

# IR Spectroscopic Study on Host-Guest Interaction of Montmorillonite with Benzothiazolium Compounds

<sup>a</sup>V. LUPTÁKOVÁ, <sup>b</sup>I. HORVÁTH, <sup>c</sup>A. PERJÉSSY, and <sup>b</sup>K. PUTYERA

<sup>a</sup>Department of Inorganic Chemistry, Faculty of Natural Sciences,  
Comenius University, CS-842 15 Bratislava

<sup>b</sup>Institute of Inorganic Chemistry, Slovak Academy of Sciences, CS-842 36 Bratislava

<sup>c</sup>Department of Organic Chemistry, Faculty of Natural Sciences,  
Comenius University, CS-842 15 Bratislava

Received 14 March 1991

Montmorillonite is able to adsorb the benzothiazolium compounds (the chemicals with the properties of fungicides and the plant growth stimulators) from their aqueous solutions *via* a cation exchange mechanism. The interaction was explained evaluating the IR spectra alteration during the adsorption. There were no significant changes registered in the vibration bands of montmorillonite when benzothiazolium compounds were adsorbed. On the other hand, the remarkable positive shifts (to higher wavenumbers from 35 to 128 cm<sup>-1</sup>) were observed in the stretching vibrations  $\nu(\text{C-H})_{\text{arom}}$  of the adsorbate molecules after their insertion in the montmorillonite interlayers. Moreover, the additional changes in the IR spectra of organic species (the shape, relative intensity, splitting, etc.) were recorded. The combined effects involving the steric and the inductive influence of the adsorbent are discussed.

Contamination of soil colloids by biologically active compounds (herbicides, pesticides, the plant growth stimulators, fertilizers, etc.) is a serious problem for the ecology. The bonding of these materials to the clay minerals is the possibility of their deactivation. Mineral montmorillonite (MMT) is known as an effective adsorbent occurring in soils due to its layered structure, non-stoichiometry, the cation exchange capacity as well as extremely large surface area and the swelling ability. Possessing these properties the MMT is able to adsorb the organic molecules in its interlayers either *via* a cation exchange mechanism or in a way of the chemical reaction (in which the surface oxygen atoms, the exchangeable cations and the water molecules present in the interlayer space of the MMT structure can take part). The mode of the interaction depends upon the chemical features of the organic adsorbate.

There are numerous reviews dealing with the MMT-organocomplexes regarding the general point of view [1-5] or the interaction of MMT with biologically active compounds in particular [6-12]. However, no information is known on the interaction of MMT with benzothiazolium (BT) compounds, which were found to act as the effective plant growth stimulators and fungicides [13, 14]. Moreover, the interaction of MMT with BT compounds can provide further information on clay organocomplexes formation process.

We have reported recently [15] that the interaction of *N*-substituted BT compounds with MMT using their aqueous solutions proceeds as a cation

exchange reaction. BT<sup>+</sup> cations enter the interlayer spaces of the MMT while the inorganic exchangeable cations and the water molecules are replaced. Their arrangement (according to the X-ray diffractometry (XRD) results) depends upon the intercalation extent (the amount of the adsorbed BT<sup>+</sup> cation) and the presence of the residual water in the interlayer space. Moreover, the presence of the sulfur atom in the BT compounds is believed to control the molecule arrangement in the interlayer space resulting from its repulsive action to the surface oxygen atoms. It was reported additionally that the course and the extent of the intercalation is influenced more by chemical than the steric properties of the *N*-substituent.

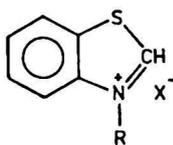
The aim of this work is to contribute to the explanation of the host-guest interaction through the study of the IR spectra of the original and adsorbed species.

## EXPERIMENTAL

The less than 2  $\mu\text{m}$  fraction of the bentonite (Jelšovský Potok, CSFR) containing  $93 \pm 3$  mass % of montmorillonite (according to the XRD and thermo-analytical results) was used as a model adsorbent. The natural MMT was converted to Ca-form using the standard cation exchange methods. According to the chemical analysis it was possible to express the following crystallochemical formula of

MMT:  $\text{Ca}_{1.06}(\text{Si}_{7.59}\text{Al}_{0.41})(\text{Al}_{3.06}\text{Fe}_{1.31}\text{Mg}_{0.63})\text{O}_{20}(\text{OH})_4$ .

