Preparation and Characterization of Organo-bentonites Modified by Different Surfactants

XIAOJIAN ZHOU[1,3], XIAOZHI WANG[1], CUILI JIN[1,3], BIN ZHAO[1], FENG YAN[2] and KE FENG[1,3,*]

[1]School of Environmental Science and Engineering, Yangzhou University, Yangzhou 225009, P.R. China
[2]Institute of Plant Nutrition, Justus Liebig University, IFC, Heinrich-Buff-Ring 26-32, 35392 Giessen, Germany
[3]Marine Science and Technology Institute, Yangzhou University, Yangzhou 225009, P.R. China

*Corresponding author: Fax: +86 514 87978626; Tel: +86 514 87979588; E-mail: fengke@yzu.edu.cn

Clay minerals with 2:1 type structure possess prodigious area of inner-surface in silicate interlayers. Inserting surfactants into the interlayers will change the characteristics of inner-surface from hydrophilic to hydrophobic ones, which significantly enlarges the capacity of clay minerals to adsorb organic pollutants. Surfactants on the inner-surface of silicates can affect the physical and chemical properties of the inner-surface and the dimension of interspace. The array forms of the surfactant molecules on the inner-surface of minerals may also influence adsorption capacity to a special organic pollutant. In the present study four surfactants, cetyltrimethylammonium bromide (CTMAB), cetylpyridinium bromide (CPB), dodecyltrimethylammonium bromide (DTMAB) and dodecylpyridiniumbromide (DPB) were selected for production of organo-bentonite. With burning and X-radial diffraction (XRD) the amount of surfactants adsorbed on the inner-surface of bentonite were measured and the molecule array forms of surfactants on the inner-surface of bentonite were discussed. The results were as follows: (1) all surfactants tested could be adsorbed onto the inner-surface of bentonite, which increased the distance between layers of elemental cells; (2) for surfactants with same length of carbon chain, one with pyridinium head is more easily adsorbed on the inner-surface of bentonite than that with trimethylammonium; for surfactants with same head but different length of carbon chains, the one with greater length is more easily adsorbed onto inner-surface of bentonite; (3) The possible molecule array forms of cetyltrimethylammonium bromide and cetylpyridinium bromide, which possess carbon chain with 16 carbon atoms, was assumed to be a pseudo-trilayer lying on the inner-surface of bentonite and those for dodecyltrimethylammonium bromide and dodecylpyridiniumbromide, which possess carbon chain with 12 carbon atoms, were assumed to be a tightly-combined lateral bilayer; (4) with increasing concentration of surfactants the molecule array forms of surfactants on the inner-surface of bentonite became complex: monolayer → lateral bilayer → paraffin-type monolayer → pseudo-trilayer.

Key Words: Organobentonite, Surfactants, Inner-surface, Molecule array forms.

INTRODUCTION

Minerals are widely used for environment remediation. Of them, bentonite stands out as one that has been broadly used extensively studied. Bentonite constitutes mainly montmorillonite of 2:1 type mineral. Compared with active carbon, bentonite possesses many advantages such as it is abundant as nature resource and cheap, it possesses higher adsorption capacity and easily regenerated.

Bentonite possesses great inner-surface. Based on calculation according to crystal structure theory, the specific area of inner-surface can be as high as 600 to 800 m^2 g^{-1}. Owing to the isomorphism replacement (Si^{4+} is replaced by Al^{3+} in tetrahedron layer and Al^{3+} by Fe^{2+}, Mg^{2+} in octahedron layer), the permanent negative charges are produced, which result in adsorption and fixation of cations such as K^+, Na^+, Ca^{2+} *etc*. on the inner-surface[1-4]. This characteristic of bentonite enables its wide application in environment remediation.

The exchangeable cations adsorbed on the inner-surface of bentonite are usually hydrated. These hydrated cations result in a water film on the inner-surface of the mineral, which makes the adsorption of hydrophobic organic pollutants difficult. This characteristic of bentonite limits its application in the environment remediation. To enhance adsorbing capability of betonite for organic pollutants, the cationic surfactants are introduced onto the inner-surface of bentonite in the way that the alkyl chains of organic cations build up an organic phase, which turns inner-surface from hydrophile into hydrophobic ones and is capable of adsorption of organic pollutants[5].

