

Thermal analysis study of heat of dehydration of tributylammonium smectites ¹

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(Received 27 February 1992)

Abstract

The dehydration of laponite and montmorillonite treated with tributylammonium chloride was studied by DSC, TG and X-ray diffraction. Dehydration of the organo-laponite took place in one stage at 320–475 K, whereas that of the organo-montmorillonite occurred in two stages, at 320–435 and 435–485 K. The first stage was attributed to loss of water of the hydrophobic hydration zone. The second stage was specific for montmorillonite and was attributed to water molecules forming hydrogen bonds with the oxygen planes of the silicate layers. Hydrogen bond formation was attributed to the tetrahedral substitution of Al for Si.

The organo-laponite has a lower molar heat of dehydration than laponite, indicating that the interlayer water clusters of the organo-clay are smaller than those of the untreated clay. The molar heat of dehydration of untreated montmorillonite is less than that of untreated laponite, indicating that water clusters in the interlayer of the former are smaller. The molar heat of dehydration of organo-montmorillonite is higher at the second dehydration stage than at the first, because at this stage water molecules which form hydrogen bonds with atoms from the oxygen plane are evolved.

In organo-montmorillonite, water molecules from the non-structured zone form water bridges between adjacent oxygen planes, thus preventing crystalline swelling. In organo-laponite, non-structured water molecules do not form strong hydrogen bonds with atoms from the oxygen plane, water bridges between adjacent oxygen planes are weak, and crystalline swelling is thus prevented to a limited extent only.

INTRODUCTION

The wettability of talc, pyrophyllite and vermiculite has recently been investigated by measuring water contact angles on freshly exposed cleavage

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¹ This paper is dedicated to Professor Loren G. Hepler on the occasion of his retirement.

surfaces [1]. Talc and pyrophyllite are hydrophobic, having water contact angles of 61–83°, whereas vermiculite is hydrophilic, having a water contact angle of 0–14° [2]. These cleavage surfaces are actually the oxygen planes of tetrahedral-octahedral-tetrahedral (TOT) silicate layers, and their hydrophilicity stems from the electron donor ability of oxygen atoms belonging to siloxane groups.

The difference between the wettability of talc and pyrophyllite, on the one hand, and that of vermiculite, on the other, was attributed to the electron density on the oxygen atoms and related to a tetrahedral substitution of Al for Si, which occurs in the latter but not in the former. In talc or pyrophyllite the actual structure of Si–O–Si results from resonance between two canonical forms [3]. In one, the bridging oxygen atom undergoes an sp hybridization and the Si–O–Si angle is equal to 180°. In addition to the two σ bonds, two π bonds are formed, involving the two oxygen non-hybridized p orbitals on each of the two silicon atoms. This structure shows no donor properties at the oxygen atom because the lone pairs are involved in the $d_{\pi}-p_{\pi}$ bonds. In the second canonical structure, the bridging oxygen atom undergoes an sp^2 hybridization and the Si–O–Si angle is equal to 120°. Two of the sp^2 orbitals are involved in the σ bonds with each of the silicon atoms. The third sp^2 orbital contains a lone electron pair, which manifests basic donor properties. The remaining unhybridized p orbital overlaps the d orbitals in both silicon atoms, so that the electron pair is delocalized over the Si–O–Si group. Resonance between the two structures should consequently yield an intermediate angle. It has indeed been found that the Si–O–Si angle in pyrophyllite is 136° [4]. As a result of the influence of the sp hybrid form, the presence of electron donating properties at the O of the Si–O–Si is reduced. This minimizes hydrogen bond interaction between the O of siloxane and the H of water [1].

Aluminium-substituted silicates, on the other hand, wherein the oxygen cannot penetrate the d orbitals of Al to form π bonds, have only the sp^2 canonical structure, and have a 120° Si–O–Al bond angle. The 120° bond angle has been observed in brittle mica [5], where almost 50% of the silicon was substituted by Al or Be. Such silicates consequently have basic properties due to the lone electron pair in a hybridized orbital. A hydrogen bond is obtained between the O of alumino-siloxane and the H of water in vermiculite but not in talc or pyrophyllite [1].

