Synthesis of N-decyl-1, 3-diaminopropanes and its flotation properties on aluminium silicate minerals [①]

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Abstract: N-decyl-1, 3-diaminopropanes (DNs) were synthesized from alkyl-amine acrylonitrile at ambient pressure. With the synthesized DNs as collectors, the flotation of kaolinite, pyrophyllite and illite was conducted and the results were interpreted in terms of the structure-activity relationship. The DNs are found to be more effective collectors than do-decyl amine, exhibiting the highest recovery over a pH range of 4 - 6. Among the DNs examined, DN_{12} shows the highest flotation efficiency. The flotation mechanisms were explained in view of the structures of reagents and aluminium silicate minerals. It is demonstrated that DNs can become new selective collectors for reverse floatation to remove aluminium sili-cate minerals from bauxite.

Key words: N-decyl-1, 3-diaminopropane; synthesis; aluminosilicate; reverse floatation; structure-reactivity relation-ship

CLC number: TD 923; TD 952   **Document code:** A

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1 INTRODUCTION

Bauxite is a major source for alumina production. Bayer process features short residence time, low energy consumption and high quality product. As a result, it is widely used to treat the bauxite of aluminum/ silicate ratio (A/ S) more than 8. Although there are abundant aluminium oxide mineral resources in China, most of them are diasporic bauxite with high aluminum content, but low A/ S ratio. Among 40 bauxite diggings, the average Al_2O_3 and SiO_2 contents are 63. 41% and 11. 59%, respectively, while the average A/ S ratio is 4 -6 [1]. This bauxite is difficult to be treated directly by the Bayer process. It is therefore highly desirable to increase A/ S ratio of bauxite by physical cleaning[2].

For this reason, the flotation desilicate-Bayer process was developed. In desilication by direct flotation, large quantity of diaspores are floated with anionic collectors. The major drawback of this process is the large collector consumption and the difficult collector removal from the concentrate to avoid its unpredicted effect in the subsequent process. The concentrate recovery is above 80% of the total feed material, conflicting with the common principle of floating less rich component and depressing the major constituents. To overcome these shortcomings, the reverse flotation was proposed. The reverse flotation desilication involves two vital components: the selective depression of diaspore and the enhanced collection of associated gangue minerals, such as kaolinite [3].

Amine, a cationic collector for oxidize ore flotation, has been used in reverse flotation of iron ores[4] and in flotation of quartz [5] and fluorite ores[6]. However, it was found that the primary amine (such as dodecyl amine) exhibits a weak collecting power for kaolinite, leading to small differences in floatability between diaspore and aluminosilicates. Therefore, it is of great interests to develop new amine family collectors.

In the present study, novel amine-based collectors, N-decyl-1, 3-diaminopropanes, are synthesized, and their effects on flotation of kaolinite, pyrophyllite and illite are investigated.
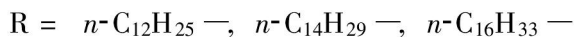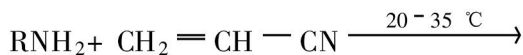
2 SYNTHESIS OF N-DECYl-1, 3-DIAMINO-PROPANES

N-alkyl cyanogens were first synthesized from primary amine and acrylonitrile[7], following the reaction below:
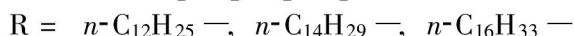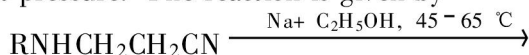

$$RNH_2 + CH_2 = CH - CN \xrightarrow{20-35\ ℃}$$

$$RNHCH_2CH_2CN$$

$$R = n\text{-}C_{12}H_{25}-,\ n\text{-}C_{14}H_{29}-,\ n\text{-}C_{16}H_{33}-$$

In general, N-decyl-1, 3-diaminopropanes are produced by reducing N-alkyl cyanogens with H_2 at high pressure in the presence of Reny Ni as catalysts[8]. Although this method of synthesis results in a high yield, it requires high pressure equipment and sophisticated fabrication of the catalyst. Instead, we use elemental sodium and ethanol as reductants to reduce N-alkyl cyanogens in ethanol (as solvent) at ambient pressure. The reaction is given by

$$RNHCH_2CH_2CN \xrightarrow{Na + C_2H_5OH,\ 45-65\ ℃}$$

$$RNHCH_2CH_2CH_2NH_2$$

$$R = n\text{-}C_{12}H_{25}-,\ n\text{-}C_{14}H_{29}-,\ n\text{-}C_{16}H_{33}-$$

The N-decyl-1, 3-diaminopropanes produced as such were dissolved in acid. The acid-insoluble component was removed by filtration. The contained 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 N-decyl-1, 3-diaminopropanes was recrystallized by evaporating the solvent and drying in a vacuum desiccate to obtain the final product in the form of white solids. The synthesized product was characterized by gas chromatography and FTIR and the results are summarized in Table 1.

