

SORPTION OF ALKYLAMMONIUM CATIONS ON MONTMORILLONITE

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ABSTRACT

Adsorption procedure of two cationic surfactants hexadecyltrimethylammonium bromide (HDTMABr) and benzyldimethylhexadecylammonium chloride (BDHDACl) onto two samples of montmorillonite was studied. Infrared spectroscopy and X-ray diffraction proved intercalation of both quaternary cations into the interlayer space of montmorillonite. An aspect of time showed not to be important for the cations adsorption.

KEYWORDS: adsorption, montmorillonite, hexadecyltrimethylammonium, benzyldimethylhexadecylammonium**1. INTRODUCTION**

The composite materials based on clay minerals are developed with aim to obtain new materials with predefined and required properties that predetermine composites to a broad range of applications both in industry and in science (Barabaszová, 2006). Clay mineral as an inorganic part of composite serves as a framework for intercalation of various organic compounds. In comparison to natural clay minerals the intercalated clay minerals – the organically modified clays (organo-clays) exhibit a higher affinity to reactions with neutral, non-polar organic molecules or anions (Ray and Okamoto, 2003; Boyd and Jaynes, 1994; Lagaly, 1994).

Intercalation of alkylammonium or alkylphosphonium cations into the clay minerals goes via ion exchange resulting in occupation an interlayer space of the clay structure. Ion exchange of primary, secondary, tertiary and quaternary alkylammonium or alkylphosphonium cations changes the hydrophilic surfaces of the clay structure into organophilic, which enables sorption or intercalation of the organic compounds (Boyd and Jaynes, 1994; Lagaly, 1994; DaSilva et al., 2006). For example, the smectite intercalated with various tetra-alkylammonium cations exhibited the significant sorption of benzene, especially in the case of tetra-methylammonium cation (Chun et al., 2003). Organically modified clays based on montmorillonite and dodecyltrimethylammonium or dioctadecyldimethylammonium cation were used for adsorption and subsequent degradation of chlorobenzene (Witthuhn et al., 2006). Hexadecyltrimethylammonium chloride was applied for modification of bentonite; the formed organo-clay complex was highly efficient (about 99 %) for

removing of humic substances from the waste waters (Anirudhan and Ramachandran, 2007). Adsorption of volatile organic compounds (benzene, tetrachloromethane) on the porous material based on organobentonites was studied in the connection with their thermal stability and the hydrophobic and adsorption properties (Zhu et al., 2005). In addition to sorption of the organic compounds, anions such as chromates or arsenites can be also accumulated onto the organo-montmorillonites (Li and Browman, 2001).

Recently, clay minerals with intercalated alkylammonium cations have found their application in the field of sensors, they are used as electrode modifiers. These modified electrodes are suitable for determination of pesticides (Manisankar et al., 2006) or anion metal complexes (Ngameni and Tonlé, 2006).

The work represents a preliminary study aimed to preparation of montmorillonite modified with alkylammonium cations that differed in a content of aromatic function group (see Fig. 1). The time aspect of the adsorption of the organic cations was included, too. Infrared spectroscopy and X-ray diffraction were used to prove a formation of the organically modified montmorillonite.

2. EXPERIMENTAL**2.1. CHEMICALS AND MATERIALS**

The chemicals used were of analytical reagent grade: hexadecyltrimethylammonium bromide (HDTMABr) (Sigma-Aldrich), benzyldimethylhexadecylammonium chloride (BDHDACl) (Fluka), ethanol 97 %.

