

Dehydration Characteristics of Cationic Surfactant-Modified Montmorillonite

양이온성 계면활성제로 표면개질된 몬모릴로나이트의 탈수 특성

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ABSTRACT : The dehydration of hexadecyltrimethylammonium (HDTMA)-exchanged montmorillonite has been studied using X-ray diffractometry (XRD) and differential scanning calorimetry (DSC). The dehydration in HDTMA-montmorillonite seems to influence the swelling behavior of the organo-clay during heating. The basal $d(001)$ spacing vs temperature curve of the HDTMA-montmorillonite has one broad swelling edge with a shoulder on the low-temperature side. We believe that the shoulder at 100°C for the HDTMA-montmorillonite is due to interlayer swelling induced by the initial rearrangement of surfactants, and the second edge at 200°C is caused by interlayer swelling resulting from the secondary vertical reorientation of alkyl chains. It seems that the dehydration of organo-clay induces a reorientation of the alkyl chains by transition to more vertical position relative to the silicate sheets, allowing instantly greater d -spacing.

Key words : dehydration, hexadecyltrimethylammonium, X-ray diffractometry, differential scanning calorimetry, swelling, organo-clay

요약: HDTMA로 표면개질된 몬모릴로나이트의 탈수현상을 X-선 회절분석기와 시차주사열량측정기(DSC)로 조사하였다. 열에 의한 HDTMA-몬모릴로나이트의 탈수작용은 유기점토의 팽창거동에 영향을 주었다. HDTMA-몬모릴로나이트의 기저 $d(001)$ 두께/온도변화 곡선은 크기가 다른 2개의 팽창피크를 보여주었다. 이것은 일차적으로 계면활성제의 정렬에 의한 점토광물의 층간팽창이 100°C 부근에서 발생하고 알킬고리의 이차적인 수직배열에 의한 층간팽창이 200°C 부근에서 일어났음을 가리킨다. 따라서, 이러한 결과는 유기점토의 탈수작용에 의해 점토 규산염층에 상대적으로 수직적인 알킬고리의 배열이 활성화되며, 소규모의 층간팽창을 야기한다는 것을 지시한다.

주요어: 탈수, HDTMA, X-선 회절분석기, 시차주사열량측정기, 팽창, 유기점토

Introduction

The adsorption of organic molecules on clay surfaces has been extensively studied (e.g., Mortland, 1970; Theng, 1974; Yariv *et al.*, 1989;

Lagaly, 1994; Lee and Kim, 2002). Most studies of ionic surfactant sorption on charged surfaces focus on the sorbed surfactant structure using sorption isotherm shapes and electrophoretic mobility data (e.g., Kibbey and Hayes,

1993). Some organic cations that are more strongly adsorbed by clay surfaces than inorganic cations have been well documented (De *et al.*, 1974; Narine and Guy, 1981). Adsorption can also proceed beyond the cation-exchange capacity (CEC) of the clay. However, very few experimental studies have been conducted to evaluate the characteristics of these oversaturated (i.e., beyond the CEC) organo-clays.

Here we investigated the uniaxial swelling and dehydration of hexadecyltrimethylammonium-montmorillonite. The structures of organo-clay and its intercalation product have been examined using X-ray diffractometry (XRD) and differential scanning calorimetry (DSC).

Materials and Methods

Montmorillonite

The natural montmorillonite sample was provided by Süd-Chemie Korea. The $<2 \mu\text{m}$ fraction was obtained by dispersing 80 g of the montmorillonite in one liter of deionised water, allowing it to stand for several hours, and separating quartz sand and heavy minerals by sedimentation. The clay (4 g) was then saturated with Na ions by washing with 0.1 M NaCl solution (200 mL), shaking, centrifuging, and decanting the supernatant solutions. This process was repeated three times. The Na-saturated montmorillonite was then washed 3~4 times with deionised water to remove excess salt until the AgNO_3 test for chloride was negative. The Na-saturated montmorillonite was freeze-dried (36 hours). The cation exchange capacity (CEC) of the Na-montmorillonite, determined by the BaCl_2 method (Hendershot and Duquette, 1986), was 104.3 cmol/kg. Its specific surface area, determined by adsorption of ethylene glycol monoethyl ether (EGME) (Carter *et al.*, 1986), was 754.8 m^2/g .

