



Cationic flotation of scheelite from calcite using quaternary ammonium salts as collector: Adsorption behavior and mechanism



Fan Yang^{a,*}, Wei Sun^b, Yuehua Hu^b, Sisi Long^a

^a School of Metallurgy Engineering, Anhui University of Technology, Ma'anshan, Anhui 243002, China

^b School of Resources and Bioengineering, Central South University, Changsha, Hunan 410083, China

ARTICLE INFO

Article history:

Received 5 May 2015

Revised 8 July 2015

Accepted 17 July 2015

Keywords:

Scheelite

Flotation

Quaternary ammonium salt

Calcite

Adsorption

ABSTRACT

Cationic flotation is a promising method for separating scheelite from calcite at room temperature, because of the significant difference between their surface charges. Three quaternary ammonium salts, i.e., didecyltrimethylammonium chloride (DDAC), trioctylmethylammonium chloride (TOAC), and dodecyltrimethylammonium chloride (DTAC), were investigated as cationic collectors in the flotation of scheelite from calcite. The flotation behaviors of scheelite and calcite with the three quaternary ammonium salts were studied using single-mineral and mixed-mineral flotations; flotation with oleate was used for comparison. The results show that flotation of scheelite from calcite was possible around pH 8 with DDAC and TOAC as collectors. The collecting powers and selectivities of these compounds for scheelite were higher than those of oleate. The molecular structures, Fourier-transform infrared spectra, and zeta potentials indicated that when quaternary ammonium salts are used as collectors, electrostatic interactions play a primary role in the flotation of scheelite from calcite. The adsorptions of the three quaternary ammonium salts fitted a general adsorption isotherm well, but the Langmuir isotherm only fitted the adsorption of DDAC well. It can be concluded from the adsorption isotherm parameters that the role of van der Waals forces is as significant as that of electrostatic forces in the interactions of quaternary ammonium salts with the two minerals, and that the selectivities of the quaternary ammonium salts for scheelite result from their large van der Waals forces, as well as the opposite charges on scheelite and calcite. The van der Waals forces of quaternary ammonium salts significantly affect the adsorption processes and consequently the isotherm plots.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Scheelite is generally recovered by flotation, because of its friability, fine mineralization, and complex associations. A silicate–sodium oleate–sodium carbonate system is usually used in the flotation of scheelite (Hanna and Somasundaran, 1976). It gives satisfactory results for the separation of scheelite from silicate gangues, but has little or no selectivity for scheelite associated with calcareous gangues. This is because of the similarity between the physicochemical surface properties of scheelite and calcite, which both contain a calcium cation (Amakonah et al., 1985; Atademir et al., 1981; Marinakis and Shergold, 1985a,b; Mishra, 1982; Pugh and Stenius, 1985; Shin and Choi, 1987; Wang, 1982).

Research on overcoming this problem has mostly focused on anionic flotation processes, using different combinations of anionic collectors or regulators, although there is a clear difference

between the surface electrical properties of scheelite and those of calcareous gangue minerals. The isoelectric point of scheelite occurs at about pH 2, whereas those of calcite and fluorite occur at pH 8.2 and 9–10, respectively (Xu and Hu, 2003). The selectivities of cationic collectors in scheelite from calcite are therefore potentially better than those of anionic collectors. Hıçyılmaz et al. (1993) studied the flotation of mixtures of scheelite and calcite with amines as collectors, and obtained concentrates containing 63.59–65.51% WO₃, with 96.54–91.41% recoveries, using dodecylamine with an acetate counterion as the collector, when washing was conducted prior to flotation.

In this study, quaternary ammonium salts were investigated as cationic collectors for scheelite. Quaternary ammonium salts (also called quaternary ammonium compounds, QACs) are usually halide salts with four alkyl groups attached to a central cationic nitrogen atom (R₄N⁺). Quaternary ammonium salts have strong surface activities and are extensively used as surfactants. Unlike ammonium (NH₄⁺), and primary, secondary, and tertiary ammonium cations, quaternary ammonium cations are permanently

* Corresponding author.

E-mail address: mcfanyang@163.com (F. Yang).

charged, regardless of the solution pH. Quaternary ammonium salts are therefore strong cationic collectors, and their performances change little under different solution conditions.

Quaternary ammonium salts have been used in flotation. [Rodrigues \(2013\)](#) achieved separation of kaolinite from hematite using dodecyltrimethylammonium bromide as the collector in the pH range 4–10. [Wang and Ren \(2005\)](#) used a combination of cetyltrimethylammonium bromide and dodecylamine chloride as the collector and quebracho as a depressant to separate quartz from iron minerals. [Wang et al. \(2004\)](#) used a quaternary ammonium collector in the reverse flotation of bauxite, and obtained a concentrate with an Al_2O_3 to SiO_2 grade ratio greater than 10, with recovery of more than 86%, in closed-circuit tests. [Abdel-Khalek et al. \(1994\)](#) used a quaternary ammonium salt in the beneficiation of Egyptian feldspar and obtained a final concentrate containing 89.5% feldspar mineral, 0.1% Fe_2O_3 , and 18.65% Al_2O_3 , which satisfies the requirements of the glass and ceramic industries. In this research, the use of three types of quaternary ammonium salt, i.e., didecyldimethylammonium chloride (DDAC), trioctylmethylammonium chloride (TOAC), and dodecyltrimethylammonium chloride (DTAC), was investigated to determine the feasibility of the use of quaternary ammonium salts as collectors for scheelite. The adsorption behaviors of the three quaternary ammonium salts were compared to identify the trends in, and mechanisms of, quaternary ammonium salt interactions with scheelite and calcite.

2. Materials and methods

2.1. Minerals and chemicals

Handpicked, high-purity scheelite and calcite, from Shizhuyuan, Hunan, China, were ground using a porcelain mill. The ground samples were wet-sieved and the fraction with particles of size less than $74\text{ }\mu\text{m}$ was collected and used in flotation tests. A portion of this fraction was further ground in an agate mortar to obtain particles of size less than $5\text{ }\mu\text{m}$ for Fourier-transform infrared (FTIR) spectroscopy and zeta potential measurements.

The three quaternary ammonium salts were provided by the Xirun Chemical Engineering and Technology Corporation (Shanghai, China). Sodium oleate, which was used as a collector for comparison, was provided by the Tianyu Oleo Chemical Corporation (Sichuan, China). Analytical-grade HCl and NaOH were used as pH modifiers. Distilled water was used in all experiments, unless otherwise stated.

2.2. Micro-flotation

Micro-flotation tests were conducted using individual and artificially mixed minerals. The mixed minerals contained equal amounts of scheelite and calcite by weight. A mineral suspension was prepared by adding 2.0 g of the fraction containing mineral particles of size less than $74\text{ }\mu\text{m}$ to 40 mL of water under agitation. The pH of the mineral suspension was adjusted to the desired value by adding concentrated NaOH or HCl stock solutions. The prepared collector solution was added to a desired concentration, and conditioned for 3 min. Flotation was performed for a total of 3 min. The floating particles and the remaining material were separately collected, filtered, and dried in a well-ventilated oven at $120\text{ }^\circ\text{C}$ for 2 h. The grades of concentrates in the mixed-mineral flotation tests were expressed as mass percentages of WO_3 . The flotation recoveries in single-mineral flotation tests were expressed as the mass ratio of the concentrate to the feed. For mixed-mineral flotation, the recovery was calculated using Eq. (1):

$$\varepsilon = \frac{\gamma\beta}{\beta_0} \quad (1)$$

where

ε is the flotation recovery,

β is the concentrate grade,

γ is the mass ratio of the concentrate to the feed,

β_0 is the feed grade (40.3% in this research).

2.3. FTIR spectroscopy

FTIR spectroscopy was used to characterize the surface species on the treated mineral particles. The samples were prepared as follows. Mineral samples of particle size less than $38\text{ }\mu\text{m}$ (less than 400 mesh) were added to a solution containing a quaternary ammonium salt at a concentration of $1.0 \times 10^{-2}\text{ mol/L}$. The suspension was ground to a pulp in a mortar for 30 min, filtered, washed three times with distilled water, and dried at $70\text{ }^\circ\text{C}$ in a vacuum drying oven. Spectroscopy was performed using a Nicolet NEXUS 670 FTIR spectrometer.

2.4. Electrokinetic measurements

Zeta potentials were measured using a Bechman Coulter DELSA-440SX zeta potential analyzer. All measurements were conducted in a 0.1 M KNO_3 background electrolyte solution. Samples were ground to a particle size of less than $5\text{ }\mu\text{m}$. A sample (0.025 g) was placed in a 50 mL beaker containing distilled water (25 mL). HCl and NaOH were added to adjust the pulp pH. After agitation for 3 min, a certain amount of collector was added, and the mixture was agitated for 5 min. The zeta potential of the obtained pulp was determined. The results presented are the averages of three independent measurements, with a typical variation of $\pm 2\text{ mV}$.

