0.15	0.16	0.05
Quartz	97.28	1.01	-	0.11	0.14	0.13	0.37	-	0.13
Feldspar	65.78	18.86	-	10.41	2.89	0.13	0.36	-	-

Table 2. Chemical composition of the spodumene ore (%)

Elements	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Li <sub>2</sub> O	BeO	Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO
Content	14.43	73.29	1.48	0.01	0.011	0.009	2.01	0.21	0.13

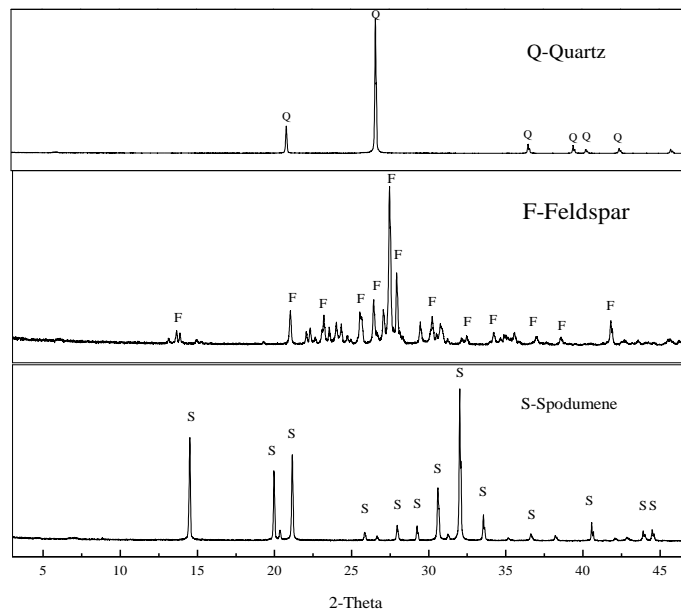


Fig. 1. XRD diffraction patterns of spodumene, feldspar and quartz

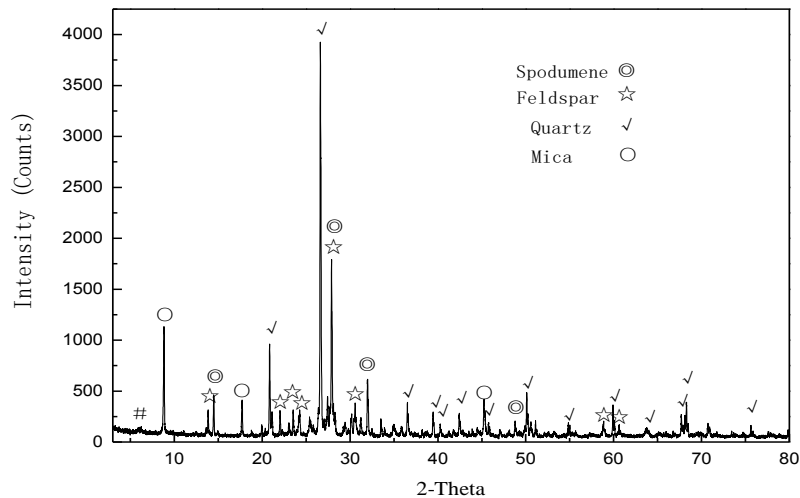


Fig. 2. XRD diffraction pattern of the spodumene ore

## 2.2 Flotation tests

Micro-flotation tests of pure minerals were carried out in a XFG-type self-aeration flotation apparatus with 40 cm<sup>3</sup> cell at 1890 rpm and room temperature. In each test, 5 g of the samples and deionized water were placed in the flotation cell. The pulp was conditioned for 2 min after each addition of reagent, including regulator and collector, and the flotation lasted for 4 min. The concentrates and tailings were filtered, dried and weighed to calculate the flotation recovery under various flotation conditions. For each condition, three experimental runs were conducted and the mean value of the data was reported.

The spodumene ore was ground in a Φ200×240 mm XMB-type steel bar mill to 70% passing 0.074 mm. The pulp was then transferred to a XFD-type flotation apparatus. Various reagents were added successively, and the pulp was conditioned for a fixed period of time, before starting flotation with

self-aeration at an air flow rate of 2.5 dm<sup>3</sup>/min. The concentrates (froth products) and tailings were separately filtrated, dried, weighed and analyzed to determine the content of Li<sub>2</sub>O. Three experimental runs were conducted for each condition and the weighted average of the data was reported.