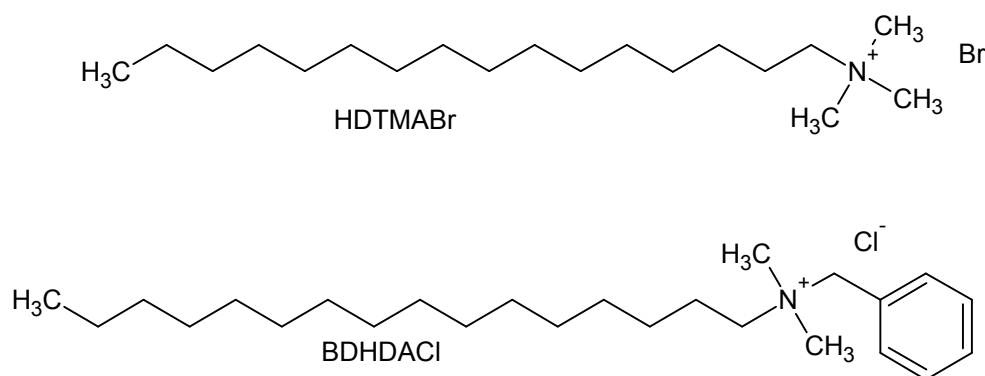


Fig. 1 Structures of alkylammonium cations.

Two samples of montmorillonites, namely MMT(SWy-2) (Crook County, USA) and MMT(JP) (Jelšový Potok, Slovakia) were treated by sedimentation and subsequent centrifugation (3000 min⁻¹, 45 min) to prepare fractions with the particle size below 10 μm. The prepared fractions were proved by means of particle size analysis (Fritsch Particle Sizer Analysette 22, Technical University, Ostrava). MMT(SWy-2) exhibited 82 % of particles with the size below 7 μm, MMT(JP) exhibited 100 % of particles with the size below 4.55 μm.

2.2. METHODS

SORPTION PROCEDURE OF ALKYLAMMONIUM CATIONS

The alkylammonium salts were dissolved in water obtaining 0.1 mol l⁻¹ solutions. The suspension of 0.5 g montmorillonite and 10 ml of the water solution of alkylammonium cation was always used for the sorption procedure performed in two modes. The first set of the suspensions was shaken thoroughly for 2.5 h at the room temperature, the second one was equilibrated without shaking for 4 days at the room temperature. All suspensions were centrifuged for 20 min (9000 min⁻¹), the obtained solids were twice washed out in 50 ml of ethanol – water mixture (1 : 2, v/v) and then in ethanol (97 %). The washed out solids were separated by centrifugation for 10 min (9000 min⁻¹). The modified montmorillonites were dried at the room temperature. A residue of bromides and chlorides was not determined in the washing solutions.

IR SPECTROSCOPY

Infrared spectra were recorded on Nicolet Avatar 320 FTIR spectrometer (ThermoNicolet, USA) equipped with a DTGS/KBr detector. The KBr pressed-disc technique (1 mg of sample and 200 mg of KBr) was used. The spectra of modified montmorillonites were measured by accumulating 64

scans at 4 cm⁻¹ resolution in the spectral range from 4000 to 400 cm⁻¹.

X-RAY DIFFRACTION

X-ray diffraction (XRD) analysis using Co-Kα (λ = 0.179 nm) radiation was carried out on a diffractometer D8 Advance (BRUKER, Germany) with VANTEC detector (Dr. Simha Martynková Gražyna, Nanotechnology Centre, Technical University, Ostrava).

3. RESULTS AND DISCUSSION

3.1. SORPTION OF ALKYLAMMONIUM CATIONS

Four samples of the organically modified montmorillonites were prepared by sorption of hexadecyltrimethylammonium bromide and benzyltrimethylhexadecylammonium chloride onto MMT(SWy-2) and MMT(JP): HDTMA-MMT(SWy-2), BDHDA-MMT(SWy-2), HDTMA-MMT(JP), and BDHDA-MMT(JP). An influence of the sorption time was studied using infrared spectroscopy. The features of absorption spectra of the organo-montmorillonites exhibited no significant differences in the dependence on the sorption time. The relative intensities of the C–H stretching vibrations at 2925 cm⁻¹ (asym. –CH₂–) and 2850 cm⁻¹ (sym. –CH₂–) were also very similar. The sorption procedure performed by shaking the suspensions of MMT and the water solution of alkylammonium cation of the given concentration for 2.5 h showed to be sufficient.