2.5. Adsorption tests

For the adsorption tests, mineral powder (2 g) was pulped to 40 mL, after addition of a desired amount of quaternary ammonium salt solution of known concentration, in a 100 mL flask. The specific surface areas of the scheelite and calcite powders were 0.26 and 0.64 g/m^2 , respectively. The suspension was equilibrated for a given period of time in a temperature-controlled water bath. After equilibration, the solids were separated by filtration using filter paper of pore size $10\text{ }\mu\text{m}$. The filtrate was analyzed by the eosin Y method, using a Unico UV-2012 spectrophotometer, to determine the amount of quaternary ammonium salt adsorbed ([Qin and Tan, 2006](#)). All the measurements were repeated in quadruplicate, and the reproducibility of the data was checked.

3. Results and discussion

3.1. Flotation of scheelite and calcite with quaternary ammonium salt as collector

The flotation behaviors of scheelite and calcite with quaternary ammonium salts and oleate as collectors were first investigated using single-mineral flotation tests. Oleate was used for comparison. The results are shown in [Fig. 1](#).

[Fig. 1\(1\)](#) shows that when DDAC was used as the collector, scheelite flotation was good, with a recovery higher than 90% above pH 3, and of almost 100% above pH 5. In contrast, the recovery of calcite increased slowly over the pH range 6–12, and reached 80% at pH 12. As calcite becomes soluble below pH 6, the acidic limit of the calcite pulp is pH 6. This means that the scheelite-collecting power of DDAC is significantly higher than that for calcite. The flotation results shown here indicate preferential flotation separation of scheelite from calcite at a pulp pH around 8.

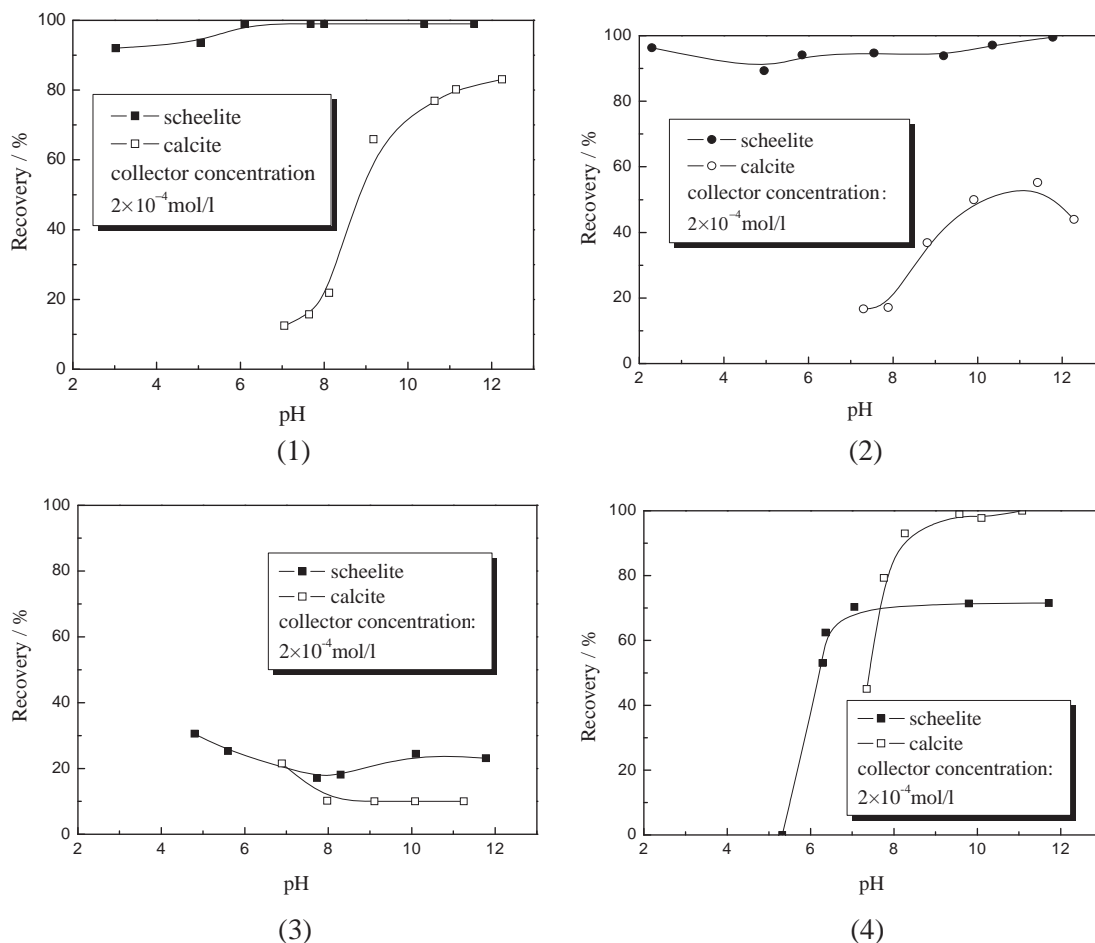


Fig. 1. Flotation recoveries of scheelite and calcite as function of pH in single-mineral flotation: (1) DDAC; (2) TOAC; (3) DTAC; and (4) oleate.

Fig. 1(2) shows that when TOAC was used as the collector, scheelite recovery was around 90% over the pH range 2–12, whereas calcite recovery increased slowly above pH 8 and reached a maximum (about 50%) at pH 10–11. These results indicate that the collecting power of TOAC is weaker than that of DDAC, but its selectivity for scheelite is higher than that of DDAC.

Fig. 1(3) shows that when DTAC was used as the collector, scheelite recovery was around 25% over the pH range of 2–12, and calcite recovery was around 10% over the pH range 7–11. This shows that the collecting power of DTAC is much weaker than those of DDAC and TOAC.

Fig. 1(4) shows that when oleate was used as the collector, the recoveries of scheelite and calcite increased with increasing pulp pH before reaching a maximum above pH 9. In contrast to the cases of quaternary ammonium salts, the calcite-collecting power of oleate was stronger than that for scheelite; the maximum calcite recovery was almost 100%, whereas that of scheelite was about 70%.

As shown in Figs. 2 and 3, the recoveries of scheelite and calcite both increased with increasing concentration of quaternary ammonium salt and then reached a maximum. The maximum recoveries of scheelite with DDAC and TOAC as the collector were more than 95%, both at salt concentration of 1×10^{-4} mol/L; recoveries of calcite reached maximum values of 60% and 40%, respectively. However, when DTAC was used as the collector, the recoveries of scheelite and calcite both increased slowly with increasing salt concentration, with maximum values of only 40% and 10%, respectively. When oleate was used as the collector, the scheelite recovery reached a maximum value of 80%, at a salt concentration of

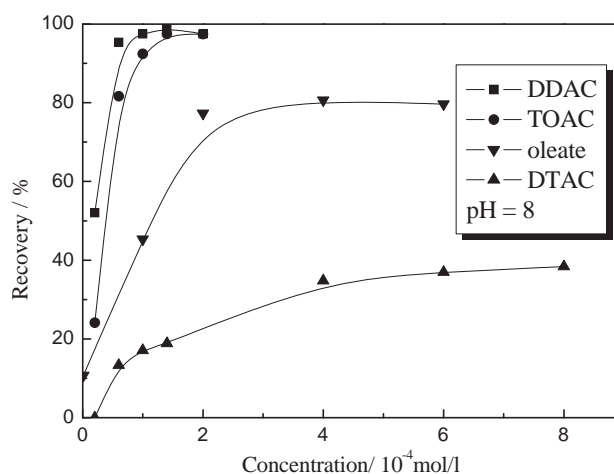


Fig. 2. Flotation recovery of scheelite as a function of concentration of quaternary ammonium salt in single-mineral flotation.

2×10^{-4} mol/L, and the recovery of calcite reached a maximum value of 95% at a salt concentration of 1×10^{-4} mol/L.

In summary, the flotation performances of DDAC and TOAC were similar; the maximum scheelite recovery was 95% around pH 8, whereas that of calcite was only 30%. The collecting power of DDAC is slightly stronger than that of TOAC, whereas the selectivity of TOAC is higher than that of DDAC. In contrast, when oleate was used as the collector, the maximum recovery of scheelite was

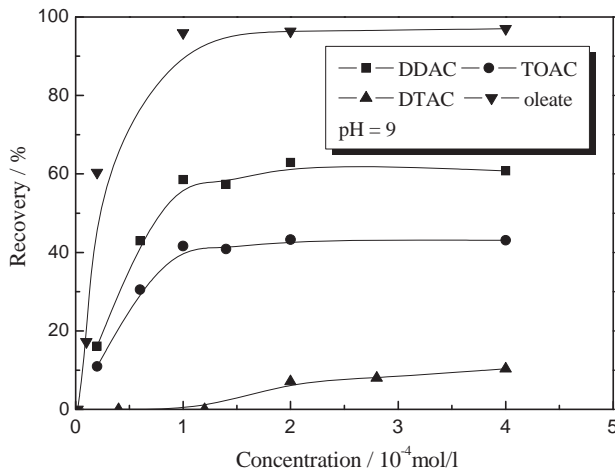


Fig. 3. Flotation recovery of calcite as a function of concentration of quaternary ammonium salt in single-mineral flotation.

