

The Kinetics of Montmorillonite Expansion in the Treatment with Hexadecyltrimethylammonium

HDTMA와 반응하는 몬모릴로나이트의 팽창 속도론

Seung Yeop Lee (이 승 엽)* · Won Jin Cho (조 원 진)

Korea Atomic Energy Research Institute, Daejeon 305-606, Korea
(한국원자력연구소 방사성폐기물처분연구부)

ABSTRACT : Surfactant adsorption by two montmorillonite types with different interlayer cations of Ca and Na was characterized by examining the time dependence of surfactant behavior on the clay surfaces. Surfactants with different micelle concentration were conducted in our experiment to observe a nonequilibrium activity of cationic surfactant on the clay over reaction periods ranging from 0.1 min to 11 days. As compared with Ca-montmorillonite (SAz), a more active intrusion of surfactant molecules into the interlayers was found in Na-montmorillonite (SWy). During a short "initiation" stage, the basal spacing of SWy montmorillonite increased rapidly with logarithmic time. For SAz montmorillonite, however, the abrupt basal spacing increase occurred at the later stage of the reaction. From the result, the difference in the adsorption behavior exhibited by the two montmorillonite types partly results from their intrinsic nature, that is, inorganic cations originally existing on the clay surfaces. Additionally, the micelle concentration of surfactants affects the development of organo-montmorillonite, especially, in the intercalant formation and stabilization under nonequilibrium.

Key words : interlayers, micelle, montmorillonite, nonequilibrium, surfactant adsorption

요약 : 층간 양이온종이 다른 두 종류의 몬모릴로나이트에 대한 계면활성제의 흡착을 통해 몬모릴로나이트 표면에서 흡착거동하는 계면활성제의 시간적인 변화를 관찰하였다. 계면활성제의 미셀 농도를 다르게 하여 시간이 경과(0.1분~11일)함에 따라 몬모릴로나이트에 대한 계면활성제의 비평형 활동성을 관찰하였다. Na-몬모릴로나이트(SWy)는 Ca-몬모릴로나이트(SAz)와 비교했을 때 계면활성제가 몬모릴로나이트 층간에 보다 활동적으로 침투 및 흡착하였다. SWy의 층간간격은 반응초기부터 시간이 경과함에 따라 급격히 팽창하였지만, SAz의 경우에는 반응 후반기에만 층간간격이 현저히 팽창되었다. 이상의 결과로부터 두 몬모릴로나이트의 서로 다른 팽창특성은 부분적으로 자신들의 본질, 즉 몬모릴로나이트 내에 존재하는 무기양 이온들의 영향 때문인 것으로 보인다. 또한, 계면활성제의 미셀 농도는 유기-몬모릴로나이트의 발달, 즉 비평형 상태에서의 유기점토복합체 형성과 안정에 큰 영향을 끼치는 것으로 보인다.

주요어 : 층간, 미셀, 몬모릴로나이트, 비평형, 계면활성제 흡착

*Corresponding Author (교신저자): lsyblue@paran.com

Introduction

Natural clay minerals with exchangeable cations can be transformed into hydrophobic organoclays by replacing the metal ions with quaternary ammonium or some other onium ions (surfactants). Such modified materials exhibit high capability to remove hydrophobic contaminants from aqueous solutions and, thus, have been recognized as very promising agents in environmental control and in the reduction of leaching, photodegradation, and volatilization of herbicides (Brixie and Boyd, 1994; El-Nahhal *et al.*, 1999; Nir *et al.*, 2000; Kwolek *et al.*, 2003). Surface active agents, surfactants, are molecules with long hydrophobic chains and hydrophilic head groups that alter solution surface tension. Surfactants are molecularly dispersed at low concentrations in aqueous solutions and form self-aggregates as their concentration increases. This class of molecules forms well-ordered associated micelles at a specific concentration called the critical micelle concentration (CMC) (Otto *et al.*, 2003).

