

Insertion of Benzothiazolium Compounds into Montmorillonite Interlayers

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Abstract. Benzothiazolium compounds exhibit pronounced antimicrobial activities and stimulation effects on plant growth. When applied to fields they can pollute soil colloids. In contact with the soil they can potentially interact with a clay fraction giving rise to clay organocomplexes. Model intercalation complexes were prepared using monoionic montmorillonite and a variety of water-soluble benzothiazolium salts. It was found that the adsorption into the silicate interlayer space proceeds via a cation exchange process. Substantial differences were observed in the extent of the reaction between non-substituted and *N*-substituted species. The sulphur atoms present in the benzothiazolium molecules repel the surface oxygen atom: this is considered to be the factor responsible for prevention of insertion of the guest cations perpendicular to the layers.

Key words. Benzothiazolium compounds, adsorption, montmorillonite.

1. Introduction

The chemicals used in agricultural management can act as pollutants when in contact with the soil and/or surface water. The best way to stop their mobility is by means of bonding to the soil clay fraction. Whether or not organic species react with clays depends upon the chemistry of the compound as well as the nature of the clay mineral. The mineral montmorillonite (MMT), forming an abundant part of soil colloids, may be considered as the most active adsorbent likely to form clay-organocomplexes. This results from its layered structure, cation exchange capacity, pronounced swelling properties and extremely high surface area.

There is an extensive amount of literature treating the interaction of MMT with organic compounds outlined in monographs and reviews [1–4], and in particular dealing with adsorption of potential pollutants [5–10]. The interaction of MMT with benzothiazolium (BT) compounds does not appear to have been studied previously.

It was reported recently [11, 12] that BT compounds (especially their 3-derivatives) may act as effective plant growth stimulants and fungicides. Occurring as cations they are water-soluble and in this way they pollute the soil colloids when used in agriculture.

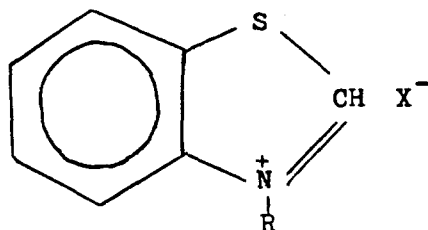
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It is the aim of this contribution to analyse the factors controlling the MMT–BT interaction using model adsorption measurements and to study the properties of the intercalation complexes obtained.

2. Experimental

2.1. MATERIALS

The structure of the BT compounds used in this study is represented by the general formula:



where R can be H (non-substituted BT compounds; abbreviation BT), CH_3 (MBT), $\text{CH}_2\text{—CH=CH}_2$ (ABT), $\text{CH}_2\text{—COO—CH}_2\text{—CH}_3$ (EBT) and $\text{CH}_2\text{—C}_6\text{H}_5$ (BBT), X is Cl, I or HSO_4 .

The non-substituted BT compound was prepared as the hydrogen-sulphate from benzothiazole according to [11]. The synthesis of *N*-substituted BT salts was accomplished by treatment of benzothiazole with the appropriate alkyl halide (Cl, I) in the reaction medium of a mixture of anhydrous dimethyl formamide and acetone (2:1) at 55–60°C [11].

The purity of the crystalline products was checked by C, H, N and S elemental analysis.

The < 2 μm fraction of the bentonite from Jelšovský Potok (Central Slovakia) was used as a model adsorbent. The montmorillonite content was 93 ± 3 wt.% according to thermogravimetric and X-ray diffraction (XRD) measurements. The natural sample was converted into the pure Ca form using the standard exchange method. The chemical composition of the MMT was (in wt.%): SiO_2 (62.7); Al_2O_3 (20.6); Fe_2O_3 (2.32); TiO_2 (0.12); CaO (3.10); MgO (3.75); K_2O (0.09); Na_2O (0.05); MnO (0.02); H_2O (15.0).

2.2. ADSORPTION MEASUREMENTS

The adsorption process was studied by suspending 1.0 g MMT (dried at 105°C), for 48 h, in aqueous solutions (25 mL) of BT compounds at concentrations of 0.001; 0.005; 0.025; 0.075; 0.050; 0.100 and 0.125 M.

