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ORIGINAL CONTRIBUTION

Thermo-infrared-spectroscopy analysis of the interaction of naphthylammonium–montmorillonite with sodium nitrite

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Abstract The deep blue organoclay color pigment (OCCP), naphthylazonaphthylammonium–montmorillonite, was synthesized in an aqueous suspension by treating montmorillonite with naphthylammonium chloride followed after 2 h by $NaNO_2$. The reddish-brown azo dye naphthylazonaphthylamine (commercial name “Solvent Brown 3”) was synthesized in an aqueous solution in the absence of clay from the same reagents. X-ray diffraction and thermo-infrared (IR) spectroscopy of organoclay prepared by treating montmorillonite with naphthylammonium chloride showed that the organoclay contained two types of tactoids with intercalated naphthylammonium cations and with naphthylammonium–naphthylamine associations. Naphthylammonium clay was obtained after thoroughly washing the latter organoclay. IR spectra of naphthylamine, naphthylammonium chloride, naphthylammonium clay, naphthylammonium–naphthylamine clay (with some naphthylammonium-clay), OCCP, and Solvent Brown 3 in KBr disks were recorded before and after thermal treatments up to 120 °C. IR spectrum of the OCCP was similar to that of Solvent Brown 3. An NH_3^+ group was identified in the spectrum of the OCCP but not in that of Solvent Brown 3. In the latter spectrum, an NH_2 group was identified, suggesting that the amine group of the azo dye in the OCCP was protonated. It appears that the difference in color between OCCP and Solvent Brown 3 resulted from the protonation of the azo molecule in the interlayer space of the clay.

Keywords Azo pigments · IR spectroscopy · Montmorillonite · Naphthylammonium–montmorillonite · Naphthylammonium–naphthylamine–montmorillonite · Naphthylazonaphthylamine · Naphthylazonaphthylammonium–montmorillonite · Organo clay color pigment (OCCP) · Sodium nitrite · Solvent brown 3

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Introduction

The interaction in aqueous systems of an anilinium cation, or its derivative, with a second aromatic molecule, which contains a powerful electron-releasing group, such as –O–H, –NHR, or $–NH_2$, followed by sodium nitrite results in the formation of a very intense colored azo dye [1–3]. We showed recently that the treatment with sodium nitrite of white anilinium–montmorillonite loaded by a second aromatic compound with an electron-releasing group resulted in an intense coloration of the clay. We assumed that an azo dye was synthesized in the clay interlayer space [4, 5]. Coloration of montmorillonite was also observed when different anilinium derivatives served as the exchangeable cation of the clay [6].

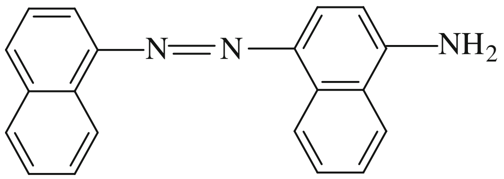
Organoclay color pigments (OCCP) are obtained by the adsorption of organic colorants into the interlayer space of smectite minerals, for example, by the adsorption of cationic dyes [6–10]. The azo clay complexes obtained by the dye synthesis inside the clay interlayer can be considered as OCCP. They are insoluble in solvents but are dispersible [2, 11]. Preliminary experiments showed that they could be used as surface coaters in the form of extremely fine particles in the range of 1 μm [6].

In most cases, the color of the azo clay complexes was similar to those of the azo dyes synthesized in aqueous media, in the absence of the clay [6]. An exception was that obtained from naphthyl-1-ammonium–montmorillonite treated with sodium nitrite, showing a color, which differed from the color of the azo dye obtained in the absence of the clay. The former organoclay was deep blue whereas the latter 4-(1-naphthylazo)-1-naphthylamine (Scheme 1), known by its commercial name Solvent Brown 3, was first red but after a few hours, became reddish-brown [12]. Adding a few drops of HCl to an aqueous suspension of Solvent Brown 3 turned the particles to grey-blue [4]. Thus, we assumed that the intercalated dye was protonated.

Recently, we described the thermo-XRD analysis of naphthylazonaphthylammonium–montmorillonite (OCCP) synthesized from naphthylammonium–montmorillonite and sodium nitrite [4, 5]. In this synthesis, naphthylammonium cations serve as the anilinium cations as well as the second aromatics, which contain powerful electron-releasing groups. The samples were heated in air at 360 °C and diffracted by X-ray. Most of the pigment did not collapse but became black at that temperature due to the formation of charcoal. Naphthylammonium–montmorillonite, on the other hand, collapsed at 360 °C. This proved that the synthesized dye was located in the clay interlayer space [13, 14].

Steps in the synthesis of naphthylazonaphthylammonium clay were previously described together with the relevant chemical equations [4]. In the first step, the clay is treated with naphthylammonium chloride. At first, naphthylammonium cations are adsorbed by cation exchange mechanism, followed by adsorption of excess naphthylamine by ion–dipole interaction. Curve-fitted X-ray diffractograms of the products of the first step showed two types of tactoids. We assumed that in one type, naphthylammonium cations intercalated the tactoids and in the second type, naphthylammonium–naphthylamine associations intercalated. Infrared (IR) spectroscopy is useful to examine this assumption. For this purpose, spectra of unwashed and washed samples were recorded. Spectra of washed samples should be diagnostic for naphthylammonium clay whereas those of unwashed samples for clay rich with naphthylammonium–naphthylamine associations [15, 16].

In the second step of the synthesis, sodium nitrite is added to the naphthylammonium–montmorillonite system. In the interlayer, nitrite ions are protonated by part of the ammonium cations to give nitrous acid and naphthylamine. The reaction between nitrous acid and the rest of naphthylammonium cations, known as diazotization, results in naphthalenediazonium–montmorillonite. The unstable naphthalenediazonium is coupled with naphthylamine to form 4-(1-naphthylazo)-1-naphthylamine dye. Because the pigment is blue, we assume that in the acidic environment of the clay interlayer, the azo dye is protonated by protons released during the coupling stage. IR spectroscopy is reliable to prove the dye synthesis and its protonation.