The adsorption of surfactants at the solid/liquid interface is important in a fundamental research. The study of cationic surfactants adsorbed onto charged solid surfaces gives insight into surface-surfactant interactions, which are usually presumed to be electrostatic in origin, and surfactant-surfactant interactions, which are thought to be a competition between electrostatic repulsion of head groups and hydrophobic attraction between alkyl chains (Theng, 1974; McDermott *et al.*, 1994). There have been numerous structural, thermodynamic, and isotherm studies of adsorption equilibria of cationic surfactants onto clay minerals (Yamaguchi and Hoffmann, 1997; Gevers and Grandjean, 2001; Koh and Kim, 2002; Lee and Kim, 2003). However, nonequilibrium interactions between surfactants and clay minerals are not still well understood. Surprisingly few investigations have been reported on organic-inorganic ion exchanged forms under nonequilibrium. The objective of the present study, therefore, is to evaluate the adsorption behavior of surfactants onto clay minerals, including the effect of surfactant forms

contacted on the clay surfaces under nonequilibrium condition. We employ an approach in which surfactant behavior and distribution on clay particles are examined as a function of time. We then relate observed time-dependent changes in the clay minerals to the sorption of surfactants to delineate the importance of the intrinsic nature of clay minerals (*e.g.* exchangeable ion types) and the aqueous surfactant forms.

Materials and Methods

Clay Samples

Wyoming Na-montmorillonite (SWy) and Arizona Ca-montmorillonite (SAz) were purchased from the Source Clay Repository (The Clay Minerals Society, Columbia, MO). Details for their mineralogical properties are listed in Table 1. The clay samples were used without further purification.

HDTMA-Clay Preparation

Hexadecyltrimethylammonium (HDTMA) bromide was obtained from Sigma-Aldrich. The HDTMA molecule consists of a 16-carbon chain tail group attached to a 3-methyl quaternary amine head group with a 1+ charge. HDTMA adsorption onto montmorillonites occurred by adding HDTMA bromide stock solution to the clay dispersion in centrifuge tubes (50 mL), bringing the solution concentration equivalent to the cation exchange capacity (CEC) of the clays used. These HDTMA stock solutions were initially added to the tubes as 4 and 40 mmol L⁻¹, respectively, with different volumes, large volume (40 mL) for 4 mmol L⁻¹ and small volume (4 mL) for 40 mmol L⁻¹, and the total aqueous solution became finally 45 mL including distilled water added. According to West and Harwell (1992), micelle formation occurs above a critical concentration of surfactant monomers, referred to as the CMC. The CMC of the pure HDTMA surfactant in H₂O is found to be ~1.0 mmol L⁻¹ (McDermott *et al.*, 1994). HDTMA surfactants in dilute aqueous solutions and in dispersions appear as an individual monomer form

Table 1. Mineralogical properties of the used montmorillonites

Sample designation	Specimen	Cation exchange capacity (meq/100 g)*	Layer charge**	Na ₂ O/CaO ratio***
SWy	SWy-2 montmorillonite	85	0.87	1.25
SAz	SAz-1 montmorillonite	123	0.97	0.02

* From Borden and Giese (2001)

** From Mermut and Lagaly (2001)

*** From Mermut and Cano (2001)

(Vinson *et al.*, 1991). However, HDTMA surfactant solutions near the CMC show a few structures that may be micelles or submicellar and monomer structures. Higher HDTMA concentration beyond the CMC shows globular micelles with larger diameter (Vinson *et al.*, 1991). Accordingly, the injected HDTMA as 4 mmol L⁻¹ had lower micellar size and concentration than those of the high concentrated HDTMA (40 mmol L⁻¹). After the HDTMA loading, the tube was gently agitated on a shaker (50 rpm) at room temperature for 11 days for equilibration; preliminary studies showed this time to be adequate for equilibration. The suspensions were centrifuged at 10,000 rpm for 15 min at 25°C and washed gently with deionized water.

