

Received March 31, 2019; reviewed; accepted June 26, 2019

Effects of single and mixed reagent systems on improved diaspore recovery

Hao Jiang, Guoyuan Xiang, Ya Gao, Sultan Ahmed Khoso, Weiwen Peng

School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China

Corresponding author: jianghao-1@126.com (Hao Jiang)

Abstract: Frothing performance and stability of sodium oleate (NaOL) alone and in presence of methyl isobutyl methanol (MIBC), octanol (OCT) and polyethylene glycol (PEG) systems were studied and compared in order to enhance flotation separation of diasporic bauxite ore. Performance of a single (NaOL) and mixed systems (NaOL-MIBC, NaOL-OCT, NaOL-PEG) was evaluated through flotation tests, three-phase dynamic froth stability tests, zeta potential measurements and adsorption analysis. The mixed systems showed a stable froth and an improved recovery with their descending order NaOL-PEG > NaOL-OCT > NaOL-MIBC. Adsorption analysis and zeta potential measurements suggested that, except NaOL adsorption, there was no significant co-adsorption of alcohols on the diaspore surface. However, adsorbed amount of NaOL on the diaspore surface was extremely high; accounts for more than 90% of the total substance used in the pulp.

Keywords: diaspore, flotation, mixed collectors, froth stability, adsorption

1. Introduction

Worldwide, the major natural resources of industrial aluminum metal are hydrated bauxite minerals, including diaspore, boehmite and gibbsite (Gibson et al., 2017). Bayer process is one of the most dominant method of bauxite upgradation method where the bauxite ore is leached with a sodium hydroxide (caustic soda) solution followed by the solid-liquid separation, cooling, precipitation, filtration and calcination, with alumina as the final product. However, it was reported in literature (Gibson et al., 2017) that the mass ratio of alumina and silica (A/S) in natural ore deposits must be greater than 8 for feeding to the Bayer process. The A/S mass ratio in diaspore type of bauxite ore is found to be less than 6 (Chen et al., 2006; Xia et al., 2010), therefore, it requires preliminary upgrading. Generally, the froth flotation physicochemical concentration method is mostly applied in China to enhance the mass ratio of A/S for adequate purification of diaspore before feeding to the Bayer process (Chen et al., 2006).

In the last few years, the mixture of different reagents have been used as collectors in flotation separation of many ores because of their better physical and chemical characteristics and synergistic effects as compared to their corresponding single reagent (Jiang et al., 2017; Rao and Forsberg, 1997; Rybinski and Schwuger, 1986). A number of studies have been carried out to design and develop the different mixed surfactant systems, such as ionic/ionic, ionic/nonionic and nonionic/nonionic, for flotation. A new collector was developed by mixing the sodium oleate with dodecyl amine hydrochloride in order to enhance the muscovite flotation (Xu et al., 2016). The flotation separation of feldspar from quartz was carried out with the mixture of two reagents sulfonate and alkyl diamine under acid conditions (Ejtemaei et al., 2014; Poorkani and Banisi, 2005). The selective flotation of spodumene from feldspar was carried out with synthetic surfactant manufactured by the mixture of sodium oleate and dodecyl ammonium with optimal molar ratio of 9:1 (Tian et al., 2017a).

Literature reported that the adsorption of collectors on the solid-liquid boundaries plays an important role in many applications such as flotation, surface wetting modification, surfactant-based

separation, foaming control, detergents and emulsification (Blanco et al., 2010; Jiang et al., 2017; Somasundaran and Krishnakumar, 1997). In recent years, a significant research has been conducted to investigate the adsorption mechanism and behavior of a single collector on the solid-liquid surfaces, but a very limited literature is available on the adsorption of mixed surfactant systems. Moreover, the use of novel mixed collectors in the applications of flotation is a recently recognized opinion. Therefore, extensive researches have been carried out to design, develop and utilize the new mixed anionic/nonionic surfactant systems for selective separation by flotation (Fang et al., 2003; Rubingh and Jones, 1982; Wang et al., 2015). In general, new developed surfactant systems typically have better surface properties than their individual compounds, because they result into a better wetting, solubilizing and foaming behavior. Furthermore, the synergistic effects of mixed collectors on the air/water surfaces and their co-adsorption on the surface of mineral have been widely reported in literature (Hao et al., 2012; Maiti et al., 2010; Rojas et al., 2010; Vora et al., 1999; Wang et al., 2014; Zhao et al., 2010). In flotation system, numerous parameters are applied as indicators for froth stability, however, there is no specific criterion to quantify froth stability up to date (Farrokhpay, 2011). It is widely acknowledged in literatures, the stability of froth is mainly measured by the dynamic and static methods (Bikerman, 1973). (Malysa et al., 1981) studied the surface rheology and frothability of acid solutions to get more understanding of the froth stability. According to (Drzymala, 2018), froth stability index (DFI) can be used as a universal external normalization parameter for flotation results. (Gourram-Badri et al., 1997) determined the frothability of methyl isobutyl methanol (MIBC) from the total froth height and found that particles in froth influenced its height. Besides, (Tao et al., 2000) related the froth stability to flotation behaviors through coal column flotation and concluded that size of coal particle and concentration of pulp stabilized/destabilized the froth to a certain extent. So, from extensive studies, it is concluded that froth stability plays a great role in the flotation in context to grade and recovery.

Amongst various mixed reagents, the mixed anionic/nonionic surfactants are more significant because they formed the natural vesicles in water phase and exert strong synergistic effects. Studies suggested that the synergistic effect reduced quantity of reagents used in industries, therefore, reducing the environmental contaminations and economic costs as well (Desai and Dixit, 1996b; Desai and Dixit, 1996a; Dixit et al., 2002; J. Penfold et al., 1997). Extensive studies on mixed reagents as collectors in the aqueous systems have been carried out, however several limitations are still existing. Hence, substantial efforts are required to understand the flotation mechanism and synergistic adsorption of mixed anionic/nonionic reagents on mineral ores.

The purpose of present study was to compare and contrast the effects of froth stability and adsorption mechanism of single anionic and mixed anionic/nonionic collectors on diaspore flotation. For this, different flotation tests were performed using micro-flotation mechanism. Zeta potential measurements and residual total organic carbon measurements were carried out to discuss the adsorption behaviors of collectors on diaspore surface and the influence of carbon chains of alcohols in mixed anionic/nonionic collectors. Three-phase dynamic froth stability tests were also measured on laboratory scale. The study offers reasonable interpretations about froth stability and adsorption mechanism of mixed anionic/nonionic collectors with different lengths of carbon chains on diaspore surfaces.

2. Materials and methods

2.1. Samples and reagents

The representative samples of diaspore were received in the form of lump from Xiaoyi city of Shanxi province, China. The samples were pulverized into fine material by using laboratory porcelain mill. The fine materials obtained were sieved to obtain three size fractions i.e. +0.074 mm, -0.074+0.038 mm and -0.038 mm. The purity of diaspore mineral was determined by using x-ray fluorescence (XRF) and x-ray diffraction (XRD) techniques. The elemental analysis and XRD results shown in Table 1 and Fig. 1 respectively, indicated that the diaspore samples are good enough in quality to use in this work. The loss on ignition (LOI) of diaspore was measured by using a thermogravimetric analyzer (TA, USA).

