



A comparison study of the flotation and adsorption behaviors of diaspore and kaolinite with quaternary ammonium collectors



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ARTICLE INFO

Article history:

Received 25 October 2013

Accepted 29 May 2014

Available online 21 June 2014

Keywords:

Diaspore

Kaolinite

Flotation

Adsorption

Quaternary ammonium collectors

ABSTRACT

The flotation and adsorption behaviors of two quaternary ammonium collectors DTAC (dodecyl trimethyl ammonium chloride) and CTAC (cetyltrimethyl ammonium chloride) on diaspore and kaolinite were investigated in this work. The flotation recovery of diaspore increases with the increase of pH and the decrease of particle size, however, the situations for kaolinite are opposite. Furthermore, the influence of pH on flotation of kaolinite decreases with the decrease of particle size, and for the fine particles (undersize 0.045 mm), the flotation recovery with CTAC which has a longer hydrocarbon chain and is believed to have a stronger collecting ability is lower than that with DTAC. The dramatic differences of the flotation behaviors between diaspore and kaolinite are correlated to the differences of their crystal structures. The morphologies of diaspore and kaolinite particles in different size were studied by SEM. The kaolinite particles have much larger specific surface areas (about 7 times) than the diaspore particles due to their layered structure. This leads to the differences of collector adsorption behaviors on kaolinite and diaspore and results in the different flotation behavior.

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1. Introduction

Diaspore-type bauxite is the major aluminum resource in China. However, for most of them, the mass ratio of Al_2O_3 to SiO_2 (A/S) is between 4 and 6, which should be improved to meet the basic condition ($A/S > 10$) of Bayer process (Liu et al., 2011; Zhong et al., 2008). The reverse flotation for silica removal was developed as an economical way to improve the A/S ratio (Hu et al., 2003; Jiang et al., 2001). Reverse flotation is widely used in mineral processing such as reverse flotation of coal (Stonestreet and Franzidis, 1992) and reverse flotation of iron ore (Dos Santos and Oliveira, 2007). In the reverse flotation of diaspore-type bauxite, gangue minerals (mainly kaolinite, etc.) are floated from valuable minerals (mainly diaspore).

During the latest ten years, many studies have been conducted to investigate the flotation behaviors of kaolinite and diaspore in order to understand and control the diasporic bauxite reverse flotation (Cao et al., 2004; Hu et al., 2003, 2005; Jiang et al., 2001; Liu et al., 2011; Ma et al., 2009; Zhong et al., 2008). Cationic collectors such as alkyl quaternary ammonium salts (Hu et al., 2003), amino amides (Zhao et al., 2003a,b), polyamine and ether amine (Cao

et al., 2004) were tested and proved to be effective collectors for bauxite reverse flotation. However, some situations such as the flotation recovery of kaolinite decreases with the pH increase (Hu et al., 2005; Jiang et al., 2001) are abnormal and their mechanisms are not very clear.

Generally, many flotation phenomena can be interpreted by considering the adsorption of collectors and modifying reagents. Several experimental techniques such as electron spin resonance (Chandar et al., 1987b; Waterman et al., 1986), UV spectroscopy and fluorescence probe studies (Chandar et al., 1987a; Somasundaran et al., 1986), and Raman spectroscopy (Somasundaran et al., 1989) have been employed to study the adsorption mechanisms as well as the structure of adsorbed collectors. The adsorption of cationic collectors on dioxide minerals is governed mainly by the electrostatic interaction and hydrophobic interaction (Cases and Villieras, 1992) which includes interaction between the collector and the surface as well as the interaction between collector molecules. Initially, collector cations adsorb physically as individual ions on the negatively charged surface sites. In this stage, the cations exchange with protons or other counterions present at the solid–water interface (Tahani et al., 1999). Once the surface charge has been neutralized, the adsorption will only increase if the interaction of the hydrophobic part of the collector for water can promote self-association and consequently, adsorption (Tahani et al., 1999).

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To make a contribution toward the understanding of the bauxite reverse flotation, the flotation and adsorption behaviors of diaspore and kaolinite in different size fractions with two quaternary ammonium collectors (DTAC and CTAC) were studied. The morphologies of the particles in different sizes were characterized by SEM and AFM. The differences of flotation behaviors between diaspore and kaolinite were interpreted by focusing on the differences of crystal structure and adsorption behaviors of collectors.

