# SECONDARY ADSORPTION OF NITROBENZENE AND *m*-NITROPHENOL BY HEXADECYLTRIMETHYLAMMONIUM-MONTMORILLONITE
## Thermo-XRD-analysis

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In the present research we studied the effect of the solvent used, whether it was polar water or a non-polar organic solvent (*n*-hexane or *n*-hexadecane), on the basal-spacing and bulk structure of the sorbate-sorbent complexes obtained by the secondary adsorption of nitrobenzene and *m*-nitrophenol by two types of organo-montmorillonites. X-ray measured basal spacings before and after thermal treatments up to 360°C. The organo-clays were synthesized, with 41 and 90% replacement of the exchangeable $Na^+$ by hexadecyltrimethylammonium (HDTMA), with mono- and bilayers of HDTMA cations in the interlayer space, labelled OC-41 and OC-90, respectively. After heating at 360°C both organo-clays showed spacing at 1.25–1.28 nm, due to the presence of interlayer-charcoal, indicating that in the preheated organo-clays the HDTMA was located in the interlayer.

The thermo-XRD-analysis of Na-clay complexes showed that from organic solvents both sorbates were adsorbed on the external surface but from water they were intercalated. *m*-Nitrophenol complexes of both organo-clays obtained in aqueous suspensions contain water molecules. Spacings of nitrobenzene complexes of OC-41 and OC-90 and those of nitrophenol complexes of OC-41 showed that the adsorbed molecules were imbedded in cavities in the HDTMA layers. Adsorption of *m*-nitrophenol by OC-90 from water and *n*-hexane resulted in an increase of basal spacing (0.21 and 0.29 nm, respectively) suggesting the existence of a layer of nitrophenol molecules sandwiched between two parallel HDTMA layers.

## Introduction

Organo-clays, prepared by the adsorption of organic ammonium cations onto clay minerals, are widely used in many sophisticated high-Tec industries and as substrates for pollution purification [1]. The replacement of the metallic cations, initially present at the exchange sites of the clay, by surfactants such as quaternary ammonium cations (primary adsorption) converts the clay into an organophilic substrate, which is capable of adsorbing polar and non-polar molecules (secondary adsorption) [2].

The objective of the present research is to follow after the effect of the solvent used in the secondary adsorption, whether it is polar water or a nonpolar organic solvent, on the basal spacing and bulk structure of the sorbate–sorbent complex. Na-montmorillonite and two types of HDTMA-montmorillonite (where HDTMA is *n*-hexadecyltrimethylammonium) were used as the adsorbing-substrates (sorbents) whereas nitrobenzene and *m*-nitrophenol as the adsorbed species (sorbates). The two organo-clays were prepared from Na-montmorillonite through replacing 41 and 90% of the exchangeable $Na^+$ by the ammonium cat-

ion (labelled OC-41 and OC-90, respectively). Adsorption by Na-clay and by the two organo-clays was carried out from water, *n*-hexane or *n*-hexadecane suspensions with the purpose to learn the effect of the solvent on the sorbate-sorbent complexes. Spacings were determined before and after thermal treatments up to 360°C [3].

Several investigators showed that the basal spacing of HDTMA-montmorillonite and other organo-clays expands as a result of a secondary adsorption (e.g. [4]). The effect on basal spacing of adsorption of a test molecule *p*-nitrophenol from aqueous solutions by HDTMA-montmorillonite and by montmorillonite modified with similar surfactants was recently studied by XRD [5–8].
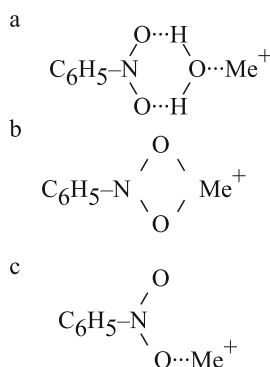
According to the VB theory the electron density in the aromatic ring of nitrobenzene differs from that of *m*-nitrophenol. In nitrobenzene the $NO_2$, being an electron-withdrawing group, imposes a deficiency of electrons on the benzene ring [9]. Hybridized oxygen-nonbonding orbitals with lone pair electrons from Si–O–Al groups in the tetrahedral sheet of montmorillonite may now overlap the π* antibonding orbitals of the nitrobenzene. Consequently, π interac-

