This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Novel Condensed Ring Carboxylic Hydroxamic Acid Studied in the Flotation Behavior of Diaspore and Aluminosilicates

Yu-Ren Jiang[a]; Li-Yi Zhou[a]; Xiao-Hong Zhou[a]; Bin-Nan Zhao[a]
[a] College of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan, P.R.China

Online publication date: 29 November 2010

To cite this Article Jiang, Yu-Ren , Zhou, Li-Yi , Zhou, Xiao-Hong and Zhao, Bin-Nan(2010) 'Novel Condensed Ring Carboxylic Hydroxamic Acid Studied in the Flotation Behavior of Diaspore and Aluminosilicates', Separation Science and Technology, 45: 16, 2475 — 2480

To link to this Article: DOI: 10.1080/01496391003733526

URL: http://dx.doi.org/10.1080/01496391003733526

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Separation Science and Technology, 45: 2475–2480, 2010

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496391003733526

Novel Condensed Ring Carboxylic Hydroxamic Acid Studied in the Flotation Behavior of Diaspore and Aluminosilicates

Yu-Ren Jiang, Li-Yi Zhou, Xiao-Hong Zhou, and Bin-Nan Zhao
College of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan, P.R.China

Flotation reagents are the critical technique in the flotation separation process for desilication. Aimed at the highly selective reagent for direct flotation of diasporic bauxite, a novel compound, dibenzo-1-(7-carboxyl-4-hydroxyl bicycle [2.2.2] octan-7,8-diyl) carboxamic acid (DBCA) with two functional groups carboxyl and hydroxamate in the same molecule, was synthesized through Diels-Alder reaction followed by oximation reaction. Subsequently, the floatability of diaspore, kaolinite, and illite was measured by using DBCA as a collector, the interaction mechanism between minerals and DBCA was investigated through zeta potential measurements and FT-IR spectrum, and the structure and property relationship of the collector were also discussed. The flotation experimental results showed that DBCA had a very strong collecting ability for diaspore, while poor activity was observed for kaolinite and illite. The interaction of DBCA on diaspore surfaces may be mainly dominated by chemical bonding as the formation of three chelation rings; however, those on the surfaces of kaolinite and illite are mainly hydrogen bonding or physical adsorption. Consequently, it is possible to separate diaspore from such aluminosilicates as kaolinte and illite employing DBCA as a collector.

Keywords aluminosilicate mineral; carboxylic hydroxamic acid; diaspore; flotation mechanism; flotation reagent

INTRODUCTION

Bauxite resources are very abundant in China, but mainly as diasporic type, with the characteristics of high alumina, high silica, and low Al_2O_3 to SiO_2 mass ratio (A/S) (A/S less than 7 possesses about 72% of the bauxite resources) (1). This type of bauxite is difficult to be treated directly by the Bayer process. It is therefore highly desirable to increase the mass ratio of A/S by flotation desilication before the Bayer process due to its highly economical efficiency (2). Theoretically, two approaches may be taken for the flotation desilication of diasporic bauxite, that is, direct flotation desilication characterized by the flotation of diaspore and the depression of aluminosilicates and reverse flotation desilication characterized by the flotation of aluminosilicates and the depression of diaspore. No matter which approach is taken, the flotation reagent is important and also the critical technique (3,4).

Recently, research on reverse flotation desilication of bauxite was very active and mainly focused on new cationic collectors for the flotation of aluminosilicate minerals or new inhibitors for the depression of diaspore. The cationic polyacrylamide and N-dodecyl-1,3-propanediamine, and modified starch and polyacrylamide as inhibitors inhibit diaspore, while it had little effect on the floatability of kaolinite (5–7). Zhang and Wei (8) reported the polysaccharide derivatives YX-2 and YF-2. Therein, YX-2 almost completely inhibited the diaspore flotation at the pH 7, and a small amount of YF-2 could separate diaspore and kaolinite. BK501 has a selective inhibitory effect on diaspore, but for kaolinite, it has some positive effects (9). Zhao et al. (10) carried out flotation experiments on three aluminosilicate minierals using N-dodecyl-1, 3-diaminopropane as a collector resulting in over 80% of the recoveries. Nevertheless, because of the well natural floatability of diaspore and a poor one of the aluminosilicate mineral, the difficulty of development of the high selective cationic collector for aluminosilicate minerals as well as the complexity of reverse flotation, (11) the desilcation by reverse flotation is still hard to put into practice.