2. Experimental

2.1. Minerals and chemicals

Kaolinite and diaspore were obtained from Xiaoguan in Henan province, China and Xiaoyi in Shanxi province, China, respectively. The samples were handpicked and ground by porcelain mill and sieved into three size fractions (0.075–0.1 mm, 0.045–0.075 mm and <0.045 mm). The purity of minerals samples determined by chemical composition analysis (Table 1) and X-ray diffractometry (XRD) indicates that they are sufficiently pure to meet the requirements of subsequent experiments.

DTAC and CTAC of analytical grade from Nanjing Robiot Co., Ltd. were used as collectors as well as frothers. Bromothymol blue (BTB) of analytical grade from Damao Chemical Reagent Factory China was used as an indicator. HCl and NaOH of analytical grade from Damao Chemical Reagent Factory China were used to adjust the pH of the system. Deionized water was used in this experiment.

2.2. Methods

Flotation tests of pure minerals were performed in a 40 mL plexiglass cell filled with distilled water by using 2 g of desired size fraction samples for each test. The rotational speed in the cell during flotation was 1600 rpm. The pH was adjusted to a desired value with addition of HCl and NaOH. The samples were conditioned with reagents for 5 min in the cell at 1600 rpm. The 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 mass of the products.

Zeta potentials were determined using a Brookhaven ZetaPlus Zeta Potential Analyzer (USA). The mineral samples were ground to <2 µm and the suspensions concentration 0.04wt% was prepared in the 1×10^{-3} mol/L NaCl solution.

The morphologies of the particles in different sizes obtained by sedimentation were characterized by SEM (JEOL, JSM-5600LV, Japan) and TMAFM (DI Nanoscope multimodeV, USA). The specific surface area of diaspore and kaolinite in different size ranges were determined by the BET nitrogen adsorption.

The amount of collectors adsorbed on minerals surfaces was determined by UV spectrophotometry (Unico UV-2012, China) in this work. At a pH 7.5–8.5 buffer solution of phosphate, the color of bromothymol blue solution will decrease due to the association reaction between quaternary ammonium salts and bromothymol blue. This phenomenon enables the determination of quaternary ammonium concentration by spectrophotometric method (Wu et al., 2002). We used the same method as that of Wu et al.

(2002) to determine the concentration of quaternary ammonium. 10.0 mL quaternary ammonium salts sample solution with unknown concentration, 2.0 mL 0.5 wt% emulsifier OP solution, 5 mL 2.5×10^{-4} mol/L bromothymol blue solution, and 2.5 mL pH 7.7 buffer solution prepared from disodium hydrogen phosphate and potassium dihydrogenphosphate were added in an 80 mL beaker. After sufficient mixing through shaking the beaker, the absorbance of the solution at 618 nm wavelength was determined by UV spectrophotometry (Unico UV-2012, China). The quaternary ammonium salts concentration of the sample solution was then determined by comparing the absorbance to the standard curve obtained at the same conditions but the known ammonium salts concentration of the sample solution. If the determined concentration exceeds 5×10^{-5} mol/L, the sample solution was diluted and retested again due to the breaking of Beer's law according to the test of standard sample.

Pure mineral sample (2 g) of desired size fraction was placed in the 40 mL plexiglass cell filled with distilled water. The pH was adjusted to a desired value with the addition of HCl and NaOH. The samples were conditioned with collectors for 5 min in the flotation cell at 1600 rpm. The solid particles were then separated by centrifugation at 12,000 r/min for 10 min. The concentration of the collector in the supernatant solution (residual collector concentration) was determined by UV spectrophotometry. The amount of collector adsorbed on the mineral particles was calculated as (Beaussart et al., 2009):

$$\Gamma = \frac{V(C_0 - C)}{mA} \quad (1)$$

where C_0 and C are the initial and supernatant concentrations, respectively; V is the solution volume; m is the amount of the particles per sample; A is the particle specific surface area.