Scheme 1 4-(1-naphthylazo)-1-naphthylamine

Experimental

Materials

Na-montmorillonite (Wyoming bentonite) from Upton, WY, USA, purchased from Ward's National Science Establishment, Inc., was ground in an agate mortar, passed through an 80-mesh sieve and suspended in distilled water. After 24 h, the clay fraction (particle size <1.5 μm [17]) was separated from the impurities by decantation. Distilled water was added to the decanted fraction to obtain 1.0 wt.% suspension. Sodium nitrite (98.6%) was supplied by Baker A R Chemical Company. Naphthyl-1-amine and naphthyl-1-ammonium chloride (98%) were supplied by Merck. They were used as received.

Methods

The preparation of samples for the thermo-IR-spectroscopy analysis

Naphthylammonium–naphthylamine–montmorillonite Three samples were prepared. In each sample to 25.0 ml of an aqueous suspension of Na-montmorillonite (1.0 wt.%), 1.5, 2.5, or 4.0 ml of 1.0×10^{-1} M naphthyl-1-ammonium chloride aqueous solution was slowly added (60, 100, or 160 mmol naphthylammonium chloride per 100 g clay, respectively). Each suspension was treated for 10 min in an ultrasonic bath (Medent supersonic cleaner mini DG-1). After 1 day aging, the clay settled to a volume of about 1.0 ml and the upper supernatant was decanted in order to remove the excess of naphthylammonium chloride. The 1.0-ml concentrated clay suspensions were air-dried on glass slides. The solids were slowly settled with a preferred orientation for the X-Ray diffraction (Philips Automatic Diffractometer, PW 1710) [13, 14]. Air-dried material was scratched from the glass slides for the thermo-IR-spectroscopy analysis. As in our previous study [4, 5], they were labelled blank-I, blank-II, and blank-III, respectively.

Naphthylammonium–montmorillonite Three samples were prepared by washing naphthylammonium–naphthylamine–montmorillonite before they were dried with triple-distilled water. Two samples were prepared from blank-I and blank-II by thoroughly washing from excess amine and chloride. They were labelled NM-I and NM-II, respectively. Carbon analysis of NM-II showed that it contained 67.5 mmol ammonium per 100 g clay [4]. A third sample was prepared from blank-III by slightly washing, leaving behind some amine, probably as ammonium–amine. It was labelled NM-III. The samples were air-dried on glass slides and scratched for the thermo-IR-spectroscopy analysis.

Naphthylazonaphthylammonium–montmorillonite Two samples were prepared by adding 2.5 or 4.0 ml $NaNO_2$

aqueous solution (1.0×10^{-1} M) to 25 ml of the aqueous suspensions of blank-II and blank-III, respectively, 2 h after they had been prepared to obtain a molar ratio [$NaNO_2$]/[$C_{10}H_7NH_3$] of 1.0 in both cases. Each suspension was treated for 10 min in an ultrasonic bath before and after adding $NaNO_2$. After 1 day aging, the clay settled to a volume of about 1.0 ml, and the upper supernatant was decanted in order to remove the excess of naphthylammonium chloride and $NaNO_2$. The settled clay suspension was poured on a glass slide. Air-dried material was scratched from glass slides for the thermo-IR-spectroscopy analysis. As in our previous study [5], they were labelled pigment B-II and pigment B-III, respectively.

Solvent Brown 3 (naphthylazonaphthylamine) The azo dye Solvent Brown 3 (naphthylazonaphthylamine) was prepared in an aqueous solution cooled in an ice bath. To 25.0 ml of triple-distilled water, 2.5 ml of naphthylammonium chloride aqueous solution (1.0×10^{-1} M) were added, followed by 2.5 ml of $NaNO_2$ aqueous solution (1.0×10^{-1} M), to obtain a molar ratio [$NaNO_2$]/[$C_{10}H_7NH_3$] of 1.0. After 1-day aging, crystals of the azo dye settled to a volume of about 1.0 ml. The upper supernatant was decanted to remove excess naphthylammonium chloride and $NaNO_2$. The 1.0-ml concentrated azo dye suspension was poured on a glass slide. Air-dried material was scratched from the glass slide for the thermo-IR-spectroscopy analysis.

Thermo-IR-spectroscopy analysis [16]

KBr disks were prepared from a 2-mg sample in 200 mg KBr. The disks were twice reground and repressed in order to homogenize them. They were heated at 60, 90, and 120 °C from 1 h up to 12 days, as stated in the text, and were then kept in a desiccator at room temperature (r.t.) Fourier transform infrared (FTIR) spectra were recorded by Bruker FTIR spectrometer (model Tensor 27) at r.t. before and after heating. During the thermal treatment, due to water evolution, the disks became opaque. Before recording the spectra, they were carefully repressed without regrinding in order to get them again transparent.

Results and discussion

X-ray diffractograms of montmorillonite treated with naphthylammonium chloride

Adsorption isotherms of various aryl and alkyl ammonium cations onto montmorillonite showed that adsorption exceeded the cation exchange capacity of the clay by an amount depending upon the interlayer cation originally present and upon the concentration of the organic salt in the reacting solution (see e.g., [18]). This excess adsorption should be associated with the formation of ammonium–amine associations in the interlayer [19].

Figure 1 shows X-ray diffractograms of blank-I and blank-III recorded at room temperature with no thermal treatment. Curve fitting of *d*(001) reflection resulted in two peak components with maxima at 1.35 and 1.58 nm, indicating the presence of two types of tactoids. The first component characterizes tactoids with monolayers of naphthylammonium cations, lying parallel to the tetrahedral–octahedral–tetrahedral (TOT) clay layers [20–22]. The second component characterizes tactoids with naphthylammonium–naphthylamine associations tilted relative to the TOT clay layers [22–24]. The intensity ratio of the 1.58-nm peak component relative to the 1.35-nm peak component depends on the amount of naphthylammonium chloride used for the preparation of the sample. It increases with the amount of the salt. Intensity ratios in the diffractograms of blank-I and blank-III (60 and 160 mmol naphthylammonium chloride per 100 g clay) are 0.85 and 1.49, respectively, indicating that the number of tactoids of naphthylammonium–naphthylamine–montmorillonite relative to that of naphthylammonium–montmorillonite increases with the applied naphthylammonium chloride salt.

