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A new collector used for flotation of oxide minerals

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Abstract: A surfactant containing a mixed aliphatic structure, with a hydrocarbon chain and a diamine group, has proven to be collector for the flotation of quartz, calamine and calcite. And research about its collecting capability was carried out in laboratory. The test results show that the flotation recovery ascends sharply with increasing the concentration of collector. When the concentration of collector reaches 1.83×10^{-4} mol/L, the flotation recoveries of quartz, calamine and calcite get their maximum of 97.64%, 91.04% and 95.99%, respectively. The flotation recoveries of quartz, calamine and calcite rise sharply with the rise of pH. And in a wide range of pH, their flotation recoveries all exceed 90%. And in the whole flotation experiment, the flotation recovery of hematite rises with the increase of collector concentration and pH, while the maximal recovery is not more than 55%. Compared with dodecylamine, the *N*-dodecylethylenediamine has strong capability to quartz and calamine, while the flotation recoveries of calcite are closely. Hydrogen binding adsorption and electrostatic adsorption occur between the collector and the surface of quartz.

Key words: *N*-dodecylethylenediamine; collecting performance; quartz; calamine; calcite; hematite

1 Introduction

Flotation is a concentration process by using particle surface composition to induce the selectivity with chemical reagents[1−5]. It is well known as the most common process in mineral separation to recover valuable minerals from gangue. It is estimated that over 2×10^9 t of ores are processed by flotation each year worldwide[6−7]. Owing to the limitation of sources and supplies of mineral raw materials and the need to treat ores of lower grades, increasing fineness and mineralogical complexity, new flotation technologies and new flotation reagents have been developed rapidly [8−10].

Cationic reverse flotation of quartz is the most important technique for the concentration of iron ores and two classes of amines are used in plant practice of cationic reverse flotation of iron ores: ether monoamine and monoamine. A combined quaternary ammonium salt was used as a collector for the flotation of quartz. It shows better selectivity and collectabality than dodecyl amine chloride and cetyl trimethylammonium bromide for the flotation of quartz from magnetite and specularite [11−14].

The purpose of this work is to synthesize one kind of new collectors containing a hydrocarbon chain of mixed aliphatic structure, with an amino group and an imino group. The collecting performances of the new collector were also studied in laboratory.

2 Experimental

2.1 Materials

The materials used in this test mainly include quartz, hematite, calcite and calamine.

The samples of hematite and quartz were taken from Qidashan plant, which is located in Liaoning Province, China. The samples prepared with hand-selected crystals by means of crusher and ball-mill were ground to <0.074 mm for investigation. The results of chemical analyses of quartz and hematite used in this study are given in Table 1.

Natural crystals of calcite from Kuandian were used in this study. The crystals were hand-ground using an agate mortar to produce (<0.1 mm) particles. Chemical compositions of calcite crystals are given in Table 2.

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Table 1 Chemical analysis results of quartz and hematite (mass fraction, %)

Sample	Fe_2O_3	SiO_2	P_2O_5	SO_3	CaO	Al_2O_3	MgO	K_2O
Hematite	96.2	3.52	0.016 7	0.020 3	0.021 9	0.196	−	−
Quartz	0.077 5	96.2	0.007 0	0.014 8	0.248	3.25	0.314	0.095 5

Table 2 Chemical compositions of calcite (mass fraction, %)

$CaCO_3$	MgO	SrO	Fe_2O_3	K_2O	MnO	Rb_2O_3	SiO_2	Al_2O_3
99.33	0.157	0.087 6	0.065 9	0.052 3	0.043 1	0.015 3	0.042 1	0.030 6

The single calamine sample used in this study was taken from oxidation zone of Changba mine, Gansu Province, China. The specimen is cut by hammer and purified by hand-sorting, then ground to <0.100 mm with ball-mill. Chemical compositions of calamine crystals are given in Table 3.

Table 3 Chemical compositions of calamine (mass fraction, %)

$PbFe_6(SO_4)_4$	$ZnCO_3$	Si	SiO_2
2.5	86	5.0	2.3

2.2 Chemicals

1-bromododecane, ethanol and ethylenediamine (analytical pure) were used in synthesis of *N*-dodecylethylenediamine(ND).

The pH regulators used in flotation test were sodium hydroxide and hydrochloric acid dissolved in distilled water.

2.3 Synthesis of ND

ND as an excellent surfactant had been synthesized by LIAO following the reaction below[15]:

$$C_{12}H_{25}Br+H_2NCH_2CH_2NH_2 \underset{\text{Ethanl}}{\overset{55\ ℃}{\rightleftharpoons}} C_{12}H_{25}NHCH_2CH_2NH_2 \qquad (1)$$

In the reaction, for the insoluble 1-bromododecane and ethylenediamine, it takes long time to react without any processing, and the reactive temperature is much higher. For this reason, we used ethanol as solvent to make the react fast in homogeneous solution at a lower temperature.