3. Results

3.1. Flotation results of diaspore and kaolinite

Fig. 1 shows the flotation results of diaspore and kaolinite with DTAC and CTAC as a function of the solution pH. The initial concentration of DTAC and CTAC are 4×10^{-4} mol/L. It is evident that the flotation recovery of diaspore with DTAC and CTAC increases with the increase of solution pH and the decrease of the particle size fraction. However, the situations are completely opposite for the flotation of kaolinite. The flotation recovery of kaolinite decreases with increasing the pH value, which is consistent with previous literatures (Hu et al., 2003; Jiang et al., 2001), but for the fine particles (undersize 0.045 mm), the decreases are mostly vanished. The flotation recovery with CTAC which has a longer hydrocarbon chain is better than that with DTAC for both diaspore and kaolinite except for the fine kaolinite (undersize 0.045 mm).

3.2. Zeta potential of diaspore and kaolinite

As shown in Fig. 2, the zeta potential of diaspore and kaolinite in water decreases with the increase of pH, and the zeta potential of diaspore is higher than that of kaolinite. These are consistent with many previous literatures (Hu et al., 2003, 2005; Liu et al., 2011).

Table 1
Chemical analyses of the pure minerals (%).

Mineral	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	LOI ^a
Diaspore	80.98	0.78	0.29	2.84	0.01	0.046	0.007	0.025	14.5
Kaolinite	39.2	43.67	0.32	1.98	0.01	0.068	0.094	0.028	13.98

^a Loss on ignition.

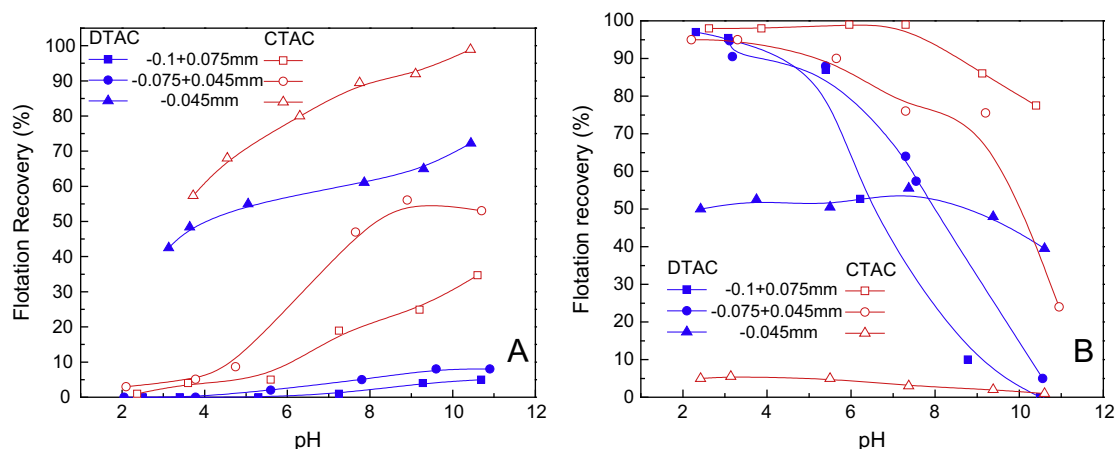


Fig. 1. The flotation results of diaspore (A) and kaolinite (B) in different size fractions with DTAC and CTAC as a function of solution pH, the initial concentration of both DTAC and CTAC are 4×10^{-4} mol/L.

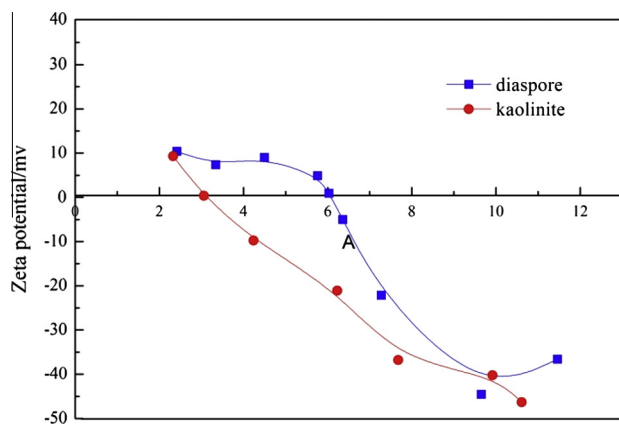


Fig. 2. Zeta potential of diaspore and kaolinite in water as a function of pH.

The IEP (isoelectric point) of diaspore and kaolinite obtained in this work are 6.0 and 3.1, respectively.

