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Near-infrared spectroscopy as an effective tool for monitoring the conformation of alkylammonium surfactants in montmorillonite interlayers

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ABSTRACT

Application of near-infrared (NIR) spectroscopy to probing the arrangement of trimethylalkylammonium cations in montmorillonite interlayers has been demonstrated. Detailed analysis of the mid-IR (MIR) and NIR spectra of montmorillonite from Jelšový Potok (JP, Slovakia) saturated with surfactants with varying alkyl chain length (even numbers of carbon atoms from C6 to C18) was performed to show the advantages of the NIR region in characterizing surfactant conformations. The position of the $\nu_{as}(CH_2)$, (~2930–2920 cm^{-1}), $\nu_s(CH_2)$ (~2860–2850 cm^{-1}), $2\nu_{as}(CH_2)$ (~5810–5785 cm^{-1}), $(\nu+\delta)_{as}(CH_2)$ (~4340–4330 cm^{-1}) and $(\nu+\delta)_s(CH_2)$ (~4270–4250 cm^{-1}) signals was used as an indicator of the *gauche/trans* conformer ratio. For all bands, a shift toward lower wavenumber on increasing the alkyl chain length from 6 to 18 carbons suggests a transition from disordered liquid-like to more ordered solid-like structures of the surfactants. The magnitude of the shift was significantly higher for $2\nu_{as}(CH_2)$ (28 cm^{-1}) than for $\nu_{as}(CH_2)$ (8 cm^{-1}) or $\nu_s(CH_2)$ (10 cm^{-1}), showing the NIR region to be a useful tool for examining this issue. Comparison of the IR spectra of crystalline alkylammonium salts and the corresponding organo-montmorillonites demonstrated a confining effect of montmorillonite layers on surfactant ordering. For each alkyl chain length the CH_2 bands of the organo-montmorillonites appeared at higher wavenumbers than for the unconfined surfactant, thus indicating a higher disorder of the alkyl chains. The wavenumber difference between corresponding samples was always higher in the NIR than in the MIR region. All these findings show NIR spectroscopy to be useful for conformational studies.

1. Introduction

The ability of clay minerals to incorporate organic species into their structures is of great interest for materials science. Most often the organoclays, prepared through the ion-exchange reaction of montmorillonite (Mt) and alkylammonium cations, are investigated because these organic/inorganic hybrid materials have found a lot of industrial applications, e.g. as fillers in polymer nanocomposites or as adsorbents in treatment of contaminated waste streams [1–6]. The behavior and properties of organoclays depend mainly on the structure and the molecular environment of the organic species within the Mt interlayers. Understanding the nature of surfactant self-assembly on the surface of montmorillonite is an important step toward optimizing the performance of organo-montmorillonites in polymer nanocomposites and other potential applications, such as removal of various contaminants where selective surface interactions are crucial [7,8].

Many techniques have been used for studying the arrangement of surfactants in the clay mineral interlayers, most often X-ray diffraction (XRD). Layer spacing of intercalate provides information on the long range order in these materials. Depending on the organic cation type, its loading density, and layer charge of the clay mineral, the alkyl chains once were thought either to lay parallel to the host layers, forming lateral mono- or bilayers, or to radiate away from the surface forming paraffin-type arrangements. In some cases, individual chains were supposed to adopt a hybrid arrangement with both lateral and paraffin-type segments leading to pseudotrilayers [9,10]. Some authors have shown that the two dimensions of the alkyl chain (i.e., c-c zig zag) can be taken into account in interpreting possible interlayer conformations based on XRD [11].

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Vaia et al. [12] was the first to show that such idealized structures, based mainly on all-*trans* segments, were misleading and that the intercalated surfactants could adopt both ordered (all-*trans*) and disordered (*gauche*) conformations. They showed that the positions of the mid-IR bands related to the $\nu_{as}(CH_2)$, $\nu_s(CH_2)$ and $\delta(CH_2)$ modes were sensitive to the organic cation arrangement, which in turn was affected by the interlayer packing density, chain length, and temperature. With increasing interlayer packing density the $\nu_{as}(CH_2)$ band was shifted from 2924.7 cm^{-1} to 2919.6 cm^{-1}, i.e. to the position characteristic for a solid-like environment with prevailing all-*trans* conformers, as observed for the crystalline alkylammonium salts. Pronounced changes were also observed as a function of chain length. The $\nu_{as}(CH_2)$ band observed for hexylammonium-saturated hectorite at 2932 cm^{-1} (a position characteristic for a liquid-like environment) was shifted to 2921 cm^{-1} for the octadecylammonium surfactant, indicating a higher portion of all-*trans* conformers. With increasing temperature the intercalated chains adopted a more disordered structure resulting from an increase in the *gauche*/*trans* conformer ratio. The authors pointed out that the large variation in CH_2 mode positions indicated a wide range of molecular environments of the chains, which was not predicted by the previously proposed idealized structures deduced from XRD.

The other IR studies, focused mainly on the effect of the long alkyl chain surfactants loading on their arrangement, confirmed that the CH_2 stretching bands are extremely sensitive to the conformational changes of the chains [13–19]. Moreover, the CH_2 scissoring mode was also found to be diagnostic. A single band near 1470 cm^{-1} indicated disordered liquid-like molecular environment, whereas the doublet near 1470 and 1460 cm^{-1} suggested an all-*trans* conformation [15]. He et al. [13] showed that with increasing concentration of the hexadecyltrimethylammonium (HDTMA) cation within the galleries of montmorillonite, varying from 0.2 cation exchange capacity (CEC) to 5.0 CEC, both the antisymmetric and symmetric CH_2 stretching absorption bands were shifted to lower frequencies elucidating the increase of ordered conformation. This is in agreement with XRD studies indicating that when there is sufficient packing density of the surfactant within the interlayer, a high degree of order ensues [20,21].

