

Received January 31, 2016; reviewed; accepted April 14, 2016

INFLUENCE OF SYNERGISTIC EFFECT BETWEEN DODECYLAMINE AND SODIUM OLEATE ON IMPROVING THE HYDROPHOBICITY OF FLUORAPATITE

Qinbo CAO^{*,**}, Bin LUO^{**}, Shuming WEN^{**}, Jinhua CHENG^{**}

* State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming, 650093, Yunnan, PR China;

** Faculty of Land Resources Engineering, Kunming University of Science and Technology, Kunming, 650093, Yunnan, PR China; e-mail: cabdxx@163.com

Abstract: The influence of synergistic effect between dodecylamine (DDA) and sodium oleate (NaOl) on the hydrophobicity of fluorapatite (FA) was investigated with contact angle, surface tension, XPS and zeta potential studies. The role of pH and the mixing ratio of surfactants on the synergistic behavior were considered. Basing on the contact angle results the suitable pH for the NaOl-DDA mixture was pH 9.5. A further study indicated that the 3:7 DDA-NaOl mixtures could notably improve the contact angle comparing to that only with DDA or NaOl. In the solution of this mixture, the DDA cation and DDA molecule both adsorb at the FA surface as revealed by the XPS spectra results. The zeta potential analysis further suggested that the adsorption of oleate at the FA surface was also improved. The presence of DDA cation and DDA molecule was expected to result in a uniform packing of surfactants at the FA surface.

Keywords: *fluorapatite, hydrophobicity, synergistic effect, mixed collectors*

Introduction

Flotation is the primary technique to upgrade phosphate ore. Oleate has been used as the apatite collector for many decades. However, oleate is an inefficient apatite collector due to its inherent disadvantages (Sis and Chander, 2003a). Improving of the efficiency of the collector has been under intensive attention (Guimaraes et al., 2005; Sis and Chander, 2003b).

The hydrophobicity of apatite determines, to some extent, the success of the flotation process. Commonly, non-ionic surfactants are used as synergists for oleate to increase the hydrophobicity of apatite (Ge et al., 2008; Sis and Chander, 2003a, c). In fact, a unique synergistic effect was also observed when a cationic collector and an anionic

collector were used together in some flotation systems (Ejtemaei et al., 2011; Hanumantha Rao and Forssberg, 1997; Vidyadhar and Hanumantha Rao, 2007; Wang et al., 2014; Xu et al., 2013).

The synergistic behavior of cationic-anionic surfactants system is mainly dependent on the presence of cation-anion complex. The formation of such complex is governed by the electrostatic attractive force between the oppositely charged groups of the surfactants and the hydrophobic force between the alkyl chains. The cation-anion complex present at the air/liquid surface can significantly lower the surface tension of solution (Alexandrova et al., 2009). Such complex can also be formed at the mineral surface improving adsorption and also the distribution of surfactants at the surface (Vidyadhar and Hanumantha Rao, 2007).

In terms of NaOl-oleate mixture, synergistic effects were observed in feldspar-quartz and muscovite-quartz flotation systems (Wang et al., 2014). In their research, limited mixing ratios and concentration levels were used to investigate the synergistic behavior of the DDA-oleate mixtures. As well known, the critical micelle concentration (CMC) has a significant impact on the flotation. Above the CMC, collector may form a bilayer/multilayer state at the mineral surface, which decreases the hydrophobicity of mineral (Fuerstenau, 2005). However, the CMCs of DDA-NaOl mixtures at different ratios have not been determined yet.

Another crucial issue for the cationic-anionic collectors system is to determine the adsorption species of collector at a mineral surface. In the case of DDA-NaOl system, both collectors are weak electrolytes. Their species distributions are governed by the pH value. Especially at an alkaline pH, DDA cation and molecule are both prevalent species in the solution, which can adsorb at a mineral surface. Unfortunately, previous study did not distinguish the adsorption species of DDA at mineral surface at an alkaline pH (Wang et al., 2014). Thus, it was still uncertain whether the synergistic mechanism of DDA-NaOl mixture was due to the formation of cation-anion complex or molecule (DDA)-anion complex.

Our understanding the DDA-NaOl system is not fully satisfied. Especially, there is no fundamental study regarding the phosphate flotation with such mixed collectors. The objective of this work is to examine the effect of the DDA-NaOl mixture on the micellization of surfactants and the hydrophobicity of apatite, as revealed by the results from surface tension tests, contact angle measurements, XPS and also zeta potential analysis.