80%, lower than that of calcite, which was almost 100%. DDAC and TOAC are therefore superior to oleate as scheelite collectors in terms of collecting power and selectivity. However, the collecting power of DTAC is significantly weaker than those of the other two quaternary ammonium salts, and gave a maximum scheelite

recovery of only 40%. The flotation tests showed that it is possible to separate scheelite from calcite using DDAC and TOAC at concentrations of 1×10^{-4} mol/L as the collector, around pH 8, at which the difference between the floatability of scheelite and that of calcite is greatest.

Micro-flotation tests of artificially mixed minerals (scheelite to calcite mass ratio of one) were conducted to investigate the flotation performances of the three quaternary ammonium salts further. Because of the presence of calcite, the pulp pH ranged from 6 to 12.

Fig. 4 shows that the flotation performances of DDAC and TOAC in mixed-mineral flotation were as good as those in single-mineral flotation. The scheelite recovery increased with increasing pH, and reached 100% above pH 9. The scheelite grade first increased, and then decreased after reaching a maximum of more than 60% around pH 8; the value of scheelite grade was slightly higher for TOAC than for DDAC. Furthermore, scheelite was not floatable below pH 7, in contrast to the case for single-mineral flotation. This could be the result of stronger competitive adsorption between Ca^{2+} and the cationic collectors in mixed-mineral flotation than in single-mineral flotation, because the solubility of calcite is greater than that of scheelite, especially under acidic and neutral conditions (Hu, 1988). Above pH 9, after reaching a maximum, the grade of scheelite decreased as calcite recovery increased. DTAC still gave a poor flotation performance, confirming that it is a weak collector for scheelite.

Although the maximum scheelite recovery with oleate as the collector was 100% above pH 11, scheelite was not separated from calcite, and the grade was almost the same before and after flotation, i.e., about 40.3%.

As in the case of single-mineral flotation, mixed-mineral flotation indicated that DDAC and TOAC have strong collecting powers and high selectivities for scheelite, and were superior to the anionic collector oleate in the flotation of scheelite from calcite. DTAC is inferior to DDAC and TOAC in scheelite flotation because of its weak collecting power.

3.2. Mechanism of quaternary ammonium salt adsorption on scheelite and calcite

3.2.1. Structural characteristics of quaternary ammonium salts

Quaternary ammonium salts are halide compounds of positively charged polyatomic ions with the structure NR_4^+ , i.e., quaternary ammonium cations, where R is an alkyl or aryl group. Quaternary ammonium salts therefore mainly differ in terms of the four substituents on the central nitrogen. DDAC, TOAC, and DTAC, which were used in this study, represent three types of quaternary ammonium salt structure as shown in Fig. 5. They contain two, three, and one long-chain alkyl substituents, respectively. These structural differences result in different flotation performances.

The central nitrogen atom is the active center of the quaternary ammonium salt during flotation. The nitrogen atom contains five valence electrons, two of which occupy the 2s orbital and the other three of which each occupy a 3p orbital. The central nitrogen atom in a quaternary ammonium salt loses a valence electron; the remaining four are hybridized, and each resides in one of the four hybrid orbitals and forms a covalent bond with a carbon atom of each of the four alkyl substituents. Consequently, the central nitrogen atom of a quaternary ammonium salt can neither donate valence electrons nor provide empty orbitals to form covalent bonds with atoms on the surfaces of calcium-containing minerals under flotation conditions. This means that quaternary ammonium salts are not chemically adsorbed on the surfaces of scheelite and calcite. Furthermore, the steric hindrance of the central nitrogen atom of the quaternary ammonium salt interacting with mineral

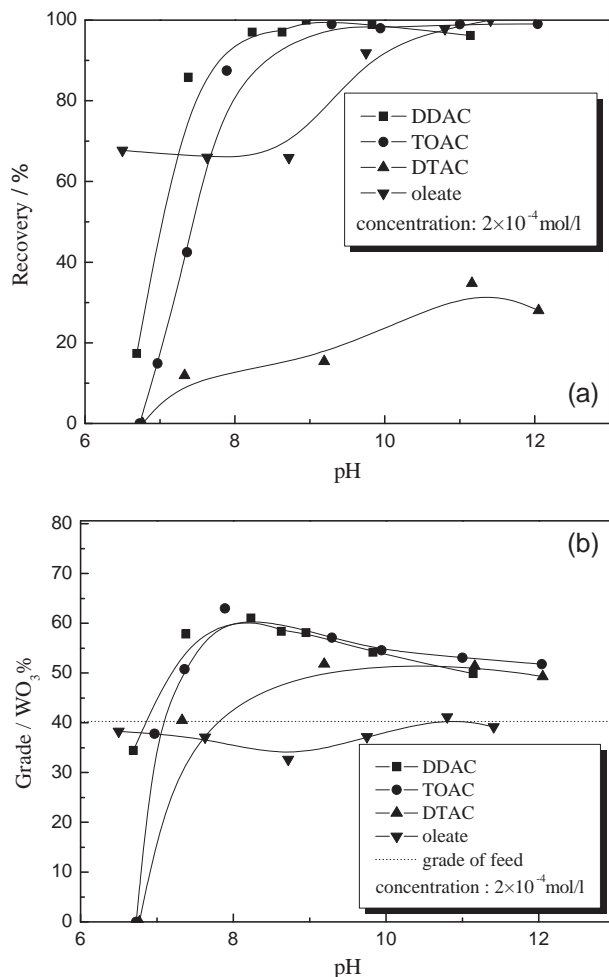


Fig. 4. Recoveries and grades for mixed-mineral flotation as function of pulp pH, with quaternary ammonium salts and sodium oleate as collectors: (a) recovery and (b) grade.

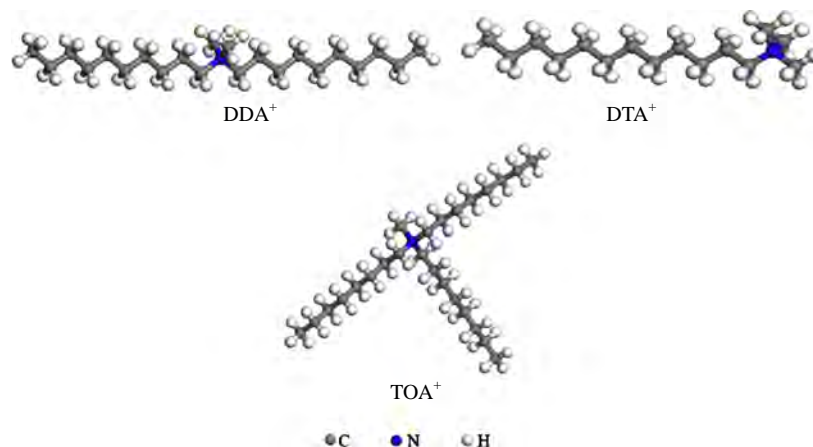


Fig. 5. Molecular structures of cations of DDAC, DTAC and TOAC.

surfaces is large, because it is surrounded by four alkyl substituents; this is also unfavorable for chemical adsorption of quaternary ammonium salts on the mineral surfaces.

It is therefore probable that physical interactions lead to scheelite flotation by quaternary ammonium salts.

3.2.2. FTIR spectroscopic analysis

FTIR spectroscopy was performed to clarify the adsorption mechanism of quaternary ammonium salts on the surfaces of scheelite and calcite. The three quaternary ammonium salts have the same functional group, and therefore they interact with minerals in the same manner; the FTIR spectroscopic analysis of the interactions of quaternary ammonium salts with scheelite and calcite was therefore performed using DDAC as an example.