### 2.3 Zeta potential measurements

The zeta potentials of the minerals were measured using a Zeta potential analyzer (Nano ZS90). A 20 mg of each sample with particle size being less than 5 μm was placed in a 50-cm<sup>3</sup> beaker, and then 40 cm<sup>3</sup> of deionized water was added into the beaker, followed by addition of reagents one by one. The pulp was allowed to stand for 3 min after being agitated using a magnetic stirrer for 5 min, and the supernatant was taken for the zeta potential measurement. Three replicates were taken and the average was reported.

### 2.4 Contact angle measurements

The contact angles of the minerals were measured using the sessile drop method. A 3S contact angle meter (GBX Company, France) with a measurement error of ±2° was used. A clean mineral crystal was placed in a beaker containing the reagent solution of interest and was agitated by using a magnetic stirrer at 1600 rpm for 10 min. The crystal was then taken out and washed by water several times before being dried in vacuum oven at 45 °C for 15 min. The contact angle was then measured 5 times, and the average of the data was adopted. Between each measurement, the crystal was cleaned by acetone, polished by sandpaper (abrasive size of 2.6 μm), and washed by deionized water.

### 2.5 Adsorption measurement

A mineral sample (2.0 g) and deionized water were added into the 40-cm<sup>3</sup> flotation cell. HCl and NaOH solution were used to adjust the pulp pH. Next, a certain amount of collector was added and the pulp was mixed for 2 min. The conditioned pulp was then transferred to a plastic tube with lid and centrifuged at 6000 rpm for 20 min. The supernatant was taken and measured by a total organic carbon analyzer (TOC) for the determination of organic carbon concentration, and the adsorption capacity of collector was calculated using Equation (1):

$$\Gamma = \frac{(C_0 - C) \times V}{1000 \times M \times 2} \quad (1)$$

where  $\Gamma$  is the adsorption capacity (mol/g),  $C_0$  and  $C$  are the organic carbon concentrations of initial and residual reagent solutions (mg/dm<sup>3</sup>), respectively,  $V$  is the volume of the pulp (dm<sup>3</sup>) and  $M$  is the molar mass of carbon in the collector molecule. In determining the collector adsorption capacity, the organic carbon concentration in the deionized water was ignored.

### 2.6 Quantum chemistry calculation

The CASTEP module in the software of Materials Studio 5.5 was used for the quantum chemistry calculations, including adsorption energy and Mulliken charge of collector components on mineral surface at different adsorption states.

## 3. Results and discussion

### 3.1 Effect of single collector on mineral flotation

Fig. 3 shows the relationship between mineral recovery and pulp pH when 6×10<sup>-4</sup> mol/dm<sup>3</sup> oleic acid was used as collector. The highest recovery of spodumene (approximately 60%) was achieved at pH 8.7 while the recoveries of feldspar and quartz were lower than 20%. The results suggest that selective flotation of spodumene from feldspar and quartz could be achieved at the pH range of 7-10.

Fig. 4 shows the relationship between the mineral recovery and pulp pH with 2×10<sup>-4</sup> mol/dm<sup>3</sup> DDA. As shown, at the pH range of 5-10, the recoveries of feldspar and quartz were over 90%, but the recovery of spodumene was less than 90%. The recoveries of all three minerals under study decreased sharply at pHs over 10, which may be caused by a decrease in the electrostatic interaction between

DDA molecules and mineral surface. The results suggest that dodecylamine is not suitable for the flotation separation of spodumene from quartz or feldspar.