Various infrared techniques have been applied to investigating the conformation of loaded surfactants in organoclays in the mid-IR region. Most often, the KBr pressed disk technique was utilized to prepare samples to acquire transmission spectra [12–18]. The utilisation of IR-transparent windows, such as CaF_2, has hitherto been rather rare [19]. In some studies reflection techniques such as Attenuated Total Reflection (ATR) or Diffuse Reflectance Infrared Fourier Transform (DRIFT) were applied as well [13,14,22]. Ma et al. [14] showed that the transmission spectra obtained by KBr technique were more suitable to probe the conformational ordering of the confined amine chains within the clay galleries rather than ATR, while the ATR and/or DRIFT techniques were more proper to explore the water in organoclays. Direct comparison of the sensitivity of different MIR methods in following changes in organic cations ordering has not been reported yet.

The magnitude of the wavenumber shift of the $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ modes differs depending on the changes in the ratio of *gauche*/all-*trans* conformers. For example, Osman et al. [19] probed the conformation of mono-, di-, tri-, and tetraalkylammonium cations of varying chain length (C4, C8, and C18) self-assembled on montmorillonite platelets at varying temperature. While no shift of the CH_2 bands of C4-4C4, C8-4C8 and C18 was found up to 70 °C, the $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ bands of 3C18 and 4C18 were upward shifted by ~5 cm^{-1} and ~2.5 cm^{-1} with increasing temperature, indicating a more disordered structure. The $\nu_{as}(CH_2)$ band of 2C18 showed a similar increase in wavenumber with temperature but the shift was only 1.5 cm^{-1}. In 2C18, the accuracy of line position determination of $\nu_s(CH_2)$ did not allow the detection of the wavenumber shift with temperature (a shift smaller than 1 cm^{-1} was expected). It is apparent that in some cases the sensitivity of the MIR spectroscopy is not sufficient to identify subtle conformational modifications of the surfactants.

In addition to MIR, near-IR spectroscopy also provides useful information on clay mineral structure [23–28]. Its utilization in organo-clay research is not so common, in spite of such benefits as speed, simplicity of sample preparation and the non-destructive character of the technique [29–35]. Investigations of the self-assembly of surfactants in clay minerals by IR spectroscopy have so far been almost exclusively limited to the mid-infrared region. As the overtone (2ν) and combination ($\nu + \delta$) modes of CH_2 groups appearing in the near-IR spectra of organo-clays are directly related to the fundamental CH_2 vibrations, their positions should also reflect the modification of the alkyl chain arrangements. To the best of our knowledge, however, only in our paper [32] the effect of the surfactant size (C8-4C8, C16 and 2C16) on the position of the $2\nu(CH_2)$ and $(\nu + \delta)(CH_2)$ bands has been even briefly mentioned. A systematic methodological study focused on the potential of NIR spectroscopy to monitor the conformation changes of surfactants in clay mineral has been missing so far.

The goal of the present work was to fill this gap and analyze in detail the first CH overtone and combination regions of a montmorillonite saturated with trimethylalkylammonium cations of gradually increasing alkyl chain length. The primary intention was to show the higher sensitivity of NIR than MIR spectroscopy to recognize the alkyl chain conformation within the montmorillonite interlayers. The effect of alkyl chain length on the organo-cation arrangement was documented as well. The comparison of the IR spectra of organo-Mts with that of the bulk alkylammonium salts used for their preparation has enabled us to demonstrate the effect of montmorillonite platelets on the surfactant configuration.

2. Experimental

2.1. Materials

The raw bentonite, from the Slovak deposit Jelšový Potok (JP), was suspended in distilled water, Na-saturated by repeated treatment with 1 M NaCl, and the <2 μm fraction was collected. The excess salt was removed by washing with deionized water until the $AgNO_3$ test for chlorides gave a negative result. The sample was dried at 60 °C and ground to pass a 0.2 mm sieve. The cation exchange capacity (CEC) of Na-JP (0.98 mmol/g) was determined spectroscopically with a 0.01 M solution of copper (II)-triethylenetetraamine, $[Cu(Trien)]^{2+}$, using the method introduced by Meier and Kahr [36].

The organo-montmorillonites were prepared from Na-JP and alkylammonium salts with increasing length of alkyl chain, from trimethylhexylammonium (C6) to trimethyloctadecylammonium (C18). The organic salts were used as received from Sigma-Aldrich. Two grams of Na-JP were dispersed in 400 ml of distilled water and stirred overnight. An ethanolic solution (100 ml), containing the alkylammonium salt in an amount corresponding to 105% of the CEC of Na-JP, was slowly (2 ml/min) added to the stored suspension of montmorillonite under extensive stirring (500 RPM). Afterwards, the slurry was stirred for another 24 h at 40 °C and left to cool to laboratory temperature. The final product was obtained by repeated centrifugation and washing out with water to remove soluble side products (NaBr) created during the cation-exchange procedure. The obtained samples will be denoted as *CN*-JP, where $N = 6, 8, 10, 12, 14, 16$ and 18.