HDTMA Isotherm

The adsorption of hexadecyltrimethylammonium

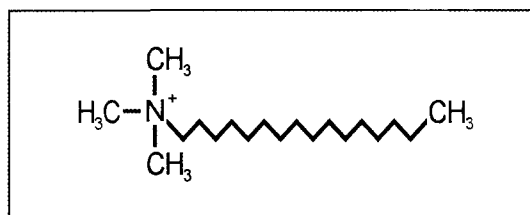


Fig. 1. The structure of HDTMA surfactant.

(HDTMA) cations (Fig. 1) on montmorillonite was measured using HDTMA bromide obtained from Sigma-Aldrich. The batch equilibration isotherm was determined on 20 mg clay samples weighed into 25 mL centrifuge tubes. 10 mL of water solutions containing quantities of HDTMA equivalent to 0.01 to 3.0 times the CEC were added to these tubes. These suspensions were then shaken for 2 days on a shaker at 200 rpm at 25°C. The mixture was centrifuged to yield a clear supernatant solution (8000 rpm for 20 min) and the HDTMA concentrations were measured using a TOC analyzer (TOC-8L, Yanaco).

HDTMA-montmorillonite Preparation

The organo-clay was obtained from montmorillonite by exchanging the Na^+ ions, initially present in that clay, with HDTMA ions. To this end, the HDTMA-bromide was dissolved in warm, deionised water. Na-saturated montmorillonite (0.1 g) was put into 25 mL centrifuge tubes containing different volumes of aqueous organic cation solutions (4.0 cmol L^{-1}) with 2.5 times the CEC of the clay, and distilled water was added to bring the total volume to 20 mL. The tubes were shaken on a reciprocating shaker at room temperature for 2 days. The suspension was centrifuged at 8,000 rpm for 20 min at 25°C and the supernatant was decanted, and then the organo-clay was examined by XRD and DSC.

X-ray Diffraction Analysis

Samples (10 mg) of the organo-clay were oriented on glass slides and dried over dry P_2O_5

in a desiccator for 3 days. The $d(001)$ -values were recorded using CuK α radiation and an automated X-ray diffractometer (Rigaku Geigerflex RAD3-C) with a graphite monochromator. The operating condition of XRD was at 40 kV/30 mA in a step scan mode. The scanning speed was $0.02\ 2\theta\ s^{-1}$ and slit set was 1° - 0.15° - 0.5° .

The variation in basal spacings of organo-clay as a result of heat treatment was determined using a Bruker AXS instrument equipped with small-angle X-ray scattering (SAXS), and a general area detector diffraction system (GADDS). This equipment can give small angle diffraction patterns of each organo-clay before and after heating. Heating was carried out using a high-temperature controller and the peaks were measured by an area detector. We used CuK α radiation at 40 kV and 40 mA (1.6 kW) with a beam time of 300 sec. A quartz capillary tube (Charles Supper Co.) of 0.5 mm diameter was

used for holding several mg of clay on the XRD system.

DSC Measurement

A DSC model *Labsys* (Setaram, France) was used for thermal analysis in a flow of dry argon. Approximately 20 mg of HDTMA-montmorillonite was heated in an aluminium crucible of 100 μ L capacity at a heating rate of $10^\circ\text{C}/\text{min}$ up to 300°C .

