Journal of Thermal Analysis, Vol 26 (1983) 49–64

EFFECT OF TEMPERATURE ON THE CONFORMATION OF DIBENZOTROPONE ADSORBED ON MONTMORILLONITES

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(Received July 6, 1982)

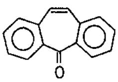
The nature of the adsorption complex formed between dibenzotropone (DBT) and montmorillonite at elevated temperatures is strongly dependent on the interlayer cations. This was shown by electronic and IR spectra, by X-ray diffraction, and by study of the effects of gradual heating of the samples on these analyses. All samples exhibited significant red shifts of the electronic spectra of DBT into the visible range. These red shifts are attributed to two factors, both contributing to the enhancement of the tropylium planar character of DBT: hydrogen-bonding of acidic interlayer water to the carbonyl group, imparting positive charge to the tropone ring; and π interactions between the aromatic moiety and the oxygen planes. The position of the maximum was temperature-dependent for Cu-, Ni-, Al- and Fe-montmorillonites, for which heating (100°) under vacuum increased the red shift. The organic molecule assumes a planar conformation and is oriented parallel to the clay layers. IR spectra confirming this conformational orientation of DBT are discussed.

The basal spacings of the DBT montmorillonite associations depend on the number of water and DBT sheets present in the interlayers. Layers with one or two sheets of DBT and with up to two sheets of water could be distinguished, leading to a maximum spacing of 20.4 Å.

Adsorbent-adsorbate interactions induce spectral changes as compared to solution measurements [1, 2]. These spectral changes, which may include shifts in adsorption bands, changes in extinction coefficients, changes in band shape and the appearance or disappearance of bands, are a direct result of (a) the non-symmetry of the adsorbate environment as compared to a symmetrical solvation shell, resulting in adsorbate conformational changes and (b) chemical and physical irregularities and inhomogeneities of the surface, giving rise to special adsorbate-surroundings interactions not usually found in solution [3].

Adsorption of organic cationic dyes by montmorillonite generally causes distinct shifts of the absorption maxima in the visible spectrum (metachromasy). Bergmann and O'Konski [4] attributed such shifts to dye-dye interactions on the surface of montmorillonite, a reaction similar to the aggregation of dye molecules in aqueous solutions. In these dye clusters π interactions between parallel aromatic moieties result in shifts in the electronic spectrum. Yariv and Lurie [5] showed, however, that spectral shifts also occur with dye-montmorillonite complexes in which only monolayers of the cationic dye methylene blue were sorbed in montmorillonite interlayers. They concluded that the metachromasy is due to π interaction between the aromatic cations and the electron-rich oxygen planes of montmorillonite. According to Yariv, Lahav and Lacher [6], such interactions may increase the stability of the adsorbed species. For example, the cationic radical benzidine blue is converted into benzidine brown within seconds in aqueous solution, whereas it persists when adsorbed on montmorillonite. Short-range interaction between the cationic radical and the oxygen plane stabilizes benzidine blue.

Studies of the mechanism of metachromasy due to adsorption on montmorillonite have so far been confined to cationic entities. Preliminary experiments indicated that a significant red shift occurs on sorption of the neutral molecule dibenzotropone (DBT: 5 H-dibenzo[a, d]cyclohepten-5-one):



A yellow color is developed when this colorless molecule is adsorbed on clay. It is the purpose of the present study to elucidate the nature of the association between montmorillonite and this molecule and the effect of thermal treatment on the staining of various monoionic montmorillonites.

Experimental

Materials

Montmorillonite from Wyoming (Wards #25), exchanged with various cations, was used for the experiments. DBT, recrystallized from ethanol, was kindly supplied by Teva Plantex Pharmaceuticals. Its purity was confirmed by thin-layer chromatography and by NMR. CH_2Cl_2 was redistilled and purified by shaking with concentrated sulfuric acid.

Preparation of specimens

Electronic spectra were recorded of clay samples sedimented on quartz slides from 0.1–1.0% aqueous suspensions. The slides were immersed in a solution of DBT in CH_2Cl_2 for periods ranging from 24 to 48 hours. They were examined in an air-dried state and subsequently after heating under vacuum for 60 minutes at 100°. To prevent dehydration, the samples were coated with paraffin oil. Preliminary experiments indicated that the presence of the paraffin film did not affect the spectrum. Finally the paraffin was dissolved in CH_2Cl_2 and the sample was reexamined after exposure to air humidity.