Experimental

Materials and reagents

Sodium oleate (NaOl) and dodecylamine (DDA) hydrochloride were both AR grade and were purchased from Sigma Aldrich. Dilute HCl and NaOH solutions were used to adjust the pH. The molar ratio of DDA to NaOl was used to represent the composition of the surfactants mixture. Fluorapatite (FA) samples were obtained from the Geological

Museum of Yunnan Province, China. Further XRD analysis indicated that the purity of the FA was 99%. All the experiments were performed with deionized water (DI) at 298 K.

Surface tension experiments

A GBX 3S instrument was used to measure the surface tension of surfactant solution. The platinum ring (9.45 mm in diameter) and all the glassware were cleaned with chromic acid and rinsed with abundant DI water. The platinum ring was further flame treated to remove organic contamination. Thirty cm³ of solution was used for each test. Each sample was tested three times, and the measurement error was less than 1 mN/m.

Contact angle tests

The dynamic captive-bubble method was employed to measure the contact angle of the FA surface with the GBX 3S instrument. Before each test, the FA crystal was first cleaned with ethanol and DI water. The crystal was polished with 1000 and 4000 grit sandpaper, and was further treated with Ar plasma for 5 min. The FA crystal was placed on two stable supports in a measurement cell filling with 100 cm³ of solution. The condition time was kept as 10 min. Then, an air bubble (2–3 mm) was released from a U-shape springy under the FA surface. After the bubble attached the FA surface, the contact angle was analyzed with the GBX 3S instrument. The variation of the contact angle measurement was less than $\pm 2^\circ$.

XPS study

Fluorapatite powder (0.1 g, $-5 \mu\text{m}$) was added into 100 cm³ of the 3:7 DDA-NaOI solution ($3.0 \times 10^{-4} \text{ mol/dm}^3$). The suspension was conditioned for 24 hours. The pH of the suspension was maintained by adding dilute NaOH solution. After the adsorption achieved equilibrium, the FA sample was carefully filtered and further air-dried for the XPS study. The XPS experiments were performed on a PHI 5000 Versa Probe II equipped with an Al target. All the spectra were recorded with the pass energy was 46.95 eV in a chamber at pressures less than 10^{-8} Pa. The scanning area was 1 mm \times 0.3 mm. The XPS spectra were analyzed with MultiPak software and fitted with the Gauss–Lorentz function.

Electrokinetic analysis

A Nano ZSP device was employed to measure the electrophoretic mobility of apatite sample. The zeta potential was further calculated with the Smoluchowski equation based on the electrophoretic mobility results by the instrument. The collector solution was prepared by $1 \times 10^{-3} \text{ mol/dm}^3$ of NaCl solution to maintain the ion strength. The sample of 0.1 g of FA ($-5 \mu\text{m}$) was conditioned with 100 cm³ of collector solution for 20

min with stirring at 300 rpm. After the condition, 10 cm³ of suspension was used for the test. Every sample was measured 20 times.

Results and discussion

Influence of pH

The influence of pH on the contact angle of the FA with NaOl, DDA and 1:1 NaOl-DDA mixture is shown in Fig.1. The concentration for each collector was 1·10⁻⁴ mol/dm³ and the total concentration of 1:1 mixture was also 1·10⁻⁴ mol/dm³. For DDA collector, the contact angle increased with the increasing in pH. The point of zero charge (PZC) of the FA is below pH 7 (Yuehua and Zhenghe, 2003). It was expected that the negative FA surface in a basic solution will favor the adsorption of DDA cations. In terms of NaOl, the contact angle reached maximum at pH 8. However, further increasing pH generated a reduction in the contact angle. The reason for the NaOl results was discussed in the later section.

It was also found that the 1:1 DDA-NaOl mixture exhibited a synergistic effect causing improvement of hydrophobicity of FA. The maximum contact angle with this mixture was obtained at pH 9.5, which was higher than that with either DDA or NaOl at the same pH. Additionally, it was observed the precipitation of collectors occurred in the solution at pH 11. Such precipitation could adsorb and/or aggregate the dissolved surfactant species, leading to a decrease in the contact angle. It was indicated that pH 9.5 was suitable for the application of the 1:1 DDA-NaOl mixture.

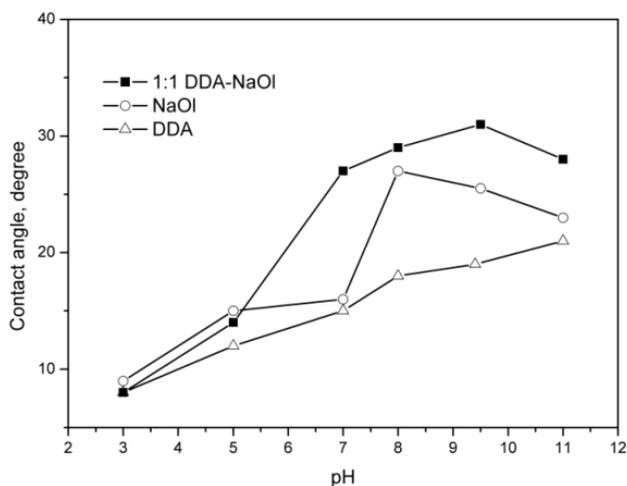


Fig. 1. Contact angles of FA with collectors as a function of pH (concentrations of DDA, NaOl and their mixtures all were 1·10⁻⁴ mol/dm³)

