

6th Workshop of Slovak Clay Group



CLAY MINERALS AND SELECTED NON-RAW
MATERIALS IN MATERIAL SCIENCE, INDUSTRIAL
APPLICATIONS AND ENVIRONMENTAL TECHNOLOGY

BOOK OF ABSTRACTS



May 27 – 28, 2019, Banská Bystrica, Slovakia

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MOLECULAR AGGREGATION OF XANTHENE DYE IN COLLOIDAL DISPERSIONS OF LAYERED SILICATE: THE EFFECT OF IONIC STRENGTH

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Keywords: rhodamine 123 | molecular aggregation kinetics | montmorillonite

The interaction of cationic organic dyes with particles of layered nanomaterials leads to the formation of dye molecular aggregates at colloidal particle interface [1]. This phenomenon results in an apparent change of the spectral and photophysical properties of dyes. Dye molecular aggregation has been intensively studied focusing mainly on colloidal systems of smectites. The results of numerous research articles confirm the significant effect of the structure and surface properties of smectites on dye molecular aggregation [2]. Our previous study, which was focused on the effects of dye surface concentration reported a close relationship between changes in the stability of montmorillonite (Mt) colloid after dye adsorption and the course of rhodamine 123 (R123) molecular aggregation [3]. Although the effects of various parameters on this phenomenon have been intensively investigated, some details of the mechanism of the formation of dye molecular aggregates in heterogeneous reaction systems have not yet been explained. The identification of the processes involved in dye aggregation is essential to understand the principles of dye/smectite interaction. It is also important for the purpose of investigating the possibilities of using organic dyes as molecular sensors for the characterization of colloidal particles.

The objective of the present work was the investigation of the effect of ionic strength on the molecular aggregation of R123 in colloidal dispersions of Mt. The ionic strength was altered by changing the concentration of an inert electrolyte (NaNO₃). The kinetics of dye aggregation was measured using the combination of a stopped-flow rapid mixing device and the UV-Vis spectrophotometer equipped with a diode array detector. Subsequently, the analysis of the spectral data matrix in a visible range by chemometric method resulted in spectral and concentration profiles of R123 monomers and aggregates. Reaction rates and half-lives of the formation of R123 aggregates were estimated using a non-linear regression analysis of the concentration profiles of the respective dye species.

The interaction of R123 with Mt particles led to rapid adsorption of dye molecules. Subsequently, the association of adsorbed R123 cations resulted in the formation of oblique J-aggregates of the dye over reaction time. The mechanism of their formation was described by two parallel processes, both of which proceeded by first-order reaction kinetics but differ in their rate constants. The extent of dye molecular aggregation slightly increased with the ionic strength. Significant effect of the concentration of the inert electrolyte on the rate constants was observed: Increasing the ionic strength increased the rate of the processes involved in dye molecular aggregation. However, the variation of the rate constant did not follow the equation describing the kinetic salt effect. In addition, a linear dependence of the rate constant on the reciprocal value of Debye length indicates, that the formation of R123 J-aggregates is mainly controlled by the rate of the diffusion of Mt particles in the colloidal systems.

Acknowledgement:

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SPECTRAL PROPERTIES OF HYBRID SYSTEMS BASED ON ORGANOMODIFIED SMECTITES AND RHODAMINE 6G

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Keywords: laser dye | organoclays | emission | spectroscopy

Organo-modified smectites are nowadays extensively studied in order to prepare functional materials suitable for advanced applications. Smectites in their unmodified forms are often studied as carriers for laser dyes that influence their final luminescent properties. Systems based on smectites modified with alkylammonium cations have shown to be effective in preventing dye aggregation, a phenomenon that reduces dye luminescence (e.g. SASAI et al., 2009). The aim of this work was to study the effect of organic cations on the final properties of organoclays and to investigate the interactions within hybrid systems with laser dye rhodamine 6G (R6G).

Synthetic saponite Sumecton (Sum) and natural montmorillonite Kunipia (Kun) were used to prepare organoclays via exchange process of initial Na⁺ for tetraoctylphosphonium (TOP⁺) and tetraoctylammonium (TOA⁺) cations in amounts equal to 25, 50, 75, 100% of the initial clay mineral cation exchange capacity. Elemental analysis showed a substantial increase of the amount of carbon present in the samples. Basal spacing expanded upon exchange from 1.2 nm up to 2.25 nm for sample with the highest content of organic phase. IR spectra in the middle (MIR) and near infrared (NIR) regions collected for organo-smectites reflected the amount of organic phase loaded to samples and the band areas of stretching (ν), bending (δ) and of the first overtones (2ν) rised in order of increasing carbon content. The shapes of the C-H absorption bands were modified compared to the pure organic salts spectra.

The UV/VIS absorption and fluorescence spectra provided information on the R6G species formed within the systems. UV/VIS spectra of both Sap/R6G and Mt/R6G exhibited bathochromic shifts and the formation of H- and J-aggregates. The increase in dye concentration induced a decrease in absorbance of the main absorption band centered at ~ 535 nm and enlarging the contribution of the bands at shorter (H-band) and longer (J-band) wavelengths. A predominant contribution of H-aggregates was detected in the spectra of Mt/R6G due to higher layer charge of Mt on contrary to the Sap. Visual comparison of the powders of initial clay minerals after R6G adsorption upon illumination with UV-lamp showed emission only for Sum. The presence of surfactants reduced the tendency of the dye cations to self-associate and promoted the formation of fluorescent J-type aggregates and the emission was more enhanced for TOA-Sum and on contrary to initial Kun was detected also for TOA-Kun samples (Fig. 1).

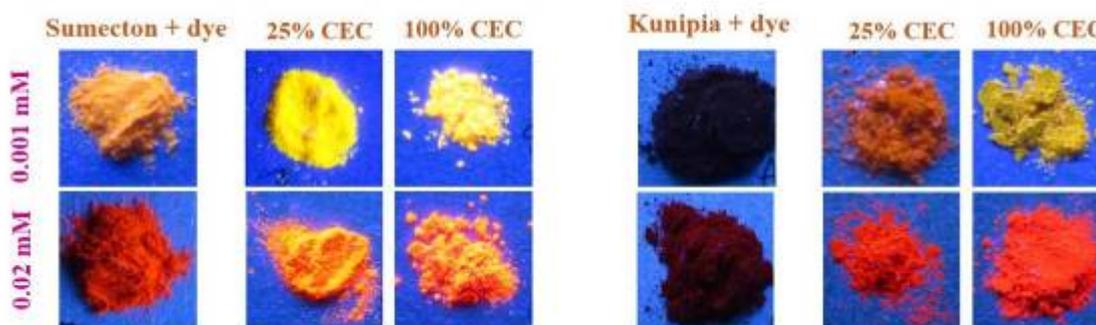


Figure 1. Rhodamine 6G samples of TOA-Sum and TOA-Kun upon illumination with UV-lamp.

The emission spectra of TOA- and TOP-Sum displayed significantly higher intensities of the bands compared to TOA- and TOP-Kun. The emission spectrum of rhodamine 6G cations incorporated in TOP⁺, TOA⁺-samples showed bathochromic effect dependent on the both, dye and organic content used for preparation of the samples. The increase in dye loading initiated the appearance of new emission band at longer wavelengths. However, significant drop in the intensity was observed for samples with the highest dye concentration, i.e. 0.02 and 0.08 mmol/g of sample (Fig. 2). The influence of organic surfactant loading was observed and for samples with the higher content of TOA⁺ or TOP⁺ (100%) the higher intensity was registered in emission spectra compared to samples with 25% of organic cation loading (Fig 2).