As the adsorbates the following BT compounds were used:



	R	X
I	$\text{CH}_2\text{-CH=CH}_2$	Br
II	$\text{CH}_2\text{-C}_6\text{H}_5$	Br
III	$\text{CH}_3$	I
IV	$\text{CH}_2\text{-COOC}_2\text{H}_5$	Br
V	H	$\text{HSO}_4$

The benzothiazolium compounds were prepared according to [13].

The MMT–organocomplexes were prepared by saturation of the powder sample of MMT (1.0 g) dried at 105 °C with aqueous solution of BT salt ( $25\text{ cm}^3$ ,  $c = 0.125\text{ mol dm}^{-3}$ ). The contact time under stirring was 48 h. Then the supernatant was removed and the wet solid was washed to remove the nonadsorbed BT salt, dried at 60 °C and carefully ground. The amount of released  $\text{Ca}^{2+}$  was determined in the liquid phase and the retention extent of the organic matter in the solid phase was determined using CHN analyzer (Hewlett–Packard).

IR spectra of the reactants (before intercalation) and of the intercalated compounds were recorded using a spectrometer Specord M 80 (Zeiss, Jena) in the region of  $\tilde{\nu} = 400\text{--}4000\text{ cm}^{-1}$  when nujol suspension and/or KBr disks were used. The IR results are presented in Figs. 1 and 2. The parts of the spectra giving no information about the studied systems are omitted.

## DISCUSSION

It is well known that the intercalation of the organic matter into clay interlayer space gives rise to the changes in the IR spectra of the interacting species [16]. The intensities and the wave-number of the individual bands can be altered as a result of the combined steric and inductive effect of the adsorbent. The interpretation of these changes provides an information on the mode of bonding of the organic molecule to the surface of the adsorbent and the mechanism of the mutual interaction can be easier defined.

E.g. the bonding of amino acids to MMT was explained studying the changes in IR spectra of histidine after its interaction with the exchangeable

