

Mechanisms of flotation separation of diasporite and kaolinite by quaternary ammonium salt DTAL^①

CHEN Xiang-qing(陈湘清), HU Yue-hua(胡岳华), WANG Yu-hua(王毓华)

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

Abstract: The FTIR spectroscopy indicates that the adsorption of quaternary ammonium salt DTAL on the diasporite and kaolinite is physical adsorption. The adsorption of cationic surfactants measured by two-phase titration shows that the adsorption on the kaolinite is notably more than that on diasporite. The adsorption isotherm on kaolinite is linear while that of DTAL on diasporite is two-step flat form. The analysis on the cationic ions of kaolinite supernatants shows that kaolinite releases plenty of crystalloid structure ions which counteract the crystalloid charge because of the adsorption of the cationic surfactant. The mechanisms of the quaternary ammonium salt DTAL on flotation separation of diasporite and kaolinite include ion exchange interaction as well as electrostatic force.

Key words: quaternary ammonium salt; adsorption; cationic ion; mechanism

CLC number: TD 923; TD 952

Document code: A

1 INTRODUCTION

In reverse flotation of diasporic bauxite, it is required to float the silicates, such as kaolinite, pyrophyllite and illite, in order to obtain high ratio of $\text{Al}_2\text{O}_3/\text{SiO}_2$ concentrate. The collectors in reverse flotation usually are the cationic surfactants, for example, quaternary ammonium salt. There are a lot of researchers on the flotation behavior of the silicates^[1-5]. Fuerstenau et al^[6] and Sun et al^[7] summarized in detail the crystal chemistry, electrical double layer properties and their correlation with flotation behavior of silicate such as orthosilicates, sheet silicates, framework silicates. As for the sheet silicates which are the major silicious minerals in the diasporic bauxite, some researchers studied their flotation behavior or their interaction mechanisms with the alkylamine or other nitrogenous organic collector^[8-10]. And also there are some researches on the flotation of silicates with quaternary ammonium species as collector^[11, 12]. Bittencourt^[11] gained the high purity gibbsite concentrate which included 97.4% Al_2O_3 and whose recovery was 90% by separating kaolinite from bauxite concentration with the quaternary ammonium salt at pH= 6. Wang^[12] studied the flotation behavior of sheet silicates, kaolinite, pyrophyllite and illite by quaternary ammonium DTAL.

The adsorption of surfactant on mineral particles plays an important role in the interfacial phenomena at the solid/liquid interface and mineral flotation.

Therefore, the adsorption mechanisms and characteristic have been very interesting subjects. It is generally accepted that ionic surfactant adsorbs readily due to electrostatic interaction on oppositely charged surfaces in the low concentration range^[8, 9, 13-16]. With an increase in surfactant concentration, the adsorption increase sharply above the hemimicelle concentration (HMC)^[13]. Consequently, various adsorption models have been proposed by many coworkers, for example, the reverse-orientation model^[13, 17, 18], the two-step model^[14, 19], and the small surface micelle model^[15, 20].

We previously reported the effective separation of kaolinite from diasporite by quaternary ammonium compound (DTAL) which is a kind of cationic surfactant^[12]. In this article the mechanisms of the adsorption of DTAL on diasporite and kaolinite was studied by solution Fourier Transfer Infrared (FTIR), adsorption measurement and chemical analysis.

2 EXPERIMENTAL

2.1 Material

The pure mineral samples of kaolinite and diasporite were from Xiaoguan and Pingdingshan in Henan Province, China, respectively. The lump ore was hand-picked, ground by porcelain mill, and screened to 0-0.098 mm. Collector was a quaternary ammonium compound (DTAL). Sodium hydroxide and hydrochloric acid were used as pH adjusters. Distilled

① **Foundation item:** Project (G1999064901) supported by the National Key Fundamental Research and Development Program of China; project (59925412) supported by the National Science Fund for Distinguished Young Scholar

Received date: 2003-09-15; **Accepted date:** 2004-01-12

Correspondence: CHEN Xiang-qing, PhD; Tel: + 86-731-8830482; E-mail: xiangqingchen@tom.com

water was used in all experiments.