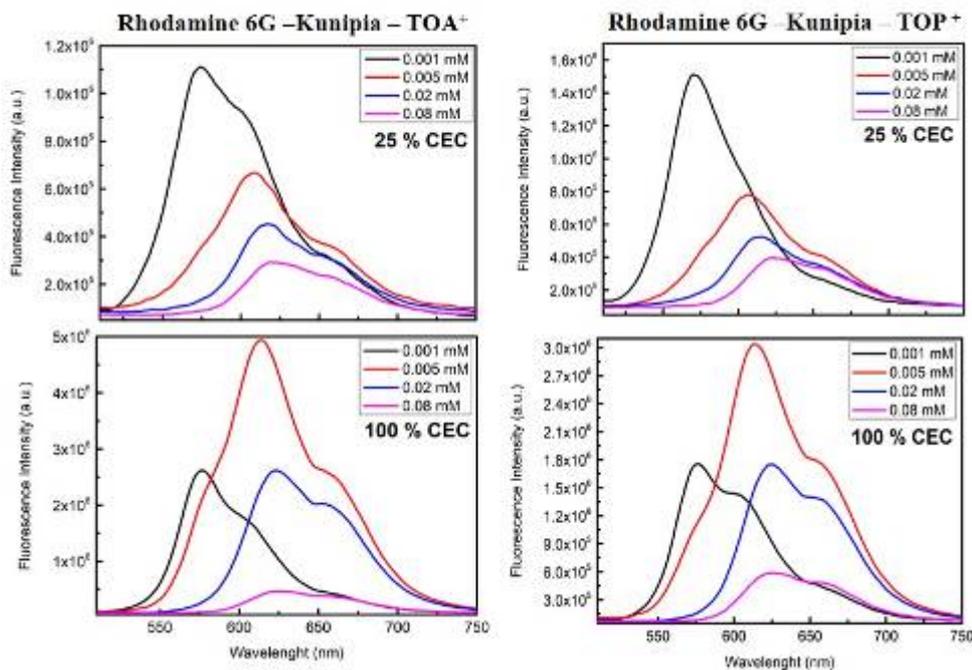


Figure 2. Emission spectra of organo-modified Kunipia

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FRET AND POISSON DISTANCE DISTRIBUTION MODEL AS THE TOOLS FOR THE CHARACTERIZATION OF THE DYE SURFACE CONCENTRATION ON THE SMECTITE PARTICLES

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Keywords: Energy transfer | hybrid nanomaterial | Poission distance distribution

Hybrid nanomaterials based on layered silicates and laser dyes could exhibit outstanding optical and photophysical properties. However, the photoactivity of such hybrids is strongly dependent on the dye's concentration on the clay surface. High concentration of dyes often leads to the formation of supramolecular assemblies with reduced photoactivity. Considering high sensitivity of Förster resonance energy transfer (FRET) on the distance between interacting particles FRET was used to obtain the main distances between the molecules of dyes adsorbed on the clay mineral surface. FRET could be easily determined experimentally using steady-state and time-resolved fluorescence spectroscopies. Using these techniques FRET efficiency was calculated and its trend with increasing surface concentration of the dyes was determined. The experimental results were supplemented with the Poisson distance distribution model. The model was applied to describe the characteristics of the dye molecules distribution on the Sap particles. High surface concentrations of dyes led to a relatively narrow distribution of distances, whereas lower surface concentrations were characterized by a broader distribution of distances. The expected values of FRET efficiency were calculated as a function of the interparticle distances. The theoretical and the experimental results of FRET efficiencies were in good agreement. The theoretical model presents an excellent tool suitable for the prediction of the photophysical properties of hybrid systems based on organic dyes and inorganic nanoparticles. The statistical approach for the characterization of the distance distribution between dye cations adsorbed on the clay mineral surface brought a considerably higher accuracy than a simpler model using average interparticle distances.

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WHAT DO WE KNOW ABOUT THE MECHANISM OF DYE MOLECULAR AGGREGATION IN COLLOIDS OF INORGANIC NANOPARTICLES?

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Keywords: metachromasia | cationic dyes | smectites | photophysical properties | visible spectroscopy

Metachromasia is known for almost a hundred years. The manifestations of this phenomenon is a significant change in the color of certain organic dyes. Metachromasia is related to the molecular aggregation of dyes with the molecular structure based on planar conjugated or heteroaromatic systems. The molecular aggregation of cationic dyes in colloids of layered nanoparticles, namely of clays, has been well documented.

The beginnings associated with attempts to interpret the molecular aggregation of the organic dye, methylene blue, in clay colloidal systems were full of problems and accompanied by intense discussions among scientists. It was a mystery how methylene blue reacted in the presence of various clay minerals. Sometimes it behaved very differently in colloids of the same type of smectite. In other cases, the same molecular aggregates were formed in the colloidal systems of smectites of different structure.

These contradictions were explained by the influence of negative layer charge. The greater the charge of the layers, the greater the density of the adsorbed dye cations, which leads to the formation of sandwich-type H-aggregates. The lower charge density leads to a partial suppression of the aggregation and formation of J-aggregates, or to the adsorption of dye cations in the form of non-aggregated molecules. Since the surface charge of the layers is not related to the structural type of smectite, the molecular aggregation does not necessarily depend on the type and structure of the mineral.

Another mystery of this phenomenon is the reaction mechanism. Molecular aggregation in homogeneous systems is an almost instantaneous reaction driven by diffusion processes. On the other hand, processes in colloidal systems with clays are relatively slow and spectral equilibrium is achieved after relatively long times, e.g. minutes to hours.

It has been suggested that the course of the reaction reflects the flocculation processes, which secondarily affect the molecular aggregation. Indeed, these factors in some cases significantly affect the phenomenon, but our experiments have not confirmed the dominant effect of colloid stability. The mystery is the relatively large half-life of the slow process. This implies that the formation of aggregates must overcome a relatively high energy barrier. However, this contradicts the fact that molecular aggregation is actually a phenomenon in which only non-covalent interactions take place. Such processes should be logically very fast, almost instantaneous, as has been observed in homogeneous systems.

Our recent experiments shed more light on the mechanism of molecular aggregation. The aggregation of rhodamine 123 (R123) in montmorillonite (Mt) colloids was measured using visible spectroscopy. The spectra were sampled using spectrophotometer equipped with a diode-array detector. For the data, from which the basic trends for the determination of the reaction mechanism were derived, uncompromising criteria were set up: Several thousand spectra were analyzed chemometrically. The spectral properties were interpreted using an exciton model. The concentration profiles were analyzed to find the mechanism and parameters of the reaction kinetics.

The oblique aggregates were the main reaction product and the reaction was described by two first-order parallel processes. The extent and the rates of molecular aggregation increased with the reaction temperature (T). The interaction between dye cations and the surface of colloidal particles played a crucial role in the process. The dependence of the reaction rate on T did not follow an Arrhenius kinetics. The linear relationship between the rate constants and T indicates the role of particle diffusion processes which explains slow rates.

The scheme of the whole process can be divided into two stages:

The first stage of the reaction takes place almost instantaneously after mixing the components and involves adsorption of the dye molecules onto the surface of the particles. This process is fast and diffusion-controlled. In part, it may lead to the aggregation of dye molecules, but part of the molecules may remain in a non-aggregated state. It is possible, adsorption of the cations stabilizes this state and prevent further diffusion of the molecules.

The second stage of the reaction is the very slow formation of molecular aggregates, but often involves also the change of the aggregates of one type to another. In this case, these processes take a relatively long time to form a spectral balance. If the dye molecules were not sufficiently fixed by adsorption, there would be nothing to prevent their very fast migration on the surface of a particle, or possibly interparticle migration. However, the fast migration is not the case as experimentally proven. On the other hand, the effect of T on these slow processes suggests that not the diffusion of molecules but rather the diffusion of colloidal particles controls the kinetics of dye molecular aggregation. The linear relation of the rate to T is in accordance with the Einstein and Smoluchowski law for the diffusion of colloidal particles. Particle-particle interactions and / or collisions seem to be the activation steps to promote a temporal desorption or exchange of dye molecules between the particles. The collisions between particles, which can destabilize the electrical double layer surrounding the particles, can break an energetic barrier to temporarily liberate dye molecules, which allows the system to re-form new aggregates and to shift more towards a thermodynamic equilibrium.

