

Effects of particle size and chain length on flotation of quaternary ammonium salts onto kaolinite

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Abstract Effects of particle size and chain length on flotation of quaternary ammonium salts (QAS) onto kaolinite have been investigated by flotation tests. Dodecyltrimethylammonium chloride (DTAC) and cetyltrimethylammonium chloride (CTAC) were used as collectors for kaolinite in different particle size fractions (0.075~0.01 mm, 0.045~0.075 mm, 0~0.045 mm). The anomalous flotation behavior of kaolinite have been further explained based on crystal structure considerations by adsorption tests and molecular dynamics (MD) simulation. The results show that the flotation recovery of kaolinite in all different particle size fractions decreases with an increase in pH. As the concentration of collectors increases, the flotation recovery increases. The longer the carbon chain of QAS is, the higher the recoveries of coarse kaolinite (0.075~0.01 mm and 0.045~0.075 mm) are. But the flotation recovery of the finest kaolinite (0~0.045 mm) decreases with chain lengths of QAS collectors increasing, which is consistent with the flotation results of unscreened kaolinite (0~0.075 mm). It is explained by the froth stability related to the residual concentration of QAS collector in mineral pulp. In lower residual concentration, the froth stability becomes worse. Within the range of flotation collector concentration, it's easy of CTAC to be

completely adsorbed by kaolinite in the particle size fraction (0~0.045 mm), which led to lower flotation recovery. Moreover, it is interesting that the coarser particle size of kaolinite is, the higher flotation recovery is. The anomalous flotation behavior of kaolinite is rationalized based on crystal structure considerations. The results of MD simulations show that the (001) kaolinite surface has the strongest interaction with DTAC, compared with the (00 $\bar{1}$) face, (010) and (110) edges. On the other hand, when particle size of kaolinite is altered, the number of basal planes and edge planes is changed. It is observed that the finer kaolinite particles size become, the greater relative surface area of edges and the more the number of edges are. It means that fine kaolinite particles have more edges to adsorb fewer cationic collectors than that of coarse kaolinite particles, which is responsible for the poorer floatability of fine kaolinite.

Introduction

Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) is a mineral that has a wide range of applications in industry, such as ceramics, paper, paints, plastic and so on. Kaolinite has an important role because of its high abundance in nature, relatively pure chemical composition, and well characterized crystal structure (Chassagne et al. 2009). Kaolinite is also the dominant silica-bearing minerals in Chinese diasporic bauxites. Diasporic-bauxite is a major source for aluminium oxide production in China, which is characterized by its low mass ratio of Al_2O_3 to SiO_2 (A/S) (Zhong et al. 2008). This kind of bauxite ores cannot be treated economically by Bayer's process unless A/S in the ores is improved higher than 8. For the economical utilization of Chinese diasporic bauxites, reverse flotation for silica (especially kaolinite) removal to increase A/S has been proved to be an efficient method (Xia et al. 2009). In the case of flotation desilication, cationic collectors display a superior

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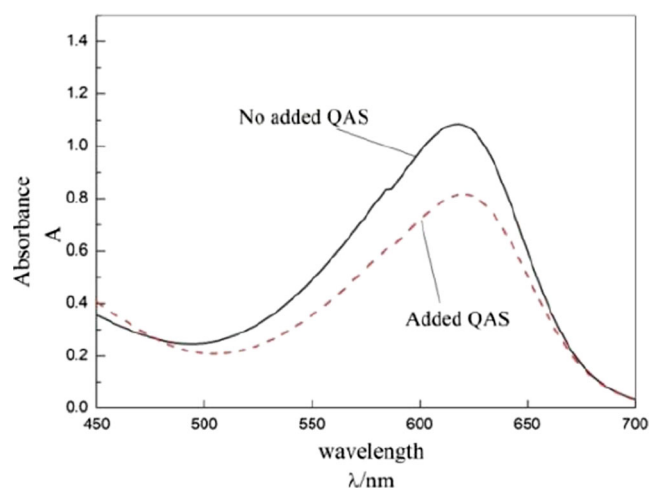