Adsorption of surfactants onto inner-surface of betonite changes not only the physical-chemical properties of the inner-surface of bentonite but also its interspace dimension and microenvironment in the interspace. The array forms of surfactant molecules on the inner-surface may also influence the adsorption of pollutants.

In this study, we used four surfactants (DTMAB, CTMAB, DPB, CPB) to produce organobentonite. Possible molecule array forms of the adsorbed surfactants were postulated.

EXPERIMENTAL

Bentonite used was primarily Na^+ montmorillonite from Hunan, China. Its cation exchange capacity (CEC) is 58.2 cmol/kg. Four surfactants, cetyltrimethylammonium bromide (CTMAB), cetylpyridinium bromide (CPB), dodecyltrimethyl-ammonium bromide (DTMAB) and dodecylpyridiniumbromide (DPB) were of chemical grade and applied to produce organobentonite.

Preparations of cation organobentonite: A series of cation organobentonites were synthesized by mixing bentonite with aqueous solutions of different surfactants at different concentrations. A total of 30 g of previously dried bentonite was mixed with 1000 mL of aqueous solutions containing CTMAB, CPB, DTMAB and DPB. The amount of each surfactant in aqueous solution was equal to CEC of bentonite. The mixtures were subjected to mechanical stirring in a 60 ℃ water bath for 2 h. Thereafter, the bentonites were separated from water by vacuum filtration and washed 5 times by distilled water. The organobentonites were dried at 80 ℃, activated for 2 h at 105 ℃ and mechanically ground with a mortar and pestle to smaller than 80 mesh. The bentonites modified with four surfactants are described as CTMAB, CPB, DTMAB and DPB.

CTMAB has a long carbon chain, was used for further study. The amount of CTMAB equivalent to 0.7 CEC or 1.4 CEC of bentonite was added to aqueous solution. The procedure used for the preparation of organobentonite was the same as before. The samples obtained in this way were named as 0.7 CTMAB, 1.0 CTMAB and 1.4 CTMAB.

The amount of surfactant adsorbed on the inner-surface of bentonite was measured by burning. Organobentonite (W_1) was dried at 120 ℃ for 4 h and then put into a desiccator for cooling. The sample was then weighed (W_2) and transported into a muffle oven, heated at 400 ℃ for 4 h. After cooling, the weight of sample was determined (W_3). Based on W_1, W_2 and W_3, the losses of water (W_1-W_2) and organic matter, namely surfactant adsorbed, (W_2-W_3) were calculated.

X-ray diffraction (XRD-D8, Japan, Cu target, 40 kV, 30 mA, scan range 2-50º, scan speed 3º (2θ)/min was used to identified the array forms of surfactant molecules on the inner-surface of bentonite. According to the size of mineral inter-space and the size of organo-cations, convergency state of surfactants in interlayer was deduced.

RESULTS AND DISCUSSION

The amount of surfactants adsorbed onto inner-surface of bentonite. For all organobentonite samples prepared with different surfactants, burning treatment caused a weight loss (Table-1), which implies that bentonite adsorbed the surfactant. For 1.0 CEC treatment the organobentonites modified with CTMAB or CPB, which possess longer carbon chain, had greater weight loss than that modified with DTMAB or DPB. After burning at 400 ℃, the weight loss of CTMAB and CPB treatments were 12.51 % and 12.58 %, respectively. However,

for DTMAB and DPB treatments they were only 8.84 % and 8.63 %. This result shows that (1) the surfactant with long carbon chain can be much easily adsorbed onto the inner-surface of bentonite than those with short carbon chain; (2) for the surfactants with same carbon chain length, but different heads, no significant discrepancy in weight loss ratio was observed, which indicates that the structure of polar heads has little effect on the process of surfactant adsorption onto the inner-surface of bentonite; (3) after 120 ℃ treatment, the weight loss of CTAMB treatments of 0.7 CEC, 1.0 CEC, 1.4 CEC were 3.43, 3.51 and 3.56 %, respectively, which indicates a similar water content for all three samples (Table-1). After high temperature treatment, however, the weight loss of organobentonite samples were 6.97, 12.51 and 17.82 %, which indicates a dose-dependent adsorption of surfactant molecules onto the inner-surface of bentonite.