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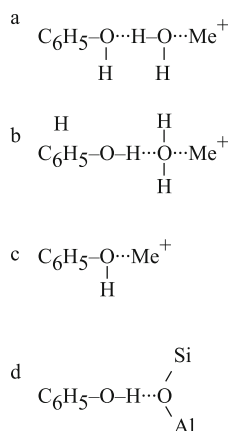\*    Author for correspondence: yarivs@vms.huji.ac.il

tions between the clay-O-plane and the adsorbed nitrobenzene occur [10, 11]. In *m*-nitrophenol the NO$_2$ group also withdraws electrons, but the OH, being an electron-releasing group, imposes a high electron density on the ring and lone-pair electrons of atoms from the clay-O-plane are repelled from the π* antibonding orbitals.

The adsorption of nitrobenzene by homoionic montmorillonites was previously studied applying IR spectroscopy and XRD [12]. It was found that the nitro group was bound to the exchangeable metallic cation via a water bridge. The water molecule, being coordinated to the cation, donated a proton to the nitro group. After thermal dehydration of the clay, nitro groups directly coordinated the metallic cations (Scheme 1). In the case of exchangeable Na$^+$, which forms unstable hydrates, the nitro groups coordinated the cations already before any thermal treatment.

The adsorption and mechanochemical adsorption of phenol and some derivatives by homoionic montmorillonites was previously studied by IR spec-

troscopy and XRD [13–15]. It was found that the phenol groups were bound to metallic cations through water bridges in which water molecules hydrating the cations either accepted or donated protons to OH groups. After dehydration the oxygens of the OH groups directly coordinated the metallic cations. As well, phenols donated protons to the clay-O-plane to form H-bonds (Scheme 2).

## Experimental

### Materials

Wyoming bentonite (Na-montmorillonite, [(Al$_{3.07}$Ti$_{0.01}$Fe$_{0.40}$Mg$_{0.49}$)(Si$_{7.79}$Al$_{0.21}$)O$_{20}$(OH)$_4$]·Na$_{0.75}$ [16] with cation exchange capacity of 90 meq/100 g) was purchased from Fisher Scientific Company (USA); moisture content of the freeze-dried bentonite was 1–2 mass/mass% (determined by oven-drying at 105°C).

Preparation of the HDTMA-exchanged sorbents involved (1) obtaining homogeneous 1.5 mass/mass% bentonite suspension in water by stirring four hours; (2) slow adding of the HDTMA bromide solution (0.03 M; 1–1.5 mL min$^{-1}$) during 5–6 h; (3) additional 15 h stirring. Finally, a suspension was centrifuged, and dissolved C was determined in supernatant using C/N Formacs analyzer. Sodium bromide was removed from the organo-clay complex by multiple washing with distilled water, until negative reaction with AgNO$_3$. Two obtained organo-clay sorbents washed and freeze-dried were labeled as OC-41 and OC-90 (with the moisture contents 2.8 and 0.7 mass/mass%, respectively; determined by oven-drying at 105°C). Number in the label indicates the extent of replacement of exchangeable cation found from the solid phase C content (Thermo-Finnigan C/N analyzer) which is in agreement with values calculated from change in the aqueous HDTMA concentration due to adsorption (for two organo-clays, 41 and 90%, as compared with 43 and 89%, respectively).