Species distribution diagrams

The above contact angle results with NaOl and the 1:1 NaOl-DDA mixture should be understood from the species distributions of DDA and NaOl at different pH values, as illustrated in Fig. 2. The calculation details for the data of these diagrams can be found in the paper of Dianzuo and Yuehua (1988).

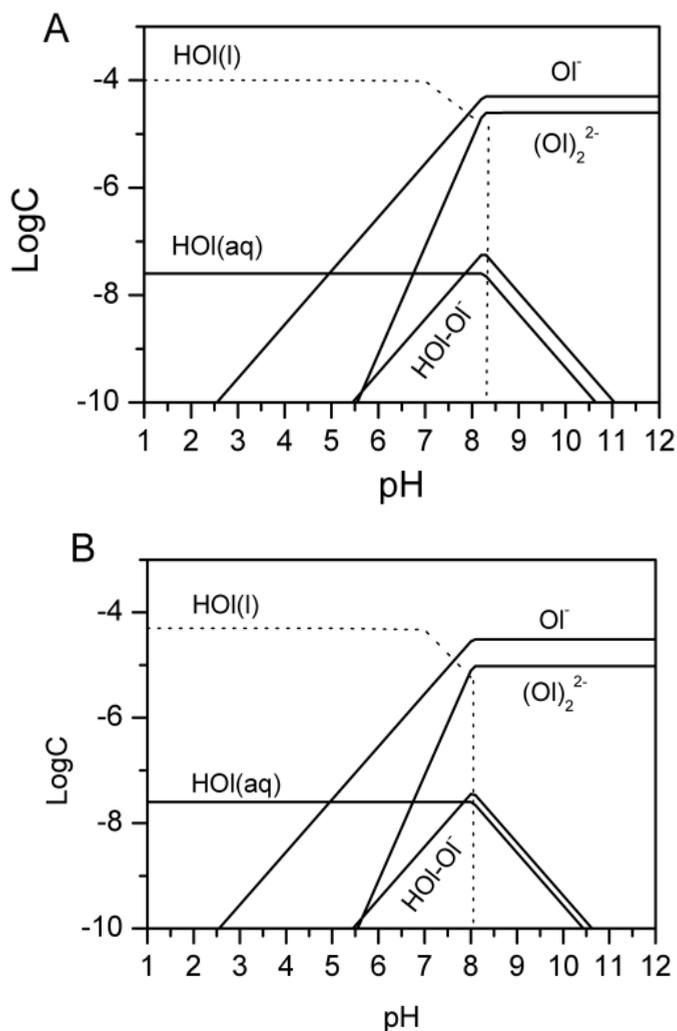


Fig. 2. Species distribution diagrams of oleate (A, $1 \cdot 10^{-4}$ mol/dm³; B, $5 \cdot 10^{-5}$ mol/dm³) as a function of pH

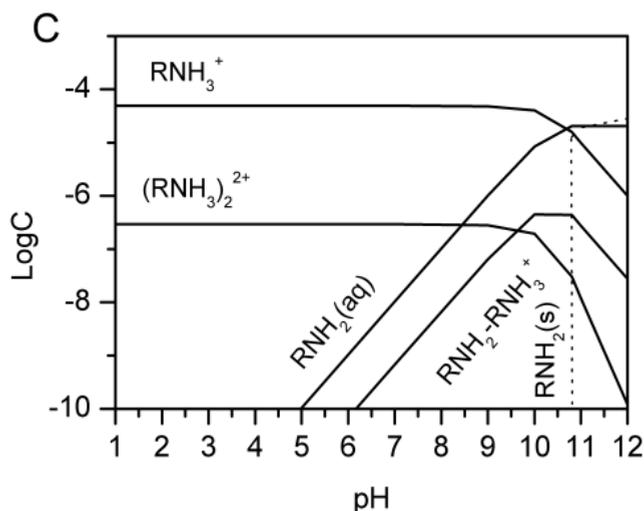


Fig. 2C. Species distribution diagrams of DDA (C, $5 \cdot 10^{-5}$ mol/dm³) as a function of pH

Figures 2A and 2B show that the oleate ion was the major species in the oleate solution at $\text{pH} > 7$. In basic solutions the oleate ion is efficiently chemisorbed at the FA surface and further precipitation of calcium dioleate at high concentrations (Lu et al., 1998) occurs. It was noticed that the concentration of ion-molecule complex (HOI-OI^-) peaked at around $\text{pH} 8$. Due to the high surface activity of the HOI-OI^- (Ananthapadmanabhan and Somasundaran, 1988), the most hydrophobic FA surface was obtained at $\text{pH} 8$. The concentration of such complex was negligible at $\text{pH} 11$, while at such high pH oleate dimmer could adsorb at the FA surface, which could cause the relative low hydrophobicity at this pH (Vucinic et al., 2010).