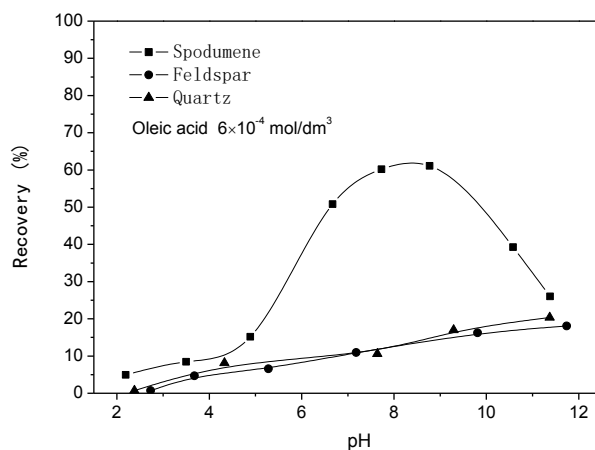


Fig. 3. Mineral recovery vs. pulp pH in the presence of oleic acid

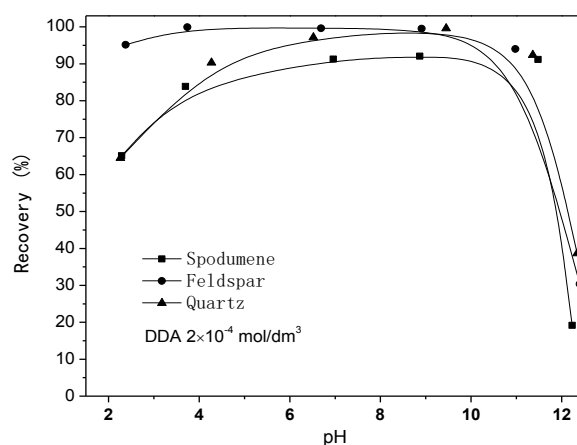


Fig. 4. Mineral recovery vs. pulp pH in the presence of DDA

Combining Figs. 3 and 4, one can see that for the flotation of spodumene, oleic acid showed relatively good selectivity but low collectability, in contrast to relatively good collectability but poor selectivity achieved by using dodecylamine. Further flotation tests were carried out using a mixture of oleic acid and dodecylamine to explore the possibility of achieving both good selectivity and good collectability for spodumene flotation.

### 3.2 Effect of mixed collectors on mineral flotation

Fig. 5 shows the flotation test results obtained using YOA (a mixture of oleic acid and dodecylamine with a molar ratio of 10:1) as collector at different pulp pHs, and the concentration of YOA is  $6 \times 10^{-4}$  mol/dm<sup>3</sup>. It is clear that the collector blending gave both good collectability and good selectivity, which outperformed dodecylamine or oleic acid alone. More specifically, at pH 8.7, the flotation recovery of spodumene reached about 85%, which was 25 percentage points larger than what was achieved using oleic acid alone, and the recoveries of feldspar and quartz remained below 20%.

### 3.3 Flotation of the spodumene ore using mixed collectors

Further flotation experiments were carried out to examine the performance of YOA in the flotation of spodumene from the pegmatite ore, following the procedure depicted in Fig. 6. For comparison, flotation tests with oleic acid were also carried out while keeping other experimental conditions the

same. Table 3 shows that YOA gave better collecting ability and selectivity than oleic acid in the flotation of spodumene ore. When 400 g/Mg YOA was used as collector, a concentrate (grade of 2.85% Li<sub>2</sub>O) was obtained with Li<sub>2</sub>O recovery being 93.13%. This result shows that combining oleic acid and dodecylamine makes it possible to improve the flotation separation of spodumene from the pegmatite ore.

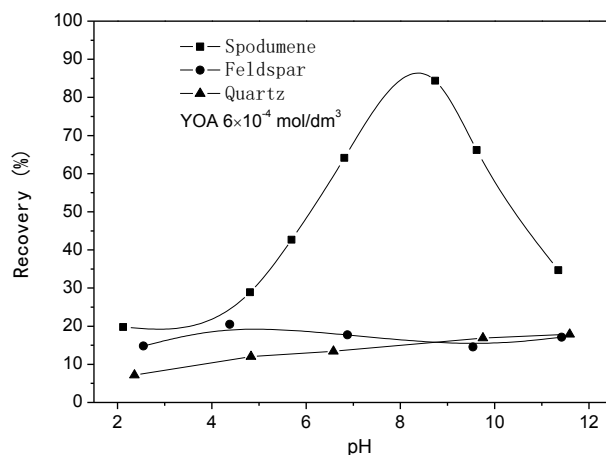


Fig. 5. Mineral recovery vs. pulp pH in the presence of YOA (a mixture of oleic acid and dodecylamine)

Subsequently, closed circuit flotation tests were carried out by using YOA as collector, following the flowsheet shown in Fig. 7, and the results are shown in Table 4.