3.3. Particle morphology and specific surface area

Fig. 3 shows the SEM micrograph of diaspore and kaolinite particles of the size smaller than $10 \mu\text{m}$. As shown in Fig. 3, the diaspore particles are stumpy rods with length-diameter. Kaolinite particles are thin slice is.

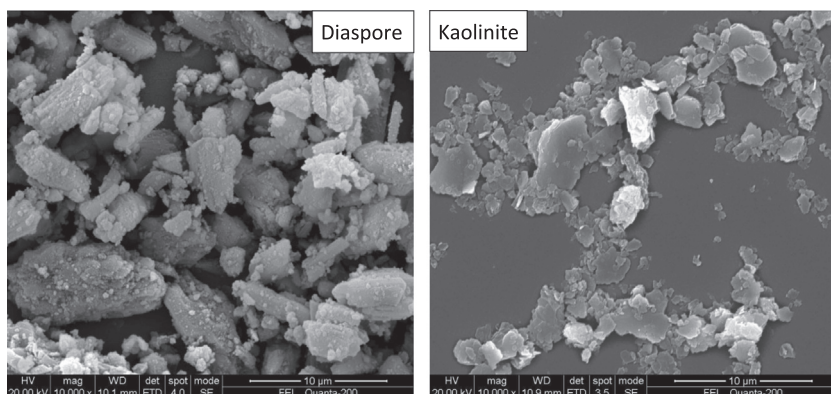


Fig. 3. SEM micrographs of diaspore and kaolinite of the particle size under $10 \mu\text{m}$.

The specific surface areas of diaspore and kaolinite in different size fractions determined by the BET test were shown in Table 2. As the particle size decreasing, the specific surface area of both diaspore and kaolinite increases, and the specific surface area of kaolinite is much larger than that of diaspore (about 6–7 times).

3.4. Adsorption of collectors

The adsorption measurements of DTAC and CTAC on diaspore and kaolinite were shown in Figs. 4 and 5 as a function of pH. The initial concentration of both DTAC and CTAC are 4×10^{-4} mol/L. The adsorbed collector density on diaspore and kaolinite increases with the increase of hydrocarbon chain length. As shown in the Figs. 4 and 5, there are four main differences of the adsorption behaviors between diaspore and kaolinite: (1) the adsorbed collector density of diaspore increases dramatically with increasing the pH, while that on kaolinite just has a slight increase; (2) the adsorbed collector density on diaspore is larger than that on kaolinite for a given size fraction; (3) the adsorbed collector density on diaspore increases but that on kaolinite decreases with the decrease of particle size; (4) the residual collector concentration of diaspore solution is much larger than that of kaolinite solution. The lowest collector residual concentration of diaspore solution in this study is about 1×10^{-4} mol/L, while that of kaolinite solution is too low to be detected.

The adsorption isotherms of DTAC and CTAC on diaspore and kaolinite surface were shown in Fig. 6. As shown in Fig. 6, the adsorbed densities of CTAC are all higher than that of DTAC in

Table 2
Specific surface areas of diasporite and kaolinite in different size fractions.

Size range/mm	Diasporite (m^2/g)	Kaolinite (m^2/g)	K/D
$-0.1 + 0.075$	1.519	10.013	6.59
$-0.075 + 0.045$	1.562	11.632	7.45
-0.045	2.173	14.246	6.56

K/D is the ratio of the specific surface area of kaolinite to that of diasporite in the same size fraction.

the same size fraction. The adsorption isotherms of DTAC and CTAC on diasporite surface have a sharp increase and then reach the maximum, while those on kaolinite surface also have a sharp increase then a slight increase and reach the maximum finally. The adsorbed densities on kaolinite surface reach maximum at higher residual concentration (equilibrium concentration) than those at diasporite surface. The maximum adsorbed densities of DTAC and CTAC on kaolinite surface are higher than those on diasporite surface. The adsorbed amount of DTAC and CTAC on kaolinite surface decreases with the decrease of particle sizes. However, that on diasporite surface increase as particle sizes decreasing.