DDA ion, soluble DDA molecule and ion-molecule complex were all major species in the DDA solution at $\text{pH} 9.5$ (Fig. 2C). When DDA and oleate were both added into the solution of $\text{pH} 9.5$, the DDA cationic species and oleate anions could form cation-anion complex in the solution. The negative FA surface at $\text{pH} 9.5$ also favored the adsorption of DDA cations, which promoted the formation of cation-anion complex at the FA surface. On the other hand, DDA molecules can also act as a non-ionic surfactant co-adsorbing at the FA surface. Consequently, the presence of DDA cations/molecules at the FA surface could produce a tight packing of surfactants. Thus, the hydrophobicity of FA was notably improved.

The contact angle results in Fig.1 also shows that the FA surface with the 1:1 DDA-NaOl was more hydrophobic at $\text{pH} 9.5$ than that at $\text{pH} 8$. In fact the FA surface is more negative at $\text{pH} 9.5$ (Yuehua and Zhenghe, 2003). The negative FA surface benefited the adsorption of the DDA cationic species. Furthermore, the concentration of DDA molecule at $\text{pH} 9.5$ also increased to some extent when compared to that at $\text{pH} 8$

(Fig. 2B), which also could contribute to the improvement in the contact angle. In both cases, a more hydrophobic surface was generated at pH 9.5.

Surface tension results

The critical micelle concentrations (CMCs) of DDA and NaOl were measured as $1.5 \cdot 10^{-4} \text{ mol/dm}^3$ and $1 \cdot 10^{-3} \text{ mol/dm}^3$ at pH 9.5 respectively. In terms of the DDA and NaOl mixtures, the surface tension results were classified into two categories as shown in Fig. 3.

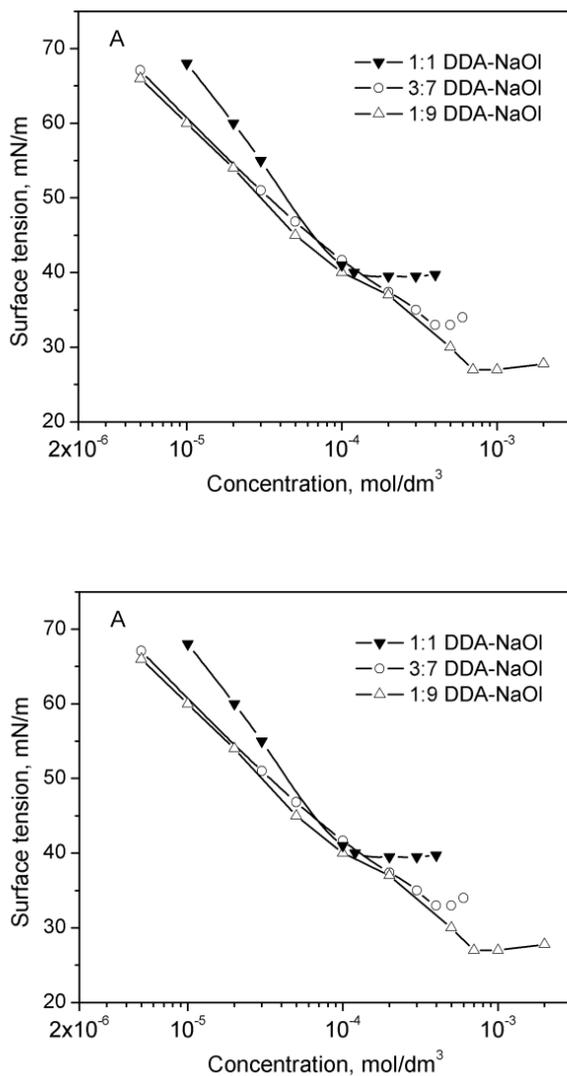


Fig. 3 Surface tension results of DDA-NaOl mixtures at pH 9.5

When the DDA content in the DDA-NaOl mixture was equal to or less than 50% (molar fraction), the surface tension reached a minimum value at a certain concentration before the occurrence of precipitation. Thus, the CMC for the DDA-NaOl mixture (DDA content $\leq 50\%$) could be measured (Fig. 3A). Differently, for the 7:3 and 9:1 DDA-NaOl mixtures (Fig. 3B), the precipitation of surfactants occurred in solution at a low concentration ($8 \cdot 10^{-5} \text{ mol/dm}^3$). The solubility limits of these two mixtures were not high enough for surfactants to form micelles.