In summary, the results of recent investigation indicate the complex processes involving particle-particle and particle-dye interactions play the key roles in the mechanism and affect reaction kinetics parameters of dye molecular aggregation.

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HALLOYSITE NANOCARRIERS FOR EFFICIENT DELIVERY OF IRINOTECAN: BASED ON EXPERIMENTAL DATA AND MOLECULAR SIMULATIONS.

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Keywords: halloysite | drug delivery system | molecular simulation

A Halloysite, a clay mineral of kaolinite group, presents a tubular morphology and has recently been tested and proposed as a drug delivery system due to the unique structure, the entrapment properties and the biocompatibility with the human body. An enriched sample of halloysite from the Dragon mine (Utah, USA) was investigated as a potential oral administration carrier of irinotecan for colon cancer treatment. The irinotecan-loaded halloysite nanotubes were coated by the anionic copolymer Eudragit S100 (in ratio 3:1) in order to provide enteric release properties. The samples were characterized by UV-Vis spectrophotometry, XRD, TEM, TGA and DLS. The entrapment efficiency of the drug in the nanotubes reached 84.42 ± 3.10 %. Drug release experiments were performed, and the drug release was minimal in simulated stomach conditions (pH 1.2) and significant higher in the first two hours in simulated colon conditions (pH 7.4).

In order to study and model the interaction of irinotecan cations with the halloysite nanotubes, the classical molecular simulation methods were used. Mutual interactions between irinotecan cations and halloysite were described. The drug cations seem to remain closer to the outer surface of the halloysite nanotubes. The energetically preferred position, as derived from the geometry optimization results, it is when the longitudinal axis of the irinotecan cations are along to the longitudinal axis of the nanotubes. Based on the molecular dynamic simulations, 6 drug cations are loaded in a 5-ring halloysite tube. This drug loading value is in agreement with the molar weight ratio of the components obtained experimentally. Halloysite can be a promising carrier of irinotecan for colon cancer treatment and molecular simulation methods can help in understanding the mechanisms of drug interaction with the halloysite carrier.

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NEW APPROACH TO THE DETERMINATION OF WATER IN PERLITES BY INFRARED METHODS

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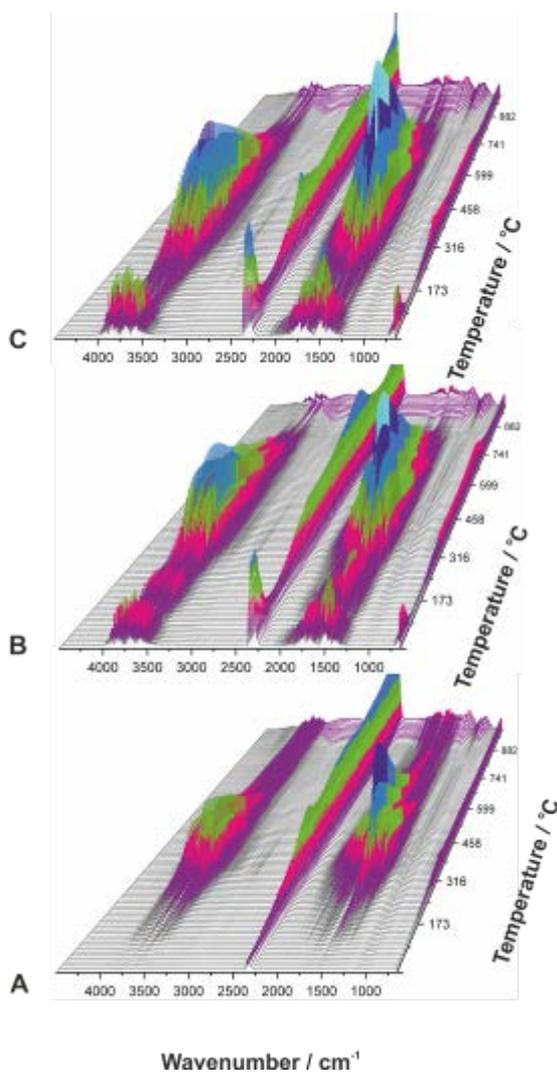
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Keywords: perlite | water molecules | water adsorption | thermal analysis | infrared spectroscopy

Perlite (PL) belongs to the group of silicate industrial rocks that's economically interesting deposits occur also in Slovakia therefore detailed studies of their properties have received a great deal of attention not only due to their industrial potential but also from the scientific point of view. Water plays an important role in the application of this material. PI contains a various types of water, especially important are water molecules trapped in the inner pores and microcracks causing the expansion when rapidly heated. The potential of a near-infrared (NIR) spectroscopy and NMR spectroscopy to water molecules types in perlites (PI) has been investigated.

Perlite samples from different localities (Lehôtka pod Brehmi – SK, Jastrabá skala – SK, Viničky – SK) with variable amount of water and textures were studied. The water in PI samples was investigated mainly by modern methods of NIR spectroscopy, supplemented with traditional gravimetric and thermal analysis. The amount of water in PI samples was investigated by NIR DRIFT accessory. The combination band of water molecules $(\nu+\delta)_{\text{H}_2\text{O}}$ near 5240 cm^{-1} was used to water quantification because the region is free from the other silicates bands and can be used to provide information on the water content in samples. The area of this band reflects the amount of molecular water in PI samples. The $(\nu+\delta)_{\text{H}_2\text{O}}$ band areas plotted as a function of water content obtained from the thermogravimetric analysis (TG) and loss on ignition (LOI) showed correlation $R^2 = 0.78$ and 0.74 , respectively. Internal standards have been used to improve water quantification. The hexadecyltrimethylammonium bromide (HDTMA) and talc (GP-1) were used as internal standards because of their very low affinity to water and absence other vibration bands in area of the water band. In HDTMA standard the area of the first overtone of CH groups (near 5800 cm^{-1}) was used to normalize spectra while in GP-1 the combination vibration band of structural OH groups from talc (near 4180 cm^{-1}) was used. This way the correlations with TG and LOI analyses for HDTMA were 0.89 and 0.86 , respectively, and for GP-1 0.88 and 0.86 , respectively. The extent of hydration was followed by NIR UpDRIFT accessory enabling the measurements of the samples directly in closed glass vials. The $(\nu+\delta)_{\text{H}_2\text{O}}$ band was used to characterize the hydration properties of the samples hydrated at 100 % relative humidity for 2 weeks. Difference in the area of $(\nu+\delta)_{\text{H}_2\text{O}}$ band of hydrated and dried sample reflects the quantity of adsorbed water. NIR spectra as well as gravimetric analysis proved very poor hydration ability. The maximal amount of adsorbed water was only 3.3 mass %. Dehydration properties of PI samples were monitored by special NIR DRIFT temperate cell susceptible to in-situ measurement of the spectra in a temperature range $25\text{-}800^\circ\text{C}$. With increasing temperature the area of $(\nu+\delta)_{\text{H}_2\text{O}}$ band fell down in different ways. The slow decline of band intensity reflected the H_2O held strongly within structure while the significantly decrease already at low temperatures points to the presence of weakly bound water molecules.

