INFRARED STUDY OF THE EFFECTS OF THERMAL TREATMENT ON MONTMORILLONITE-BENZIDINE COMPLEXES
II. Li-, Na- K-, Rb- and Cs-montmorillonite

M. Lacher[1], N. Lahav[1] and S. Yariv[2]

[1]THE SEAGRAM CENTRE FOR SOILS AND WATER RESEARCH
[2]DEPARTMENT OF INORGANIC AND ANALYTICAL CHEMISTRY, THE HEBREW UNIVERSITY OF JERUSALEM, JERUSALEM 91904, ISRAEL

Li-, Na-, K-, Rb- and Cs-montmorillonites were saturated with benzidine, these organo-clay complexes heated under vacuum to 200°C and IR spectra recorded at various temperatures. Benzidine is mostly bound to interlayer cations through water molecules, except in Cs-clay where bonding to hydrophobic water and to water molecules which are hydrogen bonded to the oxygen plane predominates. During the thermal treatment water is lost and alkali cations coordinate directly with benzidine. In Cs-, and to some extent also in Rb- and K-montmorillonite, benzidine is oxidized to semiquinone and quinoidal cation during the thermal treatment.

Keywords: montmorillonite-benzidine complexes

Introduction

In previous investigations [1–10] the adsorption of aniline and its derivatives ($ArNH_2$) have been used for the examination of surface acidity of montmorillonite (MONT). Anilines associate with water molecules of the hydration spheres of exchangeable cations. In these associations the aniline-NH_2 groups react either as proton acceptors (Type A) or as donors (Type B). With transition metals, NH_2 groups donate electrons to the cation, which is a Lewis acid site (Type C). On reaction with strong Brönsted acids $ArNH_2$ becomes $ArNH_3^+$ (Type D), whereas only hydrogen bonds are formed when aniline reacts with weak acids. IR spectroscopy was applied to determine whether the molecular anilines react as proton donors or acceptors, and to differentiate between basic and acid sites on the clay surface. In the latter case IR spectroscopy was used to define whether the anilines were bound to Lewis or Brönsted acid sites. In addition, IR was used to

differentiate between ionic (protonated) and molecular anilines adsorbed on montmorillonite, and the strength of the surface acidity was thereby determined qualitatively.

The purpose of the present investigation was to study the effects of temperature on surface acidity of montmorillonite and on proton transfer between the different sites inside the interlayer space. Because of their high vapour pressure and ease of evaporation, anilines are not reliable for this study at elevated temperatures. Benzidine (I, BEN) which is not evolved from the clay at 200°C, is suitable for this purpose. In part I of this research [11] IR thermospectrometry was used to study reactions occurring during the thermal treatment of montmorillonite saturated with benzidinium cation or with benzidinium-benzidine (BENH-MONT) or BEN·H·BEN-MONT, respectively). We followed proton transfer between the interlayer space and skeletal OH groups of aluminosilicate layers. In the present paper we describe reactions occurring during the thermal treatment of Li, Na-, K-, Rb- and Cs-MONT saturated with benzidine.

Benzidine adsorbed on montmorillonite gives an oxidation radical which is dark blue [12–14]. However, except for Cs-MONT, the IR spectra obtained in the present study are characteristic for benzidine and we can presume that only a trace amount of the benzidine is oxidized, and is not observed in our IR spectra.
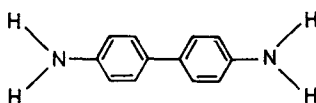
I, BEN

Experimental

BEN was supplied by BDH. Montmorillonite was supplied by Fisher (Wyoming bentonite B-235). The clay was saturated with various cations, and self-supporting films prepared as previously described [1]. They were immersed for three days in a 5% CCl4 solution of BEN and washed for very short periods in pure CCl4. IR spectra were recorded on a Bruker FTIR Spectrophotometer, 113v and a Perkin-Elmer Spectrophotometer, model 237, in a vacuum cell supported by KBr windows, as they were progressively heated up to 200°C, and in air before and after the thermal treatment. Interlayer spacings of the films before and after the thermal treatment were determined with a Seifert Iso-Debyeflex IIIa X-ray diffractometer.