**Scheme 1** Three associations formed between nitro group, water molecules and exchangeable metallic cations in the interlayer space of montmorillonite, where Me$^+$ is the exchangeable metallic cation [12]

**Scheme 2** Four associations formed between phenol group, water molecules and exchangeable metallic cations in the interlayer space of montmorillonite, where Me$^+$ is the exchangeable metallic cation [13–15]

Sorbate-sorbent complex preparation

100 mg of a freeze-dried sorbent was mixed in a vial with a certain volume of an organic compound solution in a needed solvent (as detailed in the Table 1). Aqueous solutions included also 200 mg L$^{-1}$ of sodium azide (for minimizing a microbial degradation of organic compounds). Sorbent+solution systems

**Table 1** Details on the preparation of sorbate–sorbent complexes

| Compound | Sorbent | Solvent | Solvent volume/ML | Initial compound conc./mg L$^{-1}$ | Sorbed conc./ mg kg$^{-1}$ |
|---|---|---|---|---|---|
| Nitrobenzene | Na-clay | water | 2.0 | 1300 | 6800 |
| Nitrobenzene | Na-clay | $n$-C$_{16}$H$_{34}$ | 1.0 | 2700 | 16000 |
| Nitrobenzene | OC-41 | water | 3.0 | 1300 | 20600 |
| Nitrobenzene | OC-41 | $n$-C$_{16}$H$_{34}$ | 1.0 | 2700 | 13500 |
| Nitrobenzene | OC-90 | water | 10.0 | 1300 | 75000 |
| Nitrobenzene | OC-90 | $n$-C$_{16}$H$_{34}$ | 0.5 | 2700 | 7500 |
| *m*-Nitrophenol | Na-clay | water | 1.0 | 9000 | 17800 |
| *m*-Nitrophenol | Na-clay | $n$-C$_{16}$H$_{34}$ | 10.0 | 65 | 6600 |
| *m*-Nitrophenol | OC-41 | water | 5.0 | 5200 | 38100 |
| *m*-Nitrophenol | OC-41 | $n$-C$_6$H$_{14}$ | 20.0[a] | 78 | 50000 |
| *m*-Nitrophenol | OC-90 | water | 5.0 | 2000 | 65000 |
| *m*-Nitrophenol | OC-90 | $n$-C$_6$H$_{14}$ | 20.0[b] | 78 | 90000 |

[a]There were four consecutive saturation steps in which a supernatant was replaced by new 20 mL portion of a fresh solution. This was done in order to reach higher extent of the organo-clay saturation by a sorbate. [b]As above, there were five consecutive saturating treatments; each was by the new 20 mL hexane solution of *m*-nitrophenol

were prepared in triplicate. Suspensions were equilibrated during 72 h in darkness at 22±2°C on a shaker table. Then, vial content was centrifuged; the solid sorbate-sorbent complex phase was separated and used in further X-ray measurements.

*Methods*

Organic solute concentration was measured in the equilibrated supernatant phase. For that, nitrobenzene and *m*-nitrophenol aqueous concentrations were determined using Shimadzu HPLC (UV diode array detector; RP-18 column 5 μm; Lichrocart 250-4; HPLC-cartridge Ecopack, Lichrospher 100; mobile phase acetonitrile: water 70:30; 1 mL min$^{-1}$). In *n*-hexadecane solutions, nitrobenzene was measured with GC FID Varian 3300 (column J&W DB-5, 30 m; i.d. 0.53 mm; film thickness 1.5 μm). In order to obtain *m*-nitrophenol concentrations in a hydrocarbon solution, extraction with aqueous NaOH and the following HPLC analysis were applied (details in [17]).

Sorbed concentrations of organic compounds (per mass of a dry sorbent) were found from change of solution concentrations. In this calculation, possible losses of organic compounds not related to sorption by clays were accounted in separated duplicated blank tests (solution without sorbent). Control tests were carried out also with suspended sorbent (without solute) in order to check the possibility for release of organic cations from HDTMA-exchanged clays. No such release was found as revealed by measuring dissolved organic carbon concentrations (Combustion TOC Analyzer, Formacs).