The FTIR spectra of scheelite and calcite before and after conditioning with 2×10^{-4} M DDAC solution are shown in Figs. 6 and 7. In the spectrum of scheelite treated with DDAC solution, the new bands at 2928.62 and 2858.37 cm^{-1} are attributed to C–H stretching vibrations, and the band at 1483.93 cm^{-1} is attributed to the C–H bending vibration (Xie et al., 2001). The appearance of these bands confirmed that DDAC was adsorbed on the scheelite surface. No band indicating chemical adsorption was observed, excluding

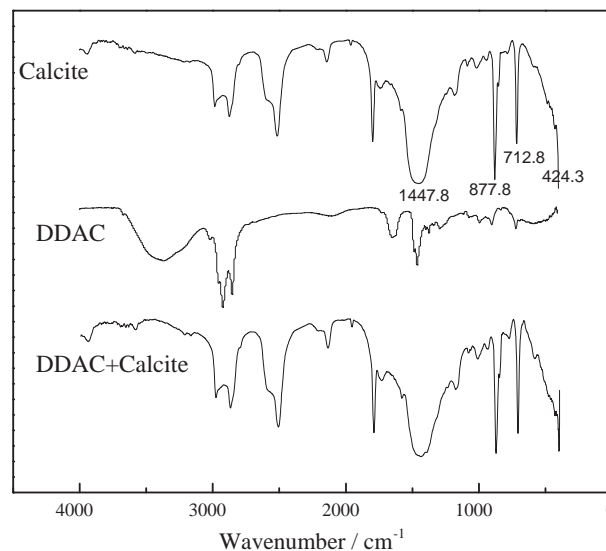


Fig. 7. FTIR spectra of calcite before and after treatment with 2×10^{-4} mol/L DDAC solution (natural pH, i.e., 9).

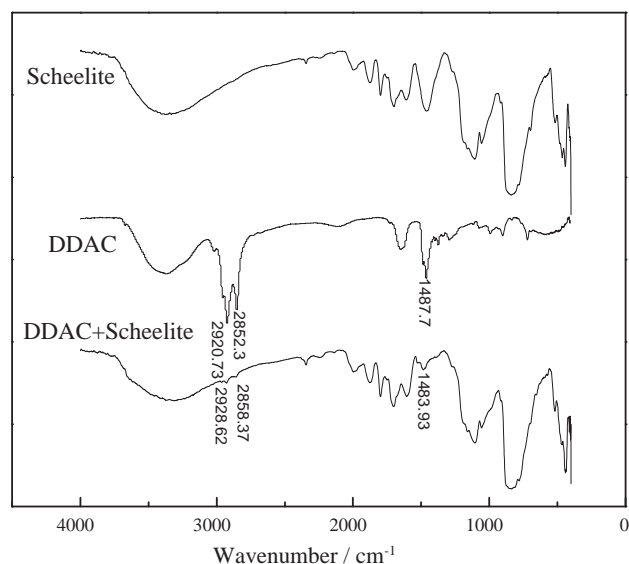


Fig. 6. FTIR spectra of scheelite before and after treatment with 2×10^{-4} mol/L DDAC solution (natural pH, i.e., 7.8).

the possibility of chemical adsorption of DDAC in scheelite flotation.

Fig. 7 shows that no new band appeared in the FTIR spectrum of calcite after treatment with DDAC solution. DDAC was therefore not adsorbed on the calcite surface after treatment; this is consistent with the flotation results for calcite with DDAC.

3.2.3. Zeta potential measurements

Structural and FTIR spectroscopic analyses excluded the possibility of chemical adsorption of quaternary ammonium salts on the surfaces of scheelite and calcite. Electrostatic interactions, which are major physical interactions, were therefore investigated using zeta potential measurements.

The surface zeta potentials of scheelite and calcite in the absence of collectors, and the results for mixed-mineral flotation, are shown in Fig. 8. The maximum difference between the scheelite and calcite surface potentials occurred around pH 8, at which scheelite was negatively charged and calcite was positively charged. In the same pH range, the flotation recovery and grade of scheelite also reached their maximum values. Above pH 9, the calcite became negatively charged and the collecting power of DDAC for calcite increased; therefore the flotation grade of

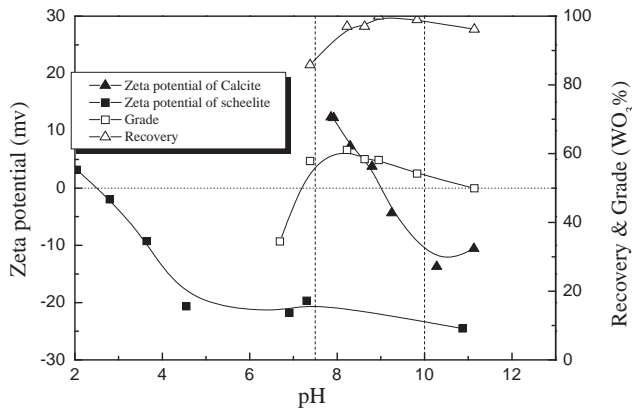


Fig. 8. Surface zeta potentials of scheelite and calcite in absence of collectors as a function of pH, and grades and recoveries of scheelite concentrates in mixed-mineral flotation as a function of pH at DDAC concentration of 2×10^{-4} mol/L.

scheelite decreased. These results imply that electrostatic interactions play a primary role in the flotation separation of scheelite from calcite when DDAC is used as the collector.

Fig. 9 shows the relationships between the surface zeta potentials of scheelite and calcite and solution pH in the presence of quaternary ammonium salts at different concentrations. Fig. 9(1) shows that when the concentration of DDAC increased, the zeta potential–pH curve shifted positively, but its shape was almost unchanged. When the concentration of DDAC reached 2×10^{-3} mol/L, the zeta potential of scheelite increased on average by as much as 120 mV. This indicates that significant adsorption of DDAC on the scheelite surface occurred.

The zeta potential–pH curve of calcite also shifted positively when the concentration of DDAC increased, but with a smaller magnitude than in the case of scheelite. This suggests that DDAC was adsorbed on the calcite surface, but the adsorbed amount was smaller than that on scheelite. No characteristic band for DDAC was therefore observed in the FTIR spectrum of calcite treated with DDAC solution, because the adsorption of DDAC on calcite was so weak that the DDAC was washed away during sample preparation. The difference between the adsorption behaviors of DDAC on scheelite and calcite can therefore be explained by the difference between the surface charges on the minerals. Scheelite was more negatively charged than calcite; therefore the electrostatic interactions between DDAC and scheelite were stronger, and more DDAC was adsorbed on scheelite. Furthermore, the positive shift of the zeta potential–pH curve of calcite occurred even in the pH range at which calcite was positively charged.

As shown in Fig. 9(3)–(6), when TOAC and DTAC were used, the zeta potential–pH curves of scheelite and calcite all showed positive shifts, but of different magnitudes. The shift for TOAC was close to that for DDAC, but much larger than that for DTAC. DTAC adsorption was much weaker than those of TOAC and DDAC; this is consistent with the flotation results.

Fig. 10 shows the relationships between the zeta potentials of scheelite and calcite and the concentrations of the three quaternary ammonium salts. The curves for DDAC, TOAC, and DTAC can all be divided into two parts, i.e., a low-concentration part and a high-concentration part. At low concentrations, the zeta potentials of scheelite and calcite slowly increased with increasing concentration, whereas at high concentrations, they increased sharply. This indicates two adsorption regimes. This can be explained by a two-step adsorption mechanism (Gao et al., 1987); i.e., the surfactant molecules are adsorbed individually through electrostatic interactions in the first step, and then adsorbed through surfactant associations in the second step, usually at a high rate, until the adsorption reaches saturation. Fig. 10 shows that for DDAC and

TOAC, the second step of scheelite adsorption started before neutralization of its surface charge, whereas for DTAC, it occurred after neutralization. In addition, the zeta potential of calcite was nearly constant in the first adsorption step for the three quaternary ammonium salts, indicating that they were initially adsorbed on the calcite surface by ion exchange.

3.3. Critical micelle concentrations (CMCs) of quaternary ammonium salts

The critical micelle concentration (CMC), an important parameter for surfactants, is the concentration at which a surfactant solution begins to form large amounts of micelles; this is an indication of the surface activity of the surfactant. In flotation, the CMC is usually used to measure the collector hydrophobicity (Wang, 1982). The surface tensions of solutions of the three quaternary ammonium salts and oleate at different concentrations were measured and plotted as a function of concentration; the results are shown in Fig. 11. The concentration at the inflexion point of the curve, marked with arrows in the figure, is the CMC. As the data in Table 1 shows, the order of the CMCs of the four surfactants was DDAC < TOAC < oleate < DTAC. The CMC of DTAC was the largest; therefore it was the least hydrophobic. This explains the poor scheelite-collecting power of DTAC. In addition, the lowest surface tensions of the three quaternary ammonium salt solutions were all lower than that of oleate. Micelles of the quaternary ammonium salts were therefore more hydrophobic than those of oleate.

The free energy of micellization can be calculated from the CMC using Eq. (2) (Graf and Kappl, 2006):

$$\Delta G_m = RT \ln \text{CMC} \quad (2)$$

The free energy of micellization indicates the strength of the hydrophobic association of a surfactant. The lower the free energy of micellization is, the stronger the hydrophobic association. The order of the association strengths was DDAC > TOAC \approx oleate > DTAC.

