Interaction of Benzotriazole with Ca- and Cu-Monoionic Forms of Montmorillonite

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The mode of interaction of benzotriazole compounds from their aqueous solutions with Ca- and Cu-montmorillonite was studied in order to obtain the data on the possibility of their immobilization in the structure of the solid porous substrate. Among the factors controlling the intercalation process pH of saturated solution and the nature of exchangeable cation appeared to be the most influential. Using XRD, elemental analysis, and IR spectroscopy the extent and mechanism of benzotriazole retention were determined. Whereas the interaction with Ca-monoionic form follows the mechanism of cation-exchange reaction (when benzotriazolium is intercalated), the coordination compounds of benzotriazole (as ligands) with Cu(II) in the interlayer are formed when Cu-montmorillonite is used. Moreover, the IR results revealed the chemical alteration of benzotriazole compounds quenched in the montmorillonite interlayer as a consequence of the host—guest interaction.

Among numerous organic species there are the heterocyclic compounds (containing one benzene ring in their structure) the interaction of which with clay minerals was studied rather rarely. It is known that these compounds represent important, widely used chemical agents. Unfortunately, many of them exhibit pronounced carcinogenic effects [1] and because of their solubility in water they behave as dangerous water and/or soils pollutants. Therefore, it is necessary to try to solve the problem of their immobilization (fixation) using suitable solid host substrate (porous crystal with appropriate adsorption abilities). It is also known that mineral montmorillonite could be used as one of the suitable hosts exhibiting desirable properties.

We have studied recently the interaction of montmorillonite (MMT) with a series of benzothiazolium compounds [2-4] which are used for the fungicides and pesticides production. Benzotriazole, on the other hand, is one of the most effective corrosion inhibitors for staining and tarnishing of many metals and can be incorporated into lacquers, polishes, and fluids as cleaning solutions and detergents [5]. The schematic structure of benzotriazole species studied in this work is given in Formula 1.

The inhibiting action of BTAH compounds is based on their ability to form the coordination complexes preferentially with the transition metals as described in [6, 7].



Previously, Heller-Kallai and Yariv [8, 9] studied the interaction of indole with MMT. The structure of indole molecule is similar to BTAH with the exception of the acidity (BTAH is a stronger acid) and the presence of additional two nitrogen atoms with lone electron pairs in the BTAH molecule. Consequently, during interaction with MMT it can be expected that it will act as a proton donor (contrary to numerous organic molecules behaving in the MMT interlayer as proton acceptors [10]). Nevertheless, the difference in behaviour of indole and BTAH during insertion into MMT interlayer can be brought about by the existence of nitrogen atoms with lone electron pairs in the BTAH structure. Concerning this it can be expected that BTAH species will form a ligand-like bond with the exchangeable cations of MMT contrary to indole molecules which are not able to form the coordination compounds even in the solution.



Fig. 1. IR spectra of Ca- and Cu-montmorillonite saturated by BTAH₂Cl.

EXPERIMENTAL

Monoionic samples of Ca- and Cu-montmorillonite were obtained by repeated saturation of a sample of Jelšový Potok montmorillonite of the composition $Ca_{0.48}(Si_{7.59}Al_{0.41})(Al_{3.06}Fe_{0.34}Mg_{0.63})O_{20}(OH)_4$ with appropriate 0.1 M chloride solution. After saturation the samples were washed and stored. Benzotri-

ration the samples were washed and stored. Benzotriazole was obtained from Lachema, Brno as a reagent grade and was additionally purified by recrystallization (2 times) from the aqueous ethanol solution. BTA chloride was prepared by the addition of stoichiometric amount of HCl. The chemical composition of BTAH₂Cl was checked determining H, C, N, and Cl using elemental analysis.

At the intercalation procedure 1 g of monoionic MMT was treated with 100 cm^3 of appropriate aqueous solution of BTAH during 48 h at room temperature. pH of the solutions was controlled by the addition of HCl or NaOH.