X-ray measurements

Few mg of freeze-dried sorbents were mixed with few drops of water or organic solvent and thoroughly stirred. These suspensions and those of the sorbate–sorbent complexes were air-dried (35–40% humidity) on microscope glasses during several days, until the solvents were completely evaporated, to give dry oriented samples. Powders of freeze-dried sorbents and dry oriented samples of the different sorbents and sorbate-sorbent complexes were diffracted by X-ray before any thermal treatment and after heating at 150, 300 and 360°C during three hours at each temperature. X-ray diffractions in air-atmosphere were carried out at room temperature by Phillips Automatic Diffractometer (PW 1710) with a Cu tube anode between 2 and 40° (2θ).

## Results and discussion

The basal spacings of the different oriented samples recorded before any thermal treatment and after heating them at 360°C, together with the amounts of adsorbed nitrobenzene and nitrophenol are gathered in Table 2. Most diffractograms recorded before the thermal treatment show almost integral order of 00l reflections, suggesting that the reproducibility of the recorded spacing is in the range of about ±0.005 nm. On the other hand after the thermal treatment they show poor integral order of reflections with reproducibility in the range of ±0.010 nm. Table 3 depicts basal spacings of the three sorbents before and after the secondary adsorption, settled from aqueous

**Table 2** Basal spacings (in mm) of sorbents (freeze-dried and air-dried from aqueous or organic solvent suspensions) and sorbate-sorbent complexes (air-dried from aqueous or organic solvent suspensions), before and after heating the samples three hours at 360°C and the amounts of adsorbed sorbates in the complexes (in mmol per 100 g clay)

| Sorbent | Solvent | Untreated sorbent basal spacing/nm | | Nitrobenzene treated sorbent | | | Nitrophenol treated sorbent | | |
| | | 25°C | 360°C | Sorption mmol/100 g | Basal spacing/nm | | Sorption mmol/100g | Basal spacing/nm | |
| | | | | | 25°C | 360°C | | 25°C | 360°C |
| Na–clay | freeze–dried | $1.12^{-}$ | $0.97^{-}$ | | | | | | |
| | water | $1.25^{*}$ | $0.97^{+}$ | 6.0 | $1.23^{*}$ | $1.26^{-}$ | 13.0 | $1.27^{*}$ | $1.25^{-}$ |
| | hexane | $1.26^{-}$ | $0.97^{+}$ | nd | nd | nd | nd | nd | nd |
| | hexadecane | $1.26^{-}$ | $0.97^{+}$ | 13.0 | $1.21^{-}$ | $0.99^{-}$ | 5.0 | $1.26^{-}$ | $0.97^{+}$ |
| OC–41 | freeze–dried | $1.41^{*}$ | | | | | | | |
| | water | $1.45^{+}$ | $1.28^{*}$ | 17.0 | $1.38^{*}$ | $1.26^{-}$ | 27.0 | $1.42^{+}$ | $1.25^{-}$ |
| | hexane | $1.42^{+}$ | $1.28^{*}$ | nd | nd | nd | 36.0 | $1.40^{+}$ | $1.27^{-}$ |
| | hexadecane | $1.42^{+}$ | $1.28^{*}$ | 11.0 | $1.40^{*}$ | $1.26^{-}$ | nd | nd | nd |
| OC–90 | freeze–dried | $1.82^{-}$ | | | | | | | |
| | water | $1.81^{+}$ | $1.28^{*}$ | 61.0 | $1.78^{+}$ | $1.24^{-}$ | 47.0 | $2.02^{-}$ | $1.26^{-}$ |
| | hexane | $1.82^{+}$ | $1.27^{-}$ | nd | nd | nd | 65.0 | $2.11^{*}$ | $1.26^{-}$ |
| | hexadecane | $1.83^{-}$ | $1.29^{*}$ | 6.0 | $1.78^{+}$ | $1.28^{*}$ | nd | nd | nd |

$^{*}$Integral order of reflections; $^{+}$integral to a smaller extent; $^{-}$non-integral; nd – not determined

suspensions, recorded before and after heating them at 150, 300 and 360°C.