Sodium oleate (NaOL) and three types of alcohols as methyl isobutyl methanol (MIBC), octanol (OCT) and polyethylene glycol (PEG) were used as collectors in flotation tests. The pH of solution was adjusted by using HCl and NaOH chemicals. All tests were performed in deionized water.

Table 1. Chemical composition of diaspore sample (mass fraction, %)

sample	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	LOI
diaspore	80.86	0.82	0.24	2.81	0.01	0.049	0.008	0.029	14.62

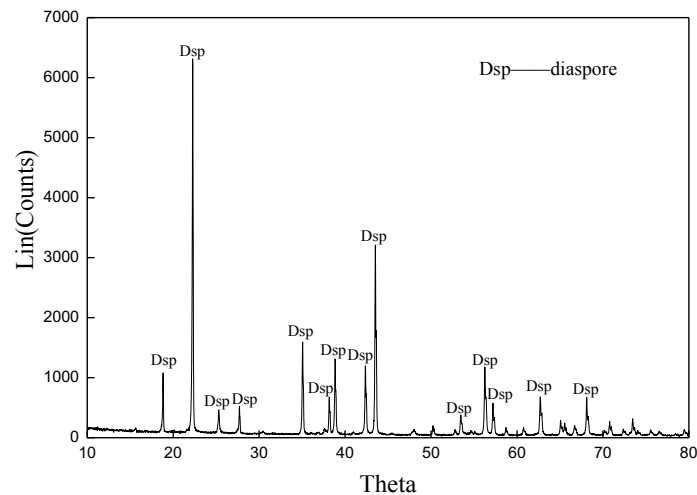


Fig. 1. X-ray diffraction results of diaspore sample

2.2. Flotation tests

Micro-flotation tests were carried out in 40 cm³ flotation cell with a fixed impeller speed of 1500 r/min. In each test, the pulp was prepared by adding 2 g of mineral and 35 cm³ of deionized water to the flotation cell and agitated for 1min to homogenize the dispersed sample particles. The pH of the pulp was adjusted to desired values by adding HCl or NaOH chemicals. After adjustment of pH, collectors with a certain concentration were added in the pulp and conditioned for 3 min. The flotation process continued for 3 min before the flotation products were collected, filtered, dried and weighed. The flotation recovery was calculated using the mass of the products. All flotation tests were performed three times with the same procedure and conditions. The average of all three tests was calculated.

2.3. Three-phase dynamic froth stability tests

For three-phase dynamic froth stability tests, as shown in Fig. 2, the pulp was made by adding 2 g of mineral sample and 35 cm³ of deionized water to the 40 cm³ flotation cell and agitated for 5 min. The reagent system is consistent with the micro-flotation exactly. The froth stability was carried out with a vertical glass column having length of 85 cm and an inner diameter of 4 cm. Bottom of the glass column was equipped with an intake valve connecting with an airflow controller to keep the airflow at 0.14 dm³/min. The prepared pulp was then placed into a column. Once the inflatable valve was opened, the froth raised up inside the column and stopped after a while to reach a constant height depending on operating conditions and the froth stability. The froth height, using the pulp-froth interface as the reference, was measured as a function of time. According to (Bikerman, 1973), the dynamic froth stability (Σ) was calculated as the ratio of steady-state froth volume to volumetric flow rate of air:

$$\Sigma = \frac{V_f}{Q} = \frac{H_{max} \times A}{Q} \quad (1)$$

where V_f is the steady-state froth volume, Q is the volumetric flow rate of air, H_{max} is the total froth height which measured experimentally, and A is the cross-sectional area of the column.

2.4. Residual total organic carbon measurements

The amount of total organic carbon (TOC) in the pulp was measured directly by using TOC-L_{CPH} type total organic carbon analyzer (SHIMADZU, Japan). For this, 2 g of mineral sample was placed in the 200 cm³ plexiglass filled with 40 cm³ mixed surfactant solution whose concentration has been known. The suspension was agitated for 40 min in a vapor-bathing vibrator and then centrifuged at 9000 r/min for 30 min. Then the supernatant was collected for TOC measurements. All the analysis experiments of TOC were performed at 25 °C.

2.5. Zeta potential measurements

The zeta potential measurements were carried out by using a Coulter Delsa 440sx Zeta potential analyzer (USA) equipped with a rectangular electrophoresis cell. For these tests, mineral samples were ground to 2 μm particle size and the suspension was prepared by adding 40 mg of mineral samples to the 80 cm³ desired solutions containing 1 mM KNO₃ as supporting electrolytes. After that, the suspension was conditioned for 6 min by using a magnetic stirrer to ensure the adequate dispersion of fine mineral particles. After settling for 10 min, the supernatant of dilute fine particle suspension was taken for the zeta potential measurements.

3. Results and discussion

3.1. Crystal structure and flotation results

Crystal structure of diaspore [α -AlO(OH) or Al₂O₃·H₂O] is much different from common layer-structured aluminosilicates like illite, kaolinite and pyrophyllite. Its crystal structure is shown in Fig. 3. It is so difficult to separate pure enough diaspore from these aluminosilicates owing to their close dissemination characteristics. There was no any impurity elements in the crystal structure of pure diaspore (Hill, 1979). It had been proved that a few Al³⁺ can be replaced by Fe³⁺ in the form of isomorphism in a diaspore crystal structure (Hazemann et al., 1992; Kellen, 1978). Diaspore was composed of hexagonal close-packed oxygen sheets with aluminum atoms filling two-thirds of the octahedral interstice sites (Hill, 1979; Newman, 1987). Each occupied-octahedron shares four edges with adjacent aluminum octahedrons, making double chains formed in the direction of c axis. Each unit is joined together by sharing the apical oxygen atom. Aluminum atoms occupy octahedrally coordinated sites in the same way to form strips of octahedrons. When aimed to grinding, diaspore usually breaks along (010) crystal planes where the bond force is the weakest. The comminution can destroy covalent/ionic of Al-O bonds, making the surface ionic or unsaturated.