Infrared spectra were obtained from self-supporting films prepared by sedimentation from 1% aqueous suspension. The films were immersed in 5% solutions of DBT in CH_2Cl_2 for periods ranging from 4 to 19 days (series 1). Samples were examined in an air-dried state and subsequently heated in a vacuum cell. Spectra were recorded at room temperature, 80°, 140° and 200°, and after cooling under vacuum. The film was then withdrawn from the vacuum cell, exposed to air humidity for 24 hours and reexamined.

X-ray diffraction patterns were recorded of the same self-supporting films used for IR spectroscopy (series 1). The films were mounted on glass slides with sellotape. In addition, another series of samples was prepared (series 2) by sedimenting clay samples directly onto glass slides. These were alternately wetted with DBT solution and air-dried throughout a period of about 3 weeks.

Electronic spectra were recorded on a Varian Techtron model 635 spectrograph, IR spectra on a Perkin–Elmer 457 IR spectrometer and X-ray diffraction patterns on a Philips PW 1730 diffractometer.

Results and interpretation

Electronic and infrared spectra and X-ray diffraction patterns were studied. The results will be reported in separate sections, but interpretation was sometimes impossible without having recourse to the conclusions reached via one of the other methods.

Electronic spectra

All the spectra show a slight increase in turbidance in the 450–650 nm range due to light scattered by the solid phase. The ratio $dA/d\lambda$ (where A is the absorbance and λ is the wavelength) is almost constant. Below this range electronic absorption gives rise to an absorption band at 313–316 nm for both adsorbed and non-adsorbed molecules. The electronic spectra of adsorbed DBT, however, do differ from the non-adsorbed species by showing an additional absorption with a maximum at 378–386 nm. This absorption imparts a yellow color to the organo-clay association. Non-adsorbed molecules are colorless. At room temperature the spectrum of DBT-treated Fe-montmorillonite differs from those of the other samples examined.

The spectra recorded after heating to 100° under vacuum can be divided into two groups. The first, the spectra of Cs-, Na- and Mg-montmorillonites, hardly differ from those of the unheated samples. The positions of the maxima remained essentially unchanged, but the wavelength at which the value of $dA/d\lambda$ begins to increase, i.e. the commencement of the electronic absorption band, was shifted from about 435 to 460 nm. This resulted in a slight intensification of the yellow color. In contrast, the spectra of DBT-treated Fe-, Al-, Ni- and Cu-montmorillonites showed appreciable changes after heating. The electronic absorption band commenced at about 530 nm, leading to a strong intensification of the color. With Al- and Fe-montmorillonites

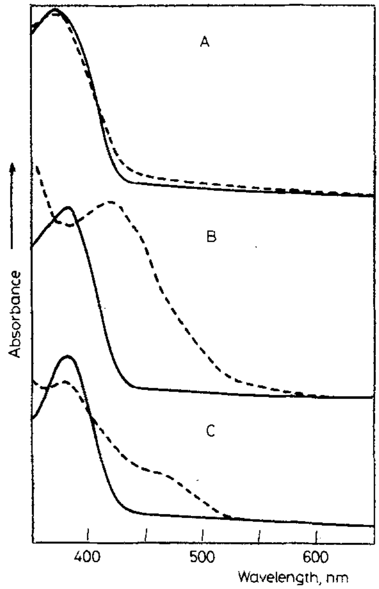


Fig. 1 Electronic spectra of DBT-treated a) Cs-montmorillonite, b) Ni-montmorillonite, c) Fe-montmorillonite, ——— RT; — — — sample heated at 100°C under vacuum, covered with paraffin oil and cooled to RT

the intensity of the band at about 380 nm decreased and a shoulder appeared at about 480 nm. With Cu- and Ni-montmorillonites the maximum of the band was shifted to higher values (Table 1 and Figure 1).

After removal of the paraffin coating and rehydration of the samples in air the spectra of all the samples were identical with those of the corresponding air-dried specimens. A red shift of the type observed on adsorption, which was intensified on

Table 1 The effect of thermal treatment on the absorption maximum (in nm) of monoionic montmorillonite treated with DBT

Exchangeable cation	Absorption maximum, nm	
	Room temperature	Heated at 100°
Na	378	380
Cs	382	378
Mg	382	388
Cu	386	410
Ni	385	420
Al	385	380, 470*
Fe	380	380, 480*

*shoulder

heating, may be due to a change in the configuration of the molecule, to interaction between the adsorbed molecules and the clay surfaces, or to both these effects.

On heating above 100° the specimens turned dark due to graphitization of minor amounts of organic molecules. It was therefore impossible to record electronic spectra of samples heated above 100°.

Infrared spectra

Some features of the spectra of self-supported films of specimens of series 1, recorded under ambient conditions, are presented in Table 2. The corresponding bands in the spectra of DBT in dilute and concentrated CH_2Cl_2 solutions and in a KBr disk are included for comparison.