Analyses of HDTMA and Inorganic Concentrations

Amount of adsorbed HDTMA on the clay under nonequilibrium condition was determined using an elemental analyzer EA 1110 (CE Instrument, Italy). The concentration of inorganic cations (Na⁺ and Ca²⁺) released from the montmorillonites via the exchange with HDTMA was measured using an inductively coupled plasma atomic emission spectrophotometer ICPQ 1000 (Shimadzu, Tokyo, Japan).

X-ray Diffraction

Samples (10 mg) of the organoclay taken from nonequilibrium experimental states were dried at 25°C as oriented aggregates on glass slides. The d_{001} values were recorded using CuK α radiation from an automated X-ray diffractometer (XRD)

(Rigaku Geigerflex RAD3-C, Japan) with a graphite monochromator. The operating condition of XRD was at 40 kV/30 mA in a step scan mode. The scanning speed was 0.02° 2 θ s⁻¹ and the slit set was 1°, -0.15 mm, -0.5°.

Results

A characteristic change of montmorillonite surface was investigated when HDTMA cations with initial different surfactant forms were loaded on the clay dispersion for a period of nonequilibrium time. During the reaction between the clay and HDTMA surfactants, $d(001)$ diffraction peak of SWy montmorillonite shifted toward the lower 2 θ region, showing the expansion of the interlayer space (Fig. 1). The basal spacing (d_{001}) increased gradually up to 1.84 nm (Fig. 1(a)) depending on the time reacted with HDTMA surfactants. However, there were some unexpected layer expansions to 2.09 nm for the clay reacted with high micellar (HM) HDTMA (40 mmol L⁻¹). Such a large layer expansion occurred within several hours did not happen in the case of low micellar (LM) HDTMA condition (4 mmol L⁻¹). In addition, the diffraction patterns with higher layer expansion showed much broader peak widths relative to the other diffraction patterns (Fig. 1(b)). In LM-HDTMA condition, there was just a gradual increase of basal spacings without highly expanded interlayers during cation exchange reaction (Fig. 1(a)). On the other hand, there was not a rapid increase of basal spacings in SAz montmorillonite as compared with SWy montmorillonite, except later great layer expansion to 2.47 nm just after 48 h reaction (Fig. 2). In that case, the surfactant arrangement in the interlayer was changed from