After equilibration the suspension was centrifuged and the released Ca was determined. The solid phase was then washed carefully, using deionized water, and dried at 105°C. The nitrogen content (as a measure of adsorbed organic) was determined by CHN elemental analysis (Hewlett Packard). Typical adsorption isotherms are shown in Figures 1 and 2. Additional data on adsorption measurements are given in Table I.

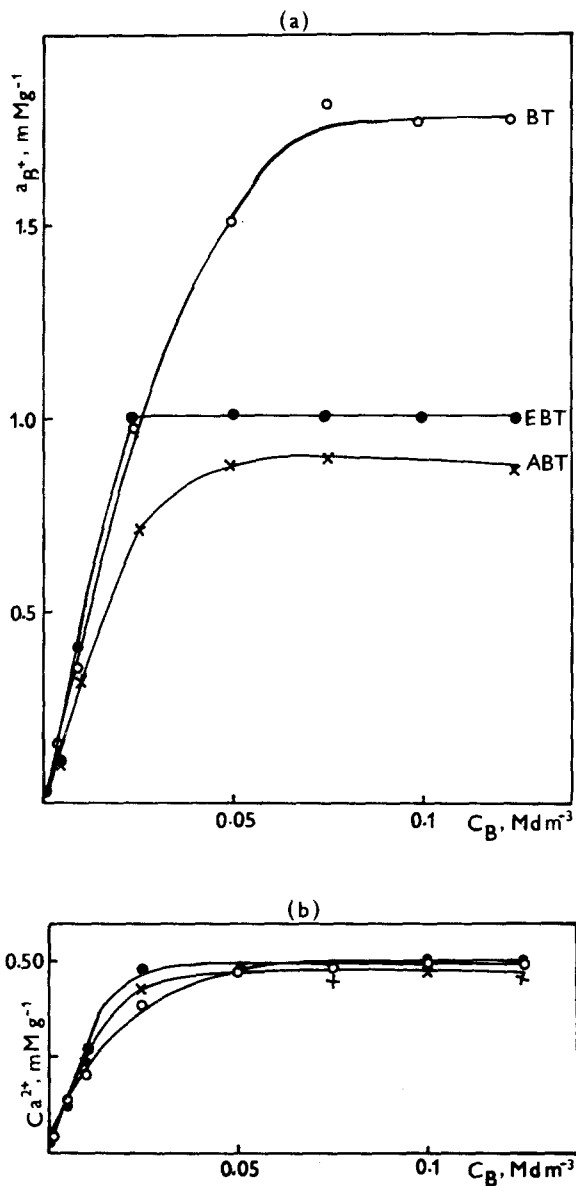


Fig. 1. (a) Adsorption isotherms for BT, EBT and ABT compounds (concentration of saturation solution C_B vs. the amount adsorbed a_B). (b) Ca^{2+} released during base adsorption.

2.3. X-RAY DIFFRACTION ANALYSIS

The washed and dried intercalated solid products were studied as smears on glass slides. The d_{001} values are illustrated in Figures 3 and 4. Additional data are given in Table I.

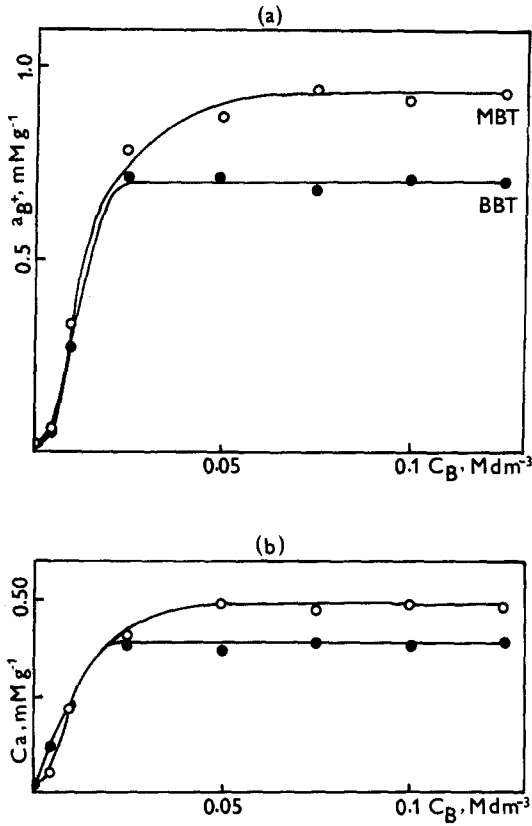


Fig. 2. (a, b) As in Fig. 1 for MBT and BBT.