Direct flotation has been proved to be an efficient method to desilicate for bauxite, and it has been put into practice on a commercial scale and has been employed in several factories in China for years. However, it still has some limitation, (2) such as high collector consuming, massive forth producing, trouble in dewater, and disadvantage in metallurgy. The recent research on direct flotation was principally focused on the flotation process using traditional anionic reagents such as fatty acids, phosphonic acids, and their modified or combined compounds (12–14). Unfortunately, the existing flotation reagents for direct desilication are relatively poor in selectivity, while the design and synthesis of new structural features of the

---

Received 16 December 2009; accepted 26 February 2010.

Address correspondence to Yu-Ren Jiang, College of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan 410083, P.R. China. Tel.: +86-731-88836834; Fax: +86-731-88859988. E-mail: jiangyr@mail.csu.edu.cn, zhouliyi0817@163.com

collectors was paid little attention and the efficient reagents of bauxite are not found yet. Moreover, it is still difficult to highly efficiently separate diaspore from bauxite by direct flotation, for the recovery of an acceptable bauxite concentrate was not very high on a commercial scale (2,15). Thus, it is necessary to find and synthesize new efficient reagents for direct flotation.

Previously, we synthesized a new structural collector COBA (16), which had a relatively strong collecting ability for diaspore while poor for kaolinite and possessed much better selectivity than salicylic hydroxamic acid (HOBA). Its collecting performance was mainly dominated by such difference of polar group as the electronegativity, topological connectivity index, the group cross-section size, and hydrophobicity. The results showed that the molecule with structural features of carboxyl and hydroxamate group is a good potential flotation reagent. However, such a structural characteristic reagent has not been reported by others.

The present work focuses on designing a compound which possesses both carboxyl group and hydroxamate with the structural characteristic of collector. As a result, dibenzo-1-(7-carboxyl-4-hydroxyl bicycle [2.2.2] octan-7, 8-diyl) carboxamic acid (DBCA) was developed as a collector for the flotation of such typical mineral in diasporic bauxite as diaspore, kaolinite, and illite, for the first time. The results of the flotation test and mechanism investigation indicate that it is possible to separate the diaspore from the aluminosilicate minerals using DBCA as a collector.

EXPERIMENTAL

Synthesis

In order to synthesize the target compound, dibenzo-1-(7-carboxyl-4-hydroxyl bicycle [2.2.2] octan-7,8-diyl) carboxamic acid (DBCA), with two functional groups of carboxyl and hydroxamate in the same molecule, anthracen-9(10*H*)-one (compound **a**) was selected as the start raw material, reacted with maleic monoester (compound **b**) by Diels-Alder reaction (17,18) to give the key intermediate (compound **c**) followed by oximation reaction (19,20) employing hydroxamine hydrochloride in the presence of alkali condition to gain a salt of DBCA, which was acidified to obtain the target compound DBCA.

The synthesis procedure was presented as follows. A mixture of anthrone (0.02 mol) and maleic monoester (0.04 mol) in glacial acetic acid was boiled under reflux for 30 min, during which time crystals formed. The mixture was cooled and the precipitates were filtered off, recrystallized in acetic acid and dried to give compound (**c**) with a yield of 89.6%. Under stirring at room temperature, sodium ethoxide (0.02 mol) ethanol solution was slowly dropped into compound (**c**) (0.02 mol) in ethanol. When the drop of sodium ethoxide ethanol solution finished, hydroxylamine hydrochloride (0.024 mol) was added into the mixture. Waiting for the mixture was stirred for 8–10 min, and then NaOH (0.044 mol) in ethanol was added to the mixture dropwise within 1 h at room temperature. Subsequently, the mixture was allowed to be heated at the temperature of 40–50°C and stirred for 3 h. The solution was reduced by evaporating at 30°C, and then a yellow precipitate was obtained as salt of DBCA. Finally, the yellow precipitate was recrystallized in water and acidified to pH = 3–4 using 5 wt% HCl to give the desired product (DBCA, white crystal powder) with a yield of 75.1%. m.p: 271.5–272.5°C. IR spectra measured by FT-IR-750 infrared spectrophotometer (Nicolet Corporation, USA): 3250–3550 cm^{-1} (-OH, -NH), 1679 cm^{-1} (C=O). Elemental analysis by Varian EL (III) elemental analyzer, found (%): C, 66.40; N, 4.32; H, 4.68; calculated for $C_{18}H_{15}NO_5$ (%): C, 66.46; N, 4.31; H, 4.65.

