

## NEAR-INFRARED SPECTROSCOPIC ANALYSIS OF ACID-TREATED ORGANO-CLAYS

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**Abstract**—The potential use of near-infrared (NIR) spectroscopy as a characterization tool for organo-clays would be a great asset but little work has been done in this regard because the application of NIR to clay mineral studies is a relatively new phenomenon. The purpose of this study was to use NIR spectroscopy to investigate the effect of alkylammonium cations on the acid dissolution of a high-charge montmorillonite (SAz-1). Detailed analysis of the spectra of  $\text{Li}^+$ ,  $\text{TMA}^+$  (tetramethylammonium), and  $\text{HDTMA}^+$  (hexadecyltrimethylammonium) saturated SAz-1 montmorillonite in the NIR region was achieved by comparing the first overtone ( $2\nu$ ) and combination ( $\nu+\delta$ ) bands of  $\text{XH}$  groups ( $X = \text{O}, \text{C}$ ) with the fundamental stretching ( $\nu$ ) and bending ( $\delta$ ) vibrations observed in the mid-infrared (MIR) region. Comprehensive analysis of the vibrational modes of  $\text{CH}_3\text{-N}$ ,  $\text{CH}_3\text{-C}$ , and  $\text{-CH}_2\text{-C}$  groups of  $\text{TMA}^+$  and  $\text{HDTMA}^+$  cations detected in the MIR and NIR regions was also performed. Both MIR and NIR spectra demonstrated that exchange of  $\text{Li}^+$  by  $\text{TMA}^+$  only slightly improved the resistance of SAz-1 layers to dissolution in 6 M HCl at 80°C, while exchange by the larger  $\text{HDTMA}^+$  cations almost completely protected the montmorillonite layers from acid attack. Use of NIR spectra in reaching these conclusions was crucial. Only in the NIR region could the creation of SiOH groups be monitored, which is an important indicator of the acidification of the montmorillonite surface. The OH-overtone region in the spectra of Li-SAz-1 and TMA-SAz-1 revealed that the SiOH band near  $7315\text{ cm}^{-1}$  increases in intensity with enhanced acid treatment. In contrast, no SiOH groups were identified in the NIR spectra of HDTMA-SAz-1 treated in HCl, indicating that  $\text{HDTMA}^+$  completely covers the inner and outer surfaces of the montmorillonite and hinders access of protons to the  $\text{Si-O}^-$  bonds created upon acid treatment.

**Key Words**—Acid Treatment, Alkylammonium Cations, NIR Spectroscopy, Organo-clays, Structural Modifications.

### INTRODUCTION

The technique of near infrared (NIR) spectroscopy, covering the spectral range  $12,000\text{--}4000\text{ cm}^{-1}$ , is undergoing dynamic development and spreading into many areas of science and technology (Bokobza, 1998; Williams and Norris, 1987, Workman and Weyer, 2008). The interest in the method arises from improvements in NIR spectrometers, the development of chemometric methods, and the introduction of optical fibers allowing transfer of NIR energy and information. Among the advantages offered by NIR spectroscopy, speed, simplicity of sample preparation, and the non-destructive nature of the technique are the most attractive. The method appears well suited to on-line quality control in various branches of industry (Williams and Norris, 1987; Prüfer and Mamma, 1995), for analysis of the minerals on Earth (Hunt and Salisbury, 1970) and Mars (Bishop *et al.*, 2004; Bishop *et al.*, 2008a), or for exploration of soils (Malley *et al.*, 2002) and clay deposits (Dill *et al.*, 2005) by portable IR analyzers. NIR spectroscopy has also been used for clay-mineral characterization (Petit *et*

*al.*, 1999; Madejová and Komadel, 2001; Gates *et al.*, 2002; Frost *et al.*, 2002; Petit, 2005; Gates, 2005; Gionis *et al.*, 2007; Bishop *et al.*, 2008b), including investigation of structural changes occurring upon heating of smectites saturated with small exchangeable cations (Madejová *et al.*, 2000; Petit *et al.*, 2002; Pálková *et al.*, 2003; Madejová, 2005). Recently, NIR spectroscopy was used successfully to monitor the acid dissolution of Fe-bentonite (Madejová *et al.*, 2007) and different kinds of naturally occurring clay minerals, showing the effects of the structure, chemical composition, and the availability of the interlayer space on the extent of dissolution (Madejová *et al.*, 2009).

One of the most frequently used modifications of clay minerals is the intercalation of organic species into their interlayers (Yariv and Cross, 2001; Theng, 1974). Of the spectroscopic techniques, infrared spectroscopy in the MIR region ( $4000\text{--}400\text{ cm}^{-1}$ ) is often used to characterize the interactions of organic substances with clay minerals (Breen *et al.*, 1997; Yariv, 2001; Zhu *et al.*, 2005; Frost *et al.*, 2008; Ōnal and Sankaya, 2008). The inorganic exchangeable cations in smectites are frequently replaced by quaternary alkylammonium cations to modify their properties and to change the surface of smectite to make it more hydrophobic (Boyd *et al.*, 1988; Stevens and Anderson, 1996). The presence of alkylammonium cations also affects the rate of dissolution of smectites in acids

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(Breen and Watson, 1998; Moronta *et al.*, 2002). The MIR spectra clearly show that the long-chain alkylammonium cations restrict access of protons to the layers so the extent of acid attack is reduced (Breen *et al.*, 1997). A few studies have reported on the use of NIR spectroscopy in adsorption studies of organic molecules on smectites (Zhou *et al.*, 2008) and none, to our knowledge, on the NIR study of acid-treated organo-clays.

This study revealed the potential of NIR spectroscopy in investigations of organo-clays. The NIR spectra of two alkylammonium derivatives of montmorillonite were analyzed in detail and the influence of the size of alkylammonium cations on the dissolution rate of organo-clays in HCl was determined. Results revealed that NIR spectra can be used successfully to characterize organic molecules adsorbed on Cheto montmorillonite and to identify structural changes occurring upon chemical treatment of organo-clays.

## EXPERIMENTAL

### Materials

The fine fraction of bentonite from Cheto (SAZ-1), Arizona, USA, obtained from the Source Clays Repository of The Clay Minerals Society was used in this study. The bentonite was suspended in distilled water, Li-saturated by repeated treatment with 1 M LiCl, and the <2  $\mu\text{m}$  fraction collected. The suspension was washed free of excess salts, dried at 60°C, and ground to pass a 0.2 mm sieve in order to prepare the Li-SA-1 sample. Organo-clays were prepared by cation exchange reactions of the Li-SA-1 with tetramethylammonium (TMA<sup>+</sup>) chloride or hexadecyltrimethylammonium (HDTMA<sup>+</sup>) bromide. Alkylammonium salts were dissolved in a 50:50 (by volume) mixture of distilled water and ethanol. The amount of organic cation used for exchange was three times (HDTMA<sup>+</sup>) and seven times (TMA<sup>+</sup>), respectively, the cation exchange capacity (CEC) of the montmorillonite. The suspension of montmorillonite and organic solution was stirred for 16 h at ~60°C. The excess alkylammonium salts were removed by repeated washing with a mixture of ethanol and distilled water. The dried samples are referred to as HDTMA-SA-1 and TMA-SA-1.

The Li-, TMA-, and HDTMA-SA-1 samples were further dissolved in 6 M HCl at 80°C for 2 and 6 h. After the acid treatments, the samples were filtered, washed with de-ionized water, centrifuged, dried, and ground as described above.