Absorption bands at 3300–3400 cm^{-1} and 1620–1625 cm^{-1} in all the spectra indicate that all the samples contain water. The vibration frequency of the C = O group (band A) is reduced from 1640 cm^{-1} for DBT in dilute solution to 1600–1605 cm^{-1} for molecules adsorbed on montmorillonite. The differences in band A (the C = O absorption) between samples saturated with different cations are insignificant, indicating that DBT is similarly bonded in all the specimens, probably by H-bridges to water molecules.

Several changes occur in the skeletal vibrations on sorption by montmorillonite. Band B is reduced from 1593 cm^{-1} in dilute solution to 1575 cm^{-1} on clay surfaces. Band C is absent from the spectrum of DBT in dilute solution but occurs in those of DBT in concentrated solution, in KBr disks and in the adsorbed state. Band C, which is intense and sharp in the spectrum of DBT in KBr disks, becomes very weak and broad on adsorption of DBT on montmorillonite. Bands E, F and H occur as doublets in the spectra of DBT in solution or in KBr disks, but as singlets in those of the adsorbed species.

The perturbations of the skeletal vibrations on sorption indicate that some interaction occurs between the skeleton of the organic molecules and the clay surfaces. DBT is non-planar in the unconstrained form [7], which causes bands E, F and H to appear as doublets. Their conversion to singlets on adsorption of DBT by clays suggests that the molecule assumes an approximately planar configuration in the clay interlayers.

The spectrum of DBT-Fe-montmorillonite differs from the other samples in several respects:

1) there is a base-line shift towards lower transmittance from 1750 cm^{-1} downwards;
2) band B is very broad and overlaps band C;
3) the maximum of band B appears at 1560 cm^{-1}, i.e. at an appreciably lower wavelength than with other specimens;
4) band D shows a tail towards lower wavenumbers;
5) band E is broad compared with the corresponding band in other spectra.

These features indicate that at least some of the DBT sorbed by Fe-montmorillonite is bonded differently from that in other samples.

Table 2 Characteristic absorption bands (in cm^{-1}) of DBT in CH_2Cl_2 solutions, in a KBr disc and adsorbed by various monoionic montmorillonites

Band	Assignment	CH_2Cl_2 solution		KBr disc	Adsorbed by monoionic montmorillonite		
		Dilute	Concentrated		Na, Cs, Mg, Cu, Ni	Al	Fe
A	C = O	1640	1630	1634	1606	1600	1600
B		1593	1590	1588	1576	1575, 1560 sh 1540 sh	1560 v, br
C			1480 1465	1480 1460 sh	1475	1480	1480
D		1420	1420	1425 w 1415	1422	1424	1420
E		1322 1305	1320 1303	1315 1300	1328 * 1310 sh *	1330 1310 sh	1330 1310 sh
F		810 804	808 803	807 793	807	803	800
G				770	775 vw	775 vw	775 vw
H		765– 710	765– 710	737 723	726	726	726
I		690	675	692 677	678 sh	675 v, br	665

*These absorptions appear at 1320, and 1305 and 690 cm^{-1} in the spectrum of Cs-montmorillonite

Abbreviations: sh — shoulder, w — weak, br — broad, v — very

The spectrum of DBT-treated Al-montmorillonite has many features in common with that of Fe-montmorillonite. Band B has a shoulder at 1560 cm^{-1}, is very broad and shows some overlap with band C.

Polarized spectra

When DBT-saturated films of Na-, Cs-, Mg-, Ni-, Cu- and Al-montmorillonites were tilted by 45° with respect to the IR beam, changes occurred in the relative intensities of some skeletal vibrations. The intensity of band E increased considerably relative to that of B (Table 3). The magnitude of band A remained approximately unchanged relative to that of B, but it is difficult to estimate its intensity due to overlap of the bending vibrations of water. These features were observed with specimens exposed to ambient conditions both before and after heating under vacuum.

Cs-montmorillonite saturated with DBT gave rise to a 12.4 Å spacing (Table 4), corresponding to a monolayer of organic material arranged with the aromatic rings approximately parallel to the clay surfaces. It follows that band B is an in-plane and E an out-of-plane vibration. The similarity of the polarized spectra demonstrates that most or all of the organic molecules in the other specimens with larger basal spacings also assume an orientation parallel to the clay surfaces. Since the intensity of band A relative to that of B was fairly independent of the angle of incidence of the beam, the $C = O$ group must also be oriented approximately parallel to the clay sheets.