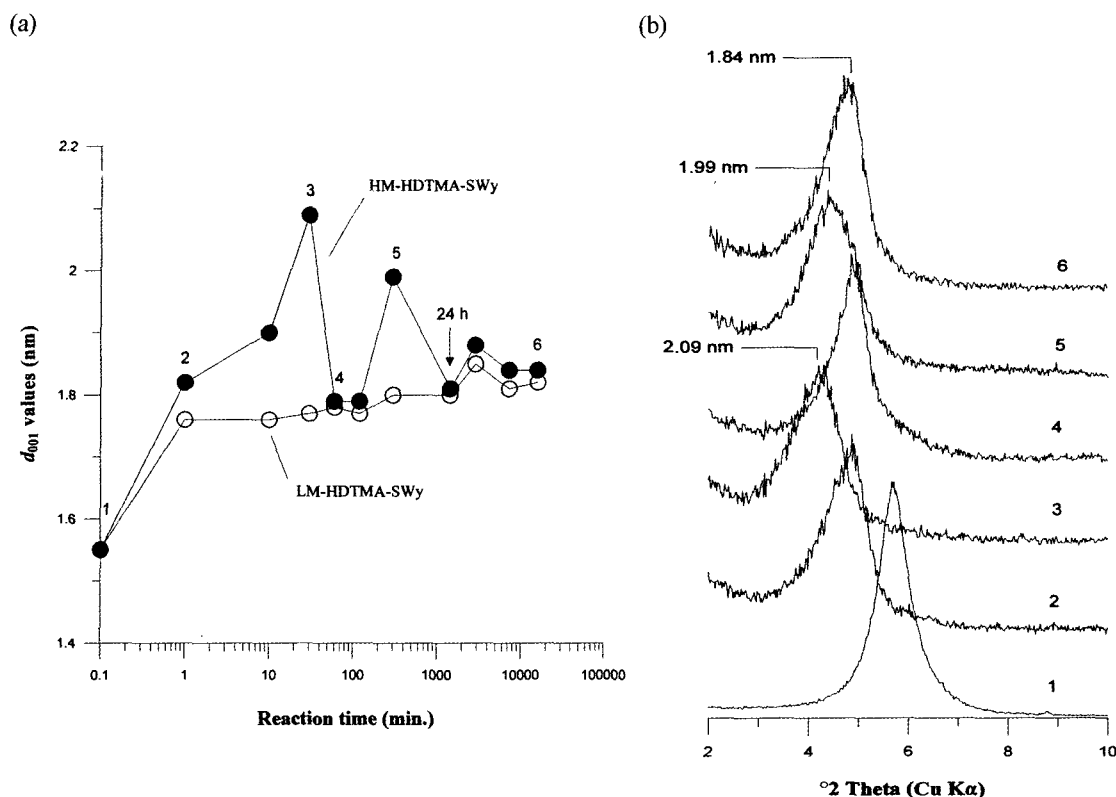


Fig. 1. (a) Basal spacing variation and (b) XRD patterns of SWy montmorillonite depending on the reaction time after the HDTMA was loaded. The numbers on the XRD curves (b) indicate the ones on the d -values variation (a).

lying parallel to the silicate layer forming a single-layered or double-layered structure to standing up with an angle to the silicate layers forming paraffin-type structure (Lagaly, 1994). This indicates that the chain orientation of the surfactants within the silicate layers seems to depend on the time that the clay is interacting with surfactants.

During the cation exchange reaction with HDTMA, the metal ions (Na^+ and Ca^{2+}) existing on internal and external clay surfaces were replaced little by little by HDTMA cations. Both SWy and SAz montmorillonites showed that the metal ions on the clay minerals were easily released into aqueous solution at the beginning of HDTMA loading (Fig. 3). In SWy montmorillonite, HM-HDTMA significantly affected the metal ions to be much more released from clay surfaces from the beginning as compared with LM-HDTMA

(Fig. 3(a)). Relatively slow rate ion exchange with HDTMA occurred on the LM-HDTMA-SWy. On the contrary, the LM surfactant interacted with SAz preferably expedited the release of metal ions relative to the HM surfactant (Fig. 3(b)). After 24 hrs reaction, however, the release pattern of ions by LM surfactant became similar to that by HM surfactant, showing a finally higher release of ions into aqueous solution.

Discussion

The most widely used technique for the study of intercalated surfactants in the silicate galleries is X-ray diffraction (XRD), which provides information on the layering structure of surfactant (Li and Ishida, 2003). The orientation of the intercalated alkylammonium molecules was indirectly

