

A series of aminoamides used for flotation of kaolinite

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Abstract: N-(2-aminoethyl)-dodecanamide, N-(3-dimethylaminopropyl)-dodecanamide, and N-(3-diethylaminopropyl)-dodecanamide used as collectors were studied for the flotation of kaolinite in the absence of additives at different pulp pHs as well as different collector contents. The effectiveness of the long chain aminoamides on pure kaolinite was demonstrated in laboratory scale flotation tests. The adsorption mechanism of the aminoamides onto kaolinite was investigated through zeta potential determinations and infrared spectrometry. The $-98 \mu\text{m}$ size fractions of kaolinite, taken from Jiaxian Henan of China, were used in flotation. The hydrophilic group size of the aminoamides has a relatively less influence upon the floatability of pure kaolinite. The results suggest either the static-electric force or the coordinating bond adsorption mechanism of the aminoamides onto kaolinite depends on pulp pH.

Key words: aminoamide; kaolinite; flotation; mechanism

1 Introduction

Diaspore is the main bauxite resources in China. More often, Kaolinite as the intergrowth is present in diaspore. The mass ratio of alumina to silica ($\text{Al}_2\text{O}_3/\text{SiO}_2$) is less than 7. Seeking an appropriate collector for flotation of kaolinite from diaspore to meet production of alumina (Al_2O_3) through the advanced Bayer process is an important task in the initial process.

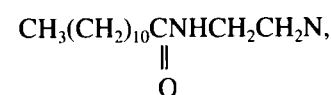
Dlugosz *et al.* [1] had investigated the flotation of kaolinite from raw material of the Maria III deposit with dodecylamine chloride as a collector resulting in a content containing 80% kaolinite with 97% yield. Troendle *et al.* [2] indicated that the yield of kaolinite with amine hydrochlorides is greater than that with amine acetates with kaolin from Hirschau (Pfalz) and kaolin from Tischenreuth (Pfalz). A strong reduction in kaolinite yield can be seen at the pH of the sludge >8 when using dodecylammonium chloride. The highest enrichment degrees have been achieved with hexylamine-HCl. A number of investigators have studied the zeta potential (ζ) of kaolinite as a function of pH [3]. These investigators all agree that the zeta potential (ζ) is negative except at quite acidic pH values. The actual shapes of the curves reported by the several authors vary considerably. There are also many investigations on kaolinite flotation from diaspore in China [4-13]. The present investigation studies the flotation

behavior of kaolinite when using a series of aminoamides as collectors. According to the infrared spectra of kaolinite, the hydrophilic group size of aminoamides as well as the zeta potential of kaolinite, the adsorption mechanism had been discussed.

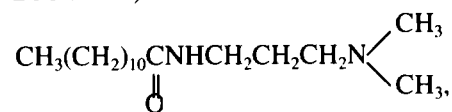
2 Experimental

2.1 Reagents

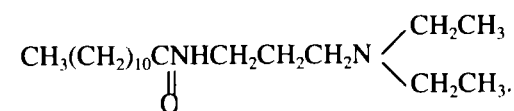
The N-(2-aminoethyl)-dodecanamide (denoted AEDA):



N-(3-dimethylaminopropyl)-dodecanamide (denoted DMAPDA):



and N-(3-diethylaminopropyl)-dodecanamide (denoted DEAPDA):



The collectors synthesized in the laboratory were used in microflotation experiments. The collector contents used in this study were expressed as the mass of collector per litre of pulp ($\text{g}\cdot\text{L}^{-1}$). In view of the low

contents used in the tests, all collectors were added to the flotation pulp as a $2 \text{ g}\cdot\text{L}^{-1}$ solution in ethanol. The effect of ethanol on flotation was found to be negligible according to the preliminary tests.

Kaolinite as a pure mineral sample was obtained from Jiaxian, Henan province (China) and contained 44.22wt% SiO_2 and 37.6wt% Al_2O_3 . The loss of ignition was about 14.79wt% and the kaolinite had a specific surface area of $16.29 \text{ m}^2\cdot\text{g}^{-1}$ as determined by the BET method. An X-ray diffraction study of the material indicated that it was a high grade kaolinite. A $-96 \mu\text{m}$ fraction of kaolinite were used in microflotation. The HCl and NaOH used to adjust pH were of reagent grade.

2.2 Methods

(1) Electrophoretic measurements.