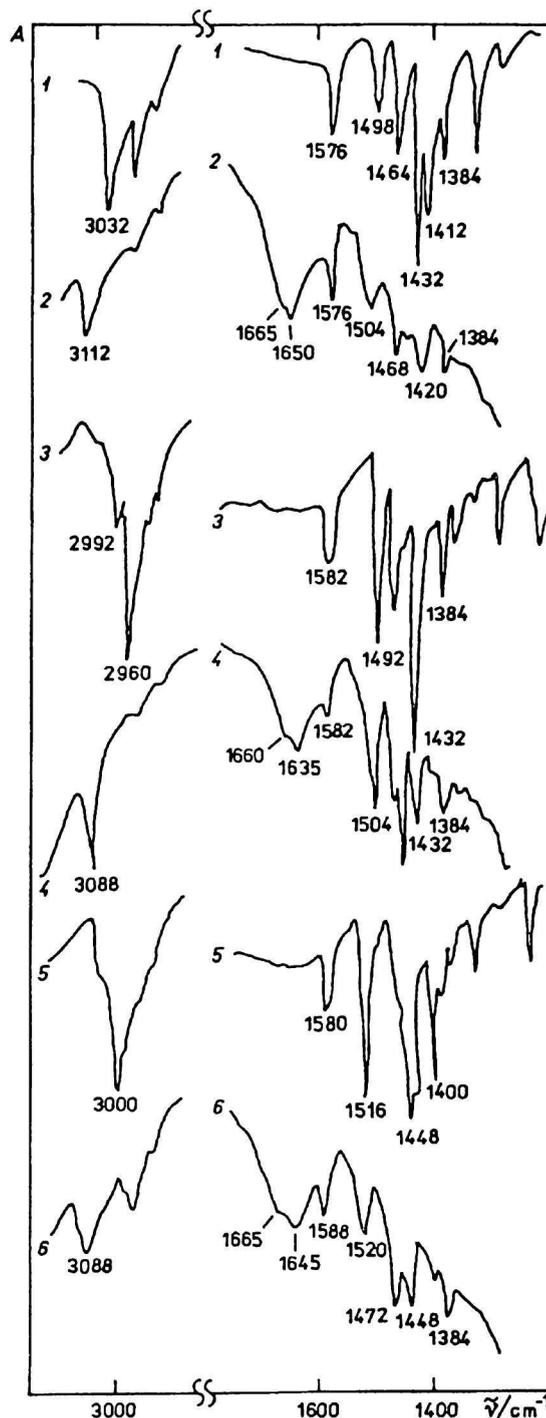


Fig. 1. IR spectra of the organic compounds before and after adsorption on montmorillonite. 1. I, 2. II—MMT, 3. II, 4. II—MMT, 5. III, 6. III—MMT.

cations and the interlayer water molecules present in MMT structure [17]. At the interaction of the aromatic dyes with the MMT surface, using the spectroscopic methods also the interaction of the  $\pi$ -electrons of the benzene ring has been proved [18]. Similarly, IR spectroscopy was used to study the interaction of the pesticide Chlordimeform or herbicide Roundup with the MMT [19].

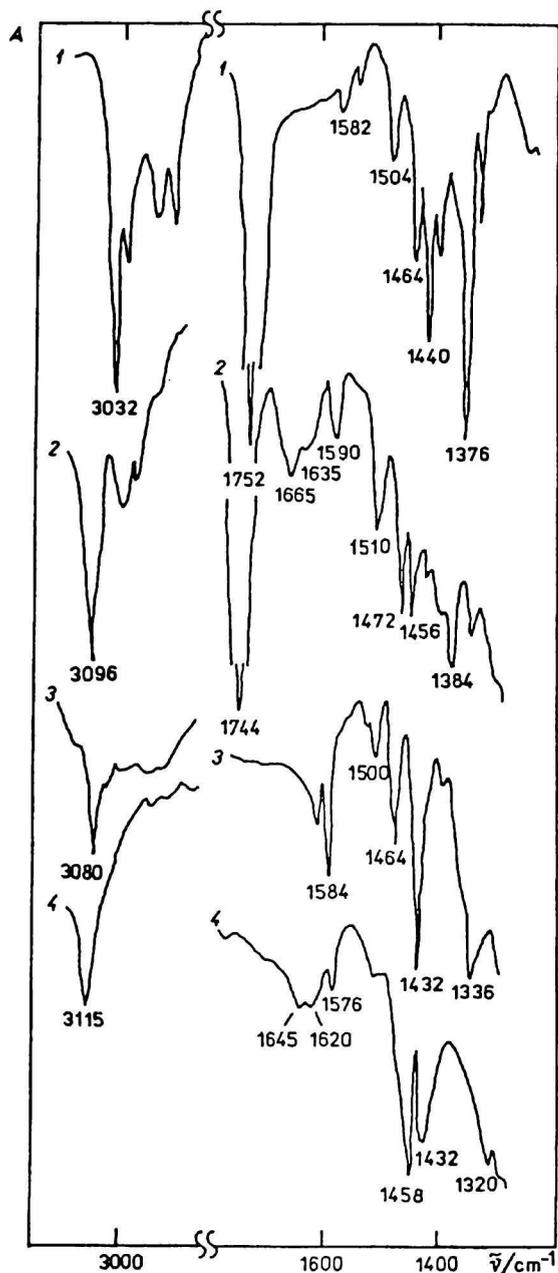


Fig. 2. IR spectra of the organic compounds before and after adsorption on montmorillonite. 1. IV, 2. IV-MMT, 3. V, 4. V-MMT.

In this work we studied the IR spectra of BT compounds before and after adsorption in the MMT interlayer. The shift of the band corresponding to the  $\nu(\text{C-H})_{\text{arom}}$  stretching vibrations seems to be the most significant alteration according to Figs. 1 and 2. Table 1 shows these shift values depending on the nature of the individual organic cation.