### FTIR spectroscopy

The IR spectra were obtained using a Nicolet Magna 750 Fourier transform infrared spectrometer. For the spectra in the NIR region, a PbSe detector, CaF<sub>2</sub> beam splitter, and the DRIFT technique were used. For the MIR region, a DTGS detector, a KBr beam splitter, and the KBr pressed-disk technique (1 mg of sample and

200 mg of KBr) were used. For each sample, 128 scans with a resolution of 4  $\text{cm}^{-1}$  were recorded.

Spectra manipulations were performed using the OMNIC software package (Nicolet Instruments Corp.). The accuracy in determining the positions of the absorption bands was  $\pm 1 \text{ cm}^{-1}$ . In order to find the location of a peak appearing in the spectrum as a shoulder, a Fourier Self Deconvolution (FSD) routine and second-derivative operation (with OMNIC default parameters) were used. The difference between the wavenumber values obtained did not exceed 2  $\text{cm}^{-1}$ . The assignment of the absorption bands of natural clay minerals in the MIR region follows Farmer (1974). The assignments of the bands in the NIR region together with relevant references are given in the Results and Discussion section below.

## RESULTS AND DISCUSSION

### Identification of MIR bands characteristic of TMA<sup>+</sup> and HDTMA<sup>+</sup> cations

The absorption bands associated with OH, NH, and CH functional groups dominate in the spectra of organo-clays taken in the NIR region. These absorptions arise from overtones of fundamental stretching vibrations or combinations involving stretching ( $\nu$ ) and bending ( $\delta$ ) modes of XH ( $X = \text{O}, \text{N}, \text{C}$ ) groups. Overtone bands occur when a fundamental vibrational mode is excited with two or more quanta, whereas combination bands represent the coupling between different vibrational modes. A NIR spectrum, however, cannot be interpreted in as straightforward a manner as a MIR spectrum. While the MIR spectra exhibit well defined peaks related to fundamental modes, the NIR spectra often contain broad bands resulting from several overlapping peaks. In addition, the presence of Fermi resonances can also increase the complexity of the NIR spectra (Bokobza, 1998). For identification of individual bands related to CH overtones and combination modes of CH<sub>3</sub> and CH<sub>2</sub> groups present in the NIR spectra of TMA-SA-1 and HDTMA-SA-1, the MIR spectra of Li-SA-1 and both organo-clays (Figure 1) were analyzed.

The characteristic bands assigned to stretching and bending vibrations of O-H and Si-O groups of Li-SA-1 montmorillonite occur in the 4000–3400  $\text{cm}^{-1}$  and 1200–400  $\text{cm}^{-1}$  regions (Figure 1a). The OH stretching band appears at 3620  $\text{cm}^{-1}$ , while the AlAlOH and AlMgOH bending bands are observed at 916  $\text{cm}^{-1}$  and 843  $\text{cm}^{-1}$ , respectively. The Si-O stretching mode is at 1033  $\text{cm}^{-1}$ , and the Si-O-Al and Si-O-Si bending vibrations absorb at 519  $\text{cm}^{-1}$  and 465  $\text{cm}^{-1}$ , respectively. Exchange of inorganic Li<sup>+</sup> cations with TMA<sup>+</sup> and HDTMA<sup>+</sup> modified the shape of the MIR spectra of organo-clays (Figures 1b,c). In addition to OH and Si-O vibrations, the absorption bands related to CH-stretching and -bending vibrations became visible. The MIR spectra of compounds containing TMA<sup>+</sup> and HDTMA<sup>+</sup>

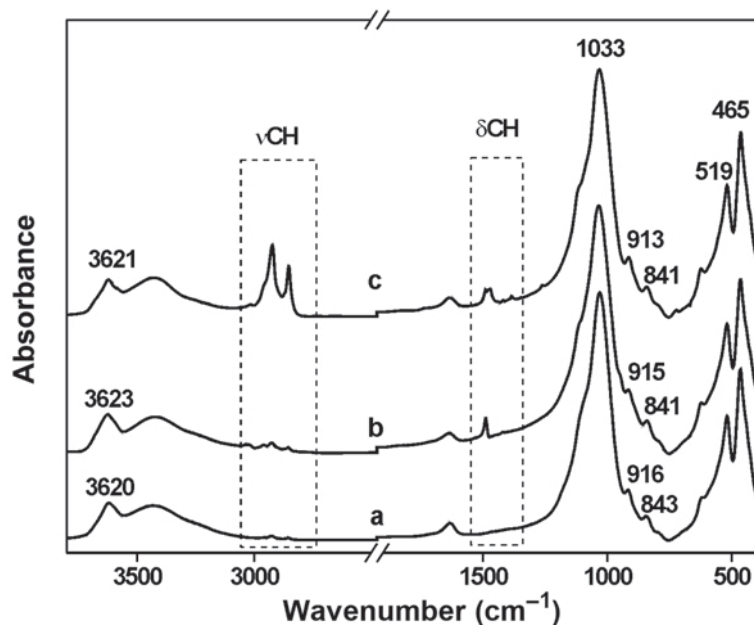


Figure 1. MIR spectra of Li-SAz-1 (a), TMA-SAz-1 (b), and HDTMA-SAz-1 (c).

cations should show asymmetric ( $\nu_{as}$ ) and symmetric ( $\nu_s$ ) stretching (at  $\sim 3050$ – $2800$   $\text{cm}^{-1}$ ), asymmetric ( $\delta_{as}$ ) and symmetric ( $\delta_s$ ) bending (at  $\sim 1500$ – $1300$   $\text{cm}^{-1}$ ), and rocking (at  $\sim 1280$ – $1000$   $\text{cm}^{-1}$ ) vibrations of  $\text{CH}_3$  and  $\text{CH}_2$  groups together with  $\nu_{\text{CN}}$  ( $\sim 950$ ,  $750$   $\text{cm}^{-1}$ ) and  $\delta_{\text{CNC}}$  ( $\sim 450$   $\text{cm}^{-1}$ ) modes (Zeegers-Huyskens and Bator, 1996). However, only  $\text{CH}_3$  and  $\text{CH}_2$  stretching and bending bands were clearly visible in the MIR spectra of organo-clays, the other absorptions occurring below  $1100$   $\text{cm}^{-1}$  were overlapped by stronger Si-O bands of the montmorillonite (Figure 1).

Comparing the CH-stretching and -bending regions in the spectra of TMA-SAz-1, HDTMA-SAz-1, and of the salts used for their preparation, *i.e.* TMA-Cl and HDTMA-Br, revealed (Figure 2) that two CH stretching bands,  $\nu_{as}\text{CH}_3$  and  $\nu_s\text{CH}_3$ , are expected to be present in the spectrum of TMA-Cl. However, Figure 2A,a shows instead a complex pattern for TMA-Cl with several overlapping bands and shoulders. Similar to other tetra-alkylammonium ions (Zeegers-Huyskens and Bator, 1996), more bands in Figure 2A resulted from a Fermi resonance interaction with a  $\delta\text{CH}_3$  level. The most pronounced absorption near  $3015$   $\text{cm}^{-1}$  corresponds to  $\nu_{as}\text{CH}_3$  vibration while the bands near  $2960$   $\text{cm}^{-1}$  and  $2920$   $\text{cm}^{-1}$  have been reported for  $\nu_s\text{CH}_3$  (Zeegers-Huyskens and Bator, 1996). The intense band at  $1488$   $\text{cm}^{-1}$  is assigned to the  $\delta_{as}\text{CH}_3$  vibration while the  $\delta_s\text{CH}_3$  mode gives an absorption band with peaks at  $1404$   $\text{cm}^{-1}$  and  $1399$   $\text{cm}^{-1}$  (Figure 2B,a). Less intense and more diffuse  $\text{CH}_3$  bands in the spectrum of TMA-SAz-1 (Figures 2A,b and 2B,b) indicate less organic phase in the organo-clay than in TMA-Cl. A shift of the  $\nu_{as}\text{CH}_3$  band to higher wavenumber ( $\sim 3030$   $\text{cm}^{-1}$ ) reflects the

interaction of the  $(\text{CH}_3)_4\text{N}^+$  cations with the montmorillonite layers. Both the positions and assignments of the  $\text{CH}_3$  bands observed in the MIR spectrum of TMA-SAz-1 are listed in Table 1.