The ND produced was dissolved in acid. The acid-insoluble component was removed by filtration. H_2O and ethanol in the filtrate were removed by evaporation at a reduced pressure. The liquid remained was treated with alkali aqueous solutions. High grade ND was recrystallized by evaporating the solvent and drying in a vacuum desiccate to obtain the final product in the form of ceraceous white solids.

2.4 Flotation test

The flotation experiments with single minerals were conducted in a 40 mL XFG flotation cell. Initially, 5.0 g of the minerals were conditioned with distilled water for 3 min, and the suspension pH was adjusted to the desired value, and then collector was added. The mixture was agitated for 2 min with stirring by a four-bladed plastic propeller rotating at 1 460 r/min before flotation for 5 min. The flotation results are reproducible.

2.5 Spectroscopic study

Spectroscopic studies were carried out using an FTIR spectrophotometer. A pellet made of a mixture of 1 mg samples and 100 mg of KBr was prepared. In order to verify the nature of species adsorbed in the quartz-aqueous solution interface, fine quartz particles were put in an aqueous solution of amine acetate collector with concentration of 1.14×10^{-2} mol/L (at pH=10.5) for 60 min. Then, the particles were separated by filtration, thoroughly rinsed with distilled water at the same pH (10.5) and dried at room temperature[16−17].

3 Results and discussion

3.1 Characterization of ND

In order to analyze the new synthetic collector, the infrared transmission spectrum of it is given in Fig.1.

As expected, the group of strong bands between 3 000 and 2 750 cm^{-1} are assigned to the stretching vibrations of —CH_2— and —CH_3 groups. The region

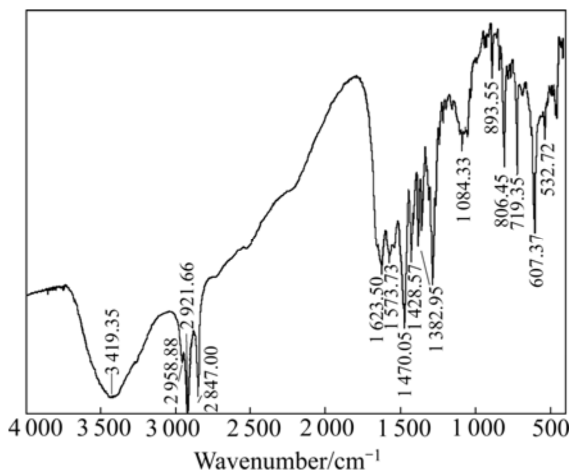

Fig.1 Infrared transmission spectrum of ND

between 3 200 and 2 220 cm^{-1} is called ‘the ammonium band’ and is diagnostic of the protonation of the former amine. The bending vibrations of $-CH_2-$ and $-CH_3$ groups occur at the peaks of 1 470 cm^{-1} and 1 382 cm^{-1}. The peak at 719 cm^{-1} is assigned to the vibrations of $\left(CH_2\right)_n$ ($n\geqslant 4$).

In order to characterize the synthesized crystalloid, C, H, N contents were analyzed to be 74.00%, 13.96% and 12.04%, which are near to the academic contents of ND, 73.68%, 14.04% and 12.28%, respectively.

According to the specific assignment explanation of the infrared transmission spectrum and the element content analysis of the synthesized ceraceous crystalloid, it is ND undoubtedly.

3.2 Froth flotation test

The collecting capability of ND compared with dodecylamine was studied and the results are shown in Figs.2−5.

Fig.2 shows recoveries of the four minerals as functions of collector concentration. ND has a strong catchabality to quartz, calamine and calcite. When the collector concentration is less than 1.5×10^{-4} mol/L, the flotation recoveries of the three minerals ascend sharply with increasing concentration of collector. Nevertheless, the flotation recoveries increase steadily with further augment of the concentration. When the concentration of collector reaches 1.83×10^{-4} mol/L, the flotation recoveries of quartz, calcite and calamine get their maximum of 97.64%, 96.21% and 91.18%.

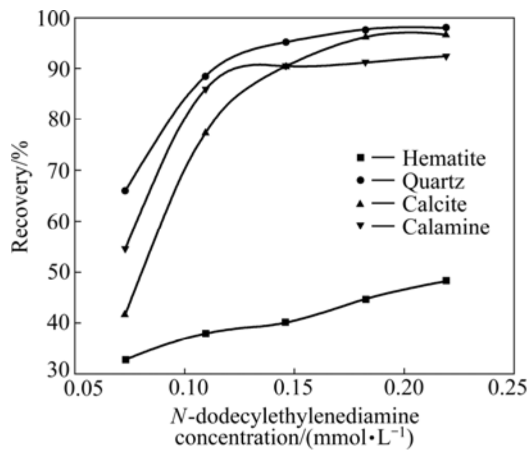

Fig.2 Effects of ND concentration on minerals recoveries

The catchabality of ND to hematite is infirmness and the flotation recovery is not more than 50% under the experimental condition. The flotation recovery of hematite increases with the increase of collector. When the dosage is less than 2.19×10^{-4} mol/L, the recovery ascends linearly.