The zeta potential (unit: mV) was measured using a COULTER DELSA 440 (Doppler Electrophoretic Light Scattering Analyzer) manufactured by Langley Ford Instruments Division of Coulter Electronics of New England Inc. For electrophoretic measurements, kaolinite was ground to about $-5 \mu\text{m}$ in a hand mortar and pestle. The content of solids in the mineral suspensions was about 0.01wt%.

(2) Infrared adsorption spectra.

The kaolinite samples were well ground in a porcelain mortar and then dispersed in a pressed KBr disk. A grating Fourier transform infrared spectrometer NEZUS 470-FT-TR was used for the infrared spectrophotometry studies. The spectra over the range $4000\text{--}500 \text{ cm}^{-1}$ were collected in order to find out the functional radicals on the surface of the kaolinite particles and whether or not the collector has been adsorbed on the surface of the kaolinite.

(3) Specific surface area.

The specific surface areas of the samples were determined by corresponding nitrogen adsorption isotherms at -195.8°C (the liquid nitrogen temperature), obtained from a NOVA 1000 & 2000 high speed surface area & pore size analyzer made in Quanta Chrome (USA) after outgassing the samples at 110°C for 1.5 h. The BET (Brunauer, Emmett, and Teller) method was used for the corresponding calculations.

(4) Laboratory flotation tests.

Flotation experiments were carried out using XFG-1600 laboratory flotation machine with a 35 mL plexiglass cell. 3 g of $-98 \mu\text{m}$ pure kaolinite mixed with 30 mL distilled water was used in flotation studies. Flotation was conducted by the examination of

parameters such as pulp pH and collector content. The pulp was stirred 1 min at 1750 r/min and then conditioned for 3 min with reagent grade HCl or NaOH, after that the collector was added and flotation was carried out for 5 min. The materials floated on the surface of pulp were collected and then dried as well as weighed for flotation recovery calculations.

3 Results and discussion

3.1 Pure kaolinite flotation with aminoamide

A number of aminoamides were tested to find out the effect of collectors on kaolinite floatability. In the absence of additives the recovery curves as a function of pH are presented in figure 1.

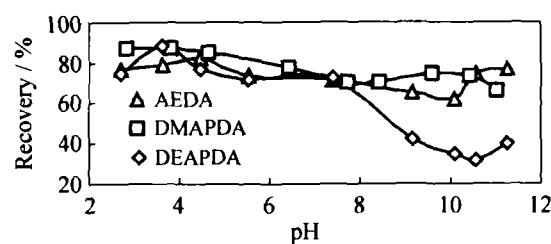


Figure 1 Floatability of kaolinite with different aminoamides as a function of pH.

The aminoamide contents are 4.9×10^{-2} , 5.7×10^{-2} and $6.3 \times 10^{-2} \text{ g}\cdot\text{L}^{-1}$ for AEDA, DMAPDA and DEAPDA respectively. Figure 1 shows a relatively high recovery of kaolinite in the acidic pH range. The maximum kaolinite floatabilities are observed in the pHs about 4.5, 2.8, 3.6 respectively for AEDA, DMAPDA and DEAPDA. The flotation recoveries go beyond 82%, 87% and 88% respectively. A relatively small pH dependence of flotation was noted with AEDA. In the middle part of the curve for the AEDA, the recovery of kaolinite was relatively less than the rest of the curve, which may be due to the operator factor or other random errors. Generally speaking, the floatability of kaolinite in the acidic conditions is greater than that in the alkaline region. The variations of pH do not give marked effect on the recovery when using AEDA or DMAPDA as a collector. Figure 1 shows that the collecting power of AEDA is close to that of DMAPDA as well as DEAPDA, especially in the acidic pH range. The recovery decreases gradually with increasing pulp pH. The results seem to indicate the need for an acidic environment for flotation of kaolinite when using an aminoamide as a collector. Figure 2 shows the results of floatability studies as a function of aminoamide content at flotation pH values of 4.5, 2.8 and 3.6 respectively for AEDA, DMAPDA and DEAPDA.

The recovery increases with an increasing content

of DMAPDA and DEAPDA up to a certain limit. The results show that the collecting power of DMAPDA is better than that of AEDA, same as DEAPDA. On the full line portion of the curves, the kaolinite recovery exhibits a certain degree of dependence on collector content. More than 94% recovery of kaolinite could be achieved by using $0.14 \text{ g}\cdot\text{L}^{-1}$ of DMAPDA and about 93.5% when DEAPDA dosage goes beyond $0.2 \text{ g}\cdot\text{L}^{-1}$.