Results

A representative adsorption isotherm of HDTMA on montmorillonite is presented in Fig. 2. The maximum HDTMA adsorption occurs beyond the CEC, showing about 2.5 CEC, probably via nonpolar interactions of the alkyl groups of exchanged HDTMA with the excessively adsorbed HDTMA. Narine and Guy

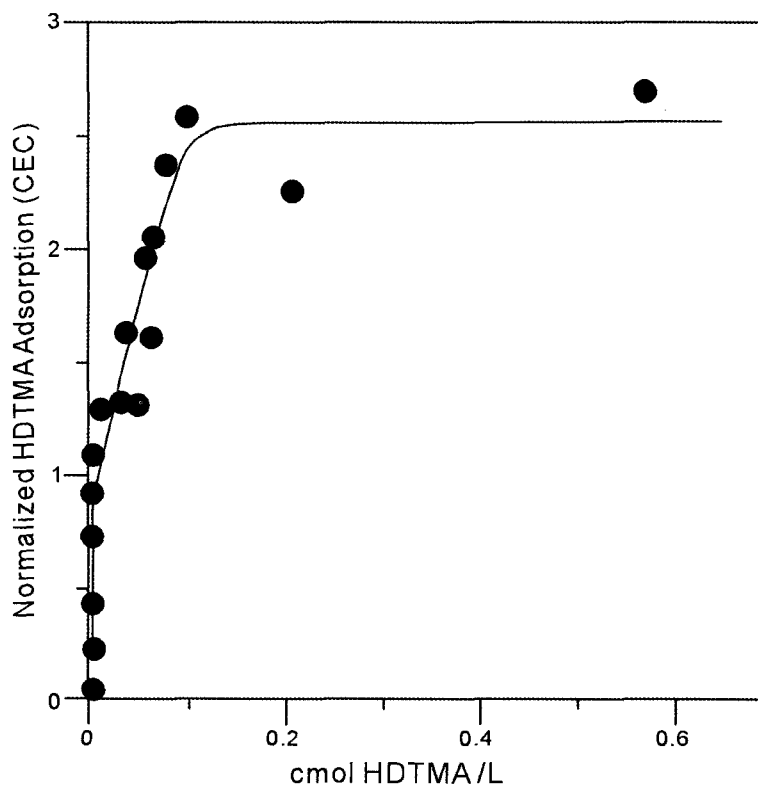


Fig. 2. Adsorption isotherm of HDTMA-Br in Na-saturated montmorillonite.

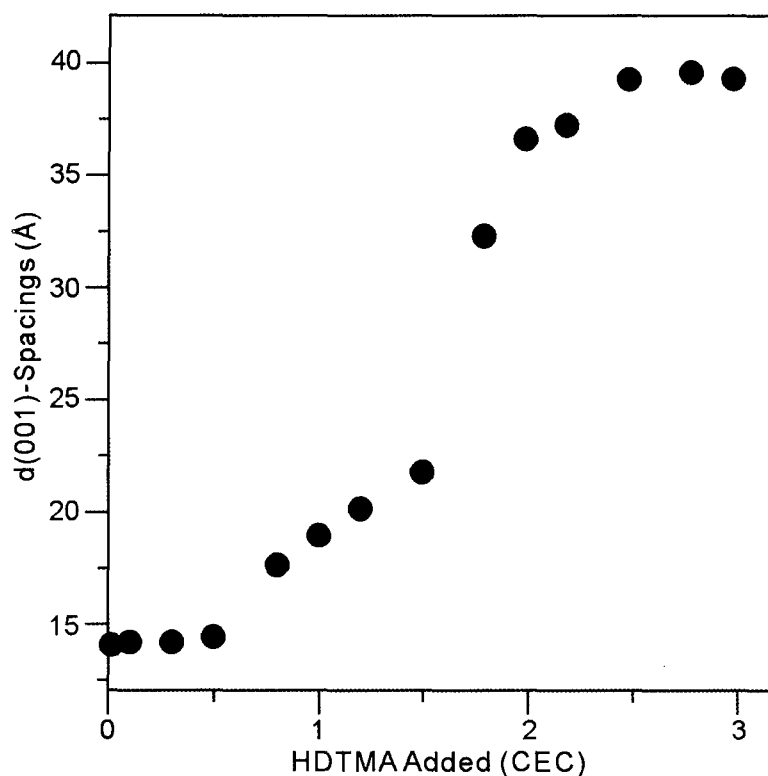


Fig. 3. d -spacings of HDTMA-montmorillonite at dry state (<5% relative humidity) as HDTMA loading increased (normalized to CEC).