Smectites are supposed to be more hydrophilic than talc or pyrophyllite. The advancing contact angles of water on natural hectorite and montmorillonite have recently been determined by the capillary rise method: they are 63° and 42.5° respectively [2,6], the former substance being less hydrophilic. These values are lower than those of the hydrophobic talc or pyrophyllite, but are very different from that of the hydrophilic vermiculite.

The adsorption of water by smectite minerals occurs mainly into their

interlayer space. Three zones were distinguished in the interlayer space of smectites, A_m , A_o and B_{om} [7]. In zone A_m , water has the hydrophilic hydration structure, and the attenuation of molecular motion is obtained from the strong polarizing field of the exchangeable cation. In zone A_o , water has the hydrophobic hydration structure and the clay/water interface exerts an ordering influence on the water structure, reducing the thermal amplitude of the intermolecular vibrations. Zone B_{om} is a disordered zone separating the ordered zones A_o and A_m .

The interlayer space of smectites is bordered by oxygen planes, and it is expected that interlayer water structures and the heat of hydration (or dehydration) will be affected by the tetrahedral substitution. A comparison between the dehydration of organo-Wyoming bentonite and that of organo-laponite seems to give information on the effect of tetrahedral substitution on the structure of the adsorbed water. Montmorillonite, by definition, obtains its negative charge from octahedral substitution, but most montmorillonites, including Wyoming bentonite, have some tetrahedral substitution as well [8,9]. Laponite is a synthetic hectorite with no tetrahedral substitution [10]. In the present study, differential scanning calorimetry (DSC) curves of montmorillonite and laponite treated with different amounts of the organic cation tributylammonium ($TBAH^+$) were investigated and molar heats of water desorption were compared. The positive charge density of this tertiary ammonium cation is too low to cause hydrophilic hydration corresponding to zone A_m . Its large size, however, leads to disruption of the hydrophobic hydration structure A_o , and consequently the non-structured zone B_{om} should be relatively large. Molecules in zone B_{om} are proton donors, and may form hydrogen bonds with oxygen planes of smectite minerals [11]. They may form water bridges between two parallel oxygen planes and thereby restrict any swelling of the smectite [12]. In the present communication the enthalpy and temperature of dehydration related to water of zone B_{om} of Wyoming bentonite are compared with those of laponite. The DSC study was supplemented by thermogravimetry (TG) and by X-ray diffraction (XRD).

EXPERIMENTAL

Laponite XLG (a synthetic Na-hectorite) was kindly donated by Laporte Industries Ltd., UK. Montmorillonite (Wyoming bentonite) was supplied by Ward's Natural Establishment, Inc., USA. Tributylamine (TBA) was supplied by Fluka. An aqueous solution of the ammonium chloride salt ($[TBAH]Cl$) was prepared by neutralizing an aqueous solution of the amine with HCl.

TBAH-smectites were prepared by saturating 1 wt.% aqueous suspensions of the clays with different amounts of the $[TBAH]Cl$ solutions, as indicated in the tables and in the text. After 24 h the solid phase was

separated by centrifugation and washed with distilled water until no chloride remained. It was then washed with methanol, acetone and carbon tetrachloride and dried in the ambient atmosphere. By this treatment Na^+ , which initially populates the exchange positions of both smectites, is replaced by TBAH^+ [13,14]. In general, when the amount of the organic cation exceeds the cation exchange capacity of the clay, an ammonium–amine association is obtained in the interlayer space [15]. In the present study only small amounts of TBA were adsorbed by both clays, and we assume that an ammonium–amine association was not obtained in the interlayer space.

The degree of saturation of the clay was measured by carbon determination using a Leco carbon analyser.

Samples of 20–50 mg were used for the DSC runs and 100–200 mg were used for the TG runs. The DSC instrument was a Perkin-Elmer Delta Series DSC7. The TG was a home-made apparatus. The heating rate for both thermal analyses was $10^\circ\text{C min}^{-1}$. The net DSC curve was obtained in the following manner. The sample was heated to 525 K (first run). After cooling in the DSC cell to room temperature, it was reheated. The second run was taken as the baseline. The net DSC curve was obtained by subtracting the baseline from the curve of the first run. All runs were carried out under a flow of nitrogen (an inert atmosphere). Oriented samples for XRD were prepared by drying aqueous suspensions on glass slides. The XRD patterns were recorded on a Philips diffractometer.

