

Flotation of kaolinite and diaspore with hexadecyl dimethyl benzyl ammonium chloride

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Abstract: Tertiary amine was synthesized from fatty amine and formaldehyde. And then the synthesized tertiary amine was used to react with benzyl chloride to synthesize hexadecyl dimethyl benzyl ammonium chloride (1627) at ambient pressure. Using the synthesized 1627 as collector, the flotation properties of diaspore and kaolinite were investigated by single mineral and mixed mineral test. The flotation mechanism of diaspore, kaolinite and 1627 was discussed based on FTIR spectra. The results show that the mass ratio of aluminum to silicate achieves 15.02 and the recovery of alumina in concentrate is 43.07% using 1627 as a collector. The 1627 is found to be a more effective and a promising collector for reverse flotation to remove aluminum-silicate minerals from bauxite.

Key words: kaolinite; diaspore; hexadecyl dimethyl benzyl ammonium chloride; dodecyl amine; reverse floatation; infra-red spectrum

1 Introduction

There are abundant bauxite resources in China, most of which are diasporic bauxite, with high mass ratio of alumina to silica (almost in the range of 4–6)^[1–3]. Aluminum-silicate minerals are major gangue minerals in bauxite^[4], generally in the form of kaolinite, illite, pyrophyllite, feldspar and so on. The floatability of pyrophyllite is better than that of kaolinite. It is therefore crucial to strengthen the collecting power for kaolinite^[5–6]. In alumina industry of our country, sintering process and united process^[7] are mainly used to produce alumina. However, the major disadvantages of the two methods are a large productive energy consumption, a long technological process and a high construction investment, when compared with Bayer process. The Bayer process requires mass ratio of aluminum to silicate(A/S) in raw material beyond 10. It is greatly desirable to increase A/S ratio in bauxite to fit the Bayer process. Depressing aluminum-silicate minerals and directly floating diaspore have been proved to be an efficient method to desilicate from bauxite with anionic collector^[8]. But this process has drawbacks, such as a large consumption of collector, difficult to dehydrate concentrate and to remove collector from the concentrate for avoiding its unpredictable effect in the subsequent process. For these reasons, the reverse flotation process to float aluminosilicate minerals has been paid attention^[9].

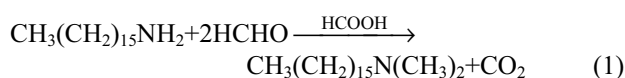
Dodecyl amine(DDA) is usually used in reverse flotation of iron ores, quartz and fluorite ores. However, it is found that the dodecyl amine exhibits a weak collecting power and selective ability^[10–11]. So it is greatly important to explore a new type of collector. In this work, the flotation characteristics and mechanism of diaspore and kaolinite were mainly discussed with hexadecyl dimethyl benzyl ammonium chloride (1627) as collector.

2 Experimental

2.1 Synthesis of hexadecyl dimethyl benzyl ammonium chloride

Collector 1627 was first synthesized from fatty amine and formaldehyde^[12].

In general, there are two ways to achieve alkylation: direct alkylation and deoxidation alkylation^[13]. The latter is better. The synthesis route was to use fatty amine and formaldehyde as raw material and formic acid as reductant^[12]. The adding sequence of reagent was in the order of fatty amine, formic acid, formaldehyde. The reaction is as follows:

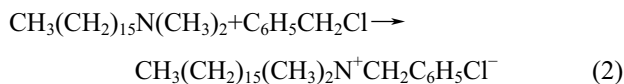


Then the obtained tertiary amine and benzyl chloride were mixed according to the mass ratio of 1.57:1.00^[14] and reacted at 80 °C for 4 h. The reaction is^[15]:

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The final product is yellow liquid, and the yield of this synthetic method reaches 90%.

2.2 Mineral samples

Lumps of diaspore and kaolinite, taken from Xiaoyi, Shanxi Province, were crushed, handpicked and ground in a porcelain mill. The material size is less than 74 μm. The sample purity is above 90%. The artificial mixed minerals in the test were composed of kaolinite and illite in the terms of A/S ratio of 5. The chemical compositions of mineral samples are listed in Table 1.