The amount of adsorbed guest molecules (a_{org} values) was checked using Hewlett—Packard analyzer on C and N. IR spectra were taken on a spectrometer Specord M 80 (Zeiss, Jena) from KBr discs and nujol suspension. The X-ray diffractometer used was Philips PN 1650 with Cu $K\alpha$ radiation.

RESULTS AND DISCUSSION

The aim of the present work was to determine the extent of intercalation and the role of the particular saturation conditions as well as to investigate the mode of the host—guest interaction.

The stoichiometric ion-exchange reaction proceeds

Table 1. Interaction of BTAH₂Cl with Ca-Montmorillonite

Sample	$\frac{c}{\text{mol dm}^{-3}}$	$\frac{a_{\rm org}}{\rm mmol~g^{-1}}$	$\frac{r\left(\mathrm{Ca_{rel}^{2+}}\right)}{\mathrm{mmol}\ \mathrm{g}^{-1}}$	<u>d001</u> nm	
1	0.010	0.06	0.03	1.40	
2	0.025	0.17	0.15	1.38	
3	0.050	0.33	0.30	1.37	
4	0.075	0.79	0.35	1.36	
5	0.100	1.09	0.41	1.38	
6	0.125	1.74	0.43	1.49	
7	0.150	1.92	0.44	1.48	

c - concentration of saturation solution, $a_{\rm org}$ amount of ${\rm BTAH}_2^+$ adsorbed, $r\left({\rm Ca}_{\rm rel}^{2+}\right) - {\rm Ca}^{2+}$ released from the MMT interlayer, d_{001} - interlayer distance after adsorption.

when Ca-MMT is saturated with BTAH₂Cl solution at $c = 0.1 \text{ mol dm}^{-3}$ Two absorption bands at $\tilde{\nu} = 1245$ cm^{-1} and 1295 cm^{-1} belonging to $BTAH_2^+$ are present in IR spectra of the BTAH₂⁺-montmorillonite complex. The intensity of the broad band at $\tilde{\nu} = 1845$ cm^{-1} attributed probably to overtones (Fig. 1) increases with the increasing amount of the cation present in the MMT complex. The $\nu(NH)$ vibration bands occur in the region above 3000 cm^{-1} . The third band at $\tilde{\nu} = 1215 - 1220 \text{ cm}^{-1}$ occurs when higher amounts (> 1.0 mmol) of organic matter are adsorbed. This band indicates the adsorption of neutral BTAH species. Simultaneously, the broad absorption band at $\tilde{\nu} = 2500 - 2900 \text{ cm}^{-1}$ can be attributed to the associated NH groups indicating the formation of BTAH associates in the MMT interlayer. These complexes have a low content of the water and X-ray d_{001} spacing (1.48 nm, Table 1) gives the evidence on almost

Sample	рH	$\frac{a_{ m org}}{ m mmol g^{-1}}$	$\frac{r\left(\mathrm{Ca}_{\mathrm{rel}}^{2+}\right)}{\mathrm{mmol}\;\mathrm{g}^{-1}}$	<u>d₀₀₁</u> nm	
8	2.5	1.06	0.20	1.46	
9	4.0	0.36	0.19	1.45	
10	5.0	0.19	0.20	1.47	
11	6.0	0.14	0.15	1.45	
12	7.0	0.56	0.05	1.51	
13	8.5	0.21	0.19	+	
14	9.5	0.08	0.09	+	
15	11.0	0.05	0.08	÷	

Table 2. Interaction of BTAH with Ca-Montmorillonite at $c = 0.1 \text{ mol dm}^{-3}$ and in the pH range 2.5—11

+ - broad, diffuse reflections.

perpendicular orientation of BTAH molecules towards the oxygen sheet of the MMT matrix.

At the saturation of Ca-MMT with BTAH solution the BTAH free base molecules are adsorbed in considerably less extent (corresponding to the CEC value) also at higher c values. Increased $a_{\rm org}$ values were determined in high acidic conditions (pH = 2.5; Table 2). However, the adsorption of BTAH₂⁺ formed can be considered as well in this particular case, even though the release of Ca²⁺ cations was not complete.

