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SORPTION OF N-SUBSTITUTED BENZOTHIAZOLIUM COMPOUNDS ON MONTMORILLONITE

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N-substituted benzothiazolium compounds are potential chemicals for pesticides and herbicides production. In this way they are able to contaminate the soil as well as earth's water. On the basis of cation exchange reaction mechanism is mineral montmorillonite able to adsorb benzothiazolium compounds from their aqueous solutions and in this manner to prevent their polluting activity. In this interaction layered clay-organocomplexes are formed exhibiting mostly disordered structure with irrational sequence of 00 l spacings. Chemical and steric characteristics of organic adsorbates influenced the extent of the retention as well as the stability of the organocomplex formed.

INTRODUCTION

Benzothiazolium compounds are commonly used in industrial production of dyes, additives, catalysts etc. [1, 2]. It was reported recently [3], that N-substituted benzothiazolium (BT) salts exert the significant biological activity. They may be used as a stimulators of plant growth as well as the pesticides and fungicides. In this connection they can potentially contact the soil and to react with the clay fraction giving rise to the clay-organocomplexes. The bonding between the clay mineral and the organic compound should be sufficiently strong to prevent the contamination of the environment.

Generally, it is known [4] that the electrostatic and van der Waal's forces are responsible for the clay-organic interaction in the first stage of the clay-organocomplexes formation. Then, the short-range forces (like in the chemical reaction) may dominate depending on the surface properties of clay mineral and the chemical characteristics of interacting adsorbate.

In this work the retention of selected N-substituted BT compounds on montmorillonite (MMT) — as the most abundant adsorbent occuring in soils — was studied in order to define the properties of the complexes formed using the methods of X-ray diffraction (XRD), thermal analysis (TA) and infrared spectroscopy (IR).

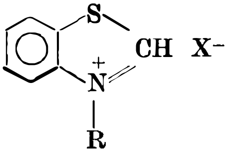
EXPERIMENTAL

Materials

Calcium form of montmorillonite (the fraction less 0.002 mm extracted from bentonite Jelšový Potok — Central Slovakia) was used as an adsorbent. Its chemical composition was (the contents of oxides in wt. %):

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	H_2O
62.7	20.6	2.32	0.12	3.10	3.75	0.09	0.05	14.97

N-substituted BT compounds were used as adsorbates. Their chemical composition may be derived from the formulae:



where R stands alternatively for H (benzothiazolium, BT); CH_3 (3-methylbenzothiazolium, MBT); $CH_2—CH=CH_2$ (3-alylbenzothiazolium, ABT); $CH_2—C_6H_5$ (3-benzylbenzothiazolium, BBT); $CH_2—COO—C_2H_5$ (3-etoxycarbonylmethylbenzothiazolium, EBT) and X stands for Br, I or HSO_4.

The compounds were prepared according the methods described in [1].

Adsorption procedure

The adsorption proceeded from aqueous solutions containing 0.1 M of BT salt in 1 dm^3 using the standard batch technique at room temperature. The solid/solution ratio was 1 g of MMT (dried at 105 °C) per 50 cm^3 of solution. The contact time took 48 hr. After equilibrating the solid phase was filtered off, washed with deionized water carefully and dried at 50 °C. The solution was analyzed for Ca^{2+} using standard titration method and the amount of the organic species adsorbed on MMT was evaluated from nitrogen content determined by CHN Hewlett-Packard analyzer. The results are in Table I.

Table I

Equilibrium amounts of organic cations adsorbed ($a_{org.}$) and Ca^{2+} released per 1.0 g of adsorbent (MMT) following the reaction scheme (1)

Sample	$a_{org.}$		Ca^{2+}	
	(mmol . g^{-1})	(mg . g^{-1})	(mmol . g^{-1})	(mg . g^{-1})
Ca-MMT	—	—	0.53	21.28
BT-MMT	1.78	242.3	0.51	20.70
ABT-MMT	0.90	158.6	0.47	19.03
BBT-MMT	0.71	161.5	0.43	17.54
MBT-MMT	0.90	135.2	0.45	18.40
EBT-MMT	1.05	233.4	0.50	20.04

Clay-organocomplexes characterization

X-ray diffraction method (XRD)

XRD method was applied to measure the changes in c-dimensions of textured samples (d_{001} spacings) using Philips PW 1050 difractometer (CuK_α radiation filtered by Ni at 35 kV and 20 mA). The results are shown in Fig. 1.