Temperature depended IR spectra of gaseous products collected during thermal analysis may indicate the temperature region the water species are evolved from the samples. Spectra showed the absorption



bands accompanied by rotational vibrations of water vapour, stretching mode between 4000-3500 cm⁻¹ and corresponding bending mode spread below 2000 cm⁻¹. 3D FTIR spectra provide wide profiles along temperature axis with the intensities of the bands increasing or decreasing based on content of water species evolved from the samples. The spectra of the sample with the lowest mass loss determined from thermal analysis (3.4%) showed also the lowest intensities of the bands in 3D spectra within temperature region 200-800°C (Fig. 1A), while intensity reached higher values for samples with the more water present, e.g. 4.1 and 4.3% based on thermal analysis (Fig. 1B,C). Weakly held water was removed at lower temperatures and is reflected in the appearance of the bands within temperature region below 200°C. Despite relatively small differences in the water content or mass loss between samples, IR spectra of gaseous product reflected reliably even those small variations within water content between perlite samples.

Figure 1. Temperature dependent 3D FTIR spectra of samples: PL-29a (A), PL-72b1 (B), PL-95 (C).

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NEAR-IR SPECTROSCOPY AND ORGANOCCLAYS

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Keywords: infrared spectroscopy | clay minerals | pyridine | acid treatment | organoclays

This work introduces the major benefits of near-infrared (NIR) spectroscopy in organoclays research. The identification of specific bonds “not visible” in the mid-infrared (MIR) region, characterization of acid-treated organo-montmorillonites (O-Mt), pyridine adsorption on acid-treated Mt, and the conformation of organic cations in montmorillonite interlayers are discussed.

Selected O-Mt, perspective fillers in clay polymer nanocomposites, were prepared from Na-Mt and organic cations containing octylammonium chain(s), hexadecylammonium chain(s) or a benzene ring with or without a reactive double bond. Based on the stretching (ν) and bending (δ) vibrations observed in the MIR region, the first overtone ($2\nu_{XH}$) and combination ($\nu+\delta$)XH modes of XH groups (X=O,C,N) were identified. The changes in the intensity of the ($\nu+\delta$)H₂O band allowed the comparison of the amount of water adsorbed on Mt surface. The NIR spectra were extremely useful in identification of NH₂⁺, NH⁺ and H₂C=C groups, which were difficult to recognize in the MIR region of O-Mt due to overlapping with other absorption bands (MADEJOVÁ et al., 2011).

The effect of the surfactant size on the extent of Mt dissolution in HCl was confirmed for O-Mt prepared from Na-Mt and tetraalkylammonium salts of alkyl-chains length increasing from methyl- Me₄N to pentyl- Pe₄N. A new band near 7315 cm⁻¹ due to SiOH overtone revealed creation of reaction product, protonated silica phase. The less stable were Na- and Me₄N-Mt, Et₄N- and Pr₄N-Mt were slightly more resistant mainly at short reaction times. Bu₄N-Mt and Pe₄N-Mt showed the least structural modifications within 8 hours treatments. Bulky alkylammonium cations, covering the inner and outer surfaces of montmorillonite, prevent effectively the access of protons to the layers protecting thus the mineral from degradation in the acid (MADEJOVÁ et al., 2012).

NIR spectra of pyridine adsorbed on untreated and acid-treated montmorillonite were analyzed with intention to distinguish different pyridine species adsorbed on montmorillonite surface. The effect of the mineral structure modification on the formation of acid sites was discussed together with the strength of the pyridine bonding on montmorillonite surface. After exposure of Mt to pyridine vapours the intensity of the ($\nu+\delta$)H₂O band diminished indicating the partial replacement of water molecules by pyridine. The CH overtone band corresponding to physisorbed and/or H-bonded pyridine appeared near 6000 cm⁻¹. Disappearance of the SiOH band in the NIR spectra of acid-treated samples revealed that silanol groups as weak Brønsted acid sites formed H-bonds with pyridine-nitrogen (MADEJOVÁ et al., 2015).

The understanding the arrangement/conformation of organic cations (surfactants) is an important step toward optimizing the performance of O-Mt in their applications where selective surface interactions are crucial. Detailed information on the local conformation of surfactants provides IR spectroscopy. The positions of the bands related to the vibrations of the CH₂ groups were used as an indicator of the disordered *gauche*/ordered *trans* conformer ratio. Shift of the bands to lower wavenumbers confirmed the increase of *trans* conformers. The comparison of the MIR and NIR spectra of montmorillonite saturated with trimethyl-alkylammonium cations with varying alkyl chain length (even numbers of carbon atoms from C6-C18) showed significantly higher downward shift of CH₂ bands in the

NIR than in MIR spectra favouring the utilization of the NIR region for examining the conformation issue (MADEJOVÁ et al., 2016).

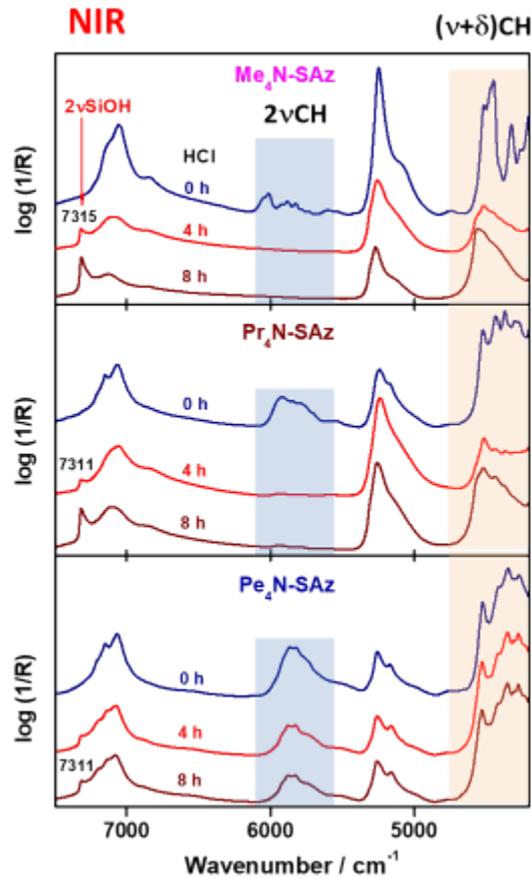


Figure 1. NIR spectra of organo-smectite acid untreated and treated in HCl for 4 and 8 h.

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DENSITY FUNCTIONAL THEORY STUDY OF ATRAZINE-BEIDELLITE INTERCALATES

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Keywords: organoclay | IR spectra | DFT

Atrazine (A), an herbicide widely used in the past, presents a negative impact on the environment [1]. Clay minerals, such as beidellite (Bd), are able to adsorb and immobilize organic contaminant, like atrazine, from soil and waste waters. Clay minerals are highly hydrophilic hence Bd shows a very limited adsorption capacity for hydrophobic organic pollutants. However, a higher adsorption of organic molecules/cations can be obtained by modifying the clay surface by organic surfactants.

Beidellite displays its substitutions predominantly in the tetrahedral sheets. The tetrahedral charge distribution improves the stability of prepared organoclays compared to the octahedral one [2].

This study aims the characterization of the interactions between the $[\text{Na}(\text{H}_2\text{O})_4]^+$ and tetramethylphosphonium cations (TMP) with A in the interlayer space of Bd, the way of keying of atrazine into Bd structure, the analysis of the bands of IR spectra by means of calculated vibrational modes, and calculate the intercalation energy to reveal the stability of the structure.

Density Functional Theory (DFT) in solid state and PBE functional [3] with D3 method for involving dispersion correction [4], was used for study of interactions in A-Bd and intercalation energies. Moreover, the vibrational spectra were calculated by means of *ab initio* molecular dynamics method (AIMD) to show possible hidden bands in the experimental FTIR spectra.

Three models were proposed: 1. A intercalated in the Bd (A-Bd); 2. TMP as organic surfactant intercalated in the Bd (TMP-Bd); 3. A and TMP cation, intercalated in the Bd (ATMP-Bd) (Fig.1).