Flotation Performance

The individual minerals of diaspore, kaolinite, and illite were obtained from Henan, China. All the individual mineral samples were hand-picked, and ground in porcelain mill with agate ball to pass 74 μm. The purity of the minerals was identified at least 90% (the results of mineralogical analysis by X-ray). Analytical grade sodium hydroxide and hydrochloric acid solution were used for the pH control. 0.1 mol/L of DBCA aqueous solution was newly prepared before its use. Distilled water prepared in our laboratory was used in all tests.

Flotation tests were performed in a XFG-35 flotation machine with 30 mL effective cell volume. The impeller speed was fixed at 1650 rpm. In each test, 2.0 g mineral samples were dispersed in 30 mL distilled water. After adjusting suspension pH to a desired value, a desired dosage aqueous solution of DBCA was added and the suspension was stirred for 5 min, and then the froth product was gathered for 5 min. The floated and unfloated fractions were collected and dried separately. The mass of the solid in each fraction was determined and used to calculate the recovery.

FT-IR Spectroscopy

In order to characterize the nature of the interaction between the collector and the minerals, the infrared spectra of collector as well as samples with or without collectors pretreated are measured by the KBr technique spec pure KBr was dried at 120°C for 4–6 hours, then ground in agate mortar into powder inside, and then an appropriate amount of KBr, together with samples powder was grown, and finally pressed into the tablet. Model FT-IR-750 Infrared spectrophotometer from Nicolet CO., USA was used to obtain the IR spectra. The mineral samples were ground to be less than 2 μm in an agate mortar before being conditioned with 2×10^{-2} mol/L collectors.

Zeta Potential Measurement

Zeta potential was measured on a Delsa-440SX Zeta potential instrument (Brookhaven Corporation, USA).The mineral sample was further ground to less than 5 μm in an agate mortar. The mineral suspension containing 0.01% (mass fraction) solid was dispersed in a beaker for 15 min by using 1×10^{-3} mol/L KNO_3 solution as a supporting electrolyte, and then HCl or NaOH was added to adjust the desired pH value. The measurement error was found to be within ±0.5 mV after at least three measurements in each condition.

RESULTS AND DISCUSSION

Collecting Behavior of DBCA on Minerals at Different pH Value or in Different Concentration

The impact of the pH value on the diaspore, kaolinite, and illite flotation using 2×10^{-4} mol/L DBCA as a collector was presented in Fig. 1 The results showed that in the pH range of 3∼7 the recovery of diaspore rises with increasing pulp pH value, while in the pH range of 7∼11, the recovery of diaspore decreases with the increase of pH value. At pH around 7, the diaspore has very good floatability with the flotation recovery above 97%. This pH value happens to be commonly reported as the range of the pKa value of hydroxamic acid (21), so such a coincidence was often used as an interpretation of the flotation peak. As for aluminosilicates, with the increase of pH value there was slight growth in the floatabilty of kaolinite and slight decrease in that of illite. However, DBCA did not present strong collecting ability to the two aluminosilicate minerals in the whole tested pH range from 3 to 11.

