

An infrared study of adsorption of *para*-nitrophenol on mono-, di- and tri-alkyl surfactant intercalated organoclays

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Abstract

Infrared spectroscopy has been used to study the adsorption of *para*-nitrophenol on mono-, di- and tri-alkyl surfactant intercalated montmorillonite. Organoclays were obtained by the cationic exchange of mono-, di- and tri-alkyl chain surfactants for sodium ions [hexadecyltrimethylammonium bromide (HDTMAB), dimethyldioctadecylammonium bromide (DDOAB), methyltrioctadecylammonium bromide (MTOAB)] in an aqueous solution with Na–montmorillonite. Upon formation of the organoclay, the properties change from strongly hydrophilic to strongly hydrophobic. This change in surface properties is observed by a decrease in intensity of the OH stretching vibrations assigned to water in the cation hydration sphere of the montmorillonite. As the cation is replaced by the surfactant molecules, the *para*-nitrophenol replaces the surfactant molecules in the clay interlayer. Bands attributed to CH stretching and bending vibrations change for the surfactant intercalated montmorillonite. Strong changes occur in the HCH deformation modes of the methyl groups of the surfactant. These changes are attributed to the methyl groups locking into the siloxane surface of the montmorillonite. Such a concept is supported by changes in the SiO stretching bands of the montmorillonite siloxane surface. This study demonstrates that *para*-nitrophenol will penetrate into the untreated clay interlayer and replace the intercalated surfactant in surfactant modified clay, resulting in the change of the arrangement of the intercalated surfactant.

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1. Introduction

Organoclays may be synthesised by ion exchange of the mono or divalent cations (for example Na⁺, Mg²⁺ or Ca²⁺) with a large organic cation such as hexadecyltrimethylammonium bromide. The properties of these materials change from hydrophilic to hydrophobic/lipophilic. These clays then have useful properties, for example the removal of oil, toxic chemicals and humic materials from water [1–3]. These modified clay minerals, organoclays, represent a family of materials which have a lot of applications in a range of key areas, such as adsorbents for organic pollutants [4,5], rheological control agents [6], reinforcing fillers for plastics and electric materials [7–9].

The influence of montmorillonite surfaces on the chemical and physical properties of adsorbed H₂O molecules has been the subject of a number of recent studies using structural, thermodynamic, spectroscopic and computational methods. Generally, the position of the ν_2 mode of H₂O decreases and H₂O stretching band shifts to higher wavenumber upon lowering the H₂O content in cation-exchanged montmorillonite. At the same time, the cation type is determinative for total water content retained in clay minerals. However, to the best of our knowledge, there are few reports about the role of sorbed H₂O molecules in organoclays and it is very important for the application of organoclays. Hence, the situation of the sorbed H₂O molecules in organoclays at different surfactant concentrations is discussed in this paper. Recently FTIR spectroscopy using ATR and KBr pressed disk techniques has been used to characterize sorbed water and HDTMA⁺ in organoclay [10,11]. It was found that sorbed water content decreases with the intercalation of HDTMA⁺. In this

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work we extend these studies to the changes in the surfactant upon intercalation and to the adsorption/absorption of a test molecule namely *para*-nitrophenol on the organoclay. Attenuated total reflection (ATR) technique is used to study the changes in structure of the organoclay formed between a montmorillonitic clay and hexadecyltrimethylammonium bromide and the adsorbed *para*-nitrophenol.

2. Experimental

2.1. Materials

Montmorillonite ($\text{Na}_{0.053}\text{Ca}_{0.176}\text{Mg}_{0.1} \cdot n\text{H}_2\text{O}$)[$\text{Al}_{1.58}\text{Fe}_{0.03}\text{Mg}_{0.39}$][$\text{Si}_{3.77}\text{Al}_{0.23}$] $\text{O}_{10}(\text{OH})_2$ used was primarily Ca–Mt from Neimeng, China. The montmorillonite was cation exchanged with sodium ions by repeated reaction with sodium carbonate. Its cation exchange capacity (CEC) is 90.8 mequiv./100 g. The *para*-nitrophenol and surfactants (HDTMAB, DDOAB, and MTOAB) used were of analytical grade chemical reagents. The aqueous solubility of *para*-nitrophenol is 1.6×10^4 mg/L at 25 °C. The surfactants used were hexadecyltrimethylammonium bromide labeled HDTMAB [$\text{CH}_3(\text{CH}_2)_{15}\text{NBr}(\text{CH}_3)_3$], dimethyldioctadecylammonium bromide labeled DDOAB [$\text{CH}_3(\text{CH}_2)_{17}]_2\text{NBr}(\text{CH}_3)_2$, methyltrioctadecylammonium bromide labeled MTOAB [$\text{CH}_3(\text{CH}_2)_{17}]_3\text{NBr}(\text{CH}_3$).