Results and discussion

Infrared spectra of BEN and BEN·2HCl in CsCl disks

IR spectra of BEN and of BEN·2HCl, recorded in CsCl disks, are shown in Fig. 1. Assignments and wavenumbers of principal absorption bands are summarized in Table 1. Spectra of films of BENH- and BEN·H·BEN-MONT and of films of Li- and Cs-MONT saturated with BEN are also listed in the table.
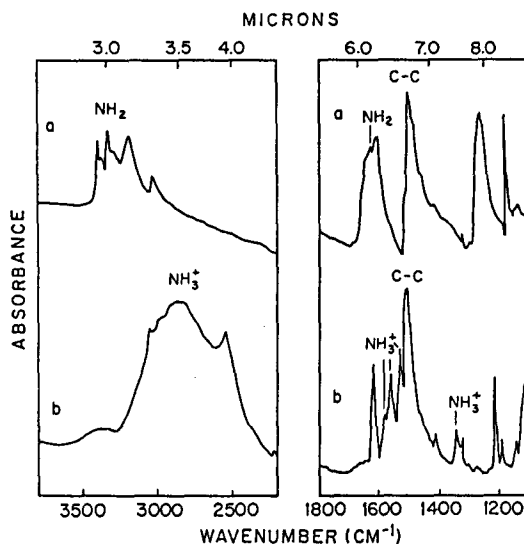

Fig. 1 IR spectra of (a) BEN and (b) BEN·2HCl in CsCl disks

A very dilute CCl_4 solution of BEN shows two NH_2 stretching bands at 3470 and 3390 cm^{-1} and a C–N stretching band at 1280 cm^{-1}. The KBr disk of BEN shows splitting of the NH_2 vibrations to four stretching and two bending vibrations (Table 1). The C–N vibration shifts slightly to a lower frequency and at the same time two very weak absorptions are observed at 1294 and 1320 cm^{-1}. The shift to lower frequencies is characteristic for NH_2 groups which form hydrogen bonds by proton acceptance, whereas the shift to higher frequencies characterizes NH_2 groups which donate protons for hydrogen bond formation. A combination band at 3180 cm^{-1} in the spectrum of the solid BEN, can be attributed to hydrogen bonds between amine groups of neighbouring molecules in the BEN crystal (NH···N group) [15]. This band is characteristic for the solid phase and does not appear in the spectrum of the dilute CCl_4 solution.

In the spectrum of BEN·2HCl the location of the C–N band is shifted to lower frequencies compared to its location in the spectrum of the amine. In the spectrum

Table 1 Assignments and wavenumber (cm^{-1}) of principal absorption bands in the spectra of BEN, BEN·2HCl, BENH-MONT, BEN·H·BEN-MONT, and Li- and Cs-MONT saturated with BEN and the principal associations A – K and Q (see text) characterized by the different absorption bands. Spectra recorded at room temperature

Assignment	CsCl disks		Benzidinium(*)	Benzidinium-benzidine(**)	Films of montmorillonite	
	Benzidine	Benzidinium-dichloride			Li-MONT/benzidine	Cs-MONT/benzidine
NH$_2$ f.a.	–	–	3480vwbr H	3490vw	–	–
H$_2$O h.w.	–	–	–	—	–	3445–3405, 3360sh
NH$_2$ as.&	3395m, 3365w	–	3380w f.a.	3375m E	3390w A	3400+vw F
sym. stret.	3323m, 3285sh	–	3310vw f.a.	3315w E	3320m A	3340+vw F
NH··O c.b.	–	–	3215vbr D∞	3215vbr D∞, 3200w E	3200vwbr B	3235 G
NH··N c.b.	3180	–	–	–	–	–
H$_2$N·HOH$_2^+$ c.b.	–	–	–	3140w E	–	–
CH aromatic	3030vw, 3010sh	3060w, 3005sh	3080vw, 3045vw	3080vw, 3045vw	3030vw	3030vw
NH$_3^+$ stret.	–	2850vbr	2930vbr D	2925vbr vw D	2925vw D	2925vw D
NH$_3^+$ c.b.	–	2555m	2610mbr D	2600vw D	2600vw D	2600vw D
BENHBEN c.b.	–	–	–	2570mbr E	–	–
p.s.	1900vw	1910m br	–	–	–	–
NH$_2$, H$_2$O def.	1645sh, 1624	–	1620	1622	1616	1625
C–C ring	1602	1607	1610+wsh	1613+wsh E	–	1625