TABLE-1
WEIGHT LOSS RATE (%) OF ORGANO-BENTONITE UNDER DIFFERENT TEMPERATURES

Temp. (ºC)	CTAMB			1.0 DTMAB	1.0 CPB	1.0 DPB
	0.7CEC	1.0CEC	1.4CEC			
120	3.43	3.51	3.56	3.61	1.60	1.71
400	6.97	12.51	17.82	8.84	12.58	8.63

Effects of different surfactants on the space between interlayers of bentonite: The space of 1.258 nm between interlayers of bentonite (d_{001}) makes sure that the mineral used belongs to typical Na-bentonite. After treatment with different surfactants the spaces between interlayers of 4 organo-benotonite samples increased as follows: original (1.258 nm) < DPB (1.730 nm) < DTMAB (1.774 nm) < CPB (1.994 nm) < CTMAB (2.050 nm) (Fig. 1). This result shows that the interlayer spaces of bentonite modified with surfactants of long alkyl chain increased much more than those with short alkyl chain.
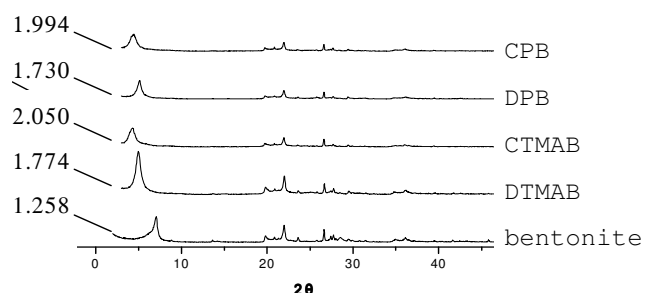

Fig. 1. XRD of organobentonite modified by different surfactants

Effects of surfactant concentrations on interspace of bentonite: With increasing concentration of CTMAB, the interspace (d_{001}) of organobentonite samples showed an increasing tendency as following: original (1.258 nm) → 0.7CEC (1.756 nm) → 1.0CEC (2.050 nm) → 1.4CEC (1.986 nm). It is noticeable that with increasing concentration of CTMAB the angle (2θ) of diffraction for organobentonite revealed a remarkable excursion to smaller angle. For example the angle of diffraction changed from 7.02º (original) to 5.028º (0.7CEC) and for 1.0 CEC and 1.4 CEC they were 4.30º and 4.46º, respectively.

TABLE-2
WEIGHT LOSS OF ORGANOBENTONITE MODIFIED BY DIFFERENT SURFACTANTS AT HIGH TEMPERATURE

Surfactant	m.w.	Weight loss (%) of organic matter	m.w. ratio (Weight loss ratio)			
			CTMAB	DTMAB	CPB	DPB
CTMAB	269	8.00	1 (1)			
DTMAB	213	5.23	1.26 (1.53)	1 (1)		
CPB	306	10.98	0.88 (0.73)	0.70 (0.48)	1 (1)	
DPB	249	6.92	1.08 (1.56)	0.86 (0.76)	1.23 (1.59)	1 (1)

Weight loss percentage of organic matter = weight loss percentage of organo bentonite at 400 ℃ - weight loss percentage of organo bentonite at 120 ℃ (based on Table-1)

TABLE-3
EFFECTS OF ORGANIC SURFACTANTS ON THE INTERLAYER SPACE OF BENTONITE

	Original bentonite	Organo bentonites					
		0.7 CTMAB	1.0 CTMAB	1.4 CTMAB	1.0 DTMAB	1.0 DPB	1.0 CPB
Space between two layers (nm) (d_{001})	1.258	1.756	2.050	1.986	1.774	1.730	1.994
Interspace (nm)	0.298	0.796	1.090	1.026	0.814	0.77	1.034