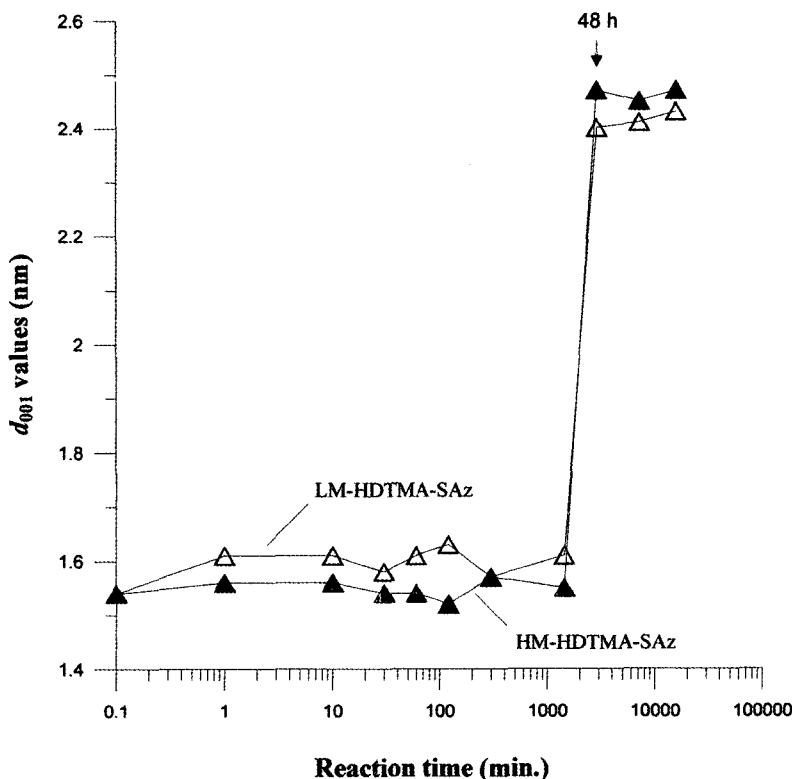


Fig. 2. Basal spacing variation of SAz montmorillonite depending on the reaction time after the HDTMA was loaded.

obtained on the basis of the basal d value. In our experiment, the structure of intercalated surfactants in the interlayer was also presumed by d values measured using the XRD. As HDTMA loading began, the interlayer expansion of montmorillonite was significantly influenced by the surfactant forms in aqueous solution as shown in Fig. 1 and 2. It means that an evolution of clay swelling under nonequilibrium condition is affected by the state of surfactant loaded. Especially, the change of interlayer thickness by HM-HDTMA on the SWy montmorillonite became greater during cation exchange reaction, showing some highly expanded layers (Fig. 1(a)) and significantly adsorbed HDTMA from the beginning (Table 2). As the ion exchange progressed, such a segregative adsorption of the HDTMA cations on the internal region was developed as the pathway for preferential adsorption of the cationic surfactants on the Na-montmorillonite. Addition-

ally, the XRD patterns exhibiting broader peak widths for the HM-HDTMA-SWy samples indirectly indicate an early stage of the disordered (Imai *et al.*, 2003) and not fully arranged HDTMA molecules in the interlayer. This could signify that there was a preliminary stage of randomly adsorbed HDTMA molecules on the interlayer surface, suggesting an unstably adsorbed micellar phase which contributed to enlarge the interlayers to some degree. The formation of highly expanded layers during the reaction seems to be driven by diffusion of micellar phase into the interlayer region. It indicates that HDTMA surfactants preferentially adsorbed in the interlayer region rather than external surfaces of the Na-SWy montmorillonite under nonequilibrium condition. Meanwhile, it may be difficult for the unstably intercalated phase to stay for a long time in the interlayer region due to an excessive charge caused by the bulky adsorption of cationic surfactants.