The IR absorption bands at $\tilde{\nu} = 1215 \text{ cm}^{-1}$ and 1270 cm⁻¹ [11—13] in IR spectra of the sample 8 indicate the presence of both BTAH and BTAH₂⁺ in the MMT interlayer. The $\nu(\text{NH})$ vibration bands are less developed and the interlayer water release does not seem to be complete.

The small portion of neutral BTAH adsorbed is present even in Ca-MMT samples saturated at pH = 7. This is evident from the IR patterns of the sample 12 exhibiting the bands at $\tilde{\nu} = 1220 \text{ cm}^{-1}$ and 1270 cm⁻¹ only (Table 5). The ν (NH) bands in the $\tilde{\nu}$ region of 2600—2800 cm⁻¹ are of low intensity as a sign of a possible intermolecular BTAH association. The basal spacings d_{001} (Table 2) reflect, similarly as in the previous case, the perpendicular orientation of heterocyclic molecules towards the silicate surface.

All Ca-MMT complexes with BTAH or $BTAH_2^+$ exhibited the same colour as an original, nontreated sample of MMT (light cream). Not any intercalation of BTAH in Ca-MMT proceeded in alkaline conditions (pH higher than 7.0).

The interaction of benzotriazole compounds with Cu-MMT followed clearly a different mechanism (compared with Ca-MMT). This results from the transition metal characteristics of Cu atoms, *e.g.* their ability to interact with BTAH or conjugated base BTA⁻ In Cu(II) complexes BTAH can form mono-, bi- and/or tridental ligands [6, 14—16]. Consequently, only a small portion of Cu(II) was released during interaction of BTAH₂Cl and Cu-MMT. Moreover, it could be supposed that majority of these released Cu(II) originated from the external surfaces of MMT (Table 3).

Table 3. Interaction of BTAH₂Cl with Cu-Montmorillonite

Sample	$\frac{c}{\text{mol dm}^{-3}}$	$\frac{a_{\rm org}}{\rm mmol~g^{-1}}$	$\frac{r\left(\mathrm{Cu}_{\mathrm{rel}}^{2+}\right)}{\mathrm{mmol}\ \mathrm{g}^{-1}}$	<u>d001</u> nm	
16	0.010	0.24	tr	1.30	
17	0.025	0.77	tr	1.33	
18	0.050	1.14	0.05	1.55	
19	0.075	1.24	0.05	1.55	
20	0.100	1.23	0.05	1.56	
21	0.125	1.29	0.05	1.55	

tr - traces.

Table 4. Interaction of BTAH with Cu-Montmorillonite at $c = 0.1 \text{ mol dm}^{-3}$ and in the pH range 2.5—11

Sample	рН	$\frac{a_{\rm org}}{\rm mmol~g^{-1}}$	$\frac{r\left(\mathrm{Cu}_{\mathrm{rel}}^{2+}\right)}{\mathrm{mmol}\;\mathrm{g}^{-1}}$	<u>d001</u> nm	
22	2.5	1.64	tr	+	
23	4.0	1.63	tr	+	
24	5.0	1.63	0	+	
25	6.0	1.50	0	1.27	
26	7.0	0.84	0	1.25	
27	8.5	1.10	0	1.25	
28	9.5	0.87	0	1.26	
29	11.0	0.84	0	1.26	

In further development the colour of Cu-MMT complexes changed during interaction to light green (sample 17) or light blue (samples 18-21).

The data on insertion of a BTAH free base in the Cu-MMT interlayer are given in Table 4. It was found that higher amounts (higher than the CEC value) were adsorbed at stronger acidic conditions at c = 0.1 mol dm⁻³ However, the insertion of BTAH was not accompanied by the release of Cu(II) from the MMT interlayer. On the contrary, the formation of coordination bond of neutral BTAH molecules with Cu(II) is supposed in acidic environment, *e.g.* at pH = 2.5. This is indicated by the occurrence of the vibration bands at $\tilde{\nu} = 1220$ cm⁻¹ and 1275 cm⁻¹.