The determined CMCs decreased in the order: NaOl $<$ 1:9 DDA-NaOl $<$ 3:7 DDA-NaOl $<$ 1:1 DDA-NaOl $<$ DDA. It was suggested that the CMC of DDA-NaOl mixture decreased with the increasing in the DDA content in the solution. However, the lowest CMC was only $1 \cdot 10^{-4} \text{ mol/dm}^3$ with 1:1 DDA-NaOl, which was slightly lower than that of DDA ($1.5 \cdot 10^{-4} \text{ mol/dm}^3$). It appeared that the DDA-NaOl mixtures exhibited a limited synergistic effect on lowering the CMC at the pH 9.5.

Contact angles dependence on mixing ratio of collectors

To further reveal the influence of the mixing ratio on the synergistic behavior of DDA-NaOl mixture, the contact angles with NaOl, DDA and their mixtures were measured and the results are shown in Figs 4 and 5. The highest contact angle with NaOl was 36.2° at $5 \cdot 10^{-4} \text{ mol/dm}^3$ (Fig. 4) while the FA surface became less hydrophobic at the concentrations higher than $5 \cdot 10^{-4} \text{ mol/dm}^3$. Since FA dissolves readily by releasing ions into solution, oleate can precipitate in the form of calcium-dioleate in the solution. The oleate salt/oleate can form multilayer adsorption at the FA surface, which is attributed to the decreasing contact angle at such high concentrations (Sis and Chander, 2003a).

It was noticed that the maximum contact angle was much smaller than our previous result, i.e., 80° of equilibrium contact angle, which was obtained with the sessile-droplet method using DI water as a droplet (Cao et al., 2015). In fact the difference in methodology could induce a notable discrepancy in contact angle results for FA with oleate. In the work of Sis and Chander (2013a) the equilibrium contact angle at FA surface reached 80° with 1 mg/dm^3 ($3.3 \cdot 10^{-6} \text{ mol/dm}^3$) of oleate, which was measured with sessile-droplet method using collector solution as droplet. However, Lu et al. (1998) reported that using DI water as droplet, the receding contact angle with oleate was less than 35° at $1 \cdot 10^{-5} \text{ mol/dm}^3$, and was in the region from 35° - 60° at $1 \cdot 10^{-4} \text{ mol/dm}^3$ depending on the size of droplet. Due to the nature of captive-bubble method, the results from this method were close to receding contact angles. Thus, the results were lower than our previous results. On the other hand, since the bubble capture was involved in the measurement, the result from captive-bubble method was considered more representative than that with the sessile-droplet method.

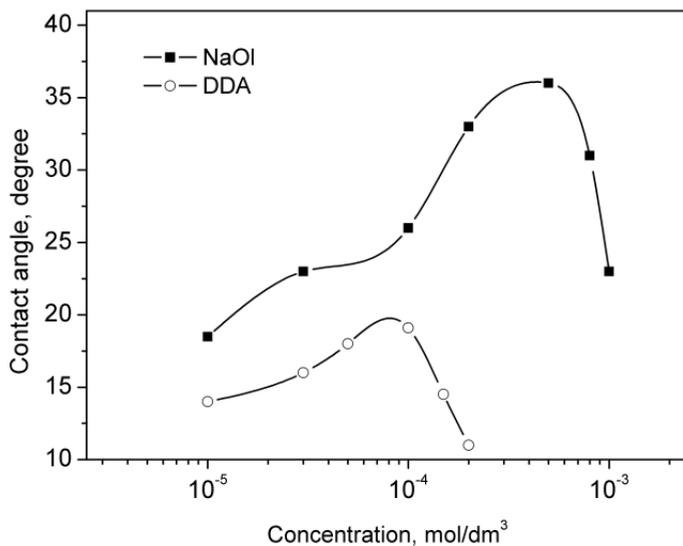


Fig. 4. Contact angles at FA surface depending on the NaOI and DDA concentrations at pH 9.5