*Thermo-XRD-analysis of the sorbents before the secondary adsorption*

The freeze-dried sorbents before suspending in water or in organic solvents were examined by X-ray diffraction as powders. The $d$(001) reflection of freeze-dried Na-montmorillonite is 1.12 nm (non-integral) and those of OC-41 and OC-90 are 1.41 (integral) and 1.82 nm (non-integral), respectively. The spacing of Na-clay suggests that water has not been completely removed during the freeze-drying. The spacings of OC-41 and OC-90 suggest that lateral mono- and bilayers of HDTMA cations, respectively, are present in the clay-interlayers with the long chain being parallel to the clay layers [5, 18].

Freeze-dried Na-clay suspended in water adsorbs water. After air-drying the suspended Na-clay an oriented sample is obtained with a basal spacing at 1.25 nm and an integral order of reflections, characteristic for Na-clay with a water monolayer sandwiched between the clay layers [19, 20]. According to Mamy [21], the monolayer hydrate in smectite with no tetrahedral substitution consists of tetrahedral distribution of water molecules arranged in a strained hexagonal icelike configuration, with intermolecular H-bonds between neighboring water molecules. This is a hydrophobic water structure (water zone $A_o$ in Yariv's terminology [22, 23]). Because of its low charge $Na^+$ does not break water structure of zone $A_o$ and fits into interstitial cavities [24]. Forces acting between these water-layers and the clay layers are mainly long-range van der Walls and electrostatic

(the water layer is positively charged due to the inclusion of $Na^+$ cations). The basal spacing of the clay is determined by the width of the hydrophobic water layer.

At 150°C water evolves and the remaining water molecules form planar hydrates of $Na^+$ by ion-dipole interactions (water zone $A_m$ [22]). Due to the polarizing power of the metallic cations water molecules in zone $A_m$ are proton donors [25] and are H-bonded to the clay-O-planes at sites where Al substitutes Si (at Si–O–Al groups in the clay tetrahedral sheet) [26–30]. These H-bonds restrict swelling and consequently, the basal spacing drops to 1.19 nm (Table 3). This hypothesis is based on a study of partial dehydration of Mg-vermiculite [31].

The basal spacing of samples obtained after air-drying of several days *n*-hexane- or *n*-hexadecane-suspensions of freeze-dried Na-clay is 1.26 nm (Table 2). The van der Waals diameter of carbon is >0.34 nm suggesting that this spacing is too small to account for the presence of hydrocarbon molecules in the interlayer. It seems that during the drying of the suspension on the microscope glass atmospheric water has been adsorbed.

After heating at 360°C the freeze-dried Na-clay and the samples obtained by air-drying aqueous, *n*-hexane or *n*-hexadecane-suspensions, spacing at 0.97 nm is recorded (Table 2), indicating dehydration and collapse of the clays.

Table 2 shows that in an aqueous suspension the freeze-dried OC-41 swells from 1.41 to 1.45 nm, indicating water adsorption. This spacing is too small to account for a separate water-layer. To accommodate the organophilic–hydrophilic nature of HDTMA, water and $Na^+$ and the hydrophobic nature of montmoril-

**Table 3** The effect of the thermal treatment on the basal spacings (in nm) of Na-clay and hexadecyltrimethylammonium-montmorillonite (OC-41 and OC-90) unloaded and loaded with nitrobenzene and *m*-nitrophenol sedimented from aqueous suspensions and air-dried

| Sorbent | Sorbate | Effect of the thermal treatment/nm | | | |
|---|---|---|---|---|---|
| | | 25°C | 150°C | 300°C | 360°C |
| Na-clay | water | 1.25 | 1.19 | 1.01 | 0.97 |
| | nitrobenzene | 1.23 | 1.26 | 1.25 | 1.25 |
| | *m*-nitrophenol | 1.27 | 1.23 | 1.29 | 1.26 |
| OC-41 | water | 1.45 | 1.43 | 1.31 | 1.28 |
| | nitrobenzene | 1.38 | 1.38 | 1.28 | 1.26 |
| | *m*-nitrophenol | 1.42 | 1.38 | 1.26 | 1.25 |
| OC-90 | water | 1.81 | 1.77 | 1.34 | 1.28 |
| | nitrobenzene | 1.78 | 1.78 | 1.31 | 1.24 |
| | *m*-nitrophenol | 2.02 | 1.63 1.41 | 1.28 | 1.26 |