2.2. Preparation of the organoclay

The syntheses of organoclay hybrids were undertaken by each of the following procedure: The pure Ca–Mt was added into Na_2CO_3 solution, stirred for 3 h with 800 rpm and drops of HCl were added into the suspension to dissolve the CO_3^{2-} . Then the suspension was washed several times with deionized water until it was chloride free and dried at 108 °C. Such a treated montmorillonite is designated as Na–Mt. The clarifying surfactant solution was obtained when certain amounts surfactants were added into hot distilled water. Then special amounts Na–Mt were added into the above-mentioned solution and the mixtures were stirred slightly in order to avoid the yield of spume in an 80 °C water bath for 2 h. The water/Na–Mt mass ratio is 10. Then the suspension was subsequently washed with distilled water for four times. The moist solid material was dried at 60 °C and ground with a mortar. The obtained surfactant modified montmorillonites were labeled as 0.5CEC-S, 0.7CEC-S, 1.5CEC-S, 2.5CEC-S, 0.5CEC-D, 0.7CEC-D, 1.5CEC-D, 2.5CEC-D and 1.5CEC-T, respectively. The symbols S, D and T mean HDTMAB, DDOAB, and MTOAB separately.

2.3. Adsorption of the *para*-nitrophenol on the organoclay

A total of 0.2 g of different type montmorillonites were combined with 30 mL of different concentration of *para*-nitrophenol solution whose initial pH value is about 5.0 in 50 mL Erlenmeyer flasks with glass caps. The flasks were shaken for different times at certain temperature on a shaker at 150 rpm. After being centrifuged at 3500 rpm for 10 min, the *para*-nitrophenol

concentration in the aqueous phase was determined by a UV-260 spectrophotometer at 317 nm, the detection limits being 0.05 mg/L. The *para*-nitrophenol uptake on the montmorillonite was calculated by the following equation: $Q = (C_0 - C_t)V/m$, where Q is the *para*-nitrophenol uptake, C_0 the initial concentration, C_t the equilibrium concentration, V the column of *para*-nitrophenol solution and m is the quality of sorbents. In order to get the optimum sorption of *para*-nitrophenol from aqueous solutions, conditions were modified according to specific parameters. The losses of the *para*-nitrophenol by both photochemical decomposition and volatilization were found to be negligible during adsorption [12].

2.3.1. Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–550 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s . Spectral manipulation such as baseline adjustment, smoothing and normalization were performed using the GRAMS[®] software package (Galactic Industries Corporation, Salem, NH, USA).