Fig.3 shows the effect of dodecylamine concentration on minerals flotation. Dodecylamine has stronger collecting performance to calcite than the other three minerals. When the collector concentration gets to 1.5×10^{-4} mol/L, the flotation recovery achieves equilibrium, namely, the flotation recovery keeps invariable with continual rise of the concentration.

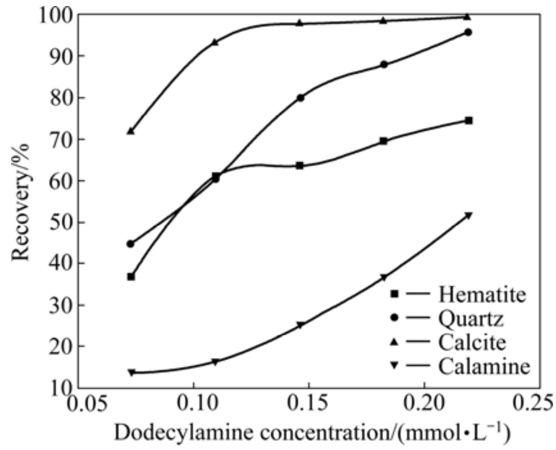

Fig.3 Effects of dodecylamine concentration on minerals recoveries

The flotation recoveries of hematite and quartz increase with the enhancement of collector concentration, and collecting capability of dodecylamine to quartz is better than that to hematite clearly. Although the flotation recovery of calcite is accretion with the augment of collector concentration, the recovery is less than 50% in the whole experimental concentration range.

By comparing Fig.3 with Fig.2, it can be concluded that ND has stronger capability to quartz than dodecylamine, while the flotation recovery of hematite with ND as collector is poorer than that with dodecylamine. So, ND can be used as collector in the reverse flotation of hematite by adding proper depressor such as amylum.

Figs.4 and 5 show the effects of pH on flotation recoveries of the minerals.

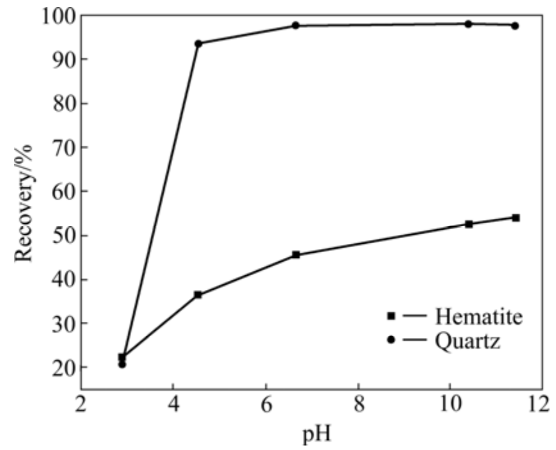

Fig.4 Effects of pH on flotation of hematite and quartz at $c(ND)=1.83\times10^{-4}$ mol/L

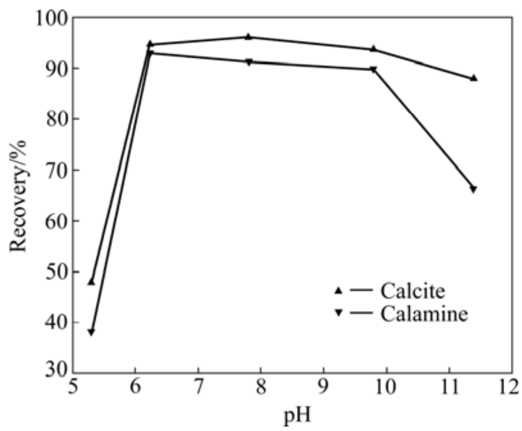

Fig.5 Effects of pH on flotation of calcite and calamine at c(ND)=1.83×10^{-4} mol/L

The flotation recoveries of quartz and hematite increase with the rise of pH. With increase in pH, the flotation recovery of quartz rises sharply until pH=4.6. When pH reaches 6, the flotation recovery of quartz achieves more than 90% and with the further increase of pH, the recovery keeps steadily. Along with increasing pH, the flotation recovery of hematite rises, while the maximum recovery of hematite is no more than 55% under the experimental conditions.