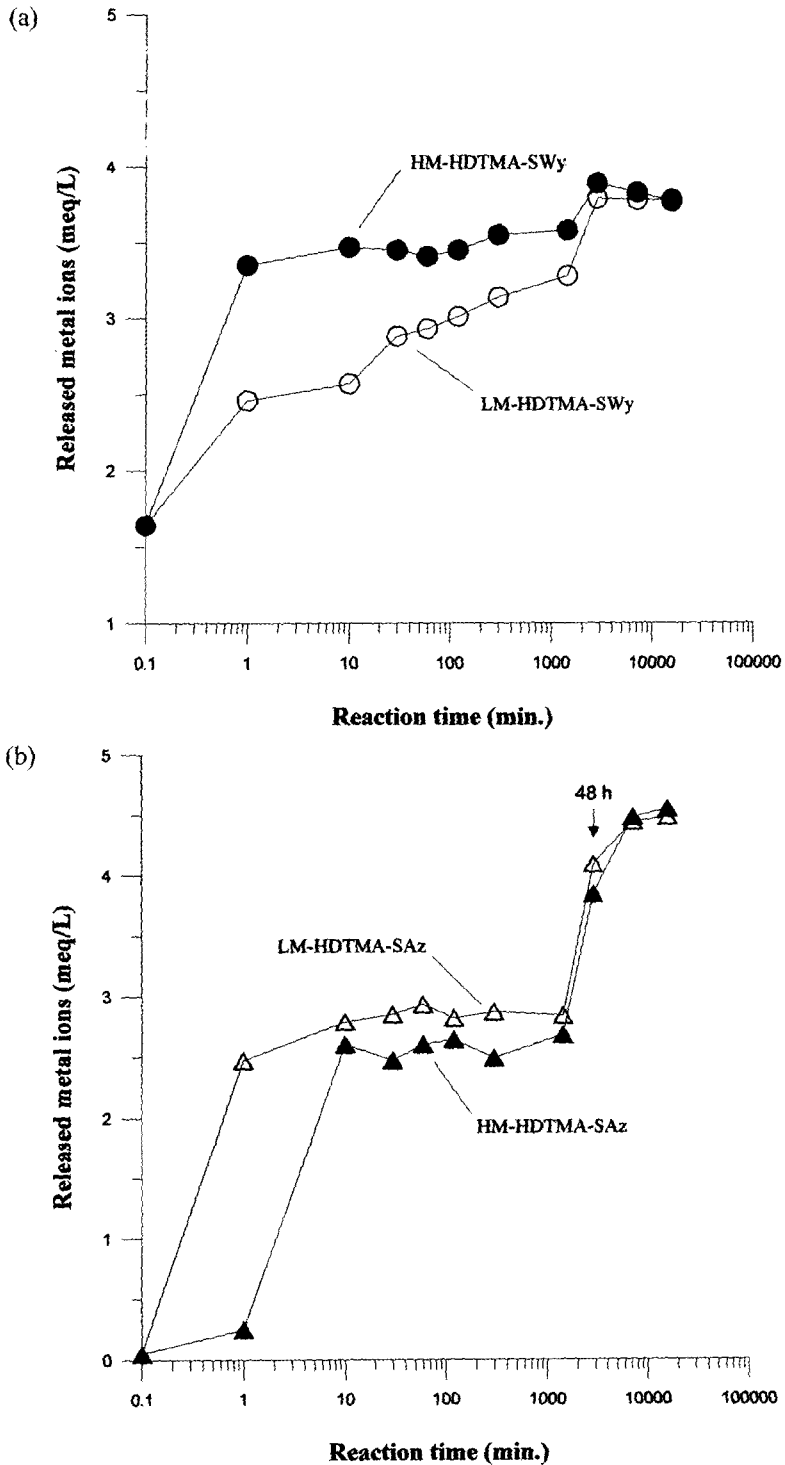


Fig. 3. The release trends of exchangeable metal ions from (a) SWy and (b) SAz montmorillonites vs. the reaction time after the HDTMA was loaded.

Table 2. Total organic carbons of the HDTMA-adsorbed montmorillonites

Reaction time (min.)	SWy		SAz	
	HM-HDTMA (g/100 g)	LM-HDTMA (g/100 g)	HM-HDTMA (g/100 g)	LM-HDTMA (g/100 g)
0.1	0.05	0.05	0.01	0.01
1	14.56	9.23	0.47	15.49
10	15.23	10.85	22.94	17.63
30	14.92	10.68	-	-
60	16.65	10.92	17.18	20.89
120	13.13	10.46	-	20.53
300	16.41	12.49	24.35	20.09
1440	15.30	12.74	24.23	20.99
2880	16.46	15.56	21.51	22.56
7200	16.65	16.19	22.14	22.13
15840	16.79	16.39	22.37	22.26

From the reason, the bulky cationic surfactants intruded in the interlayer may be going to balance the charge with the surface anions, partly migrating from there to aqueous solution. If such an alternate movement of cationic surfactant around the internal or edge sites occurred, there would be a considerable fluctuation of interlayer spacing as shown in Fig. 1a, and gradually perturbed from the bulky to an individual surfactant phase, eventually distributed self-assembly on the surfaces (Chen *et al.*, 1992; Schulz and Warr, 2000; Lee and Kim, 2002).