Thermo-IR-spectroscopy analysis of naphthylamine and naphthylammonium chloride

IR spectra of these compounds were recorded in KBr disks, before any thermal treatment and after heating the disks at different temperatures up to 120 °C. Before the thermal treatment, small water bands were identified in the IR spectra. At 60 °C, the disks dehydrate. The skeleton absorption bands of

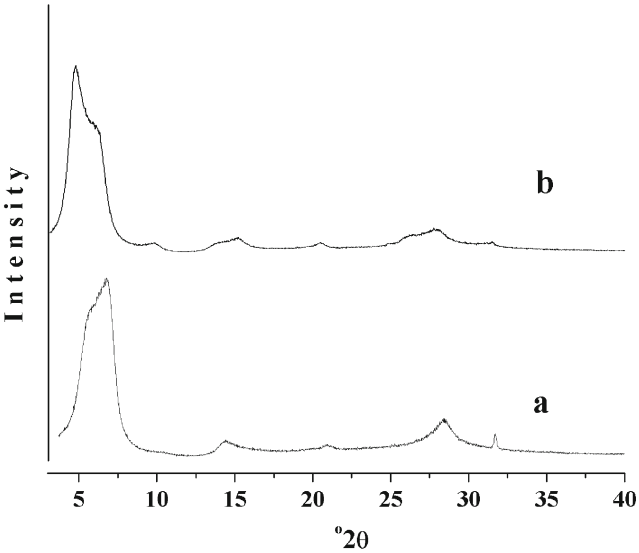


Fig. 1 X-ray diffractograms of Na-montmorillonite saturated with naphthylammonium chloride, (*a*) 60 and (*b*) 160 mmol ammonium per 100 g clay (blank-I and blank-III, respectively), recorded at room temperature

naphthylammonium chloride and of naphthylamine do not show any change during the thermal treatment, indicating that in KBr disks, these compounds do not decompose even after 12 days at 120 °C. Figure 2 depicts the spectra of KBr disks of naphthylammonium chloride and naphthylamine. The location of the different absorption bands and their assignments are gathered in Table 1.

Thermo-IR-spectroscopy analysis of naphthylammonium–montmorillonite

Before the thermal treatment, the stretching and bending bands of the adsorbed water overlap the NH_2 and NH_3^+ bands in the spectroscopic regions >2,800 and 1,700–1,600 cm^{-1}. Reliable spectra of these regions in KBr disks of NM-I and NM-II are obtained after drying the disks at 120 °C during 5 days. Longer thermal treatments at 120 °C result in a slight decrease of the bands. Most characteristic bands in the region 1,600–1,250 cm^{-1} are detectable in the presence of water. Thus, the thermal stability of the complexes is determined from changes in that spectroscopic region. NM-III (with a small excess of amine) slowly loses some free amine during the thermal treatment. This is shown from a decrease in the intensity of the C(aromatic)-NH_2 stretching band at 1,273 cm^{-1} with the thermal treatment.

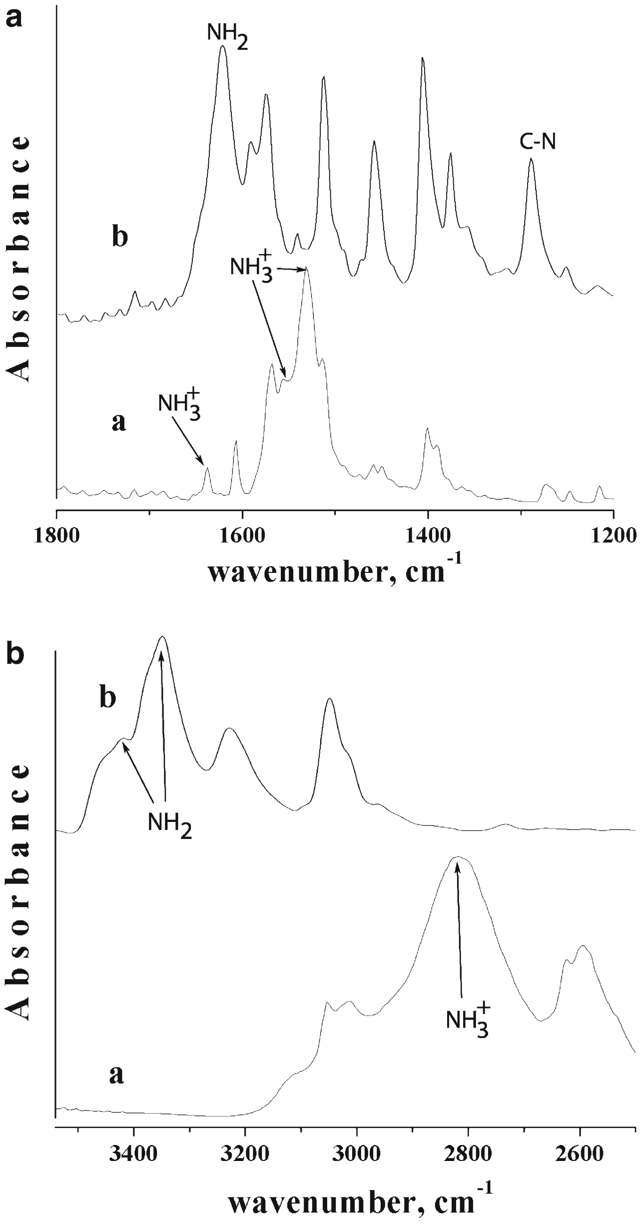


Fig. 2 Infrared spectra of KBr disks of (*a*) naphthylammonium chloride and (*b*) naphthylamine, after heating the disks at 120 °C for 5 days

Figure 3 depicts the spectra of KBr disks of NM-II and NM-III after being heated at 120 °C for 5 days. The locations of the different bands and their assignments are gathered in Table 1. A broad band with a maximum at 3,394 cm^{-1} in both spectra is attributed to O–H stretching frequency of highly acidic water. The appearance of this band indicates that desorption of water is not complete at 120 °C. Consequently, the recorded maxima of NH_2 stretching bands are not unequivocal. Large organic cations in the interlayer break the water structure and the latter band becomes highly acidic [24]. Water in bentonite absorbs at 3,446 cm^{-1}. When it becomes acidic, the absorption shifts to lower frequencies [25].

The spectrum of NM-I (not shown) is similar to that of NM-II, but the bands of the organic groups are weaker. Comparing the spectra of NM-I and NM-II with that of naphthylammonium chloride (Table 1) proves that the principle-adsorbed species in the thoroughly washed samples are naphthylammonium cations. The spectrum of NM-III shows shoulders of NH_2 (at 3,318, 1,618, and 1,273 cm^{-1}, the latter band is not shown in the figure) in addition to naphthylammonium bands. A shoulder at 3,318 cm^{-1} suggests the presence of ammonium–amine association [26].