Fig. 1 Absorption spectra of BTB solution

collecting power for the silicate minerals. Thereby various cationic collectors have been extensively studied in recent years. The main collectors cover alkylamines, tertiary amine, quaternary ammonium, acylamide, ether amine, polyamine, amidoamine and so on (Zhao et al. 2003; L-y et al. 2009; Liu et al. 2011). In summary, these cationic surfactants used as collectors in silicate minerals flotation cannot be widely applied because of many shortcomings. But quaternary ammonium is well characterized by stability in solution, low toxicity, light irritation and low corrosive, etc. At the same time, quaternary ammonium is less influenced by pH and existing in the form of ions in a wide range of pH (Y-h et al. 2003). With all these advantages, QAS draw more and more attention in the field of mineral processing.

As we all know that the particles size of mineral plays a significant role in flotation. And there is an optimum particle size range for a given flotation system, usually 10–100 μm (Santana et al. 2008). Generally, in the optimum particle size range, the finer particle size of mineral is, the higher flotation recovery is. Many important physicochemical factors related to particle size have been identified. For example, in particle-bubble interaction, particle size is known to play a critical role in the probability of particles colliding with bubbles,

Table 1 Parameters for geometry optimization of kaolinite

optimization parameters	conditions
Task	Geometry Optimization
Functional	GGA+PBESOL
k-point set	3*3*4
SCF tolerance	1.0×10^{-6} eV/atom
Energy cutoff	340Ev

attachment of particles to bubbles after collision, as well as remaining attached in the pulp phase (Chipfunhu et al. 2012). Fine particles typically show slow recovery rates, owing to decreased particle-bubble collisions, and are prone to entrainment. In contrast, recovery rates of coarse particles are affected by the disruption of bubble-particle aggregate in turbulent zones, as well as a decrease in buoyancy of the particle-bubble aggregate relative to the pulp (Miettinen et al. 2010).

Although the adsorption of amine on kaolinite has been studied thoroughly (JIANG et al. 2011; Y-h et al. 2005; Ma et al. 2009), few studies focus on relationship between the particle size and chain length of cationic collectors and kaolinite flotation. In this paper, the comparative effects of particle size on the flotation of DTAC and CTAC onto kaolinite have been investigated. This study aimed to profoundly investigate the role of particle size and carbon chains length on kaolinite flotation. Furthermore, the anomalous behaviours of kaolinite flotation with QAS collectors is explained from crystal structure.

Materials and methods

Materials

Kaolinite obtained from Xiaoyi, Shanxi province in China. The samples were hand-picked, crushed and ground in a laboratory porcelain mill. Some -0.074 mm fractions

Fig. 2 The standard curves of QAR standard solutions

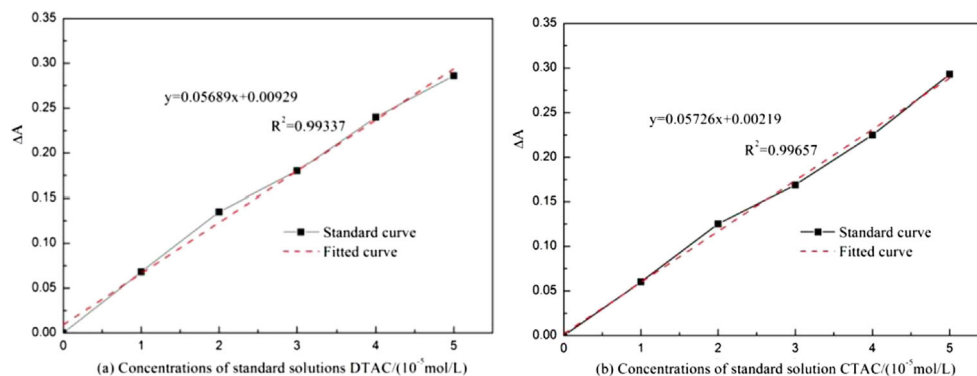


Table 2 Parameters in MD simulation of DTAC adsorbed on kaolinite surface

Task	Fixed pressure/Fixed loading	
Calculation parameters	Equilibration steps	10,000
	Production steps	100,000
Energy parameters	Sample interval	50 steps
Electrostatic terms	Summation method	Ewald & Group
	Accuracy	0.001 kcal/mol
	Charge group cutoff	12.5 Å
	Buffer width	0.5 Å
Van der Waals terms	Cutoff distance	12.5 Å
	Spline width	1 Å
	Buffer width	0.5 Å