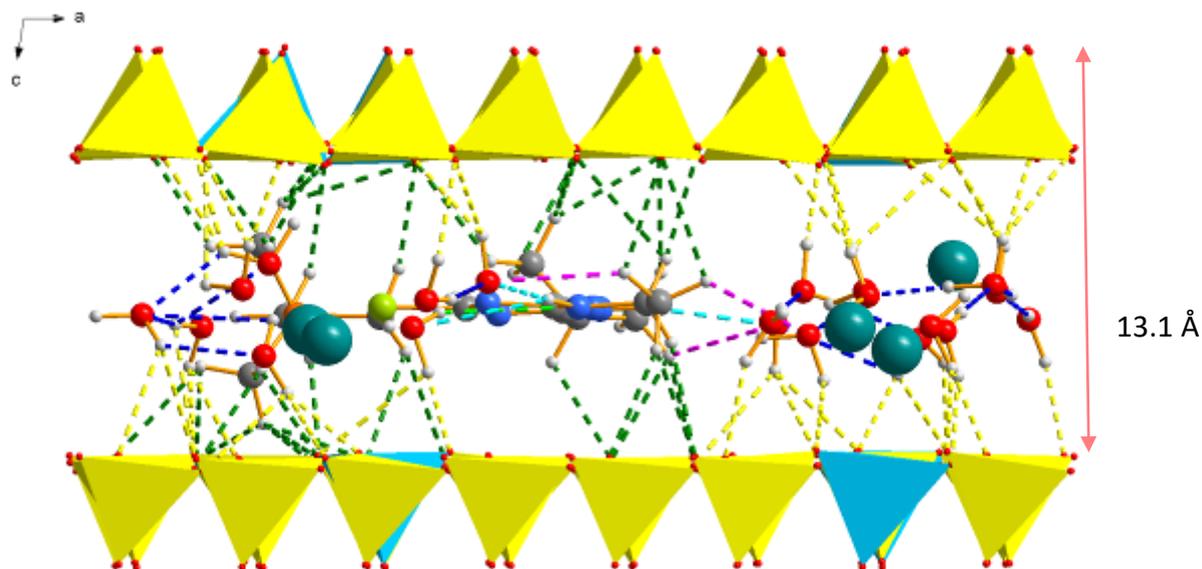


Figure 1. Hydrogen bonds in ATMP-Bd model (yellow dash - $\text{O}_w\text{-H}\dots\text{O}_b$, blue dash - $\text{O}_w\text{-H}\dots\text{O}_w$, green dash - $\text{C-H}\dots\text{O}_b$, magenta dash - $\text{C-H}\dots\text{O}_w$, light blue dash - $\text{N-H}\dots\text{O}_w$, light green dash - $\text{O-H}\dots\text{N}$).

The results revealed that in the optimized models, atrazine has a flat arrangement in Bd interlayer space. The interactions that form the intercalates are mostly weak hydrogen bonds. The presence of TMP cation in the interlayer space improves the interactions of atrazine.

Acknowledgements:

Authors are grateful for the financial support by the Slovak Research and Development Agency APVV-15-0741, APVV-15 0479 and VEGA 02/0021/19.

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THE INFLUENCE OF THE ORGANIC CATION ON THE WATER UPTAKE BY CLAY MINERALS: SPECTROSCOPIC STUDY

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Keywords: organoclay | IR spectra | near infrared spectroscopy | NMR spectroscopy

Modification of a clay mineral surface with quaternary alkylammonium cations results in a hybrid inorganic/organic material with surface properties considerably different from unmodified sample. Question of hydrophobicity/hydrophilicity of clay minerals come forward due to their possible industrial applications including for instance their utilization as fillers in polymer-clay nanocomposites. Exposing unmodified smectite to water molecules causes their penetration between the layers followed by swelling of the structure. The extent of swelling depends on several factors, mainly on the nature of the interlayer cations. The influence of organic cation size on the water vapour uptake by montmorillonite was examined and the comparative study with unmodified clay mineral was provided. The organoclays were prepared from Li-saturated SAz-1 montmorillonite (Li-SAz) and tetramethylammonium- (TMA⁺) or hexadecyltrimethylammonium- (HDTMA⁺) salts and consequently samples were characterised with several methods (e.g. IR spectroscopy, CHN elemental analysis, ¹H MAS NMR and ¹³C MAS NMR). The CHN elemental analysis was used to determine the carbon content in the samples. The results showed that TMA-SAz and HDTMA-SAz contained 1.2 mmol/g and 1.1 mmol/g of organic cation, respectively. The presence of organic cation affected also a specific surface area (SA) of the samples. The SA increased significantly after the exchange of Li⁺ for TMA⁺ from 68 to 246 m²/g, while the presence of the long chain HDTMA caused drop in surface area to about 10 m²/g. Prepared samples were exposed to water vapour under various relative humidity (RH) and the water content was determined. Water adsorption/desorption isotherms obtained for all three samples displayed similar shape with hysteresis loop upon desorption process. According the isotherms Li-SAz adsorbed the highest amount of water. A downward shift in the adsorption isotherms observed for both, TMA-SAz and HDTMA-SAz confirmed decreasing amount of water in order Li- > TMA- > HDTMA-. The hydration of montmorillonites caused also the changes in their near-infrared spectra. Presence of water in dried Li-SAz indicated the first overtone 2ν_{OH} near 7054 cm⁻¹ together with shoulder at 6830 cm⁻¹ and the combination mode (ν+δ)_{H₂O} at 5235 cm⁻¹. These bands belong to either strongly H-bonded and/or to physisorbed water molecules. The bands of water were observed also in dried organo-exchanged samples; however their intensity was significantly reduced compared to Li-SAz due to lower water content present on the samples after exchange. In particular, large HDTMA⁺ caused pronounced changes in the combination band (ν+δ)_{H₂O} and this band of relatively low intensity compare to Li-SAz and TMA-SAz was split into three-components reflecting the variability of H-bonded water molecules. Upon hydration, the intensity of both, first 2ν_{OH} overtone and (ν+δ)_{H₂O} combination mode gradually increased. Differences in the level of hydration between samples observed already in the adsorption isotherms are reflected in the degree of the increase in the intensity of overtones 2ν_{H₂O} and combination vibrations (ν+δ)_{H₂O}.

To follow the changes in water content the ¹H MAS NMR spectroscopy was employed. Spectra of Li-S showed resonance with a chemical shift of 1.6 ppm assigned to the resonance of hydrogens from the

structural OH groups present in the octahedral sheets of clay mineral layers (Fig. 1Aa). Signal at 4.2 ppm belongs to the hydrogens from water molecules. The spectrum of dried TMA-S (Fig. 1B-a) and HDTMA-S (Fig. 1C-a) showed at 3.3 and 1.6 ppm signals of hydrogens from CH₃⁻ and CH₂⁻ groups due to introduction of organic cations to the smectites. Upon hydration an increase in the intensity of the signal at 4.2 ppm relative to the signals of hydrogens present in the structural OH or in CH₂⁻ and CH₃⁻ groups was registered for all samples. Hydration influenced also positions of the in the ¹³C MAS NMR spectra of organosmectites. The presence of H₂O molecules close to the cation's headgroup affected the signals of inner -CH₂- groups in HDTMA-S causing the intensity of disordered *gauche* conformers (31.1 ppm) overtook the intensity of ordered *all-trans* conformers (33.0 ppm) for sample hydrated at RH=100%.