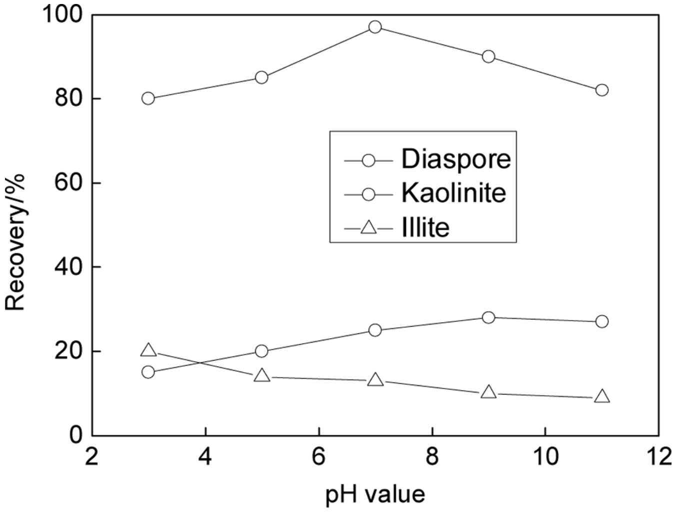


FIG. 1. Effect of pH value on the flotation of minerals using 2×10^{-4} mol/L DBCA as a collector.

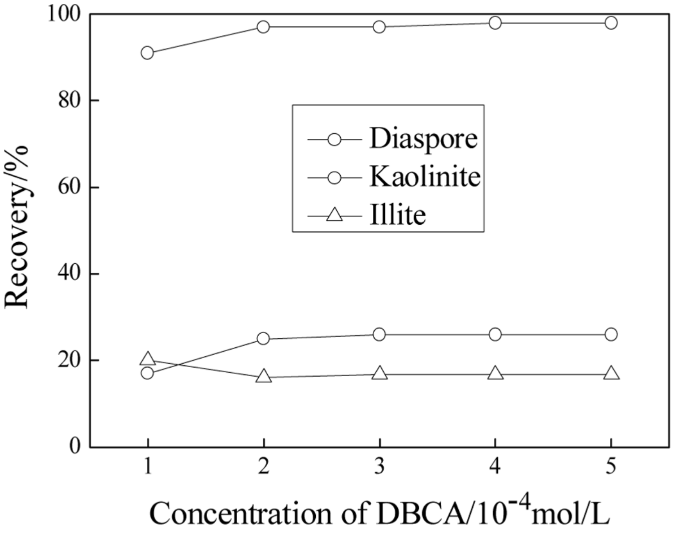


FIG. 2. Effect of DBCA concentration on mineral flotation at pH 7.0.

At a fixed pH 7, Fig. 2 presented the flotation results of diaspore, kaolinite, and illite with different concentration of DBCA. It was shown that, when the concentration of DBCA increasing from 1×10^{-4} mol/L to 5×10^{-4} mol/L the recovery of diaspore almost remained unchanged with a basically recovery of 97%. Also, the floatability of the two aluminosilicate minerals varied little, and the recovery of kaolinite kept a level no more than 26% while that of illite maintained less than 17% in the tested DBCA concentration.

Concluded from Figs. 1 and 2, the flotability of the three minerals is in the order of diaspore > kaolinite > illite when using DBCA as a collector, and it possesses very good collecting ability to diaspore and poor collecting activity to either kaolinite or illite. This means that DBCA has a good selectivity for diaspore flotation. Accordingly, the diaspore may be possibly separated from kaolinite and illite by using DBCA as a collector.

FT-IR Spectra of Minerals Treated or Untreated by DBCA

Figure 3 presented the IR spectra graph of diaspore, kaolinite, and illite with and without DBCA. According to the infrared spectra of DBCA, the reagent characteristic absorption peaks appeared at 3250–3550 cm^{-1}(-OH, >NH), 1679 cm^{-1} (>C=O) and others, etc. After being conditioned by DBCA, the appearance or disappearance of the characteristic absorption peaks was observed on diaspore, kaolinite, and illite, and a different shift of wavenumber happened in the IR spectra between the reagent and different mineral.