unscreened were used in the experiments, and others were screened to three different size fractions (0.075~0.1 mm, 0.045~0.075 mm, and 0~0.045 mm). Chemical composition analysis and X-ray diffractometry (XRD) were used to study the characteristics of chemical and mineral compositions. The purity of as-preparation kaolinite is 90 % by chemical analysis and X-ray diffraction. The BET surface area kaolinite in different size fractions were measured at 10.013, 11.632 and 14.246 m²/g for 0.075~0.1, 0.045~0.075, and 0~0.045 mm, respectively.

DTAC and CTAC of chemical pure from Nanjing Robiot Co., Ltd were used as collectors. Bromothymol blue (BTB), phosphate and emulsifier *op*-10 were used in absorption tests. HCl and NaOH were used adjust the pH of the system. The water for all experiments was deionized water.

Flotation

Flotation tests were carried out in a 40 mL hitch groove flotation cell. Mineral particles prepared (2 g) were placed in a plexiglass cell, and then filled with deionized 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 dry weight of the products.

Adsorption measurements

UV spectrophotometry was used to measure the absorption amount of QAS collectors. In pH=7.5~8.5 phosphate buffer solution, QAS cationic surfactants react with BTB by ion association, which reduces the concentration of BTB. As shown in Fig. 1 that the color of solution becomes weak after adding QAS, and the weakened degree of color is proportional to concentrations of QAS. In this way, UV spectrophotometry is available to determine concentrations of QAS in solution. In the presence of QAS, maximum reduction of BTB absorption spectra was showed at 618 nm in Fig. 1. Because absorption peak at 618 nm is relatively stable, 618 nm was selected as determination wavelength in later adsorption tests. 10.0 ml of BTB solution with concentration of 0.25Mmol/L was treated by QAS standard solution of different concentrations for colour fading, respectively. The decrement values of absorbance (ΔA) at 618 nm were fitted by standard linear equation, the results are showed in Fig. 2.

A certain amount of a collector, 2.0 mL 0.5 % (mass fraction) of emulsifier *op*-10, 10.0 mL 2.5×10^{-4} mol/L BTB solution and 5.0 mL phosphate buffer solution of pH7.7 were added in a 50 mL volumetric flask. Thereafter, added with deionized water to make 50 ml. The absorbance of solution with different concentration of cationic collectors was obtained by using a UV-2012 spectrophotometer with a wave length of 618 nm. The adsorbed amount of cationic collectors was calculated based on the absorbance. The amount of collector adsorbed on the mineral particles was calculated as:

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

Fig. 3 Flotation recovery of unscreened kaolinite with DTAC and CTAC as a function of pH(a) and collector concentration(b)