(1981) likewise found that large organic cations adsorb on clays in excess of the CEC due to the formation of organo-cation aggregates on the clay surface.

The d -spacings of dry (dried at <5% relative humidity) montmorillonite are shown in Fig. 3. As the HDTMA loading increased from 0.01 CEC to 3 CEC, the d -spacings of montmorillonite increased from 14.1 to 39.8 Å. No further change in the d -spacing was observed at higher HDTMA loadings. At loading levels ≥ 1.5 CEC, the d -spacing abruptly increased from 21.7 to 32.2 Å, indicating the transition of pseudotrimolecular layer (21.7 Å) to paraffin complex (>22 Å) (Lagaly, 1994).

Fig. 4 shows the displacement of the (001) peak of highly hydrated HDTMA-smectite (~ 0.6 g H₂O g⁻¹ dry weight clay) with increasing temperature up to 450°C at a heating rate of 2°C/min. Up to 200°C, the d (001) or basal

spacing gradually increased. However, above 200°C, the d (001) spacing gradually decreased with increasing temperature. At the same time, the d (001) line became broad and weak. The sample finally became disordered at 450°C.

Fig. 5 is a d (001) spacing/temperature diagram for the HDTMA-montmorillonite. The curve in this figure has one smooth edge at 200°C with a shoulder on the low temperature side at about 100°C. It is characterized by 3 stepwise basal spacing changes: (1) expansion of the d (001) spacing to 42.4 Å up to 100°C, (2) further expansion to about 44 Å between 150°C and 200°C, and (3) the gradual collapse of d (001) spacing to about 24 Å between 200°C and 500°C.

In the case of Na-montmorillonite without adsorbed HDTMA, it shows a characteristic dehydration curve with three distinct steps of basal spacing collapses (Fig. 6).