The spectra of DBT-treated Fe-montmorillonite did not show any significant changes with orientation of the films relative to the incident beam. It appears that when Fe is present in the interlayers, DBT assumes different orientations. The polarized spectra alone cannot provide any information beyond the fact that an arrangement of the organic molecules parallel to the clay surfaces cannot predominate.

Table 3 Ratios of intensities of band *E* (I_E) and band *B* (I_B) in IR spectra of DBT heated montmorillonites recorded with the beam perpendicular (I) and parallel (II) to the clay sheets

Exchangeable cation	I_E/I_B (I)	I_E/I_B (II)	% *
Na	0.54	0.64	19
Cs	0.45	0.56	24
Mg	0.70	0.83	19
Cu	0.74	0.86	16
Ni	0.68	0.85	25
Al	0.86	0.93	8
Fe	–	–	–

*% increase of I_E relative to I_B resulting from tilt of specimen

Table 4 Basal spacings of DBT heated montmorillonites, Å

Cation	Series 1			Series 2	Series 3	
	air dried	56% RH	200° + vacuum	air dried	air dried	200° + vacuum
Na	19 vs 10.5 s 6.48 w br 4.96 w br	18 br 10.3 br 6.45	11.7 s, vbr 6.45 vw, br 4.9 vw, br	12.4 *	17.7 vs 12.5 sh 10.6 s 6.41 w	19.2 vs, br 10.0 vs. as 6.43 vw, br 4.95 w
Mg	18.2 vs 10.0 m, br 6.63 vw 4.99 w	18.6 vs 10.1 m, br	20.2 *	18.4 s 12.0 vw 10.2 vw 6.91 vw, br		
Cu	19.8 vs, br 12.7 sh 10.5 vs, br	20.2 vs 12.3 sh 10.6 vs, br	20.2 *	19.6 vs, br 12.4 sh 11.5 s, br 6.48 w, br		
Ni	20.2 *	20.2 *	20.2 *	18.8 vs 12.0 sh 10.2 mw 6.48 w, br		
Fe	20.15 *	20.4 *	20.2 *	20.15 *		
Al	20.1 *	20.0*	20.2 *	20.0 *		
Cs					12.4 *	11.9 vs 6.06 vw, br 5.30 vw, br

* Integral series of reflections.

Abbreviations: s — strong, m — moderate, w — weak, v — very, sh — shoulder, br — broad, as — asymmetric

They are compatible with an arrangement

a) with part of the DBT molecules oriented with their aromatic rings parallel to the clay surfaces, while others assume an approximately perpendicular orientation, and
b) with the organic molecules tilted at a definite angle or randomly to the clay surfaces.

In view of the similarity of the basal spacings of DBT-saturated Fe-montmorillonite to those of other samples, the first alternative seems more probable.

Changes in the IR spectra on heating

With all the samples studied the intensities of the bands at about 3400 cm^{-1} and 1620–1625 cm^{-1} decreased simultaneously and progressively on heating, but weaker bands persisted throughout. This supports the assignment of the band at 1620–1625 cm^{-1} to deformation vibrations of hydrogen-bonded water and demonstrates that the presence of some water is essential for the organo-clay complex.

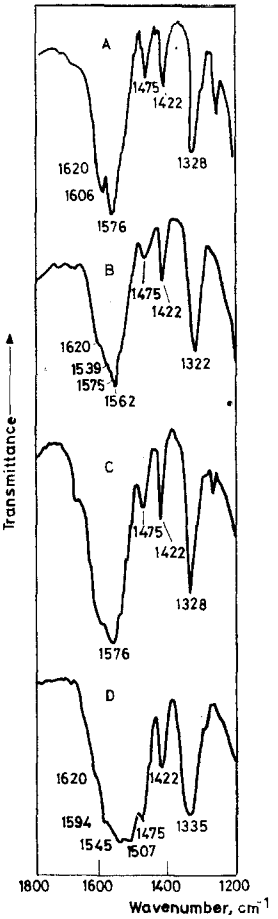
The position of band A was shifted on heating, from 1600–1606 cm^{-1} to 1595–1598 cm^{-1}, except with Fe-montmorillonite, where it appeared at 1592 cm^{-1}. This small shift, which is practically independent of the interlayer cations, together with the fact that some water molecules are retained throughout the entire thermal treatment, indicates that the $C=O$ groups of DBT remain coordinated to water molecules even at 200° under vacuum. The small shift in the absorption bands may be due to the increased acidity of the remaining water molecules.

Band B became broad and was shifted to lower wavenumbers. This may reflect an increase in π interaction between the aromatic moiety and the clay surfaces. The extent of the broadening and the temperature at which it occurred depend on the interlayer cations. In most spectra it led to overlap with band C, resulting in a shift of the base-line of band C towards lower transmittance (Figs 2–5). With some specimens the intensities of bands E and H were enhanced on heating.

