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Study on quantitative structure–activity relationship of quaternary ammonium salt collectors for bauxite reverse flotation

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ABSTRACT

Microflotation tests were performed on such pure minerals as diaspore and kaolinite to detect their respective flotation behaviors and flotation selectivity, in which 20 quaternary ammonium salts were applied as collectors to explore the relationship between the structure and selectivity of quaternary ammonium salt so as to investigate the probability of application of QSAR in the development of flotation reagents. Based on the selection and calculation of quantization parameters, topological parameters and selectivity indices of the reagents, a model with robust predictive abilities was established. The results showed that the shape of molecule, total energy and hydrophobic property were the three major factors affecting the selectivity of collectors. The better matching degree of molecular chain length and molecular configuration and the more negative total energy of the reagent were, the more efficient the reverse flotation separation of aluminum-silicate minerals would be.

1. Introduction

Since diasporic-bauxite in China is characterized by high content of aluminum oxide and silica but low mass ratio of aluminum oxide to silica (A/S = 4–6), from which bayer process cannot economically produce aluminum oxide due to the high sodium hydroxide and energy consumption caused by high-silica (Luo et al., 2001; Zhang et al., 2002). Therefore, it is necessary to remove aluminosilicate minerals such as kaolinite to increase the mass ratio of aluminum oxide to silica (Hu et al., 2001; Wang et al., 2003a,b; Zhang et al., 2001). Reverse flotation provides a promising way to remove silicates. As a matter of fact, flotation technology has been extensively applied as a pretreatment prior to bayer process (Hu and Wang, 2004). Recently the cationic amine collectors were considered the most efficient agents and investigated quite intensively (Liu et al., 2009; Zhong et al., 2008; Zhao et al., 2007), which, however, still had their shortcomings such as weak selectivity, low flotation speed and a large amount of foam and so on (Wang et al., 2004; Zhao et al., 2005; Yu et al., 2008; Wang et al., 2003a,b). Thus, bauxite reverse flotation process still has a long way to go before it can be put into commercial use, to which the design and development of high-selectivity collectors for aluminosilicate gangue minerals (mainly kaolinite) are very critical (Chen et al., 2005).

It is known that chemical reactivity and physicochemical properties of organic compounds are decided by their molecular structure. On the basis of the activity determination of a series of derivatives of the known leading compound, the quantitative-relation that brings out the dependence of a property or activity on entire molecular or its substructural fragment is called quantitative structure–activity relationship (QSAR) (Li, 1992). Since corresponding relations between compounds structure and activity has already been found, QSAR, a successful method of drug development and pharmacological study in medical field, will be very helpful to deepen the understanding of drug mechanism, avoid blindness at work, save manpower, material, resources and money, etc., which has also been extensively used in agricultural chemistry, pharmaceutical chemistry and toxicology (Kar and Roy, 2010; Frid and Matthews, 2010). In minerals processing field, however, this advanced process was researched by only a few scholars (Natarajan and Nirdosh, 2003, 2008). To provide basic data for research in this field and explore cationic collector database, this paper focused on QSAR research of quaternary ammonium salt collector and indicated that collector structure and flotation selectivity were closely linked, which provided new insights into the design and development of novel high efficient collector of reverse flotation for diasporic-bauxite.

2. Materials and methods

2.1. Materials and reagents

Samples of diaspore and kaolinite were obtained from Xiaoyi, Shanxi province of Northern China, which were crushed, hand-selected, and ground in a porcelain mill with agate ball. After being

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sieved, the −0.074 mm fraction with its purity being above 90% was chosen for microflotation tests. Chemical compositions of diaspore and kaolinite samples were listed in Table 1.

The flotation collectors were divided into three series: single long alkyl chain structure, double long alkyl chain structure and stellate configuration. The first series includes: 0831, 1031, 1231, 1222, 1227, 1431, 1427, 1631, 1622, 1627, 1831; the second includes: D8, D10, D12, D16, D18; and the third: T4, T8, T12, F4. All the collectors were 99.9% analytical reagents purchased from Xiamen Pioneer Technology Co. Ltd. Analytical grade of sodium hydroxide and hydrochloric acid was used for pH control. Details of all reagents were given in Table 2 and Fig. 1.

2.2. Flotation tests

Single mineral flotation tests with diaspore and kaolinite were conducted in a 40 mL flotation cell, each using 3 g of mineral samples in 40 mL of distilled water. After the desired amount of reagents (pH controller or collector) was added, the pulp was agitated for 3 min. Since the pH of suspension was adjusted and the collector was completely dispersed, a 4–5 min flotation period was necessary. The concentrate and tailing samples were filtered, dried, and weighed to calculate the flotation recovery under various flotation conditions.