RESULTS

Carbon analysis

The percentage of carbon in untreated laponite and montmorillonite was 0.26 and 0.24 respectively. The percentage of carbon in clays treated with different amounts of $[\text{TBAH}]\text{Cl}$ was determined and, after the subtraction

TABLE 1

Adsorption of TBAH^+ by laponite (in millimoles per 100 g clay) calculated from the carbon content (%) and loss of water (wt.%) determined by TG

Ratio of TBA to clay in preparation of samples (mmol TBA per 100 g clay)	Adsorption of TBA by laponite (mmol TBA per 100 g clay)	Loss of water (wt.%)
0	0	13.07
2	1	19.78
10	4	17.65
20	6	18.10
40	8	18.29
80	15	19.55

TABLE 2

Adsorption of TBAH⁺ by montmorillonite (in millimoles per 100 g clay) calculated from the carbon content (%) and loss of water (wt.%) determined by TG

Ratio of TBA to clay in preparation of samples (mmol TBA per 100 g clay)	Adsorption of TBA by montmorillonite (mmol TBA per 100 g clay)	Loss of water (wt.%)	
		(a)	(b)
0	0	9.08	–
10	6	13.31	1.20
20	8	13.74	1.24
40	18	11.86	1.22
80	25	9.30	1.16

Key: (a) first stage of dehydration; (b) second stage of dehydration.

of the percentage of carbon of untreated clays, the amount of TBAH⁺ adsorbed by the different samples was calculated (Tables 1 and 2).

DSC curves

Figure 1 shows the DSC curves of untreated laponite and of laponite treated with different amounts of TBAH⁺ in the range 300–525 K. There is a single endothermic peak, lying between 320 and 475 K, which represents the dehydration of the clay. At this stage, interparticle and interlayer water is evolved. The peak maximum in the DSC curve of untreated laponite is located at 406 K. The maximum shifts to lower temperatures when the clay is treated with TBA. With an adsorption of 4 mmol TBA per 100 g clay it shifts only very slightly, but with greater adsorptions the shifts are very high. For example, with 15 mmol TBA per 100 g clay the peak maximum is at 374 K. This shift of the peak temperature results from the hydrophobic effect of the adsorbed organic cation [16].

Figure 1 also shows DSC curves of untreated montmorillonite and of montmorillonite treated with different amounts of TBA, in the range 300–525 K. There is a single endothermic peak in the DSC curve of untreated montmorillonite, extending between 320 and 425 K, which represents the dehydration of the clay and the evolution of interparticle and interlayer water. The peak is asymmetric with a maximum at 412 K. The peak maximum shifts to lower temperatures when the clay is treated with TBA. With an adsorption of 18 mmol TBA per 100 g clay it is located at 387 K. With 25 mmol TBA per 100 g clay the peak splits into two maxima at 377 and 391 K. This shift of the peak temperature results from the hydrophobic effect of the adsorbed organic cation.

A more striking effect of the organic cation on the curves of montmorillonite is the appearance of an extensive shoulder in the range 435–485 K. This is an indication that the dehydration of TBAH-montmorillonite takes place in two stages. The first stage is similar to the dehydration of laponite,