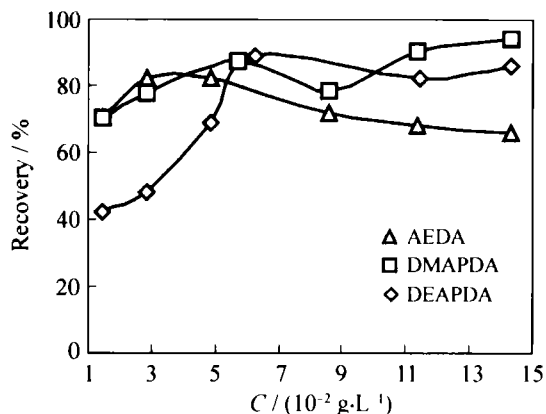


Figure 2 Recovery of kaolinite as a function of aminoamide content at flotation pH levels of 4.5, 2.8 and 3.6 for AEDA, DMAPDA and DEAPDA respectively.

3.2 Adsorption mechanism

(1) Electrokinetic investigations.

The zeta potential of kaolinite was deemed to be a comparatively important factor to understand the interaction between the collector and kaolinite surface. **Figure 3** shows the zeta potential of kaolinite as a function of pH. It can be seen that only one sign reversal of zeta potential appears, situates at a pH value around 3.99, so the isoelectric point (IEP) appears to be about at pH=3.99.

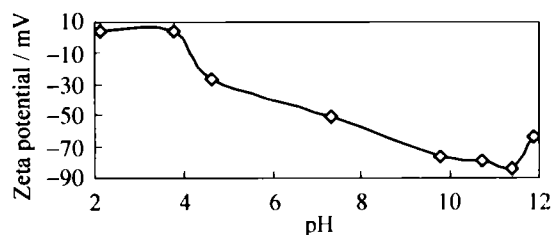


Figure 3 Zeta potential of kaolinite as a function of the pH of solution.

The zeta potential is negative over a wide pH-range. This is attributable to the isomorphous exchange of surface ions. Si^{4+} can be replaced by Al^{3+} ions, and Al^{3+} by Mg^{2+} . This leads to the formation of the negatively charged surface of oxygen. This permanent negative charge is independent of pH. Na^+ ions may dissolve out of the basal plane of kaolinite surface. This dissolution process results in negatively charged $\text{Al}-\text{O}^-$ being left behind on the surface. At the same time, when kaolinite is crushed under water, the broken

$\text{Si}-\text{O}-\text{Si}$ bonds at the surface react with water molecules to form a surface silicic acid. Ionization of this surface silicic acid also makes the mineral surface electrified with negative charge. In addition, because the more the pulp pH increases, the more the zeta potentials are negative, the hydroxyl ions in water may be coordinated with surface Si^{4+} or Al^{3+} (positive surface sites) to lead the surface of kaolinite bearing still more negative charges.

According to zeta potential curves, we may consider that the surface of kaolinite is negatively charged in a wide pH range except at quite acid pH values. The cationic surfactants should adsorb readily onto kaolinite in the above pH value range. In addition, zeta potentials were measured at various pH values following the interaction between kaolinite and aminoamides.

Because of the alkalinity of aminoamides (Lewis base), the protonation of aminoamides can take place in a certain pH range, leading to the formation of cationic surfactants being positively charged. The cationic aminoamide as a counter-ions is drawn by electrostatic force at the interfacial layer. The flotation behavior of kaolinite is highly dependent on the formation of cationic aminoamides in the acidic range as well as the neutral region.

Figure 4 exhibits the phenomenon that zeta potentials of kaolinite all change into positive values except for the quite alkaline pH region, which means that the aminoamide molecules positively charged have been adsorbed onto kaolinite surface through electrostatic force leading to the surface becoming more positive. The negatively charged kaolinite surface is neutralized by positively charged aminoamide molecules. It may reverse the overall kaolinite surface charges that the positively charged aminoamide molecules are adsorbed in quantity on the kaolinite surface. The results at quite alkaline pH values indicate that zeta potentials of kaolinite remain negative values, but in the pH region above the isoelectric point the collector shifts the zeta potential fairly toward the positive value direction as compared with kaolinite alone. This may be the results of aminoamide molecules competing strongly with hydroxyl ions for the coordination with Al^{3+} or Si^{4+} (positive surface sites).