Table 1 Continued

Assignment	CsCl disks		Films of montmorillonite			
	Benzidine	Benzidinium-dichloride	Benzidinium(*)	Benzidinium-benzidine(**)	Li-MONT/benzidine	Cs-MONT/benzidine
NH_3^+ as.	–	1572vw	1577w D	–	–	–
sym.	–	1553	1550wsh D	1552m D	–	–
def.	–	1518	1530m D	–	1528vw D	1530vw D
C–C ring	1502	1496	1503	1505	1503	1503
	1412vw	1407vw	1405vw	1410vw	1412vw	1405vw
NH_3^+ rocking	–	1340w, 1325w	1330w D	1370–1350vw D	–	–
C–NH···O	–	–	–	1320m E	1335vwsh B	1320vwsh G
C–N stret.	1265	1208	1208sh D	1251 E, (1208sh D)	1250 A	1263 F
p.s.	1177	1187m	–	–	–	–
C–H def.	1132w, 1095w	1141m, 1070m	–	–	–	–
	848, 816	810	–	–	–	–
	747, 701	794m, 700vw	–	–	–	–

f.a. - free amine; h.w. - hydrophobic water; p.s. - aromatic band associated with para substitution; c.b. - combination band; + observed after vacuum; ∞ water molecules hydrogen bonded to ammonium groups; * contains free amine; ** contains benzidinium ion

of BENH-MONT this band overlaps and Si–O absorption and is not always detected. The frequency of the NH$_3^+$ band depends inversely on the strength of the hydrogen bonds which this cation forms with the different proton acceptors. It is located at 2850, 2930 and 3080–3220 cm^{-1} in the spectra of BEN·2HCl, BENH-MONT and of dehydrated BENH-MONT, respectively.

Infrared spectrum of BEN adsorbed by Li-, Na-, K- and Rb-MONT

When BEN is adsorbed by Li-MONT, two NH$_2$ stretching, one NH$_2$ bending and one C–N stretching vibrations are observed (Fig. 2). The NH$_2$ bending vibration overlaps water and C–C vibrations. These vibrations shift from their locations in the spectrum of a solution of BEN in CCl$_4$ to lower frequencies. The shift of the NH$_2$ frequencies is an indication of the involvement of this group in hydrogen bonds, whereas the shift of the C–N absorption to a lower frequency is an indication that N atoms in these hydrogen bonds accept protons. The changes in the spectrum of BEN due to adsorption are similar to the changes which were previously observed when anilines were adsorbed by Li-MONT, and similarly they indicate that in the interlayer space the following association between BEN, water molecules and Li is obtained (type A).
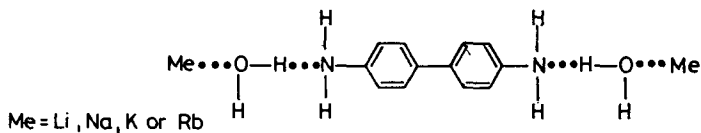
Association Type A

BEN is also adsorbed by Na-, K- and Rb-MONT but the amount adsorbed decreases with increasing size of the exchangeable cation. Only very small amounts of BEN were adsorbed during the three days that K- or Rb-films were immersed in the BEN solution. The principal features of the spectra of BEN adsorbed by these films are similar to those of BEN adsorbed by Li-MONT, indicating that type A association is obtained with these cations in the interlayer space. However, the shifts of the NH$_2$ and C–N stretching bands from 3470 and 1280 cm^{-1}, respectively (their non-perturbed location), are smaller than with Li, indicating that the interlayer acidity is reduced with increasing size of exchangeable cation. Consequently, weaker hydrogen bonds are formed between water and BEN in these organo-clay complexes.

The NH$_2$ band in the spectra of K- and Rb-MONT has a tail ranging up to 3480 cm^{-1}, representing residual hydrophobic water.

In the spectrum of BEN adsorbed by Li-MONT a very weak and broad absorption appears at 3200 cm^{-1}, accompanied by a very weak shoulder at 1335 cm^{-1}.
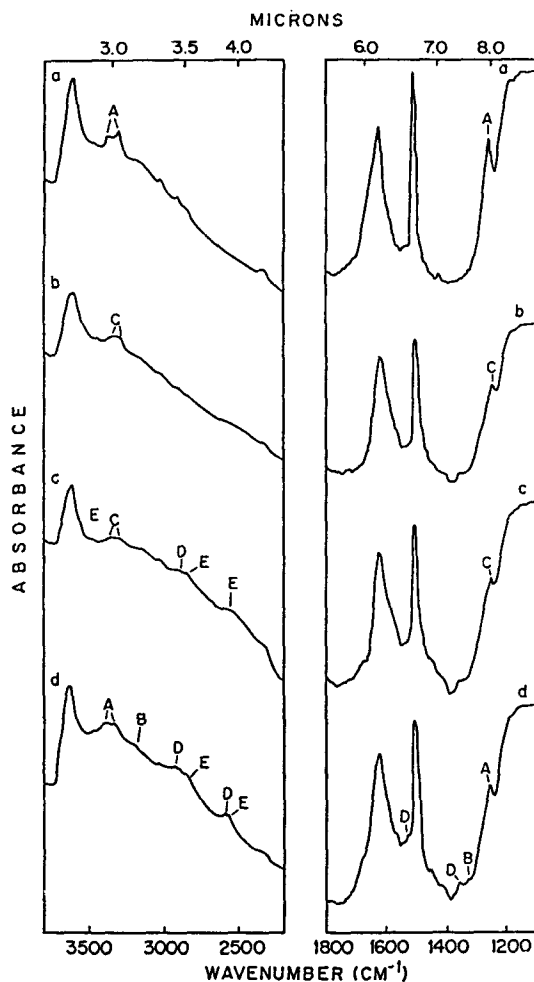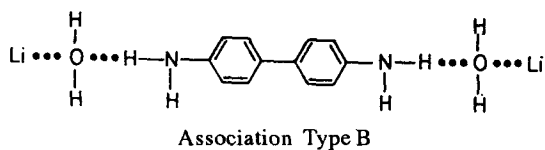
Fig. 2 IR spectra of film of Li-MONT saturated with BEN (a) air-dried, (b) after heating at
150°C under vacuum, (c) after heating at 200°C then cooling to room temperature under
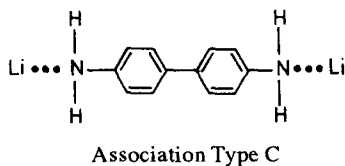vacuum, (d) rehydrated (72 h at room temperature – ambient conditions)