The organic cations used in this work represent the group of the compounds containing the substituent at the same site. Therefore the correlation of the wavenumbers values for  $\nu(\text{C-H})_{\text{arom}}$

Table 1. The Wavenumbers of the  $\nu(\text{C-H})_{\text{arom}}$  Vibration Maxima of the BT Compounds before and after Their Adsorption on MMT

Compound	$\tilde{\nu}/\text{cm}^{-1}$		$\Delta\tilde{\nu}/\text{cm}^{-1}$
	Before	After	
I	3032	3112	80
II	2960 (2992)	3088	128 (96)
III	3000	3088	88
IV	3032	3096	64
V	3080	3115	35

with Taft's constants  $\sigma^*$  of the individual substituents was made [20, 21]. It was found to be nonlinear correlation. A similar result was obtained in case of the correlation of the observed changes of wavenumber values with the induction  $\sigma_I$  and/or steric constants of the individual substituents. The absence of these correlations may be due to the electronic inhomogeneity of the MMT interlayer space containing the variable amounts of the residual  $\text{Ca}^{2+}$  cations as well as the water molecules after the adsorption.

The organic cations adsorbed are situated between two layers of the oxygen atoms from the tetrahedral sheets of the MMT structure and the alteration in the wavenumber value may be due to the electron-donor effect. This can bring about the electron transfer in the direction  $\text{C} \leftarrow \text{H}$  resulting in the enhanced values of the wavenumbers. Nevertheless, the extent of this alteration can be additionally modified by another factors as well.

It was reported recently [22, 23] that the positive charge is dispersed over the whole heterocyclic ring of BT compound. Moreover, a higher charge density occurs on the benzene ring than on the thiazole one contributing to the observed alterations in the wavenumber. Additionally, the mentioned shift to the higher wavenumbers supports the suggestion that the hydrogen atoms from the benzene ring do not take part in any hydrogen bond.

The alteration in  $\tilde{\nu}(\nu(\text{C-H})_{\text{aliph}})$  was impossible to evaluate because of their extremely low intensities.

As a consequence of an electron-donor effect of the oxygen atoms (from the MMT structure) the electron transfer in  $\text{N} \rightarrow \text{C}$  bond can be expected (the bonding of the substituent to the heterocyclic ring). Then, the highest electron density occurs in the geometric centre of the bond enhancing its order. Due to this effect the higher stability of these adsorbed cations compared with the nonadsorbed ones could be explained. The  $\text{N} \rightarrow \text{C}$  bond is supposed to be the weakest one

as far as nonadsorbed cations are concerned. Unfortunately, its vibration was not possible to detect due to its overlapping with the intense Si—O vibration.

Small shifts with the intensity changes were observed also in the range of ring vibrations of the heterocycle [22] in the region of  $\tilde{\nu} = 1300\text{--}1600\text{ cm}^{-1}$ . It is suggested that in these alterations the different orientation of benzothiazolium derivatives quenched between the silicate layers, e.g. the rotation around the N—C bond of the *N*-substituent, is involved.

There were not registered any significant changes in the IR spectra of the MMT structure after adsorption. This evidences that e.g. OH groups present in the MMT structure do not interact with the organic cations. The stretching vibration  $\nu(\text{Al—OH})$  at  $\tilde{\nu} = 3624\text{ cm}^{-1}$  remains constant with the exclusion of 3-benzylbenzothiazolium bromide (*II*) where a slight negative shift to  $\tilde{\nu} = 3618\text{ cm}^{-1}$  was recorded. In this case, the splitting of the band corresponding to the  $\nu(\text{Si—O})$  vibrations in the region of  $\tilde{\nu} = 1040\text{ cm}^{-1}$  to two absorption maxima at 1024 and 1048  $\text{cm}^{-1}$  was registered. The similar alteration of  $\tilde{\nu}(\nu(\text{Si—O}))$  was found for the compounds *I* (1048  $\text{cm}^{-1}$ ) and *IV* (1032  $\text{cm}^{-1}$ ). However, the significance of these alterations is questionable due to the complexity of the broad band of  $\nu(\text{Si—O})$  vibrations at all. Regarding the small changes of  $\tilde{\nu}(\nu(\text{Si—O}))$  it can be considered that also the steric interaction of the individual organic cations in the interlayer space of the MMT can contribute to the shifts of  $\tilde{\nu}(\nu(\text{C—H})_{\text{arom}})$ .