In the alkaline region, an aminoamide cation must be changed into a free aminoamide molecule, and the aminoamide as a Lewis base can attack the Al^{3+} or Si^{4+} (positive surface sites) on kaolinite surface to form a coordinating bond. An hydroxyl anion may be replaced by the aminoamide molecule. The electric condition and zeta potential of kaolinite are attributed to the strong influence of aminoamide collectors on min-

eral surface.

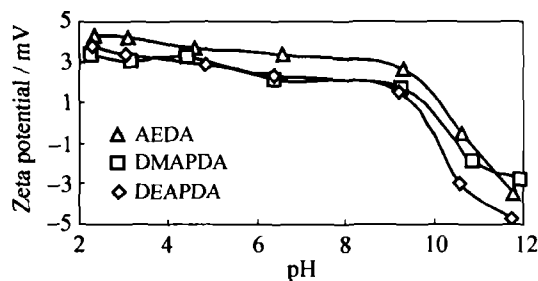


Figure 4 Zeta potential of kaolinite as a function of pH in the presence of $0.11 \text{ g}\cdot\text{L}^{-1}$ aminoamides.

(2) Infrared spectrophotometry studies.

Infrared spectrophotometry studies were carried out to determine chemical groups on kaolinite surface as well as whether aminoamide molecules were adsorbed onto kaolinite surface.

In figure 5 (a), the bands at 3695 , 3621 and 3450 cm^{-1} correspond to the stretching vibration of the Si-O-H or Al-O-H bonds from kaolinite surface. The double peaks at 3695 and 3621 cm^{-1} may be attributed respectively to the asymmetric and symmetric stretching vibration of HO-Si-OH (or HO-Al-OH), which can lead to the shift of O-H stretching vibration frequency. The bands at 3085 , 2920 and 2851 cm^{-1} in figure 5 (b) correspond to the stretching vibrations of the CH-H (mainly) and $\text{CH}_2\text{-H}$ bond of the hydrocarbon chains of *N*-(3-aminoethyl)-dodecanamide, while the band at 1640 cm^{-1} was attributed to the stretching vibration of the carbonyl group (C=O) and the bands at $3600\text{-}3000 \text{ cm}^{-1}$ to the stretching vibration of the N-H bond. In figure 5 (c), the bands at 2920 and 2851 cm^{-1} correspond to the stretching vibration of the C-H bond from the *N*-(3-aminoethyl)-dodecanamide hydrocarbon chain, at 1640 cm^{-1} corresponding to the stretching vibration of the C=O bond (amide I band), which confirms the adsorption of the *N*-(3-aminoethyl)-dodecanamide molecule onto kaolinite

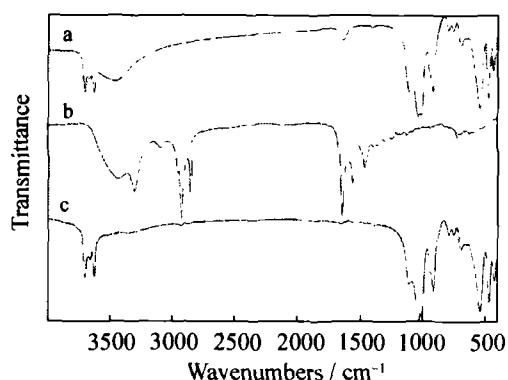
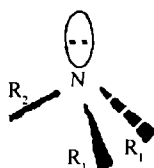


Figure 5 Infrared spectra of kaolinite: (a)—kaolinite; (b)—*N*-(2-aminoethyl)-dodecanamide (AEDA); (c)—kaolinite after exposed to *N*-(2-aminoethyl)-dodecanamide solution at $\text{pH}=3$.

surface. The presence of the C-H bands and amide I band is evidence that a few adsorbed collectors are present at the kaolinite surface. The infrared spectra of kaolinite after adsorption from DMAPDA and DEAPDA aqueous solution ($143 \text{ mg}\cdot\text{L}^{-1}$) are similar to that of AEDA. Although infrared spectra can establish whether the collectors have been adsorbed onto kaolinite surface, yet, we consider the adsorption type (chemisorption or physisorption) has not been so readily resolved with the infrared technique.

(3) Effect of aminoamide structure.