2.3 Flotation

Flotation tests were conducted in a 40 mL mechanical flotation cell. The impeller speed was fixed at 1 650 r/min. In each test, 3.0 g mineral sample was dispersed in 30 mL distilled water. After adjusting pH of suspension to a desired value, collector was added, and the resultant suspension was conditioned for 4 min. The flotation time was fixed as 4 min. The floated and unfloted fractions were collected and dried separately. The mass of solids in each fraction was determined accurately and used to calculate the recovery.

2.4 Infrared spectrum

The FT-IR spectra were obtained with PE system 2002 FTIR-740 (Nicolet Corporation, USA) to characterize the nature of the interaction between collector and minerals. The diffuse reflectance infrared (DRI) spectra were measured on air-dried powders whose size less than 5 μm after dealing with collector.

3 Results and discussion

3.1 Flotation of kaolinite and diaspore

The flotation recoveries of kaolinite using DDA and 1627 as collectors as a function of pH are given in Fig.1. From Fig.1, it can be seen that the recovery of kaolinite decreases with increasing the pulp pH using 1627 or DDA as collector. The collecting ability of 1627 for kaolinite is better than that of DDA.

The flotation recoveries of diaspore using DDA and

1627 as collectors as a function of pH are shown in Fig.2. It can be seen that diaspore has a better floatability in the pH range of 8–10. Obviously, the collecting ability of 1627 for diaspore is weaker than DDA. The flotation recovery is about 80% using DDA as a collector and 50% using 1627 as a collector.

The flotation responses of kaolinite and diaspore as a function of reagent dosage using DDA and 1627 as collectors are shown in Fig.3 and Fig.4, respectively. With the increase of collector dosage, the recoveries of kaolinite and diaspore increase. Collector 1627 exhibits stronger collecting power for kaolinite in the pH range of

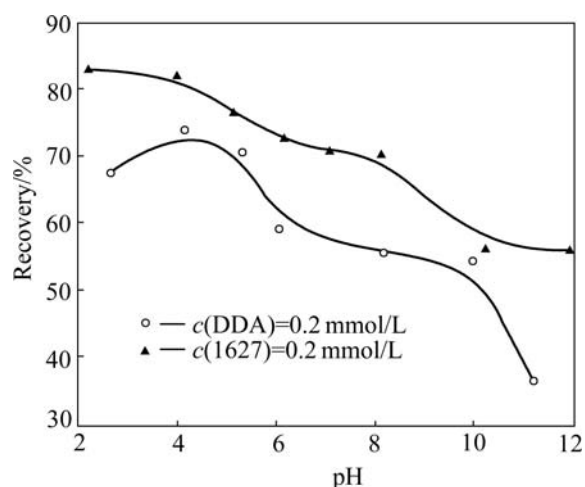


Fig.1 Flotation recoveries of kaolinite as function of pH using 1627 and DDA as collectors

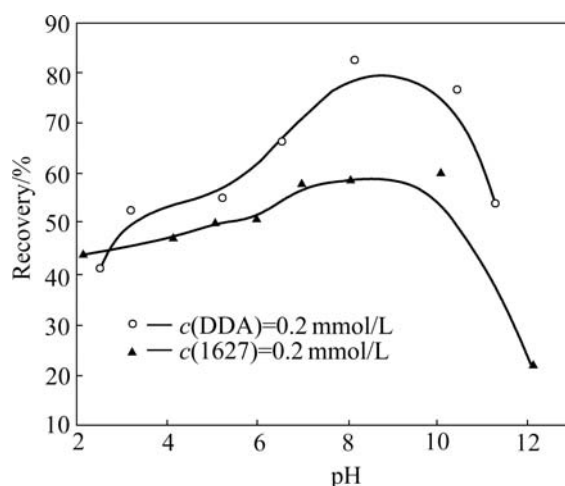


Fig.2 Flotation recoveries of diaspore as function of pH using 1627 and DDA as collectors

Table 1 Chemical compositions of mineral samples (mass fraction, %)

Sample	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	H ₂ O	Loss
Kaolinite	39.2	43.67	0.32	1.98	0.01	0.068	0.094	0.028	13.65	13.98
Diaspore	80.98	0.78	0.29	2.84	0.01	0.046	0.007	0.025	14.06	14.5