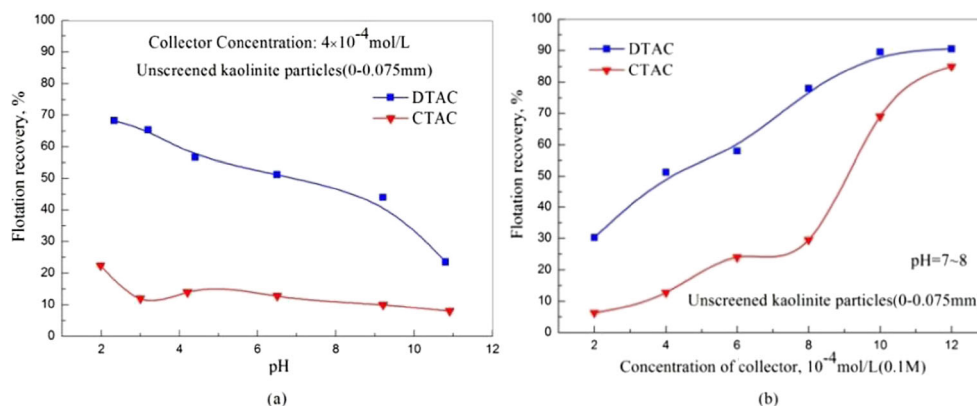
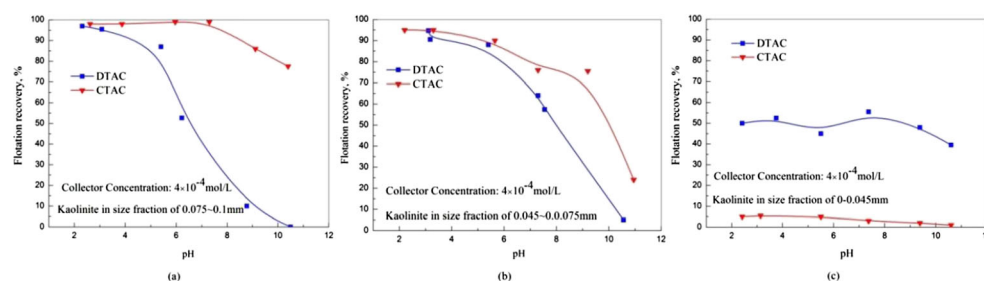


Fig. 4 Flotation recovery of kaolinite in different size fraction 0.075–0.1 mm (a) 0.045–0.075 mm (b) 0–0.045 mm (c) with DTAC and CTAC as a function of pH



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 mineral specific surface area.

Molecular dynamics simulations

All calculations were performed in the framework of the MD, using the Material Studio 5.0 (MS) package. CASTEP module included in MS software was adopted to optimize the crystal structure of kaolinite. The unit cell parameter is $a=5.149 \text{ \AA}$, $b=8.934 \text{ \AA}$, $c=7.384 \text{ \AA}$, $\alpha=91.930^\circ$, $\beta=105.0420^\circ$, $\gamma=89.791^\circ$ after geometry optimization, which is well consistent with literature (Y-h and Liu X-w 2003). The optimization parameters are listed in Table 1. Then, a 2D periodic surface cell is created from the unit cell of the mineral at the cleavage planes (001), (00 $\bar{1}$), (010) and (110), respectively. Meanwhile, DTAC molecule was optimized using DMol3 module.

Finally, Sorption module was employed to calculate adsorption sites and adsorption energies by Fixed pressure and Fixed loading task. DTAC was as adsorbate, while kaolinite was as adsorbent. The simulation parameters are shown in Table 2.

SEM analysis

The morphologies of the kaolinite (0–0.045 mm) adsorbed DTAC in acid solution (pH=3) and alkaline solution (pH=10)

were characterized using a scanning electron microscope (SEM, TM-1000, Hitachi, Japan) with an accelerating voltage of 20 kV. Before characterization, Well dispersed-kaolinite samples were freeze-dried and then were coated with a thin layer of gold.

Results

Flotation

Figure 3a shows the recovery of unscreened kaolinite (0–0.075 mm), using the collectors DTAB and CTAC, respectively, as a function of pH. The results showed that the flotation recoveries of kaolinite for DTAC and CTAC decrease with increasing in pH. The recovery of kaolinite with DTAC changed in the range of 70–20 %, while the recovery of kaolinite with DTAC changed in the range of 20–5 %. It is obvious that the flotation behavior of kaolinite is different from the other oxides and silicates (Schulz and Warr 2002; Rodrigues et al. 2013). It is generally believed CTAC with longer carbon chains as a collector is much more efficient than DTAC. Surprisingly, quite the case of kaolinite is the opposite. As carbon chain length of collectors increase, the flotation recovery of kaolinite decreases. In other words, the collecting power for kaolinite (0–0.075 mm) is in the order of DTAC > CTAC. The recovery–collector dosage curves of kaolinite at pH 7~8 are presented in Fig. 3b. It shows that the recovery of