lonite-O-plane (the tetrahedral substitution of Si by Al is small and the Si–O–Al sites are already occupied by the positive heads of HDTMA) the following arrangement is suggested. The adsorbed water forms hydrophobic three-dimensional clusters of few molecules arranged in a strained hexagonal icelike configuration, with intermolecular bonds between neighboring molecules, penetrating into cavities in the HDTMA layers [22]. Exchangeable Na cations, which have not been replaced by HDTMA cations, should be located inside the icelike clusters. Thus the monolayer shape of HDTMA cations is preserved but with an increment in its width.

The swelling of OC-41 in organic solvent suspensions, from 1.41 to 1.42 nm, (Table 2) is too small to account for any change in the HDTMA monolayers. If solvent molecules intercalate, they probably imbed cavities in the HDTMA monolayers.

Spacing of samples obtained by air-drying aqueous, *n*-hexane or *n*-hexadecane suspensions of freeze-dried OC-90 are 1.81–1.82 nm, similar to that of freeze-dried sample (1.82 nm) indicating that the HDTMA bilayer shape of the sorbent is preserved and that adsorbed solvent molecules, if intercalate, imbed cavities in the HDTMA cation monolayers (Table 2). Adsorbed water molecules probably form hydrophobic clusters inside the cavities.

Shrinkage of spacings occurs during heating at 150°C OC-41 and OC-90 obtained from aqueous suspensions due to partial dehydration (Table 3). At temperatures >250°C the first air-oxidation step of the HDTMA cations takes place [3, 32, 33]. At this step most of the organic hydrogen is oxidized to form $H_2O$ and the residual carbon and nitrogen form charcoal. The basal spacings at 1.31–1.34 and 1.28 nm recorded at 300 and 360°C, respectively, indicate the presence of monolayer charcoal in the interlayer. This observation proves that before the thermal treatment HDTMA cations were located inside the interlayers of the organo-clays. Table 2 shows that heating at >250°C OC-41 and OC-90 air-dried from the organic solvent suspensions, also results in the formation of intercalated charcoal.

*Thermo-XRD-analysis of the sorbents after the secondary adsorption*

In most cases the effect of secondary adsorption of nitrobenzene or nitrophenol on the basal spacings of the sorbents is small (Table 2) and conclusions based on these changes on whether the adsorbed species intercalates or is located on the external surface, should be taken cautiously. In the case of Na-clay sorbent, which is collapsed at 360°C, thermo-XRD-analysis is reliable for this purpose. After heating at 360°C spacing of

Na-clay-nitrobenzene or *m*-nitrophenol complexes prepared from aqueous suspensions is ≈1.25 nm, indicating the presence of intercalated charcoal [3, 32, 33]. On the other hand, if prepared from *n*-hexadecane suspensions, at 360°C these complexes collapse to spacing at 0.97 nm, indicating absence of charcoal in the interlayer. To conclude, if adsorption by Na-clay takes place from aqueous suspensions nitrobenzene and *m*-nitrophenol intercalate, but from organic solvents, under the conditions applied here, adsorption occurs on the external surfaces of the clay.

When nitrobenzene is adsorbed by both organo-clays from aqueous or *n*-hexadecane suspensions, spacings of OC-41-nitrobenzene and OC-90-nitrobenzene complexes decrease compared with those of the solvent-treated sorbents before the secondary adsorption (Table 2). From the spacings it is obvious that the lateral HDTMA mono- or bilayer shapes in OC-41 or OC-90, respectively, persist and that nitrobenzene does not form a separate layer in the clay-interlayer. It appears that nitrobenzene molecules are imbedded in cavities between the quaternary ammonium cations. The decrease in basal spacing indicates that the interaction between the clay-O-plane and the organic layers becomes stronger after the secondary adsorption, probably due to π interactions between O atoms and aromatic rings of the imbedded nitrobenzene molecules. In these complexes the aromatic rings should be oriented coplanar or almost so to the clay-O-planes for the π interaction to occur [11].