The NH_3^+ stretching band appears at 2,820 cm^{-1} in the spectrum of naphthylammonium chloride salt. It splits into two weak bands at 2,926 and 2,857 cm^{-1} in the spectra of the clay complexes. The deformation bands are shifted from 1,637 and 1,533 cm^{-1} in the spectrum of the chloride salt to 1,625 and 1,542 cm^{-1}, respectively. According to previous studies of aromatic ammonium–montmorillonites [27], these shifts are attributed to the hydration of the NH_3^+ group with water oxygens accepting protons from the ammonium to form H bonds.

In general, ring vibrations of ammonium cations are only slightly shifted as a result of adsorption by the clay. A C–C ring vibration in the spectrum of NM-II appears at 1,517 cm^{-1} before the thermal treatment. After heating the disk at 90 °C, it splits into two bands at 1,516 and 1,508 cm^{-1}. As a result of dehydration, there is a better contact between the clay-O-plane and the aromatic ring, accompanied by π interaction. In this π interaction, oxygen-lone pair electrons overlap the π^* antibonding orbitals of the rings [16]. This thermal splitting is also observed in the spectrum of NM-I but not in the spectrum of

Table 1 Assignments and maxima (in cm^{-1}) of the absorption bands in the infrared spectra of naphthylamine, naphthylammonium chloride, naphthylammonium–montmorillonite-II (NM-II), naphthylammonium–montmorillonite-III (NM-III) and naphthylammonium–naphthylamine–montmorillonite (blank-III)

	Naphthyl–amine	Naphthyl–ammonium chloride	Naphthyl–ammonium mont-II	Naphthyl–ammonium mont-III	Naphthylammonium–naphthylamine–mont (blank-III)
H_2O			3,393 m. br	3,394 m. br	3,447 w
NH_2 as stret	3,418 m			3,394 m	3,399 m
NH_2 sym stret	3,348 vs			3,365 sh	3,363 m
Ammonium–amine				3,318 w	3,327 sh
NH...O cb			3,224 w	3,221 w	3,257 w
NH...N cb	3,229 m				
NH...Cl^- cb		3,109 sh			
CH aromatic	3,044 s	3,055	3,065 w	3,061 w	3,065 w
CH aromatic	3,016 m	3,016	3,015 vw	3,016 vw	3,016 vw
NH_3^+ stret		2,820 vs	2,926 m	2,928 m	2,926 m
			2,857 w	2,858 m	2,854 w
NH_3^+ cb		2,629 sh	2,569 w br	2,573 w	
		2,598 m			
H_2O def			1,647 w	1,647 w	1,650 vw
			1,635 m	1,636 m	1,636 vw
NH_3^+ def		1,637 w	1,625 s	1,625 s	1,625 vw
NH_2 def	1,622 vs			1,618 w	1,618 vw
C–C ring	1,591 m	1,607 m	1,602 sh	1,602 m	1,594 vw
C–C ring	1,576 s	1,570 s	1,576 vw	1,577 vw	
NH_3^+ def		1,557 s	1,559 w	1,559 w	
NH_3^+ def		1,533 vs	1,542 m	1,542 m	
C–C ring	1,514 vs	1,514 s	1,516 s	1,517 s	
			1,508 m		
C–C ring and CH def	1,458 s	1,460 vw	1,458 m	1,458 m	
		1,451 vw			
C–C ring	1,406 vs	1,402 m	1,398 s	1,399 s	1,417 m
	1,375 m	1,390 m	1,384 s	1,386 vw	1,384 m
	1,358 w		1,362 vw	1,361 vw	
NH_3^+ rocking			1,339 vw	1,337 vw	
C–N stret	1,289 m			1,273 w	1,272 vs

Spectra of KBr disks were recorded at room temperature after hearting the disks at 120 °C for 5 days

Mont Montmorillonite, *stret* stretching, *def* deformation, *as* asymmetric, *sym* symmetric, *cb* combination band, *vs* very strong, *s* strong, *m* medium, *w* weak, *vw* very weak, *sh* shoulder, *br* broad

NM-III. To conclude, π interactions occur in naphthylammonium clay but not in the presence of excess naphthylamine, where the NH_2, being an electron-releasing group, imposes a high electron density on the ring, and lone pair electrons from the clay-O-plane are repelled from the π* antibonding orbitals.

The C–C ring vibration at 1,384 cm^{-1} is very weak in the spectrum of NM-I and NM-II recorded before the thermal treatment. It intensifies with the temperature. This intensification during the thermal treatment is not observed in the spectrum of NM-III.

Thermo-IR-spectroscopy analysis of naphthylammonium–naphthylamine–montmorillonite

The interaction of organic ammonium–montmorillonite with molecular amine results in the association of the amine with the ammonium cation in the interlayer space. Some investigators suggest that in the ammonium–amine associations, there are H bonds in which the ammonium-NH_3^+ groups donate protons to the amine-NH_2 groups [22, 27]. In this case, the structure of naphthylammonium–naphthylamine association in the interlayer should be:

$$C_{10}H_7-NH_3^+ \bullet\bullet\bullet NH_2-C_{10}H_7$$

Other investigators suggest that water takes part in this association. In the first stage, the ammonium-NH_3^+ groups donate protons to water molecules or clusters to form hydronium cations. In the second stage, two amine molecules are hydrogen bonded with the protonated water by accepting