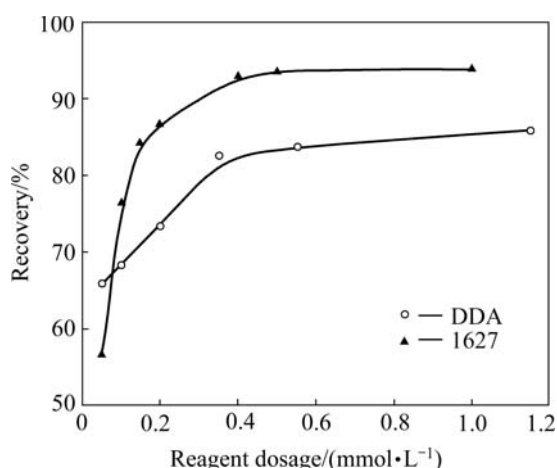


Fig.3 Relationship between recovery of kaolinite and reagent dosage (pH=5.0–5.5)

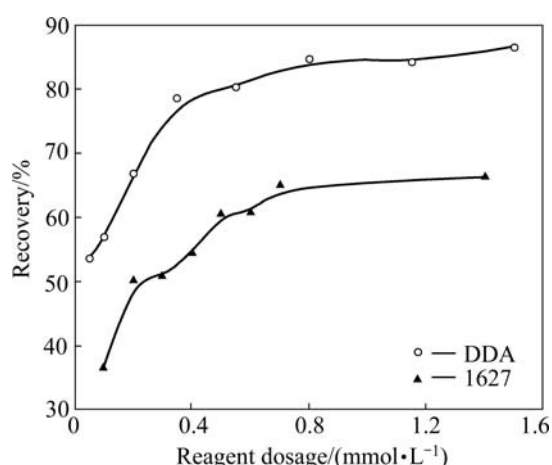


Fig.4 Relationship between recovery of diaspore and reagent dosage (pH=5.0–5.5)

5.0–5.5. But the collecting ability of 1627 for diaspore is weaker than that of DDA. It suggests that 1627 is a more effective collector for reverse flotation of aluminosilicate minerals from diaspore.

3.2 Separation of artificial mixed minerals

The reverse flotation separation of artificial mixture was carried out by using 0.2 mmol/L 1627 as collector, and adjusting pH of pulp to 5.0–5.5. Table 2 lists the results of the separation test.

From Table 2, it can be seen that the mass ratio of Al_2O_3 to SiO_2 in the feed is 5.00 and that in concentrate with 43.07% in recovery of alumina is 15.02. The result

indicates that the collector 1627 has a better selectivity, but its collecting power is not strong enough.

4 Infrared spectrum analysis

4.1 Infrared spectrum analysis of 1627 adsorption on diaspore

Infrared spectra of 1627, diaspore, and diaspore conditioned with 0.2 mmol/L 1627 are presented in Fig.5. There is O—H stretching at $2\,921\text{--}3\,007\text{ cm}^{-1}$ in the spectrum of diaspore. The peaks at $2\,119$ and $1\,985\text{ cm}^{-1}$ are due to vibration of O—H. The peaks at $1\,082$ and 973 cm^{-1} are due to bending vibration of O—H. The peak at 752 cm^{-1} is due to stretching of Al—O. The distinct peaks of collector 1627 at $2\,919$ and $2\,850\text{ cm}^{-1}$ are due to stretching of —CH₃ and —CH₂, respectively. The peak around $1\,300\text{ cm}^{-1}$ is due to stretching of C—N^[16]. The peaks in the range of $1\,400\text{--}1\,600\text{ cm}^{-1}$ are due to —CH₃ and —CH₂ deformation. The peaks in the ranges of $1\,006\text{--}1\,203\text{ cm}^{-1}$ and $698\text{--}730\text{ cm}^{-1}$ are vibrating modes of —CH₃ and —CH₂ on the surface, respectively. After adding 1627, new stretching of C—N appears at $1\,344\text{ cm}^{-1}$, deformation vibration of —CH₃ and —CH₂ appears at $1\,469$ and $1\,592\text{ cm}^{-1}$, respectively. The evidences mentioned above demonstrate that 1627 is adsorbed by diaspore. The characteristic peaks of diaspore at $2\,921$, $2\,119$ and 752 cm^{-1} do not shift, indicating that the adsorption of 1627 on diaspore is dominated by very weak physical adsorption.