Replacement of one methyl group in the  $(\text{CH}_3)_4\text{N}^+$  cation with a longer alkyl chain, as in the  $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3$  cation, significantly modified the shape of the spectra of HDMA-Br and HDTMA-SAz-1 (Figures 2C,D). The  $\text{CH}_3$ -N,  $\text{CH}_3$ -C,  $\text{CH}_2$ -N, and  $\text{CH}_2$ -C groups should be considered for analysis of the vibration modes in the spectra of HDTMA<sup>+</sup>. However, resolving unambiguously the absorption bands of individual groups in the MIR region is quite difficult due to overlap. The spectrum of HDTMA-Br shows a complex band in the  $3050$ – $3000$   $\text{cm}^{-1}$  region with two absorptions at  $3030$   $\text{cm}^{-1}$  and  $3017$   $\text{cm}^{-1}$  corresponding to the  $\nu_{as}\text{CH}_3$ -N vibrations (Figure 2C,a). Based on comparison with the TMA-Cl spectrum, the absorption at  $2958$   $\text{cm}^{-1}$  should be due to  $\nu_s\text{CH}_3$ -N vibrations, while the  $2943$   $\text{cm}^{-1}$  band may be related to  $\nu_{as}\text{CH}_3$ -C. The assignment of the bands at  $2918$   $\text{cm}^{-1}$  and  $2850$   $\text{cm}^{-1}$  is unambiguous; these two strong bands originate from  $\nu_{as}\text{CH}_2$ -C and  $\nu_s\text{CH}_2$ -C modes, respectively. The weak band at  $2871$   $\text{cm}^{-1}$  corresponds to  $\nu_s\text{CH}_3$ -C. The C-H bending region of HDTMA-Br revealed several bands (Figure 2D,a). The  $\delta_{as}\text{CH}_3$ -N vibrations absorb at  $1487$   $\text{cm}^{-1}$ , while the bands at  $1473$   $\text{cm}^{-1}$  and  $1463$   $\text{cm}^{-1}$  correspond to asymmetric bending vibrations of  $\text{CH}_2$ -C groups. The weak bands below  $1430$   $\text{cm}^{-1}$  might be related to  $\delta_s\text{CH}_3$ -N and/or  $\delta_s\text{CH}_2$ -C.

In comparison with HDTMA-Br, the MIR spectrum of HDTMA-SAz-1 contained less intense and fewer resolved bands corresponding to C-H vibrations (Figures 2C,b and 2D,b). Only  $\nu_{as}\text{CH}_2$ -C and  $\nu_s\text{CH}_2$ -C vibrations

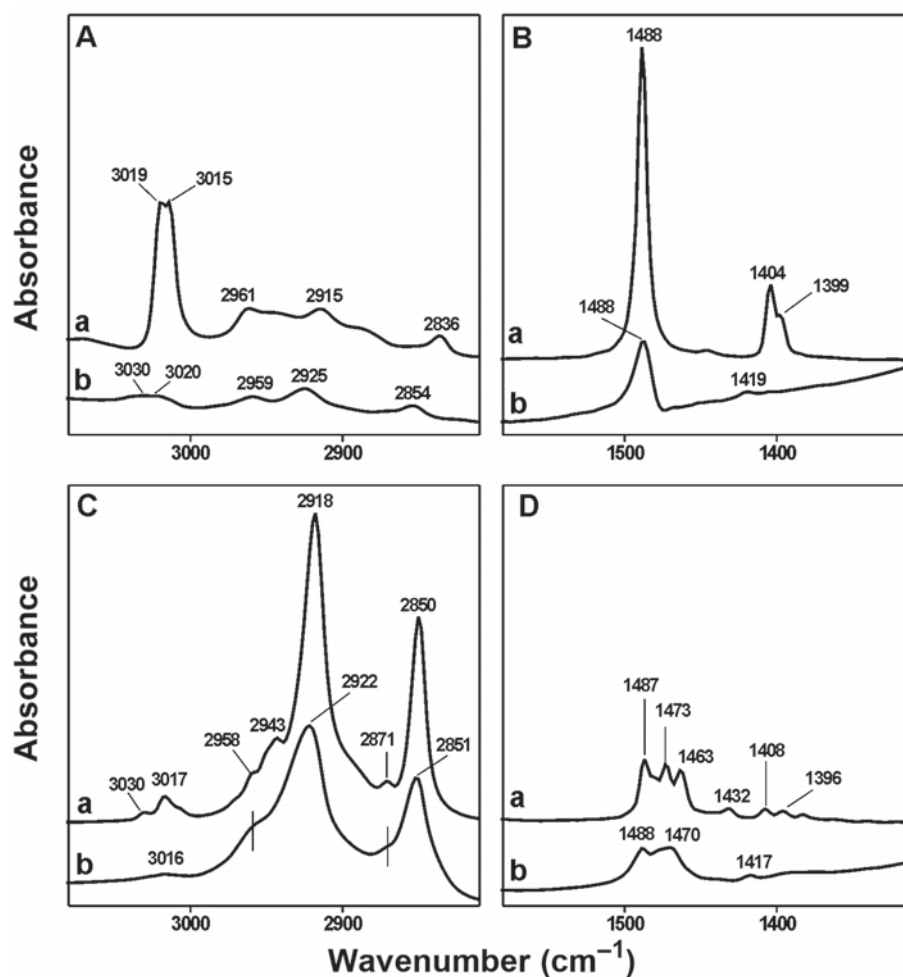


Figure 2. CH stretching (A) and bending (B) regions of TMA-Cl (a) and TMA-SA-Z-1 (b), and CH stretching (C) and bending (D) regions of HDTMA-Br (a) and HDTMA-SA-Z-1 (b).

absorbing at  $2922\text{ cm}^{-1}$  and  $2851\text{ cm}^{-1}$  are clearly recognized; other C-H stretching modes appear as broad shoulders or weak inflections. Using the FSD routine, the positions for  $\nu_{\text{as}}\text{CH}_3\text{-N}$  and  $\nu_{\text{s}}\text{CH}_3\text{-C}$  were identified at  $3016\text{ cm}^{-1}$  and  $2872\text{ cm}^{-1}$ , respectively. A broad shoulder near  $2960\text{ cm}^{-1}$  is due to  $\nu_{\text{s}}\text{CH}_3\text{-N}$  overlapping a band near  $2950\text{ cm}^{-1}$  related to  $\nu_{\text{as}}\text{CH}_3\text{-C}$ . Corresponding deformation modes of  $\text{CH}_3$  and  $\text{CH}_2$  groups were observed in the  $1500\text{--}1400\text{ cm}^{-1}$  region. The  $\delta_{\text{as}}\text{CH}_3\text{-N}$  vibrations give rise to a band at  $1488\text{ cm}^{-1}$ , while a broad band near  $1470\text{ cm}^{-1}$  is caused by vibrations of  $\delta_{\text{as}}\text{CH}_2\text{-C}$  groups. A weak band near  $1417\text{ cm}^{-1}$  may be attributed to a symmetric C-H deformation mode (Table 2).