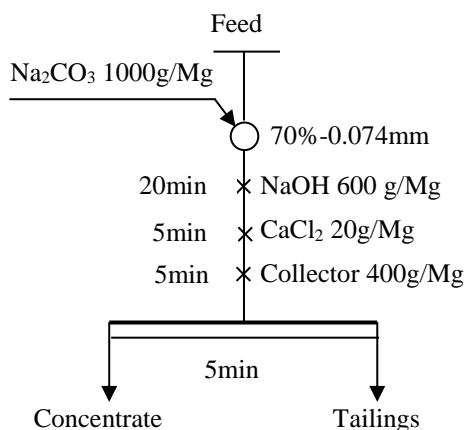


Fig. 6. Single-stage flotation flowsheet for comparison of different collectors

Table 3. Test results of flotation separation of spodumene from the pegmatite ore with different collectors

Collectors	Products	Yield(%)	Grade of Li <sub>2</sub> O (%)	Recovery of Li <sub>2</sub> O (%)
Oleic acid	Concentrate	37.84	3.31	85.20
	Tailings	62.16	0.35	14.80
	Feed	100.00	1.47	100
YOA	Concentrate	46.73	2.85	93.13
	Tailings	53.27	0.18	6.87
	Feed	100.00	1.43	100

It can be seen from Table 4 that with using YOA as collector, a concentrate (grade of 5.59% Li<sub>2</sub>O) was produced from the flotation feed with 1.47% Li<sub>2</sub>O where 85.24% of Li<sub>2</sub>O was recovered to the

concentrate. This spodumene flotation outcome is considerably better than those obtained by others (Liu, 2008; He, 2009; Luo et al., 2012).