Table I. Adsorption and XRD characteristics of the intercalation compounds at full saturation ($[B^+] = 0.125 \text{ M}$)

Compound	$a_{\text{org.}}$ (mM/g)	$\text{Ca}^{2+}_{\text{released}}$ (mM/g)	d_{001} (nm)	CTOL (nm)
BT-MMT	1.78	0.51	1.67	0.82
BBT-MMT	0.72	0.43	1.50	0.65
MBT-MMT	0.92	0.45	1.44	0.59
ABT-MMT	0.90	0.47	1.46	0.59
EBT-MMT	1.02	0.50	1.62	0.68

CTOL = 'corrected thickness of the organic layer' according to [14]; montmorillonite (MMT): $\text{Ca}^{2+} = 0.53 \text{ mM g}^{-1}$; $d_{001} = 1.50 \text{ nm}$.

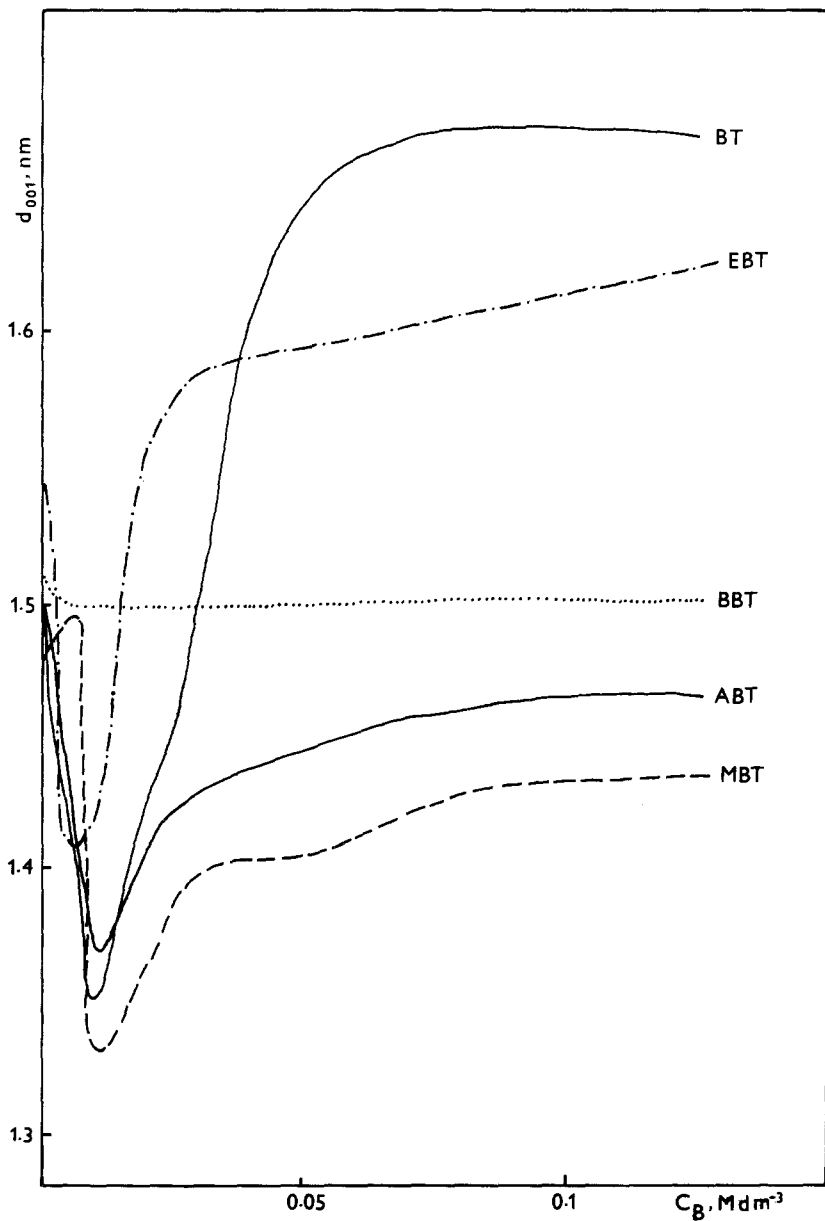


Fig. 3. The change of the d_{001} spacing of MMT during adsorption of BT compounds (d_{001} checked at $C_B = 0.001, 0.005, 0.010, 0.025, 0.050, 0.075, 0.100$ and 0.125 M).