With DBT-Na-montmorillonite these spectral changes were observed at 140°, but became more pronounced at 200°. With DBT-Mg-montmorillonite they occurred already at 80°, but were small and remained small even at higher temperatures. With Ni-montmorillonite they were appreciable at 80° and increased further on heating (Fig. 2).

DBT-Cu-montmorillonite showed drastic changes at 80°. Band B was very broad and the base-line of band C was shifted strongly towards lower transmittance. The maxima of bands C and D were displaced to lower values. At 140° these changes were still evident, though to a lesser extent. They disappeared when the film was heated at 200° (Fig. 3). These features may indicate that π interaction between interlayer Cu ions and DBT occurs in clay interlayers on heating, but that the complex is destroyed at more elevated temperatures.

With DBT-treated Fe-montmorillonite band B, which was broad in the room-temperature spectrum, was broadened further on heating. The intensities of bands D and H were greatly increased relative to those of other bands. The tail of band D



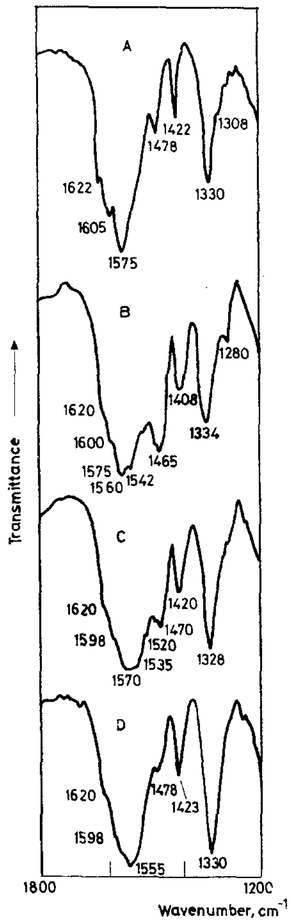
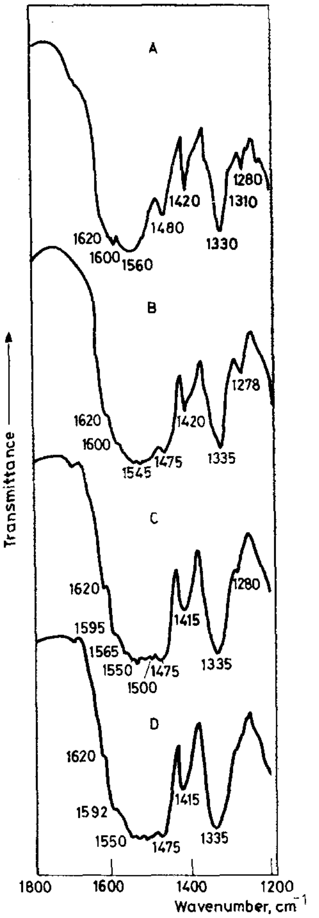


Fig. 2 Infra-red spectra of DBT-trated a) Na-montmorillonite, RT; b) Na-montmorillonite, 200°C, vacuum; c) Ni-montmorillonite, RT; d) Ni-montmorillonite, 200°C, vacuum

Fig. 3 Infra-red spectra of DBT-Cu-montmorillonite a) RT; b) 80°C, vacuum; c) 140°C, vacuum; d) 200°C, vacuum

towards lower wavenumbers became very pronounced. Band E was broadened and shifted to higher wavenumbers (Fig. 4). The spectra of heated samples of Al-montmorillonite became progressively more similar to those of the corresponding Fe-exchanged samples.

The principal change observed in the spectra of DBT-Cs-montmorillonite on heating at 80° is the attenuation of the deformation and stretching bands of water at 1620–1625 and 3400 cm^{-1}, respectively. At higher temperatures a new peak de-



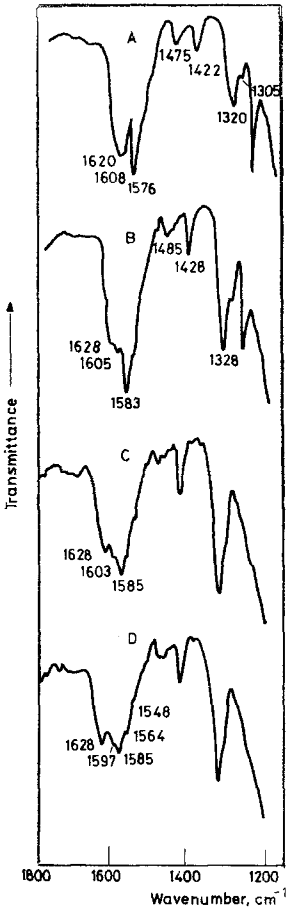


Fig. 4 Infra-red spectra of DBT-Fe-montmorillonite a) RT; b) 80°C, vacuum; c) 140°C, vacuum; d) 200°C, vacuum