#### Identification of NIR bands characteristic of Li-SA-Z-1, TMA-SA-Z-1, and HDTMA-SA-Z-1

The NIR spectra of Li-, TMA-, and HDTMA-SA-Z-1 montmorillonites (Figure 3) revealed bands in the  $8000\text{--}4000\text{ cm}^{-1}$  region, which derive from the first overtone ( $2\nu\text{OH}$  and  $2\nu\text{CH}$ ) and combination ( $(\nu+\delta)\text{OH}$

and  $(\nu+\delta)\text{CH}$ ) modes of fundamental stretching and bending vibrations. As a result of the anharmonic character of vibrations, the positions of the bands are lower than the theoretical values calculated from the wavenumber values of the corresponding MIR bands (Bokobza, 1998; Balan *et al.*, 2007; Workman and Weyer, 2008). Petit *et al.* (2004) showed that the location of the first OH-overtone band in NIR spectra of various clay minerals is  $\sim 170\text{ cm}^{-1}$  less than the value calculated from the  $\nu\text{OH}$  positions. The calculated average value of the anharmonicity constant was  $-86.5\text{ cm}^{-1}$ . This parameter is unique for each bond because it depends on the nature and environment (*e.g.* formation of hydrogen bonds, intermolecular interactions, *etc.*) of vibrating groups. Balan *et al.* (2007) reported that the anharmonicity constant increases from  $-93$  to  $-300\text{ cm}^{-1}$  when the OH-stretching frequency decreases from  $3700$  to  $2900\text{ cm}^{-1}$ , suggesting that the anharmonicity of the OH bond increases with the strength of the H-bonding between the OH group and the surrounding oxygens. Thus, substantial variability in

Table 1. Positions and assignments of the CH<sub>3</sub> bands observed in the NIR and MIR spectra of TMA-SAz-1 and the theoretically calculated values of overtone and combination modes.

Observed position (cm <sup>-1</sup> )	Assignment	Calculated value <sup>+</sup> (cm <sup>-1</sup> )
6048	2ν <sub>as</sub>	6060; (2 × 3030)
6014	2ν <sub>as</sub>	6040; (2 × 3020)
5920	ν <sub>as</sub> + ν <sub>s</sub>	5945; (3020 + 2925)
5880	2ν <sub>s</sub>	5918; (2 × 2959)
5825	2ν <sub>s</sub>	5850; (2 × 2925)
4471*	(ν + δ) <sub>as</sub>	4518; (3030 + 1488)
4447	(ν + δ) <sub>as</sub>	4508; (3020 + 1488)
4324	ν <sub>s</sub> + δ <sub>s</sub>	4378; (2959 + 1419)
4268*	ν <sub>s</sub> + δ <sub>s</sub>	4344; (2925 + 1419)
4203	ν <sub>as</sub> + r <sup>#</sup>	4327; (3030 + 1297)
4105	ν <sub>as</sub> + r <sup>#</sup>	4222; (2925 + 1297)
3030	ν <sub>as</sub>	
3020*	ν <sub>as</sub>	
2959	ν <sub>s</sub>	
2925	ν <sub>s</sub>	
1488	δ <sub>as</sub>	
1419	δ <sub>s</sub>	

<sup>+</sup> value calculated from the observed fundamental vibrations  
<sup>\*</sup> wavenumber value obtained by FSD and/or 2<sup>nd</sup> derivative  
<sup>#</sup> CH<sub>3</sub> rocking vibrations observed only in the spectrum of (CH<sub>3</sub>)<sub>4</sub>N-Cl

the differences between the observed and calculated OH- and CH-band positions can be expected in the organo-clays studied.

The NIR spectrum of Li-SAz-1 (Figure 3a) shows a broad, complex band at 7060 cm<sup>-1</sup> containing overlapping contributions of the first overtone of structural

Table 2. Positions and assignments of the CH<sub>3</sub> and CH<sub>2</sub> bands observed in NIR and MIR spectra of HDTMA-SAz-1 and the theoretically calculated values of overtone and combination modes.

Observed (cm <sup>-1</sup> )	Assignment	Calculated value <sup>+</sup> (cm <sup>-1</sup> )
6039	2ν <sub>as</sub> CH <sub>3</sub> -N	6060; (2 × 3030) <sup>#</sup>
5998	2ν <sub>as</sub> CH <sub>3</sub> -N	6032; (2 × 3016)
5911*	2ν <sub>s</sub> CH <sub>3</sub> -N	5920; (2 × 2960)
5864*	2ν <sub>as</sub> CH <sub>3</sub> -C	5886; (2 × 2943) <sup>#</sup>
5785	2ν <sub>as</sub> CH <sub>2</sub> -C	5844; (2 × 2922)
5688	2ν <sub>s</sub> CH <sub>3</sub> -C	5744; (2 × 2871) <sup>#</sup>
	2ν <sub>s</sub> CH <sub>2</sub> -C	5702; (2 × 2851)
4463	(ν <sub>as</sub> +δ <sub>as</sub> )CH <sub>3</sub> -N	4518; (3030 + 1488)
4440	(ν <sub>as</sub> +δ <sub>as</sub> )CH <sub>3</sub> -N	4504; (3016 + 1488)
4330	(ν <sub>as</sub> +δ <sub>as</sub> )CH <sub>2</sub> -C	4392; (2922 + 1470)
4255	(ν <sub>s</sub> +δ <sub>s</sub> )CH <sub>2</sub> -C	4268; (2851+1417)
4156		complex band
3016	ν <sub>as</sub> CH <sub>3</sub> -N	
2960*	ν <sub>s</sub> CH <sub>3</sub> -N, ν <sub>as</sub> CH <sub>3</sub> -C	see text
2922	ν <sub>as</sub> CH <sub>2</sub> -C	
2872*	ν <sub>s</sub> CH <sub>3</sub> -C	
2851	ν <sub>s</sub> CH <sub>2</sub> -C	
1488	δ <sub>as</sub> CH <sub>3</sub> -N	
1470	δ <sub>as</sub> CH <sub>2</sub> -C	
1417	δ <sub>s</sub> CH <sub>2</sub> -C, δ <sub>s</sub> CH <sub>3</sub> -N	

<sup>+</sup> value calculated from the observed fundamental vibrations  
<sup>\*</sup> wavenumber value obtained by FSD and/or 2<sup>nd</sup> derivative  
<sup>#</sup> vibrational band observed only in the spectrum of HDTMA-Br

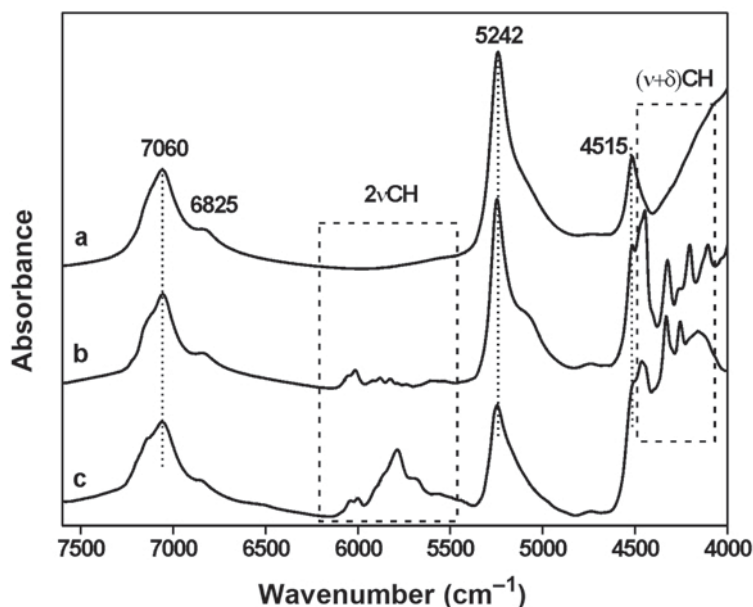


Figure 3. NIR spectra of Li-SAz-1 (a), TMA-SAz-1 (b), and HDTMA-SAz-1 (c)