4. Discussion

4.1. Crystal structure and specific surface area and zeta potential

The crystal structure of diasporite consists of hexagonal closest packed oxygen sheets with Al filling two thirds of the octahedral site. Each occupied octahedron shares four edges with adjacent Al octahedral to form double chains in the *c* axis direction. These units are joined to similar units by sharing the apical oxygen. Aluminum ions occupy octahedrally coordinated sites between layers in such a way to form strips of octahedral (Liu et al., 2003). Therefore, diasporite particles often are in the shape of stumpy rods as shown in Fig. 3. On the other hand, kaolinite, as one kind of 1:1 clay, has crystal units of one silica tetrahedral layer alternating with one alumina octahedral layer. The two sheets of each crystal unit of kaolinite are held together by oxygen ions, which are mutually shared by the silicon and aluminum ions in their respective sheets. These units, in turn, are held together rather tightly by hydrogen bonding (Sadek et al., 2006). Therefore, the kaolinite particles are always thin slice with two basal planes (001) and (00 $\bar{1}$) and the edge surfaces (110) and (010) (Hu et al., 2005). This could be confirmed in Fig. 3. The difference of the particle shape between

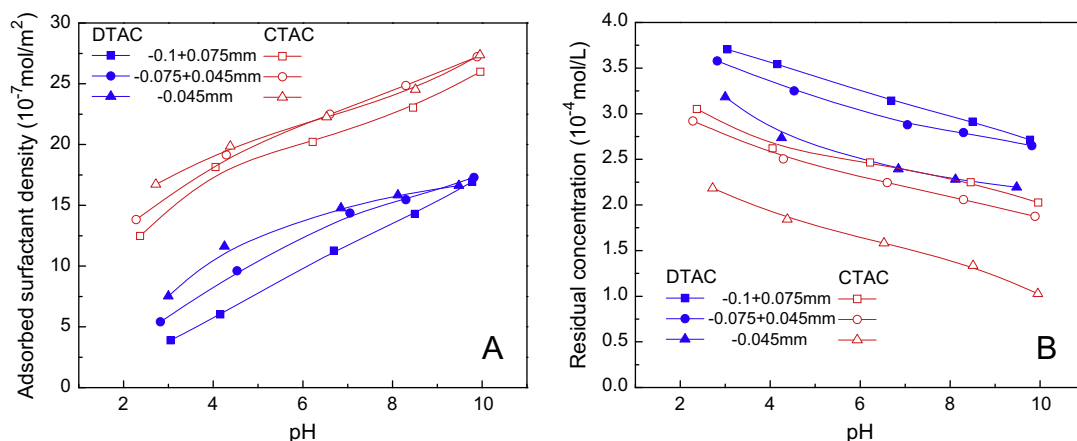


Fig. 4. The adsorbed collector density on diasporite surfaces (A) and corresponding residual concentration in diasporite solution (B) in different size fractions as a function of pH, in the initial concentration of DTAC and CTAC, $4 \times 10^{-4} \text{ mol/L}$.

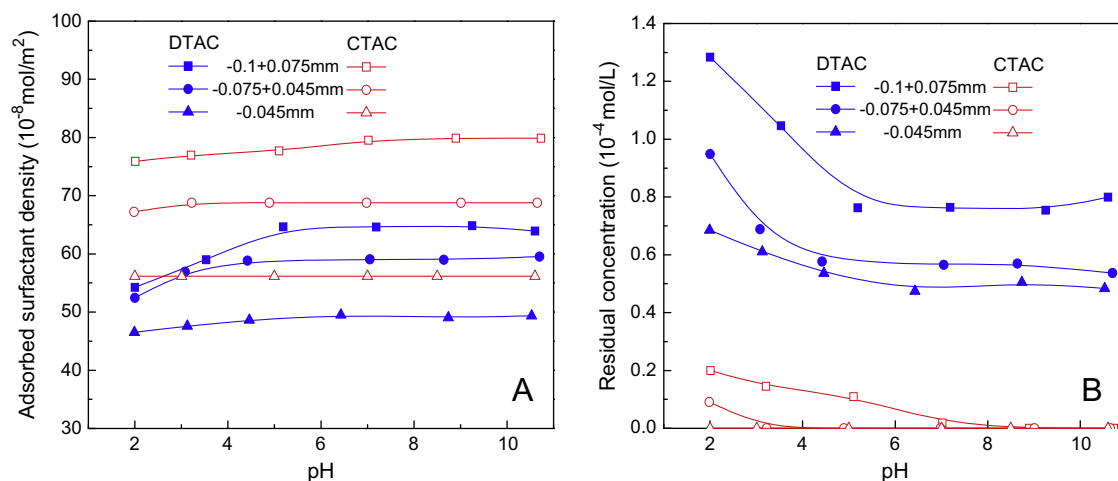


Fig. 5. The adsorbed collector density on kaolinite surfaces (A) and corresponding residual concentration in kaolinite solution (B) in different size fractions as a function of pH, in the initial concentration of DTAC and CTAC, $4 \times 10^{-4} \text{ mol/L}$.