The shift to the lower wavenumbers of  $\nu(\text{CO})$  vibrations (from 1752 to 1744  $\text{cm}^{-1}$ ) was observed when the compound *IV* was adsorbed. It reflects the electron-donor action of the surface oxygen atoms (from the MMT tetrahedra sheets). Moreover, the joining of CO group to the residual water molecules through the hydrogen bond can be suggested.

The bands corresponding to the bending  $\delta(\text{H—O—H})$  vibrations of the residual interlayer water exhibit a low intensity because of its low amount in the intercalated compounds. The splitting of these bands was observed in the region of  $\tilde{\nu} = 1630\text{ cm}^{-1}$  giving two maxima at the higher wavenumbers compared with the nontreated MMT (Table 2).

The stretching vibrations of the bonds of residual water in the region of  $\tilde{\nu} = 3400\text{ cm}^{-1}$  are almost not detectable or they appear at lower wavenumbers. This gives an evidence that the residual water molecules are joined to the organic adsorbates molecules with the hydrogen bond. In the case of the substituted BT compounds the H bond can be formed by hydrogen atom present at the

**Table 2.** The Selected IR Absorption Bands of Original MMT and Intercalation Complexes

Sample	$\tilde{\nu}/\text{cm}^{-1}$		
	$\delta(\text{H—O—H})$	$\nu(\text{Si—O})$	$\nu(\text{Al—OH})$
Ca—MMT	1630	1040	3624
<i>I</i> —MMT	1650, 1665 sh	1048	3624
<i>II</i> —MMT	1635, 1660 sh	1024, 1048	3618
<i>III</i> —MMT	1635, 1665	1032	3624
<i>IV</i> —MMT	1645, 1665 sh	1040	3624
<i>V</i> —MMT	1620, 1645	1040	3624

site C-2 of the thiazole ring. The other possibility is to form the hydrogen bond by means of —NH group present in the nonsubstituted BT compound the retention extent of which exceeds in 70 % the cation exchange capacity of the MMT. The stretching vibration  $\nu(\text{N—H})$  at  $\tilde{\nu} = 2560\text{ cm}^{-1}$  occurring in the spectra of the nonsubstituted BT compound (*V*) disappeared after its adsorption. But this feature does not exclude the suggestion on the possibility of the formation of the polymerized nonsubstituted BT molecules in the MMT interlayers.

## CONCLUSION

The comparison of the IR spectra of the original and adsorbed (in MMT interlayers) BT compounds offered the data on the nature and characteristics of the formed intercalation complexes. The lack of significant changes in the IR spectra of the MMT structure after adsorption provided the suggestion that the surface oxygen atoms of the MMT structure do not interact directly with the entering organic molecules.

On the other hand, remarkable shifts of  $\nu(\text{C—H})_{\text{arom}}$  vibration maxima to higher wavenumbers can be a proof of the electron-donor effects of the surface oxygen atoms of the MMT on the intercalating adsorbates molecules. It was found that the observed alterations reflect the chemical nature of the *N*-substituent bonded to the benzothiazolium heterocyclic ring.

The IR spectra of the intercalation complexes indicated clearly the presence of the residual water molecules in the MMT interlayers. It is suggested that these water molecules do interact with the adsorbed BT compounds and in this way they influence the arrangement of the adsorbed molecules in the interlayer space. This knowledge contributes significantly to the explanation of the X-ray diffraction results indicating the thickness of the individual organic layer in the MMT interlayer space [15].

*Acknowledgements.* The authors are indebted to Dr. V. Sutoris for providing the samples of benzothiazolium compounds.