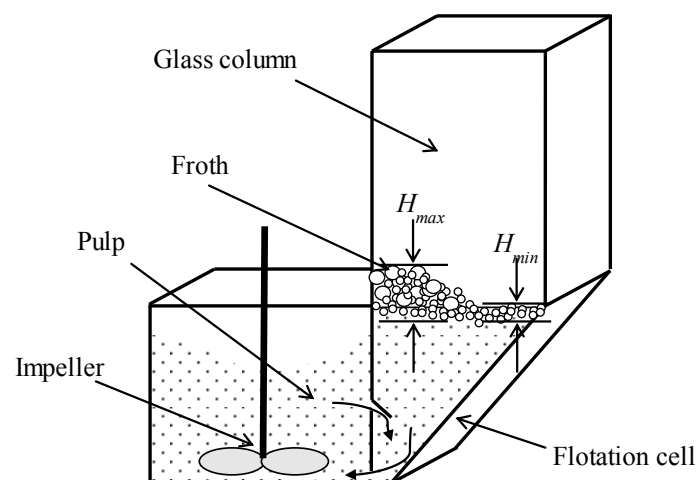


Fig. 2. Diagram of modified micro flotation cell used for froth stability tests

Flotation tests were conducted mainly to characterize the collecting properties of a single collector NaOL and mixed collectors (NaOL/alcohols). Literature reported that pH has great influence on the

surface properties of minerals during flotation process (Fuerstenau and Pradip, 2005). The flotation recovery of diaspore in different size fractions as a function of pH is shown in Fig. 4. The initial concentrations of both single and mixed collectors are 10^{-4} mol/dm³ ($C=10^{-4}$ mol/dm³). Mole fraction of NaOL in mixed NaOL/alcohols collectors is controlled at 0.60 ($x(\text{NaOL})=0.60$). It can be seen from Fig. 4 that the flotation recovery increases sharply to above 90% with increasing of pH values from 2 to 10 and then decreases slightly irrespective of the types of collectors and the size of particles. However, it is quite clear from the Fig. 4 that the collecting performance of mixed collectors is much better than that of a single collector. Flotation tests conducted with NaOL and NaOL/alcohols showed following recovery order: NaOL-PEG > NaOL-OCT > NaOL-MIBC > NaOL while the pulp pH was within 10 (see Fig. 4). The flotation results suggested that recovery of diaspore can be enhanced to a certain level with

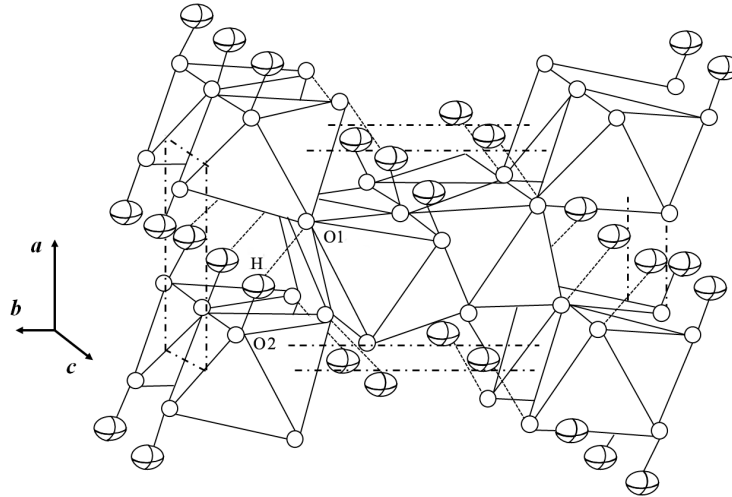


Fig. 3. Schematic diagram of crystal structure of diaspore

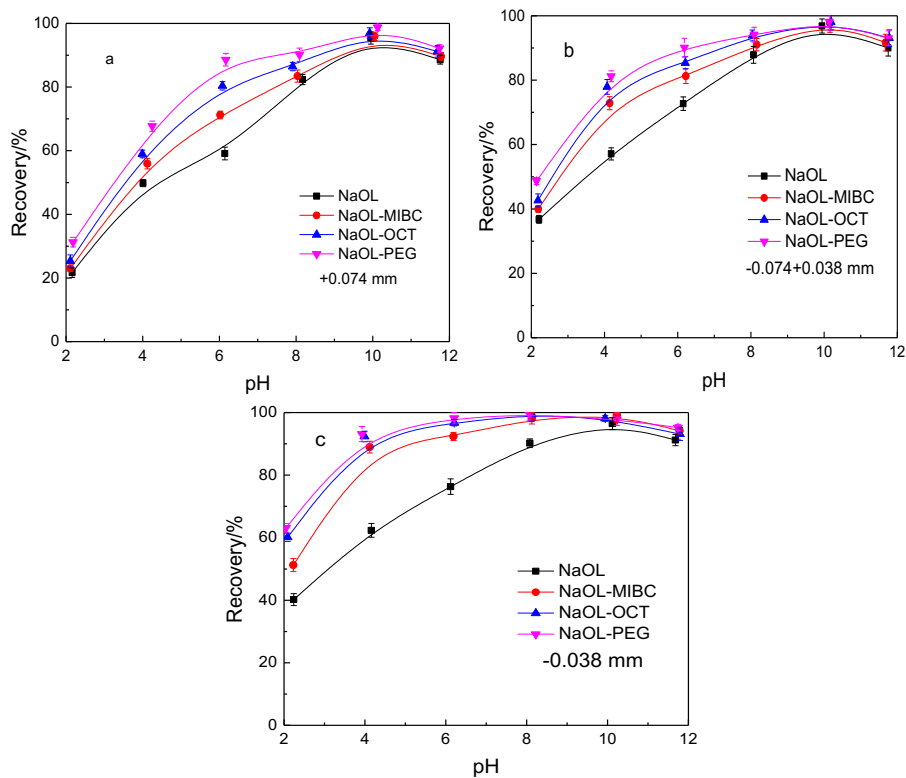


Fig. 4. Flotation recovery of diaspore in different size fractions with different collectors as a function of pH ($C = 10^{-4}$ mol/dm³, $x(\text{NaOL}) = 0.60$)

addition of alcohols. Furthermore, enhanced recovery obtained from NaOL-PEG is mainly due to its larger carbon chains. Therefore, it is confirmed that, the larger carbon chains of alcohols, higher the collecting ability of mixed NaOL/alcohols collectors. Moreover, it is seen that recovery is almost equal in all size fractions when pH is above 10 (see Fig. 4). However, the finer size fraction shows somewhat higher potential to raise the recovery which may be attributed to the fact that fine-grained diaspore can be floated more easily and/or can produce more stable froth.

The effect of collector concentrations on diaspore flotation at $\text{pH}\approx 7.0$ is presented in Fig. 5. Mole fraction of NaOL in mixed NaOL/alcohols collectors was kept same i.e. at 0.60 ($x(\text{NaOL})=0.60$). It can be seen from Fig. 5(a) that the flotation recovery increases extensively when the mixed or single collector concentration was less than $10^{-4}\text{mol}/\text{dm}^3$. Fig. 5(a) further showed that by increasing collectors' concentration from $10^{-4}\text{mol}/\text{dm}^3$, the recovery achieved from mixed collector NaOL-PEG, as PEG has the longest carbon chain relative to OCT and MIBC, reaches at maximum and remain unchanged. While in case of a single NaOL and other mixed collectors of NaOL-MIBC and NaOL-OCT, recovery continues to increase very slowly with increasing concentrations. Moreover, as seen in Fig. 5(a) that floatability of diaspore is almost identical by all four kinds of collectors when their concentration reaches $10^{-3}\text{mol}/\text{dm}^3$. In addition, the synergistic effect of mixed collectors is more significant and the collecting ability is apparently stronger than that of single NaOL when the concentration is less than $8 \times 10^{-4}\text{mol}/\text{dm}^3$. The situations of Fig. 5(b) and Fig. 5(c) are similar to that of Fig. 5(a). The difference is that the flotation recovery of -0.038 mm diaspore with NaOL slightly decreases when the concentration exceeds $4 \times 10^{-4}\text{mol}/\text{dm}^3$ and the finer particles promote the recovery relative the coarse particles.