2.2 FTIR

The 0.2 mL 0.2% (mass fraction) kaolinite or diaspore slurry was mixed with the 0.8 mL DTAL solution with concentration of 5×10^{-3} mol/L and 0.1 mol/L respectively. Then 0.8 mL distilled water was added. After airproof and vibration for 24 h, the slurry was measured on the Nicolet FTIR instrument, and ATR FTIR spectra were recorded.

2.3 Adsorption measurement

In order to keep the same condition of flotation, 3 g kaolinite or diaspore sample was put into flotation cell with volume of 25 mL. After 22 mL water was added, the cell was hanged and stirred by the impeller of the laboratory XFG flotation machine for 3 min. The adsorption was divided into two parts: 1) the adsorption of 4×10^{-4} mol/L DTAL at different pH values and 2) the adsorption of different concentration DTAL at the pH=6. In part 1, the pH of the slurry was regulated to the desired value, then 4×10^{-4} mol/L DTAL solution was interacted with the slurry for 5 min; in part 2, after regulating the pH=6, the desired concentration DTAL was interacted with the slurry for 5 min. After that, the slurry was spilled to centrifugal tube and run for 10 min in the GL-20G-II refrigerant centrifugal machine, whose centrifugal velocity is 230 r/s. 2 mL supernatants were analyzed for the concentration of the cationic surfactant DTAL by two-phase titration technique^[21].

2.4 Chemical analysis of inorganic cation concentration in kaolinite slurry

8 g kaolinite (0.098–0.15 mm) and 200 mL distilled water were mixed in the beaker and stirred by the magnetic stirrer for 30 min. Then the slurry was equally divided into two parts: one was interacted with 10 mL 5×10^{-3} mol/L DTAL solution and the other was interacted with 10 mL distilled water for 4 h on the stirring. After that, the slurry was spilled to centrifugal tube and run for 10 min in the GL-20G-II refrigerant centrifugal machine, whose centrifugal velocity is 230 r/s. 40 mL total supernate was analyzed for the concentration of the inorganic cation Na^+ , K^+ , Ca^{2+} and Mg^{2+} .

3 RESULTS AND DISCUSSION

3.1 FTIR spectra

The FTIR spectra of DTAL, kaolinite and kaolinite interacted with DTAL are shown in Fig. 1. The FTIR spectra of diaspore and diaspore interacted with

DTAL are shown in Fig. 2. It can be seen from Fig. 1 and Fig. 2 that the peaks at 2925 cm^{-1} and 2856 cm^{-1} are due to the asymmetric and symmetric stretching vibration of C—H bond, whose theoretic peaks are at the range of $2850\text{--}3000\text{ cm}^{-1}$. The three peaks under 1500 cm^{-1} are due to the curving vibration of C—H bond. Peaks at the range of $1020\text{--}1220\text{ cm}^{-1}$ attributed to C—N bond stretching vibration are not found because their intensities are very weak^[22]. The peaks at 905 cm^{-1} , 961 cm^{-1} and 1483 cm^{-1} are the characteristic peaks of quaternary ammonium group from the standard FTIR. The peaks at 2925 cm^{-1} and 2856 cm^{-1} both appear in the FTIR spectra of kaolinite and diaspore which are interacted with DTAL, and their different intensity may be due to the different interaction concentration of DTAL. This indicates the adsorption of DTAL on kaolinite and diaspore. But there isn't any shift of the peaks in the FTIR, so the adsorption of DTAL on kaolinite and diaspore may be mainly of physical interaction.