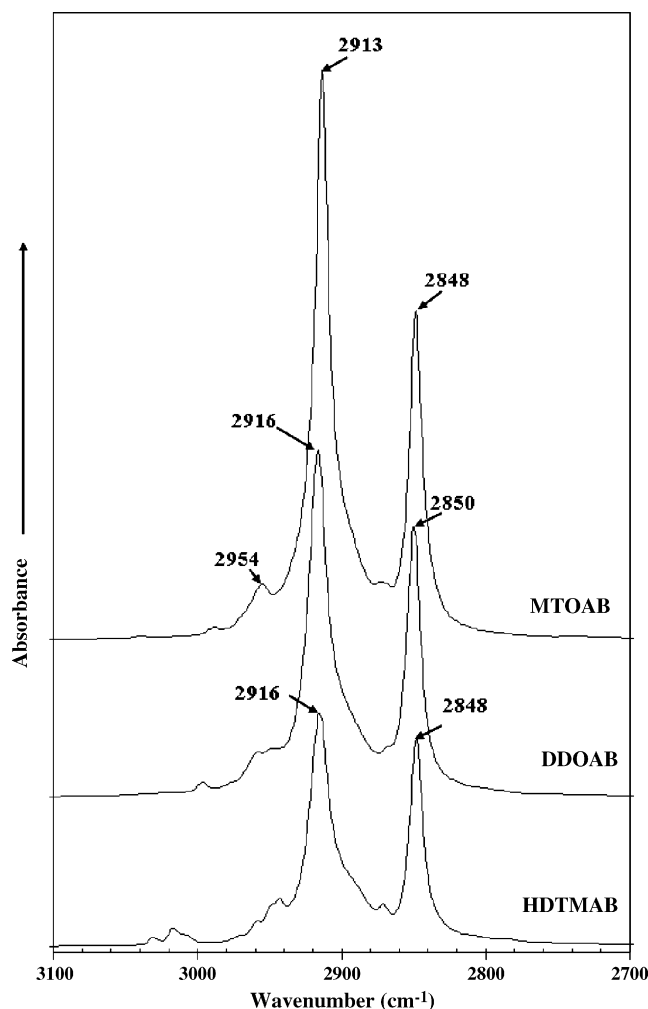


Fig. 1. Infrared spectra of the surfactants HDTMAB, DDOAB, MTOAB in the 2700 to 3100 cm^{-1} region.

3. Results and discussion

3.1. Infrared spectroscopy

The infrared spectroscopy of the montmorillonitic clay modified with hexadecyltrimethylammonium bromide (HDTMAB), dimethyldioctadecylammonium bromide (DDOAB), methyltrioctadecylammonium bromide (MTOAB) may be divided into sections according to the functional groups. The CH stretching region of the three-surfactant molecules in the 2700–3100 cm^{-1} region are shown in Fig. 1. The infrared spectra of the CH stretching 2700–3100 cm^{-1} region of montmorillonite, with and without adsorbed *para*-nitrophenol, 1.5 CEC-single-alkyl chain, with and without adsorbed *para*-nitrophenol, 1.5 CEC-double-alkyl chain, with and without adsorbed *para*-nitrophenol, 1.5 CEC-triple-alkyl chain, with and without adsorbed *para*-nitrophenol are shown in Fig. 2. The infrared spectra of the OH stretching 2700–3100 cm^{-1} region of montmorillonite, with and without adsorbed *para*-nitrophenol, 1.5 CEC-single-alkyl chain, with and without adsorbed *para*-nitrophenol, 1.5 CEC-double-alkyl chain, with and without adsorbed *para*-nitrophenol, 1.5 CEC-triple-alkyl

chain, with and without adsorbed *para*-nitrophenol are shown in Fig. 3.

3.2. CH stretching region

Pnp does not show any bands in the CH stretching region, nor does the montmorillonite. Infrared bands are observed for the surfactant molecules in the 2700–3100 cm^{-1} region at around 2954, 2913 and 2848 cm^{-1} . These bands are assigned to the CH antisymmetric and symmetric stretching modes. For the 1.5CEC loaded organoclays, stretching modes are observed at 2954, 2922 and 2850 cm^{-1} . It is observed that the CH antisymmetric stretching modes show a slight shift to higher wavenumbers upon intercalation of the surfactant molecules. A previous study proposed that both the frequencies of antisymmetric and symmetric CH_2 stretching modes of amine chains are extremely sensitive to the conformational changes of the chains and their wavenumbers will decrease as the increase of ordered conformers within clay interlayers, and only when the chains are highly ordered (all-trans conformation), the narrow absorption bands appear around 2916 cm^{-1} ($\nu_{\text{as}}(\text{CH}_2)$) and 2848 cm^{-1} ($\nu_{\text{s}}(\text{CH}_2)$) in the infrared spectrum [13]. However, our present study indi-