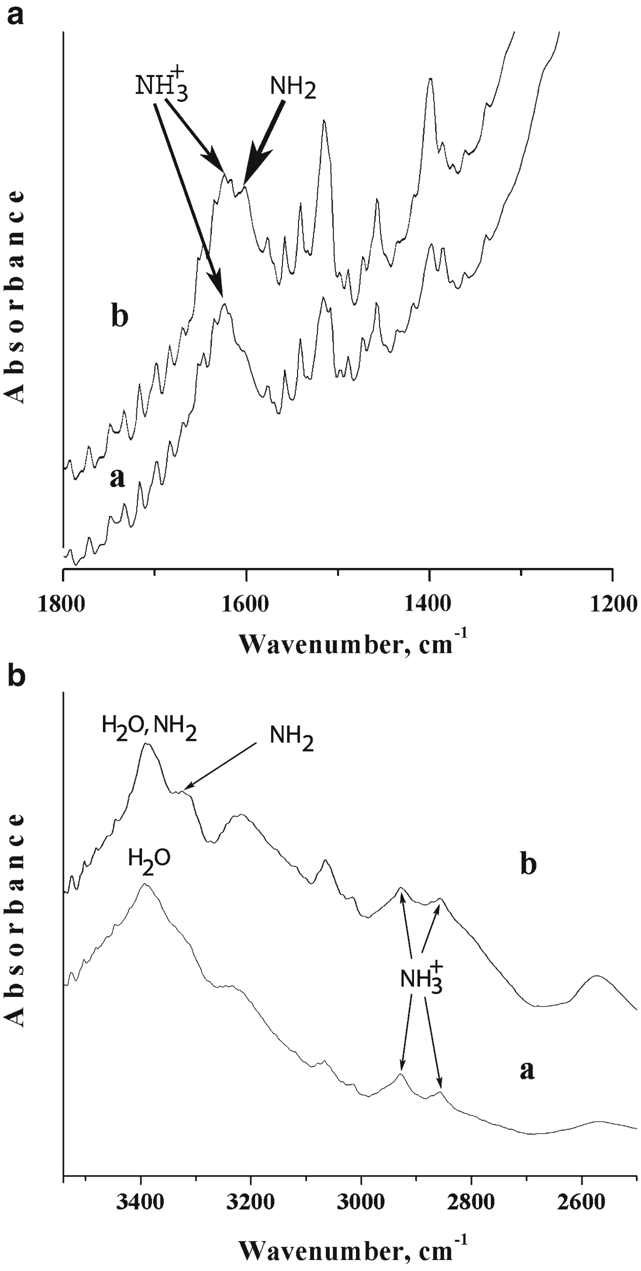


Fig. 3 Infrared spectra of KBr disks of (*a*) naphthylammonium–montmorillonite-II and (*b*) naphthylammonium–montmorillonite-III, after heating the disks at 120 °C for 5 days

protons [19, 28, 29], and the structure in the interlayer space should be:

$$C_{10}H_7{-}NH_2 \bullet\bullet\bullet [H_3O]^+ \bullet\bullet\bullet NH_2{-}C_{10}H_7$$

IR spectra of ammonium–amine–montmorillonite complexes of aniline or benzidine and of various derivatives of aniline were previously investigated [26, 29]. When the ammonium–montmorillonites were immersed in the corresponding amine liquids or solutions, the clays adsorbed the amines. The diagnostic bands of NH_3^+ group and the ring vibrations became very weak or disappeared even after short periods of immersion. The NH_2 and CN stretching bands persisted but shifted to lower frequencies compared with their locations in the spectra of the corresponding neutral amines. These shifts are characteristic of amines in which the N atoms, acting as proton acceptors, participate in hydrogen bonds [16].

Based on the X-ray diffractograms in Fig. 1 showing that the fraction of tactoids with ammonium–amine association increases with the ammonium salt used in the preparation, for the IR study of naphthylammonium–naphthylamine–clay, blank-II and blank-III are used.

To identify characteristic bands of the adsorbed naphthylammonium–naphthylamine, the disks are dried at 120 °C. At lower temperatures, absorptions of the adsorbed water overlap characteristic NH_2, NH_3^+, and ammonium–amine bands in the regions >2,800 and 1700–1600 cm^{-1}. Before the thermal treatment, only bands at 1,417, 1,384, and 1,272 are traced. IR spectra of thermally treated KBr disks of blank-III heated at 120 °C 1 h, 5 days, and 12 days are depicted in Fig. 4. A disk heated 1 h at 120 °C shows very intense water stretching and deformation bands at 3,438 and 1,636 cm^{-1}, respectively, overlapping NH_2 bands. Very weak NH_3^+ bands are traced on the envelope of the H_2O stretching band at 2,926 and 2,854 cm^{-1} (Table 1), suggesting the presence of small amounts of ammonium cations. According to the X-ray diffractograms (Fig. 1), some naphthylammonium is already present before the thermal treatment.

To obtain an almost dry naphthylammonium–naphthylamine–montmorillonite, the disks were heated for 5 days at 120 °C. The spectrum of naphthylammonium–naphthylamine–montmorillonite (blank-II or blank-III) differs profoundly from that of naphthylammonium–montmorillonite (NM-II), both recorded after the same thermal treatment. The broad band with a maximum at 3,394 cm^{-1}, in the spectrum of NM-II, attributed to O–H stretching frequency of highly acidic water, does not appear in the spectrum of blank-II and blank-III. The shift of the water band to a higher frequency (3,447 cm^{-1}) indicates a decrease in its acidity in the presence of excess amine. The latter spectrum exhibits two NH_2 stretching bands with maxima at 3,399 and 3,364 cm^{-1}, which are not detected in the former spectrum. The spectrum shows weak absorptions at 2,926 and 2,854 cm^{-1}, indicating the presence of naphthylammonium cations. The very intense C–NH_2 stretching band, which appears in the spectrum of naphthylamine at 1,289 cm^{-1}, is shifted to 1,272 cm^{-1} in the spectrum of blank-II and blank-III. This intense band does not appear in the spectrum of NM-II. Most ring vibrations are not observed. Only two skeleton vibrations are observed. The intense C–C stretching band located in the spectra of naphthylamine and naphthylammonium chloride at 1,406 and 1,398 cm^{-1}, respectively, decreases in intensity and shifts to 1,418 cm^{-1}. The medium size C–C stretching band located in the spectra of naphthylamine and naphthylammonium chloride at 1,375 and 1,390 cm^{-1}, respectively, is traced at 1,384 cm^{-1}.