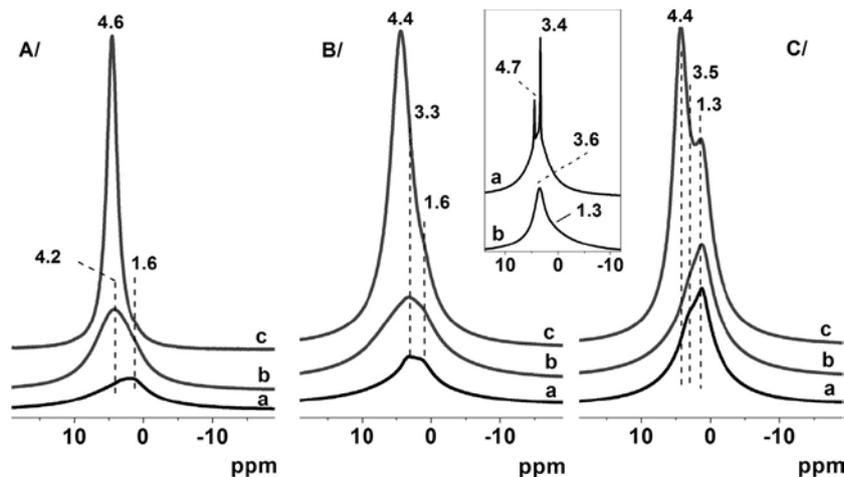


Figure 1 ¹H MAS NMR of the samples (A) Li-S, (B) TMA-S and (C) HDTMA-S: (a) dried sample, (b) hydrated at RH = 52%, and (c) 100%. Insert: spectra of pure salts (a) TMA-Cl and (b) HDTMA-Br.

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COMPUTATIONAL STUDY OF CS-HECTORITE

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Keywords: Cs-hectorite | DFT | IR

Natural or synthetic smectites like hectorites are important, widely abundant, and low-cost materials with unique physicochemical properties, such as swelling, intercalation and as well as ion-exchange properties applicable e.g. in catalytic processes or matrices in polymer nanocomposites. Controlled pore size distribution and composition of the synthetic hectorites predetermine these materials also on applicability for drug delivery purpose. In spite of the wide uses of the smectites (also hectorites) in the industry the structural characterization of clays and organoclays is very difficult because of a poor crystallinity of these materials. For investigation of these materials and their characterization some experimental methods are employed, such as Fourier transform infrared spectroscopy, ultraviolet-visible spectroscopy, contact angle measurement and atomic force microscopy, for example.

The computational methods help to eliminate the deficiency of suitable information about clay structures or to supply the obtained results and find more and more the application in this field. Except for the specific atomic positions, which enable to study e.g. hydrogen bonds, it is also possible to analyze the vibrational modes of the individual functional groups in these structures and help to describe the overlapped vibrational bands in the experimentally measured spectrum. An important factor at the use of the computational methods is proposing of the suitable representative model of the clay structure.

The primary aim of this study is to describe the structural model of Cs-hectorite based on the experimentally obtained structural data [1] in detail by means of density functional theory (DFT) method to obtain further structural information (Fig. 1) and secondly, to describe the individual calculated vibrational modes, especially in the case of overlapped bands (Fig.2).

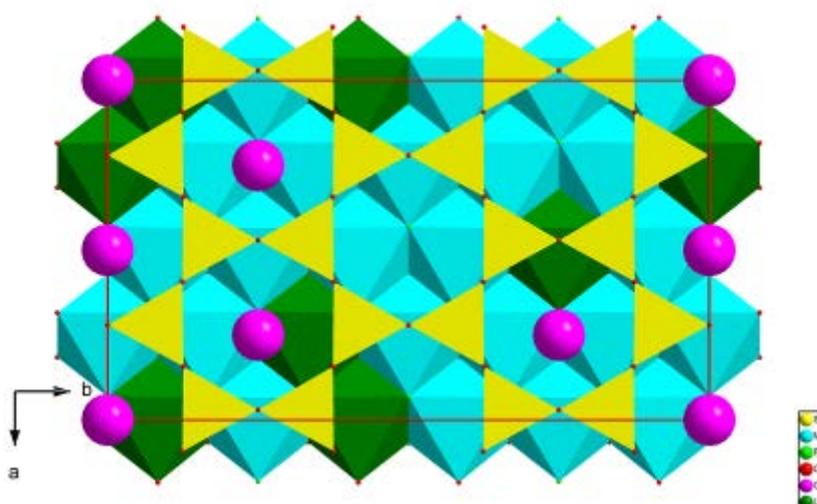


Figure 1. The structural model of Cs-hectorite.

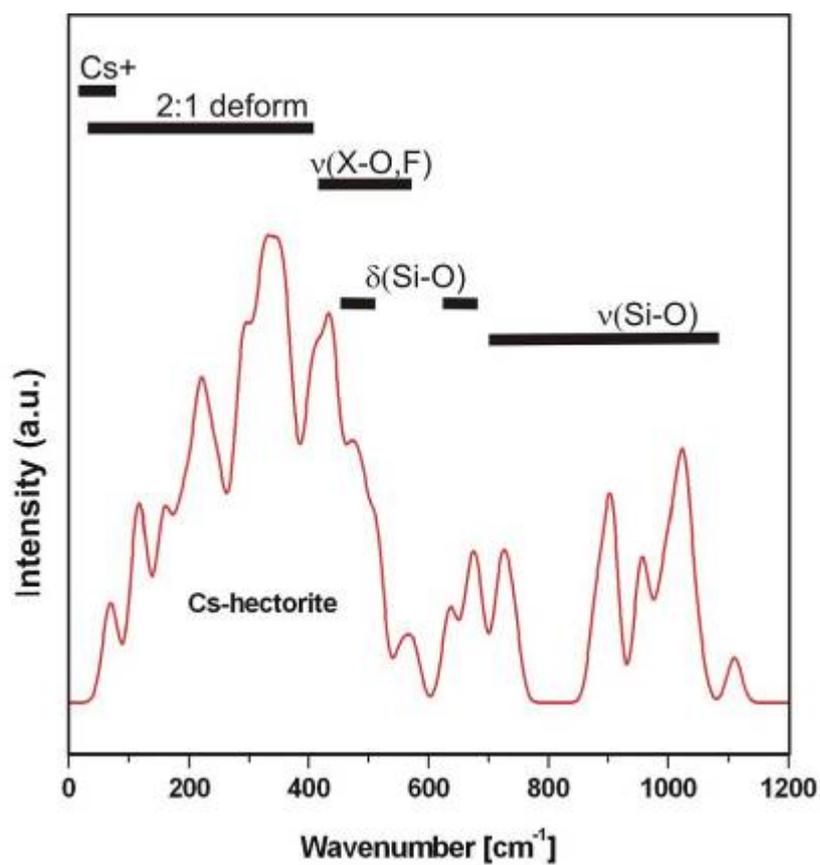


Figure 2. Analysis of the calculated vibrational spectrum of the Cs-hectorite.

Acknowledgement:

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MODERN METHODS OF IR SPECTROSCOPY AND THEIR UTILIZATION FOR CONFORMATION STUDY OF ALKYLAMMONIUM CATIONS INTERCALATED IN MONTMORILLONITES

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Keywords: near-infrared spectroscopy | organoclays | conformation | alkyl chain | gauche, trans

Infrared (IR) spectroscopy is one of the most commonly used methods for characterization of organoclays. Over the past decades, these inorganic/organic hybrid materials found application in a wide variety of industrial and scientific applications such as adsorbents of organic pollutants, pharmaceutical and cosmetic additives, reinforcing fillers for plastics, water treatment or host structures for direct intercalation of polymers. The behaviour and properties of organoclays strongly depend on the structure and arrangement of the intercalated surfactants, most often alkylammonium cations, in clay mineral interlayers. Detailed information on the arrangement of organic cations provides also near-infrared (NIR) spectroscopy.

The objective of this paper was to study the arrangement/conformation and the influence of head-group structure on self-assembly of the primary (C_n-NH_3) and quaternary $C_n-N(CH_3)_3$ alkyl ammonium surfactants in the montmorillonite interlayers. The organo-montmorillonites were prepared from a Na-saturated $<2 \mu m$ fraction of bentonite Jelšový Potok (JP, Slovakia) and from alkylammonium (C_n-NH_3) and $C_n-N(CH_3)_3$ salts with the increasing length of alkyl chain, for primary alkylammonium from C1 to C19 and for quaternary alkylammonium surfactants from C6 to C18. The X-ray diffraction analysis was used to probe the arrangement of alkylammonium cations in the interlayers. The KBr pressed disk technique was applied for measurements in the middle-IR (MIR) region and diffused reflection (DRIFT) techniques was used for NIR.