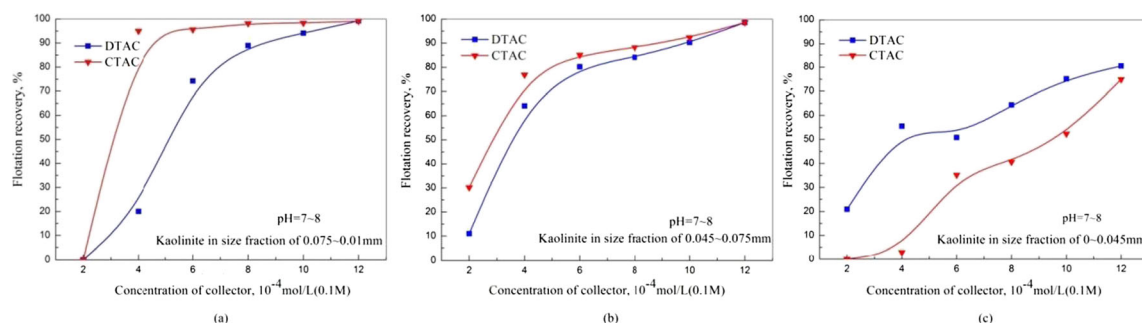
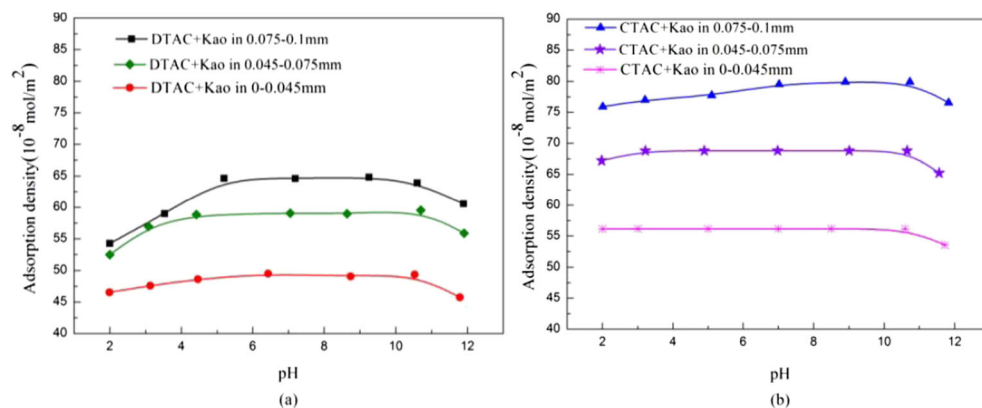


Fig. 5 Flotation recovery of kaolinite in different size fraction 0.075–0.1 mm (a) 0.045–0.075 mm (b) 0–0.045 mm(c) with DTAC and CTAC as a function of collector concentration

Fig. 6 Adsorption density of QAS collectors of kaolinite in different size fractions as a function of pH



kaolinite sharply increases with the increase of DTAC and CTAC concentration. Furthermore, as the concentration of collectors increase, the difference of flotation recovery between DTAC and CTAC is gradually reduced.