3.2. INFRARED SPECTROSCOPY

3.2.1. ORIGINAL MONTMORILLONITES

IR spectra of the original montmorillonites were found in a user FTIR spectral library of Clay Minerals (Institute of Geonics, Ostrava). The interpretation of corresponding absorption bands according to (Madejová, 1995; Madejová, 2003; Vaculíková, 2006) is presented in Table 1. The main absorption band in

Table 1 Position and assignment of the absorption bands (cm^{-1}) in IR spectra of original montmorillonites.

| Assignment | MMT(SWy-2) | MMT(JP) |
|---|------------|---------|
| OH stretching of structural hydroxyl groups | 3630 | 3626 |
| OH stretching of water | 3427 | 3427 |
| OH deformation of water | 1636 | 1637 |
| Si-O stretching of quartz | 1165 | |
| Si-O stretching (longitudinal mode) | 1120 | 1114 |
| Si-O stretching | 1049 | 1035 |
| Al-Al-OH deformation | 918 | 915 |
| Al-Fe-OH deformation | 880 | |
| Al-Mg-OH deformation | 845 | 848 |
| Si-O stretching of quartz and silica | 798 | 800 |
| Si-O stretching of quartz | 778 | - |
| Si-O | 695 | 695 |
| coupled Al-O and Si-O, out-of-plane | 621 | 626 |
| Al-O-Si deformation | 524 | 523 |
| Si-O-Si deformation | 467 | 467 |

IR spectra of montmorillonites located near 1040 cm^{-1} belongs to the Si-O stretching vibrations. The next intensive bands at 523 cm^{-1} and 467 cm^{-1} are due to the bending vibrations of Al-O-Si and Si-O-Si bonds, respectively. OH stretching modes of structural hydroxyl groups and water molecules lie in the spectral region of $3000\text{-}3800 \text{ cm}^{-1}$. The position of the hydroxyl stretching band at 3626 cm^{-1} in IR spectrum of MMT(JP) is typical for Al-rich dioctahedral layer minerals. In addition to bands common to all dioctahedral montmorillonites, the diagnostic bands of quartz as doublet at 798 and 778 cm^{-1} appear in the IR spectrum of MMT(SWy-2). A weak absorption at 800 cm^{-1} in IR spectrum of MMT(JP) confirms admixture of volcanic glass.

3.2.2. MODIFIED MONTMORILLONITES

The results of MMT(SWy-2) and MMT(JP) intercalation with HDTMA and BDHDA were evaluated by means of infrared spectroscopy. The IR spectra of the pure alkylammonium salts helped to better distinguishing the new visible absorption bands in spectra of the modified montmorillonites. These IR spectra are demonstrated in Figs. 2 - 5.

The stretching vibrations of the C-H bonds occurring in the $2800 - 2950 \text{ cm}^{-1}$ region reflect C_{16}

chains of both alkyl ammonium compounds. The absorption band at 2925 cm^{-1} and 2850 cm^{-1} corresponding to antisymmetric and symmetric stretching CH_2 were found in all IR spectra of intercalated montmorillonites (Figs. 2, 3). The bending vibrations of C-H fragments appear at 1474 cm^{-1} . The presence of benzene rings in BDHDA-MMTs confirms a two pairs of weak absorption peaks observed at 3062 cm^{-1} and 3032 cm^{-1} (Fig. 5). These absorptions are due to the stretching C-H bonds on benzene ring. A band at 1487 cm^{-1} is probably related to the bending vibration of N-H groups (Figs. 4, 5). It is evident that HDTMA and BDHDA alkylammonium cations are present in the modified montmorillonites. Both intercalation and adsorption either on the edges or on the external surfaces of MMT(SWy-2) and MMT(JP) can be considered.

3.3. X-RAY DIFFRACTION

The obtained XRD spectra of the modified montmorillonites (a typical one is on Fig. 6) were analysed to calculate the corresponding values of the basal spacing of montmorillonites. The found basal spacing of the prepared organo-montmorillonites was compared with those of the unmodified montmorillonites (Table 2).