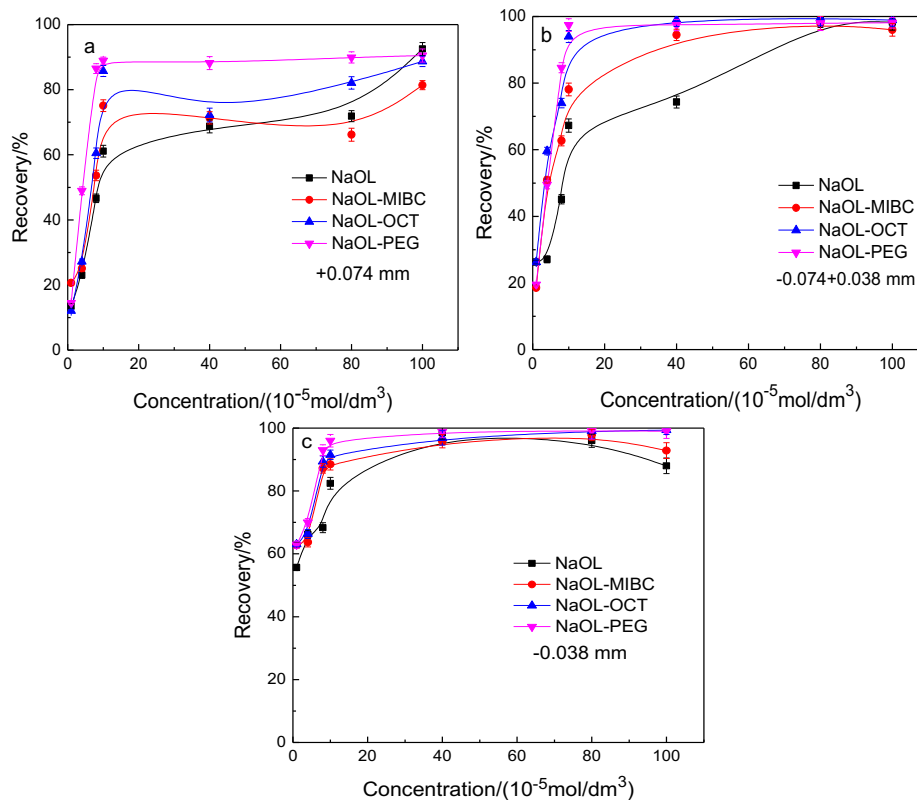


Fig. 5. Effect of collectors' concentration on flotation behavior of diaspore ($\text{pH}\approx 7.0$, $x(\text{NaOL})=0.60$)

From the flotation results of three size fractions shown in Fig. 5, it was noted the mixed collectors have more advantages over a single collector only within the certain concentration which is named as the critical advantage of concentration (C_y). The C_y values of diaspore in three size fractions $+0.074\text{ mm}$, $-0.074+0.038\text{ mm}$ and -0.038 mm are $8 \times 10^{-4}\text{mol}/\text{dm}^3$, $4 \times 10^{-4}\text{mol}/\text{dm}^3$ and $1 \times 10^{-4}\text{mol}/\text{dm}^3$ respectively. It is clear from C_y values that, the finer the size of diaspore, the smaller the value of C_y which indicated the stronger collecting ability in fine-grained diaspore.

In order to understand the effects of different mole fractions of NaOL mixed with alcohols on flotation recovery, further detailed studies were carried out. For this test, the pH and concentration of reagents were kept at 7 and 10^{-4} mol/dm³ respectively. Effects of $x(\text{NaOL})$ on flotation behavior of diaspore with mixed reagents are shown in Fig. 6. It can be seen from Fig. 6 that the recovery increases initially to the maximum level at $x(\text{NaOL}) = 0.60$ regardless of the particle size of diaspore, and then decreases marginally with increasing $x(\text{NaOL})$ from 0.60 to 1. The synergistic effect for NaOL-OCT and NaOL-PEG takes place when the mole fractions of NaOL are greater than 0.40, and for NaOL-MIBC, it requires to more than 0.50.

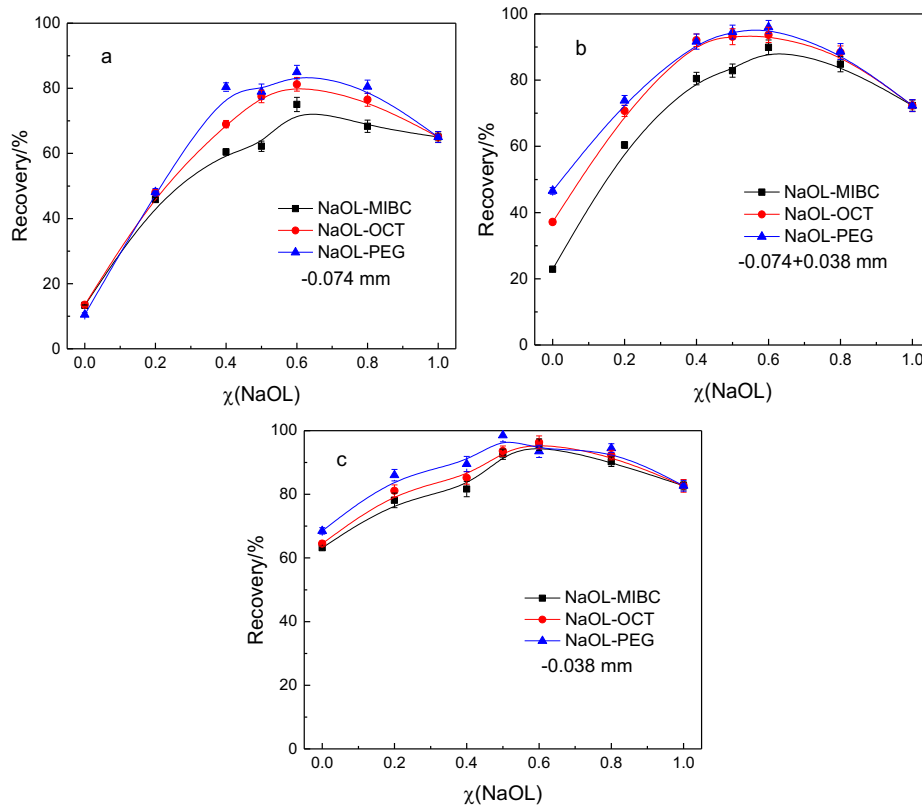


Fig. 6. Effect of $x(\text{NaOL})$ on flotation behavior of diaspore using mixed reagents ($C_{\text{mixed reagents}}=10^{-4}$ mol/dm³, pH \approx 7.0)

From the detailed investigations, it is clear that mixed collectors have a better flotation performance at a certain mole fraction and are more favorable for improving the floatability of mineral. In addition, the longer carbon chains of alcohol in mixed collectors are beneficial for the better recovery as discussed previously using results shown in Fig. 4 and Fig. 5. Flotation results for different particle size showed that the finer particle size of diaspore offers a better recovery, which can be due to the fact that fine-grained diaspore can be floated more easily and/or can produce more stable froth within the entire concentration range.