Crystal layer thickness of bentonite is 0.96 nm; interspace = space between two layers – 0.96

The precondition for modification of surface property of minerals by cation surfactants is the adsorption of the surfactants onto the inner-surface of bentonite. At 400 ℃, the organic surfactants adsorbed are decomposed and lost. So, based on the weight loss, relative amount of surfactant adsorbed on surface and in particular on the inner-surface of bentonite can be determined. The present results showed that all four surfactants used could be adsorbed onto the inner-surface of bentonite. In addition, the amount of surfactant adsorbed was related to the concentration of surfactant and to the molecular specificity of the surfactants such as the length of carbon chain and structure of polar head (Table-1). For surfactants with different molecular weight, assuming A and B, if the ratio of weight loss of organic part (A/B) is equal to that of their molecular weight, it is assumed that the number of surfactants adsorbed is same for these two surfactants. If ratio of weight loss is greater than that of molecular weight, it means that the adsorbed numbers of surfactant A is greater than that of surfactant B and if former ratio less than the latter, it implies a more adsorption for surfactant B than surfactant A. According to this principle it can be elicited from Table-2 that in comparison with CTMAB higher numbers of CPB molecules were adsorbed, although both of them have same length of carbon chain with 16 carbon atoms. For DTMAB and DPB, both have carbon chain of 12 carbon atoms, the latter could be more easily adsorbed onto the inner-surface of bentonite. By comparing the molecular structures of CTMAB, DTMAB, CPB and DPB it becomes clear that the former two surfactants possess a polar head (composed of 3 methyl groups and one N atom) and latter two surfactants contain a pyridyl head. This implies that polar head consisted of pyridyl favoured adsorption of surfactants onto inner-surface of bentonite. Based on the same analysis it can be concluded that for surfactants with same polar head structure, one with a longer carbon chain will be more easily adsorbed onto the inner-surface of bentonite. Furthermore, Fig. 2 shows that with increase of length and concentration of surfactant during production of organobentonite, the diffraction peak became wider and diffraction peak area became greater, implying that with increase of interspace of bentonite the numbers of surfactant molecules adsorbed onto the inner-surface of bentonite also increased.

Many researchers pointed out that the characteristic of organobentonite was related to the quality of bentonite, the type of surfactant and its concentration, reaction duration, reaction temperature and so on[6-9]. XRD has been often used as a suitable method to determine the interspace of organo bento-nite[10]. Based on d_{001} and thickness of cell layer of bentonite the interspace of bentonite or organobentonite can be easily determined by calculation (Table-3). According to the interspace of organobentonite and molecular size of surfactants, the molecule array forms of surfactants on the inner-surface of bentonite can be postulated. It was found that on the inner-surface of bentonite, the alkyl chain of CTMAB could be arrayed in lateral-monolayer (0.41 nm), lateral-bilayer (0.81 nm), standard trilayer (1.21 nm), or even in slope[11-13]. In addition, different array forms of surfactants may be related to charge density of interlayer[14,15].
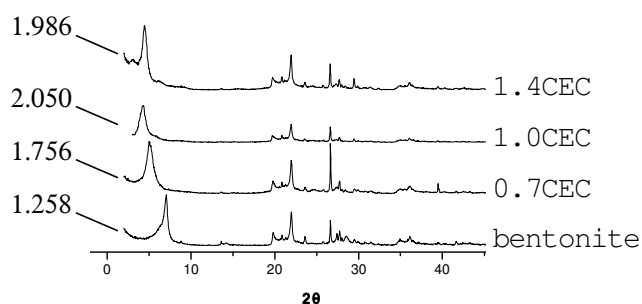