Infrared analysis (IR)

The IR spectra for adsorbent and adsorbates before and after adsorption in the region of 400—4000 cm^{-1} were recorded by Specord spectrometer (Carl Zeiss) in nujol suspension or/and KBr tablets (0.002 g of the sample in 0.3 g KBr). The selected frequencies are in Table II.

Thermal analysis (TA)

TA was used to study the amount of organic species adsorbed as well as to measure the thermal stability of the complexes formed. A DuPont 990 Thermoanalyzer, TGA 951 module was used. The sample size was 10—15 mg, the heating rate 10 °C per min. The measurements proceeded in static air and/or in nitrogen flow ($1\ cm^3\ N_2 \cdot s^{-1}$). The results are given in the form of differential thermogravimetric curves (DTG) in Figs. 2. and 3.

DISCUSSION

It may be expected that the interaction of BT^+ cations with MMT will follow the cation exchange reaction scheme:

$$Ca(MMT)_2\ (s) + 2\ BT^+X^-\ (aq.) \quad = \quad 2\ BTMMT\ (s) + CaX_2\ (aq.) \qquad (1)$$

According to the data in Table I only nonsubstituted BT and EBT compounds were able to release the amounts of Ca^{2+} cations corresponding approximately to the stoichiometric value (0.53 mmol Ca^{2+}/1 g of MMT). The remaining compounds released Ca^{2+} amounts lower in 10—20 %. Moreover, in one case only (EBT cmpd.) was achieved the stoichiometry in exchange as far as the amount of the adsorbed organic cation is concerned (theoretical value of 1.06 mmol . g^{-1}). The value for nonsubstituted BT compound exceeded the stoichiometry in the other cases the values were lower (0.71—0.90 mmol . g^{-1}). The amounts of the adsorbed species decrease in the sequence:

$$BT > EBT > MBT \quad = \quad ABT > BBT.$$

Excluding the EBT compound the extent of adsorption correlate with the size of the adsorbate which increases in the rate (the numbers in parentheses represent the cation volume in nm^3):

$$BT(0.121) < MBT(0.130) < ABT(0.246) < BBT(0.310) < EBT(0.340).$$

(The size of cations was calculated using quantum chemical data according to [9]).

This correlation indicates that the prevailing part of smaller cations are adsorbed more extensively which is unexpected regarding the rules governing the van der Waal's forces. Obviously, a chemical nature of organic species plays a significant role in the adsorption and additional studies are needed to make this phenomenon more clear (investigation of the mode of packing, steric hindrance to the diffusion in the interlayer region, etc.).

The XRD results revealed decreasing interlayer spacings in the sequence (the numbers denote d_{001} spacing value in nm):

$$BT(1.632) > EBT(1.590) > BBT(1.470) > ABT(1.422) > MBT(1.400).$$

Table II

Infrared frequencies before and after treatment (cm^{-1})

Sample	νSi—O	δH—O—H	νAl—OH	ν(C=C)	ν(C—H)$_{alkyl}$	ν(C—H)$_{aromatic}$	ν(C=N$^+$)
Ca-MMT	1040	1630	3624	—	—	—	
ABT	—	—	—	1498	2952	3032	1576
ABT-MMT	1048	1646	3624	1504	2930	3112	1576
BBT	—	—	—	1498	2890	2960	1581
BBT-MMT	1024	1644	3618	1504	2920	3088	1580
MBT	—	—	—	1516	—	3000	1580
MBT-MMT	1040	1655	3624	1520	—	3088	1588
EBT	—	—	—	1504	2928	3032	1582
EBT-MMT	1032	1645	3624	1510	2950	3096	1590
BT	—	—	—	1500	—	3080	1584
BT-MMT	1040	1620	3624	1510	—	3115	1574

ν(C—H)$_{alkyl}$ = stretching frequency attributed to (C—H) bonding in aliphatic substituent;
ν(C—H)$_{aromatic}$ = stretching vibration of (C—H) bonding in aromatic ring;

The regular layer structure (rational 001 sequences) was found for nonsubstituted BT complex only. The remaining complexes form rather disordered structures showing weak and mostly irrational 001 diffractions.