3.4. Adsorption isotherms of quaternary ammonium salts on scheelite and calcite

An adsorption isotherm is a mathematical expression that relates the concentration of an adsorbate at the interface to its equilibrium concentration in the liquid phase. Isotherm measurements are commonly used to investigate adsorption at a liquid/solid interface. In this study, the Langmuir adsorption isotherm and a general adsorption isotherm (Gu et al., 1992) were considered to describe the adsorption of quaternary ammonium salts on scheelite and calcite.

The Langmuir adsorption isotherm (Langmuir, 1918) is a typical adsorption isotherm; it is commonly observed in adsorption from solutions of surfactants, and is expressed as

$$\Gamma_1 = \frac{\Gamma_m C_1}{C_1 + a} \quad (3)$$

where

Γ_m is the surface concentration of the surfactant, in monolayer adsorption,

C_1 is the concentration of the surfactant in the liquid phase at adsorption equilibrium,

a is a constant [$=55.3 \exp(\Delta G^0/RT)$] (mol/L), at absolute temperature T , in this case around room temperature; ΔG^0 is the free energy of adsorption at infinite dilution; R is the gas constant in the ideal gas equation.

The Langmuir isotherm model assumes uniform energies of adsorption onto the adsorbent surface. It is based on the

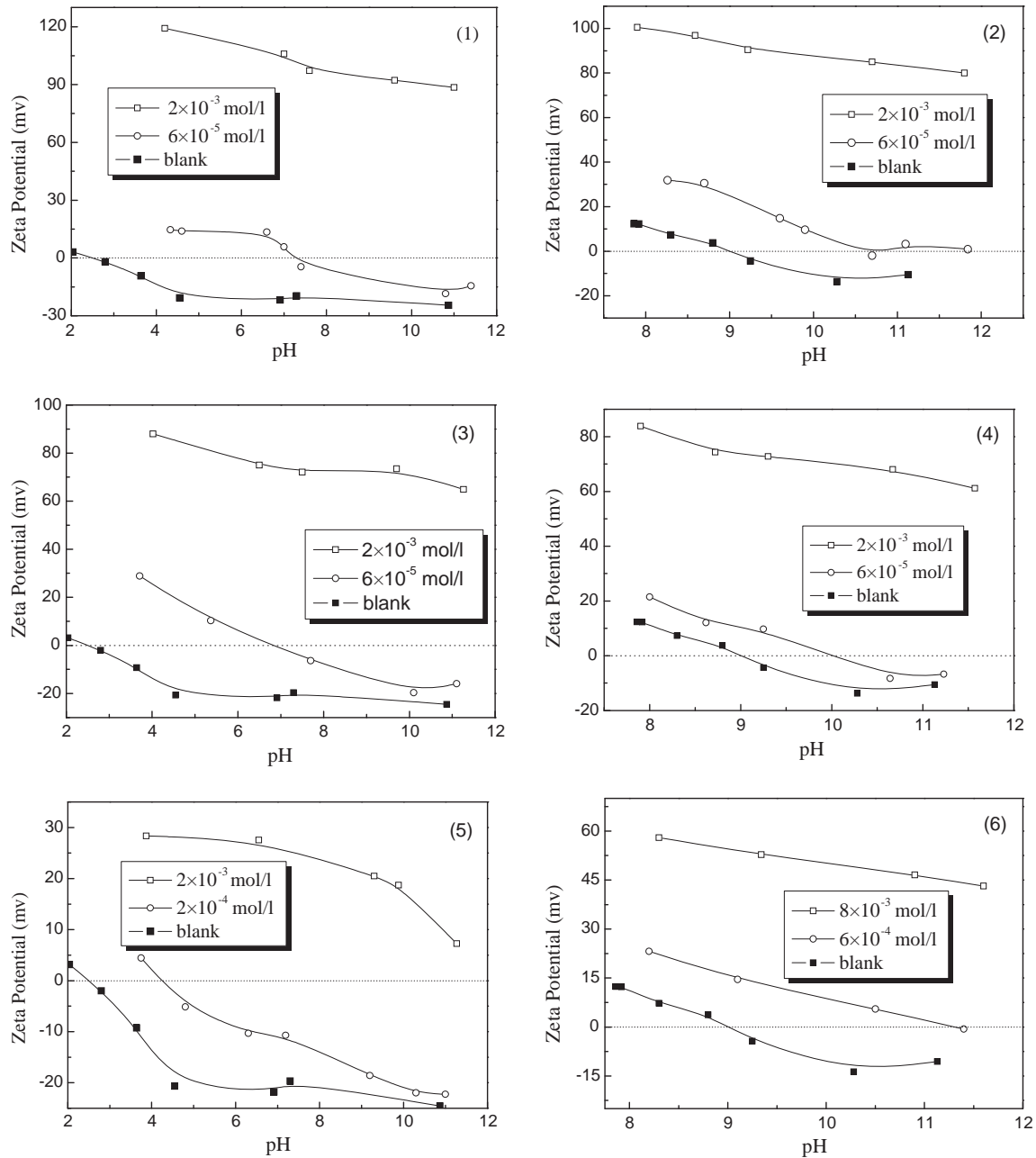


Fig. 9. Zeta potentials of scheelite and calcite as function of pH at various concentrations of quaternary ammonium salts: (1) DDAC + scheelite; (2) DDAC + calcite; (3) TOAC + scheelite; (4) TOAC + calcite; (5) DTAC + scheelite; and (6) DTAC + calcite.

assumption of monolayer adsorption onto a completely homogeneous surface with a finite number of identical sites, and with negligible interactions between adsorbed molecules. However, many surfactant solutions show Langmuir-type behavior even when these restrictions are not met (Rosen, 2004).

In terms of plot shape, surfactant adsorption isotherms can be divided into three types: L-type, S-type, and two-plateau or LS-type (Gu and Zhu, 1990; Zhu and Gu, 1989, 1990; Zhu et al., 1989). A Langmuir isotherm is a typical L-type adsorption isotherm. The general adsorption isotherm used in this research can describe various types of isotherm (including L-, S-, and LS-type). It was derived based on the two-step adsorption mechanism mentioned above, i.e., adsorption through direct interactions between surface-active species and the solid surface in the first step, and

hydrophobic interactions between the adsorbed species in the second step. The general adsorption isotherm equation is

$$\Gamma = \frac{\Gamma_{\infty} k_2 k_1 C^n}{1 + k_1 k_2 C^n} = \frac{\Gamma_{\infty} K C^n}{1 + K C^n} \quad (4)$$

where

k_1 is the equilibrium constant for surfactant monomer adsorption,

k_2 is the equilibrium constant for surfactant micelle adsorption, $K = k_1 k_2$,

C is the concentration of the surfactant in the liquid phase at adsorption equilibrium,

Γ_{∞} is the limiting adsorption amount at high concentration,

n is the number of monomers in the micelles.

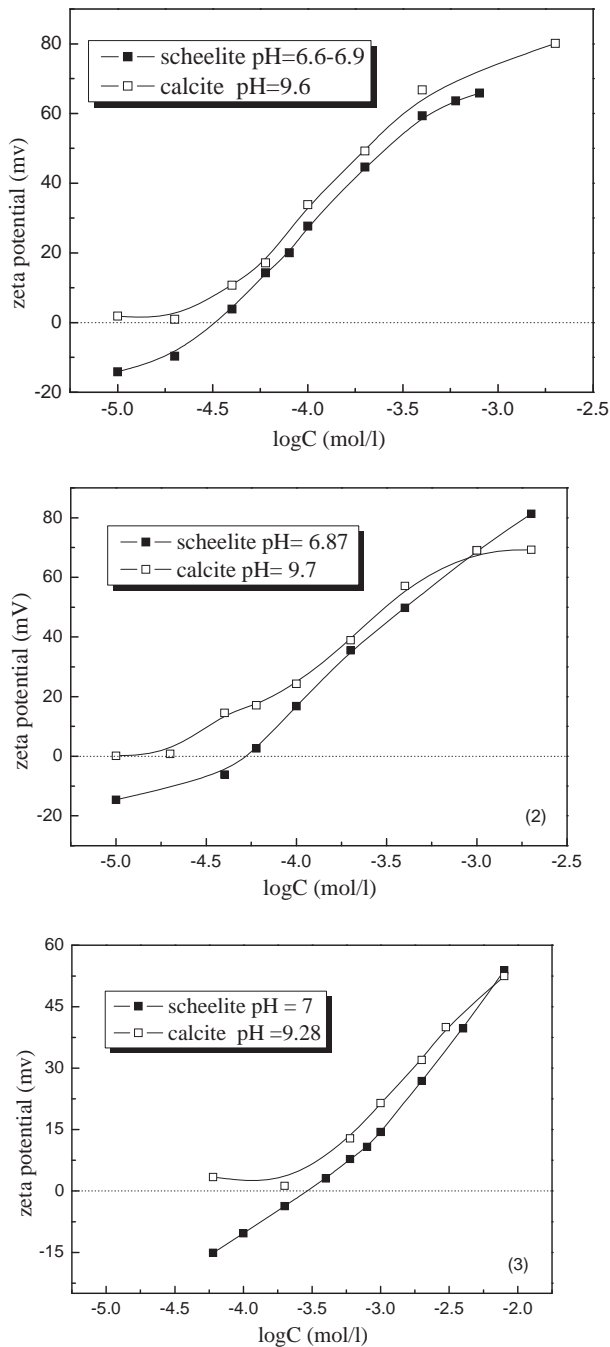


Fig. 10. Zeta potentials of scheelite and calcite as function of quaternary ammonium salt concentration at natural pH: (1) DDAC; (2) TOAC; and (3) DTAC.