3.2 Adsorption measurement

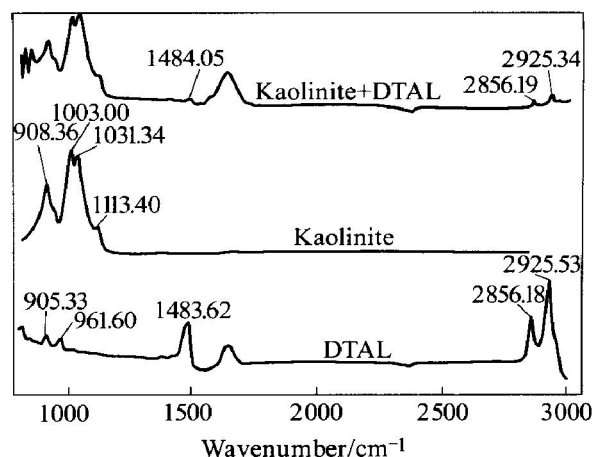


Fig. 1 FTIR spectra of kaolinite, DTAL and kaolinite interacted with DTAL

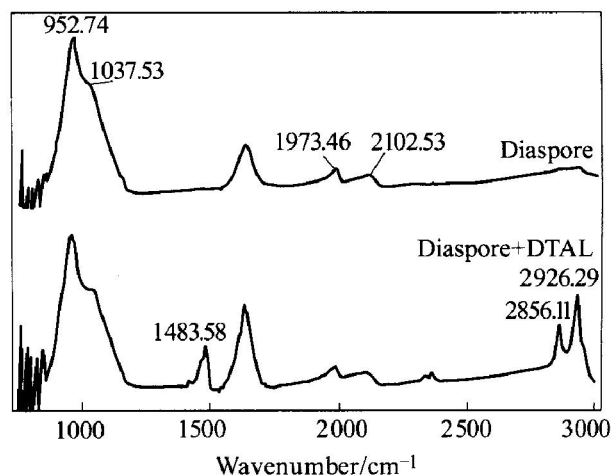


Fig. 2 FTIR spectra of diaspore before and after interaction with DTAL

The adsorption of DTAL on kaolinite and diaspore at different pH conditions is shown in Fig. 3. It can be seen that the adsorption of DTAL on kaolinite and diaspore increases with the pH value increasing. This may be due to the electrostatic interaction because the negative potential of kaolinite and diaspore increases with the pH value increasing^[12]. It can also be noticed that the adsorption of DTAL on kaolinite is much more than that on diaspore corresponding to the floatability of kaolinite and diaspore^[12]. The adsorption isotherms of different concentration DTAL on kaolinite and diaspore are presented in Fig. 4. The adsorption isotherm of DTAL on diaspore is a double plat form. At low concentration, the electrostatic adsorption corresponds to the first plat. With the increase of the concentration of DTAL to about 1.5×10^{-3} mol/L, there is an increase in the adsorption attributed to the formation of surfactant aggregated at the solid/liquid surface because of the role of hydrophobic interactions between the hydrocarbon tails. This corresponds to the second plat. While the adsorption of DTAL on kaolinite linearly increases in the experiment range with the increase of the concentration of DTAL and is much more than the adsorption on diaspore. Almost 90% of the initial concentration adsorbed is independent of the initial concentration. Obviously the electrostatic interaction can't explain the phenomena.

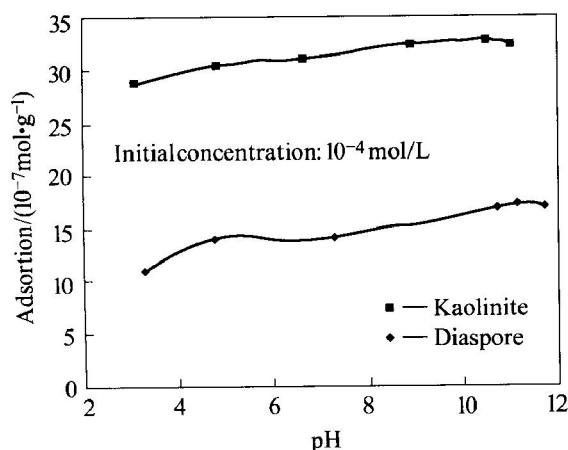


Fig. 3 Adsorption of DTAL on diaspore and kaolinite as a function of pH

3.3 Chemical analysis of inorganic cation concentration in kaolinite slurry

It is generally accepted that kaolinite has some cation exchange capacity. Organic cations are strongly preferred to the exchange sites over the Na^+ ions^[23]. The change of the cations concentration in the absence and presence of DTAL is given in Table 1. It is shown that the cations concentration is greatly increased, especially the divalent ions such as Mg^{2+} and Ca^{2+} after the addition of

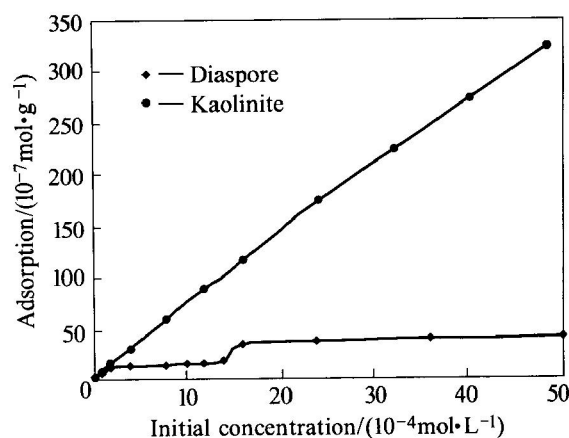


Fig. 4 Adsorption isotherms of DTAL on diaspore and kaolinite at pH= 6

Table 1 Cationic concentration of supernatant of kaolinite slurry (mg/L)