3.2. Three-phase dynamic froth stability results

The froth stability results of fine diaspore (-0.038 mm) as a function of pH are demonstrated in Fig. 7. The initial concentrations for both, single and mixed collectors, were used as 10^{-4} mol/dm³. Mole fraction of NaOL in mixed NaOL/alcohols collectors was kept at 0.60. Fig. 7 shows that the stability of the three-phase froth increases with increasing of pH. However, as seen in Fig. 7 the froth stability increases slowly and then rapidly at pH values from 2 to 10 and 10 to 12, respectively. Furthermore, the froth stability achieved for the three kinds of mixed collectors was stronger than the single NaOL at pH less than 10 (see Fig. 7). The descending order of the froth stability achieved by three kinds of mixed collectors is: NaOL-PEG > NaOL-OCT > NaOL-MIBC. Therefore, from the results of three-phase dynamic froth stability it was concluded that the mixed collectors performed better than the single

NaOL because of their more stable three-phase froth in pH range between 6 to 8, which is the best range in diaspore floatation.

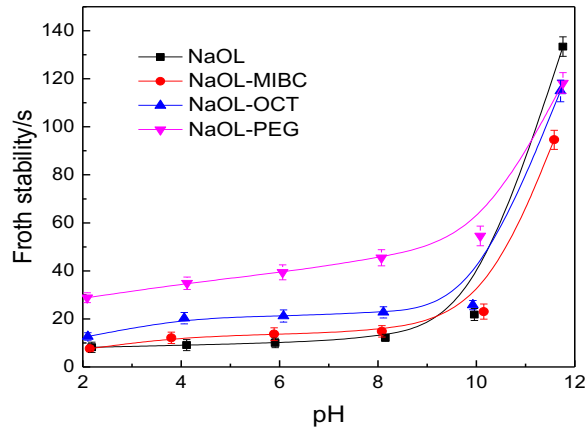


Fig. 7. Effects of pH on froth stability of diaspore under action of mixed reagents ($C=10^{-4}$ mol/dm³, $x(\text{NaOL})=0.60$)

Using NaOL-PEG, effects of different mole fractions $x(\text{NaOL})$ and concentrations on the three-phase dynamic froth stability of diaspore with particle size of -0.038 mm were investigated, and the results are summarized in Fig. 8. It can be seen from the Fig. 8 that with increasing concentrations, the froth stability under the action of single NaOL or mixed collectors gradually rises except for the single PEG, which has almost no effect on froth stability. It was noted that the mixed collectors performed better before the concentration reached to 8×10^{-4} mol/dm³ (Fig. 8), and the dynamic froth appears the most stable at $x(\text{NaOL})=0.60$ which accords with the results of floatation accurately. However, when the concentration was increased from 8×10^{-4} mol/dm³, the better the dynamic froth stability of diaspore was only achieved with the greater value of $x(\text{NaOL})$. Hence, the froth obtained by single NaOL at ($x(\text{NaOL})=1.0$) was the most stable.

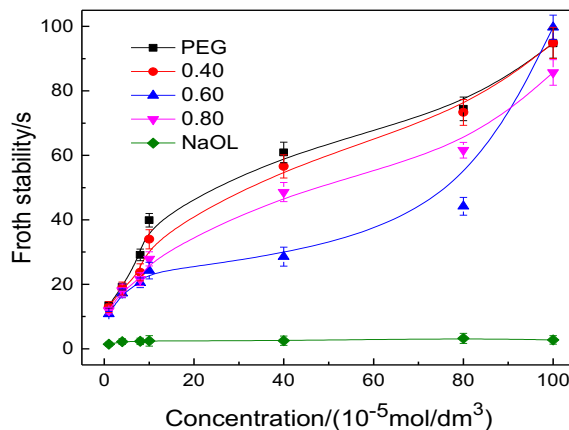


Fig. 8. Effects of concentrations of single NaOL and mixed collectors on froth stability of diaspore at $\text{pH} \approx 7.0$

It is known that the carbon chains in alcohols play a vital role in flotation of minerals. The longer the carbon chains, the better the stability and recovery. Furthermore, length of carbon chains in alcohols increase with increasing of concentration of alcohols. In present study, three different alcohols were used having different length of carbon chains. Hence, results shown in Fig. 9 indicated that the froth stability of diaspore in -0.038 mm enhances sharply and then slowly before and after 10^{-4} mol/dm³, respectively with the increase of concentration and turns out identical at 10^{-3} mol/dm³, which agrees with the results of Fig. 9 roughly. The froth stability obtained using mixed collectors is much better than single NaOL. As the PEG has longer carbon chains than OCT and MIBC, hence froth stability obtained for NaOL-PEG is better than other two NaOL-OCT and NaOL-MIBC collectors, and the

descending order obtained is NaOL-PEG > NaOL-OCT > NaOL-MIBC > NaOL. It can be inferred that different froth stability is a main reason for different flotation results.

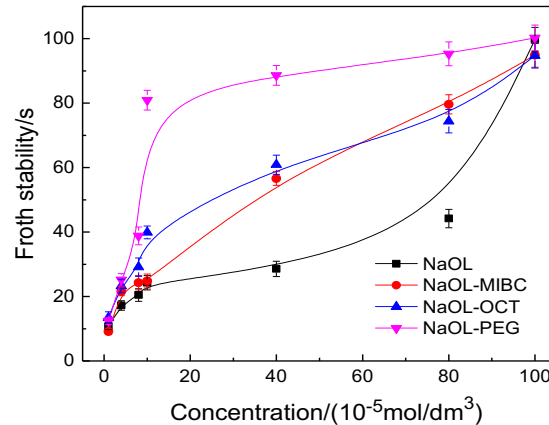


Fig. 9. Effects of single and mixed collectors on the froth stability of diaspore ($\text{pH} \approx 7.0$ $x(\text{NaOL}) = 0.60$)

From the flotation results, it is clear that the recovery obtained for fine-grained diaspore is much higher than the coarser particles. This increased recovery may be due to stronger froth stability in the finer-grained sample. Froth stability obtained for the single and mixed collectors in each size fraction at $\text{pH} = 7$ and $x(\text{NaOL}) = 0.60$ is shown in Fig. 10. It can be seen from Fig. 10 that finer diaspore particles have enhanced froth stability more than the coarser particles. Especially for -0.038 mm , the particles can keep the froth stable within the entire concentration range. Furthermore, the finer the diaspore particles, the more the froth stability is promoted in mixed reagents relative to single NaOL. (Xu et al., 2014) put forward a viewpoint through crystallographic calculation that there were more broken Al-O bonds to adsorb the oleate ions on coarse-grained diaspore surface making its hydrophobicity better. Hence it is now confirmed that the finer diaspore works better in floatation than the coarser particles owing to the appearance of much more stable flotation froth, not the increase of hydrophobicity.