3. Discussion

3.1. HOST-GUEST INTERACTION

The surface of MMT can be considered (ideally) as consisting of negatively charged oxygens (from Si and Al tetrahedra), exchangeable Ca^{2+} cations and water

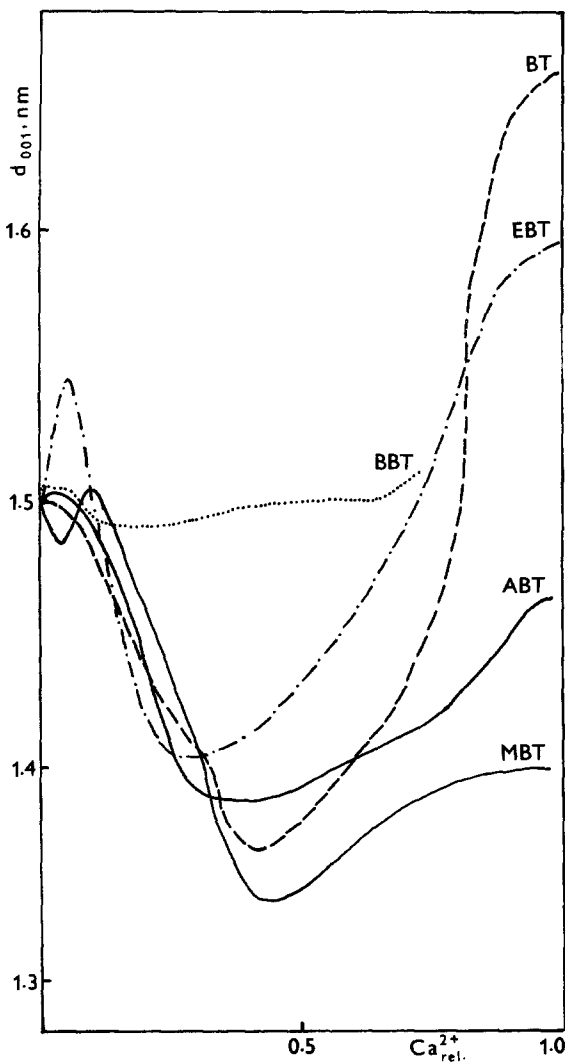


Fig. 4. The change of the d_{001} spacing of MMT vs. Ca^{2+} released from the MMT interlayer ($0.5 \text{ Ca}_{\text{rel}}^{2+}$ stands for 50% of Ca^{2+} originally present in MMT).

molecules bonded to both Ca^{2+} cations (as hydration shells) and oxygen atoms (by H-bonding).

A BT molecule consists of a 6-membered benzene ring combined with a 5-membered heterocyclic ring containing S, C and N atoms without or with a substituent in the N-site. Accordingly, the following chemical points can be taken into account as far as host-guest interaction is concerned:

(I) The functional sites in the heterocyclic ring:

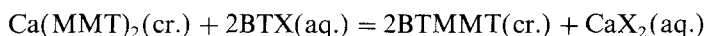
(a) a positively charged N atom in position 3 (nevertheless, some part of the charge is delocalized on the aromatic ring);

- (b) the electronegativity of the sulphur atom in position 1;
- (c) the presence of the N—H group in the nonsubstituted BT compound;
- (d) the acidity of the H atom in position 2;
- (e) the chemical and steric characteristics of the substituents linked with nitrogen in position 3.

(II) Layered structure of MMT:

- (a) the negatively charged surface with charge distributed over oxygen atoms of the tetrahedral layer;
- (b) the presence of Ca^{2+} cations and water molecules in the interlayer space.

The basic information mentioned above gives clear evidence for the polar character of both the host and guest species. Considering the negatively charged MMT surface and the positively charged BT molecules, the interaction is likely to be dominated by the cation exchange process:

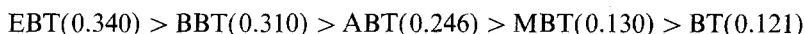


with simultaneous competition between the interlayer water and BT molecules.