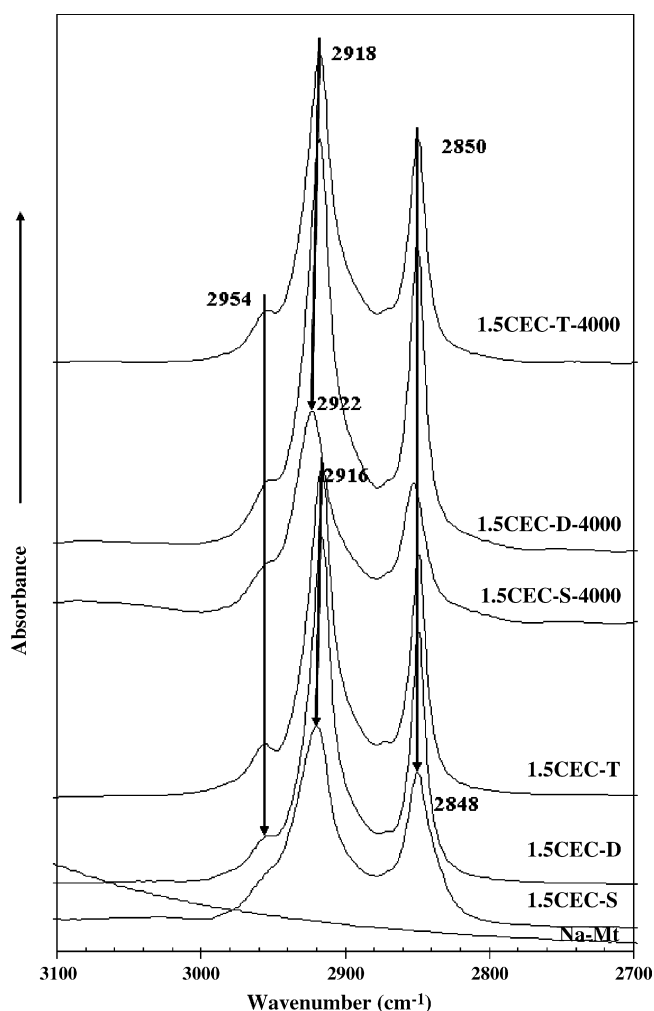


Fig. 2. Infrared spectra of the NaMt, 1.5CEC-S, 1.5CEC-D, 1.5CEC-T, 1.5CEC-S-4000, 1.5CEC-D-4000, 1.5CEC-T-4000 in the 2700 to 3100 cm^{-1} region.

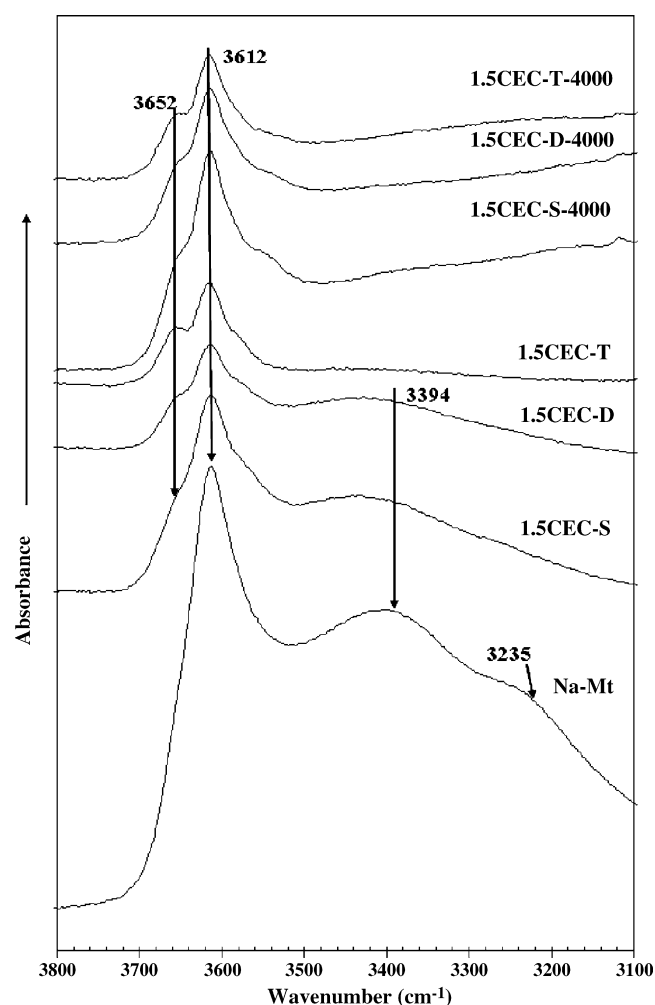


Fig. 3. Infrared spectra of the NaMt, 1.5CEC-S, 1.5CEC-D, 1.5CEC-T, 1.5CEC-S-4000, 1.5CEC-D-4000, 1.5CEC-T-4000 in the 3100 to 3800 cm^{-1} region.