This absorption is not observed in the spectra of BEN adsorbed by Na-, K- or Rb-
MONT. Previously, similar bands were attributed to hydrogen bond formation in
which the amine groups of different anilines donated protons to water molecules
coordinating the exchangeable cation (NH···O groups). A similar association be-
tween BEN, water molecules and Li is obtained (type B) to a very small extent,

$$Li \cdots \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{O}} \cdots H - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N}} - \bigcirc\!\!-\!\!\bigcirc - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N}} - H \cdots \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{O}} \cdots Li$$

Association Type B

It has been shown previously that this type of association is obtained mainly with *o*-substituted anilines and with polyvalent cations. In the next paper of this series we will show that with polyvalent cations this type of association is more significant. From the spectrum it is not clear whether only one or both NH_2 groups of a BEN molecule serve simultaneously as proton donors.

Thermal treatment of Li- and Na-MONT saturated with BEN

No spectral changes are observed after treating the films under vacuum at room temperature and even after heating them below 100°C, only the shoulder at 3200 cm^{-1}, which is characteristic for type B, disappears (Table 2). Above this temperature the films are dehydrated and a direct interaction between the metallic cation and the NH_2 group is surmised from the shifts of the NH_2 and CN stretching bands (association type C). With Na-MONT the bands shift to higher frequencies whereas with Li-MONT they shift to lower frequencies and a very weak absorption is observed at 3140 cm^{-1}. This is an indication that the Li–NH_2 bond is stronger than the Na–NH_2 bond and the NH_2 group is more perturbed.

$$Li \cdots \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N}} - \bigcirc\!\!-\!\!\bigcirc - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N}} \cdots Li$$

Association Type C

The dehydration process is complete at 200°C. At this temperature π interactions between the aromatic ring and the oxygen plane occur and the C–C stretching vibration is shifted slightly (Table 2).

When the dehydrated films are rehydrated in air at ambient temperature for at least 24 hours, a spectrum similar to the original one is obtained, i.e., association A reappears, indicating that the changes observed during the thermal treatment are not associated with oxidation or decomposition of the organic matter. Association B also appears in the spectra of both clays. With Li-MONT the amount of association B after rehydration is greater than initially, whereas with

Na-MONT it appears only after rehydration. Larger amounts of association B are developed if the films are left for several days at ambient atmosphere.

Protonation of benzidine in Li- and Na-MONT

In addition to molecular amine, Li- and Na-MONT contain trace amounts of protonated BEN (benzidinium ion, association D), which is shown by very weak stretching, deformation and rocking NH_3^+ absorptions at 2920, 1520–1575 and ≈ 1350 cm^{-1}. The cationic species is obtained from BEN by accepting protons from hydrated cations as follows:

$$[Li(HOH_m]^+ + BEN \rightarrow BENH^+ + [Li(HOH)_{m-1}(OH)] \qquad (1)$$
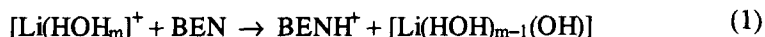
In the present study protonation of BEN occurred only to a low degree, in Li-more than in Na-MONT, because alkali cations are very weak acids. The amount of this ion increases if samples are left at ambient atmosphere for several days, or if the organo-clay films are immersed for several minutes in water. The amount of this ion also increases during the thermal treatment, as shown by the intensification of the bands at 2920 and 1560 cm^{-1}. This is an indication that the acidic strength of hydrated cations in the interlayer space increases with rise in temperature. In our next paper we will show that with polyvalent cations this type of proton donation from hydrated cations to BEN becomes more significant. It is not clear from the spectrum whether one or two NH_2 groups of a BEN molecule are protonated.