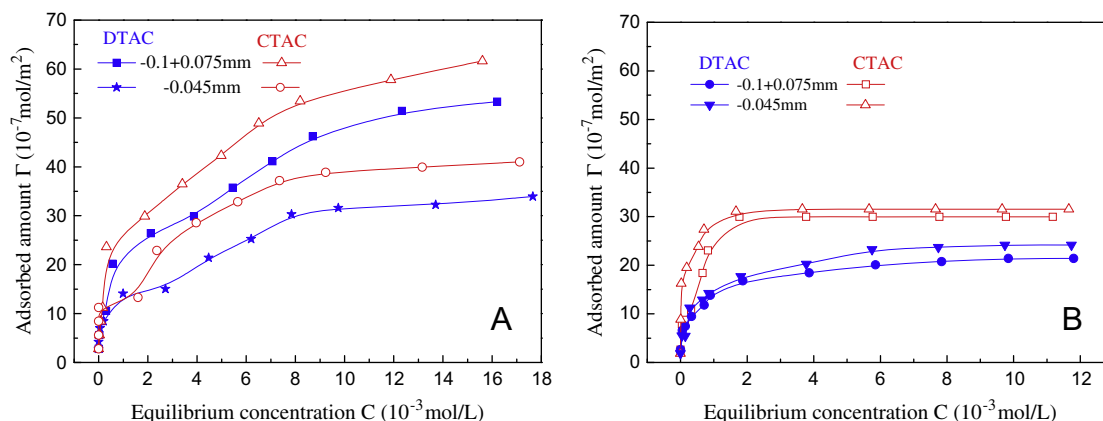


Fig. 6. Adsorption isotherms of DTAC and CTAC on kaolinite (A) and diasporite (B) in different size fractions.

diasporite and kaolinite leads to the dramatic difference of the specific surface area. As shown in Table 2, the specific surface area of kaolinite is about 7 times larger than that of diasporite of the same size fraction. At the same time, the structure of kaolinite make the charged anisotropy. The colloidal force measurements reveal that the silica tetrahedral face of kaolinite is negatively charged at $\text{pH} > 4$, whereas the alumina octahedral face of kaolinite is positively charged at $\text{pH} < 6$, and negatively charged at $\text{pH} > 8$ (Gupta and Miller, 2010). In the present work, the isoelectric point of kaolinite is $\text{pH} 3.1$, which is total charge of kaolinite. Diasporite is made of alumina octahedral and the isoelectric point is $\text{pH} 6.0$.

4.2. Collectors adsorption

As the pH increases, the zeta potential of both diasporite and kaolinite decreases (see Fig. 2). Therefore, the adsorbed collector density on diasporite and kaolinite of both DTAC and CTAC increases with pH (see Figs. 4A and 5A). The higher adsorbed collector density of quaternary ammonium with longer hydrocarbon chain (CTAC) (see Figs. 4A and 5A) indicates the important role of chain–chain interaction on the adsorption of collector. As the hydrocarbon-chain length increases, the stronger interaction of hydrocarbon chains will promote self-association and lead to an increase of adsorbed collector density (see Fig. 6). For diasporite, the adsorbed collector density increases with the decrease of the particle size (see Fig. 4A), because the particles with smaller size have higher surface free energy which makes them more likely to interact with collector. The situation for kaolinite is confusing since the adsorbed collector density decreases with the decrease of the particle size. Another confusing adsorption behavior is the lower adsorbed collector density of kaolinite with respect to diasporite of the same size fraction (see Figs. 4A and 5A). In the reverse flotation of diasporite-type bauxite, it is believed that gangue minerals, such as kaolinite, have stronger interaction with cationic collector than diasporite, and therefore, cationic collector can be used to separate diasporite from the gangue minerals (Hu et al., 2003). These two confusing adsorption behaviors may be caused by large specific surface area of kaolinite (about 7 times larger than that of diasporite). The large specific surface area of kaolinite leads to a much lower collector residual concentration in the kaolinite solution with respect to diasporite solution (see Figs. 4B and 5B). The low collector residual concentration imposes resistance on the adsorption of collector and leads to a lower adsorbed collector density of kaolinite. This is confirmed by the adsorption isotherms of DTAC and CTAC on diasporite and kaolinite surfaces (see Fig. 6). The adsorbed amount on kaolinite surfaces is higher than that on diasporite surfaces at high collector residual concentration (see