N-(2-aminoethyl)-dodecanamide, *N*-(3-dimethylaminopropyl)-dodecanamide and *N*-(3-diethylaminopropyl)-dodecanamide are aminoamides with similar the hydrocarbon chain length ($\text{CH}_3(\text{CH}_2)_{10}$), however, the difference among them is the structure of hydrophilic group. A nitrogen atom of the NH_2 group links up with two methyl groups in an *N*-(3-dimethylaminopropyl)-dodecanamide molecule, so it is a long chain tertiary amine. The *N*-(3-diethylaminopropyl)-dodecanamide connects with two ethyl groups in the site of the NH_2 group. There are no substituents for *N*-(2-aminoethyl)-dodecanamide. In case we take the matter of size into account, the volume of the hydrophilic group increases in the order: $\text{DEAPDA} > \text{DMAPDA} > \text{AEDA}$, which seemingly means that the more volume of the hydrophilic group, the more substituents hindered the collector molecule to adsorb onto kaolinite surface. The preceding experiments indicate that the collecting power of the every collector discussed above is almost identical with each other. So, we think the size of the hydrophilic group does not influence the adsorption of the collector molecule on mineral surface. In the collector molecule, a nitrogen atom uses sp^3 hybridized orbits to bond with carbon atoms of relevant substituents. The hydrophilic group located at one end of the collector molecule should take the configuration of a trihedral cone.

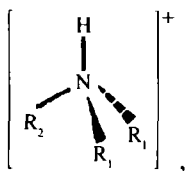


$R_1 = \text{H}, \text{CH}_3, \text{CH}_3\text{CH}_2$

$R_2 = \text{CH}_3(\text{CH}_2)_{10}\text{CONHCH}_2\text{CH}_2$,

$\text{CH}_3(\text{CH}_2)_{10}\text{CONHCH}_2\text{CH}_2\text{CH}_2$.

In the acidic or neutral condition, the aminoamide molecule as a Lewis base can capture a hydrogen ion from water to form a cationic surfactant. It's configuration as following:



$R_1 = \text{H}, \text{CH}_3, \text{CH}_3\text{CH}_2$

$R_2 = \text{CH}_3(\text{CH}_2)_{10}\text{CONHCH}_2\text{CH}_2,$

$\text{CH}_3(\text{CH}_2)_{10}\text{CONHCH}_2\text{CH}_2\text{CH}_2.$

Just now the hydrophilic group located at one end of an aminoamide molecule would be changed into tetrahedral configuration. When positively charged aminoamide ions are nearing kaolinite surface during stirring, they may regulate their direction many times and take the position of less sterically hindered effect. Finally, hydrogen atoms still face the mineral surface and interact with each other by electrostatic force. In view of the analysis above, it seems that increasing the steric bulkiness of a substituent do not weaken the interaction between collectors and kaolinite surface, which is consistent with the above experimental results of flotation. There are no obvious stereoselectivity in the above flotations.

In addition, the methyl group and ethyl group are all electron-donating substituents, their electron-donating effect can transfer to nitrogen atoms through the carbon-chains, resulting in increasing the electron density of nitrogen atoms of the aminoamide. The alkalinity of the aminoamide as a Lewis base is enhanced. This makes nitrogen atoms of the aminoamide more nucleophilic and thereby enhances the attractive force of the aminoamide toward hydrogen ions. So, the formation of cationic surfactants is more easy. In brief, the steric and electronic effects of aminoamide molecules are considerably weak toward kaolinite floatability.

4 Summary and conclusion

Three aminoamides with different substituents were used for microflotation tests of kaolinite. Maximum flotation recoveries found close to pH=4.5, 2.8 and 3.6 for N-(2-aminoethyl)-dodecanamide, N-(3-dimethylaminopropyl)-dodecanamide and N-(3-diethylaminopropyl)-dodecanamide respectively. The aminoamide collector can markedly raise zeta potentials of kaolinite in a wide pH range. The influence of varying substituents of alkyl groups on the nitrogen atom of an aminoamide molecule is not obvious for the floatability of kaolinite. Infrared spectroscopy studies showed that kaolinite surface has rich hydroxyl groups. In the acidic region, the interaction

between the aminoamide and negatively charged kaolinite surface is probably electrostatic force, while in the alkaline region, the free aminoamide molecule as a Lewis base can coordinate with Al^{3+} or Si^{4+} positive surface sites to replace the hydroxyl group linked with Al^{3+} or Si^{4+} . Kaolinite can be effectively floated when using the above-mentioned aminoamides at higher contents.

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