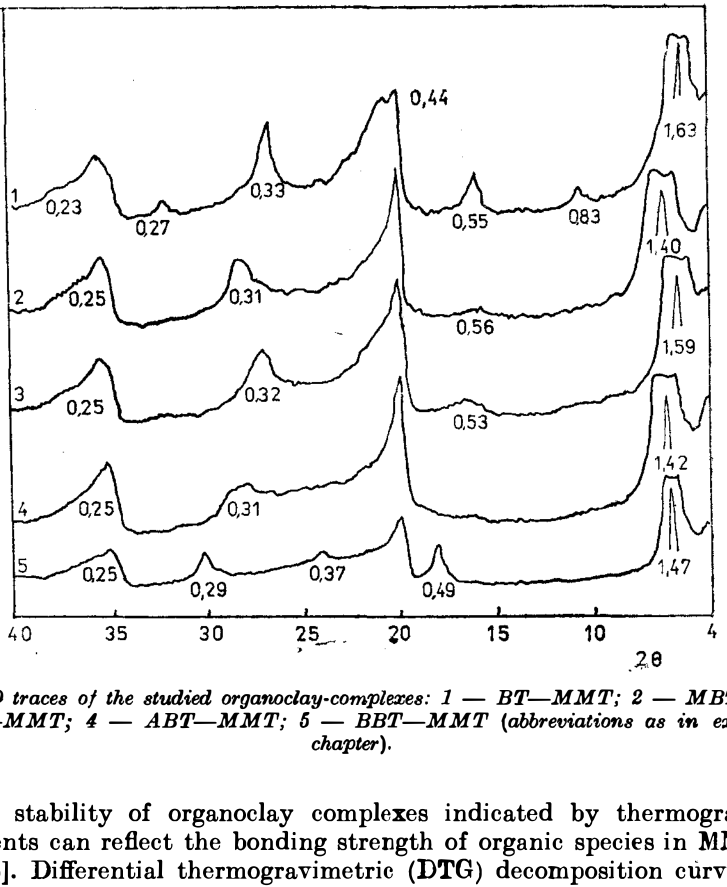


Fig. 1. XRD traces of the studied organoclay-complexes: 1 — BT—MMT; 2 — MBT—MMT; 3 — EBT—MMT; 4 — ABT—MMT; 5 — BBT—MMT (abbreviations as in experimental chapter).

Thermal stability of organoclay complexes indicated by thermogravimetric measurements can reflect the bonding strength of organic species in MMT interlayer [5, 6]. Differential thermogravimetric (DTG) decomposition curves in the temperature range 20—1000 °C are shown in Fig. 2 (measurements performed in static air) and in Fig. 3 (nitrogen flow). The curves differ in their shape and peaks localization on the T-axis expressing the variability in the chemistry of adsorbates and/or experimental conditions. The most intensive changes occur in temperature range 200—500 °C in which 8—15 wt. % (in air) and/or 12—17 wt. % (in nitrogen atmosphere) of the gaseous products are formed and escaped. However, the stepped decomposition is evident in this temperature region exhibiting 2—3 distinct DTG peaks with one dominant belonging to the largest weight loss. Considering this peak as a measure of the thermal stability for investigated complexes the following sequence may be obtained:

$$\text{MBT} > \text{ABT} > \text{BBT} > \text{EBT}$$

for both, air and nitrogen atmosphere. Accordingly, the lowest thermal stability showed complex containing the largest EBT cation decomposing at temperature lower in about 200 °C compared with complex formed by substantially smaller MBT cation.

Next reaction is MMT dehydroxylation. Nevertheless, it occurs at lower temperatures compared with non-treated CaMMT, in flowing nitrogen especially. This phenomenon was still observed previously [7], and may be explained by easier H_2O (g) diffusion in MMT interlayer due to its partial pillaring with carbonaceous residues. That's why dehydroxylation of MMT structure occured in temperature range 500—700 °C.