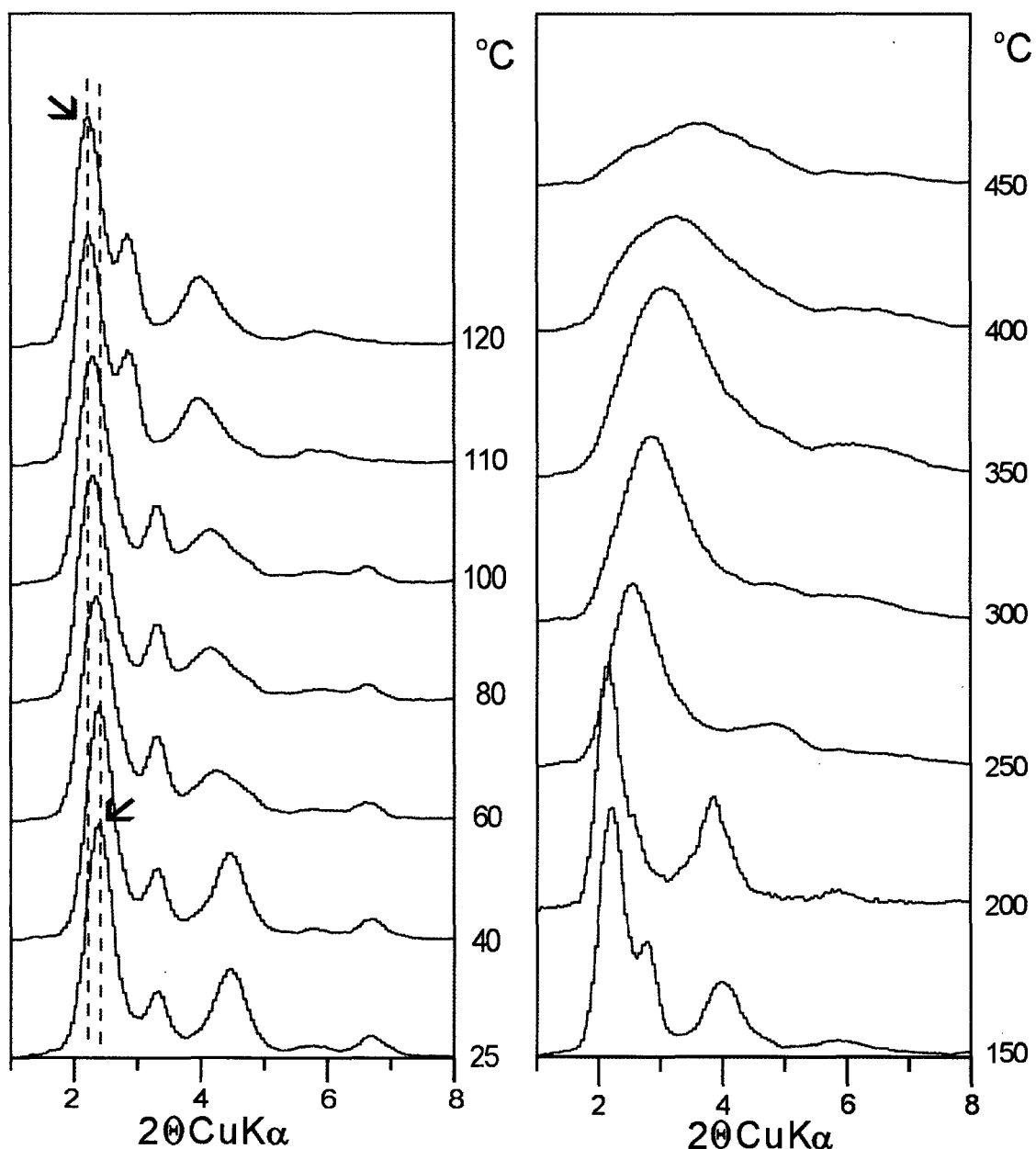


Fig. 4. Displacement of (001) peak with increasing temperature in the HDTMA-montmorillonite. Arrows indicate the minimum and maximum of $d(001)$ spacing during temperature increase (25~120°C).

Fig. 7 shows the DSC curves for HDTMA bromide, Na- and HDTMA-modified montmorillonite at a heating rate of 10°C/min. The DSC curve provides information on the difference in the energy states of water for the different saturation phases in the dehydration

process (Anderson *et al.*, 1999). In an inert atmosphere the endothermic peaks are observed at HDTMA bromide (Fig. 7), showing a strong endotherm at ~110°C and weaker endotherm at ~80°C probably due to dehydration reactions, and a second strong endotherm peaks at ~250°C

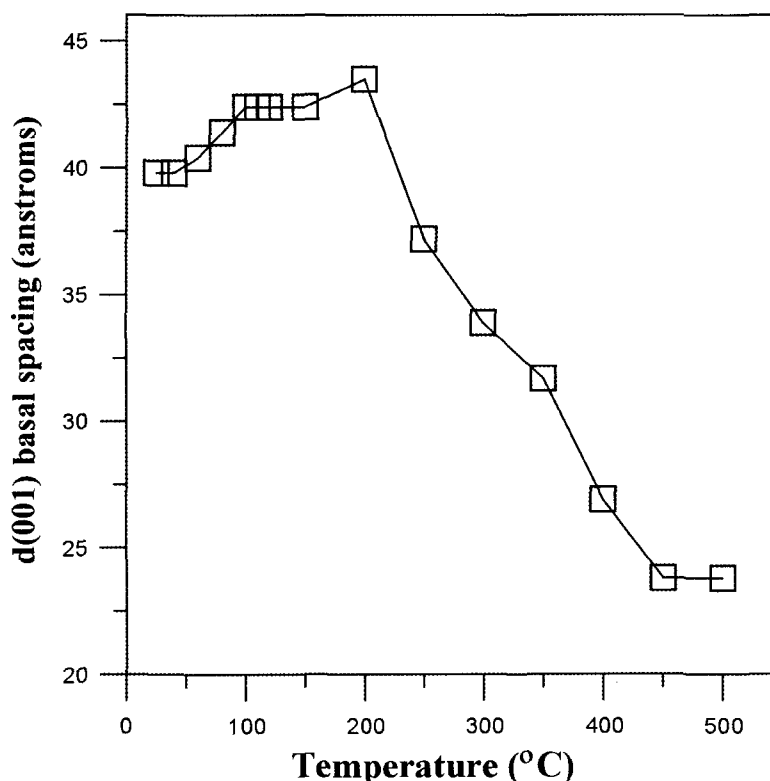


Fig. 5. Variation of $d(001)$ spacing of HDTMA-montmorillonite at different temperatures.