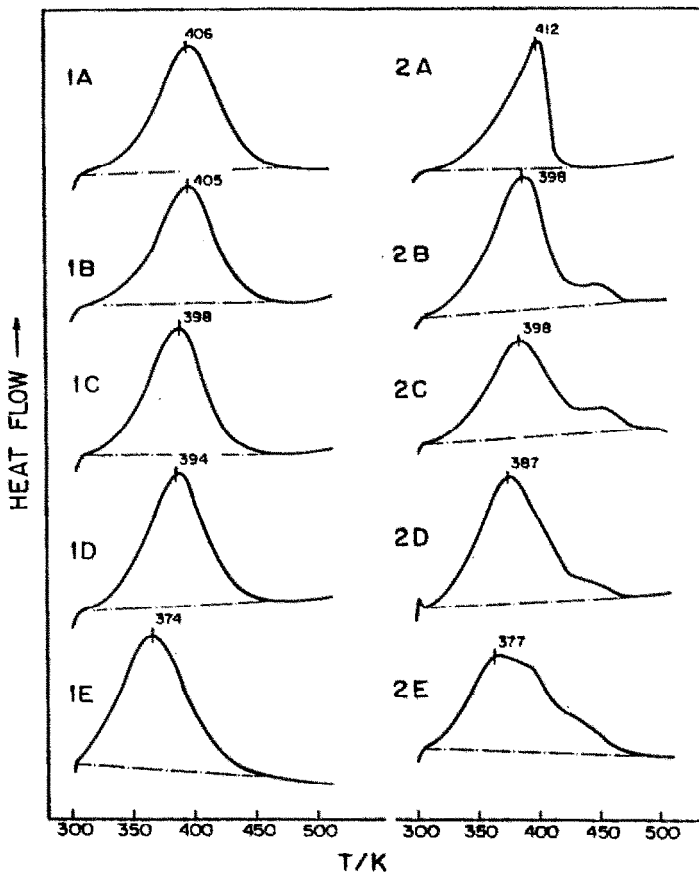


Fig. 1. DSC curves of (1) laponite, untreated (A) and saturated with 4, 6, 8 and 15 mmol TBAH⁺ per 100 g clay (B, C, D and E respectively) and of (2) montmorillonite, untreated (A) and saturated with 6, 8, 18 and 25 mmol TBAH⁺ per 100 g clay (B, C, D and E respectively).

and it is suggested that in this stage water molecules belonging to the hydrophobic hydration zone are evolved. The second stage is specific for montmorillonite, and it is suggested that in this stage water molecules which form hydrogen bonds with the oxygen plane of the aluminosilicate layer are evolved.

Thermogravimetry

In a separate series of experiments, the amount of water evolved from montmorillonite, in connection with each stage of the DSC run, was determined by TG. It should be noted that in our TG system the furnace temperature is recorded, whereas in DSC the temperature of the sample is recorded. Consequently, the two dehydration stages of montmorillonite

appear at higher temperatures in the TG as compared with the DSC runs. The first stage extends up to 465 ± 8 K in the TG run and the second up to 520 ± 10 K. Weight losses during the first and second stages are given in Table 2. The table shows that most of the adsorbed water is evolved during the first stage.

The amounts of water evolved from laponite and TBAH-laponite are much greater than those evolved from montmorillonite and TBAH-montmorillonite respectively. For both clays, there is a significant increase in the water content as a result of the treatment of the clay with TBAH⁺. However, there is no significant effect of the ratio of amine to clay on the amount of water which is adsorbed.

Heats of dehydration

Heats of dehydration were obtained from DSC peak areas. In the case of laponite, where there is a single peak, the energy per 100 g clay was obtained directly from the DSC system (Table 3). In the case of montmorillonite, dehydration energies per 100 g clay, below and above 435 K, were determined by cutting a paper sheet which had the shape of the peak into two pieces (at the 435 K position) and calculating the energy from relative weights of each piece of this paper (Table 4). Dehydration energies per mole of H₂O are gathered in Tables 3 and 4. The tables show that TBAH⁺ affects the molar heat of dehydration of both clays.

In the case of laponite, the molar heat of dehydration of untreated clay (41.6 kJ mol^{-1}) is very similar to the molar heat of vaporization of water (44.0 kJ mol^{-1} [17]), probably because water clusters in the interlayer space of untreated laponite are similar to water clusters in liquid water. The treatment of laponite with TBAH⁺ leads to a lower molar heat of dehydration. This is in agreement with decreasing hydrophilicity of the clay and may indicate that the water clusters in the interlayer are now small. In the case of montmorillonite, the molar heat of dehydration of the untreated

TABLE 3

Heat of dehydration of laponite per 100 g clay and per 1 mol H₂O

Degree of saturation (mmol TBA per 100 g clay)	ΔH (kJ per 100 g clay)	ΔH_m (kJ per 1 mol water)
0	30.19	41.6
1	33.06	30.1
4	28.14	28.7
6	28.59	28.5
8	31.54	31.1
15	25.32	23.3