DTG peak at 870 °C belongs, obviously, to the calcite decomposition. A small amount of calcite was present in CaMMT as admixture according to XRD results. Oxidation of the last carbonaceous residues in air (Fig. 2) occured in temperature range 750—800 °C.

TG analysis provided an information on the presence of the interlayer water in organoclay complexes as well. The results showed, that despite of intensive hydrophobisation of MMT surfaces the content of interlayer water took 1.5—4.5 wt. % depending on the nature of the organic cation. It is suggested that this residual molecular water might be connected with the nonexchanged Ca^{2+}

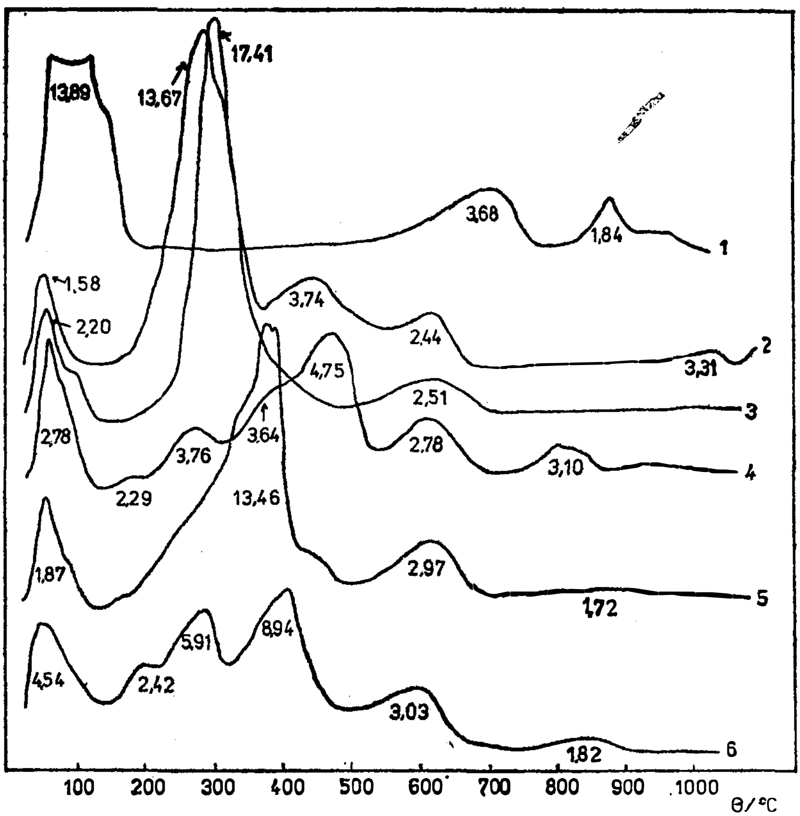


Fig. 2. DTG decomposition curves for Ca-MMT Jelšový Potok: 1 and organoclay-complexes in nitrogen flow (2 — EBT—MMT; 3 — BBT—MMT; 4 — MBT—MMT; 5 — ABT—MMT; 6 — BT—MMT). The values represent the weight losses (in wt. %) attributed to the DTG paaks.

cations present in the complexes (Table I). This is supported by typical two steps dehydration on the DTG curves up to 160 °C (Fig. 2 and 3).

The IR measurements made possible to compare the selected vibrations for nontreated species (MMT, organic adsorbates) with the same determined for organoclay complexes. The results in Table II show, that there is no significant change in stretching frequencies for Si—O and or Al—OH groups in MMT structure before and after adsorption. However, the pronounced changes can be detected for vibrations of selected functional groups in adsorbed organic cations. Surprisingly, all changes were positive e.g. the shift to the higher frequencies was observed after adsorption. This is unexpected for stretching vibrations of C—H bond in benzene structure especially, because the opposite shift was reported by [8] studying analoguous nitrobenzene adsorption on MMT.