The X-ray diffraction analysis showed basal spacing (d_{001}) in the range 1.26–1.95 nm ($C1-NH_3-JP$ – $C19-NH_3-JP$) and in the range 1.42–2.05 nm for $C6-N(CH_3)_3-JP$ – $C18-N(CH_3)_3-JP$ in dependence on the alkyl chain length (Fig. 1). The basal spacing was almost the same ($\sim 1.26 - 1.37$ nm) for montmorillonite saturated with $C1-NH_3-JP$ – $C8-NH_3-JP$ suggesting a monolayer arrangement. With further increase of the alkyl chain length the d_{001} values gradually increased from 1.41 nm ($C9-NH_3-JP$) through 1.75 nm ($C14-NH_3-JP$), 1.83 nm ($C16-NH_3-JP$) to 1.95 nm ($C19-NH_3-JP$), indicating consecutive transitions from monolayers to bilayers and pseudotrimolecular layer arrangement. The most pronounced increase of the d_{001} value was observed between $C11-NH_3-JP$ and $C12-NH_3-JP$ ($\sim 1.51-1.66$ nm). In the case of $C_n-N(CH_3)_3-JP$, monolayers were formed for samples with relatively short chain lengths ($C6-N(CH_3)_3-JP$ – $C8-N(CH_3)_3-JP$), while d_{001} values from 1.5 to 1.85 nm, observed for $C10-N(CH_3)_3-JP$ – $C14-N(CH_3)_3-JP$, indicated the transition from monolayers to bilayers. Basal spacing higher than 1.9 nm ($C16-N(CH_3)_3$ – $C18-N(CH_3)_3$) reflected the predominant pseudotrimolecular arrangement.

IR spectroscopy in the MIR and NIR regions was further used to follow the conformation of the cations. The positions of the absorption bands related to the stretching vibrations (νCH_2) and the first overtone ($2\nu CH_2$) of the methylene groups were found to be very sensitive to the alkyl chain arrangements. The MIR spectra of organo-montmorillonites ($C4-NH_3-JP$ – $C19-NH_3-JP$) showed a gradual replacement of the asymmetric $\nu_{as}CH_2$ and symmetric ν_sCH_2 stretching bands from 2935 to 2925 cm^{-1} and from 2864 to 2851 cm^{-1} , respectively. In case of organo-montmorillonites $C6-N(CH_3)_3-JP$ – $C18-N(CH_3)_3-JP$

a similar process was observed. Gradual shift of the $\nu_{as}CH_2$ and ν_sCH_2 stretching bands from 2930 to 2921 cm^{-1} and from 2861 to 2851 cm^{-1} , respectively, was found. A shift towards lower wavenumber with increasing alkyl chain length confirmed a transition from disordered (*gauche*) to more ordered (all-*trans*) conformers of the surfactants.

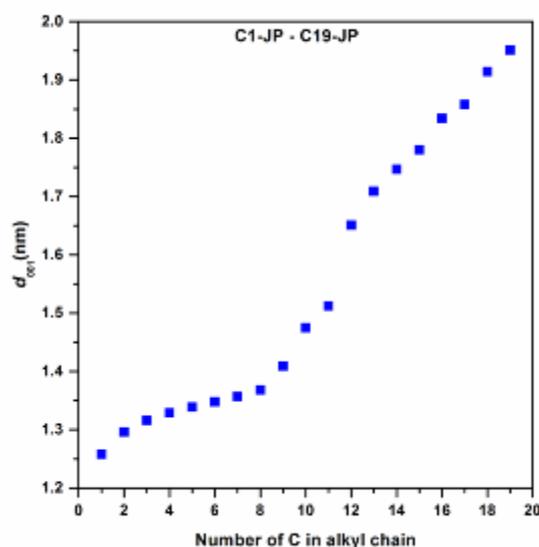


Figure 1. Dependence of basal spacing on the alkyl chain lengths in organo-exchanged samples.

The NIR spectra of organo-montmorillonites showed a broad complex $2\nu_{as}CH_2$ band in the 6100–5600 cm^{-1} , the combination ($\nu+\delta$) bands of CH_2 groups in the 4500–4000 cm^{-1} region and the band related ($\nu+\delta$) H_2O in the 5300–5100 cm^{-1} region. With the increasing number of CH_2 groups in alkyl chain the intensity of the ($\nu+\delta$) H_2O band gradually decreased indicating an increase in samples hydrophobicity. In case of C6- $N(CH_3)_3$ -JP – C18- $N(CH_3)_3$ -JP the $2\nu_{as}CH_2$ and ($\nu+\delta$) $asCH_2$ vibration modes were progressively shifted from 5810 to 5783 cm^{-1} (by 27 cm^{-1}) and from 4342 to 4329 cm^{-1} (by 13 cm^{-1}) after increasing alkyl chain length from 6 to 18. Even more significant alteration have been found for C6- NH_3 -JP – C18- NH_3 -JP samples for which the $2\nu_{as}CH_2$ and ($\nu+\delta$) $asCH_2$ bands were shifted by 38 and 24 cm^{-1} , respectively. The $-NH_3$ groups are closely attached to the surface of montmorillonite forcing extra *gauche* conformations in the chains to maintain energetically-favourable hydrogen bonds. In contrast, the $-N(CH_3)_3$ head-groups are more distant from the basal oxygens and do not form H-bonds. The absence of H-bonds facilitates a more ordered conformation of the chains. The percentage of *gauche* conformers is higher in short chains (C6, C8, and C10) with $-NH_3$ head-groups than in those with $-N(CH_3)_3$ head-groups. The effect decreases for longer chains because van der Waals interactions between the alkyl chains become dominant. It is evident, that NIR spectroscopy can provide new experimental insight into the interlayer structure of intercalated alkylammonium cations.

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STRUCTURAL AND SPECTROSCOPIC CHARACTERIZATION OF BEIDELLITE INTERCALATED WITH CHOLINE AND ACETYLCHOLINE

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Keywords: Acetylcholine-Beidellite | DFT | Vibrational spectra

Clays are lamellar aluminosilicates with a large variety of physicochemical properties, such as swelling, adsorption, surface acidity and ion exchange. They have various applications as a gelling, decolouring, water pollutant elimination, radioactive waste repository, cracking and heterogeneous catalysis [1]. Beidellite (Bd), a member of smectite clay family, intercalated with different types of organocations is comprehensively researched due to their excellent properties and various interactions using the theoretical and experimental approaches [2]. Beidellite also played an important role, e.g., as adsorbent for the removal of lead and cadmium ions from aqueous solutions [3, 4].

The aim of this work is to obtain a further information about the structure of the following organoclays – beidellite (Bd) intercalated with acetylcholine (AC) and choline (C) in hydrated (hAC-Bd and hC-Bd) and dehydrated (dAC-Bd and dC-Bd) form (**Fig. 1**) using the density functional theory (DFT) method. All calculations are performed with dispersion corrections using D3 scheme due to the weak interactions between the clay layers and intercalated compounds [5].