OH groups (2νOH) and the first overtone of stretching vibrations of H<sub>2</sub>O molecules. Considering the anharmonicity, the corresponding asymmetric stretching vibra-

tion ( $\nu_{as}H_2O$ ) should appear in the  $\sim 3630\text{--}3610\text{ cm}^{-1}$  region. The shoulder near  $6825\text{ cm}^{-1}$  is due to the first overtone of symmetric stretching vibrations of water molecules involved in strong hydrogen bonds ( $\nu_sH_2O = \sim 3430\text{ cm}^{-1}$ ). Detailed analysis of the spectral features attributed to water molecules in both the MIR and NIR regions was given by Bishop *et al.* (1994). The intense band near  $5242\text{ cm}^{-1}$  is due to  $(\nu+\delta)H_2O$  while the band at  $4515\text{ cm}^{-1}$  is attributed to a combination mode of structural OH groups (Madejová and Komadel, 2001). Displacement of hydrated  $Li^+$  with  $TMA^+$  and  $HDTMA^+$  cations in SAZ-1 affects the shape of the NIR spectra. In addition to the  $2\nu_{OH}$  and  $(\nu+\delta)OH$  bands of montmorillonite, the C-H overtone and combination bands appear in the  $6100\text{--}5500\text{ cm}^{-1}$  and  $4500\text{--}4000\text{ cm}^{-1}$  regions, respectively (Figure 3b,c). No detailed analysis of the NIR spectra of montmorillonites saturated with alkylammonium cations is available in the literature. Thus, the assignment of the C-H overtones and combination modes given in Tables 1 and 2 is based on the interpretations reported for other alkylammonium salts (Zeegers-Huyskens and Bator, 1996) and on the theoretically calculated values of overtones and combination modes using bands observed in the MIR region.

Precise assignment of the vibrational modes of CH overtone and combination regions of the two organo-clays (Figure 4) is difficult because the number of observed bands is significantly greater than predicted from the MIR spectra (Figure 2). The overtone and

combination bands may correspond to several possible combinations of C-H fundamental vibrations which are not clearly resolved in the MIR spectra of organo-clays but are visible in the MIR spectra of TMA- and HDTA-salts. Moreover, distortion of the symmetry of alkylammonium cations may lead to splitting of the C-H overtone and combination bands. Therefore some bands were assigned to the same vibrational modes (Tables 1, 2). Similar doublets were also reported for other tetraalkylammonium ions (Zeegers-Huyskens and Bator, 1996).

Both the wavenumber values of the  $CH_3$  and  $CH_2$  fundamentals and the anharmonic character of vibrations must be taken into account to find the explanation of the bands present in the spectra shown in Figure 4. Due to the anharmonicity factor, the wavenumber positions of the observed bands should be less than the calculated values. The absorption bands observed in the  $6100\text{--}5500\text{ cm}^{-1}$  region of the TMA-SAz-1 are assigned to two  $2\nu_{as}CH_3$ , two  $2\nu_sCH_3$ , and one combination ( $\nu_{as}+\nu_s$ ) $CH_3$  vibrations (Figure 4A,a; Table 1). The clearly resolved band at  $4515\text{ cm}^{-1}$  is due to the combination mode of the structural OH groups. Several strong bands appear in the  $4500\text{--}4000\text{ cm}^{-1}$  region of TMA-SAz-1 (Figure 4B,a). Some correspond to combination modes of stretching and bending  $CH_3$  vibrations present in the MIR spectrum. However, the rocking  $CH_3$  vibration must be considered to find the possible combination for the bands at

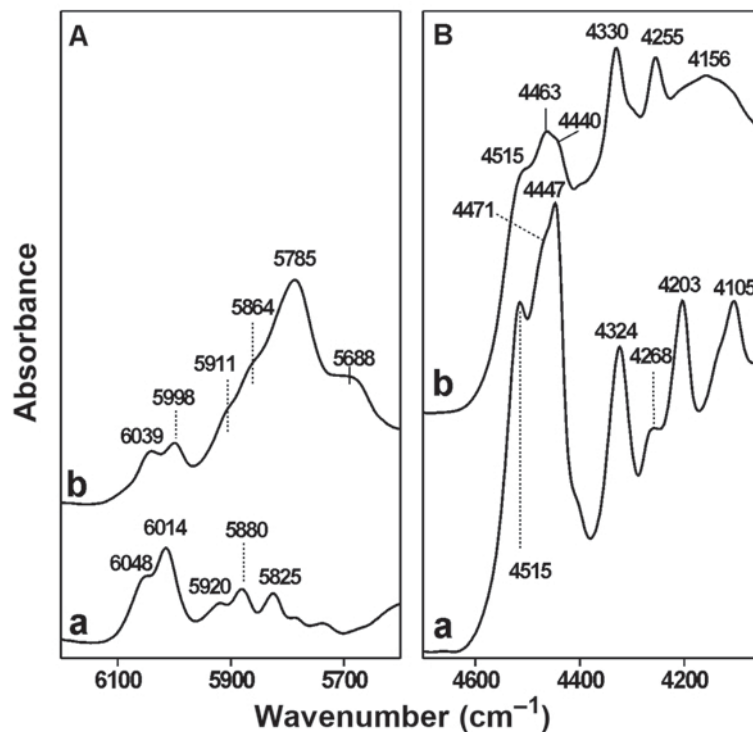


Figure 4. CH overtone (A) and combination (B) regions of TMA-SAz-1 (a) and HDTMA-SAz-1 (b).

4203  $\text{cm}^{-1}$  and 4105  $\text{cm}^{-1}$  (Table 1). No such band can be found in the MIR spectrum of TMA-SAZ-1; however, a rocking  $\text{CH}_3$  vibration at 1297  $\text{cm}^{-1}$  (not shown in Figure 2) was identified in the spectrum of TMA-Cl.

The CH overtone and combination region of the HDTMA-SAZ-1 sample (Figure 4b; Table 2) indicates that replacement of one methyl group in  $(\text{CH}_3)_4\text{N}^+$  with a longer alkyl chain,  $(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_{15}\text{CH}_3$ , made the shape of the NIR spectrum even more complex. The first CH overtones of  $\text{CH}_3$ -N groups appeared in the 6100–5900  $\text{cm}^{-1}$  region and the  $2\nu_{\text{as}}\text{CH}_2$ -C and  $2\nu_{\text{s}}\text{CH}_2$ -C bands were present at 5785  $\text{cm}^{-1}$  and 5688  $\text{cm}^{-1}$ , respectively. The broad shoulder near 5688  $\text{cm}^{-1}$  also involves the contribution of  $2\nu_{\text{s}}\text{CH}_3$ -C vibrations. The combination region revealed a shoulder near 4515  $\text{cm}^{-1}$  due to  $(\nu+\delta)\text{OH}$ . The bands at 4463  $\text{cm}^{-1}$  and 4440  $\text{cm}^{-1}$  are attributed to combination modes of  $\text{CH}_3$ -N groups, while the bands in the 4400–4000  $\text{cm}^{-1}$  range should be related to combination vibrations of  $\text{CH}_2$ -C groups (Table 2).