due to pyrolysis and liberation of the organic cations (Sullivan *et al.*, 1997). The DSC curves of Na- and HDTMA-modified montmorillonites show strong endothermic peaks at $\sim 110^\circ\text{C}$ due to dehydration reactions. The endothermic peak of Na-montmorillonite due to dehydration is not symmetrical, instead showing a steep higher temperature limb. However, the endothermic peak of the HDTMA-montmorillonite due to dehydration is approximately symmetrical, showing a broader width at half-maximum of peak compared with the Na-montmorillonite. The DSC curve of HDTMA-montmorillonite shows a peak at 116°C with a weak shoulder at 122°C .

Fig. 8 shows the thermogravimetric (TG) curves of Na- and HDTMA-modified montmorillonites. In the weight loss curves, we observed a sequential loss of mass due to both water desorption and HDTMA pyrolysis and desorp-

tion. The HDTMA-montmorillonite, whose weight loss rate is relatively slow, shows a relatively greater loss above 200°C .

Discussion and Conclusions

A dehydration experiment involving HDTMA-montmorillonite was conducted for a highly hydrated sample having $0.6\sim 0.8\text{ g H}_2\text{O g}^{-1}\text{ d.w.}$ clay in its interlayer space. In the fully hydrated phase, most of the available spaces are filled with water (Theng, 1974). Montmorillonite having a high degree of surfactant intercalation exhibits a basal spacing greater than 30 \AA (Fig. 3), indicating a close packing or aggregation of the organic cations relative to the silicate layer (Jaynes and Boyd, 1991). Such a large basal spacing suggests the conversion of flat-lying adsorption layers to a paraffin-type vertical configuration favorable for alkyl-alkyl chain

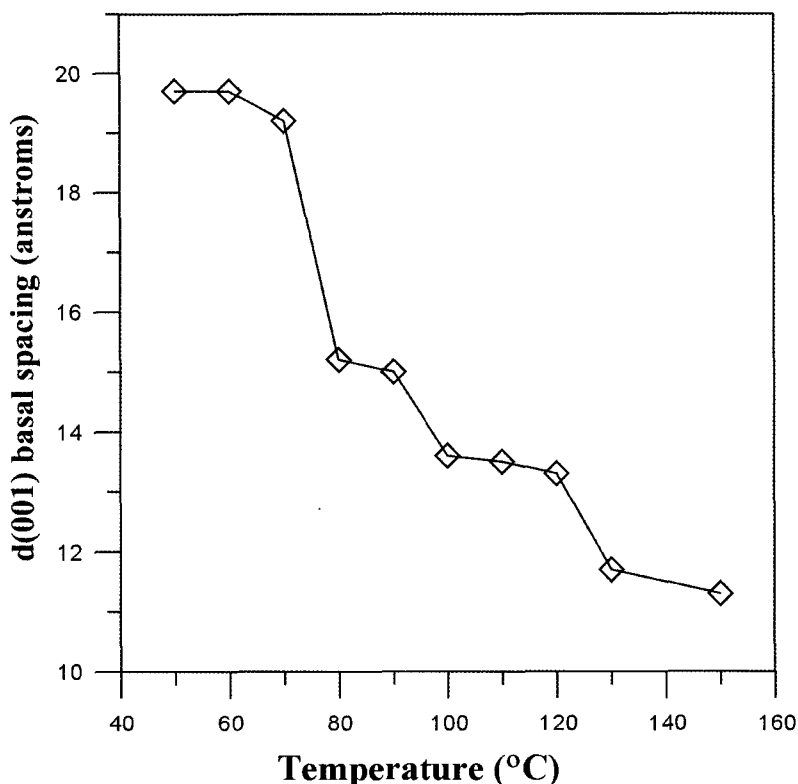


Fig. 6. Variation of $d(001)$ spacing of the hydrated Na-montmorillonite at different temperature.