From Fig.5, it can be seen that, the effects of pH on flotation of calamine and calcite are similar. With pH increasing, the flotation recoveries of the two minerals go up fleetly until pH=6.5. And then the flotation recoveries keep gently and reach their maximum at pH=6.5−10. Afterwards, the flotation recoveries decrease sharply in alkaline media.

3.3 Infrared spectrum measurement

In order to investigate the collecting mechanism of ND to quartz, the infrared spectra of ND, quartz and after contacting with ND solution were analyzed and shown in Fig.6.

It can be seen from Fig.6(b) that the vibration of Si—O stretching is characterized by 1 080.18 cm^{-1}. It is evidence that the adsorption peak of hydroxyl group is visible in Fig.6, indicating the existence of crystal water in quartz.

After contacting with ND solution, there exist the stretching liberations of —CH_3— and —CH_2— at 2 925 cm^{-1} and 2 855 cm^{-1} although they are very weak, meaning the adsorption of ND on quartz surface. And the diagnostic peaks of mineral are not changed clearly expect red-shift, meaning there is not chemical adsorption on mineral surface but electrostatic adsorption [18]. After adsorption with collector, the peak at 3 431.80 cm^{-1} shifts to 3 444.24 cm^{-1}, indicating that hydrogen binding adsorption occurs on the quartz surface [19].

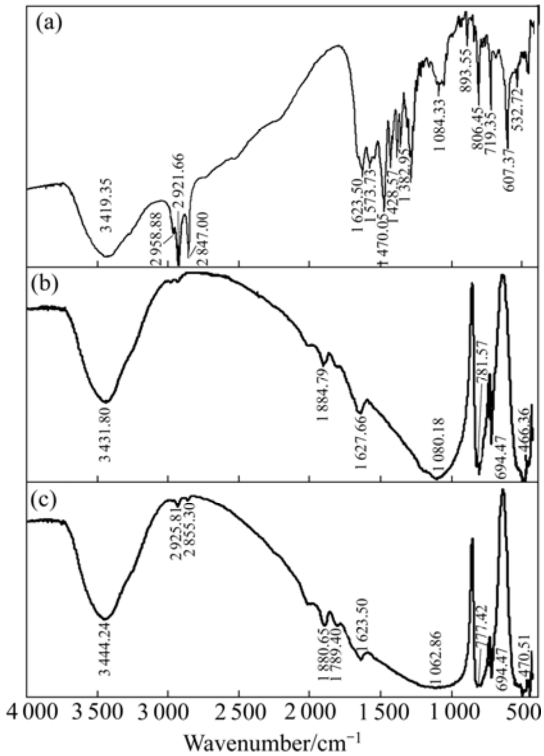

Fig.6 Infrared spectra of collector and quartz before and after acting with collector: (a) ND; (b) Quartz; (c) Quartz after acting with collector

3.4 Effect of ND structure on flotation

The electronegativity of group (χ_g) and radical size of collector reflect the acting intensity and selectivity of collector. Usually, the larger the electronegativity of group, the stronger the acting-solid intensity; and the larger the radical section size of collector, the stronger the selectivity of the collector. Electronegativity of group is not invariable for it is influenced by the contiguous atoms[20].

Amine collectors are the common oxide minerals collectors, and the bonded atom in them is nitrogen. When the hydrogen is replaced by different radicals, the electro cloud density of nitrogen is changed. So, the collect capabilities of amines are changed. ND was obtained by replacing the hydrogen of dodecylamine by radical —$CH_2CH_2NH_2$. So, ND has advantages over dodecylamine on collecting capability.

According to the calculating formulas of electro-conegativity of group[21], the electronegativities of groups in ND were worked-out and are shown in Table 4.

The electronegativity of group in ND is 3.9 and dodecylamine is 3.7. So, ND can be used as collectors

Table 4 Electronegativity of groups in ND

Group	χ_g
—NH_2	3.7
—NH—	4.1

for oxide minerals and it has stronger collectivity than dodecylamine.

4 Conclusions

1) *N*-dodecylethylenediamine was synthesized in laboratory by nucleophilic substitution reaction of 1-bromododecane and ethylenediamine in ethanol liquids.

2) ND has strong collecting capability to quartz. And when the concentration of collector reaches 1.83×10^{-4} mol/L, the flotation recovery gets its maximum of 97.64%.

3) The flotation recovery rises sharply with the increase of pH until pH=4.6; then with the further increase of pH, the recovery keeps almost unchanged. When pH=10.38, the flotation recovery achieves 98.20%.

4) Compared with dodecylamine, ND has stronger capability to quartz, while the flotation recovery of hematite with ND as collector is poorer than dodecylamine.

5) Infrared spectrum measurement indicates that hydrogen binding adsorption and electrostatic adsorption occur between ND and the quartz.

6) Electrconegativity of group in ND shows that ND has stronger collectivity to oxide minerals than dodecylamine.

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