Table 1 Content and state of synthesized products

Product	State	Content/%
$C_{12}H_{25}NH(CH_2)_3NH_2(DN_{12})$	Paste	90
$C_{14}H_{29}NH(CH_2)_3NH_2(DN_{14})$	Solid	88
$C_{16}H_{33}NH(CH_2)_3NH_2(DN_{16})$	Solid	85

3 EXPERIMENTAL

3. 1 Mineral samples and reagents

The source and the results of chemical analyses of the mineral samples used in this study are given in Table 2 .

Stock solutions of chemical purity dodecyl amine and synthesized collectors were prepared by dissolving collectors in acetate aqueous solutions at a collector to acetate molar ratio of 1∶1.

3. 2 Flotation

Flotation tests were conducted in a 40 mL mechanical float 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 suspension pH to a desired value and adding collector, the resultant suspension was conditioned for 4 min. The flotation time was fixed at 4 min. The floated and unfloated fractions were collected and dried separately. The mass of solids in each fraction was determined accurately and used to calculate the recovery.

4 RESULTS AND DISCUSSION

The flotation recoveries of kaolinite, illite and pyrophyllite using dodecyl amine (DDA) as collectors are shown in Fig. 1. From Fig. 1, it can be seen that the recovery of three aluminosilicate minerals decreases with increasing pulp pH. Over a pH range of 2-4, the flotation recovery is in the order of pyrophyllite ≈ kaolinite ≫ illite. The observed flotation characteristics can be explained in view of crystal structure and solution chemistry[9] of kaolinite, illite and pyrophyllite[10].

The flotation recoveries of aluminosilicate minerals using DN_{12}, DN_{14} and DN_{16} as collectors are shown in Figs. 2-4. In general, all the DN collectors show stronger collecting power than dodecyl amine, in particular when floating in a weak alkali or weak acid pulp. Among the three aluminosilicates, DNs exhibit stronger collecting power for kaolinite and pyrophyllite than for illite. At pH= 5, for example, the recoveries of kaolinite and pyrophyllite are greater than 80%, while for illite, it is less than 60%. Among three DNs synthesized, DN_{12} shows the best recovery for all three aluminosilicate minerals. Therefore, DN_{12} is a promising collector for reverse flotation of bauxite. To account for a significant reduction in flotation recovery at pH higher than 10, the molecular species distribution of the collectors needs to be considered. At high pH, DNs may be present as molecular precipitates so as to weaken their collecting ability. Just like alkyl amines, the more the carbon atoms, the lower the pH at which DNs start to precipitate. This trend can be seen in Figs. 2-4.

Table 2　Chemical analyses of mineral samples

Sample	Source	Grade(mass fraction)/%										Granularity /mm
		SiO_2	Al_2O_3	MgO	CaO	Fe_T	TiO_2	K_2O	Na_2O	H_2O	Burning-lose	
Kaolinite	Jiaxian, Henan	44. 22	37. 66	0. 093	0. 074	0. 54	0. 22	0. 064	0. 049	1. 19	14. 79	< 0. 098
Pyrophyllite	Qingtian, Zhejiang	61. 57	31. 10	0. 013	0. 081	0. 18	0. 19	0. 049	0. 12	0. 63	6. 53	< 0. 098
Illite	Ouhai, Zhejiang	50. 86	32. 93	0. 30	0. 080	0. 29	0. 36	7. 52	0. 18	0. 35	5. 04	< 0. 098