#### Dissolution of organo-clays in HCl

Dissolution of smectites in inorganic acids can lead to significant degradation of their structure. Protons penetrate into the layers and attack the OH groups, starting with those which are close to the isomorphous substitution sites. The resulting dehydroxylation is related to successive release of the octahedral atoms. At the same time, the transformation of the tetrahedral

sheets to a three-dimensional Si-O framework proceeds (Tkáč *et al.*, 1994; Komadel *et al.*, 1996; Komadel and Madejová, 2006). The alteration of the structure of the Li-SAZ-1, TMA-SAZ-1, and HDTMA-SAZ-1 montmorillonites treated with 6 M HCl at 80°C was first studied by MIR spectroscopy (Figure 5). As an indicator of the extent of the decomposition of the smectite structure, the absorption band at 1033  $\text{cm}^{-1}$ , corresponding to stretching vibrations of the Si-O groups, was chosen. The spectra of HCl-treated Li-SAZ-1 show a gradual shift of the Si-O band from 1033  $\text{cm}^{-1}$ , the characteristic position of tetrahedra arranged in the sheets of montmorillonite layers, to 1097  $\text{cm}^{-1}$ , *i.e.* the position of the Si-O stretching vibrations of the reaction product – amorphous silica with a three-dimensional framework (Figure 5A). Two components in the spectrum of the sample treated for 2 h reflect the presence of both the smectite with layered arrangement (1044  $\text{cm}^{-1}$ ) and amorphous silica with three-dimensional framework (1082  $\text{cm}^{-1}$ ). The position of the Si-O band after 6 h of dissolution (1097  $\text{cm}^{-1}$ ) reflects complete decomposition of the Li-SAZ-1 montmorillonite structure.

The stability of smectites in acids is changed if  $\text{Li}^+$  cations are replaced by alkylammonium ions (Figure 5B,C). Dissolution of TMA-SAZ-1 and HDTMA-SAZ-1 proceeds much more slowly. After 2 h, the Si-O band in the spectra of both samples remained at a similar position as in the untreated samples, demonstrating minimal alteration of the smectitic layers. The

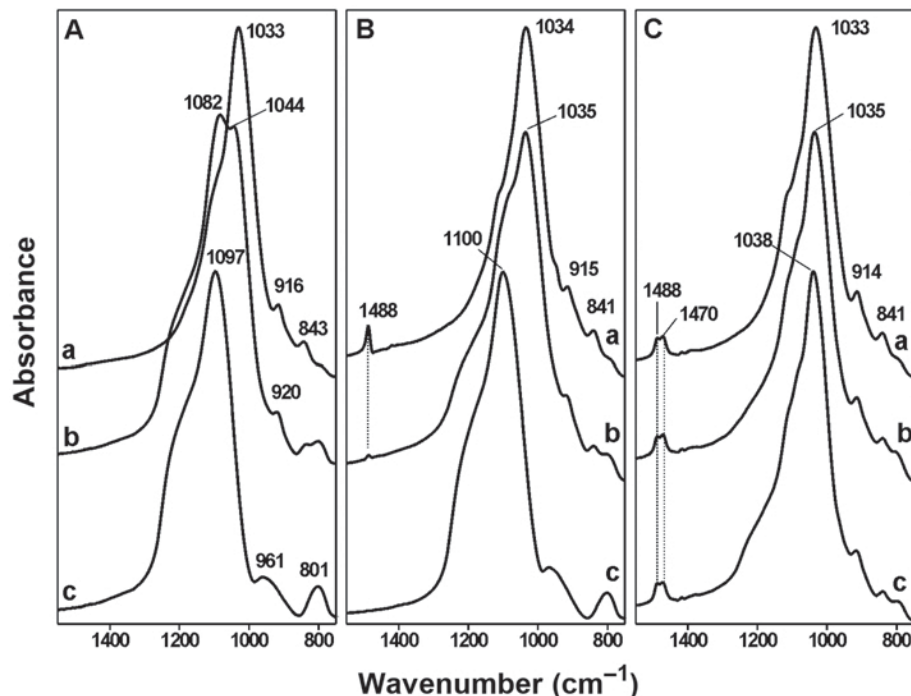


Figure 5. MIR spectra of Li-SAZ-1 (A), TMA-SAZ-1 (B), and HDTMA-SAZ-1 (C): untreated (a), treated in 6 M HCl at 80°C for 2 h (b), and 6 h (c).

almost complete disappearance of the  $1488\text{ cm}^{-1}$  band implies that  $\text{TMA}^+$  cations were fully replaced by protons. On the other hand, no changes in the CH bending region were visible for HDTMA-SAZ-1 treated for 2 or 6 h (Figure 5C,b, 5C,c). Significant differences were seen between the spectra of TMA-SAZ-1 and HDTMA-SAZ-1 treated for 6 h. While the position of the Si-O band of TMA-SAZ-1 at  $1100\text{ cm}^{-1}$  indicates the presence of only amorphous silica, just a slight change in the Si-O band position (compared to the spectrum of the untreated sample) was found for HDTMA-SAZ-1. Modification of the HDTMA-SAZ-1 structure after 6 h of treatment in 6 M HCl at  $80^\circ\text{C}$  was only minor,

confirming that long-chain alkylammonium cations ( $\text{HDTMA}^+$ ) are more resistant to displacement by  $\text{H}^+$  than cations with short chains, *i.e.*  $\text{TMA}^+$ .

Dissolution of smectites in HCl is related to gradual dehydroxylation and acidification of the surface and thus this process can be effectively followed by NIR spectroscopy (Pálková *et al.*, 2003; Madejová *et al.*, 2009). The NIR spectra of acid-treated Li-SAZ-1, TMA-SAZ-1, and HDTMA-SAZ-1 montmorillonites were compared (Figure 6) and details of the first CH overtone ( $6150\text{--}5650\text{ cm}^{-1}$ ) and CH combination ( $4650\text{--}4050\text{ cm}^{-1}$ ) regions of both organo-clays were also examined (Figure 7). The spectrum of untreated Li-

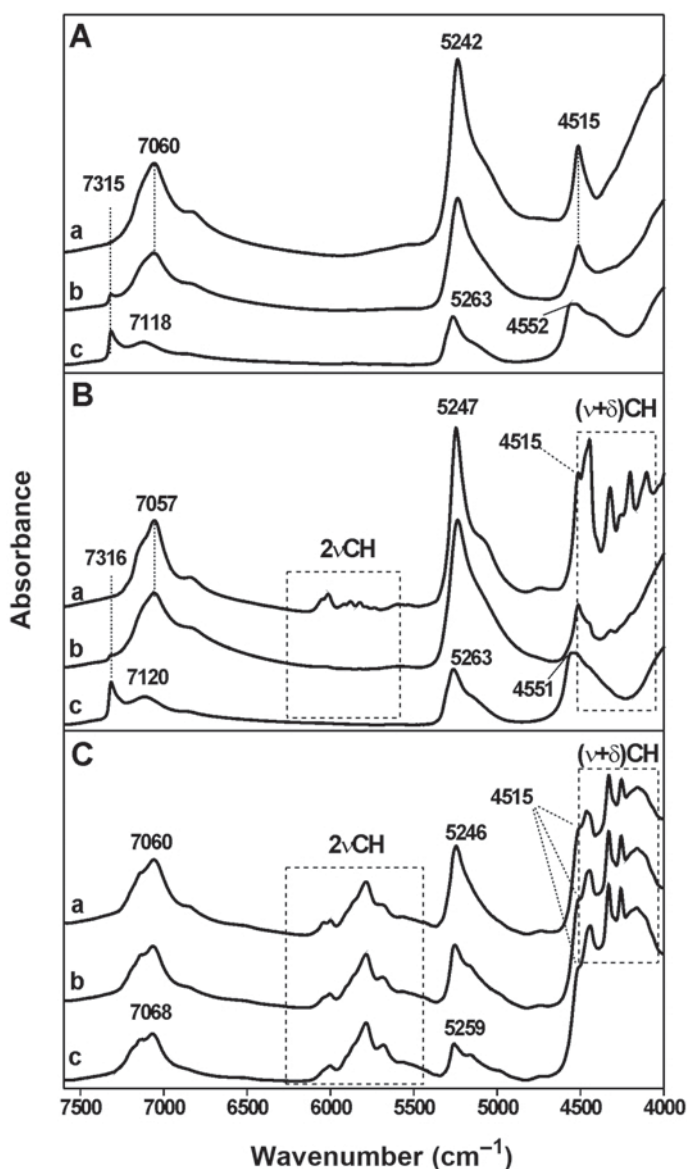


Figure 6. NIR spectra of Li-SAZ-1 (A), TMA-SAZ-1 (B), and HDTMA-SAZ-1 (C): untreated (a), treated in 6 M HCl at  $80^\circ\text{C}$  for 2 h (b), and 6 h (c).