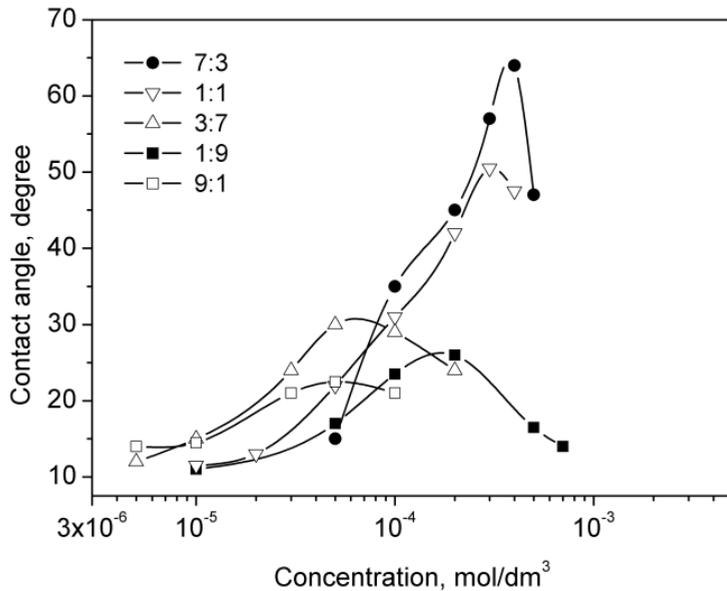


Fig. 5. Contact angles at FA surface depending on concentration and molar ratio of NaOI-DDA mixtures at pH 9.5

With regard to DDA, the highest contact angle with this collector was only 19.1° at $1 \cdot 10^{-4}$ mol/dm³. It seemed that DDA was inefficient to generate a hydrophobic FA surface. Furthermore, the main collector in the DDA-NaOl system was oleate rather than DDA. A reduction in contact angle was also observed as the DDA concentration exceeding $1 \cdot 10^{-4}$ mol/dm³ (CMC of DDA). It has been proved that at the quartz surface DDA could form bilayer structure at concentrations higher than the CMC (Wang et al., 2010). It was rational to predict that bilayer of DDA could partially be present at the FA surface and lower the hydrophobicity.

Figure 5 summarizes the contact angle results with the DDA-NaOl mixtures. It was found that only 1:1 and 3:7 DDA-NaOl mixtures had synergistic effect on improving the hydrophobicity of FA. The contact angle by these two mixtures could be higher than the maximum value with NaOl (36°). Especially for the 3:7 mixture, the contact angle reached 65° at $4 \cdot 10^{-4}$ mol/dm³, which was the highest value in this test. This result indicated that the 3:7 molar ratio of DDA: NaOl was optimal for the mixture to improve the hydrophobicity of the FA surface. It was expected that, in the solutions of 3:7 DDA-NaOl, DDA ions/molecules were present at the FA surface along with oleate species leading to a more uniform distribution and adsorption.

A reduction in contact angle was found after the contact angle reached a maximum for each DDA-NaOl mixture. For the mixture with molar ratio less than 7:3, it could be explained by the presence of a bilayer/multilayer of surfactants at the FA surface. In terms of the 7:3 and 9:1 mixtures, precipitation of surfactants accounted for the reduction in the contact angle at concentrations higher than $8 \cdot 10^{-5}$ mol/dm³.

XPS spectra and zeta potential analysis

The XPS technique was used to measure the binding energies of Ca and N atoms at the apatite surface. The aim of the study was to investigate the adsorption features of the DDA and NaOl species at the FA surface. As shown in Fig. 6A, the Ca2p peaks of FA treated with the 3:7 DDA-NaOl shifts to lower energies comparing to the Ca2p peaks of natural FA. This phenomenon was due to the shielding effect of outer layer electrons, which was caused by the surface precipitation of calcium dioleate (Cao et al., 2015).

The N1s peak was also detected for the FA sample after conditioning of the 3:7 DDA-NaOl mixture. The N1s spectrum can be separated into two individual peaks at 400.3 eV and 401.2 eV (Fig. 6B). These two peaks could be characterized by the DDA molecule and DDA cation, respectively (Chernyshova and Rao, 2001). Furthermore, the atomic concentrations of N element were 0.42% at 401.2 eV and 0.23% at 400.3 eV. It was suggested that both DDA cations and molecule adsorbed at the FA surface and the DDA cation was the major component.

The zeta potentials of FA in solutions of DDA, NaOl and 3:7 DDA-NaOl were also determined, as shown in Fig. 7. For the FA in DDA solution, the zeta potential gradually increased with the increase in DDA concentration, due to adsorption of the DDA cations. While the DDA molecule could also adsorb at the FA surface, the adsorption of this species could not change the zeta potential.