From the other point of view, the possibility of the formation of small amounts of associates cannot be excluded because of the occurrence of the band at $\tilde{\nu} = 2720 \text{ cm}^{-1}$ (typical for the associated NH groups, Table 5). Furthermore, the band at $\tilde{\nu} = 1245 \text{ cm}^{-1}$ can be attributed to the BTAH₂⁺ cations formed in the interlayer. The colour of the intercalation compound was light greenish blue.

The content of interlayer water molecules was very small. The shoulder on the band of MMT structural Al, Al—OH vibrations at $\tilde{\nu} = 3540 \text{ cm}^{-1}$ and 3580 cm⁻¹ could be attributed to $\nu(\text{OH})$ of Cu(II) hydroxide or Cu—hydroxo complex as reported in [8] for the case of indole—Cu-MMT interaction. Considering this case, the reaction in the MMT interlayer follows the scheme

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Table 5. Characteristic Bands of IR Spectra of Montmorillonites Treated with Benzotriazolium Chloride (Samples 5, 7, 16, 21) and Benzotriazole (Samples 8, 12, 22, 26, 29)

Vibration	$\tilde{\nu}/\mathrm{cm}^{-1}$										
	BTAH	$BTAH_2Cl$	5	7	8	12	16	21	22	26	29
$ u(\mathrm{NH}) $		3310 s	3175 vw 3140 w	3340 vw 3170 w	3120 vw	-	3240 w 3220 w	3480 3360 m 3330 m	3470 m 3412 m	3470 sh 3410 m	
ν(Cu—OH)				-	-	-	3550 vw	3580 sh	3580 sh 3540 w	-	
$\nu({ m H_2O})$	-	-	3400 vw	-	3400 w	3400 m	-	-	-	(3400) br	3440
ν(NH)	2400— 3200			2885 br 2830 br		2724 w	-	1.000 M	2600— 2800 br	-	
= ⁺ _N -H	-	2620 m br	2720 w	2680 w	_	_		-	2720 vw	-	
$\delta({ m H_2O})$	=	-	1655 w sh	-	1645 sh	1640 sh	1660 sh	-	1645 sh	1640 sh	1635 m
δ (C=C, C-N)	1621 m	1621 s	1624 s	1624 m	1621 m	1626 m	1624 m	1624 m	1622 m	1624 m	
δ(N—N)	1280 m 1268 m	1290 w 1240 s	1290 w 1245 w	1295 w 1245 w	1270 w 1245 w	1270 w	1285 w 1255 w	1285 w	1275 w 1245 w	1272 w	1270 w
$\delta(N-N=N)$	1210 s	-		1215 w	1214 w	1220 w	1220 w	1225 m	1220 w	1212 w	1205 w
$\gamma(CH)$	776 m 752 s	750 s	750 s	778 vw 754 s	765 vw 742 s	770 vw 750 s	750 s	775 vw 750 s	778 vw 750 s	790 m 742 s	785 m 740 s

$$\begin{split} \mathrm{BTAH} + \mathrm{Cu(II)}(\mathrm{H}_2\mathrm{O})_x &\to \mathrm{BTAH}_2^+ \\ &+ \mathrm{Cu(OH)}(\mathrm{H}_2\mathrm{O})_{x-1} \ (A) \end{split}$$

This kind of the reaction can also proceed during the adsorption of other organic nitrogenous compounds. The presence of OH groups in the spectrum of the sample 22 is shown in Fig. 2.

When Cu-MMT is treated with BTAH in acidic environment a well developed shoulder at $\tilde{\nu} = 3480$ cm⁻¹ can be observed in the ν (OH) vibration band of adsorbed water molecules at $\tilde{\nu} = 3400$ cm⁻¹ This can be attributed to the stretching vibration of free NH groups as reported in [11—13].

The amount of BTAH adsorbed decreases and is approximately equal to the CEC value when saturation proceeded at pH = 7. The colour of the sample after interaction turned to light green and the presence of small amounts of residual interlayer water was obvious from the shoulder at $\tilde{\nu} = 1640 \text{ cm}^{-1}$ on the band of complex vibration of C—C and C—N groups centred at $\tilde{\nu} = 1624 \text{ cm}^{-1}$ [14—16].