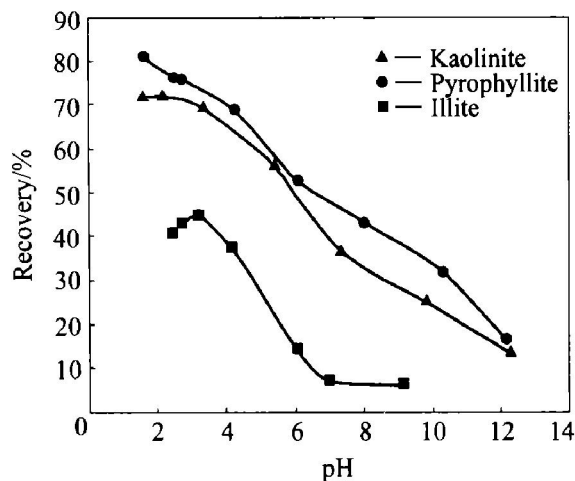**Fig. 1** Flotation recoveries of kaolinite, pyrophyllite and illite using DDA as collectors
(c (DDA) = 2×10^{-4} mol/ L)

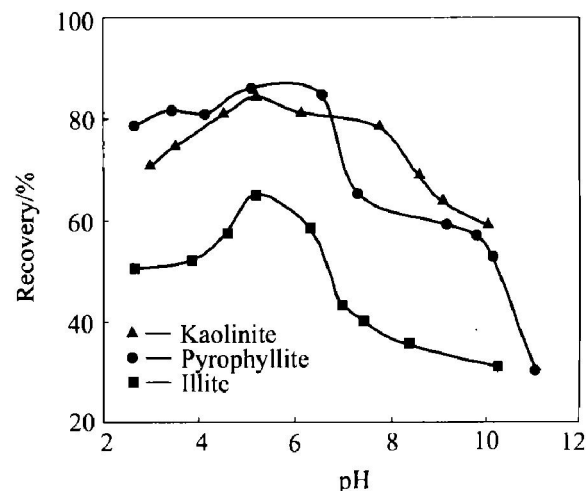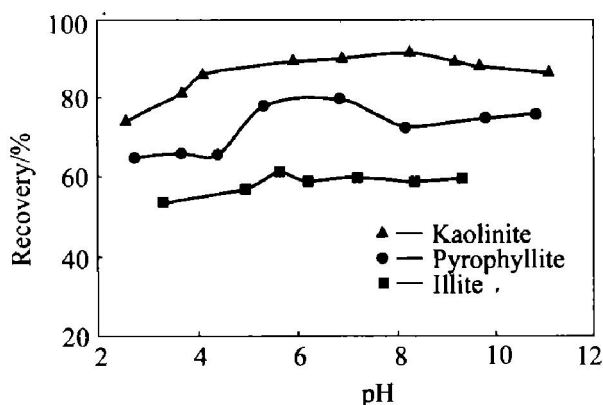**Fig. 2** Flotation recoveries of kaolinite, pyrophyllite and illite using DN_{12} as collectors
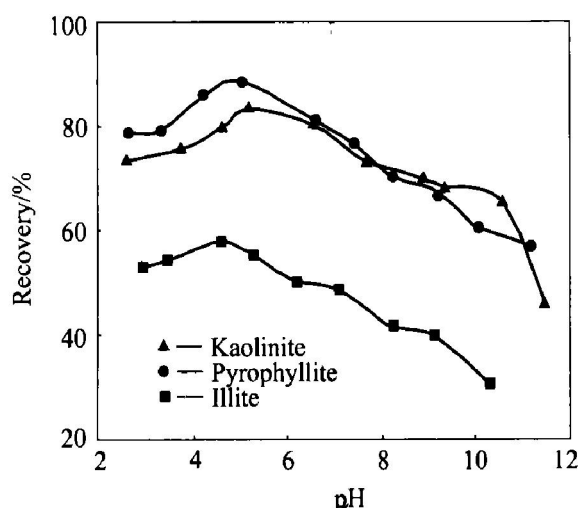(c (DN_{12}) = 2×10^{-4} mol/ L)

Fig. 3 Recoveries of three minerals at different pH using DN_{14} as collector
(c (DN_{14}) = 2×10^{-4} mol/ L)

5 ζ-POTENTIAL OF MINERALS

The ζ-potentials of aluminosilicate minerals

Fig. 4 Recoveries of three minerals at different pH using DN_{16} as collector
(c (DN_{16}) = 2×10^{-4} mol/ L)

were measured by a laser electrophoresis instrument (Brookhaven Corporation, USA). The mineral sample was ground to < 5 μm with an agate mortar. The mineral suspension was prepared in distilled water to 0. 01% solid content. After adjusting suspension pH to a desired value, the suspension was stirred for 5 min prior to filling the capillary cell for zeta potential measurement.