Fig. 5 Infra-red spectra of DBT-Cs-montmorillonite a) RT; b) 80°C, vacuum; c) 140°C, vacuum; 200°C, vacuum

veloped, at 1628 cm^{-1}, while band A decreased in intensity and was shifted from 1607 to 1597 cm^{-1}. Simultaneously, band B was displaced to 1585 cm^{-1} and two weak bands appeared at 1564 and 1548 cm^{-1} (Fig. 5). It seems reasonable to assign the band at 1628 cm^{-1} to absorption of C = O groups not coordinated to water molecules, and the band at 1585 cm^{-1} to skeletal vibrations of molecules which do not form π interactions with the oxygen sheets of interlayer cations or hydroxides. The bands at 1597, 1564 and 1548 cm^{-1} (Fig. 5), on the other hand, may be assigned to C = O and skeletal vibrations of molecules which are hydrogen-bonded with water molecules and participate in π interaction with the oxygen planes of the clay. The spectrum of the sample cooled under vacuum was identical with that recorded at

200°, confirming that the spectral features discussed depend not on the temperature, but on the amount of water present in the interlayers.

After cooling and exposure of the specimens to ambient conditions, DBT-treated Mg-, Cu- and Ni-montmorillonites gave rise to spectra that were identical with those recorded before heating. The intensities of the spectra of DBT-treated Cs- and Na-montmorillonites indicated that some of the organic material was lost on heating, but the spectra were otherwise unchanged. The spectra of DBT-treated Al- and Fe-montmorillonites were identical at this stage, but slight differences were observed between the spectra of DBT-Fe-montmorillonite before and after the thermal treatment. Bands D and E were sharper and the base-line shift below 1600 cm^{-1} was smaller than that observed during the first stage. Band B was narrower than in the original spectrum and there was less overlap with band C.

It appears that the main change that occurs on heating all the specimens is loss of water, though bridging water molecules persist throughout. Only with Cs- and Na-montmorillonites was some DBT lost on heating. With Fe-montmorillonite some DBT is differently bonded from that in other specimens and this difference persists on heating, though redistribution of the differently arranged molecules appears to occur. Changes that take place in the Al clay on heating lead to similar DBT associations. This suggests that these are associations formed by π interaction of the organic molecules with Fe- or Al-hydroxides, which, at least in part, are originally present in Fe-montmorillonite, but in Al-montmorillonite are formed on heating, which causes hydrolysis of interlayer Al. These associations are expected to be sensitive to the temperature and degree of rehydration of the specimens, as was indeed observed.

X-ray diffraction

Table 4 shows the basal spacings of the specimens after various treatments. When the reflections are non-integral, the first four are listed.

It is evident that the interlayer spacing depends on the exchangeable cation. Interpretation of the X-ray data on the basis of the powder patterns alone is difficult and other information must be taken into consideration. Infrared spectra indicated that

a) the organic molecules are oriented either parallel to or at a small angle to the clay surfaces, and
b) the $C = O$ groups are bound to water molecules and are also approximately parallel to the clay surfaces.

Bearing these considerations in mind, arrangements A, B and C can be envisaged, giving rise to repeat distances of approximately 20, 17.5 and 12.5 Å, respectively (Fig. 6). Basal spacings in the 17.7–19.2 Å region with non-integral higher orders can be attributed to random interstratification of 17.5 and 20 Å layers. However, this cannot explain the additional strong or moderate, generally broad reflection observed in the 10–11 Å region with some of the specimens. This reflection may arise from a combination of $d_{002} = 10$ Å and $d_{001} = 12.5$ Å. The specimen must then be regarded as being composed of interstratified layers of types A, B and C. The presence of some non-expanded layers ($d \approx 9.6$ Å) cannot be excluded.

DBT-Cs-montmorillonite heated under vacuum and exposed to air gave rise to a strong reflection at 11.7–11.9 Å, but no reflections at lower angles. The reflection at ~ 11.8 Å is probably due to interstratification of 12.4 Å and non-expanded layers, in agreement with the conclusion drawn from the IR spectra that some DBT is lost on heating.