No decrease in basal spacing occurs by heating at 150°C OC-41-nitrobenzene and OC-90-nitrobenzene complexes obtained from aqueous suspensions (Table 3) suggesting that water does not participate in the shapes of these complexes.

Spacings of OC-41-nitrophenol sorbate-sorbent complexes obtained from aqueous or *n*-hexane suspensions are slightly shorter than those of the sorbents sedimented from these solvents, before the secondary adsorption. Basal spacings at 1.40–1.42 nm indicate that the adsorbed *m*-nitrophenol molecules do not form separate layers, but are imbedded in cavities scattered in the HDTMA monolayers. Shrinkage after the secondary adsorption of *m*-nitrophenol from *n*-hexane indicates that the interaction between the clay-O-plane and the organic layers becomes stronger

Si  Si  Si  Al  Si  Si  Si  Si  Al  Si

O  O  O  O  O  O  O  O  O

H          H

$O_2N–C_6H_4–O$          $O_2N–C_6H_4–O$
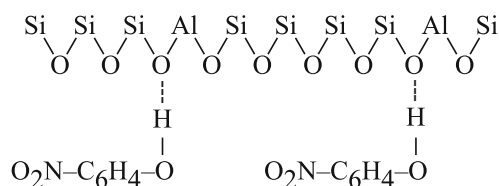
**Scheme 3** Direct interaction between *m*-nitrophenol and the clay-O-plane *via* H-bonds in which the *m*-nitrophenol donates a proton to an oxygen atom of the clay-O-plane
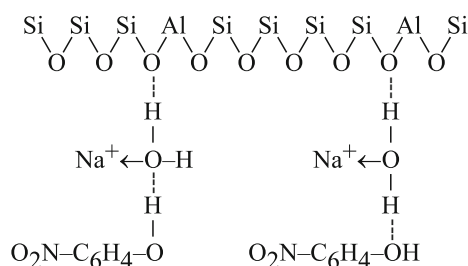
after the secondary adsorption, probably due to H-bonds in which the nitrophenol molecules donate protons to the clay-O-planes (Scheme 3).

OC-90-*m*-nitrophenol complexes obtained either from water or from *n*-hexane suspensions show swelling of 0.21 or 0.29 nm, respectively. Spacings at 2.02 and 2.11 nm characterize three organic layers in the clay interlayer space. Since the van der Waals interactions between the long chains of HDTMA cations and the siloxane groups of the clay are very strong [22, 23], it is suggested that the intercalated *m*-nitrophenol molecules form a separate layer sandwiched between two HDTMA layers.

When OC-41-nitrophenol and OC-90-nitrophenol obtained from aqueous suspensions are heated at 150°C water is evolved with a basal spacing decrease (Table 3) indicating that water participates in these sorbate-sorbent complexes. The difference in behavior between nitrobenzene and nitrophenol may be attributed to the higher hydrophilicity of the latter deduced from their aqueous solubility, that of *m*-nitrophenol is relatively high, 12.150 mg L$^{-1}$, whereas that of nitrobenzene is only 1.949 mg L$^{-1}$ [17]. Nitrophenol–water associations are formed in the interlayers of Na-montmorillonite [13–15] and probably also in the complexes of OC-41 and OC-90 obtained from aqueous suspensions.

At room temperature in the interlayer of OC-41-*m*-nitrophenol water molecules probably bridge between nitrophenol, Na$^+$ cations not replaced during the synthesis of the sorbent, and oxygens of the clay-O-plane (Scheme 4). Dehydration results in H-bonds of phenol groups with the clay-O-plane and shrinkage (Scheme 3).