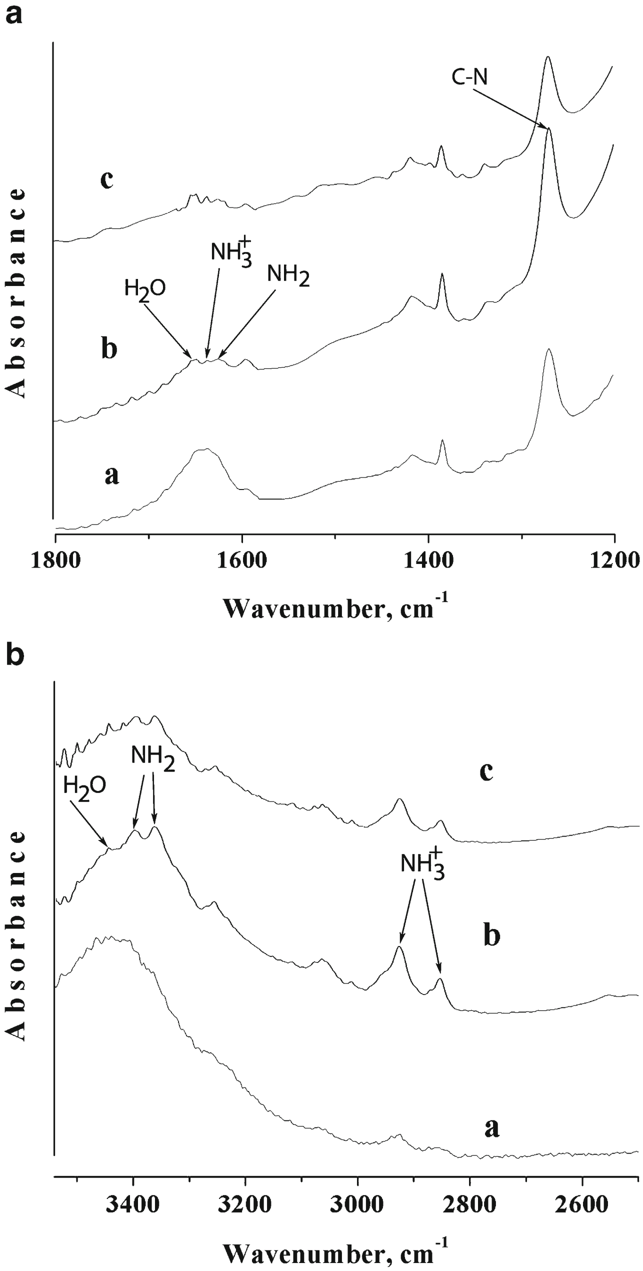


Fig. 4 Infrared spectra of KBr disks of blank-III (composed of naphthylammonium–naphthylamine–montmorillonite with some naphthylammonium–montmorillonite) after heating the disks at 120 °C for (*a*) 1 h, (*b*) 5 days, and (*c*) 12 days

With longer thermal treatments, more water is evolved together with some organic matter, in agreement with previous differential thermal analysis and thermo-XRD analysis, which showed that this organoclay complex decomposes at 120 °C [4, 5].

Thermo-IR-spectroscopy analysis of Solvent Brown 3

IR spectra of Solvent Brown 3 before and after heating the KBr disk for 5 days at 120 °C are shown in Fig. 5. The assignments of the different bands, based on band assignments in the spectra of naphthylamine and naphthylammonium chloride (Table 1), are gathered in Table 2 together with their locations and relative intensities. Two absorptions at 3,474 and 3,391 cm^{-1} before the thermal treatment, asymmetric and symmetric NH_2 stretching frequencies, prove that the non-protonated amine group is present in Solvent Brown 3. They shift to 3,482 and 3,394 cm^{-1} after dehydrating the disk at 60 °C. During the thermal treatment, these bands split, and additional shoulders appear at 3,448 and 3,371 cm^{-1}, which intensify with the temperature, suggesting the pre-

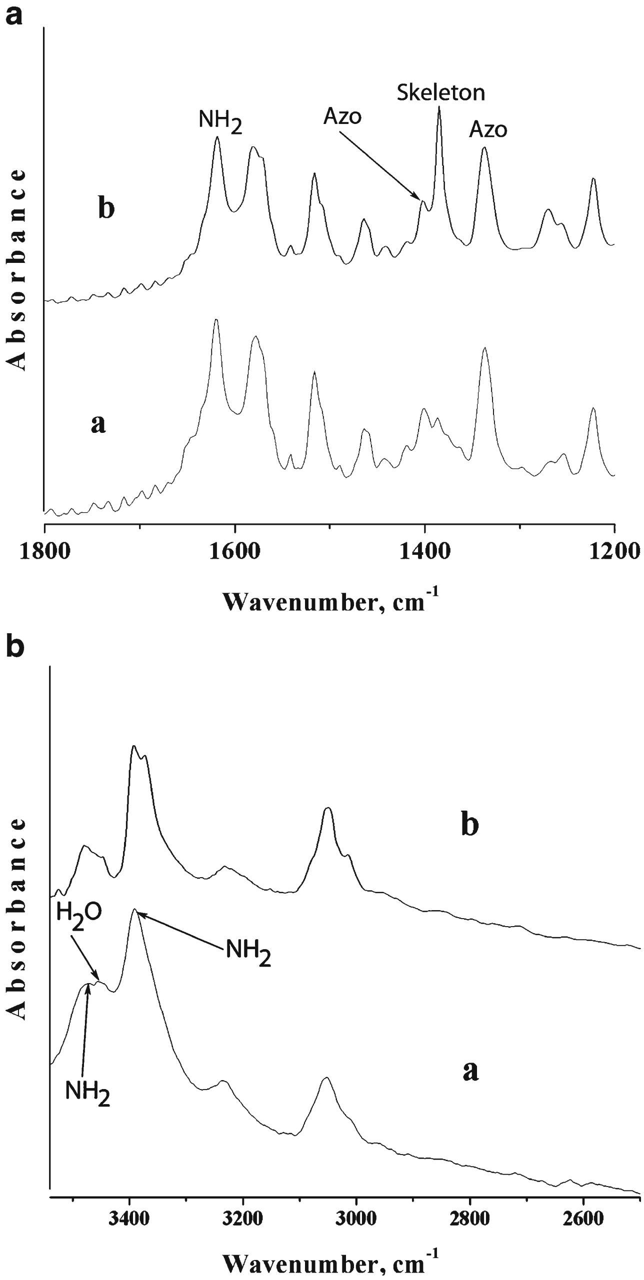


Fig. 5 Infrared spectra of a KBr disk of naphthylazonaphthylamine (Solvent Brown 3) (*a*) before thermal treatment, (*b*) after heating the disk at 120°C for 5 days

sence of intermolecular H bonds in the dehydrated crystals of the azo dye.