The values of k_1 and k_2 determine the isotherm type. If k_1 is sufficiently small, the equation reduces to an S-type equation. If k_1 is sufficiently large, an LS-type isotherm is obtained. The larger k_2 is, the steeper the second step in the isotherm.

Fig. 12 shows the amounts of the three quaternary ammonium salts adsorbed on scheelite and calcite as function of equilibrium concentration at natural pH (pH 7.8 for scheelite and pH 9 for calcite). For the three quaternary ammonium salts, adsorption increased with increasing concentration and then reached saturation at around their CMCs. Immediately before saturation, a sudden increase in adsorption was observed; this is attributed to the formation of surface aggregates, known as hemimicelles, of the surfactant molecules on the solid surface as a result of lateral interactions between hydrocarbon chains (Gao et al., 1987). This

lateral attraction force generates an additional driving force, which is superimposed on the existing electrostatic attraction, causing a sharp increase in adsorption.

Fig. 12 shows that for the three quaternary ammonium salts, the amount adsorbed on scheelite was always higher than that on calcite. The gap between the adsorbed amounts increased with increasing concentration of the quaternary ammonium salt. This is why scheelite can be separated from calcite by flotation using a quaternary ammonium salt as the collector. In addition, the order of the differences between the amounts adsorbed on scheelite and calcite for the three quaternary ammonium salts was DDAC < TOAC < DTAC. This explains why the selectivity of TOAC for scheelite was higher than that of DDAC. DTAC had the highest selectivity for scheelite, because of its high CMC, i.e. low hydrophobicity, but the amount required for flotation was so large that it was impractical to use it as collector for scheelite.

The adsorption mechanisms of quaternary ammonium salts on scheelite and calcite were further studied by fitting the adsorption data to both the Langmuir and general adsorption isotherms. Fig. 13 shows the two adsorption models for the three quaternary ammonium salts. The parameters calculated from the curves of the Langmuir and general adsorption isotherms are summarized in Table 2.

In the fitting to the Langmuir model, the correlation coefficients (R^2_{adj}) were used to measure the fitness. As shown in Table 2, the three quaternary ammonium salts showed different degrees of fitting; i.e., the Langmuir model provided the best fit for DDAC adsorption, the second best for TOAC, and the worst for DTAC. This is also shown by the variations between the graphical and analytical solutions for the three quaternary ammonium salts.

For fitting to the general adsorption model, the adsorption data were first divided into two parts, i.e., low-concentration and high-concentration parts. The two parts were then fitted by two equations transformed from the general adsorption model at low and high concentrations, respectively. No correlation coefficients were obtained for the overall fitting to the general adsorption model. However, from the variations between the graphical and analytical solutions shown in Fig. 13, it can be concluded that the general adsorption isotherm provided good fits for the adsorptions of all three quaternary ammonium salts, and this model fitted the adsorption better than the Langmuir isotherm did.

The derivation of the general adsorption isotherm equation implies that the parameters k_1 and k_2 in Eq. (4) indicate the strength of the interaction between the surfactant and the solid

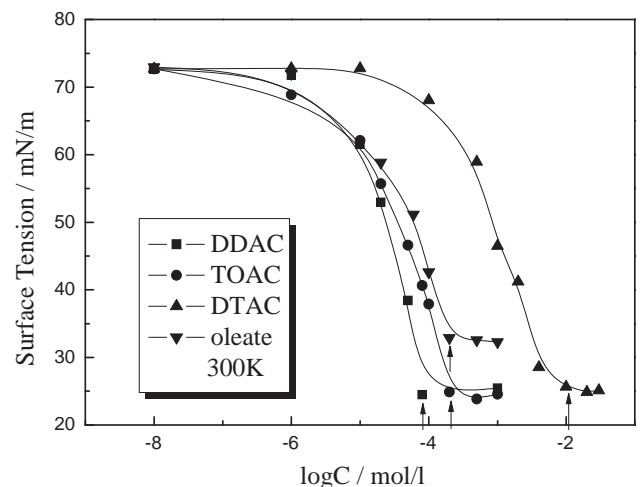


Fig. 11. Surface tensions of solutions of quaternary ammonium salts and oleate as function of concentration (pH 7.3).

Table 1
CMCs and related properties of quaternary ammonium salts and oleate.

Surfactants	CMC (mmol/l)	The lowest surface tension (mN/m)	Micellization free energy (kJ/mol)
DDAC	0.08	24.95	−23.52
TOAC	0.2	24.42	−21.23
DTAC	20	25.2	−9.75
Oleate	0.2	32.54	−21.23

surface in the first adsorption step, and the strength of the lateral hydrophobic associations between surfactants in the second adsorption step, i.e., the van der Waals forces. The larger k_1 and k_2 are, the stronger the interactions. An analysis of the values of k_1 and k_2 for the three quaternary ammonium salts could clarify the mechanism of the adsorption of quaternary ammonium salt cationic collectors on scheelite and calcite.

The data in Table 2 shows that the adsorptions of quaternary ammonium salts on scheelite and calcite were characterized by large k_2 values; DDAC had the highest k_2 , followed by TOAC and then DTAC. The general adsorption isotherms of the three quaternary ammonium salts show that the shape of the adsorption isotherm changed from LS-type to L-type as k_2 increased. The Langmuir adsorption model therefore fitted the adsorption of DDAC well, but the fitting was progressively worse for TOAC and DTAC.

The differences among the shapes of the adsorption isotherms clearly results from different adsorption processes. The relationships among them were clarified by dividing the active sites on the surface into three classes, i.e., sites with adsorbed monomers, sites with adsorbed micelles, and unoccupied sites. The isotherm of the sites with adsorbed monomers was derived from the

corresponding general adsorption isotherm. The fraction of sites with adsorbed monomers was calculated as

$$\Theta_1 = \frac{\Gamma_1}{\Gamma_\infty/n} = \frac{k_1 C}{1 + k_1 C + k_1 k_2 C^n} \quad (5)$$

where

Θ_1 is the fraction of sites with adsorbed monomers,

k_1 is the equilibrium constant for surfactant monomer adsorption,

k_2 is the equilibrium constant for surfactant micelle adsorption, C is the concentration of the surfactant in the liquid phase at adsorption equilibrium,

Γ_1 is the amount of adsorbed surfactant monomers,

Γ_∞ is the limiting adsorption amount at high concentrations, n is the number of monomers in the micelles.

The relationships were similar for scheelite and calcite; therefore only isotherms of the fractions for scheelite are shown in Fig. 14.

Fig. 14 shows that for the three quaternary ammonium salts, the fraction of scheelite sites with adsorbed monomers initially increased with increasing equilibrium concentration and then decreased after reaching a maximum. This corresponds to the two steps of surfactant adsorption, i.e., monomer adsorption in the first step and hemimicelle adsorption in the second step. The major difference among the isotherms for the three quaternary ammonium salts was the maximum fraction of sites with adsorbed monomers that could be obtained. The fraction was largest for DTAC, higher than 0.9 (90%), whereas those for DDAC and TOAC were similar, and lower than that for DTAC, about 0.7 (70%). This suggests that for DTAC, hemimicelle formation started after