The spectrum of thermal treated Li-MONT which has been cooled to room temperature, showed two very small broad absorptions at 2855 and 2565 cm^{-1} which are characteristic for ammonium-amine association (type E). These bands persist after the dehydration of the clay. This association is obtained from the interaction between benzidinium cation, water and free benzidine. In the present case only trace amounts of this association are obtained. In the next paper of this series we will show that with polyvalent cations this type of association is more significant. It is not clear from the spectrum whether only one or both NH_2 groups of a BEN molecule take part in this association.
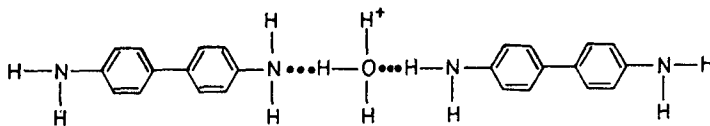
Association Type E

Table 2 Assignments and wavenumber (cm^{-1}) of principal absorption bands in the spectra of Li-, Na-, K-, Rb- and Cs-MONT saturated with benzidine, recorded at room temperature and after thermal treatments under vacuum and the principal associations A – K and Q (see text) characterized by the different absorption bands

Inter-layer cation	Temp. / °C	H$_2$O Hydrophobic water	Benzidine Assignments					Associations Relative amount is expressed by + tr - trace amounts
			NH$_2$ stretching	NH···O c. b.	H$_2$O, NH$_2$ & ring vib.	Ring vib.	CN stretching	
Li	r.t.	–	3390, 3325	3200vw	1616	1503	1335vwsh, 1250	A+++++, B+, D+
	150	–	3360, 3302	–	1616	1502br	1243	C+++++, D+
	200	–	3357, 3295	–	1613	1495	1242	C+++++, D+, E^{tr}
	rehy	–	3390, 3325	3210sh	1615	1503	1322vw, 1250	A+++++, B++, D++, E^{tr}
Na	r.t.	3455vw	3390, 3330	–	1613, 1621	1503	1254	A+++++, D+
	150	–	3390–3320	–	1615–1623	1498	1256br	A+++, C+++, D+
	200	–	3400–3330	–	1620v br	1498	1262	C+++++, D++
	rehy	–	3390, 3330	3200wsh	1620	1503	1258	A+++++, B^{tr}, D++
K	r.t.	3460–3390vw	3390, 3340	–	1630v br	1503	1255	A+++++, D+
	100	3500–3380sh	3360sh, 3320	3200vw sh	1630–1615	1500	1320vwsh, 1266	C+++++, D+
	200*	–	3360vbr sh	–	1625, 1613	1496	1598, 1320sh, 1266sh	C^{tr}, H^{tr}, Q^{tr}, D+
	rehy*	3460–3380	3370, 3345, 2870vw	3235vwsh	1630v br	1500	1595vwsh, 1320vw	A^{tr}, G^{tr}, Q^{tr}, D+

Table 2 Continued

Inter-layer cation	Temp. / °C	H₂O Hydrophobic water	Benzidine assignments NH₂ stretching	NH···O c. b.	H₂O, NH₂ & ring vib.	Ring vib.	CN stretching	Associations Relative amount is expressed by + tr - trace amounts
Rb	r.t	3450–3400w	3400, 3340		1625v br	1505	1260	A+++++, D+
	100	3500–3380sh	3360sh		1620–1605	1495	1590, 1285sh, 1260	A, C, Q, D+
	200*	3450–3380w			1620–1610	1497	1590	Q+, D+
	rehy*	3470–3350	2870vw br		1630br	1505	1600br	Q+, D+
Cs	r.t.	3405–3445	3400, 3340	3235	1625	1503	1320vwsh, 1263	F+++++, G++, D+
	u.v.	3400–3450w	3460vbr 3390–3320	3220	1620, 1612sh	1500	1263	F+++++, G+, D+
	100		2820br, 2550mbr	3200sh	1620, 1615	1497	1278sh, 1266	C+++, F+++, G+, D+
	200		2885, 2570	3200vbrw	1618–1625	1493	1595, 1313vw	Q+++++, H+, D++, I+
	rehy	3380vbr		3230	1623	1495	1595, 1323vw	Q+++++, G+, D++