The ζ-potentials of the minerals in the absence of collectors are shown in Fig. 5. An iso-electric point (IEP) was determined to be 4. 3 and 3. 6 for kaolinite and illite, while for pyrophyllite, it was less than 2. 0. With the addition of 0. 2 mol/ L DN_{12}, the IEP for kaolinite, illite and pyrophyllite shifted to 5. 8, 4. 5 and 3. 0, respectively, as shown in Fig. 6. The significant shift of IEP suggests a strong interaction of the aluminosilicate minerals with DN_{12}. Compared with DDA, DN series collectors become protonated over a wider pH range with $RN^+ H_2(CH_2)_3 NH_2$ and $RN^+ H_2-(CH_2)_3 N^+ H_3$ being the predominate species, exhibiting a cationic characteristics. The adsorption of these species on the minerals is responsible for the shift of IEPs. Since DN collectors ionize more easily (K_a (DN_{12}) = $2. 0 \times 10^{-3[11]}$) than DDA (K_a(DDA) = $4. 3 \times 10^{-4[12]}$) , a stronger adsorption and hence stronger collecting power are anticipated for DN_{12} than for DDA. Considering the IEP of diaspore being at pH 6. $2^{[9]}$, the optimum pH range for reverse floatation separation of diaspore and aluminum silicate minerals using DNs as collectors can be set between pH= 4 and 6.

6 EFFECT OF DN ALKYL STRUCTURE ON FLOTATION

Among the same type of collectors, the collecting ability of reagent becomes stronger with increasing the
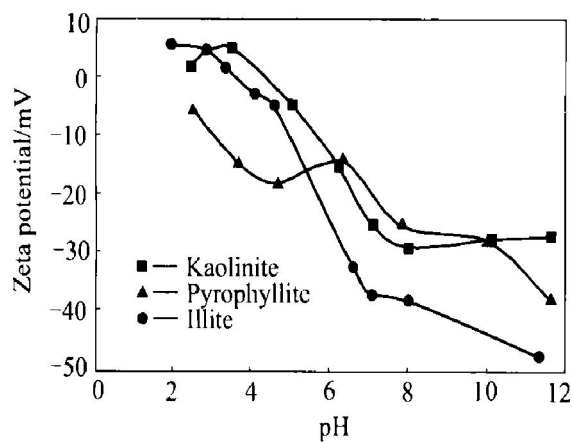
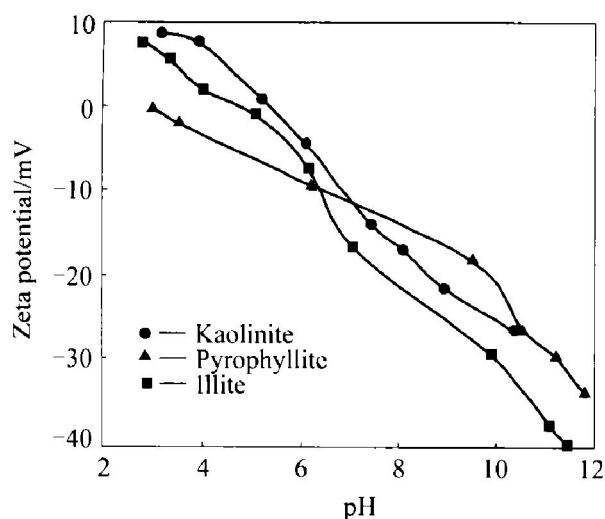**Fig. 5**   Relation of ζ-potentials of minerals and pH (no collector)

Fig. 6   Relation of ζ-potentials of minerals and pH (using DN_{12} as collector)

number of carbon atoms in alkyl chains. Table 3 lists the partition coefficient ($\lg P$) and the equivalent number (N) of carbon atoms in alkyl chains of DNs calculated by using the fragmentography arithmetic[13]. It is known that for a given collector, the larger the $\lg P$ and N, the stronger the collecting power. The data in Table 3 indicate that the collecting ability follow the order of DN_{16}> DN_{14}> DN_{12}. However the collectors should have not only the necessary but also the optimum length of hydrophobic chain. The DN_{12}, whose hydrophobic chain length is close to the optimum one for kaolinite, exhibits evident collecting effect, seen in Figs. 2 ~ 4.

Table 3   Partition coefficient and hydrophobic chains of DNs

Collector	$\lg P$	N
DN_{12}	7. 06	12. 19
DN_{14}	8. 46	14. 78
DN_{16}	9. 86	17. 37

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(Edited by YUAN Sai-qian)