Table 2 Basal spacing values $d(001)$.

| montmorillonite | $d(001)$ [\AA] | montmorillonite | $d(001)$ [\AA] |
|------------------|---------------------------|-----------------|---------------------------|
| MMT(SWy-2) | 13.6 | MMT(JP) | 15.0 |
| HDTMA-MMT(SWy-2) | 21.5 | HDTMA-MMT(JP) | 26.4 |
| BDHDA-MMT(SWy-2) | 23.3 | BDHDA-MMT(JP) | 28.4 |

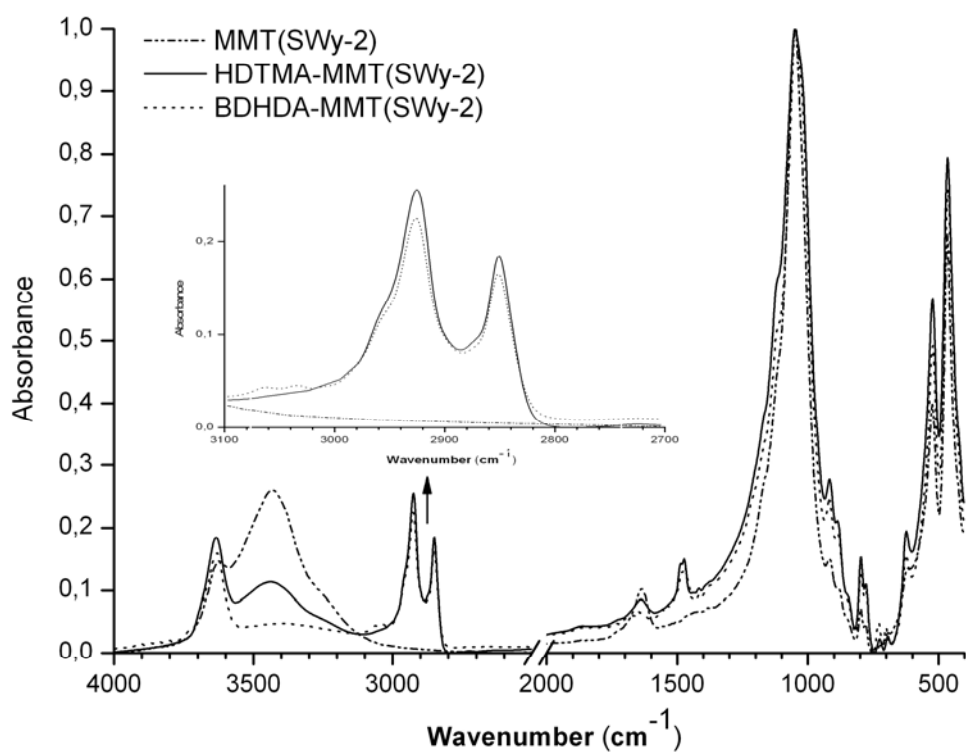


Fig. 2 IR spectra of original MMT(SWy-2) and modified HDTMA-MMT(SWy-2) and BDHDA-MMT(SWy-2).