The samples listed in Table 4 can be divided into four groups according to their sorption of DBT:

a) Al-and Fe-montmorillonites: These gave rise to integral series of reflections corresponding to $d \approx 20$ Å i.e. to type A complexes, under all the experimental conditions studied. No changes in the X-ray patterns occurred when the specimens were left to stand in air for three weeks.

b) Mg-, Cu- and Ni-montmorillonites: Type A complexes were formed after heating under vacuum and exposure to air and with Ni-montmorillonite also after prolonged exposure to DBT solution (series 1). Interstratification of complexes of types A, B and C was observed with the other samples. Cu-montmorillonite exhibited a tendency to develop non-interstratified regions of type C, in accordance with the preference of Cu for planar coordination.

c) Na-montmorillonite: Sorption of DBT by this sample depends on the experimental conditions. After prolonged immersion interstratification of A, B and C complexes was obtained (series 1). The clay retained most of the DBT on heating and the contribution of type A to the mixed layer arrangement was increased relative to the air-dried specimen. After intermittent exposure and drying (series 2), only type C was obtained.

d) Cs-montmorillonite gave rise to a type C complex on exposure to DBT. After heating in vacuum and exposure to air, layers of type C were interstratified with non-expanded layers.

The arrangement of DBT in montmorillonite interlayers is thus directly dependent on the polarizing ability of the exchangeable cations. With strongly polarizing cations arrangement A occurs, with two sheets of water and two sheets of DBT. With decreasing polarizing power there is an increasing tendency to develop arrangements of type B with two sheets of water and one of DBT, and of type C with DBT and water molecules in the same sheet only. Thermal treatment promoted the formation of type A layers. With cations of still lower polarizing ability the tendency to sorb and retain DBT is reduced and the layers tend to collapse. With Cs-montmorillonite expansion beyond a single interlayer sheet of DBT and water was not observed.

Discussion

Synthesis of the results obtained by the various methods of investigation led to the following concepts:

The IR spectra indicate that DBT is sorbed by hydrogen-bonding of the $C=O$ groups to interlayer water molecules. This imparts an effective positive charge to the organic molecules. The IR spectra also show that the molecules assume an approximately planar configuration. The 12.4 Å basal spacing of DBT-treated Cs-montmorillonite necessitates an arrangement of the organic molecules parallel to and adjacent to the clay surfaces. A bathochromic effect, manifested by the yellow coloration of the specimens and by shifts in the absorption maxima of the visible spectra, indicates that charge transfer occurs. This is confirmed by the perturbation of the skeletal vibrations observed in the IR spectra. The similarity of the visible and polarized IR spectra of DBT-Cs-montmorillonite to those of the other samples indicates that the organic molecules are similarly oriented in all the samples despite the larger basal spacings. Associations of types A and B (Fig. 6) were postulated in accordance with the observed basal spacings. The more polarizing the interlayer cations, the greater the tendency to form associations of type A.

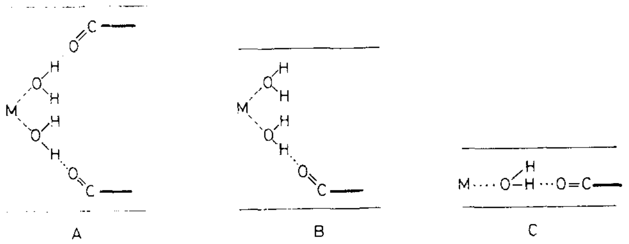


Fig. 6 Schematic sketch of configurations A (≈ 20 Å), B (≈ 17.5 Å) and C (≈ 12.5 Å)

The effects observed on heating the specimens are consistent with these concepts. The basal spacings of the specimens either remained unchanged or were increased after heating, confirming that the 20 Å basal spacing is due to a rigid arrangement of molecules in the interlayers and not merely to sheets of water and DBT molecules. If only sheets of more or less loosely bound molecules were present, heating up to 200° under vacuum would be expected to drive off some of the interlayer material, leading to smaller basal spacings. In fact, the IR spectra show that loss of water occurs, but that only Cs- and to a lesser extent Na-montmorillonite lose DBT on heating. Some water is retained throughout; since the residual water molecules are more acidic, they are expected to form stronger H-bonds. Associations of type A therefore tend to develop. These are stable and persist on rehydration of the specimens.

The spectra of DBT-Fe-montmorillonite differ from the rest. DBT-Al-montmorillonite resembles the corresponding Fe-exchanged samples after heating in vacuum. On the basis of the similarities of these specimens to other samples on the one hand and the differences, in particular the lack of polarization of the IR spectra, on the other, it was inferred that although the 20 Å basal spacing is determined by type A assemblages, some DBT molecules assume other orientations in the clay interlayers. This may be due to electron transfer interactions between H-bonded DBT and interlayer iron or aluminium hydroxides. It appears that heating DBT-Al-montmorillonite causes hydrolysis which renders such interactions possible. With Cu-montmorillonite π complexes between DBT and interlayer Cu^{2+} ions may be formed on heating, but these are destroyed at higher temperatures.