cates that only the wavenumber of antisymmetric CH_2 stretching mode is sensitive to the conformational change of amines within the clay interlayer. This is similar to our previous study on HDTMA^+ in organoclay [10] and provides another evidence for our previous proposal that the antisymmetric CH_2 stretching mode is more sensitive to the conformational ordering than the symmetric stretching mode does.

3.3. OH stretching region

No bands attributable to the surfactant molecules are observed in the OH stretching region. The infrared spectra of the pnp displays peaks at 3400 and 3318 cm^{-1} . These bands are assigned to OH stretching vibrations of the phenol unit. The first band is assigned to non-hydrogen bonded phenol OH units and the second to hydrogen bonded OH units. The intensity of this second band is greater than that of the first band. Two types of hydrogen bonding are possible (a) hydrogen bonding of pnp with itself and (b) hydrogen bonding of the pnp with water. This latter bonding is proposed as a mechanism for the adsorption of pnp on the non-reacted montmorillonite and on the organoclay with low CEC concentrations.

The infrared spectrum of the sodium montmorillonite clay displays two bands at 3612 cm^{-1} attributed to the inner OH unit within the clay structure (Fig. 3). Bands at 3394 and 3235 cm^{-1} are attributed to adsorbed water. The less intense band observed at 3235 cm^{-1} is ascribed to water hydrogen bonded to other water molecules within the interlayer of the montmorillonite. These molecules are involved with the structure of the hydration sphere of the cation within the montmorillonite interlayer. The infrared spectrum sodium montmorillonite with adsorbed pnp shows peaks in similar positions to that of the non-reacted montmorillonite. The bands at 3388 and 3235 cm^{-1} show increased intensity. This result shows that the pnp is adsorbed through hydrogen bonding to the water molecules in the cation hydration sphere.

Infrared bands for the 1.5CEC-S, D, T organoclays show bands at 3612 and 3394 cm^{-1} . The 3235 cm^{-1} band shows minimal intensity for the surfactant molecules in these spectra. Intensity in the 3394 cm^{-1} infrared band is reduced. The loss in intensity in these bands illustrates the change in surface properties upon the formation of the organoclays. The montmorillonite clay is hydrophilic and upon formation of the organoclays becomes hydrophobic. In addition a band at 3652 cm^{-1} (not