r.t. - room temperature; u.v. - room temperature under vacuum; rehy - rehydrated; c.b. - combination band; v - very, w - weak band,

m - medium band, sh - shoulder, br - broad

*Most BEN evaporates, absorptions are very weak and their locations are not accurate
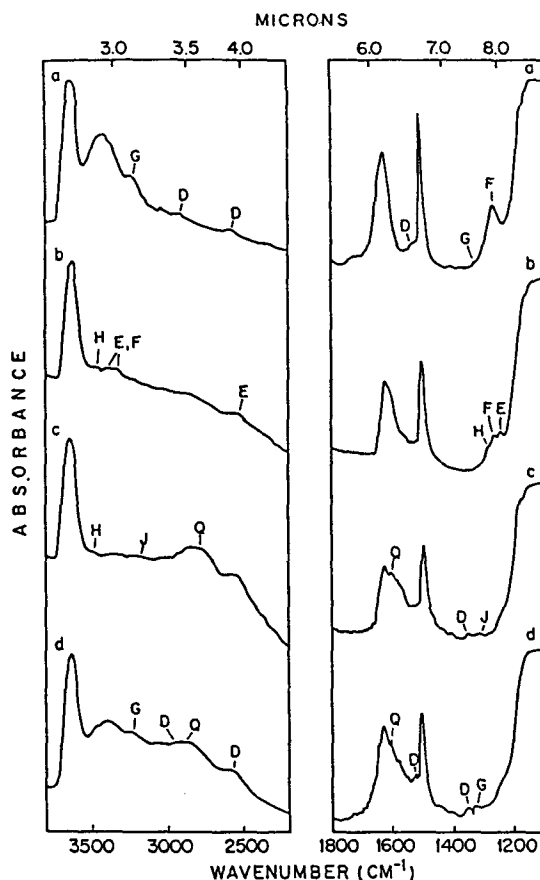
MICRONS

Fig. 3 IR spectra of film of Cs-MONT saturated with BEN (a) air-dried, (b) after heating at
    100°C under vacuum, (c) after heating the film at 200°C, then cooling to room
    temperature under vacuum, (d) rehydrated (48 h at room temperature – ambient conditions)

## Infrared spectrum of BEN adsorbed by Cs-MONT

Cs is unique in being a water structure breaker and in not forming hydrates in
the interlayer space. Cs-MONT has little tendency to retain water or to form com-
plexes with organic molecules. The spectrum of BEN adsorbed by Cs-MONT dif-
fers from those of the other clays mentioned previously. A very broad band occurs
in the NH$_2$ stretching region with a maximum at 3405–3445 cm^{-1} and a shoulder
at 3360 cm^{-1}. This band may represent water molecules which fill this space but
do not form the hydration sphere of Cs and which are non-structured
(hydrophobic water). When the film is treated under vacuum at room tempera-
ture, some of the interlayer water is evolved and two small broad bands, at-

tributed to NH_2, are observed at 3340 and 3400 cm^{-1}. The latter band has a tail ranging up to 3480 cm^{-1}, representing residual hydrophobic water. Another characteristic feature of this spectrum is the location of the C–N stretching band at 1263 cm^{-1}, close to that of the pure solid BEN.

These features which are similar to those previously observed with various anilines adsorbed by Cs-MONT, indicate that these vibrations are only slightly perturbed and that BEN is held in the Cs-MONT interlayer by weak hydrogen bonds, probably to hydrophobic water (type F).

Association Type F
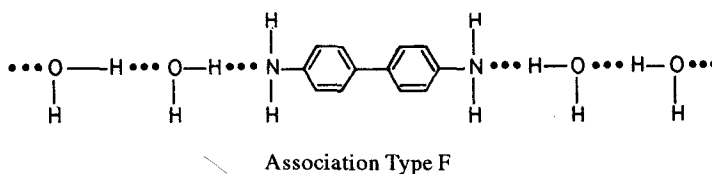
A combination band at 3235 cm^{-1} in this spectrum, is characteristic for Cs-BEN-MONT. This absorption disappears above 100°C and reappears when the thermally-treated film is rehydrated at ambient atmosphere. It can therefore be attributed to hydrogen bonds between BEN and hydrophobic water molecules in which amine groups donate protons to water oxygens (NH···O group) At the same time, these water molecules, which reveal basic properties, are probably hydrogen bonded to the oxygen plane of the MONT layer. The following association between BEN, water molecules and the oxygen plane of the aluminosilicate clay layer is surmised (type G).