The effect of particle size on kaolinite flotation for DTAC and CTAC is illustrated in Figs. 4 and 5. Figure 4 shows that with pH increasing there is a decrease in recovery for all of the three particle size fractions of kaolinite. There is a huge difference in flotation behaviors of kaolinite in different particle size fractions. As carbon chain of QAS increases, the recoveries of kaolinite in 0.075–0.1 mm and 0.045–0.075 mm increase, which is consistent with the results of other oxide minerals flotation. But in case of kaolinite in size fraction of 0–0.045 mm, the flotation recovery decreases with increasing hydrocarbon chain of QAS. That is to say, the collecting ability of collectors for fine kaolinite is CTAC < DTAC, in contrast to the general trend for the cationic flotation of oxides in which recovery increases with carbon chain. Thus it can be seen that the anomalous behaviour of kaolinite flotation is dependent on particle size. Comparing the effect of particle size on flotation, the coarser particle size of kaolinite is, the better it is floated. It can be observed visually when CTAC is used as collector, the flotation recovery of kaolinite in 0.075–0.1 mm is above 95 % in pH 2~7. While the flotation recovery of kaolinite in 0.045–0.075 mm is just about 90 % in pH range 2 to 5. Most amazing, in case of kaolinite in 0–0.045 mm, the recovery maintains fewer than 10 %. Fig. 5 shows that the recovery kaolinite in different size fraction at pH 7~8 as a function of collector concentration. As Fig. 5 explained, the DTAC and CTAC cationic collectors display a similar flotation rule, meaning that with collector dosage increasing there is an increase in recovery for all of the three particle size fractions of kaolinite. In the low collector concentration range, a flotation recovery difference between DTAC and CTAC is considerable greater. And the difference is getting less with increasing collector concentration. When the concentration was above 1.2 mmol/L, the collecting power of CTAC and DTAC for kaolinite in three size fractions is close to equal.

Adsorption

The adsorption density of QAS collectors onto kaolinite in three different size fractions as a function of pulp pH is shown in Fig. 6. With pH increasing there is a slight increase in adsorption for all of the three particle fractions of kaolinite. But the adsorption starts to decline due to the interaction between OH⁻ and QAS cation when pH is above 10. It is evident from Fig. 6 that the adsorption density increases with carbon chain of collectors increasing and particle size of kaolinite coarsening.

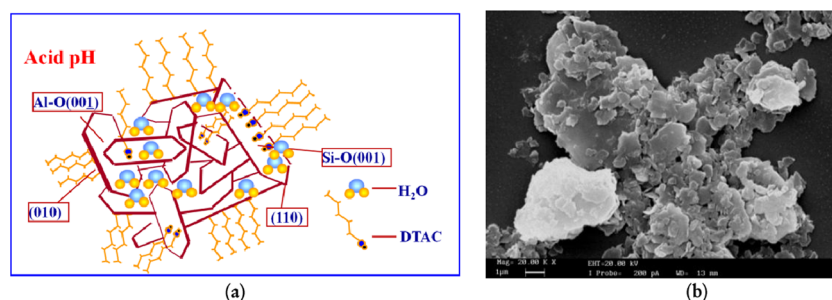
MD simulation

The MD stimulation results of DTAC adsorbed on kaolinite surfaces (001), (001̄), (010) and (110) are compared in Table 3. As illustrated in Table 3, the negative magnitude of adsorption energy is in the order (001) > (001̄) > (010) > (110). In general, the more negative the magnitude of adsorption energy shows, the more favorable the interaction between mineral surface and reagent is. Namely, the (001) kaolinite surface has the strongest interaction with DTAC, compared with the (001̄), (010) and (110) surfaces. Distance between N atom and (001̄) on Z-axis direction is an order of magnitude smaller than (001), which may be due to hydrogen bonding between (001̄) and DTAC.

Table 3 MD stimulation results of DTAC adsorbed on kaolinite surfaces

crystal plane	average adsorption amount (number/Cell)	adsorption energy of adsorbed an DTAC molecule (Kcal/mol)	Distance between N atom and crystal plane on Z-axis direction (Å)
(001)	1.806	−23.051	0.384512
(001̄)	1.848	−20.989	0.086016
(010)	2.000	−20.218	0.964783
(110)	3.000	−18.675	0.894751

Fig. 7 **a** Hydrophobic assembly structure model of kaolinite particles with adsorbed DTAC in acid solution **b** SEM of kaolinite particles with adsorbed DTAC in acid solution (pH=3)