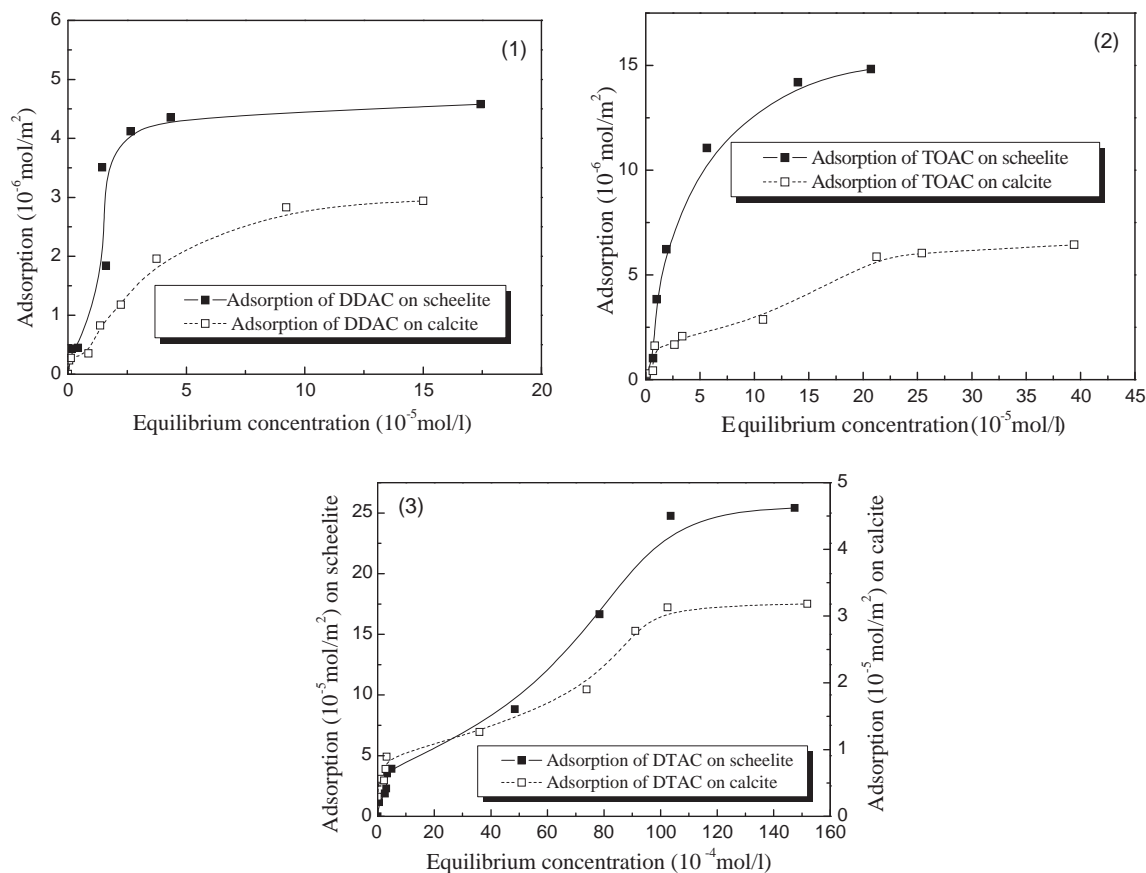


Fig. 12. Adsorption isotherms of quaternary ammonium salts on scheelite and calcite at natural pH: (1) DDAC, (2) TOAC, and (3) DTAC.

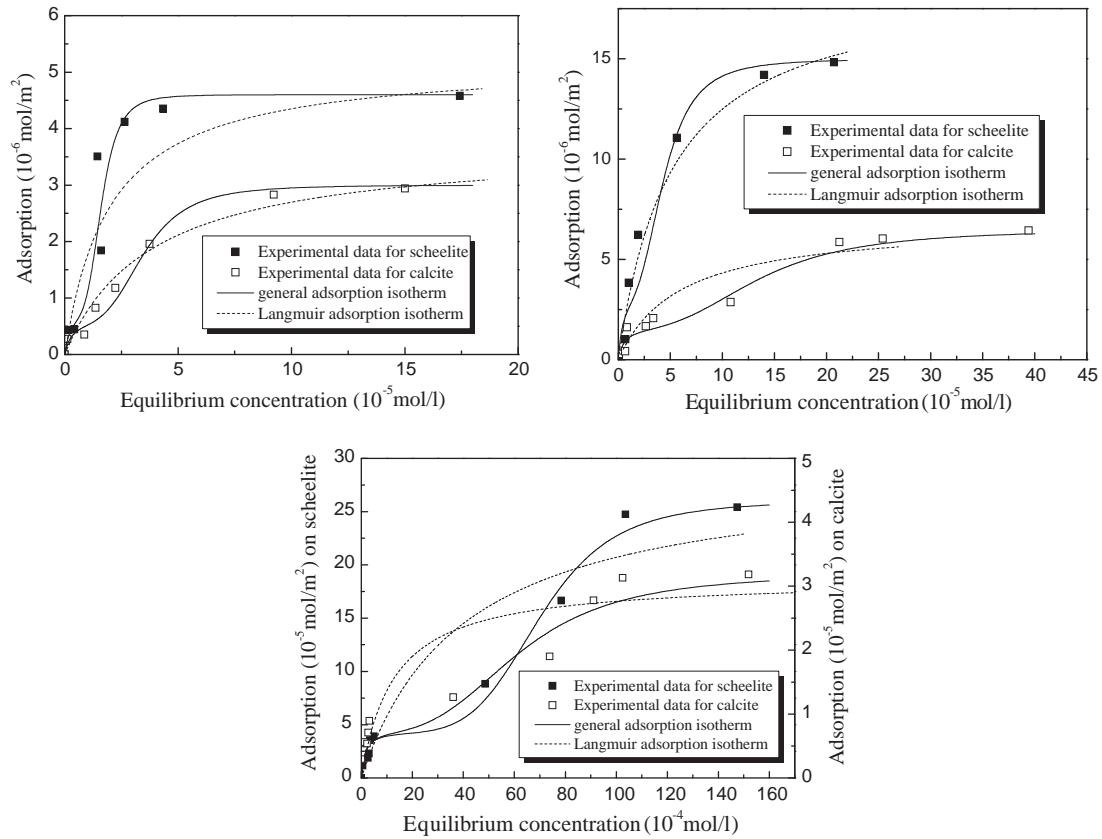


Fig. 13. Langmuir and general adsorption isotherm models fits for adsorption of quaternary ammonium salts on scheelite and calcite at natural pH.

Table 2
Adsorption isotherm parameters of quaternary ammonium salts.

Isotherm models	Parameters	Surfactants					
		DDAC		TOAC		DTAC	
		Scheelite	Calcite	Scheelite	Calcite	Scheelite	Calcite
Langmuir	Γ_m (mol/m ²)	5.210×10^{-6}	3.723×10^{-6}	1.894×10^{-5}	6.839×10^{-6}	2.899×10^{-4}	3.116×10^{-5}
	R_{adj}^2	0.937	0.949	0.837	0.805	0.751	0.883
Two-Step	k_1	3.498×10^5	3.101×10^5	1.967×10^5	1.766×10^5	7.582×10^3	6.329×10^3
	k_2	2.26×10^{20}	9.72×10^{15}	1.70×10^{13}	7.87×10^{10}	2.95×10^{10}	8.96×10^6

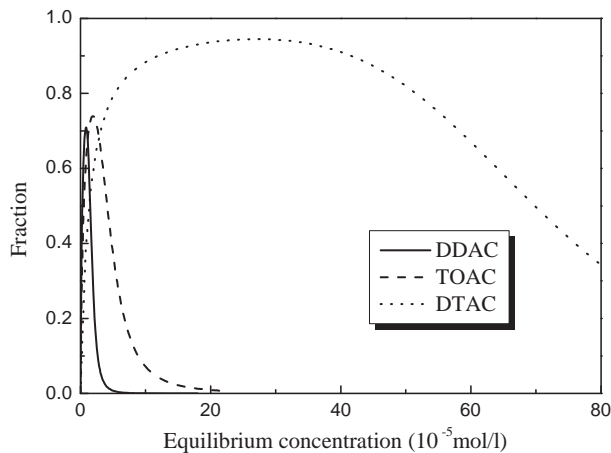


Fig. 14. Isotherms of scheelite surface sites with adsorbed monomers for three quaternary ammonium salts.

monomer adsorption almost reached saturation, whereas for DDAC and TOAC, it started earlier. This is consistent with the zeta potential measurement results; i.e., for DDAC and TOAC, the second step of adsorption on scheelite started before neutralization of the surface charge, whereas for DTAC it occurred after neutralization. These differences among the adsorption processes for DDAC, TOAC, and DTAC are reflected by their adsorption isotherms; those for DDAC and TOAC were L shaped, especially that for DDAC, whereas the DTAC isotherm was LS shaped.

It can be seen from Table 2 that the values of k_1 for the three quaternary ammonium salts were different from each other. The order is DDAC > TOAC > DTAC. This shows that the interactions between DDAC and scheelite or calcite were the strongest, followed by TOAC and then DTAC. These results suggest that in the interactions between quaternary ammonium salts with scheelite or calcite, van der Waals forces were as important as electrostatic interactions, because the charges were the same, and the van der Waals forces were large. It can be concluded from the values of k_1 that the van der Waals forces of DDAC were the largest, followed by TOAC and DTAC; this is consistent with the order of the hydrophobic associations obtained in the CMC tests. This is also

the order of the k_2 values of the three quaternary ammonium salts (DDAC > TOAC > DTAC). Moreover, these results also explain the positive shift of the zeta potential–pH curve of calcite in the presence of quaternary ammonium salts, even when the calcite was positively charged.