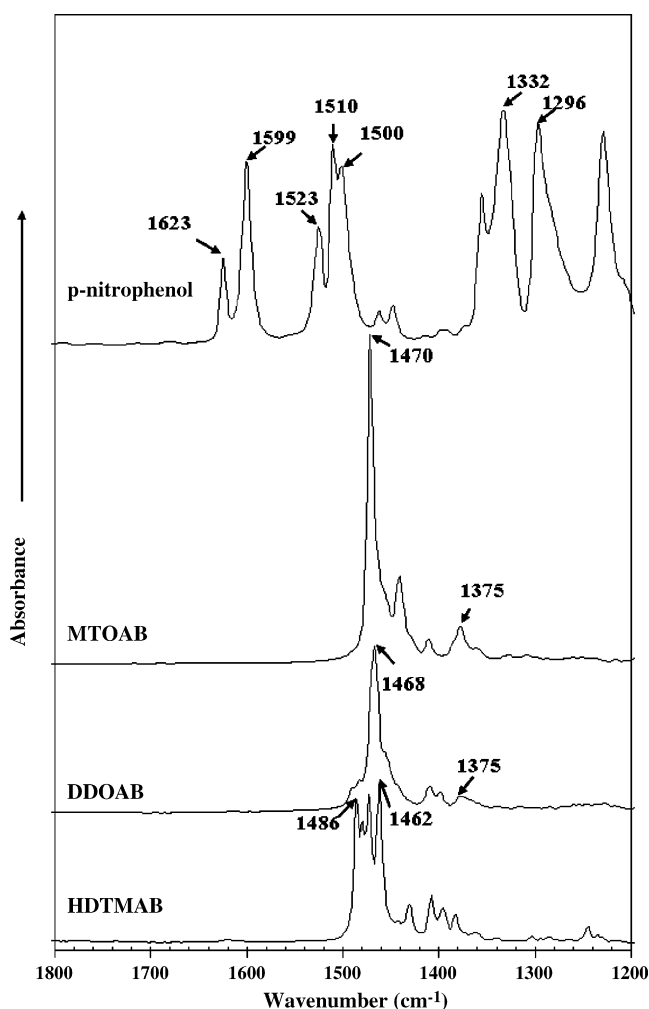


Fig. 4. Infrared spectra of the surfactants HDTMAB, DDOAB, MTOAB and paranitrophenol in the 2700 to 3100 cm^{-1} region.

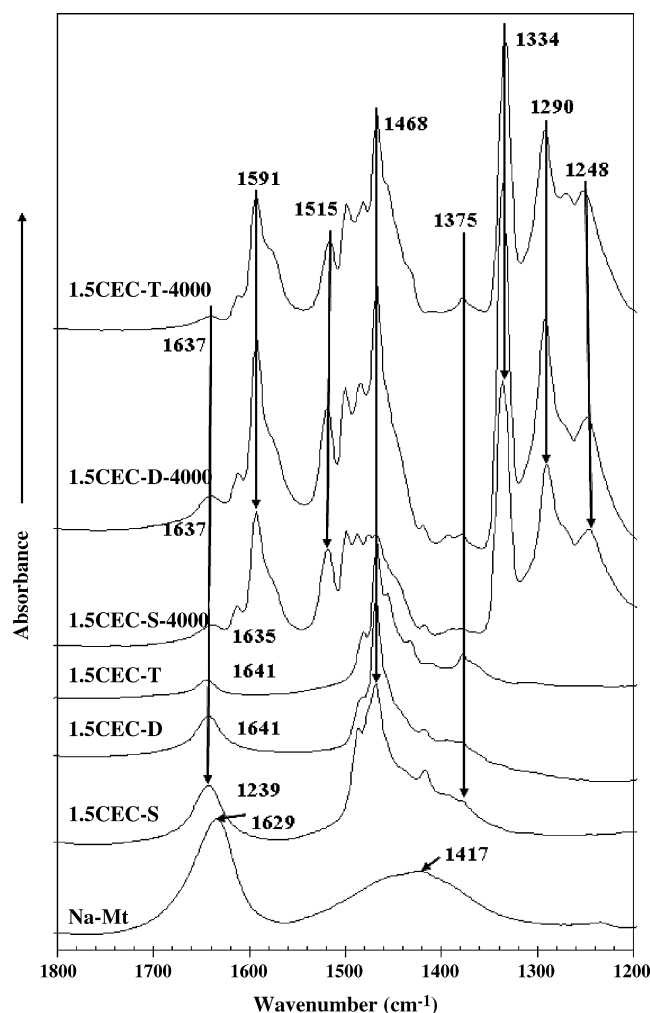


Fig. 5. Infrared spectra of the NaMt, 1.5CEC-S, 1.5CEC-D, 1.5CEC-T, 1.5CEC-S-4000, 1.5CEC-D-4000, 1.5CEC-T-4000 in the 1200 to 1800 cm^{-1} region.

observed in the infrared spectrum of the montmorillonite) is observed for all the organoclays. One possible assignment of this band is to the inner hydroxyl units of the clay, which are bonded to the surfactant molecules.