Cation species	In absence of DTAL	In presence of DTAL	Difference before and after interaction with DTAL
K^+	4.3	7.1	2.8
Na^+	3.1	3.6	0.5
Mg^{2+}	2.6	10.4	8.8
Ca^{2+}	2.3	7.9	5.6

cationic DTAL.

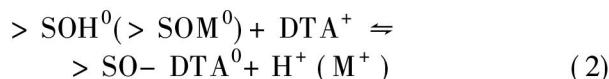
Kaolinite has layered structure with an extended sheet on the crystallographic ab plane composed of a siloxane layer of tetrahedral Si, and a gibbsite layer of octahedral Al. Both layers are connected by bridging oxygens. The arrangement of tetrahedral Si gives rise to ditrigonal cavities along the surface, which permits the existence of the small volume cationic ions. The isomorphous substitution of Si(IV) for Al(III) in the tetrahedral position develops a permanent negative charge within the siloxane layer, which accounts for the compensatory cationic ions. The layered structure kaolinite swells when water exists, which allows for the exchange and diffusion of these cationic ions: Ca^{2+} , Mg^{2+} , Na^+ , K^+ and H^+ . It is commonly believed that cationic exchange occurs due to the broken bonds around the crystal edges, the substitution within the lattice, and the hydrogen of exposed surface hydroxyls that may be exchanged.

The protonation/deprotonation or the cationic exchange of the exposed surface sites can be denoted as:



where $>\text{S}$ represents the surface site, M represents the metal cationic.

At the existence of the DTA^+ , the exchange will further occur:



This is the reason that the cationic concentration in the supernatant of kaolinite slurry increases in the presence of DTAL in the solution.

While diasporite has hexagonal compact accumulation lattice. It is difficult for the diffusion of cationic. Its exchange can only occur on the surface, which limits the adsorption of DTAL.

As mentioned above, the adsorption of DTAL on the surface of kaolinite is not only the electrostatic interaction, but also the cationic exchange process. Because of the abundance of the exchangeable cationic in the kaolinite, there allows for abundant adsorption of DTAL. The absorbed DTAL is more than 90%; while the lattice of diasporite limits its adsorption, bringing about only 50% absorption. When the kaolinite and diasporite are put together in the bulk, they will further compete for adsorption of the DTAL, then the adsorption of DTAL is little on the surface of diasporite compared with the surface of kaolinite. The more adsorption of DTAL results in hydrophobic surface corresponding to the high floatability of kaolinite. This causes the separation of kaolinite from diasporite. The high grade bauxite, whose $\text{Al}_2\text{O}_3/\text{SiO}_2$ is 10.63 and the recovery is 86.25%, was obtained by SFL regulator and DTAL collector^[12].

4 CONCLUSIONS

The solution FTIR spectroscopy indicates that the adsorption of quaternary ammonium salt DTAL on the diasporite and kaolinite is physical adsorption. The adsorption of cationic surfactants on the kaolinite is notably more than that on diasporite. The adsorption isotherm on kaolinite is linear while that of DTAL on diasporite is two-step flat form. The further analysis on the cationic ions of the supernate of kaolinite shows that kaolinite releases plenty of crystalloid structure ions which counteract the crystalloid charge because of the adsorption of the cationic surfactant. The mechanisms of the quaternary ammonium salt DTAL on flotation separation of diasporite and kaolinite include ion exchange interaction as well as electrostatic force.