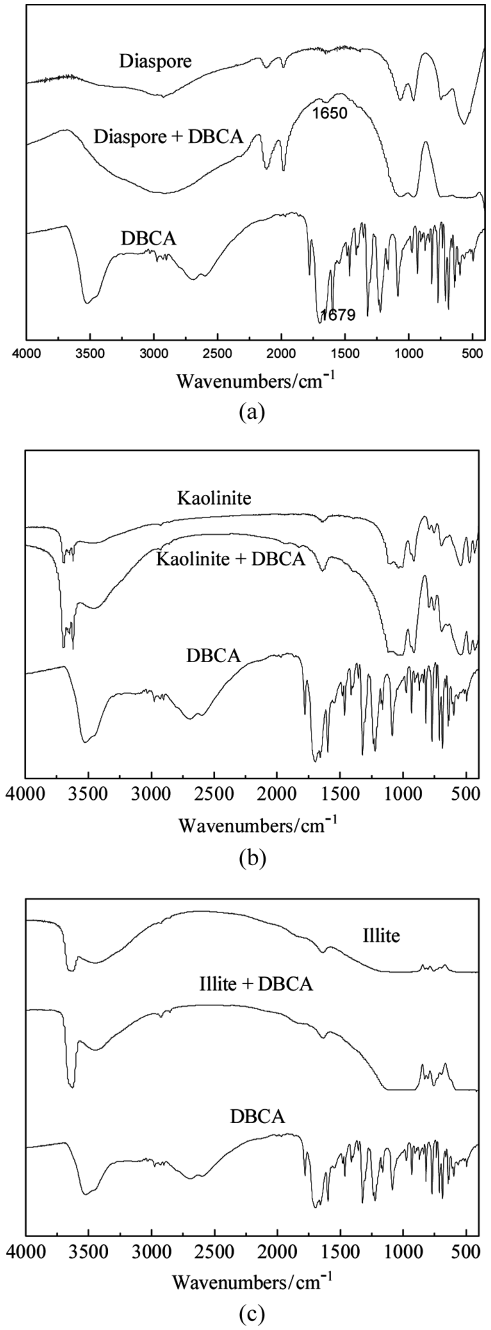


FIG. 3. FT-IR spectra of mineral with and without reagent (a) Diaspore; (b) Kaolinite; (c) Illite.

For diaspore treated by DBCA, the 3250–3550 cm^{-1} absorption band of DBCA disappeared, which should be the result from reaction of –OH in -COOH or -CONHOH with diaspore and the brokenin of O-H bond (16); At the same time, the >C=O absorption peak of the reagent shifted down to 1650 cm^{-1} from 1679 cm^{-1}, which may explain that the oxygen atom of >C=O provided the lone-pair electron to the aluminum ions on the diaspore surface to form a chemical bond.

The spectra of kaolinite treated by DBCA exhibited a peak at 1640 cm^{-1} (that was 1638 cm^{-1} without DBCA), which may be caused by the formation of N-H . . . O hydrogen bond between the group of -NHOH in DBCA molecule and the oxygen on kaolinite surface (22). Similar to kaolinite, the hydrogen bond was formed in illite with DBCA as well, where the peak of 1637 cm^{-1} shifted to the lower wavenumber and higher intensity of 1635 cm^{-1}.

To sum up, treated by DBCA, the characteristic absorption of DBCA on diaspore shifted more while those of the two aluminosilicate minerals shifted only slightly. Therefore, this may illustrate that the interaction between DBCA and the diaspore is mainly chemical adsorption, while DBCA on kaolinite and illite is hydrogen bonding or physical adsorption. Since the chemical bond is stronger than the hydrogen bond or physical adsorption, the recovery of the diaspore is at a high level and those of aluminosilicates are at a relatively low level, which is consistent with the flotation results by using DBCA as a collector.

Zeta Potential of Minerals Treated or Untreated by DBCA

Figure 4 described the relationship between the pH value and the zeta potential of diaspore, kaolinite, and illite untreated or treated by DBCA. The results presented that the isoelectric point (IEP) determined was 6.2, 3.8, and 3.0 for diaspore, kaolinite, and illite without DBCA, which are generally consistent with the previous reported literatures (16, 22). Compared with kaolinite and illite, the diaspore has a relatively higher IEP. When pH>IEP, the zeta potential of diaspore, increases rapidly with the negative growth of pH values, while pH reaching 10, it keeps nearly invariance. However, the zeta potential of kaolinite and illite falls significantly with the growth of the pH value and has no significant change when the pH reaches 6 or above.