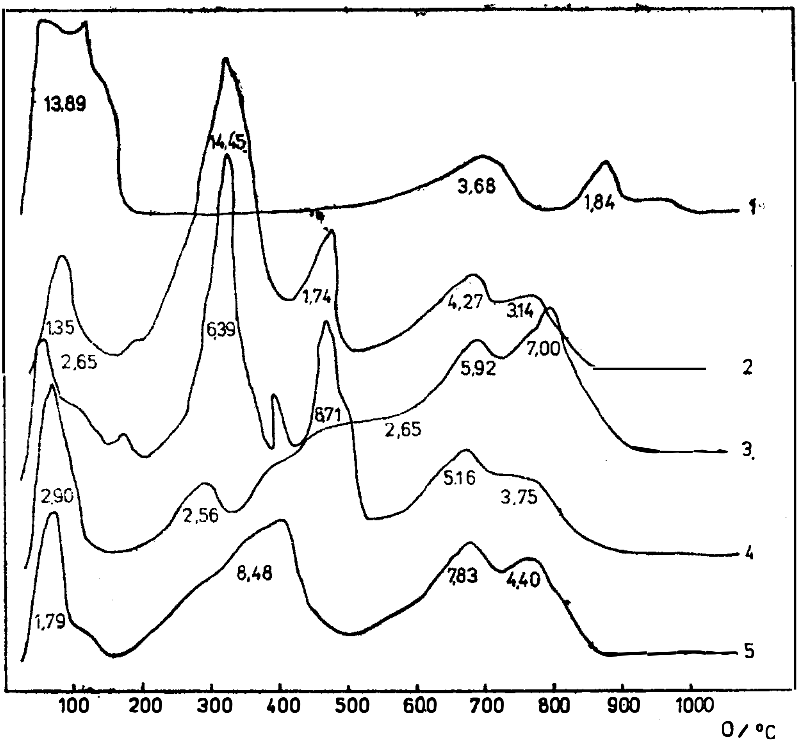


Fig. 3. DTG decompositon curves for MMT Jelšový Potok: 1 and organo-complexes after heating in static air (2 — EBT—MMT; 3 — BBT—MMT; 4 — MBT—MMT; 5 — ABT—MMT). The numerical data as in Fig. 2.

CONCLUSIONS

Water soluble BT compounds (the chemicals potentialy used for the production of a new types of herbicides and pesticides) interact with MMT on the basis of the cation exchange reaction mechanism. As a result the ionic complexes are formed.

Depending on the chemistry and size of BT compound can MMT adsorb 0.7—1.8 mmol BT compound per 1 mmol M^+ (monovalent exchangeable cation in MMT interlayer). In this way is MMT able to prevent the contamination of the environment with these pollutants.

The layered structure of the complexes is rather disordered (excluding the non-substituted BT compound) characterized by irrational 001 spacings. Obviously, the chemical and steric nature of N-substituted BT compounds prevent their regular arrangement in MMT interlayer.

The steric characteristics of BT compounds are suggested to play a significant role in thermal stability of complexes as detected by thermoanalytical study. In prevailing part, thermal stability decreased with increasing of the size of organic cation in MMT interlayer.

No changes in MMT structure were detected after adsorption of organic species using IR study. However, the additional experimental work is needed to elucidate the special bonding of BT compounds in MMT interlayer.

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SORPCIA N-SUBSTITUOVANÝCH DERIVÁTOV BENZOTHIAZÓLIA NA MONTMORILLONITE

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Vodorozpustné benzothiazóliové zlúčeniny sú biologicky aktívne zlúčeniny a okrem iného ich možno použiť pre výrobu herbicídov a pesticídov. Pôsobia tiež ako stimulátory rastu rastlín. V týchto súvislostiach prichádzajú do kontaktu s pôdou a povrchovými vodami, ktoré môžu kontaminovať. Jednou z možností ich dekontaminácie je väzba na ílové minerály za vzniku stabilných organokomplexov.

Štúdium modelových vzoriek pripravených interakciou montmorillonitu (ako potenciálneho adsorbenta nachádzajúceho se v pôdach) a vodných roztokov N-substituovaných derivátov benzothiazólia poskytlo informácie o rozsahu sorpcie a stabilite vznikajúcich organokomplexov.