The NH_2 deformation band appears at 1,619 cm^{-1}. A band at 1,272 cm^{-1} might be attributed to C–N stretching vibration. This assignment is not certain because of the possible presence of $NaNO_2$ impurities. This salt absorbs at (strong) 1,272 and (weak) 1,384 cm^{-1}.

Bassignana and Cogrossi [30] attributed a band at 1,401 cm^{-1} in the spectrum of naphthylazonaphthylamine to the –N=N– vibration of the azo dye and a band at 1,114 cm^{-1} to its C–N= vibration. In our spectrum, these bands appear at 1,404 and 1,116 cm^{-1}, respectively (the latter band is not shown in Fig. 5). An additional band at 1,336 cm^{-1}, which is not traced in the spectra of naphthylammonium chloride, naphthylamine, or sodium nitrite, the starting reagents for the azo dye appears in the spectrum of Solvent Brown 3. It should also be attributed to the azo group. This is in agreement with Guenzler and Gremlich [31], who stated that *para*-substituted azo benzenes give strong absorptions near 1,370 and 1,150 cm^{-1}.

Thermo-IR-spectroscopy analysis of naphthylazonaphthylammonium–montmorillonite

Figure 6a–c depicts the spectra of a KBr disk of pigment B-III before thermal treatment and after heating 1 h and 12 days at 120 °C. Figure 6d depicts the spectrum of a KBr disk of pigment B-II after 12 days at 120 °C. Locations of the different bands, their assignments, and relative intensities are gathered in Table 2. After 1-h heating at 120 °C, dehydration is incomplete (water band appears at 3,447 cm^{-1}). Nevertheless, NH_2 and NH_3^+ absorptions are identified on the envelope of the H_2O bands. These bands intensify upon further heating.

Comparing the spectroscopic region 1,600–1,300 cm^{-1} of Fig. 6a with that of Fig. 6b shows that the interlayer azo dye does not decompose during 1-h heating at 120 °C. In both spectra, the appearance of NH_3^+ deformation bands at 1,559 and 1,543 cm^{-1} proves that the dye is protonated. Because NH_3^+ group is not present in the reddish-brown Solvent Brown 3, the assumption that the blue azo dye in the OCCP is protonated should be correct [4, 5].

NH_2 absorptions at 3,400, 3,360, and 1,620 cm^{-1} in Fig. 6b suggest that after heating the disk 1 h at 120 °C, the OCCP contains some non-protonated naphthylazonaphthylamine in addition to the protonated naphthylazonaphthylammonium cation. A shoulder at 1,618 cm^{-1} (NH_2 deformation band) is observed for the first time after 90 °C. However, from the present study, it is not clear if the amine group already exists before the thermal treatment.

Each of the C–C ring vibrations, which, in the spectrum of Solvent Brown 3, appear at 1,580 and 1,516 cm^{-1}, split into two bands in the spectra of pigment B-II and pigment B-III (Table 2). This splitting is due to π interactions between the dye and the clay-O-plane [16].

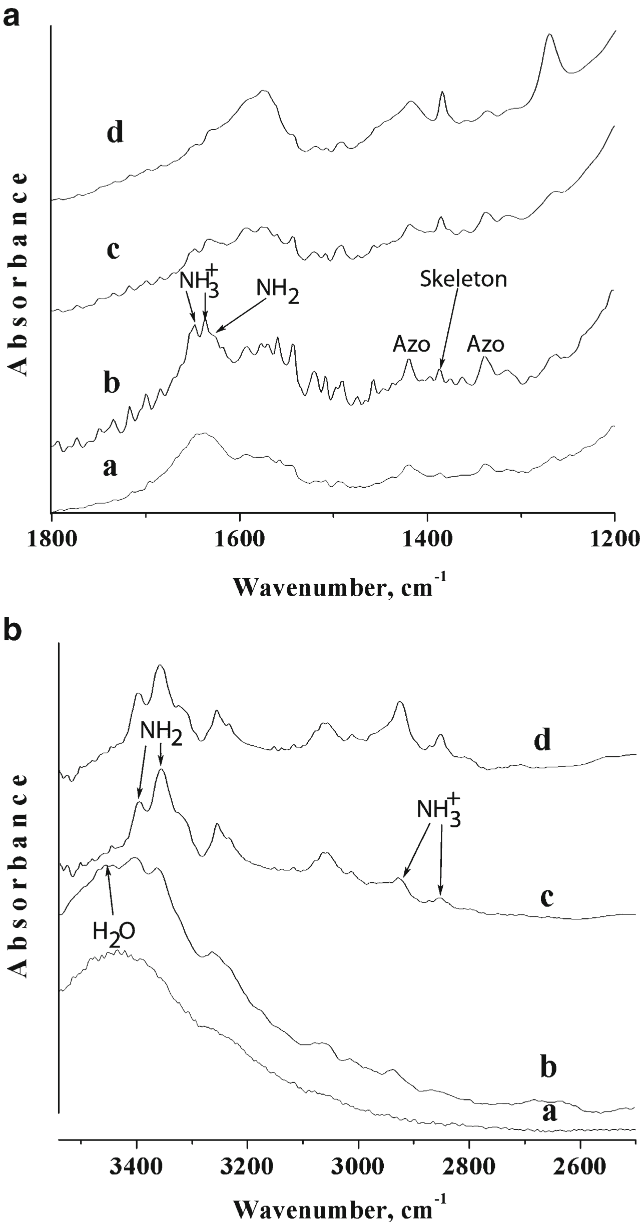


Fig. 6 Infrared spectra of a KBr disk of (*a*), (*b*), and (*c*) pigment B-III before any thermal treatment after heating the disk for 1 h and 12 days at 120 °C, respectively; (*d*) pigment B-II after heating the disk for 12 days at 120 °C

An azo band located in the spectrum of Solvent Brown 3 at 1,404 cm^{-1} is shifted in the spectrum of the OCCP to 1,419 cm^{-1}. This shift results from the overlapping of the lone pair electrons of the clay oxygens with π* antibonding orbitals of the azo dye. According to the VB model, the resonance of the azo group is described by two canonic structures:

$$\mathbf{Ar}-\mathbf{N}=\mathbf{N}-\mathbf{Ar}\ (\text{structure I})\quad \text{and}$$

$$^{-}\mathbf{Ar}{=}\mathbf{N}{-}\mathbf{N}{=}\mathbf{Ar}^{-}\ (\text{structure II})$$