Fig. 2.   XRD of organobentonite modified by different concentrations of CTMAB

CTMAB and DTMAB are composed of NH_4^+, of which 4 H^+ are replaced by 3 methyls and a cetanedecyl- or a dodecyl-, respectively. Using van der Waals semidiameter, covalence semidiameter and bond angle, the construct, size and shape of organic compound can be estimated[16]. For CTMAB with a chain length of 2.5 nm and carbon chain height of 0.41 nm and head height of 0.46 nm, its height should be 0.46 nm, if it outspreads as a lateral-monolayer[8]. DTMAB has similar molecular structure as CTMAB and therefore possess similar height of carbon chain and head height. For carbon chain of DTMAB there are only 12 atoms, 4 atoms less than that of CTMAB. Its chain length is therefore 0.45 nm shorter than

that of CTMAB. At low concentration both of them lie on the inner-surface of bentonite as lateral-monolayer[17]. If organic cations lie on the inner-surface of bentonite as lateral-monolayer, the distance between two crystal layers of bentonite should be 1.42 nm in theory, namely the height of organic cation (0.46 nm) plus thickness of crystal layer of 2:1-type minerals (0.96 nm). The values of d_{001} for organobentonites modified with four different surfactants at 1.0 CEC concentration were more than 1.42 nm (Table-3), indicating that the array of surfactants on the inner-surface of bentonite is not always lateral-monolayer. When organic cations are arrayed in lateral-bilayer, the thickness of two layers of organic cation should be about 0.92 nm, namely the interspace between contiguous layers should also be about 0.92 nm. However, the protuberant head of an organic cation can be wedged in lacuna of contiguous organic cation layer (field of carbon chain) or in hexagon hole of oxygen of silicon-oxygon layer of bentonite, which leads to a tight lateral-bilayer array. So in fact, if the surfactant molecules array as the tight lateral-bilayer, the interspace height of organobentonite will be determined by height of lateral-bilayer carbon chain, not by the height of two organic cation heads[18] and therefore, a height of about 0.82 nm should be measured for lateral-bilayer. In present study, the interspace of bentonite modified by DTMAB and DPB was estimated to be 0.814 nm and 0.77 nm, which were close to that value which is related to the array of lateral-bilayer. Brindley and Beneke studied a so-called interlock inlay model formed by multilayer alkyl chain[15,19]. Through calculation they found that for every additional layer of alkyl chain, the total height of alkyl layers would decrease 0.1 nm. According to this calculation, the height of a pseudotrilayer should be about 1.1 nm. In the present study the interspace of 1.0 CTMAB and 1.0 CPB were 1.090 nm and 1.034 nm, which were close to the value of 1.1 nm, so that the array of the surfactants on the inner-surface of bentonite should be related to pseudotrilayer array form. Similar results were also reported by Choy *et al.*[20]. Based on discussion above it becomes clear that after treatment with same mol concentration of surfactants CTAMB and CPB, both of which possess 16 carbon atom chain, the molecule array form of the surfactants on the inner-surface of bentonite can be assumed as pseudotrilayer and surfactans with 12 carbon atom chain (DTMAB and DPB) as tight bilayer.

The concentration of surfactants during the production of organobentonite could also influence their array forms in interlayer[9]. Fig. 2 shows that the d_{001} of organobentonite changed with increasing concentration of CTMAB. For 0.7 CEC, 1.0 CEC and 1.4 CEC treatments the d_{001} values of organobentonite were 1.756, 2.050 and 1.986 nm. These values correspond to interspace of 0.796, 1.090 and 1.026 nm, respectively. From these data it can be deduced that the array of surfactant molecules on the inner-surface of bentonite may mainly be in tight bilayer for 0.7 CEC treatment, while for 1.0 CEC treatment the array of surfactant molecule may mainly be in pseudotrilayer. For 1.4 CEC treatment, it is more complex. There are two peaks of 3.05 and 6.08 (Fig. 2), corresponding to interspace of 2.892 nm and 1.452 nm, respectively. These data imply that besides pseudotrilayer there may be two array forms with 1.932 nm and 0.492 nm interspace, respectively. The interspace value of 0.492 nm is close to the thickness of CTMAB (0.46 nm) and the array of CTMAB in this field of interlayer should be in monolayer. The interspace of 1.932 nm is typical for slop monolayer array form of organic cations

in silicate interlayer, which is known as Paraffin-type monolayer. According to calculation based on the length of alkyl chain (2.5 nm) and layer thickness of silicate crystal (0.96 nm), the angle between interface and alkyl chain of surfactant molecule is 50.63º. It appears that with increasing concentration of surfactant the array forms of organic cation on the inner-surface of bentonite shows a trend as follows: monolayer → bilayer → pseudotrilayer → paraffin-type monolayer. In addition, at high concentrations of surfactant, many different array forms often coexist simultaneously.