Súborom fyzikálne-chemických metód (rtg. difrakčná analýza, termická analýza, IČ spektroskopia) sa zistilo, že študované organické adsorbáty vnikajú do medzivrstvových priestorov štruktúry montmorillonitu mechanizmom iónovej výmeny. Vznikajú vrstevnaté organokomplexy vyznačujúce sa prevažne neusporiadanou štruktúrou (v smere kolmom na klad vrstiev). Termická stabilita komplexov klesá s rastúcim rozmerom molekuly adsorbátu. Metódou IČ spektroskopie sa zistilo, že po sorpcii nenastávajú význačnejšie zmeny v lokalizácii absorpčných maxím typických pre vibrácie Si—O a Al—OH v štruktúre montmorillonitu. Namerali sa však významné zmeny niektorých väzbových vibrácií adsorbovaných organických molekúl v porovnaní s východiskovou látkou.

Obr. 1. Rtg. difraktogramy študovaných organokomplexov: 1 — BT—MMT; 2 — MBT—MMT; 3 — EBT — MMT; 4 — ABT—MMT; 5 — BBT—MMT (označenia vysvetlené v texte).

Obr. 2. DTG krivky Ca-montmorillonitu Jelšový Potok 1 a pripravených organokomplexov po záhreve v prietoku N_2 (2 — EBT—MMT; 3 — BBT—MMT; 4 — MBT—MMT; 5 — ABT—MMT; 6 — BT—MMT). Číselné hodnoty znamenajú straty hmotnosti v %.

Obr. 3. DTG krivky Ca-montmorillonitu Jelšový Potok 1 a pripravených organokomplexov po záhreve na vzduchu (2 — EBT—MMT; 3 — BBT—MMT; 4 — MBT—MMT; 5 — ABT—MMT). Číselné hodnoty ako pri obr. 2.

СОРБЦИЯ N-ЗАМЕЩЕННЫХ ПРОИЗВОДНЫХ БЕНЗОТИАЗОЛИЯ НА МОНМОРИЛЛОНИТЕ

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Водорастворимые бензотиазолиовые соединения являются биологически активными соединениями, которые кроме того можно использоватъ для производства гербицидов и пентицидов. Далее они являются стимуляторами роста растений. В связи с тем они входят во взаимодействие с почвой и поверхностными водами, которые могут контаминировать. Одной из возможностей их деконтаминации может быть их связанность с илистыми материалами с образованием стабильных органокомплексов.

Исследование модельных образцов, полученных взаимодействием монтмориллонита производных бензотиазолия предоставляет инфорнации относительно потенциальього адсорбента, находящегося в почве и водных расторов N — замещенных размера сорбции и устойчивости образующихся органокомплексов.

С помощью набора физико-химических методов (трг. дифракционный анализ, термический анализ, ИК спектроскопия) было установлено, что исследуемые органические адсорбаты проникают в межслоистые пространства структуры монтморилонита механизмом ионного обмена. Таким образом возникают слопстые органокомплексы, отличающиеся прежде всего неупорядоченной структурой (в направлении перпендикулярн. к укладке слоев). Термическая стабильность комплексов понижается с растущим размером молекулы адсорбата. С помощью метода ИК спектроскопии было установлено, что после сорбции не следуют более существительные изменения в размещении абсорбционных максимумов, типичных для вибраций Si—O и Al—OH в структуре монтмориллонита. Однако нами измерялись резкие изменения некоторых связочных вибраций адсорбированных органических молекул в сопоставлении с исходным веществом.

Рис. 1. RTG дифракрограммы исследуемых органокомплексов: 1 — BT — MMT 2 — MBT — MMT; 3 — EBT — MMT; 4 — ABT — MMT; 5 — BBT — MMT (обозначения объяснятся в тексте).

Рис. 2. DTG кривые Ca-мотмориллонита Ельшовы Поток 1 и приготовленных органокомплексов после нагрева в притоке N_2 (2 — EBT — MMT; 3 — BBT — MMT; 4 — MBT — MMT; 5 — ABT — MMT; 6 — BT — MMT. Цифровые величины обозначают потери веса в %.

Рис. 3. DTG кривые Ca-монмориллонита Ельшовы Поток 1 и приготовленных органокомплексов после нагрева в воздухе (2 — EBT — MMT; 3 — BBT — MMT; 4 — MBT — MMT; 5 — ABT — MMT). Цифровые величины обозначают потери веса в %.