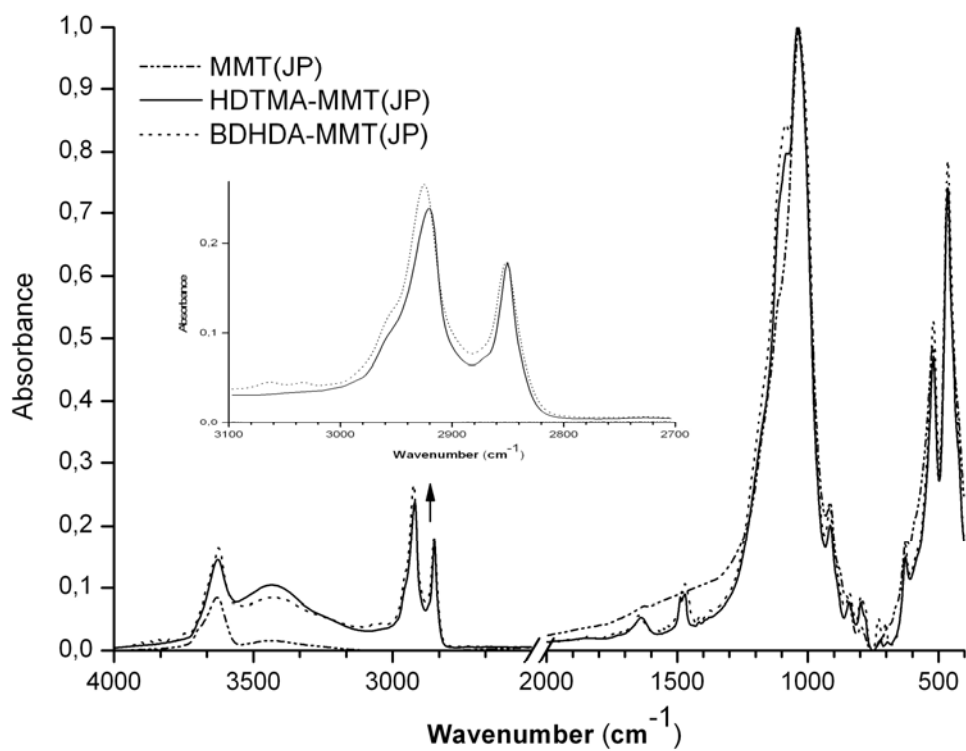


Fig. 3 IR spectra of original MMT(JP) and modified HDTMA-MMT(JP) and BDHDA-MMT(JP).

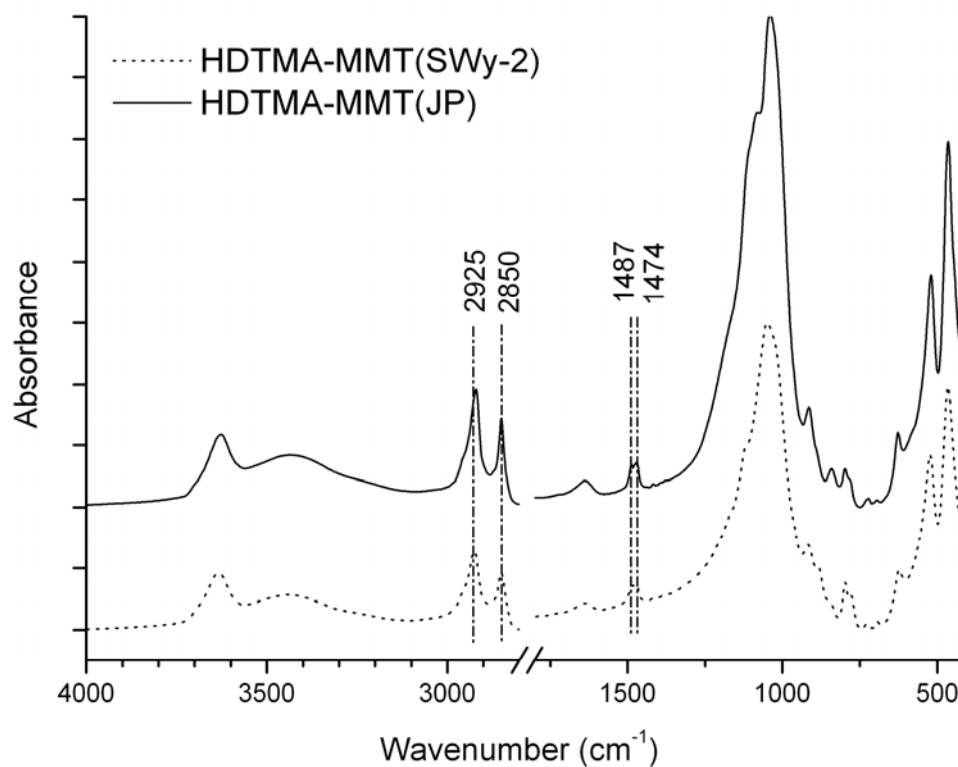


Fig. 4 IR spectra of HDTMA-MMT(SWy-2) and HDTMA-MMT (JP).