2.3. Computational methods

All the descriptors were calculated using Gaussian03 (Frisch et al., 2003) and Cerius^2 3.0 software. In order to balance the calculation accuracy and calculation time, a smaller basis set was applied to optimize the molecular structure and a larger one was used to calculate the single point energy. Now that a large number of experiments proved that the size of basis set had more impact on the calculation of single point energy than on the structural optimization (Jensen, 2007), in this study, the initial molecular models of reagents were optimized by 3-21G basis set and RHF method, and then the geometries obtained were further optimized and calculated using DFT methods at B3LYP/6-31G (D) level.

3. Results and discussion

3.1. Microflotation tests

The core of using QSAR to screen effective reagents was that all indices must be quantized, analyzed and reflected in a mathematical model. Twenty quaternary ammonium salts were tested as collectors to float the diasporic-bauxite from China. Separation efficiencies of the collectors were taken as the dependent parameter, which was defined as the difference between the % recovery of the valuable mineral and that of the gangue mineral in the float concentrate. For low-grade bauxite the separation efficiency (Es) could be expressed as Es = % kaolinite recovery -% diaspore recovery. A larger Es reflected a better reverse flotation separation effect. The quaternary ammonium salts were used in the study, whose effects on the floatability of diaspore and kaonlinite at varied pH levels were given in Fig. 2.

Table 2
Molecular formula of collectors.

Collectors	Molecular formula
0831	$C_8H_{17}(CH_3)_3NCl$
1031	$C_{10}H_{21}(CH_3)_3NCl$
1231	$C_{12}H_{25}(CH_3)_3NCl$
1222	$C_{12}H_{25}C_2H_5(CH_3)_2NCl$
1227	$C_{12}H_{25}C_6H_5CH_3(CH_3)_2NCl$
1431	$C_{14}H_{29}(CH_3)_3NCl$
1427	$C_{14}H_{29}C_6H_5CH_3(CH_3)_2NCl$
1631	$C_{16}H_{33}(CH_3)_3NCl$
1622	$C_{16}H_{33}C_2H_5(CH_3)_2NCl$
1627	$C_{16}H_{33}C_6H_5CH_3(CH_3)_2NCl$
1831	$C_{18}H_{37}(CH_3)_3NCl$
D8	$(C_8H_{17})_2(CH_3)_2NCl$
D10	$(C_{10}H_{21})_2(CH_3)_2NCl$
D12	$(C_{12}H_{25})_2(CH_3)_2NCl$
D16	$(C_{16}H_{33})_2(CH_3)_2NCl$
D18	$(C_{18}H_{37})_2(CH_3)_2NCl$
T4	$(C_4H_9)_3CH_3NCl$
T8	$(C_8H_{17})_3CH_3NCl$
T12	$(C_{12}H_{25})_3CH_3NCl$
F4	$(C_4H_9)_4NCl$

For quaternary ammonium salt collectors, the most favorable reagent selectivity could be obtained in acidic condition, which has already been concluded in previous works (Jiang, 2004). Therefore, to facilitate data processing and analysis, this paper focused on the research of selectivity in weak acidic condition (pH from 4 to 6). The recovery of minerals at pH 5 was extracted from flotation curves and shown in Table 3.

Although 11 single long alkyl chain collectors were of similar configuration, different alkyl chain lengths could also lead to a remarkably different flotabilities of diaspore and kaolinite (Fig. 2 and Table 2). The collecting ability of aluminosilicate minerals increased with an increase in alkyl chain length until a maximum (at alkyl chain of 10 carbon atom) was reached, and then declined following the increase of chain length. Compared to the other single alkyl chain collectors, 1031(10 carbon atoms in straight-chain) showed the strongest collecting ability of kaolinite, while 1627 the weakest; their recovery of kaolinite was 68.55% and 0.34%, respectively. There was a similar law for the other two series of quaternary ammonium salt collectors, in which the optimum alkyl chain length was 8 carbon atoms for double long chain collectors and 4 for stellate collectors.

3.2. Calculation of molecular structure descriptors and establishment of QSAR model

A QSAR model with good predictive abilities relied on the effective transformation of structural details of molecules into numerical quantities. As a molecular metrics, Topological indices (TIs) were extensively used to encode structural details into numbers. Over 300 TIs were illustrated; definitions and calculations thereof could be obtained from the monographs (Devillers and Balaban, 1999; Todeschini and Consonni, 2000). In addition to TIs, quantum mechanical parameters, electronic parameters, physicochemical properties and geometrical parameters that described the molecular surface area and partial atomic charges were also used in

Table 1
Chemical analytical results of pure mineral samples/%.

Samples	Grade (mass fraction) (%)									
	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	H_2O	Lost
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