Discussion

Kaolinite has two kinds of different crystal planes, one of which is the basal planes (001), the other is the edge surfaces (010) and (110). Kaolinite is a dioctahedral layered aluminosilicate of 1:1 type, therefore, each layer has two different surfaces parallel to the (001) plane. First one (001), tetrahedral, is formed from basal oxygen atoms of the tetrahedral (SiO_4) sheet, while second one (001), octahedral, is formed from surface hydroxyl groups of the octahedral (AlO_6) sheet (Šolc et al. 2011; Gupta et al. 2011). It is traditionally believed that the basal planes are permanent negatively charged, which is attributable to isomorphous substitution of lattice elements. Si^{4+} and Al^{3+} can be replaced by Al^{3+} ions and $\text{Mg}^{2+}/\text{Fe}^{2+}$, respectively (Xu L-h et al. 2013). But some studies recently show that a distinct dependence on the pH of the basal planes through surface force measurements using atomic force microscopy (AFM). (001) is negatively charged at $\text{pH} > 4$, whereas (001) is positively charged at $\text{pH} < 6$, and negatively charged at $\text{pH} > 8$ (Gupta and Miller 2010). In case of edge surfaces (010) and (110), the charge is also pH-dependent due to broken silica and alumina bonds with an iso-electric point at neutral pH of 7 (Zhao et al. 2008).

As we all know that oxides and silicates adsorb cationic collector by electrostatic interactions. When pH increases the surface charge of oxides grows more negative. So of course flotation recovery of oxides increases with an increase in pH. Conversely, as Figs. 4 and 6 demonstrate, the absorption of QAS collectors increases with pH increasing while the

flotation recovery of kaolinite decreases. The pH dependence of kaolinite flotation is opposite to that of oxides, with lower flotation recovery obtained at higher pH. This discrepancy could be attributed to the structural anisotropy of kaolinite (X-h et al. 2012).

As discussed in the Introduction, (001) is negatively charged at $\text{pH} > 4$, whereas (001) is positively charged at $\text{pH} < 6$, and negatively charged at $\text{pH} > 8$ (L-y et al. 2009). Clearly, only (001) is negatively charged in acidic solution, whereas (001), (010) and (110) are positively charged. Hence the self-aggregation between (001) and other faces of kaolinite particles is generated by electrostatic interaction. Negatively charged (001) planes will adsorb cationic DTAC. Furthermore, It has been revealed from MD stimulation results that the (001) plane has the stronger interaction with DTAC in all faces. Consequently, most of the (001) faces adsorbed hydrophobic DTAC are exposed, resulting in good floatability of kaolinite in acidic solutions. The interaction model is schematically depicted in Fig. 7a. The SEM picture of kaolinite (0–0.045 mm) adsorbed DTAC in acid solution ($\text{pH}=3$) is given in Fig. 7b. As indicated in the figure, there are self-aggregations among the kaolinite particles, which is consistent with the interaction model shown Fig. 7a.

In alkaline solution, both edges and basal planes are negatively charged. The kaolinite particles are dispersed due to electrostatic repulsion, and the system is stabilized. In this case, DTAC adsorption on the edges (010) and (110) and the basal planes (001) and (001) could contribute to the wettability of kaolinite surface and the floatability of kaolinite. As

Fig. 8 **a**Hydrophilic assembly structure model of kaolinite particles with adsorbed DTAC in alkaline solution **b** SEM of kaolinite particles with adsorbed DTAC in alkaline solution (pH=10)

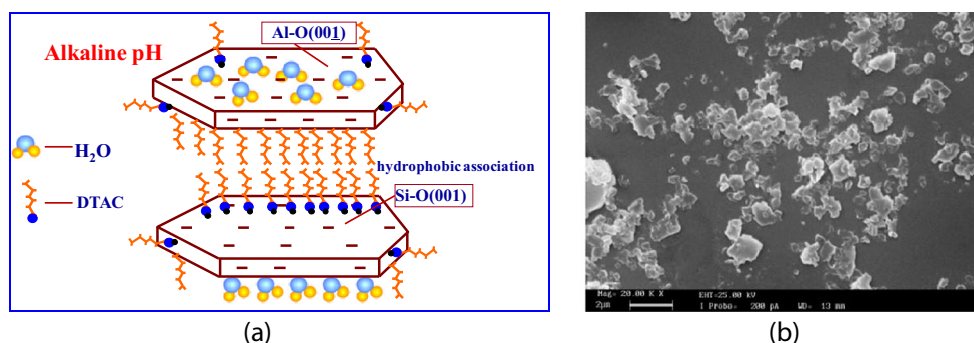
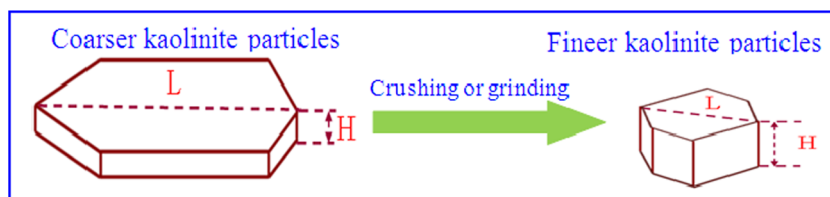