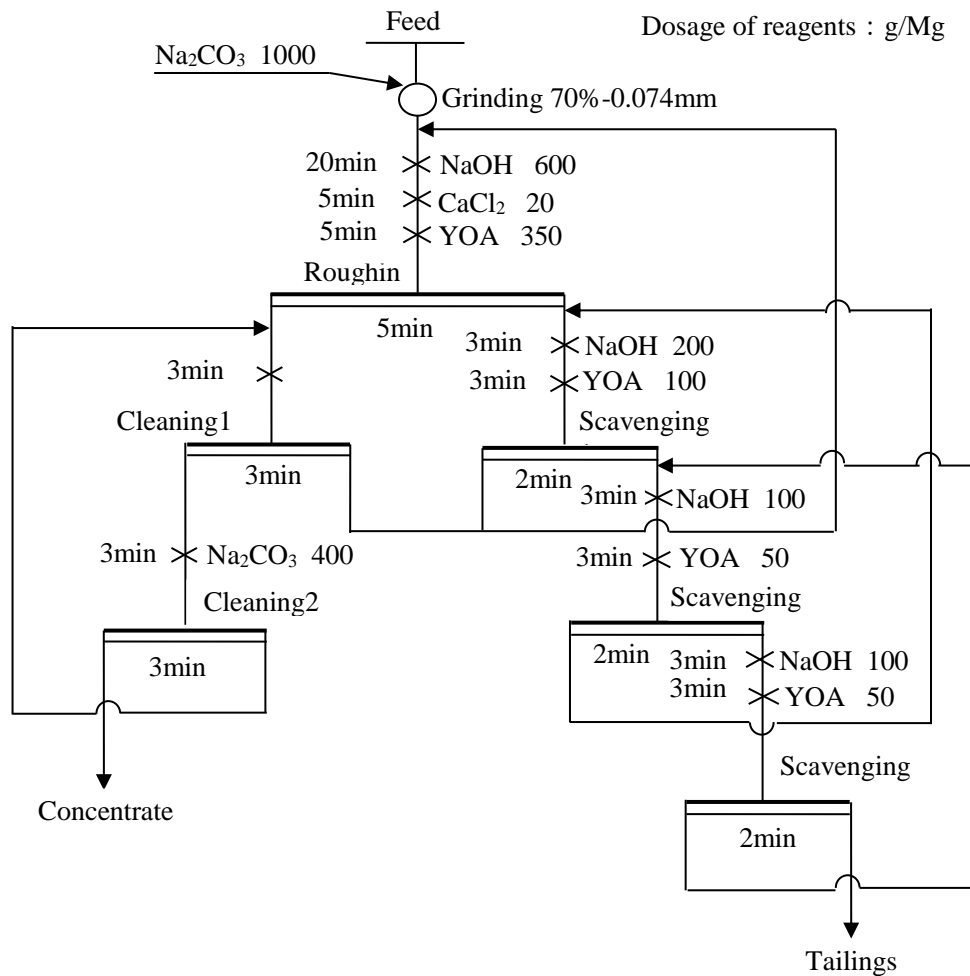


Fig. 7. Flowsheet of closed circuit tests using YOA as collector

Table 4. Results of closed circuit tests

Products	Yield (%)	Grade of Li <sub>2</sub> O (%)	Recovery of Li <sub>2</sub> O (%)
Concentrate	22.44	5.59	85.24
Tailings	77.56	0.28	14.76
Feed	100.00	1.47	100.00

### 3.4 Interaction between YOA and mineral surface

The zeta potentials, contact angles and adsorption capacity were measured in the presence of YOA, and the results are presented and discussed as follows.

#### 3.4.1 Zeta potential measurements

Fig. 8 shows the zeta potentials of the spodumene, feldspar and quartz particles as a function of pulp pH in deionized water and  $6 \times 10^{-4}$  mol/dm<sup>3</sup> YOA solution, respectively. From Fig. 8a one can see that the point of zero charges (PZCs) of spodumene, feldspar and quartz were 2.83, 2.15 and 2.33, respectively, in consistence with those reported by others (Moon and Fuerstenau, 2003; Yu et al., 2015). It was, therefore, suggested that these three minerals would be negative charged at a pulp pH over 3 where the electrostatic interaction between mineral and reagent would make it easy for these minerals

to be floated by using dodecylamine as collector. Indeed, Fig. 4 shows high recoveries of all these three minerals at pHs 3 – 11.