interactions. The vertical arrangement of HDTMA in interlayers in a hydrophobic environment results in a high density of HDTMA in the interlayer of montmorillonite. Most of the water molecules in Na-montmorillonite are coordinated or strongly associated with Na^+ (Sheng and Boyd, 1998). The hydrated Na-montmorillonite (Fig. 6) slowly collapses stepwise from low temperature up to 200°C by dehydration. In contrast, the HDTMA-montmorillonite shows unusual swelling and collapse during dehydration. The XRD patterns of HDTMA-montmorillonite at different temperatures from 40 to 200°C are similar in shape except for the swelling of the interlayer from 39.8 to 44 \AA (Figs. 4 and 5). This suggests that the interlayer HDTMA cation is considerably stable up to 200°C .

It seems that the conversion of less vertical adsorption layers to a more vertical configura-

tion occurred due to the dehydration process through the supply of heat energy and the removal of water in the interlayer environment, resulting in greater stabilization and order. Xu and Boyd (1995) suggested that the alkyl chains of HDTMA-smectite have very loose and probably less ordered arrangements in the wet state. They insisted that the reduction in contact between the hydrophobic alkyl chains and H_2O makes the HDTMA-clay exchange complex in the clay interlayers more stabilized (Xu and Boyd, 1994). Kung and Hayes (1993) also showed that during the drying process, the sorbed HDTMA molecules on silica surface appear to alter their structural arrangement to a more stabilized condition. Hence, if the pore water among alkyl chains is removed from the interlayer, the interlayer environment of organo-clay may become more organophilic, resulting in the increase of the mutual attraction between

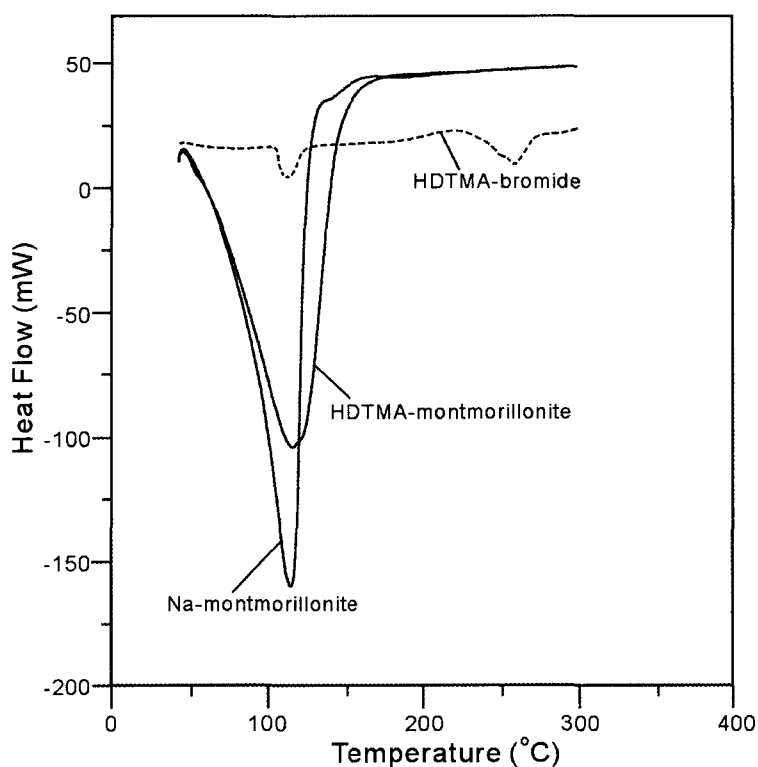


Fig. 7. Differential scanning calorimetry curves for Na- and HDTMA-exchanged montmorillonites with heating rate 10°C/min.