Fig. 9 A schematic of aspect ratio of kaolinite changing with particles size



shown in Fig. 7, the hydrophobic (001) planes is responsible for the strongest interaction with DTAC. Hydrophobic aggregation appears to occur between (001) planes by chain–chain association of DTAC molecules, and the hydrophilic (00 $\bar{1}$) planes are exposed. Such a structure that leads to poor flotation in alkaline solution is given in Fig. 8a. And it is consistent with the flotation results of Fig. 4. Figure 8(b) shows the SEM picture of kaolinite (0–0.045 mm) adsorbed DTAC in alkaline solution (pH=10). It is evident from SEM picture that kaolinite particles can fully dispersed in alkaline to be difficult to float.

When particle size of kaolinite is altered, the number of basal planes and edge planes are changed. Furthermore, the aspect ratio L/H (ratio of particle diameter to thickness) is changed, as Fig. 9 shown. It is observed that the finer kaolinite particles size becomes, the greater relative surface area of edges and the more relative number of edges are. Notably, fine kaolinite particles have a lower aspect ratio than coarse particles. It means that fine kaolinite particles have more edges to adsorb few cationic collectors, which is responsible for the poorer floatability of fine kaolinite.

In case of 0–0.045 mm kaolinite, the flotation recovery decreases with the carbon chain of collector. This discrepancy could be attributed to QSA collector being completely adsorbed onto fine kaolinite. In lower residual concentration, the froth stability becomes worse. Within the range of flotation collector concentration, it's easy of CTAC to be completely adsorbed by kaolinite in the particle size fraction (0–0.045 mm), which led to lower flotation recovery.

Conclusions

The flotation behaviour of kaolinite was found to be opposite to that of other oxide minerals. The flotation recovery decreases with pH, obtaining lower flotation recovery at higher pH. It is explained by the crystal structural anisotropy of kaolinite. In acidic solutions, the kaolinite particles are mostly self-aggregated in edge-face (001) association and face (001)-face (00 $\bar{1}$) association. And the most of hydrophobic (001) faces adsorbed DTAC are exposed, resulting in good floatability of kaolinite in acidic solutions. In alkaline solution, hydrophobic aggregation between (001) planes by chain–chain association of DTAC molecules, and the

hydrophilic (00 $\bar{1}$) planes are exposed, resulting in poor floatability of kaolinite in alkaline solution.

The flotation recoveries of coarse kaolinite (0.075~0.01 mm and 0.045~0.075 mm) increase with the carbon chain of QAS collectors. But the flotation recovery of the finest kaolinite (0~0.045 mm) decreases with chain lengths, being consistent with the flotation results of unscreened kaolinite (0~0.075 mm). Within the range of flotation collector concentration, it's easy of CTAC to be completely adsorbed by kaolinite in the particle size fraction (0–0.045 mm). In this way, the froth stability becomes worse and lower flotation recovery is obtained.

Compared with the flotation results of the different particle size fractions, the particle size dependence of kaolinite flotation is coarser kaolinite obtained higher flotation recovery. It is inferred that the finer kaolinite particles size becomes, the greater relative surface area of edges and the more relative number of edges are. It means that fine kaolinite particles have more edges to adsorb few cationic collectors, which is responsible for the poorer floatability of fine kaolinite.

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