To summarize, DBT exhibits a strong tendency to π bonding with the oxygen surfaces. Unconstrained DBT molecules are non-planar. The seven-membered ring is in the boat form and the two benzene rings are inclined at 39° to each other [7]. It appears that H-bonding with water molecules imparts a positive charge to the organic molecules and enhances the aromatic tropylium character of the central tropone ring. π interaction with the oxygen surfaces (and possibly also with interlayer iron or aluminium hydroxides and with Cu^{2+} ions) stabilizes the planar configuration. These interactions and the concomitant intensification of the color of the specimens are enhanced by heating, due to the high acidity of the remaining water molecules, which confer a greater effective positive charge on the aromatic moiety.

It is significant that DBT-Cs-montmorillonite, which loses most of its interlayer water on heating up to 200°, differs from the other samples. Only part of the DBT molecules are hydrogen-bonded after heating at 200° and give rise to π interactions. Accordingly, additional bands corresponding to skeletal vibrations, unperturbed by π bonding, appear in the IR spectra. The DBT molecules are less firmly retained, as shown by the lower intensity of the IR spectra and the basal spacing of 11.9 Å, which indicates that some interlayers have entirely collapsed. These observations provide additional confirmation of the crucial role of water: only those DBT molecules that are hydrogen-bonded to water can undergo π interactions with the oxygen surfaces.

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D. A. thanks the Bergmann Foundation for partial support of this study.

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Zusammenfassung — Die Natur der von Dibenzotropen (DBT) und Montmorillonit bei erhöhter Temperatur gebildeten Adsorptionskomplexe ist stark vom Zwischengitterkation abhängig. Dies konnte anhand von Elektronen- und IR-Spektren sowie röntgendiffraktometrischen Untersuchungen der insbesondere stufenweise erhitzten Adsorptionskomplexe gezeigt werden. Bei allen Proben wird eine signifikante Rotverschiebung der Elektronenspektren des DBT in den sichtbaren Bereich beobachtet. Diese Rotverchiebungen werden zwei Faktoren zugeschrieben, die beide zur Verstärkung des planaren Tropylium-Charakters von DBT beitragen: Wasserstoffbrückenbindung mit positiver Ladungsverschiebung zum Troponring und π-Wechselwirkungen zwischen der aromatischen Hälfte und den Sauerstoffebenen. Bei Cu-, Ni-, Al- und Fe-Montmorillonit ist die Lage des Maximums abhängig von der Temperatur, wobei Erhitzen (100°) im Vakuum die Rotverschiebung verstärkt. Das organische Molekül nimmt eine planare Konformation an und ist parallel zu den Schichten orientiert. IR-Spektren, die diese konformationelle Orientierung des DBT bestätigen, werden diskutiert. Die basalen Schichtgitterabstände der DBT-Montmorillonite hängen von der Zahl der Wasser- und DBT-Lagen im Zwischengitterraum ab. Schichten mit einer oder zwei Lagen von DBT und mit bis zu zwei Wasserlagen konnten unterschieden werden, wobei der maximale Schichtgitterabstand 20.4 Å betrug.

Резюме — Природа адсорбционного комплекса, образующегося при повышенных температурах между дибензтропоном (ДБТ) и монтмориллонитом, сильно зависит от межслоевых катионов. Это было показано электронными и ИК-спектрами, рентгено-диффракционным анализом, а также при изучении эффектов, установленными этими методами при постепенном нагреве образцов. Для всех образцов наблюдается красный сдвиг полос поглощения ДБТ в видимую область. Эти красные сдвиги приписаны двум факторам, обусловленными увеличением планарности тропилий-катиона в ДБТ: образование водородной связи межслоевой водой кислотного характера с карбонильной группой, что приводит к переносу положительного заряда на кольцо тропона и π-взаимодействием между ароматической составляющей и кислородными плоскостями. Положение максимума поглощения для монтмориллонитов меди, никеля, алюминия и железа зависит от температуры и для которых нагревание (100°) под вакуумом увеливает красный сдвиг. Предполагается, что органическая составляющая является планарной конформацией и ориентирована параллельно слоям минерала. Обсуждены ИК-спектры, подтверждающие такую конформационную ориентацию ДБТ. Основные расстояния в ассоциатах ДБТ — монтмориллонит зависят от числа молекул воды и листами ДБТ, расположенными между слоями. Слои с одним и двумя дистами ДБТ и с дистами воды до двух, могут быть разделены, давая максимальное расстояние в 20,4 Å.