the alkyl chains (tails) of surfactant molecules to become more stabilized. These arguments might explain why the organo-clay expands during the heating process. It has been well known that the surfactant-modified clays (organo-clays) are hydrophobic or organophilic in nature (Mortland, 1970; Theng, 1974; Jaynes and Boyd, 1991). The more surfactants are involved in the interlayer above the CEC, the more the interlayer space becomes hydrophobic due to the increase in alkyl chain interaction (Figs. 2 and 3). Sullivan *et al.* (1998) found that the surfactant orientation depends on the quantity of surfactant on the mineral surface, with close horizontal contact (less ordering) between the surfactant and surface at low loading levels and with a perpendicular orientation (greater ordering) at higher loading levels. Consequently, the alkyl chains in the HDTMA-montmorillonite become gradually aligned more parallel to each

other by the dehydration up to 100°C without interlayer collapse, and then tend to have a more vertical configuration between 150 and 200°C (Fig. 5).

Thermal analyses by DSC provide some informations on energy differences for water in the interlayer regions (Yariv, 1985; Pires *et al.*, 2000). The endothermic peak is related to the thermal loss of interlayer water and is associated with the hydrophobic character of the clay surface (Yariv *et al.*, 1989). In our experiments, the degree of HDTMA content has an effect on the location of the principal peak of the DSC curve (Fig. 7).

In summary, if the water molecules incorporated in the interlayer complex alkyl chains are removed by heating, the interlayer spaces are firstly expanded by rearrangement of alkyl chains at low temperature ($\leq 100^\circ\text{C}$), and secondarily by gradual perpendicular orientation

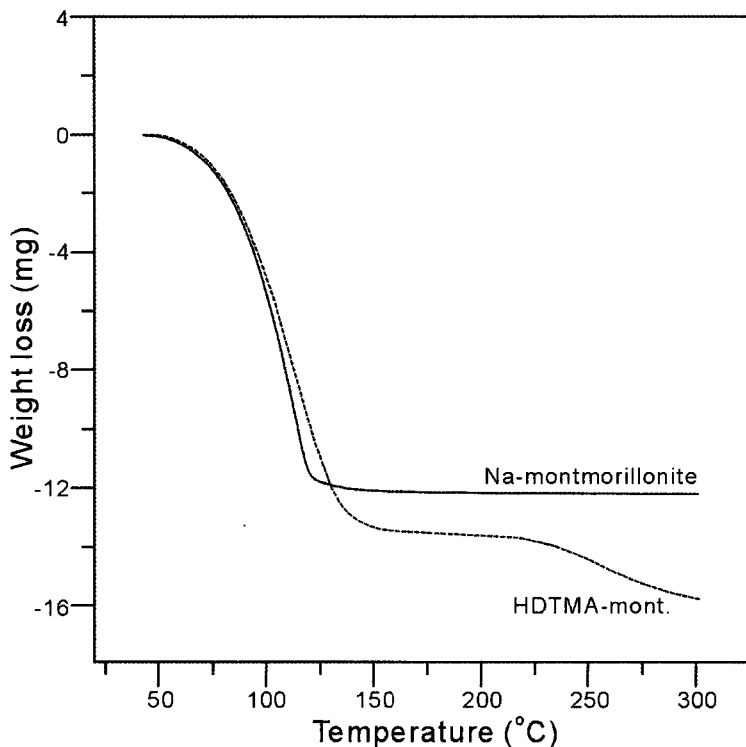


Fig. 8. Thermogravimetric curves for Na- and HDTMA-exchanged montmorillonites with heating rate 10°C/min. Initial mass (mg) of Na- and HDTMA-montmorillonite are 16.5 and 20.9, respectively.

(greater ordering) at high temperature (150~200°C), resulting in two edges in the $d(001)$ /temperature curve. We believe that the reduction of water causes a reorientation of the alkyl chains by transition to a more vertical position relative to the silicate sheets, allowing instantly greater d -spacing.

Acknowledgments

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