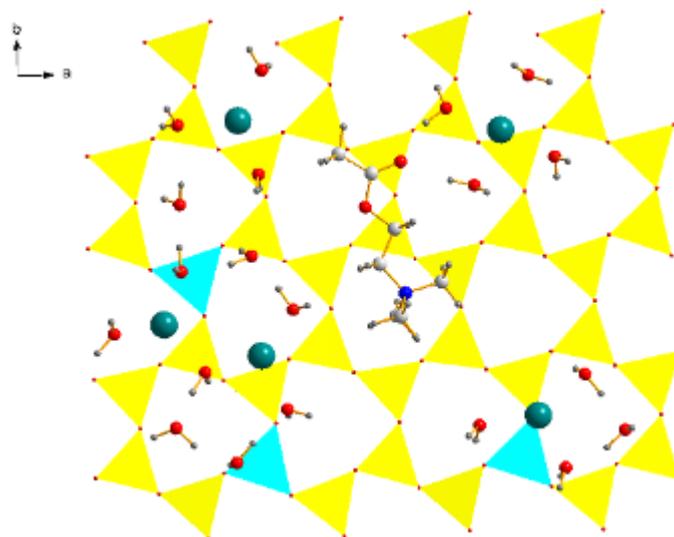


Figure 1: Optimized structure of hAC-Bd; c view.

The structural analysis of models has shown that organic cations had a quasi-planar configuration in the interlayer space and were located approximately in the middle of the structural models of beidellite mineral. For dehydrated models, sodium cations (Na^+) were placed in the centre of the hexagonal hole due to strong Coulombic interactions with a negative layer charge localized on the surface of basal oxygen atoms. The analysis of interactions in the interlayer space of Bd mineral has shown that

$[\text{Na}(\text{H}_2\text{O})_4]^+$ and AC/C cations create weak hydrogen bonds for both, dehydrated and hydrated forms. The vibrational modes of hAC/C-Bd and dAC/C-Bd were clearly identified from calculated spectra and compared with experimental measurements (see Fig. 2).

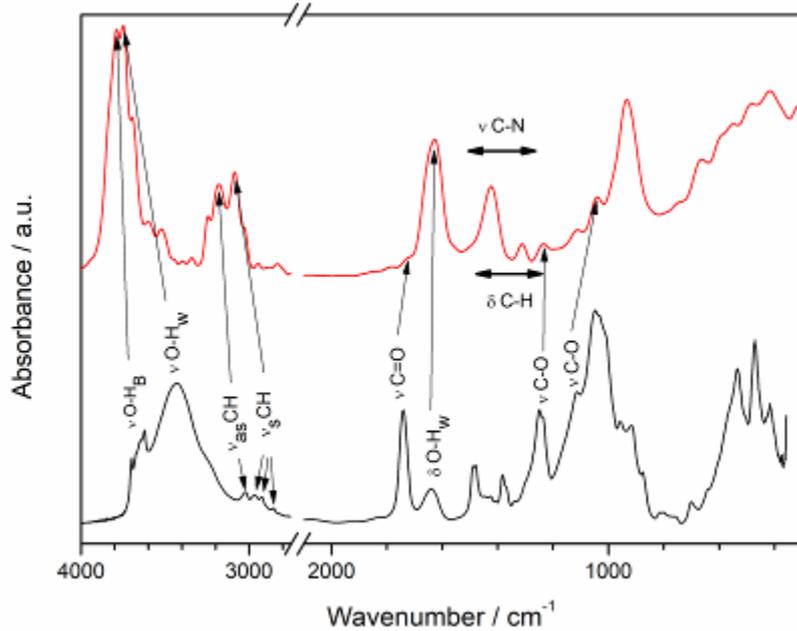


Figure 2: The experimental (black) FTIR absorption spectra and calculated (red) vibrational spectra of hAC-Bd.

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ILLITE – INDICATOR OF HYDROTHERMAL ALTERATION CONDITIONS IN EPITHERMAL DEPOSIT BANSKÁ HODRUŠA

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Keywords: illite | dehydroxylation | hydrothermal alteration

The significant presence of illite has been used for determination of temperature conditions and character of fluid that formed wall-rock alterations in the intermediate-sulphidation precious and base metal deposit Banská Hodruša at the Rozália mine. The mine is hosted by the central zone of a Miocene andesite Štiavnica stratovolcano, located in the Central Slovakia Volcanic Field on the inner side of the Carpathian arc.

Samples from different parts of the mine showed the presence of each of 1Md, 1M and 2M1 polytypes and variable ratios of all polytypes with a slight prevalence of 2M. Illite crystallinity - the "Kubler index" (KI) was used for the calculation of crystallisation temperatures using the data from the recent geothermal area in Taupo, New Zealand [1]. At least 50 measurements of KI were applied. From these samples three illite-rich samples were selected for a detail study. Two of them associated with subhorizontal vein system (292°C; 275 °C) and one related to earlier base metal stockwork mineralization that occurs close to the studied deposit (246 °C). K-Ar dating of all three samples provided ages between 12.23 and 12.67±0.35 Ma. The very similar illite ages probably show partial resetting of ages by a later hydrothermal system.

Preliminary thermal analyses indicate a potential dependence of illite dehydroxylation on crystallization temperatures. Higher temperature illites dehydroxylated over temperature of 600 °C and lower temperature illite dehydroxylated at temperature lower than 600 °C. It means that the higher temperature illites should have cis-vacant character and lower temperature ones have trans-vacant character.

Stable isotope analyses of illites (δD and $\delta^{18}O$) indicate isotopically well homogenised fluid of magmatic-meteoritic source, where the mixing took place outside of the deposit during the ascent of magmatic fluids from a deep magma chamber.

Acknowledgement: This work was supported by the grant APVV-15-0083.

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THE WEATHERING OF ROCKS AND SOIL ORGANIC MATTER FORMATION IN THE ALPINE TERRAIN DEPENDING ON ALTITUDE, THE HIGH TATRAS, SLOVAKIA

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Keywords: alpine terrain | soil | $\delta^{13}\text{C}$

The aim of this study is to determine the development of weathering in the alpine terrain depending on altitude. The basic physical and chemical properties of soil, mineralogy of soil and clay fraction and $\delta^{13}\text{C}$ of organic matter were determined for that purpose. The study of mineral composition (XRD analysis) was also performed with the aim to track source areas for mountain lakes (tarns) sediments (Veľké Hincovo pleso, 1946 m a.s.l., Biele pleso, 1612 m a.s.l. and Popradské pleso, 1494 m a.s.l.). The contribution belongs to complex paleolimnological study of High Tatras tarns with aim to determine a timing of the glacier disappearance and amplitude of climatic and ecological changes on the glacial/interglacial boundary (<http://www.geo.sav.sk/en/depovyt-apvv-15-0292/>).

The samples were collected along the altitudinal gradient from 1540 to 2350 m a.s.l that includes four altitudinal zones: supramontane zone with tree line at 1550 m a.s.l. (one sample), subalpine zone (1550-1850 m a.s.l.) with dwarf pine (*Pinus mugo*; tree samples); alpine zone (1850-2300 m a.s.l.) with rocky terrain and alpine meadows without trees (one sample) and subnival zone (over 2300 m a.s.l.) with rocky terrain and occasional snow also during the summer months (one sample). The bedrocks of studied areas are dominantly biotite-muscovite granodiorites to granites and biotite tonolite to granodiorites and glacier sediments derived from mentioned rocks [1]. The only difference is sample from Belianska kopa (1832 m a.s.l.). This bedrock is composed by Anisian and Ladinian dolomite [1]. The soils studied profile were dominated by undeveloped leptosols (rankers) and partly by podzol (determined base on FAO, [2]). The similar soil groups were defined by Kopáček et al, [3]. The initial stages of soil development are caused by their young age, the glacier retreat are predicted about 10000 cal BP and by alpine climate.

The values of $\delta^{13}\text{C}$ from the first six analysed soil samples range from -24.19 to -25.91. There is weak hint of a relationship of $\delta^{13}\text{C}$ and altitude in soil on granitic bedrocks. The increasing of $\delta^{13}\text{C}$ values with increasing of altitude, however, has to be confirmed by other measurements. Our other preliminary results shows that soil pH slightly increase with altitude and depth of soil profile. The soil pH is strongly dependent on bedrock. Any relationship between of Corg amount and the $\delta^{13}\text{C}$ was observed.

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