In the interlayer of OC-90 water molecules, quaternary ammonium cations, with charged heads and hydrophobic tails, and *m*-nitrophenol molecules, with hydrophilic groups and organophilic rings, are arranged so as to accommodate their organophilic-hydrophilic nature [34]. We assume that the organophilic field exerted by the two parallel layers of the long chain ammonium cations leads to the formation of quasi-nano-micelles in which few water molecules are surrounded by *m*-nitrophenol molecules with their OH groups directed towards the center of the water cluster. Formation of the quasi-nano-micelles minimizes the contact between water molecules or phenol OH groups and HDTMA organophilic chains. Spacing at 2.02 nm requires some 'keying' of the quasi nano-micelles into cavities in the HDTMA layers. At 150°C this complex is destroyed as can be seen from the critical decrease in basal spacing (Table 3). The idea on the formation of quasi-nano-micelles is based on studies of organic ammonium–amine associations formed in montmorillonite-interlayers with water molecules or hydronium cations bridging between amine molecules [35–37]. Further study by other methods is required to understand the nature of these quasi-nano-micelles.

There are no changes in basal spacing when these complexes obtained from *n*-hexane suspensions are heated at 150°C. The spacing of OC-41-nitrophenol before and after heating at 150°C is 1.40 nm and that of OC-90-nitrophenol is 2.11 nm. Since the boiling point of *n*-hexane is 68.75°C it appears that it does not participate in the shapes of these complexes.

When nitrobenzene or *m*-nitrophenol complexes of OC-41 and OC-90, prepared from aqueous or organic solvent suspensions are heated at >250°C charcoal is formed in the interlayers mainly from the air-oxidation of HDTMA cations.

## Conclusions

OC-41 consists of intercalated monolayers of HDTMA cations with their long chains parallel to the clay-O-planes whereas OC-90 consists of parallel bilayers of HDTMA cations.

Thermo-XRD-analysis of Na-clay complexes of nitrobenzene and *m*-nitrophenol shows that under the adsorption conditions applied here, from organic solvents both sorbents are adsorbed on the external clay-surface but from water they intercalate.

In the secondary adsorption of nitrobenzene by OC-41 and OC-90 from aqueous or organic suspensions, the HDTMA mono- and bilayer shapes, respectively, persist. The nitrobenzene molecules are imbedded in cavities between the HDTMA cations with π interactions between the clay-O-planes and the aromatic rings of the imbedded molecules.

In the secondary adsorption of nitrophenol by OC-41 from aqueous or organic suspensions, the HDTMA monolayer shape persists and the nitro-

Si  Si  Si  Al  Si  Si  Si  Si  Al  Si

O  O  O  O  O  O  O  O  O

H                    H

Na$^+$←O–H          Na$^+$←O

H                    H

O$_2$N–C$_6$H$_4$–O      O$_2$N–C$_6$H$_4$–OH

**Scheme 4** Indirect interaction between *m*-nitrophenol and the clay-O-plane through the intermediation of a water bridge. The bridging water molecule is H-bonded to the O-plane and to the nitrophenol. Left, the *m*-nitrophenol donates a proton to the oxygen atom of the water molecule. Right, the *m*-nitrophenol accepts a proton from the bridging water molecule. The bridging water molecule may also be coordinated to the exchangeable Na$^+$

phenol molecules are imbedded in cavities between the HDTMA cations. In the complex obtained from *n*-hexane, nitrophenol is H-bonded with the clay-O-plane. In that obtained from aqueous suspension it is bonded with the clay-O-plane through the intermediation of water.

In OC-90-nitrophenol complex obtained from aqueous suspension, two parallel HDTMA layers sandwich a layer of water quasi-nano-micelles surrounded by nitrophenol molecules. In the complex obtained from *n*-hexane suspension, a layer consists of *m*-nitrophenol is obtained sandwiched between two parallel HDTMA layers.

# References

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