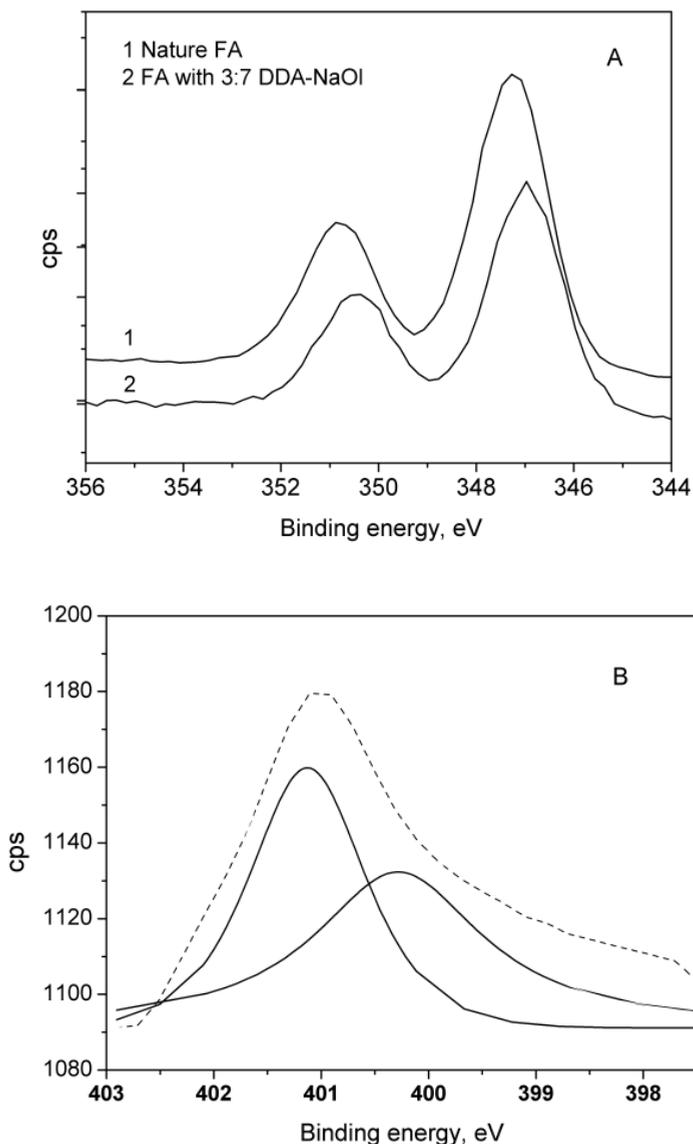


Fig. 6. XPS results of Ca2p peaks (A) and N1s peaks (B) of FA treated with the 3:7 DDA-NaOI mixture

The zeta potentials with 3:7 DDA-NaOI and NaOI were the same at $1 \cdot 10^{-5} \text{ mol/dm}^3$. Above this concentration, the zeta potential for the mixture was more negative than that with NaOI at the same concentration. The more negative FA surface is a result of improvement of oleate adsorption, since the adsorption of DDA species could not shift

the zeta potential to a negative value. The above XPS results showed that, in the solution of 3:7 DDA-NaOl, both DDA cation and molecule were present at the FA surface. Unfortunately, the zeta potential results with 3:7 DDA-NaOl could not reflect the adsorption amount of DDA species at FA surface. Further work should be done to measure the adsorption intensities of DDA species at the FA surface.

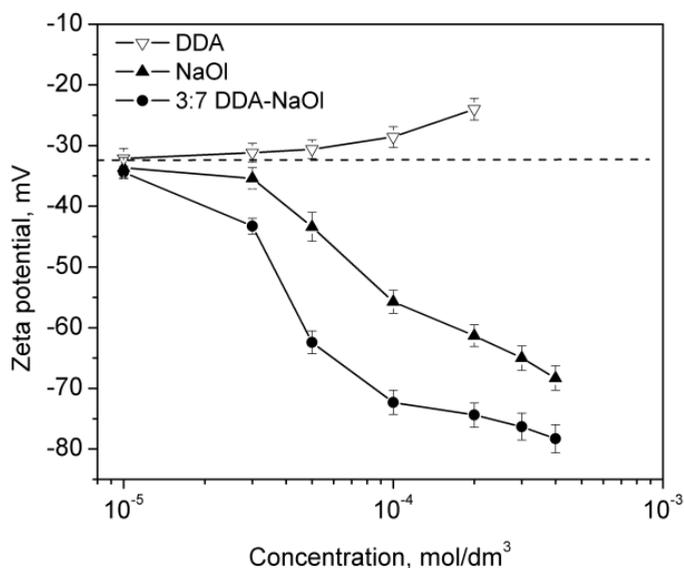


Fig.7. Zeta potentials of FA depending on concentrations of DDA, NaOl and their 3:7 mixture

Conclusions

The contact angle of FA could be improved via the DDA-NaOl mixture at pH 9.5. The benefit behavior of the surfactants mixture depended strongly on the molar ratio of DDA to NaOl. Furthermore, the 3:7 DDA-NaOl mixture exhibited notable synergistic effect on enhancing the hydrophobicity of FA. The contact angle could reach 65° with this mixture. The XPS study indicated that both DDA cations and molecules adsorbed at the FA surface, together with oleate species. Additionally, the concentration of DDA cation at the FA surface was relative higher than that of DDA molecule. The zeta potential analysis revealed that the adsorption of oleate at the FA surface was improved with 3:7 DDA-NaOl in comparison of only with NaOl. However, adsorption amount of DDA species was still uncertain from the zeta potential analysis, which should be examined with other techniques in the future.