When treated by DBCA at a different pH value, the variety of zeta potential of diaspore, kaolinite, and illite is almost the same as that without DBCA; however, diaspore has a more negative zeta potential than kaolinite or illinite in mostly tested pH range. These results present that DBCA could be adsorbed on the surface of the three minerals. Since the fact that DBCA possesses very high collecting activity to diaspore and low activity to the aluminosilicates, it can be concluded that the adsorption of DBCA on diaspore is a chemical one and those on the aluminosilicates are physical ones or hydrogen bond, which is in agreement with and confirms the conclusion resulted from IR spectra.

Analysis of the Relationship of Collector Between Structure and Properties

According to the calculation formula of group electronegativity X_g (23), group topological connectivity index

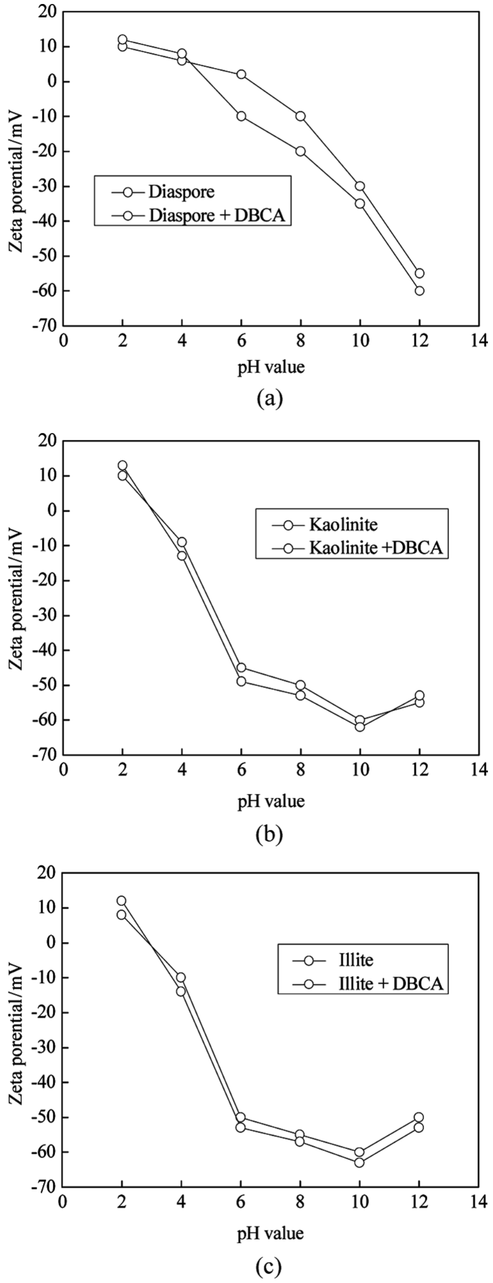


FIG. 4. Relationship between zeta potential and pH value with or without DBCA (a) Diaspore; (b) Kaolinite; (c) Illinite.

G_g (24), group cross-section size d_g (4), and hydrophobic constant (4), the indices for DBCA were calculated, the results of which associated with those of COBA and HOBA (16) and were listed in Table 1. Usually for the flotation reagent, a relatively large value of X_g or G_g indicates that the reagent is intensively adsorbed on the oxide mineral, the relatively large value of d_g shows the better selectivity of the reagent among minerals, and the relatively large value of logP gives intensive hydrophobicity resulting in high collecting ability of a collector to a mineral.

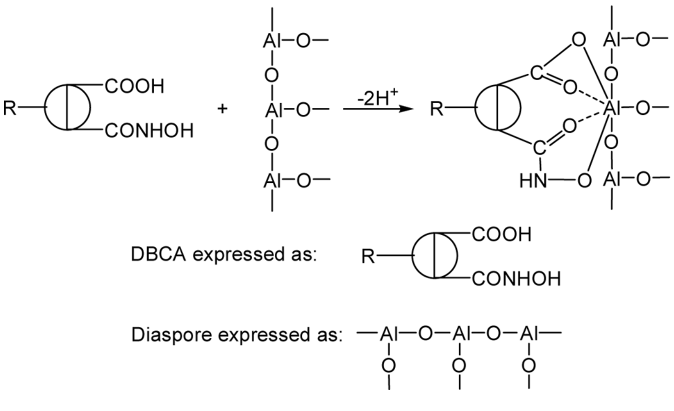
TABLE 1
The performance index of DBCA, COBA and HOBA