Association Type G
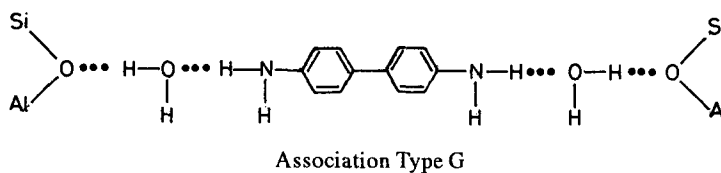
Protonation of BEN in Cs-MONT

A very weak absorption at >1700 cm^{-1} which characterizes protonated water clusters, such as H_3O^+ or $H_5O_2^+$ ions, appears in the spectrum of the film of Cs-MONT. These ions originate from the dissociation of non-structured water molecules. After vacuum treatment this absorption becomes smaller. It disappears with rise in temperature as protons migrate into the alumino-silicate layer. Being very acidic, protonated water clusters may donate protons to BEN molecules. The spectrum of the film before the thermal treatment shows very weak absorptions at

2920, 2600 and 1530 cm^{-1}, indicating that in addition to the benzidine molecules, a very small amount of benzidinium ion is present. The intensity of these bands increases during the thermal treatment, indicating that the amount of this ion increases.

Thermal treatment of Cs-MONT saturated with benzidine

The NH$_2$ and C–N stretching bands persist during the thermal treatment up to 100°C, where a new structure is shown by the appearance of shoulders at ≈3460 and 1278 cm^{-1}. This association is probably obtained without water, monomeric BEN molecules being held in the interlayer by weak van der Waals attractions (type H). In addition, the NH$_2$ becomes band very broad, extending between 3390 and 3320 cm^{-1}. Additional shoulders are detected at 2530 and 1250 cm^{-1}, characterizing the formation of trace amounts of ammonium-amine (association E).

At 150°C the NH$_2$ band is weakened and at the same time a very broad band at 2785–2875 cm^{-1} is observed. At higher temperatures this band progressively gains in intensity. When the film is rehydrated for 24 hours under ambient conditions, this newly formed band shifts to 2845–2915 cm^{-1}. Another characteristic feature of the film at 150°C is the disappearance of the CN band at 1266 or 1278 cm^{-1} and the appearance of a new band at 1595 cm^{-1} [16]. These characteristic features persist at 200°C and also after the rehydration of the film at ambient temperature.

The fact that the rehydration of the film at ambient conditions does not result in a spectrum similar to that of the original sample may indicate that most of the benzidine is oxidized. The oxidation of benzidine results in a semiquinone (blue, II) and a quinoidal cation (yellow, III, association type Q) as well as polymerization products. The changes which are observed in the spectrum are compatible with such a transformation. The perturbation of the NH$_2$ band from >3330 to ≈2850 cm^{-1} indicates that the oxidation product is highly hydrogen bonded and must therefore be positively charged.

Association Type Q

A very small and broad absorption band at 1310–1340 cm^{-1} which appears above 200°C, is probably associated with hydrogen bonds in which the NH$_2$ group of anhydrous BEN donates a proton to the oxygen plane (type J). When the clay is rehydrated the 3235 cm^{-1} band reappears, indicating that the anhydrous

BEN is rehydrated and association G is reformed. However, the intensity of this band is now weaker than before the thermal treatment.

Thermal treatment of K- and Rb-MONT saturated with benzidine

These two ions show both similarity to Li and Na by forming hydrates in the interlayer space, and to Cs by breaking the water structure in the interlayer space.

BEN evaporates during the thermal treatment or is protonated, giving benzidinium. At 200°C or after rehydration the spectra show very weak bands and therefore the locations given in Table 2 are not accurate. The thermal behaviour of BEN adsorbed by Rb-MONT is similar to that adsorbed by Cs-MONT and the organic molecule is oxidized to a quinoidal cation. The thermal behaviour of BEN adsorbed by K-MONT is more complicated. Up to 100°C it behaves like BEN adsorbed by Li- or Na-MONT, the clay dehydrates and the association of type A is converted to type C, as can be seen mainly from the shift of the C–N stretching vibration. At higher temperatures the thermal behaviour is similar to that of Cs-MONT. A weak band appears at 1598 cm^{-1} indicating some oxidation to the quinoidal structure. After rehydration trace amounts of the following associations are detected from the IR spectrum, A, G, Q and the ionic species D.

X-ray diffraction

The basal spacings of the homoionic montmorillonites, either untreated or treated with BEN, are given in Table 3. Non-integral series of reflections were obtained and the peaks of the BEN-clay complexes were broad. Spacings obtained after heating the films of BEN-treated clays at 200°C were always higher than those of the dehydrated mono-ionic montmorillonite, proving that the adsorbed organic molecules are located in the interlayer space.