## REFERENCES

1. Green-Kelly, R., *Trans. Faraday Soc.* 51, 425 (1955).
2. Mortland, M. M., *Adv. Agron.* 22, 75 (1970).
3. Theng, B. K. G., *The Chemistry of Clay-Organic Reactions*. A. Hilger, London, 1974.
4. Lagaly, G., *Phil. Trans. R. Soc. London, A* 311, 315 (1984).
5. Yariv, S., *Thermochim. Acta* 88, 49 (1985).
6. Bailey, G. W. and White, J. L., *Residue Rev.* 32, 29 (1970).
7. Mortland, M. M., *Proc. of the Int. Clay Conf.*, Mexico City, p. 469. Applied Publications Ltd., Wilmette, Illinois, 1975.
8. Hayes, M. H. B., Pick, M. E., and Toms, B. A., *Residue Rev.* 37, 1 (1975).
9. Perez Rodriguez, J. L. and Hermosin, M. C., *Proc. of the Int. Clay Conf.*, Oxford, p. 227. Elsevier, Amsterdam, 1978.
10. Hermosin, M. C. and Perez Rodriguez, J. L., *Clays Clay Min.* 29, 143 (1981).
11. Srinivasan, K. R. and Fogler, H. S., *Clays Clay Min.* 38, 287 (1990).
12. Carrado, K. A. and Winans, R. E., *Chem. Mat.* 2, 328 (1990).
13. Sutoris, V., Halgaš, J., Sekerka, V., Foltínová, P., and Gáplovský, A., *Chem. Papers* 37, 653 (1983).
14. Sutoris, V., Halgaš, J., Foltínová, P., and Sekerka, V., *Chem. Papers* 38, 247 (1984).
15. Luptáková, V. and Horváth, I., *Ceramics - Silikáty* 35, 153 (1991).
16. Gibbons, J. J. and Soundarajan, R., *Am. Lab.* 1988, 38.
17. Heller-Kallai, L., Yariv, S., and Riemer, M., *Proc. of the Int. Clay Conf.*, Madrid, p. 651. Division de Ciencias, Madrid, 1973.
18. Yariv, S., *Int. J. Trop. Agric.* 6, 1 (1988).
19. Hermosin, M. C., Cornejo, J., and Perez Rodriguez, J. L., *Clay Min.* 20, 153 (1985).
20. Hansch, C. and Leo, A., *Substituent Constants for Correlation Analysis in Chemistry and Biology*. J. Wiley, New York, 1979.
21. *Correlation Analysis in Chemistry*. Plenum Press, New York, 1978.
22. Kellö, E., Kettman, V., Miertuš, S., Vrábel, V., and Konečný, V., *Collect. Czechoslov. Chem. Commun.* 51, 1864 (1986).
23. Zahradník, P., *Chem. Papers* 44, 145 (1990).

Translated by I. Horváth

## Thermal Dissociation of Molten Complex Compounds $\text{Me}_3\text{XF}_7$ (Me = Li, Na, K; X = Ti, Zr, Hf)

V. DANĚK and R. CEKOVSKÝ

*Institute of Inorganic Chemistry, Slovak Academy of Sciences, CS-842 36 Bratislava*

Received 30 July 1991

The degree of the thermal dissociation on melting of complex compounds  $\text{Me}_3\text{XF}_7$ , where Me = Li, Na, K and X = Ti, Zr, Hf, has been calculated on the basis of the known phase diagrams of the systems  $\text{MeF}-\text{Me}_3\text{XF}_7$ . It was found that the thermal stability of the investigated complex compounds increases with the increasing size of the central transition metal as well as with decreasing polarizability of the present alkali metal cation. The substitution of the fluorine atom in the coordination sphere of the transition metal by chlorine one leads to the decrease of the thermal stability of the compound.

Besides, the enthalpies of fusion of the investigated complex compounds were calculated on the basis of the cryoscopic measurements in independent systems.

In the binary systems of alkali metal fluorides and other salts of alkali metals, such as sulfates, chromates, molybdates, tungstates, transition metal fluorides, etc., complex compounds like  $\text{Na}_3\text{FSO}_4$ ,  $\text{K}_3\text{FMO}_4$ ,  $\text{K}_3\text{TiF}_7$ ,  $\text{K}_3\text{ZrF}_7$ , etc. are formed. These compounds exhibit a lowered symmetry of the coordination sphere of the central atom of the complex anion. Owing to this fact and obviously a relatively high energetic state such compounds undergo often at melting a more or

less extended thermal dissociation, in some cases they melt even incongruently. Evidences of such behaviour may be found e.g. in [1, 2].

Into this group belong also  $\text{Me}_3\text{XF}_7$  compounds, where Me represents an alkali metal and X represents titanium, zirconium, and hafnium. The thermal stability of the complex  $\text{XF}_7^{3-}$  anion depends on the chemical nature of the central transition metal as well as of the present alkali metal. Besides  $\text{F}^-$ , in some cases also the ion  $\text{Cl}^-$