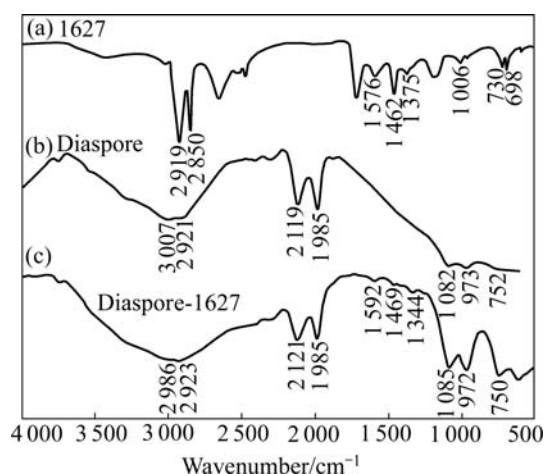


Fig.5 FTIR spectra of 1627 (a), diaspore (b) and diaspore-1627 (c)

Table 2 Test results of flotation of artificial mixed minerals using 1627 as collector

Sample	Yield/%	Grade/%		Recovery/%		A/S
		Al_2O_3	SiO_2	Al_2O_3	SiO_2	
Concentrate	37.67	76.74	5.11	43.07	14	15.02
Tailing	62.33	61.29	18.98	56.93	86	3.23
Feed	100	71.09	14.21	100	100	5.00

4.2 Infrared spectrum analysis of 1627 adsorption on kaolinite

Infrared spectra of collector 1627, kaolinite, and kaolinite in the presence of 0.2 mmol/L 1627 are shown in Fig.6. It is clear that the IR of kaolinite-1627 is different from that of kaolinite. The distinct peaks appeared at 1 576 and 1 462 cm^{-1} are due to vibration of aromatic ring in the infrared spectrum of 1627.

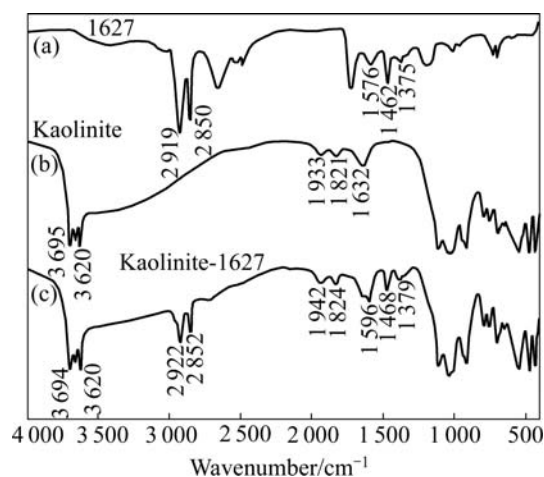


Fig.6 FTIR spectra of 1627 (a), kaolinite (b) and kaolinite-1627 (c)

In the infrared spectrum of kaolinite treated with 1627, new peaks appear at 2 922 and 2 852 cm^{-1} , which are contributed to the stretching vibration of $-\text{CH}_3$ and $-\text{CH}_2$. And the characteristic peaks of 1627 are transferred to 1 596 and 1 468 cm^{-1} , indicating that the adsorption of 1627 on kaolinite is dominated by strong physical adsorption.

4.3 Effect of structure of 1627 on flotation property

There is a benzyl on atom N of 1627, and the electron-pair on atom N of amidogen can conjugate benzene ring, but electron-pair on alkyl of DDA cannot. Therefore, it can be speculated that the offering electronic effect of benzyl is stronger than that of alkyl. The electronegativity of 1627 is 5.05. Consequently, the ability of 1627 combined with kaolinite through electrostatic force is better than that of DDA.

In sum, the collecting ability and the selectivity of cationic collector 1627 for kaolinite are better than those of DDA, and the pH range of flotation is wider.

5 Conclusions

1) Hexadecyl dimethyl benzyl ammonium chloride is synthesized by the means of deoxidation alkylation at an ambient pressure, using fatty amine and formaldehyde as raw material and formic acid as reductant. The yield of this synthetic method reaches 90%.

2) The mass ratio of aluminum to silicate achieves 15.02 and the recovery of alumina in concentrate is 43.07% using 1627 as collector.

3) The collecting ability of 1627 for kaolinite is stronger than that of DDA, while the collecting ability of 1627 for diasporite is weaker than that of DDA. Therefore, 1627 is a suitable collector for bauxite reverse flotation.

4) It should focus on improving the process technology in order to not only increase the mass ratio of aluminum to silicate but also improve the alumina recovery in concentration.

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