For the same quaternary ammonium salt, the difference between the k_2 values for scheelite and calcite were as significant as those among the three quaternary ammonium salts. If we take DDAC as an example, k_2 for adsorption on scheelite was larger by five orders of magnitude than that on calcite. This indicates that the lateral hydrophobic associations between DDAC molecules adsorbed on scheelite in the second adsorption step were much stronger than those on calcite. This is probably because more DDAC was adsorbed on scheelite in the first adsorption step than on calcite, because DDAC interacted more strongly with scheelite than with calcite, as a result of their different surface charges. The larger number of molecules adsorbed on scheelite than on calcite acted as anchors, which facilitated the formation of hemimicelles in the second adsorption step. As a consequence of micellization in the second adsorption step, the large van der Waals forces of DDAC further increased the adsorption gap between scheelite and calcite. Therefore, in addition to the opposite charges on scheelite and calcite, the selectivities of the quaternary ammonium salts for scheelite were the result of large van der Waals forces.

4. Conclusions

- (1) Three quaternary ammonium salts (DDAC, TOAC, and DTAC) were investigated as cationic collectors in the flotation of scheelite from calcite. Single-mineral and mixed-mineral flotations indicated that DDAC and TOAC were superior to oleate as collectors for scheelite with respect to collecting power and selectivity. It was possible to separate scheelite from calcite using DDAC or TOAC at concentrations of 1×10^{-4} mol/L as the collector around pH 8, at which the difference between the floatability of scheelite and that of calcite was largest. The collecting power of DTAC was significantly weaker than those of the other two quaternary ammonium salts, with maximum scheelite recovery of only 40%.
- (2) Based on the molecular structures and FTIR spectra, we excluded the possibility of chemical adsorption of the quaternary ammonium salts on scheelite and calcite surfaces. Zeta potential measurements indicated that electrostatic interactions played a primary role in the flotation separation of scheelite from calcite with quaternary ammonium salts. Adsorption isotherm analysis showed that van der Waals forces also played an important role in the interactions of quaternary ammonium salts with scheelite and calcite. The quaternary ammonium salts showed selectivities not only because scheelite and calcite were oppositely charged, but also because of the large van der Waals forces of the collectors.
- (3) Zeta potential and adsorption measurements indicated that two steps were involved in the adsorption of quaternary ammonium salts on scheelite and calcite, i.e., monomer adsorption through direct interactions between surfactants and solids in the first step, and hemimicelle adsorption through lateral hydrophobic associations between surfactants in the second step. The adsorption on calcite was much weaker than that on scheelite. A two-step adsorption isotherm fitted the adsorption of all three quaternary ammonium salts well, but the Langmuir adsorption isotherm only fitted DDAC well. It was concluded from analysis of the isotherms that the van der Waals forces of the quaternary ammonium salts determined the adsorption processes,

and therefore the plots of their isotherms. DDAC had the highest van der Waals forces; therefore the second step, i.e., micelle adsorption, occurred early, before the first step, i.e., monomer adsorption, reached saturation, and consequently its isotherm was L type.

Acknowledgment

The authors would like to thank the State Key Program of National Natural Science Foundation of China (Grant No. 50834006) for financial support.

References

- Abdel-Khalek, N., Yehia, A., Ibrahim, S., 1994. Technical note beneficiation of Egyptian feldspar for application in the glass and ceramics industries. *Miner. Eng.* 7 (9), 1193–1201.
- Amakonah, J.O., Somasundaran, P., Ananthapadmanabhan, K.P., 1985. Effect of dissolved mineral species on the dissolution precipitation characteristics of calcite and apatite. *Colloids Surf.* 15, 295–307.
- Atademir, M.R., Kitchener, J.A., Shergold, H.L., 1981. The surface chemistry and flotation of scheelite, II. Flotation "collectors". *Int. J. Miner. Process.* 8 (1), 9–16.
- Gao, Y., Du, J., Gu, T., 1987. Hemimicelle formation of cationic surfactants at the silica gel–water interface. *J. Chem. Soc. Faraday Trans. 1: Phys. Chem. Condens. Phases* 83 (8), 2671–2679.
- Graf, K., Kappl, M., 2006. *Physics and Chemistry of Interfaces*. John Wiley & Sons, New Jersey.
- Gu, T., Zhu, B.Y., 1990. The S-type isotherm equation for adsorption of nonionic surfactants at the silica gel–water interface. *Colloids Surf.* 44, 81–87.
- Gu, T., Zhu, B.Y., Rupprecht, H., 1992. Surfactant adsorption and surface micellization. *Prog. Colloid Polym. Sci.* 88, 74–85.
- Hanna, H.S., Somasundaran, P., 1976. Flotation of salt-type minerals. In: Fuerstenau, M.C. (Ed.), *Flotation: A.M. Gaudin Memorial Volume*, vol. 1. American Institute of Mining, Metallurgical, and Petroleum Engineers, New York.
- Hiçiyilmaz, C., Atalay, Ü., Özbayoglu, G., 1993. Selective flotation of scheelite using amines. *Miner. Eng.* 6 (3), 313–320.
- Hu, Y.H., 1988. Solution chemistry calculation, diagram method and the research on flotation behaviors of salt-type minerals. PhD Thesis, Central South University, China.
- Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* 40 (9), 1361–1403.
- Marinakakis, K.I., Shergold, H.L., 1985a. Influence of sodium silicate addition on the adsorption of oleate by fluorite, calcite and barite. *Int. J. Miner. Process.* 14 (3), 177–193.
- Marinakakis, K.I., Shergold, H.L., 1985b. The mechanism of fatty acid adsorption in the presence of fluorite, calcite and barite. *Int. J. Miner. Process.* 14 (3), 161–176.
- Mishra, S.K., 1982. Electrokinetic properties and flotation behavior of apatite and calcite in the presence of sodium oleate and sodium metasilicate. *Int. J. Miner. Process.* 9 (1), 59–73.
- Pugh, R., Stenius, P., 1985. Solution chemistry studies and flotation behavior of apatite, calcite and fluorite minerals with sodium oleate collector. *Int. J. Miner. Process.* 15 (3), 193–218.
- Qin, Z.H., Tan, R., 2006. Spectrophotometric method for determination of cationic surfactants with eosin Y and its reaction mechanism. *Chin. J. Anal. Lab.* 25 (10), 110–114.
- Rodrigues, O.M.S., 2013. Kaolinite and hematite flotation separation using etheramine and ammonium quaternary salts. *Miner. Eng.* 40, 12–15.
- Rosen, M.J., 2004. *Surfactants and Interfacial Phenomena*. John Wiley & Sons, New Jersey.
- Shin, B.S., Choi, K.S., 1987. Adsorption of sodium metasilicate on calcium minerals. *Miner. Metall. Process.* 2, 226.
- Wang, D.Z., 1982. *The Interaction Mechanism and applications of Flotation Reagents*. Metallurgy Industry Press, Beijing.
- Wang, Y.H., Hu, Y.H., He, P.B., Gu, G.H., 2004. Reverse flotation for removal of silicates from diaspore-bauxite. *Miner. Eng.* 17 (1), 63–68.
- Wang, Y.H., Ren, J.W., 2005. The flotation of quartz from iron minerals with a combined quaternary ammonium salt. *Int. J. Miner. Process.* 77 (2), 116–122.
- Xie, J.X., Chang, J.B., Wang, X.M., 2001. *Application of Infrared Spectroscopy in Organic Chemistry and Pharmaceutical Chemistry*. Science Press, Beijing.
- Xu, Z.H., Hu, Y.H., 2003. Interaction of amphoteric amino phosphoric acids with calcium-containing minerals and selective flotation. *Int. J. Miner. Process.* 72 (1–4), 87–94.
- Zhu, B.Y., Gu, T., 1989. General isotherm equation for adsorption of surfactants at solid/liquid interfaces. Part 1. Theoretical. *J. Chem. Soc. Faraday Trans. 1: Phys. Chem. Condens. Phases* 85 (11), 3813–3817.
- Zhu, B.Y., Gu, T., 1990. Reverse hemimicelle formation of 1-decanol from heptane at the solution/graphite interface. *Colloids Surf.* 46 (2), 339–345.
- Zhu, B.Y., Gu, T., Zhao, X.L., 1989. General isotherm equation for adsorption of surfactants at solid/liquid interfaces. Part 2. Applications. *J. Chem. Soc. Faraday Trans. 1: Phys. Chem. Condens. Phases* 85 (11), 3819–3824.