Table 2 Assignments and maxima (in cm^{-1}) of the absorption bands in the infrared spectra of naphthylazonaphthylamine (Solvent Brown 3) and of naphthylazonaphthylammonium–montmorillonite (OCCP)

	Solvent Brown 3 before thermal treatment	Solvent Brown 3 120 °C/5 days	Pigment B-III before thermal treatment	Pigment B-III 120 °C/1 h	Pigment B-III 120 °C/12 days	Pigment B-II 120 °C/12 days
H_2O	3,455 m		3,430 vs	3,447 s		
NH_2 as stret	3,474 m	3,482 w		3,400 s	3,394 m	3,398 m
		3,448 w				
NH_2 sym stret	3,391 vs	3,394 vs		3,360 s	3,356 s	3,364 s
		3,371 s				
$H_2N..HO$ cb					3,321 sh	3,321 sh
NH…O cb				3,257 w	3,260 m	3,252 m
NH...N cb	3,235 w	3,234 w		3,237 vw	3,237 w	3,237 w
CH aromatic	3,052 m	3,052 s		3,054 m	3,060 m	3,059 w
CH aromatic	3,015 sh	3,016 m		3,009 vvw	3,009 vw	3,009 vw
NH_3^+ stret				2,940 m	2,936 m	2,928 m
				2,854 w	2,854 w	2,854 w
NH_3^+ and/or H_2O def	1,647 w sh		1,648 vs	1,647 s	1,648 m	1,633 w sh
			1,637 vs	1,636 vs	1,633 s	
NH_2 def	1,620 vs	1,619 s		1,620 sh	1,620 vw	1,620 w sh
C–C ring			1,595 s	1,592 m	1,593 vs	1,593 w sh
C–C ring	1,579 vs	1,580 vs	1,578 s	1,577 m	1,577 vs	1,576 vs br
			1,572 s	1,570 m	1,570 vs	
NH_3^+			1,559 s	1,559 s	1,559 s	–
NH_3^+			1,543 m	1,543 s	1,543 s	1,543 w sh
C–C ring	1,516 s	1,516 s	1,519 vw	1,520 m	1,520 w	1,519 vw
			1,508 vw	1,510 m	1,509 w	1,508 vw
			1,492 w	1,492 w	1,492 m	1,492 w
C–C ring and CH def	1,465 m	1,465 m	1,456 vw	1,456 w	1,457 vw	–
			1,437 vw	1,437 vw	1,437 vw	
Azo group	1,405 m	1,401 m	1,419 m	1,419 m	1,419 m	1,419 m
Skeleton	1, 384 m	1,384 vs	1,387 w	1,387 w	1,387 m	1,384 m
Azo group	1,336 s	1,336 s	1,337 m	1,337 m	1,337 m	1,337 w

Spectra of KBr disks were recorded at room temperature before thermal treatment and after different thermal treatments
Stret Stretching, *def* deformation, *as* asymmetric, *sym* symmetric, *cb* combination band, *vs* very strong, *s* strong, *m* medium, *w* weak, *vw* very weak, *sh* shoulder, *br* broad, *h* hour, *d* day

Structure I contributes to the double bond character of the N=N group whereas structure II contributes to its single bond character. The shift from 1,404 to 1,419 cm^{-1} indicates that the double bond character of the N=N group is higher in the naphthylazonaphthylammonium–montmorillonite compared with that in Solvent Brown 3. Namely, the contributions of structure I to the overall resonance increase. The electron density in the naphthyl skeleton is smaller and the postponement of the lone pair electrons of the clay oxygens from π* antibonding orbitals of the naphthyl skeletons is weaker in structure I than in II. In conclusion, this shift is associated with the π interactions between the clay and the dye.

After 12 days at 120 °C (Fig. 6c), the pigment is dehydrated with some decomposition shown by a decrease of the NH_3^+ deformation bands and broadening of C–C ring vibrations. Fig. 6d shows that with smaller amounts of intercalated azo dye (pigment B-II), there is a critical change in the 1,700–1,500 cm^{-1} spectroscopic region. The 1,576 cm^{-1} C–C ring vibration becomes the most intense, and all other absorptions appear as shoulders. This may indicate a thermal condensation of the azo dye inside the interlayer space. It should be noted that the bands of the azo group and those of NH_2 and NH_3^+ persist after this thermal treatment.

Correlation between π interactions and the clay-basal spacing

There is a correlation between the existence of π interactions between the aromatic rings and the clay-O-plane and the basal spacing of the clay. The IR study of the OCCP with a basal spacing at 1.28 nm showed π interactions between the clay-O-plane and the intercalated naphthylazonaphthylammonium, which has four aromatic rings per one cation. Interactions of π between the clay-O-plane and the intercalated naphthylammonium, which has only two aromatic rings per one cation, were identified in naphthylammonium–montmorillonite with a basal spacing at 1.35 nm. On the other hand, no π interactions between the clay-O-plane and the intercalated naphthylammonium–naphthylamine associations were identified by IR spectroscopy. The basal spacing of these tactoids is at 1.58 nm and we assume that the associations are tilted relative to the TOT clay layers [22–24].

Conclusions

1. The IR spectrum of the organic component in the OCCP differs from those of naphthylammonium–montmorillonite and naphthylammonium–naphthylamine–montmorillonite proving that the treatment of the clay with naphthylammonium chloride and sodium nitrite resulted in the formation of a new azo compound.
2. The IR spectrum of the organic component in the OCCP is similar to the spectrum of naphthylazonaphthylamine (Solvent Brown 3). Splitting of C–C ring vibrations and a shift in the N=N frequency in the spectrum of the OCCP compared with that of Solvent Brown 3 (Table 2) are due to π interactions between the clay-O-plane and the intercalated dye.
3. Protonation of amine groups of the intercalated azo dye in the OCCP has been proved by the appearance of NH_3^+ bands in the IR spectrum of this complex. These bands do not appear in the spectrum of Solvent Brown 3. As a consequence the OCCP is deep blue and Solvent Brown 3 is reddish-brown.
4. The frequencies of the NH_3^+ bands in the IR spectra of naphthylammonium clay and OCCP are shifted from their location in the spectrum of naphthylammonium chloride due to the hydration of the NH_3^+ group in the interlayer.

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