TABLE 4

Heat of dehydration of montmorillonite calculated for the two stages of the dehydration per 100 g clay and per 1 mol H₂O

Degree of saturation (mmol TBA/100 g clay)	ΔH (kJ per 100 g clay)		ΔH_m (kJ per 1 mol water)	
	(a)	(b)	(a)	(b)
0	13.82	0.0	27.4	0.0
6	18.53	2.36	26.4	35.4
8	14.56	2.63	19.1	38.2
18	19.74	2.33	30.0	34.4
25	18.00	2.84	34.9	44.1

Key: (a) 320–435 K; (b) 435–485 K.

clay is less than the molar heat of vaporization of water, and also is less than the molar heat of dehydration of untreated laponite, probably because water clusters in the interlayer of untreated montmorillonite are smaller than water clusters in liquid water or in laponite. The molar heat of dehydration of TBAH-montmorillonite is high in the range 435–485 K as compared with that in the range 320–435 K.

X-ray diffraction

Figure 2 shows XRD curves of untreated clays and of clays treated with different amounts of TBAH⁺. In the diffractograms of laponite there is a very broad peak extending between a 2θ angle of $< 3^\circ$ and 9° , indicating that the samples are inhomogeneous and randomly interstratified. The peak maximum in the XRD curves of untreated laponite or of samples with amine-to-clay ratios of 1, 4 and 6 mmol TBA per 100 g clay is located at 1.35 nm. The maximum shifts to higher c spacings (maximum at about 1.6 nm and a shoulder at about 1.7 nm) with higher amine-to-clay ratios.

In the diffractograms of montmorillonite and of montmorillonite treated with different amounts of TBAH⁺, the peaks are sharper than in those of laponite, indicating that the samples are relatively homogeneous and better oriented. They become sharper with increasing amounts of TBA. The peak maximum in the diffractogram of untreated montmorillonite is located at 1.2 nm. The maximum shifts to higher c spacings (1.38–1.41 nm) when the clay is treated with TBA.

The effect of the adsorption of TBAH⁺ on the c spacing is an indication that the organic cation is located in the interlayer space and thus should have an effect on the structure of the interlayer water. The difference in shapes between the diffractograms of laponite and montmorillonite indicates that the former swells with larger amounts of water, and that many tactoids of laponite have an interlayer with a c spacing larger than 1.7 nm.

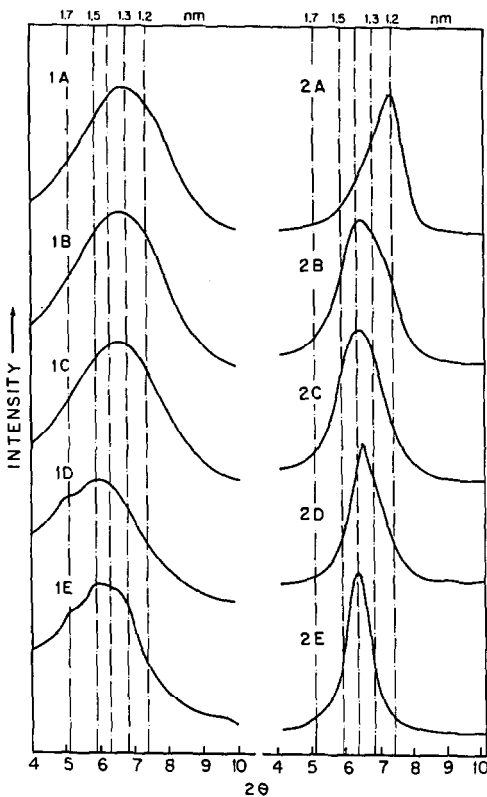


Fig. 2. X-ray diffractograms of (1) laponite, untreated (A) and saturated with 4, 6, 8 and 15 mmol TBAH⁺ per 100 g clay (B, C, D and E respectively) and of (2) montmorillonite, untreated (A) and saturated with 6, 8, 18 and 25 mmol TBAH⁺ per 100 g clay (B, C, D and E respectively).

These results, together with the TG study, show that TBAH⁺ prevents crystalline swelling of montmorillonite, but not of laponite.