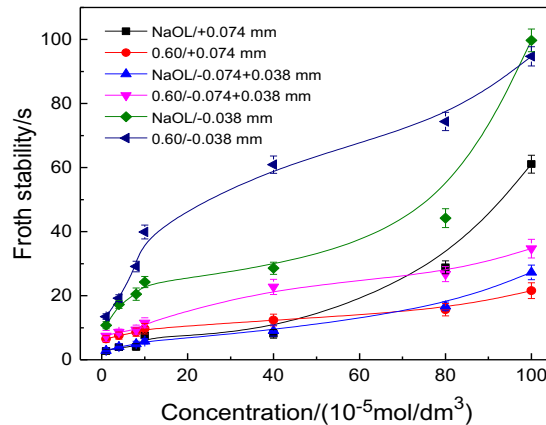


Fig. 10. Effects of mixed reagents on the froth stability of diaspore with different size fractions ($\text{pH} \approx 7.0$ $x(\text{NaOL}) = 0.60$)

3.3. Residual total organic carbon analysis

The adsorbed concentration and organic carbon of reagents on the surface of diaspore in -0.038 mm size at different initial concentrations were investigated and the results obtained are summarized in Fig. 11 (a) and (b), respectively. During investigations, the pH and the value of $x(\text{NaOL})$ were maintained at 7.0 and 0.60, respectively. It can be seen from Fig. 11 (a) that the adsorbed amount of a single NaOL collector on the diaspore surface increases linearly with initial concentrations and accounts for more than 90% of the total amount of substance in the pulp. But, on the other hand, the adsorption by alcohols PEG, OCT and MIBC on the surface is extremely low, just accounting for nearly 5%. Hence, the

concentration of NaOL used as a frother is very low making the froth stability poor which is not favorable for flotation. Moreover, as depicted in Fig. 11 (b), the amount of adsorbed organic carbon on the mineral surface raises linearly and is almost equal for all mixed collectors.

It is clear in this investigation that mixed collectors do not show a significant co-adsorption on diaspore surface and the adsorbed reagent is mainly NaOL, while the alcohol is only slightly adsorbed. Hence after being adsorbed, the concentrations of NaOL in the pulp, which also acts as frother, are approximately equal among three mixed reagents and alcohols are too. Then, the higher the alcohol activity due to its length of carbon chain, the better the three-phase dynamic froth stability. This is why the froth stability increased with the growth of the carbon chain in alcohols in mixed reagents system shown in Fig. 9.

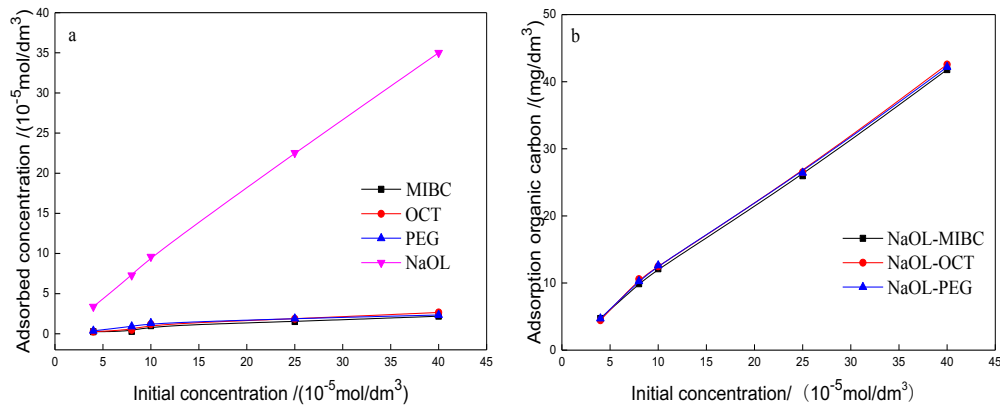


Fig. 11. Adsorbed concentration (a) and organic carbon (b) of reagents on diaspore surface at different initial concentrations ($x(\text{NaOL})=0.60$, $\text{pH}\approx 7.0$)

Furthermore, it has been calculated that the relative molecular mass of PEG is 1.97 times of that of NaOL. It means that greater the $x(\text{NaOL})$ value in mixed NaOL-OCT, the higher the amount of initial TOC. Therefore, according to the curve of adsorbed TOC in Fig. 12, it can conclude that there is more TOC adsorbed on the mineral surface with increasing of $x(\text{NaOL})$, as more NaOL is adsorbed (Fig. 11). Hence the lack of frother deteriorates the stability of three-phase dynamic froth.

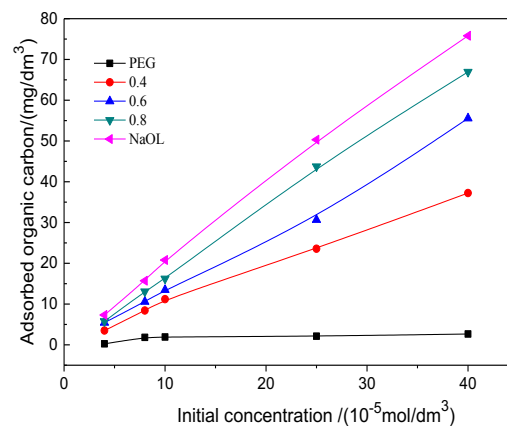


Fig. 12. Adsorbed TOC of NaOL-PEG on surface of diaspore in -0.038 mm as a function of initial concentration ($\text{pH}\approx 7.0$)

3.4. Zeta potential analysis

The zeta potential measurement has been widely used as an efficient method to interpret the trend of the modification performance caused by the presence of reagents (Tian et al., 2017b). The electrokinetic phenomenon of mineral suspension was studied in this work. The curves obtained from zeta potential measurements as a function of pulp pH are demonstrated in Fig. 13. It can be seen that the zeta potential of diaspore in water decreases with the increase of pH. Furthermore, the isoelectric point (IEP) of

diaspore samples obtained by reading the intercept of the trend lines with horizontal is about 6.8, which is according to the previous results in range of 5.8–7.7 (Barbian et al., 2003; Parks, 1965; Yoon et al., 1979). In case of single and mixed system, the zeta potential shows a downward trend as a whole with increasing pH (see Fig. 13). However, as compared to single NaOL, the mixed reagents have not reduced sufficiently the zeta potential of diaspore, which is in agreement with the results given in Fig. 11 (b) that there is no significant difference in co-adsorption on diaspore surface between NaOL and three types of alcohols PEG, OCT and MIBC. As to the flotation results, longer carbon chains of alcohols can lower more the zeta potential value.