SAZ-1 contained a complex band related to  $2\nu\text{OH}$  and  $2\nu\text{H}_2\text{O}$  at  $7060\text{ cm}^{-1}$ ,  $(\nu+\delta)\text{H}_2\text{O}$  at  $5242\text{ cm}^{-1}$ , and  $(\nu+\delta)\text{OH}$  at  $4515\text{ cm}^{-1}$ . The OH overtone region of Li-SAZ-1 treated with 6 M HCl for 2 h at  $80^\circ\text{C}$  (Figure 6A,b) revealed a decrease in the intensity of the band at  $7060\text{ cm}^{-1}$  proving a release of OH groups and/or of the central atoms from the octahedral sheets. Moreover, the appearance of a new band at  $7315\text{ cm}^{-1}$  assigned to the first SiOH overtone (Pálková *et al.*, 2003) confirmed the acidification of the Li-SAZ-1 surface. Partial dehydroxylation of Li-SAZ-1 after 2 h of dissolution in HCl is also reflected in the decreased intensity of the combination band at  $4515\text{ cm}^{-1}$ . The lesser intensity of the  $(\nu+\delta)\text{H}_2\text{O}$  band at  $5242\text{ cm}^{-1}$  suggests fewer water molecules in the sample. Destruction of the smectite layers resulted in a smaller amount of exchangeable cation and, consequently, the amount of water adsorbed decreased.

The increased intensity of the  $2\nu\text{SiOH}$  band ( $7315\text{ cm}^{-1}$ ), and the reduced intensity and shift in

position of the overtone band from  $7060\text{ cm}^{-1}$  to  $7118\text{ cm}^{-1}$ , together with the appearance of the  $(\nu+\delta)\text{SiOH}$  band at  $4552\text{ cm}^{-1}$ , confirmed that 6 h of dissolution of Li-SAZ-1 resulted in the creation of protonated amorphous silica. Concurrently, the  $(\nu+\delta)\text{H}_2\text{O}$  band, the intensity of which decreased significantly in comparison with that of the untreated Li-SAZ-1, shifted from  $5242\text{ cm}^{-1}$  to  $5263\text{ cm}^{-1}$  (Figure 6A,c). An upward shift of the  $(\nu+\delta)\text{H}_2\text{O}$  band provides evidence that  $\text{H}_2\text{O}$  molecules adsorbed on the surfaces of destroyed layers and/or amorphous silica are less hydrogen bonded than those in the untreated clays. A more detailed discussion of the changes in the  $(\nu+\delta)\text{H}_2\text{O}$  region was given by Madejová *et al.* (2009).

Comparing the NIR spectra of samples Li-SAZ-1 and TMA-SAZ-1 before and after HCl dissolution for 2 h (spectra b in Figure 6A,B) found that exchanging  $\text{Li}^+$  with  $\text{TMA}^+$  reduces the extent of alteration of SAZ-1 by acid dissolution. The  $2\nu\text{SiOH}$  band in TMA-SAZ-1 (Figure 6B,b) is weaker than that in the Li-SAZ-1

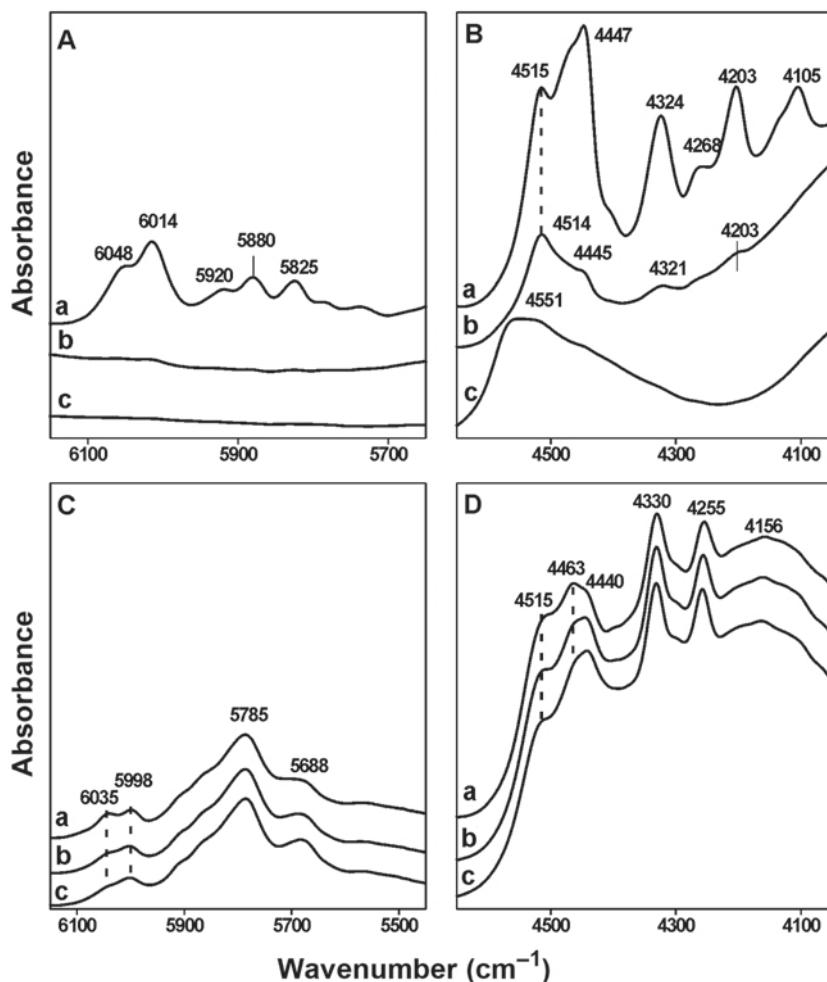


Figure 7. CH overtone and combination regions of TMA-SAZ-1 (A, B) and HDTMA-SAZ-1 (C, D): untreated (a), treated in 6 M HCl at  $80^\circ\text{C}$  for 2 h (b), and 6 h (c).

spectrum (Figure 6A,b) and no clear decrease in the intensity of the  $2\nu\text{OH}$  band is visible in the TMA-SAZ-1 spectrum. While the first CH overtone region (Figure 7A,b) showed the disappearance of all bands after 2 h of acid dissolution, the CH combination region (Figure 7B,b) retained some spectral features even after this treatment, indicating it is a more sensitive region in terms of the relics of the  $\text{CH}_3$  groups. (Figure 7B,b). Although the  $(\nu+\delta)\text{OH}$  band at  $4515\text{ cm}^{-1}$  dominates in this region, the presence of the shoulders near  $4445\text{ cm}^{-1}$ ,  $4321\text{ cm}^{-1}$ , and  $4203\text{ cm}^{-1}$  confirms that not all the  $\text{TMA}^+$  cations were exchanged by protons upon 2 h of treatment. The NIR region distinguishes more sensitively the presence of  $\text{TMA}^+$  than does the MIR spectrum (Figure 5) in which the inflection due to  $\delta\text{CH}_3$  vibrations can be only barely resolved in the spectrum of the sample treated for 2 h. The shape of the NIR spectrum of TMA-SAZ-1 dissolved for 6 h is similar to that of Li-SAZ-1; no bands due to  $\text{TMA}^+$  were detected. The intensities of the SiOH overtone ( $7316\text{ cm}^{-1}$ ) and combination (near  $4551\text{ cm}^{-1}$ ) bands indicate pronounced degradation of the montmorillonite structure (Figure 6B).