Only the bands representing adsorbed neutral BTAH are present in the region of N—N and/or N=N vibrations. Moreover, the increasing intensity of the ring stretching vibration band can be observed at $\tilde{\nu} = 1388 \text{ cm}^{-1}$ The band of out-of-plane deforma-

tion vibrations of benzene ring at $\tilde{\nu} = 742 \text{ cm}^{-1}$ is shifted to a lower frequency and the increase of intensity of the second $\gamma(\text{CH})$ band at $\tilde{\nu} = 790 \text{ cm}^{-1}$ can be observed simultaneously (Fig. 2). Accordingly, the formation of the coordination bond between neutral BTAH and Cu(II) atoms in the interlayer space of Cu-MMT is evident.

Intercalation complexes of Cu-MMT and compounds formed in alkaline conditions (pH above 7.0) exhibit an intensive green colour. The presence of residual interlayer water in these complexes can be proved. Their IR patterns are different from those of the complexes of compounds prepared at acidic or neutral conditions.

Firstly, the vibration bands of N—H groups as well as the complex vibration bands of C—C and C—N groups centred at $\tilde{\nu} = 1621 \text{ cm}^{-1}$ are absent at all. The band at $\tilde{\nu} = 1635 \text{ cm}^{-1}$ of the sample 29 belongs only to $\delta(\text{OH})$ vibrations of H₂O, that have been confirmed by the disappearance of this band after heating at 150 °C for 2 h. On the other hand, after heating the sample 26 at $\tilde{\nu} = 1624 \text{ cm}^{-1}$ the band remains present that confirms the coordination of BTAH on Cu. The spectra show two out-of-plane vibration bands of C—H at $\tilde{\nu} = 740 \text{ cm}^{-1}$ and $\tilde{\nu} = 785$ cm⁻¹ and the increased intensity of the second band especially. This is typical for IR data obtained for the





Fig. 2. IR spectra of BTAH—Cu-montmorillonite prepared at various pH of the saturation solution.

 $Cu(BTA)_2$ complex according to [14, 15]. And it was found that the composition of the interlayer complex corresponds with the ratio Cu:BTA = 1:2. In conclusion, it is evident that Cu(II)-bis(benzotriazenido) complex is formed but it cannot be excluded that $[Cu(BTA) (BTAH)]^+$ cation is formed as well.

The presence of H_3O^+ in the Cu-MMT interlayer can be assumed as a consequence of $Cu(BTA)_2$ formation to compensate a negative charge of the MMT structure. This can be indicated by the shoulder at $\tilde{\nu} = 1680-1690 \text{ cm}^{-1}$ on the $\delta(OH)$ bending vibration band of adsorbed water molecules. The band centred at $\tilde{\nu} = 1705 \text{ cm}^{-1}$ can be attributed to the presence of H_3O^+ The shoulder at $\tilde{\nu} = 1170 \text{ cm}^{-1}$ occurring on the Si—O vibration band can belong to the OH bending vibrations of H_3O^+ , too [17]

CONCLUSION

Mineral montmorillonite (MMT) seems to be a suitable solid substrate for the adsorption and immobilization of benzotriazole (BTAH) compounds from their aqueous solutions. The extent and mechanism of BTAH intercalation depends on pH of the solution and the kind of the exchangeable cation.

A typical ion-exchange process results from the interaction of $BTAH_2Cl$ salt and Ca-MMT. However, when Cu(II) monoionic form of MMT was used, the BTAH compounds were fixed in the MMT interlayer by the coordination bond.

Furthermore, IR spectroscopic study of the intercalated compounds revealed a chemical alteration of BTAH (polymerization) as a consequence of the host—guest interaction and the H_3O^+ presence could be anticipated from the IR spectra of Cu(II)-MMT intercalated species.

XRD data gave the evidence of the most probable arrangement of BTAH molecules quenched in the MMT interlayer.

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