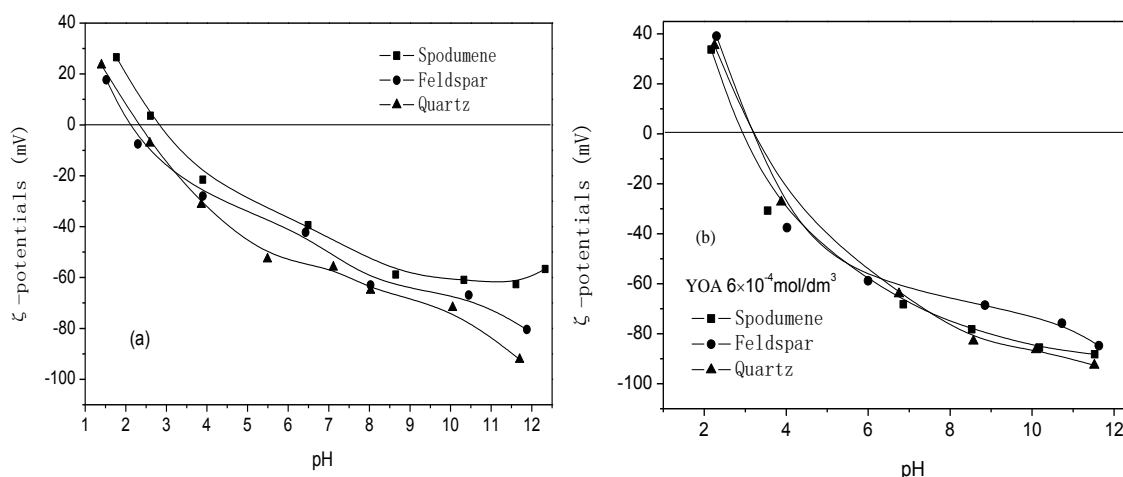


Fig. 8.  $\zeta$ -potential vs. pH in (a) deionized water and (b) YOA solution

Fig. 8b shows the zeta potential values measured at different pHs in the YOA solution. Compared to Fig. 8a, at acidic pHs lower than 3.2, the positive zeta potentials of the minerals in the YOA solution were slightly higher than those in deionized water, probably owing to adsorption of dodecylamine ions. At a given pH over 3.2, especially at the alkaline pH range, the zeta potential of the minerals in the YOA solution was more negative than those in deionized water, especially the spodumene, implying that oleate ions were adsorbed on these minerals surfaces.

#### 3.4.2 Contact angles measurements

Fig. 9 shows the contact angles of spodumene, feldspar and quartz in deionized water and  $6 \times 10^{-4}$  mol/dm<sup>3</sup> YOA solution. In deionized water, the contact angles of minerals were lower than  $16^\circ$  at the entire pH range under study, indicating that three minerals were naturally hydrophilic, and the hydrophilicity followed the order of Quartz > feldspar > spodumene. In the YOA solution, however, the contact angles of these three minerals increased greatly at the pH range of 4-10 and at a given pH, the contact angle of spodumene was greater than those of feldspar and quartz. The difference in contact angle between spodumene and silicate minerals was the biggest at the pH range of 7-10. In other words, after the adsorption of YOA, the hydrophobicity of spodumene was stronger than that of feldspar or quartz.

#### 3.4.3 Measured adsorption capacity of YOA on minerals

The adsorption quantity of YOA on minerals in the solution with initial YOA concentration of  $6 \times 10^{-4}$  mol/dm<sup>3</sup> was measured, and the results are shown in Fig. 10. The adsorption quantity of YOA on each of these three minerals reached the maximum around pH 8.7 and at a given pH, the adsorption quantity of YOA on spodumene was larger than that of feldspar or quartz, in consistence with the results shown in Figs. 8 and 9. Compared with our previous work on the adsorption quantity of oleic acid on spodumene with initial concentration of  $6 \times 10^{-4}$  mol/dm<sup>3</sup> (Yu et al., 2015), the adsorption quantity of YOA on spodumene obtained in the present work was larger.

#### 3.4.4 Computational results of the adsorption state of YOA on spodumene

The adsorption energies of YOA on spodumene at different states were calculated, and the results are shown in Table 5. The adsorption energies of the four states were all negative, which means that the four adsorption states of YOA on spodumene were all possible. Note, however, that the dominated adsorption states of YOA should be (a), (b) and (d).

In order to study the influence of ion-molecule association on YOA adsorption, the Mulliken charges of -COO group at the different states were calculated, and the results are shown in Table 6.



The association of oleic acid ion and oleic acid or dodecyl amine molecule allowed the charges of the carboxyl group to become more negative compared to that of oleic acid ion without the association. A highly negative charge of -COO group should be beneficial for the adsorption of collector molecules on the Al sites of spodumene. It is, therefore, likely that in using YOA as collector for spodumene flotation, the association of oleic acid ions with dodecyl amine molecules plays an important role in determining the flotation performance.