DISCUSSION

In both of the untreated smectites used in the present study, sodium is the original exchangeable cation. Being monovalent and relatively small, sodium does not break the interlayer water structure and is located in cavities. The structure of zone A₀ depends on the degree of hydrophilicity of the oxygen plane [18]. In the vicinity of a hydrophobic oxygen plane, such as that of Na-laponite, large hydrophobic water clusters are obtained. The organization of the water molecules is such that they are arranged in the strained hexagonal ice-like configuration and are closely linked to one another by hydrogen bonds. Protons of the water molecules are not necessarily directed toward the hydrophobic oxygen planes, and hydrogen

bonds are not formed between water molecules and oxygen atoms of the silicate surfaces, or, if formed, are very weak. For montmorillonite saturated with sodium, Mamy [19] suggested that the monolayer hydrate consists of a tetrahedral distribution of water molecules, arranged in a strained hexagonal ice-like configuration with intermolecular hydrogen bonds formed between neighbouring water molecules. Since some of the water molecules have protons inside ditrigonal cavities of the silicate surface, and since some silicon atoms are substituted by aluminium atoms, hydrogen bonds are formed between water molecules and Al–O–Si oxygen atoms in the silicate surface and the net of the hydrogen bonds between the adsorbed water molecules is broken in places. Thus the water structure in the interlayer of Na-laponite is less strained than in the interlayer of Na-montmorillonite. Less water is held by the latter in an ambient atmosphere and its molar heat of dehydration is smaller.

Introducing organic matter into clay interlayers renders them hydrophobic [16]. In the present study this is shown from the shift of the endothermic peak maximum to lower temperatures. This shift increases with increasing ratios of TBAH⁺ to clay. Because this ratio has only a slight effect on the amount of adsorbed water (Table 1), a shift of the DSC peak maxima to lower temperatures should result from the decrease in the size of the water clusters of zone A_o. Thus TBAH⁺ serves as a water structure breaker in both smectites.

Organic aliphatic ammonium cations restrict the swelling of montmorillonite to 1.35 ± 0.05 nm. The explanation for this phenomenon can be as follows. The proton in TBAH⁺ is not accessible to form hydrogen bonds with water molecules because of steric hindrance. In addition, the positive charge density of the organic ion is too small to cause hydrophilic hydration corresponding to zone A_m. The large size of the organic ion, however, leads to disruption of the hydrophobic hydration structure A_o. Some of the water in the interlayer is non-structured (zone B_{om}) and forms water bridges between adjacent oxygen planes, thus preventing crystalline swelling. Organic ammonium cations resemble Cs⁺ in this respect [12].

Water molecules of zone B_{om} which form strong hydrogen bonds with the oxygen plane of montmorillonite, should evolve at a temperature higher than that of the evolution of water of zone A_o. Indeed, the DSC curves show that this water is lost above 435 K, and Table 4 shows that the molar heat of dehydration above 435 K is much higher than that below this temperature.

In TBAH-laponite, where there is no tetrahedral substitution, the hydrogen bonds of water molecules of zone B_{om} with the oxygen plane are very weak, and this water is evolved together with water of zone A_o. Thus, in contrast to the DSC curves of TBAH-montmorillonite, curves of TBAH-laponite do not show a distinct peak of water evolution at temperatures above 435 K. The molar heat of dehydration of TBAH-laponite is less than

that of untreated laponite because of the smaller water clusters which are present in the organo-clay. Because water molecules from the non-structured zone (zone B_{om}) do not form strong hydrogen bonds with atoms from the oxygen plane, water bridges between adjacent oxygen planes are weak, and crystalline swelling is thus prevented to a limited extent only. This is the reason that the water content of laponite is twice that of montmorillonite and that the XRD peaks of laponite are very broad, starting with a 2θ angle smaller than 3° .

ACKNOWLEDGEMENTS

The authors thank Mr. Yoetz Deutsch from the Geological Survey, Jerusalem, for the carbon analysis. They also thank Dr. Harold Cross for reading the manuscript and for his useful comments and suggestions. Our thanks to Laporte Industries, UK, for the kind donation of the laponite sample.

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