Reagent	X_g	G_g	d_g/nm	logP
DBCA	4.1(-COOH),3.8(CONHOH)	0.90	91	1.30
COBA	4.1(-COOH),3.8(CONHOH)	0.86	87	1.01
HOBA	3.9(-OH),3.8(-CONHOH)	0.80	73	0.60

Analyzed from the HSAB principle, the three reagents belong to the hard base type flotation reagents while diaspore, kaolinite, and illite are the hard acid type minerals, but kaolinite and illite is relatively softer than the diaspore. Seen from Table 1, compared with COBA and HOBA, the DBCA has a relative higher value of G_g, d_g and logP. These present the foot that the DBCA possesses highly intensive adsorption force on the diaspore, high selectivity, and high hydrophobicity, which leads to very high collecting activity to the diaspore and low collecting activity to aluminosilicate minerals when DBCA is employed as a collector.

Analysis of Adsorption Model of DBCA on Diaspore Surface

In the polar group of the DBCA, the oxygen atoms of >C=O and –OH in the carboxyl group –COOH, the oxygen atoms of >C=O and –NHOH in the hydroxamate group all have lone-pair electron whose negative value of net charge is relatively high, which indicates that these oxygen atoms may become the possible bonding atoms in DBCA. The negative value of the net charge of the above minerals is big. The net charges of the isolated molecules are −0.7300, −0.7886, and −0.9345 respectively, which indicates that the four O atoms may be the bonding atoms of the DBCA with the mineral. Meanwhile, the distance of these oxygen atoms is 4∼6 atoms which are in accordance with the requirement to form the five to seven membered rings. These characteristics combined with the evidence provided by IR spectra and zeta potential mentioned above,



SCH. 1. Adsorption model of DBCA on diaspore surface.

an adsorption model of DBCA on diaspore surface is suggested as Scheme 1, where four oxygen atoms in the polar group of DBCA donate electrons to the aluminum atom on the diaspore surface to form three cycle chelation rings.

CONCLUSION

By implanting the carboxyl and hydroxamate into the same molecule, a novel collector DBCA was synthesized for the first time. It possesses very high collecting activity to the diaspore and low collecting ability to kaolinte or illite. The essential of DBCA for highly selective flotation of diaspore may be the four oxygen atoms in its polar group donate electrons to the aluminum atom on the diaspore surface to form three chelation rings. It is possible to separate diaspore from the aluminosilicate minerals using DBCA as a collector.

ACKNOWLEDGEMENTS

The research was supported by a grant from the National Natural Science Foundation of China (20876180), for which the authors wish to express their appreciation.