Fig. 6). As the particles size of kaolinite decreasing, the increased specific surface area leads to a lower collector residual concentration and the stronger resistance on the adsorption of collector results in a decrease of adsorbed collector density. It is interesting to note that the slight increment of kaolinite with increasing pH (see Fig. 5B) may also due to the strong resistance from the low collector residual concentration in the solution.

4.3. Flotation behavior

The flotation behavior of diasporite can be explained by classical understanding of cationic flotation of oxides and silicates. As pH increases, the increased adsorbed collector density (see Fig. 4A) results in the increase of hydrophobicity on diasporite particles surfaces, and consequently, the increase of flotation recovery (see Fig. 1A). The increase of diasporite flotation recovery with the decrease of particle size and the increase of hydrocarbon chain length is also due to the increase of adsorbed collector density and hydrophobicity.

The flotation behaviors of kaolinite are more complicated with respect to those of diasporite. As the pH increases, the mild increase of adsorbed collector density (see Fig. 5A) has not led to the increase but the decrease of kaolinite flotation recovery (see Fig. 1B). It seems difficult to explain the flotation behavior of kaolinite particles under size 0.045 mm which is almost independent with solution pH value (see Fig. 1B) from this consideration. It is also confusing that the flotation recovery of kaolinite under size 0.045 mm with CTAC which has a longer hydrocarbon chain and thus has a stronger collecting ability is lower than that with DTAC (see Fig. 1B). The decrease of kaolinite flotation recovery with the particle size may be attributed to the decreased adsorbed collector density. However, at pH above 8.0 , the flotation recovery with DTAC of kaolinite under size 0.045 mm is much larger than that of kaolinite in particle size above 0.045 mm . These dramatically different flotation behaviors of kaolinite from those of diasporite in this work are believed to be correlated with the differences of adsorption behavior and aggregation of kaolinite particles because electrostatic attraction may take place between positively charged faces and negatively charged faces. At the same time, the froth stability plays the other important role. In this work, the collector quaternary ammonium also acts as frother: one portion of the collector adsorbs on the mineral surface and changes the particle hydrophobicity, and the other remains in the pulp to stabilize the froth. The flotation recovery of kaolinite under size 0.045 mm with CTAC attributes to the too low collector residual concentration.

5. Conclusions

Due to the difference of particle morphology between diasporite and kaolinite, the specific surface area of kaolinite is about 7 times larger than that of diasporite with the same particle size fraction. This intrigues many different adsorption behaviors between diasporite and kaolinite: (1) adsorbed collector density of diasporite increases dramatically with increasing the pH, while that of kaolinite just has a slight increase; (2) adsorbed collector density of diasporite is larger than that of kaolinite at the same size fraction; (3) residual concentration of diasporite solution is much larger than that of kaolinite solution. The lowest collector residual concentration of diasporite solution in this study is about 1×10^{-4} mol/L, while that of kaolinite solution is too low to be detected. As the particle size decreasing, the flotation recovery of diasporite increases but that of kaolinite decreases reversely.

There are several anomalous kaolinite flotation behaviors in this work. The flotation recovery of kaolinite undersize 0.045 mm with DTAC is much larger than that of with CTAC and is almost independent on pH. The flotation recovery of kaolinite above the particle size of 0.045 mm decreases with increasing pH. The anomalous flotation behavior attributes to adsorption behavior and aggregation as well as the froth stability because quaternary ammonium acts as collector and frother.

Acknowledgements

The authors would like to thank the Project support by National Natural Science Foundation of China Grant Nos. 50974134 and 51304162 and the National Basic Research Program of China Grant No. 2005CB623701 for this research.

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