Acid dissolution of HDTMA-SAZ-1 for 2 or 6 h produced no pronounced changes in its NIR spectra (spectra b and c in Figures 6C, 7C, and 7D). Only an upward shift and a slight decrease in the intensities of the  $2\nu\text{OH}$  and  $(\nu+\delta)\text{H}_2\text{O}$  bands in the spectrum of HDTMA-SAZ-1 treated for 6 h indicate partial modification of the montmorillonite structure. Only minor changes in the CH overtone and combination regions of HDTMA-SAZ-1 were observed after 6 h of treatment (Figures 7C and 7D). An initial doublet at  $6035\text{ cm}^{-1}$  and  $5998\text{ cm}^{-1}$ , corresponding to  $2\nu_{\text{as}}\text{CH}_3\text{-N}$ , merged into one broader peak after acid treatment while a shoulder near  $5688\text{ cm}^{-1}$  became better resolved. Similarly, the modification of the  $(\nu+\delta)\text{CH}_3\text{-N}$  bands at  $4463\text{ cm}^{-1}$  and  $4440\text{ cm}^{-1}$  can be recognized in the CH combination region of acid-treated HDTMA-SAZ-1 (Figure 7D). Apparently the terminal  $(\text{CH}_3)_3\text{-N}$  groups are more sensitive to HCl treatment than are the  $-\text{CH}_2\text{-C}$  groups.

The NIR spectra of HDTMA-SAZ-1 contained, however, one unexpected feature. No SiOH overtone near  $7315\text{ cm}^{-1}$  can be distinguished in the spectrum of HDTMA-SAZ-1 treated for 6 h, although a small upward shift of the  $\nu\text{Si-O}$  band (Figure 5) and changes in the bands at  $7060\text{ cm}^{-1}$  and  $5246\text{ cm}^{-1}$  (Figure 6) indicate at least some, though minimal, decomposition of the montmorillonite layers. The presence of a SiOH overtone was found to be a very sensitive indicator of the creation of SiOH groups on the clay mineral surface (Pálková *et al.*, 2003). For example, the SiOH overtone was unambiguously identified in the spectrum of acid-treated illite-smectite even when no intensity alteration of the  $2\nu\text{OH}$  overtone and no change in the  $\nu\text{Si-O}$  band position were observed (Madejová *et al.*, 2009). The

absence of SiOH overtone in the spectra of acid-treated HDTMA-SAZ-1 can only tentatively be explained because no additional results obtained by other methods (*e.g.* NMR spectroscopy or CHN analysis) are available at the moment. Even though the disruption of the octahedral sheets of the HDTMA-SAZ-1 after 6 h of treatment in HCl is very limited, some  $\text{Si-O}^-$  groups should still have been created. The  $\text{HDTMA}^+$  released as a result of their partial replacement by  $\text{H}^+$  may compensate the unsaturated charge of  $\text{Si-O}^-$  groups. Consequently, no Si-OH band can be distinguished in the NIR spectrum of acid-treated HDTMA-SAZ-1. However, this hypothesis, as was mentioned above, requires verification by other analytical methods.

Both MIR and NIR spectra confirm the different influence of quaternary alkylammonium cations on the acid dissolution of SAZ-1 montmorillonite. In comparison with  $\text{Li}^+$ , the effect of  $\text{TMA}^+$  cations on the dissolution in 6 M HCl is distinguished only after short treatments (*i.e.* 2 h), while after a longer period (*e.g.* 6 h) the extent of dissolution is the same as that of Li-SAZ-1. On the other hand, the  $\text{HDTMA}^+$  cations almost completely prevent decomposition of the montmorillonite layers even after 6 h of acid exposure. The properties of alkylammonium derivatives of clay minerals depend on the layer charge of smectite and on the type of alkylammonium cation used (Klapyta *et al.*, 2001; Slade and Gates, 2004; Kooli and Magusin, 2005; Lagaly *et al.*, 2006). Alkylammonium cations with short alkyl chains ( $\text{TMA}^+$ ) are located on the montmorillonite surface as discrete units isolated by uncovered mineral surface that can act as potential access for protons. Due to the high layer charge of SAZ-1, a large part of the siloxane surface is covered with  $\text{TMA}^+$  and, therefore, the rate of dissolution of TMA-SAZ-1 is reduced somewhat in comparison with that of Li-SAZ-1. The arrangement of  $\text{HDTMA}^+$  in the smectite interlayers is different, however. The charged head-groups of  $\text{HDTMA}^+$  are in direct contact with the siloxane surface while long alkyl chains create a pseudotrimolecular and bimolecular configuration (Lagaly *et al.*, 2006; Slade and Gates, 2007). They also cover the minerals' outer surfaces. Taking into account the high charge of SAZ-1 montmorillonite and the size of the  $\text{HDTMA}^+$ , only a limited part of the HDTMA-SAZ-1 surface can interact with protons. Decelerated dissolution of HDTMA-SAZ-1 reflects a combination of two factors; *i.e.* the poor ability of the organo-clay to swell in aqueous media and limited access of protons to the layers.

## CONCLUSIONS

The application of NIR spectroscopy to the study of acid-treated alkylammonium derivatives of SAZ-1 montmorillonite has great potential as a characterization tool for clay mineral-organic molecule interactions. Based on the fundamental vibrations observed in the MIR region,

the  $2\nu\text{CH}$  and  $(\nu+\delta)\text{CH}$  bands have been identified in the NIR spectra of organo-clays. The NIR spectra of acid-treated Li-SAZ-1 showed a pronounced decrease in the intensities of structural OH overtone and combination bands, indicating a substantial degradation of the structure. The first SiOH overtone near  $7315\text{ cm}^{-1}$  indicates acidification of the montmorillonite surface and/or creation of a partly protonated silica phase during acid dissolution of the clay mineral. The IR spectra confirm that the dissolution rate of TMA-SAZ-1 in 6 M HCl at  $80^\circ\text{C}$  is only slightly reduced compared to that of Li-SAZ-1, while the long-chain HDTMA<sup>+</sup> cation protects the montmorillonite layers from acid attack. The IR spectra in both the MIR and NIR regions provide information regarding the different dissolution rates of Li-, TMA-, and HDTMA-SAZ-1. Spectra in the NIR region, however, more sensitively reflect the changes in alkylammonium cations during acid treatment. In addition, only the NIR region can monitor the creation of SiOH groups – an important indicator of the surface acidification of montmorillonite. That no SiOH groups were found in the NIR spectrum of HDTMA-SAZ-1 dissolved in 6 M HCl at  $80^\circ\text{C}$  for 6 h indicates that the HDTMA<sup>+</sup> completely covers the inner and outer surfaces of montmorillonite and blocks access by protons to the unsaturated Si-O<sup>-</sup> groups of the SAZ-1.

Detailed analysis of the NIR spectra of alkylammonium derivatives of smectites is important for further interpretation of spectra of various organic species adsorbed on clays. The results achieved in this study may also help soil mineralogists using portable field spectrometers utilizing NIR radiation. Acidification of soils, for example, is currently a frequently investigated environmental problem. Accurate interpretations of NIR spectra of acid-treated organo-clays could contribute to more precise analyses of the results obtained directly in the field.

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