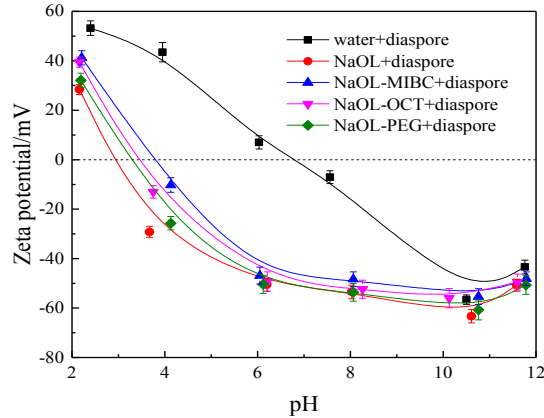


Fig. 13. Zeta potential of diaspore in single and mixed reagents system as a function of pH ($C=10^{-4}$ mol/dm³, $x(\text{NaOL})=0.60$)

Effects of NaOL and NaOL-PEG with different mole fractions $x(\text{NaOL})$ on the zeta potential of diaspore as a function of concentrations are demonstrated in Fig. 14. As seen in Fig. 14, the zeta potential of diaspore is negative throughout the whole experimental concentration ranges and decreases with increasing of concentration. This shows that with increasing of reagent concentration, more and more reagents are adsorbed on the mineral surface. Moreover, the zeta potentials of diaspore are $x(\text{NaOL}) = 0.60$, NaOL and $x(\text{NaOL}) = 0.80$ in descending order indicating that an apparent co-adsorption between NaOL and PEG is promoted at $x(\text{NaOL}) = 0.80$ in comparison with other two curves, which encourages the adsorption of reagents on the diaspore surface.

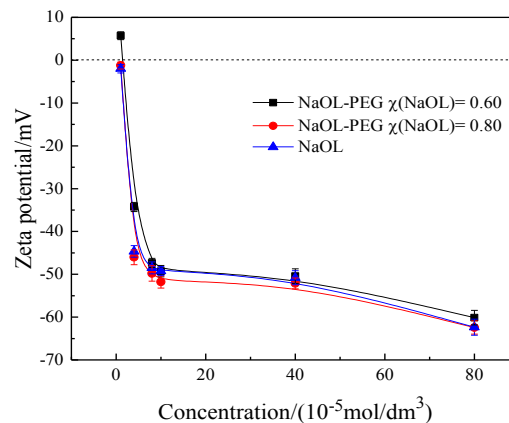


Fig. 14. Effects of NaOL and mixed reagents concentration on zeta potential of diaspore (pH \approx 7.0)

4. Conclusions

Collecting performance and froth stability of sodium oleate (NaOL) alone and in the presence of isobutyl carbinol methanol also called methyl isobutyl carbinol (MIBC), octanol (OCT) and polyethylene glycol (PEG) in flotation of natural diaspore were studied through flotation experiments, three-phase dynamic froth stability tests, zeta potential measurements and adsorption analysis. The results obtained can be summarized as follows.

- 1) As compared to NaOL alone, mixed systems (NaOL-PEG, NaOL-OCT, NaOL-MIBC) showed an improved recovery at pH<10. The optimum concentration and mole fraction of NaOL were observed at about 10^{-4} mol/dm³ and $x(\text{NaOL}) = 0.60$, respectively. Furthermore, the recovery achieved from fine-grained diaspore was relatively higher than coarse-grained.
- 2) Results of three-phase dynamic froth stability tests indicated that the froth obtained from mixed systems was more stable than single NaOL, and becoming more and more stable with increasing carbon chains in alcohols. The following descending of mixed systems was obtained: NaOL-PEG > NaOL-OCT > NaOL-MIBC.
- 3) Zeta potential and adsorption analysis showed that there was no significant adsorption of alcohols on diaspore surface. However, NaOL adsorption on the diaspore surface was extremely high and accounts for more than 90% of the total substance used in the pulp.

Acknowledgements

Authors of this paper proudly acknowledge the financial support from the National Natural Science Foundation of China (Grant Nos. 51674207, 50974134, and 51304162), the Joint Funds of National Natural Science Foundation of China (No. U170420015), the Key Laboratory of Hunan Province for Clean and Efficient Utilization of Strategic Calcium-Containing Mineral Resources (No. 2018TP1002).

References

- BARBIAN, N., VENTURA-MEDINA, E., CILLIERS, J.J., 2003. *Dynamic froth stability in froth flotation*. Minerals Engineering, 16(11), 1111-1116.
- BIKERMAN, J.J., Foams. 1973, Springer Berlin Heidelberg.
- BLANCO, E., RODRIGUEZ-ABREU, C., SCHULZ, P., RUSO, J.M., 2010. *Effect of alkyl chain asymmetry on cationic mixtures of hydrogenated and fluorinated surfactants*. Journal of Colloid & Interface Science, 341(2), 261.
- CHEN, X.Q., CHEN, X.H., JUNWEI, M.A., CHEN, Z.Y.J.L.M., 2006. *Study on the research of lower grade bauxite dressing and desilication*.
- DESAI, T.R., DIXIT, S.G., 1996a. *Interaction and Viscous Properties of Aqueous Solutions of Mixed Cationic and Nonionic Surfactants*. Journal of Colloid & Interface Science, 177(2), 471-477.
- DESAI, T.R., DIXIT, S.G., 1996b. *Coadsorption of Cationic-Nonionic Surfactant Mixtures on Polytetra Fluoroethylene (PTFE) Surface*. Journal of Colloid & Interface Science, 179(2), 544-551.
- DIXIT, S.G., VANJARA, A.K., NAGARKAR, J., NIKOORAZM, M., DESAI, T., 2002. *Co-adsorption of quaternary ammonium compounds – nonionic surfactants on solid-liquid interface*. Colloids & Surfaces A Physicochemical & Engineering Aspects, 205(1-2), 39-46.
- DRZYMALA, J., 2018. *Evaluation of flotation reagents by normalization procedures*. Physicochemical Problems of Mineral Processing, 54.
- EJTEMAEI, M., GHARABAGHI, M., IRANNAJAD, M., 2014. *A review of zinc oxide mineral beneficiation using flotation method*. Advances in Colloid & Interface Science, 206(2), 68.
- FANG, X., ZHAO, S., MAO, S., YU, J., DU, Y., 2003. *Mixed micelles of cationic-nonionic surfactants: NMR self-diffusion studies of Triton X-100 and cetyltrimethylammonium bromide in aqueous solution*. Colloid & Polymer Science, 281(5), 455-460.
- FARROKHPAY, S., 2011. *The significance of froth stability in mineral flotation – A review*. Advances in Colloid & Interface Science, 166(1-2), 1-7.
- FUERSTENAU, D.W., PRADIP, 2005. *Zeta potentials in the flotation of oxide and silicate minerals*. Advances in Colloid & Interface Science, 114-115(114-115), 9.
- GIBSON, B., WON YEN, D.G., CHELGANI, S.C., 2017. *A review of pretreatment of diasporic bauxite ores by flotation separation*. Minerals Engineering, 114, 64-73.
- GOURRAM-BADRI, F., CONIL, P., MORIZOT, G., 1997. *Measurements of selectivity due to coalescence between two mineralized bubbles and characterization of MIBC action on froth flotation*. international journal of mineral processing, 51, 197-208.
- HAO, L.S., DENG, Y.T., ZHOU, L.S., YE, H., NAN, Y.Q., HU, P., 2012. *Mixed micellization and the dissociated Margules model for cationic/anionic surfactant systems*. Journal of Physical Chemistry B, 116(17), 5213.
- HAZEMANN, J.L., MANCEAU, A., SAINCTAVIT, P., MALGRANGE, C., 1992. *Structure of the aFe x Al 1:x OOH*