REFERENCES

- [1] Smolik J J, Harman E, Fuerstenau D W. Surface characteristics and flotation behavior of aluminosilicates [J]. Trans AIME, 1966, 235: 367 - 375.
- [2] Cases J M. On the normal interaction between adsorbed species and adsorbing surface [J]. Trans Soc Mining Eng AIME, 1970, 247(2): 123 - 127.
- [3] Soc Mining Eng, Choi H S, Oh J. Surface properties and floatability of kyanite and andalusite [J]. J Inst Min Metall Japan, 1965, 21: 614 - 621.
- [4] Manser R M. Handbook of Silicate Flotation [M]. Stevenage: Warren Spring Laboratory, 1975.
- [5] Smith R W, Akhtar S. Cationic flotation of oxide and silicates [A]. Fuerstenau M C. Flotation—A M Gaudin Memorial Volume [C]. AIME, 1976. 87.
- [6] Fuerstenau D W, Fuerstenau M C. The flotation of oxide and silicate minerals [A]. King R P. The Principles of Flotation [C]. Johannesburg: South African Inst of Min & Met, 1982. 109 - 158.
- [7] SUN C Y, YIN W Z. The Principles of Silicates Flotation [M]. Beijing: Science Press, 2001. 74 - 195.
- [8] JIANG H, HU Y H, QIN W Q, et al. Mechanism of flotation for diasporite and aluminium silicate with alkyl amine collectors [J]. The Chinese Journal of Nonferrous Metals, 2001, 11(4): 688 - 692. (in Chinese)
- [9] CAO X F, HU Y H, JIANG Y R, et al. Flotation mechanism of aluminium silicate minerals with N-dodecyl 1, 3 diamino propane [J]. The Chinese Journal of Nonferrous Metals, 2001, 11(4): 693 - 696. (in Chinese)
- [10] HU Y H. Progress in flotation of silica [J]. Trans Nonferrous Met Soc China, 2003, 13(3): 656 - 662.
- [11] Bittencourt L R, Lin C L, Miller J D. Flotation recovery of high purity gibbsite concentrates from a Brazilian bauxite ore [A]. Advanced Material—Application of Mineral and Metallurgical Processing Principles [C]. Colorado: Society of Mining Engineers of AIME, 1990. 77 - 85.
- [12] WANG Y H, HU Y H, CHEN X Q. Aluminium silicate flotation with quaternary ammonium salts [J]. Trans Nonferrous Met Soc China, 2003, 13(3): 715 - 719.
- [13] Somasundaran P, Fuerstenau D W. Mechanism of alkyl sulfonate adsorption at alumina-water interface [J]. J Phys Chem, 1966, 70(1): 90 - 96.
- [14] Harwell J H, Hoskins J C, Schechter R S, et al. Pseudophase separation model for surfactant adsorption: isomerically pure surfactants [J]. Langmuir, 1985, 1(2): 251 - 262.
- [15] GAO Y, DU J, GU T. Hemimicelle formation of cationic surfactants at the silica gel-water interface [J]. J Chem Soc Faraday Trans 1, 1987, 83(8): 2671 - 2679.
- [16] ZHU B, GU T. General isotherm equation for adsorption of surfactants at solid/liquid interface [J]. J Chem Soc Faraday Trans 1, 1989, 85(11): 3813 - 3817.
- [17] Böhmer M R, Koopal L K. Adsorption of ionic surfactants on variable charge surfaces. 1. Charge effects and structure of adsorbed layer [J]. Langmuir, 1992, 8: 2649 - 2659.
- [18] Böhmer M R, Koopal L K. Adsorption of ionic surfactants on variable charge surfaces. 2. Molecular architecture and structure of the adsorbed layer [J]. Langmuir, 1992, 8: 2660 - 2665.
- [19] Yeskie M A, Harwell J H. On the structure of aggregates of adsorbed surfactants: The surface charge density at the hemimicelle/admicelle transition [J]. J Phys Chem, 1988, 92(8): 2346 - 2352.
- [20] Rupperecht H, Gu T. Structure of adsorption layers of ionic surfactants at solid/liquid interface [J]. Colloid Polym Sci, 1991, 269: 506 - 522.
- [21] Masahiro T, Hiromi M, Nakamichi Y. Determination of cationic surfactants by two-phase titration [J]. Anal Chem, 1981, 53: 1957 - 1959.
- [22] XU S. Organic Chemistry (2nd ed.) [M]. Beijing: Higher Education Press, 1981. 86 - 95. (in Chinese)
- [23] Van Olphen H. An Introduction to Clay Colloid Chemistry [M]. Xu J transl. Beijing: Agriculture Press, 1982. 168 - 171. (in Chinese)

(Edited by YUAN Sai-qian)