3.4. HCH and HOH bending vibrations

The infrared spectra of pnp and the surfactant molecules in the 1200–1800 cm^{-1} region are shown in Fig. 4. The bands between 1375 and 1486 cm^{-1} for the surfactant molecules are attributed to HCH bending modes. Pnp infrared spectrum shows a number of bands at 1623 assigned to OH deformation modes; 1599 ascribed to C=C aromatic stretching vibrations, 1523 attributed to antisymmetric NO_2 stretching vibrations; 1485 described as C–H in-plane bending vibrations; 1332 and 1296 cm^{-1} described by symmetric NO_2 stretching vibrations + C–O stretching vibrations [14]. When the pnp is adsorbed on the montmorillonite shifts in the position of the bands are observed (Fig. 5). The band at 1599 shifts to 1594 cm^{-1} ; 1523 shifts to 1510 cm^{-1} ; 1332–1340 cm^{-1} ; 1296–1281 cm^{-1} . The shifts in these bands provide strong indication that the

pnp has reacted with the montmorillonite clay surfaces. The band at 1629 cm^{-1} is assigned to water bending modes of the water in the hydration sphere within the clay interlayer. The intensity of this band decreases with surfactant loading. The band also shifts to higher wavenumber ($\sim 1640 \text{ cm}^{-1}$) in the organoclays.

3.5. SiO stretching region

The infrared spectra of the surfactant molecules and pnp in the 600–1200 cm^{-1} are shown in Fig. 6. The infrared spectrum of pnp shows a number of strong absorptions at 1178, 1122, 850, 754 and 625 cm^{-1} (Fig. 6). The first two bands are attributed to C–H in-plane bending vibrations. The band at 754 cm^{-1} is assigned to NO_2 wagging vibrations.

The infrared spectra of the organoclays with and without the adsorbed *para*-nitrophenol are shown in Fig. 7. The infrared spectrum of the non-treated montmorillonite displays bands 972, 908, 849 and 833 cm^{-1} . These bands are attributed to SiO stretching and bending vibrations. Other bands are ascribed to the intercalated surfactant molecules.

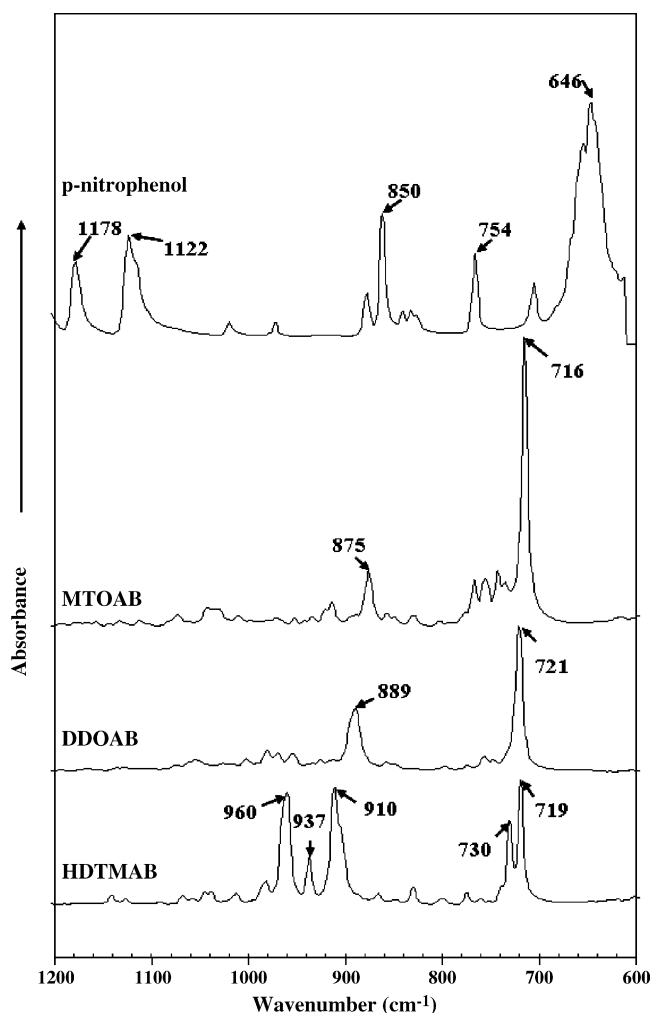


Fig. 6. Infrared spectra of the surfactants HDTMAB, DDOAB, MTOAB and paranitrophenol in the 600 to 1200 cm^{-1} region.