- solid solution*. *Physics & Chemistry of Minerals*, 19(1), 25-38.
- HILL, R.J., 1979. *Crystal structure refinement and electron density distribution in diaspore*. *Physics & Chemistry of Minerals*, 5(2), 179-200.
- PENFOLD, J., STAPLES, E.J., TUCKER, I., THOMPSON, L.J., 1997. *Adsorption of Mixed Cationic and Nonionic Surfactants at the Hydrophilic Silicon Surface from Aqueous Solution: Studied by Specular Neutron Reflection*. *Langmuir*, 13(25), 6638-6643.
- JIANG, H., JI, W., YANG, Q., XU, L., ZHAO, C., HU, Y., 2017. *Synergistic adsorption and flotation of new mixed cationic/nonionic collectors on muscovite*. *Minerals* 7(5).
- KELLEN, W.D., 1978. *Diaspore recrystallized at low temperature*. *Physica Status Solidi*, 4(1), K19-K22.
- MAITI, K., BHATTACHARYA, S.C., MOULIK, S.P., PANDA, A.K., 2010. *Physicochemistry of the binary interacting mixtures of cetylpyridinium chloride (CPC) and sodium dodecylsulfate (SDS) with special reference to the catanionic ion-pair (coacervate) behavior*. *Colloids & Surfaces A Physicochemical & Engineering Aspects*, 355(1), 88-98.
- MALYSA, K., LINKENHEIMER, K., MILLER, R., HARTENSTEIN, C., 1981. *Surface elasticity and frothability of n-octanol and n-octanoic acid solutions*. *Colloids & Surfaces*, 3(4), 329-338.
- NEWMAN, A.C.D., 1987. *Chemistry of clays and clay minerals*. *Clay Minerals*, 22(4), 485-486.
- PARKS, G.A., 1965. *The Isoelectric Points of Solid Oxides, Solid Hydroxides, and Aqueous Hydroxo Complex Systems*. *Chemical Reviews*, 65(2).
- POORKANI, M., BANISI, S., 2005. *Industrial use of nitrogen in flotation of molybdenite at the Sarcheshmeh copper complex*. *Minerals Engineering*, 18(7), 735-738.
- RAO, K.H., FORSSBERG, K.S.E., 1997. *Mixed collector systems in flotation*. *International Journal of Mineral Processing*, 51(1-4), 67-79.
- ROJAS, Y.V., CHI, M.P., LOU, X., 2010. *Dynamic surface tension studies on poly(N -vinylcaprolactam/ N -vinylpyrrolidone/ N , N -dimethylaminoethyl methacrylate) at the air-liquid interface*. *Colloids & Surfaces A Physicochemical & Engineering Aspects*, 355(1-3), 99-103.
- RUBINGH, D.N., JONES, T., 1982. *Mechanism of detergency in systems containing cationic and nonionic surfactants*. *Ind.eng.chem.prod.res.dev*, 21(2), 176-182.
- RYBINSKI, W.V., SCHWUGER, M.J., 1986. *Adsorption of surfactant mixtures in froth flotation*. *Langmuir*, 2(2), 639-643.
- SOMASUNDARAN, P., KRISHNAKUMAR, S., 1997. *Adsorption of surfactants and polymers at the solid-liquid interface*. *Colloids & Surfaces A Physicochemical & Engineering Aspects*, s 123-124, 491-513.
- TAO, D., LUTTRELL, G.H., YOON, R.H., 2000. *A parametric study of froth stability and its effect on column flotation of fine particles*. *International Journal of Mineral Processing*, 59(1), 25-43.
- TIAN, J., XU, L., DENG, W., JIANG, H., GAO, Z., HU, Y., 2017a. *Adsorption mechanism of new mixed anionic/cationic collectors in a spodumene-feldspar flotation system*. *Chemical Engineering Science*, 164, 99-107.
- TIAN, J., XU, L., DENG, W., JIANG, H., GAO, Z., HU, Y., 2017b. *Adsorption mechanism of new mixed anionic/cationic collectors in a spodumene-feldspar flotation system*. *Chem. Eng. Sci.*, 164,, 99-107.
- VORA, S., GEORGE, A., DESAI, H., BAHADUR, P., 1999. *Mixed micelles of some anionic-anionic, cationic-cationic, and ionic-nonionic surfactants in aqueous media*. *Journal of Surfactants & Detergents*, 2(2), 213-221.
- WANG, L., HU, Y., SUN, W., SUN, Y., 2015. *Molecular dynamics simulation study of the interaction of mixed cationic/anionic surfactants with muscovite*. *Applied Surface Science*, 327(327), 364-370.
- WANG, R., LI, Y., LI, Y., 2014. *Interaction Between Cationic and Anionic Surfactants: Detergency and Foaming Properties of Mixed Systems*. *Journal of Surfactants & Detergents*, 17(5), 881-888.
- XIA, L., ZHONG, H., LIU, G., 2010. *Flotation techniques for separation of diaspore from bauxite using Gemini collector and starch depressant*. *Transactions of Nonferrous Metals Society of China*, 20(3), 495-501.
- XU, L., HU, Y., DONG, F., GAO, Z., WU, H., WANG, Z., 2014. *Anisotropic adsorption of oleate on diaspore and kaolinite crystals: Implications for their flotation separation*. *Applied Surface Science*, 321, 331-338.
- XU, L., HU, Y., TIAN, J., WU, H., WANG, L., YANG, Y., WANG, Z., 2016. *Synergistic effect of mixed cationic/anionic collectors on flotation and adsorption of muscovite*. *Colloids & Surfaces A Physicochemical & Engineering Aspects*, 492, 181-189.
- YOON, R.H., SALMAN, T., DONNAY, G., 1979. *Predicting points of zero charge of oxides and hydroxides*. *Journal of Colloid & Interface Science*, 70(3), 483-493.
- ZHAO, S., ZHU, H., LI, X., HU, Z., CAO, D., 2010. *Interaction of novel anionic gemini surfactants with cetyltrimethylammonium bromide*. *Journal of Colloid & Interface Science*, 350(2), 480-485.