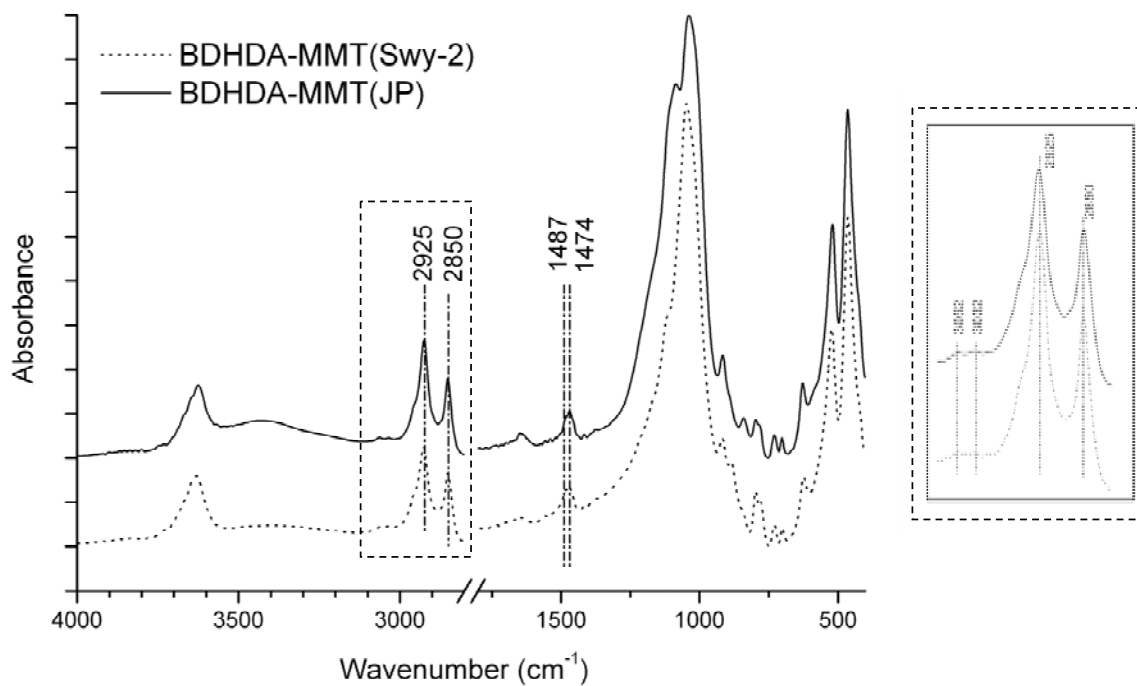


Fig. 5 IR spectra of BDHDA-MMT(SWy-2) and BDHDA-MMT (JP).