In SAz montmorillonite, although there was a considerable adsorption of HDTMA onto the clay from the beginning (Table 2), the increase of d value was insignificant (Fig. 2). The interlayer of SAz montmorillonite was slightly expanded by cationic surfactants and the limited expansion continued for some time (24 h). The slight increase of d value may imply the difficulty of approach to the internal exchangeable sites by the surfactant molecules, suggesting that most SAz montmorillonite external charge sites are preferably compensated by HDTMA cations. Only few surfactant molecules with monomer HDTMA could access the interlayer galleries during the reaction. At the low micelle (LM) concentration, the probability of alkyl chain overlapping is low (Li and Ishida, 2002), resulting in the high dispersion in aqueous solution of the surfactant molecules. It means that the presence of free monomer (LM)

surfactants could effectively make an influence on the interlayer expansion as well as on the cation exchange in SAz (Fig. 3(b)). On the other hand, as can be seen from Fig. 2, most micelles (HM) of HDTMA did not make the increase of d value and were probably adsorbed on the edges and external surfaces of SAz. This indicates that the adsorbed surfactant consisted of molecules lying in interleaved aggregate structures on the external surface for quite a time after surfactant loading. Only monomer forms of surfactants can be slightly diffused into the internal surfaces of the SAz clay and caused a slight interlayer expansion.

According to Xu and Boyd (1995), in aqueous solution, Na-montmorillonite was fully dispersed, providing full access of HDTMA to interlayer exchange sites, while Ca-montmorillonite suspension was flocculated prior to HDTMA addition. The face-to-face aggregation of clay particles limited the access of HDTMA to the interlayer sites. As a result, the replacement of Ca^{2+} ions by HDTMA may occur primarily along the edges and external surfaces of the flocks. This caused the limited interlayer intercalation of HDTMA manifesting a completely different d -spacing variation unlike the Na-SWy montmorillonite.

Consequently, surfactant forms, metal ions, and treatment time are very important factors in the development of an intercalated structure. HDTMA molecules access different regions or domains of montmorillonite depending on the clay type. It is

further reasonable to expect that HDTMA molecules access different surface sites at different times and rates as HDTMA loading begins. The dynamics of sorption processes of this nature were particularly observed in our nonequilibrium condition used here for the two montmorillonite types.