All air-dried alkali-MONTs form monolayers of water (c spacing of an untreated film <13.6 Å). After being saturated with BEN, Li- and Na-MONT, which adsorb considerable amounts of BEN, show spacings greater than 14.5 Å characteristic of a bi-layer. The other clays show spacings nearer to that of a monolayer. After thermal treatment, the BEN-saturated montmorillonites can be divided into three groups. The basal spacing of the first group (Li-MONT) is determined by association B. The second group (Na- and K-MONT) is determined by association A, whereas the third group (Rb- and Cs-MONT) is determined by the semi-quinone and quinoidal cation.

The aromatic rings of BEN are negatively charged. In association B the negativity of the rings is reinforced; in configurations A, C or Q it is reduced. It is reasonable to assume that the negatively charged clay surface will repel negatively charged organic rings and attract those which are positively charged. In the arrangement of association B the plane of the organic molecule is repelled by the oxygen planes and is consequently inclined at a large angle to them. Water

Table 3 Basal spacings of air-dried and benzidine-treated monoionic montmorillonite (Å)

Inter- layer cation	Untreated MONT		BEN-saturated MONT	
	Air-dried	After heating at 200°C under vacuum	Air-dried	Rehydrated after heating at 200°C under vacuum
Li	12.37	9.80	14.97	15.10
Na	13.59	9.70	16.05	12.89 v br
K	11.85	9.90	12.18	13.48–13.80
Rb	11.70	10.10	11.33–11.62	11.55–11.78
Cs	12.71	11.20	13.00	12.18

v br - very broad

molecules acting as proton acceptors tend to form stronger hydrogen bonds with the oxygen surfaces, due to the weaker bonding within the molecules. The interlayer separation is therefore equivalent to the thickness of two water molecules and is equal to 15 Å [17].

* * *

References

1 S. Yariv, L. Heller, Z. Sofer and W. Bodenheimer, Isr. J. Chem., 6 (1968) 741.
2 S. Yariv, L. Heller and N. Kaufherr, Clays Clay Miner., 17 (1969) 301.
3 L. Heller and S. Yariv, Proc. Int. Clay Conf. Tokyo, 1 (1969) 741.
4 S. Yariv and L. Heller, Isr. J. Chem., 8 (1970) 935.
5 L. Heller-Kallai, S. Yariv and M. Riemer, Clay Miner., 10 (1973) 35.
6 S. Yariv and L. Heller-Kallai, Clays Clay Miner., 21 (1973) 199.
7 P. Cloos, A. Moreale, C. Broers and C. Badot, Clay Miner., 14 (1979) 307.
8 A. Moreale and R. Van Bladel, Clay Miner., 14 (1979) 1.
9 A. Moreale, P. Cloos and C. Badot, Clay Miner., 20 (1985) 29.
10 Y. Soma and M. Soma, Clay Miner., 23 (1988) 1.
11 M. Lacher, S. Yariv and N. Lahav, Thermal Analysis, Proc. 6th Int. Conf. Therm. Anal., Bayreuth, 2 (1980) 319.
12 N. Lahav and S. Raziel, Isr. J. Chem., 9 (1971) 683.
13 D. T. B. Tennakoon and M. J. Tricker, J. Chem. Soc. Dalton Trans., (1975) 1802.
14 S. Yariv, N. Lahav and M. Lacher, Clays Clay Miner., 24 (1976) 51.
15 H. Wolff and D. Mathias, J. Phys. Chem., 77 (1973) 2081.
16 R. E. Hester and K. P. J. Williams, J. Chem. Soc. Faraday Trans., 77 (1981) 541.
17 Z. Sofer, L. Heller and S. Yariv, Isr. J. Chem., 7 (1969) 697.

Zusammenfassung — Li-, Na-, K-, Rb- und Cs-Montmorillonite wurden mit Benzidin gesättigt, diese Organotonkomplexe im Vakuum bis 200°C erhitzt und bei verschiedenen Temperaturen IR-Spektren von ihnen aufgenommen. Benzidin ist zum größten Teil über Wassermoleküle an den Kationen der Trennschicht gebunden, ausgenommen ist Cs-Ton, wo Bindungen an hydrophobem Wasser und an Wassermolekülen, die an der Sauerstoffebene wasserstoffgebunden sind, vorherrschen. Bei der Wärmebehandlung wird Wasser abgegeben und Alkalikationen werden direkt am Benzidin koordiniert. In Cs- und zu einem gewissen Ausmaße auch in Rb- und K-Montmorillonit wird Benzidin bei der Wärmebehandlung zu Semiquinon und einem quinoidalem Kation oxidiert.