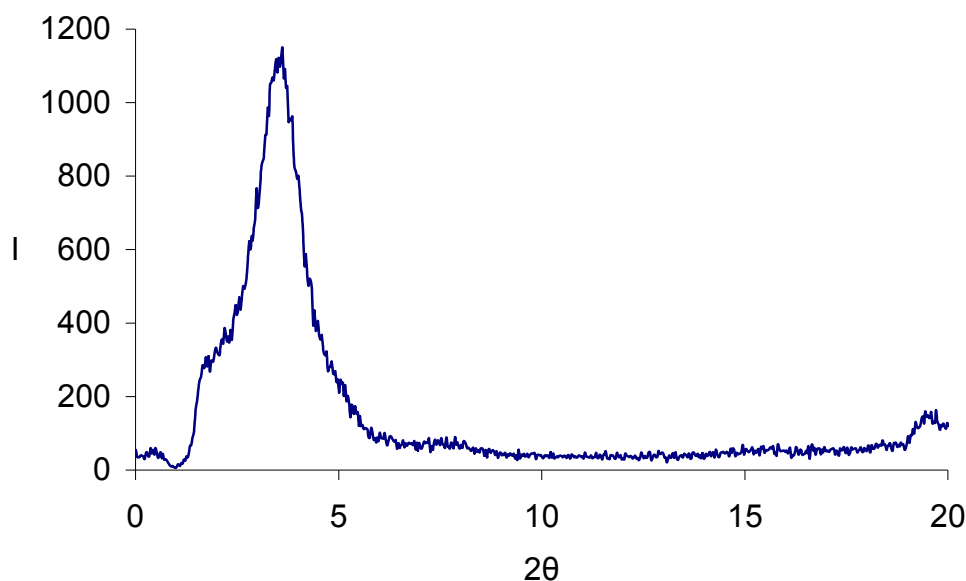


Fig. 6 XRD spectrum of BDHDA-MMT(JP).

The enhancement of the value $d(001)$ indicates an intercalation of alkylammonium cations into both types of montmorillonites. The higher intercalation of benzyldimethylhexadecylammonium is caused by a system of π electrons present in benzene nucleus in the BDHDA structure (Fig. 1). The same results were found in the case of pyridinium rings (Praus et al., 2006). Such types of structures are attached to montmorillonite not only by the electrostatic forces due to the ion exchange but also by means of additional interactions. Both induced interactions between benzene nucleus and clay layer surface and π - π interactions of the neighbouring benzenes are supposed.

Montmorillonite MMT(JP) exhibited the higher sorption of both alkylammonium cations as follows from the higher values of basal spacing. This fact can be probably explained by an inhomogeneous distribution of layer charge of the used montmorillonites. The charge range is $0.25 - 0.36 e^-$ in the case of MMT(JP) (Čumakov et al., 2000) and $0.26 - 0.42 e^-$ (Mermut and Lagaly, 2001) in the case of MMT(SWy-2). Unexpectedly, the extent of the intercalated alkylammonium cations is opposite to cation exchange capacity of the studied montmorillonites measured formerly (Navrátilová and Vaculíková, 2006) - 0.46 mol kg^{-1} (MMT(JP)) and 0.76 mol kg^{-1} (MMT(SWy-2)). This result proves that not only the ion exchange of the organo cations takes place during their sorption.

An arrangement of the organic cations in the interlayer space of montmorillonite can be also

estimated according to the obtained $d(001)$ values. In agreement with the older conclusions (Lagaly, 1994) the arrangement of both cations differs. As the typical $d(001)$ value for bilayer arrangement is 17.6 \AA , the obtained values (Table 2) suggest more than bimolecular structure of the intercalated cations. The type MMT(SWy-2) exhibits rather pseudotrimolecular arrangement – the polar constituents of molecule are attached to the silicate layer, those nonpolar are twisted together forming the trilayer. The $d(001)$ values of MMT(JP) correspond to a paraffin-type of arrangement – the ammonium groups are attached to the silicate layer, the nonpolar chains are oriented under the tilt angle 46.3° (HDTMA) and 41.1° (BDHDA). However, an accurate boundary between these two structures cannot be found.

4. CONCLUSION

The organo-montmorillonites HDTMA-MMT(SWy-2), BDHDA-MMT(SWy-2), HDTMA-MMT(JP), and BDHDA-MMT(JP) exhibited IR spectra giving evidence about sorption or intercalation of the alkylammonium cations. The most intense valence bands at 2925 cm^{-1} and 2850 cm^{-1} relate to the stretching vibrations of C-H bonds of alkyl chains. Benzene nucleus was identified according to the bands at 3062 cm^{-1} and 3032 cm^{-1} .

The content of aromatic ring contributed to the higher intercalation due to the induced interactions between aromatic ring and clay layer surface and due to π - π interactions of aromatic ring. The pseudotrimolecular arrangement of the intercalated alkyl-

ammonium cations is supposed in the case of MMT(SWy-2), the arrangement of a paraffin-type is considered in the case of MMT(JP).

It can be concluded that intercalation of alkylammonium cations takes place both via ion exchange and via other interactions, such as induced and π - π interactions. The montmorillonites modified with alkylammonium cations are supposed to exhibit significant altered properties with regard to sorption of organics and anions.

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