References

- Borden, D. and Giese, R.F. (2001) Baseline studies of the clay minerals society source clays: cation exchange capacity measurements by the ammonia-electrode method. *Clays Clay Miner.*, 49, 444-445.
- Brixie, J.M. and Boyd, S.A. (1994) Treatment of contaminated soils with organoclays to reduce leachable pentachlorophenol. *J. Environ. Quality*, 23, 1283-1290.
- Chen, Y.L., Chen, S., Frank, C., and Israelachvili, J. (1992) Molecular mechanisms and kinetics during the self-assembly of surfactant layers. *J. Colloid Interface Sci.*, 153, 244-265.
- El-Nahhal, Y., Nir, S., Polebusova, T., Margulies, L., and Rubin, B. (1999) Reduction of photodegradation and volatilization of herbicides in organoclay formulations. *Appl. Clay Sci.*, 14, 105-119.
- Gevers, C. and Grandjean, J. (2001) A multinuclear magnetic resonance study of synthetic clays suspended in water and in dodecyltrimethylamine oxide solutions. *J. Colloid Interface Sci.*, 236, 290-294.
- Imai, Y., Nishimura, S., Inukai, Y., and Tateyama, H. (2003) Differences in quasicrystals of smectite-cationic surfactant complexes due to head group structure. *Clays Clay Miner.*, 51, 162-167.
- Koh, S.M. and Kim, J.Y. (2002) Comparison of some physicochemical properties and adsorption of organic cations between Ca- and Na-bentonites. *J. Miner. Soc. Korea*, 15, 243-257.
- Kwolek, T., Hodorowicz, M., Stadnicka, K., and Czapkiewicz, J. (2003) Adsorption isotherms of homologous alkyltrimethylbenzylammonium bromides on sodium montmorillonite. *J. Colloid Interface Sci.*, 264, 14-19.
- Lagaly, G. (1994) Layer charge determination by alkylammonium ions. In: Mermut, A.R. (ed). *Layer Charge Characteristics of 2:1 Silicate Clay Minerals*, The Clay Minerals Society, Boulder, Colorado, 2-46.
- Lee, S.Y. and Kim, S.J. (2002) Expansion of smectite by hexadecyltrimethylammonium. *Clays Clay Miner.*, 50, 435-445.
- Lee, S.Y. and Kim, S.J. (2003) Dehydration behaviour of hexadecyltrimethylammonium-exchanged smectite. *Clay Miner.*, 38, 225-232.
- Li, Y. and Ishida, H. (2002) A differential scanning calorimetry study of the assembly of hexadecylamine molecules in the nanoscale confined space of silicate galleries. *Chem. Mater.*, 14, 1398-1404.
- Li, Y. and Ishida, H. (2003) Concentration-dependent conformation of alkyl tail in the nanoconfined space: hexadecylamine in the silicate galleries. *Langmuir*, 19, 2479-2484.
- McDermott, D.C., McCarney, J., Thomas, R.K., and Rennie, A.R. (1994) Study of an adsorbed layer of hexadecyltrimethylammonium bromide using the technique of neutron reflection. *J. Colloid Interface Sci.*, 162, 304-310.
- Mermut, A.R. and Lagaly, G. (2001) Baseline studies of the clay minerals society source clays: layer-charge determination and characteristics of those minerals containing 2:1 layers. *Clays Clay Miner.*, 49, 393-397.
- Mermut, A.R. and Cano, A.F. (2001) Baseline studies of the clay minerals society source clays: chemical analyses of major elements. *Clays Clay Miner.*, 49, 381-386.
- Nir, S., Undabeytia, T., Yaron-Marcovich, D., El-Nahhal, Y., Polebusova, T., Serban, C., Rytwo, G., Lagaly, G., and Rubin, C. (2000) Optimization of adsorption of hydrophobic herbicides on montmorillonite preadsorbed by monovalent organic cations: interaction between phenyl rings. *Environ. Sci. Technol.*, 34, 1269-1274.
- Otto, W.H., Britten, D.J., and Larive, C.K. (2003) NMR diffusion analysis of surfactant-humic substance interactions. *J. Colloid Interface Sci.*, 261, 508-513.
- Schulz, J.C. and Warr, G.G. (2000) Adsorbed layer structure of cationic surfactants on clays (mica is not a typical substrate for adsorption studies). *Langmuir*, 16, 2995-2996.
- Theng, B.K.G. (1974) *The Chemistry of Clay-Organic Reactions*. Adam Hilger, London, 343 pp.
- Vinson, P.K., Bellare, J.R., Davis, H.T., Miller, W.G., and Scriven, L.E. (1991) Direct imaging of surfactant micelles, vesicles, discs, and ripple phase structures by cryo-transmission electron microscopy. *J. Colloid Interface Sci.*, 142, 74-91.
- West, C.C. and Harwell, J.H. (1992) Surfactants and

- subsurface remediation. Environ. Sci. Technol., 26, 2324-2330.
- Xu, S. and Boyd, S.A. (1995) Cationic surfactant adsorption by swelling and nonswelling layer silicates. Langmuir, 11, 2508-2514.
- Yamaguchi, Y. and Hoffmann, H. (1997) Interaction between saponite and cationic, zwitterionic and nonionic surfactants. Colloid. Surface. A, 121, 67-80.
-
- 2004년 11월 26일 원고접수, 2004년 12월 15일 게재승인.