Conclusion

Surfactants can be adsorbed onto the inner-surface of bentonite and lead to an increase of interspace. For surfactants with same length of carbon chain, one with polar head consisted of pyridyl is much easily adsorbed onto the inner-surface of bentonite. For surfactants with same polar head structure, one with longer carbon chain is more easily adsorbed onto the inner-surface of bentonite. Surfactants with 16 carbon atom chain (CTMAB, CPB) array on the inner-surface of organobentonite mainly as pseudotrilayer and those with 12 carbon atom chain (DTMAB and DPB) arrayed mainly in tight bilayer. With increasing concentration of surfactant during the production of organobentonite, the array forms of organic cation on the inner-surface of bentonite present a trend as follows: monolayer → bilayer → pseudotrilayer → paraffin-type monolayer → many array forms coexist simultaneously.

REFERENCES

1. R. Zhu, T. Wang, F. Ge, W. Chen and Z. You, *J. Colloid. Interf. Sci.*, **335**, 77 (2009).
2. Y. Shen, *Chemosphere*, **44**, 989 (2001).
3. G.E. Christidis, *Appl. Clay Sci.,* **13**, 79 (1998).
4. G.J. Churchman, M. Askary, P. Peter, M. Wright, M.D. Raven and P.G. Self, *Appl. Clay Sci.*, **20**, 199 (2002).
5. J. Wagner, H. Chen and B.J. Brownawel, *Environ. Sci. Technol.*, **28**, 231 (1994).
6. R. Zhu, T. Wang, J. Zhu, F. Ge, P. Yuan and H. He, *Chem. Eng. J.*, **160**, 220 (2010).
7. D. Plachá, G.S. Martynková and M.H. Rümmeli, *J. Colloid. Interf. Sci.*, **327**, 341 (2008).
8. H. He, R.L. Frost, T. Bostrom, P. Yuan, L. Duong, D. Yang, Y. Xi and J.T. Kloprogge, *Appl. Clay Sci.*, **31**, 262 (2006).
9. X. Wen, H. He, J. Zhu, Y. Jun, C. Ye and F. Deng, *J. Colloid. Interf. Sci.*, **299**, 754 (2006).
10. R.A. Vaia, R.K. Teukolsky and E.P. Giannelis, *Chem. Mater.*, **6**, 1017 (1994).
11. S. Xu and S.A. Boyd, *Langmuir*, **11**, 2508 (1995).
12. S. Xu and S.A. Boyd, *Environ. Sci. Technol.*, **29**, 3022 (1995).
13. W.F. Jaynes and S.A. Boyd, *Soil Sci. Soc. Am. J.*, **55**, 43 (1991).
14. A.V. Richard, K.T. Rachel and P.G. Emmanuel, *J. Chem. Mater.*, **6**, 1017 (1994).
15. K. Beneke and G. Lagaly, *J. Clay Miner.*, **17**, 175 (1982).
16. X.R. Zhang, X.Q. Pei and Q.H. Wang, *J. Appl. Polym. Sci.*, **111**, 2980 (2009).
17. H. He, Y. Ma, J. Zhu, P. Yuan and Y. Qing, *Appl. Clay Sci.*, **48**, 67 (2010).
18. A.V. Faridi and S. Guggenheim, *Clays Clay Miner*, **45**, 859 (1997).
19. G.W. Brindley and W.F. Moll, *Am. Miner*, **50**, 1355 (1965).
20. J.H. Choy, S.Y. Kwak and Y.S. Han, *Mater. Lett.*, **33**, 143 (1997).