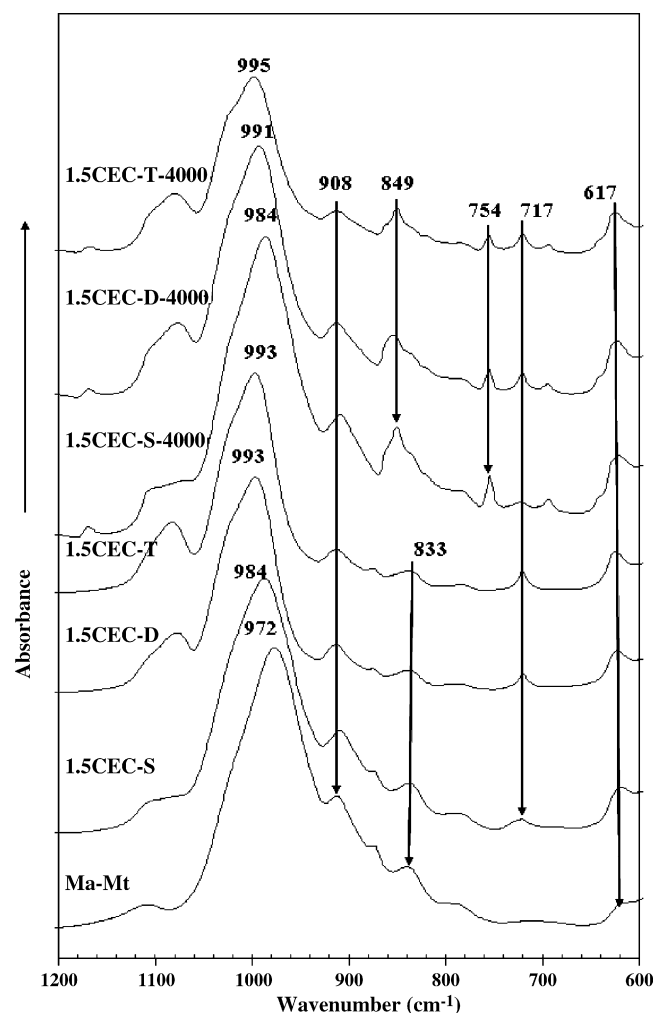


Fig. 7. Infrared spectra of the NaMt, 1.5CEC-S, 1.5CEC-D, 1.5CEC-T, 1.5CEC-S-4000, 1.5CEC-D-4000, 1.5CEC-T-4000 in the 600 to 1200 cm^{-1} region.

4. Conclusions

Infrared ATR techniques were used to study the changes in the band positions and intensity of both the surfactant molecules [hexadecyltrimethylammonium bromide labeled HDTMAB $[\text{CH}_3(\text{CH}_2)_{15}\text{NBr}(\text{CH}_3)_3]$, dimethyldioctadecylammonium bromide labeled DDOAB $[\text{CH}_3(\text{CH}_2)_{17}]_2\text{NBr}(\text{CH}_3)_2$, methyltrioctadecylammonium bromide labeled MTOAB $[\text{CH}_3(\text{CH}_2)_{17}]_3\text{NBr}(\text{CH}_3)$] and the montmorillonite. Changes in both the wavenumber and the intensity of the bands occur at the 1.5 CEC concentration level. Bands which are attributed to water stretching vibrations decrease in intensity as the ion exchange of the sodium from the montmorillonite occurs. Marked changes occur in the surface properties of montmorillonitic clay when the cation Na^+ is replaced with an organocation, in this case HDTMAB, DDOAB or MTOAB.

The clay changes from being hydrophilic to hydrophobic and the clay becomes lipophilic upon formation of the organoclay. This result is very important for the application of organoclays for the adsorption of *para*-nitrophenol from aqueous systems. *para*-Nitrophenol apparently hydrogen bonds to the water in the cation hydration sphere. As the loading of the surfactant increases the amount of available water decreases. The *para*-nitrophenol then interacts with the clay surface replacing or removing some of the surfactant molecules. At the same time, this study demonstrates that *para*-nitrophenol will penetrate into the Na–montmorillonite interlayer, resulting the expand of the interlayer. However, the influences of the adsorbed *para*-nitrophenol on the structure of organoclay are complicated. Generally, *para*-nitrophenol will replace the intercalated surfactant and has a significant influence on the clay interlayer structure, i.e., the arrangement of the intercalated surfactant.

This finding is very important for the application of organoclays as sorbents for organic pollutants.

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