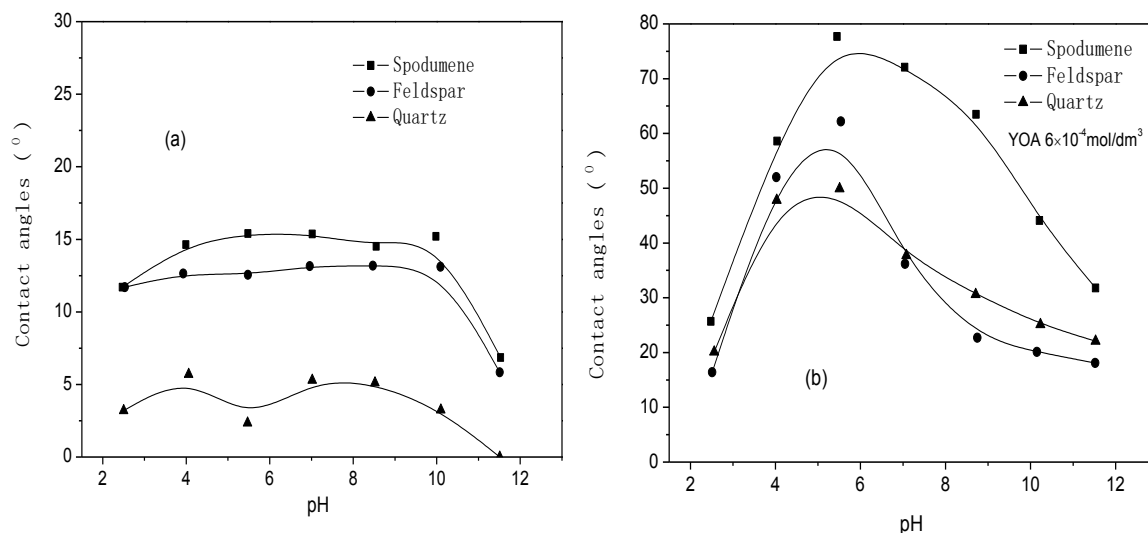


Fig. 9. Contact angles vs. pH in (a) deionized water and (b) YOA solution

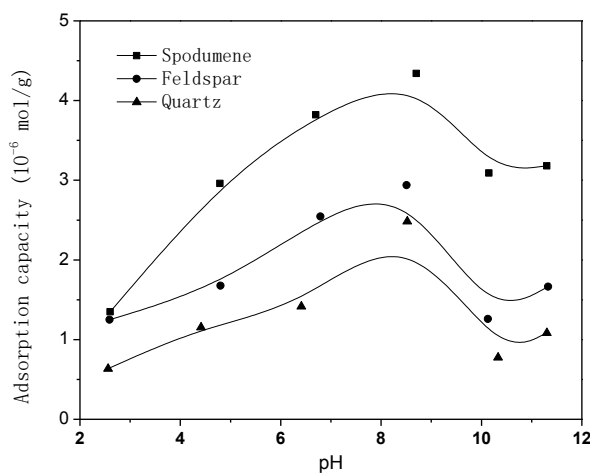


Fig. 10. Adsorption quantity of YOA vs. pulp pH

Table 5. Adsorption energy of YOA on spodumene surface

Adsorption states	adsorption energy((kJ/mol)
(a) Oleic acid ions adsorb on Al atoms, dodecyl amine ions adsorb on O atom	-364.25
(b) Association of oleic acid and dodecyl amine ions adsorb on Al atoms by COO- group	-428.19
(c) Oleic acid ions adsorb on Al atoms, dodecyl amine molecules adsorb on O atom	-133.09
(d) Association of oleic acid ions and dodecyl amine molecules adsorb on Al atoms by COO- group	-337.54

Table 6. The Mulliken charges of the -COO group

States	Mulliken charge (e)			
	O1	O2	C	-COO group
Oleic acid ion	-0.46	-0.47	0.73	-0.20
Association of ion and molecule of oleic acid	-0.48	-0.51	0.70	-0.29
Association of oleic acid ion and dodecyl Amine molecule	-0.52	-0.52	0.73	-0.31

#### 4. Conclusions

Flotation tests for pure minerals (spodumene, quartz and feldspar) and a real ore (spodumene ore) were carried out at laboratory scale. Use of YOA, a mixture of oleic acid and dodecylamine with the molar ration of 10:1 led to effective flotation separation of spodumene from quartz and feldspar, manifested by good selectivity and good collectability. A spodumene concentrate with grade of 5.59% Li<sub>2</sub>O was produced from the feed with grade of 1.48% Li<sub>2</sub>O where 85.24% of Li<sub>2</sub>O was recovered to the concentrate. The zeta potential, contact angle and adsorption capacity measurements showed that YOA was easier to adsorb on the surface of spodumene than on the surface of quartz or feldspar, with the spodumene surface being more hydrophobic than that of feldspar or quartz. This experimental observation was consistent with the computational results of the adsorption energies of YOA on spodumene. The latter suggests that in using YOA as collector for spodumene flotation, the association of oleic acid ions and dodecylamine molecules could play an important role in enhancing the flotation performance.

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