REFERENCES

1. Huang, C.B.; Wang, Y.H.; Chen, X.H.; L, Y.; Hu, Y.M.; Yu, F.S. (2005) Review of research on desilication of bauxite ores by reverse flotation. *Metal Mine.*, 1 (6): 21–24.
2. Xu, Z.H.; Plitt, V.; Liu, Q. (2004) Recent advances in reverse flotation of diasporic ores A-Chinese experience. *Miner. Eng.*, 9 (10): 1007–1015.
3. Li, H.P.; Hu, Y.H.; Jiang, Y.R.; Wang, D.Z.; Cao, X.F. (2001) Flotation reagents for desilication from Bauxite. *Multipurpose Utilization of Mineral Resources*, 1 (6): 31–35.
4. Wang, D.Z. (1982) *Flotation Reagents Fundamentals and Applications*; Metallurgical Industry Press: Beijing, 50–169.
5. Liu, G.Y.; Lu, Y.P.; Dai, T.G. (2003) Reverse flotation with cationic polyacryamide (CPAM) polymers to separate kaolinite from diaspore. *Metal Mine.*, 1 (2): 48–50.
6. Li, H.P.; Hu, Y.H.; Jiang, Y.R. (2001) Interaction mechanism between modified starches and aluminum-silicate minerals. *Chin. J. Nonfer. Met.*, 11 (4): 697–701.
7. Hu, Y.H.; Cao, X.F.; Li, H.P. (2003) Synthesis of N-decyl-1, 3-diaminopropanes and its flotation properties on aluminium silicate minerals. *Trans. Nonfer. Met. Soc. China.*, 13 (2): 417–420.
8. Zhang, Y.H.; Wei, D.Z. (2004) The separation of kaolinite and diaspore by reverse flotation. *Non-Fer. Met.*, 1 (2): 45–47.
9. Zhang, Y.H.; Wu, X.Q.; Zeng, K.W. (2006) Development and application of BK501 depressor in silica removal from bauxite by reverse flotation. *Metal Mine.*, 1 (11): 41–44.
10. Zhao, S.M.; Wang, D.Z.; Hu, Y.H.; Liu, B.D.; Xu.J. (2003) The fotation behaviour of N-(3-aminopropyl)-dodecanamide on three aluminosilicates. *Miner. Eng.*, 16 (12): 1391–1395.
11. Gao, S.L.; Li, X.A.; Wei, D.Z.; Fang, P.; Jia, C.Y.; Liu, W.G.; Han, C. (2008) Beneficiation of low-grade diaspric bauxite with hydrocyclone. Trans. *Nonfer. Met. Soc. China.*, 18 (2): 444–448.
12. Liu, S.H.; Fang, Q.X. (2004) Commentary on present situation of research into bauxite desilication technology. *Mining and Metallurgy*, 13 (4): 24–30.
13. Jiang, H.; Hu, Y.H.; Xu, J.; Wang, D.Z. (2001) Solution chemical mechanism of diaspore flotation using anionic collectors. *Mining and Metallurgical Engineering*, 21 (2): 27–33.
14. Chen, X.Q.; Bai, W.Q.; Yan, W.Z. (2006) Status and research progress of bauxite floatation desilication. *Light Metals*, 1 (2): 8–12.
15. Liu, P.W.; Zhang, L.H.; Zhang, X.F.; Pei, Y. (2000) Theoretical basis of new technology in predesilicification and bauxite dressing Bayer-Process and industry technique of new technology. *J. Chem. Ind. Eng.*, 51 (6): 734–739.
16. Jiang, Y.R.; Hu, Y.H.; Cao, X.F. (2001) Synthesis and structure—activity relationships of carboxyl hydroxidoxime in bauxite flotation. *Chin. J. Nonfer. Met.*, 4 (11): 702–706.
17. Cohen, D.; Ian, T.M. (1968) Diels-Alder Adducts of 9-Anthrol. *J. Chem. Soc.*, 1 (7): 793–795.
18. Harrison, R.; Synergistic, B.R. (2002) Catalysis of anthrone Diels-Alder reactions. *Org. Lett.*, 4 (10): 1711–1713.
19. Wang, W.H.; Liu, W.S.; Wang, Y.W.; Li, Y.; Zheng, L.F.; Wang, D.Q. (2007) Self-assembly and cytotoxicity study of waterwheel-like dinuclear metal complexes: the first metal complexes appended with multiple free hydroxamic acid groups. *J. Inorg. Biochem.*, 101 (2): 297–304.
20. Braish, T.F.; Fox, D.E. (1992) Synthesis of 2-bromo-4, 5-difluorobenzoic acid. *Synth. Comm.*, 22 (21): 3067–3074.
21. Che, L.P.; Yu, Y.F.; Pang, J.X.; Yuan, J.Z.; Wang, X.T. (2004) Synthes, properties and role mechanism of hydroximic acidas collectors of RE mineral flotation. *Chinese Rare Earths*, 25 (3): 49–54.
22. Liu, G.Y.; Zhong, H.; Hu, Y.H.; Zhao, S.G.; Xia, L.Y. (2007) The role of cationic polyacrylamide in the reverse floation of diasporic bauxite. *Miner. Eng.*, 20 (13): 1191–1199.
23. Wang, D.Z.; Lin, Q.; Jiang, Y.R. (1996) Molecular design of regents for mineral and metallurgical processing, Central South University of Technology Press: Changsha, 52–204.
24. Cao, Y.C.; Jiang, Y.R.; Xue, Y.L. (2000) Quantitative correlation between group connectivity index and property of flotation reagent. *J. Cent. South Univ. Technol.*, 7 (1): 25–28.