Acknowledgments

The financial support provided by the Ph.D. Programs Foundation of Ministry of Education of China 20135314120007. Additionally, this work was also prompted by collaborative research supported by NSF grant No. 51304089.

References

- ALEXANDROV L., RAO K.H., FORSBERG K.S.E., GRIGOROV L., PUGH R.J., 2009. *Three-phase contact parameters measurements for silica-mixed cationic-anionic surfactant systems*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 348(1-3), 228-233.
- ANANTHAPADMANABHAN, K.P., SOMASUNDARAN, P., 1998. *Acid-soap formation in aqueous oleate solutions*. Journal of Colloid & Interface Science, 122(1), 104-109.
- CAO Q., CHENG J., WEN S., LI C., BAI S., LIU D., 2015. *A mixed collector system for phosphate flotation*. Minerals Engineering, 78, 114-121.
- CHERNYSHOVA I.V., RAO K.H., 2001. *Mechanism of coadsorption of long-chain alkylamines and alcohols on silicates. Fourier transform spectroscopy and X-ray photoelectron spectroscopy studies*. Langmuir, 17(9), 2711-2719.
- EJTEMAEI M., IRANNAJAD M., GHARBAGHI M., 2011. *Influence of important factors on flotation of zinc oxide mineral using cationic, anionic and mixed (cationic/anionic) collectors*. Minerals Engineering, 24(13), 1402-1408.
- FUERSTENAU D.W., PRADIP, 2005. *Zeta potentials in the flotation of oxide and silicate minerals*. Advances in Colloid & Interface Science, 114-115(30), 9-26. .
- GE Y.Y., GAN S.P., ZENG X.B., YU Y.F., 2008. *Double reverse flotation process of collophanite and regulating froth action*. T Nonferr Metal Soc, 18(2), 449-453.
- GUIMARAES R.C., ARAUGO A.C., PERES A.E.C., 2005. *Reagents in igneous phosphate ores flotation*. Minerals Engineering, 18(2), 199-204.
- HANUMANTHA RAO K., FORSSBERG K., 1997. *Mixed collector systems in flotation*. International Journal of Mineral Processing, 51(1-4), 67-79.
- HU Y., XU Z., 2003. *Interactions of amphoteric amino phosphoric acids with calcium-containing minerals and selective flotation*. International Journal of Mineral Processing, 72(1-4), 87-94.
- LU Y., DRELICH J., MILLER J.D., 1998. *Oleate Adsorption at an Apatite Surface Studied by Ex-Situ FTIR Internal Reflection Spectroscopy*. Journal of Colloid and Interface Science, 202(2), 462-476.
- SIS H., CHANDER S., 2003a. *Adsorption and contact angle of single and binary mixtures of surfactants on apatite*. Minerals Engineering, 16(9), 839-848.
- SIS H., CHANDER S., 2003b. *Reagents used in the flotation of phosphate ores: a critical review*. Minerals Engineering, 16(7), 577-585.
- SIS H., CHANDER S., 2003c. *Improving froth characteristics and flotation recovery of phosphate ores with nonionic surfactants*. Minerals Engineering, 16(7), 587-595.
- VIDYADHAR A., HANUMANTHA RAO K., 2007. *Adsorption mechanism of mixed cationic/anionic collectors in feldspar-quartz flotation system*. Journal of Colloid and Interface Science, 306(2), 195-204.

- VUCINIC D.R., RADULOVIC DEUSIC S.D., 2010. *Electrokinetic properties of hydroxyapatite under flotation conditions*. Journal of Colloid and Interface Science, 343(1), 239-245.
- WANG D., HU Y., 1988. *Solution chemistry of Flotation*. Hunan Science and Technology Press, China. 31-37.
- WANG L., SUN W., HU Y.-H., XU L.-H., 2014. *Adsorption mechanism of mixed anionic/cationic collectors in Muscovite – Quartz flotation system*. Minerals Engineering, 64(1), 44-50.
- WANG X., LIU J., DU H., MILLER J.D., 2010. *States of Adsorbed Dodecyl Amine and Water at a Silica Surface As Revealed by Vibrational Spectroscopy*. Langmuir, 26(5), 3407-3414.
- XU L., WU H., DONG F., WANG L., WANG Z., XIAO J., 2013. *Flotation and adsorption of mixed cationic/anionic collectors on muscovite mica*. Minerals Engineering, 41(2), 41-45.