Adsorption measurements (Figures 1, 2) roughly confirmed the validity of the equation. The adsorption of BT^+ cations is accompanied by the simultaneous release of the Ca^{2+} cations from the clay. The final equilibrium retention values (saturation at 0.125 M) decrease in the order (Table I):



No clear correlation was found between the retention extent and the size of the individual cation (Table II), which decreases in the sequence (the calculated cation volumes in nm^3):



Thus, the chemical nature of the substituent can be responsible for the differences in the extent of retention.

The highest retention was found for non-substituted BT (around 70% beyond the exchange capacity of MMT). Obviously, the presence of the N—H group is significant in this case. H-bonding may occur between the N—H group and the surface oxygens, giving rise to the mixed ionic and molecular complexes.

Table II. Size characteristics (cartesian coordinates) of benzothiazolium compounds

Compound	Coordinate (nm)		
	x	y	z
BT	0.663	0.370	0.494
BBT	1.004	0.418	0.731
MBT	0.614	0.418	0.504
ABT	0.823	0.418	0.716
EBT	0.984	0.418	0.828

Despite the differences in their size, MBT and ABT were found to have almost the same retention values.

The lowest retention was exhibited by voluminous BBT (around 30% less than CEC of MMT). At the same time it was able to displace only around 80% of Ca^{2+} cations from the interlayer. It is possible that diffusion prevented larger insertion of this large molecule containing two benzene rings.

EBT is the only compound with oxygens in the substituents. Its retention is very close to the theoretical cation exchange value (1.06 mM g^{-1}), even though its size is very near to that of BBT.

Analyzing the experimental data on adsorption according to Giles *et al.* [13] a slightly 'S'-shaped curve was observed in some cases at the beginning of the adsorption (Figures 1 and 2). This is typical of the retention of polar molecules from polar solvents. A plateau occurs mostly beyond 0.05 M dm^{-3} (concentration of the saturating solution) and indicates the full saturation of the host's surface and a monolayer arrangement of the guest molecules.

3.2. XRD MEASUREMENTS

The adsorption measurements showed clearly that BT compounds intercalate into the MMT interlayer competing for the Ca^{2+} exchangeable cations as well as the interlayer water molecules. Using XRD analysis it was possible to measure the change of the thickness of the interlayer space during adsorption.

The correlation of d_{001} values of BTMMT complexes with the amount of BT compound added to the saturated solution is shown in Figure 3. It can be seen that small additions of BT compounds can change the MMT 001 spacings dramatically. Excluding the BBT sample there is a pronounced minimum in d_{001} at $[\text{B}^+] = 0.005\text{--}0.015 \text{ M g}^{-1}$. This is consistent with the contraction of the MMT structure from 1.5 nm (original d_{001} spacing of Ca^{2+} -MMT) to 1.33–1.41 nm, depending on the type of cation. At the same time a similar minimum can be observed using the correlation of d_{001} with the Ca^{2+} released (Figure 4). It occurs between 30–40% of exchanged Ca^{2+} , excluding the BBT compound again.

If we consider the thickness of the dehydrated MMT layer to be 0.95–0.96 nm then the 1.3–1.4 nm spacings observed represent 0.35–0.45 nm for the interlayer space. These values are very near to the y coordinate of all the investigated BT^+ cations (Table II), indicating their flat arrangement in the interlayer at the beginning of the adsorption.

The voluminous BBT compound represents a special case in this connection. It enters the interlayer space without changing the d_{001} spacing of MMT and this remains constant up to the equilibrium. Additional studies are needed to understand this behaviour.

On increasing the equilibrium concentrations of $[\text{B}^+]$ beyond 0.02 M g^{-1} the thickness of the interlayer space increases rapidly achieving the maximum value at around 0.075 M g^{-1} corresponding to the beginning of the plateau in Figures 1 and 2.

Using d_{001} values of fully saturated samples it was possible to derive the so called 'corrected thickness of the organic layer (CTOL)' according to Green–Kelly [14]: the CTOL value is derived from the d_{001} value of the organoclay complex by adding

0.1 nm as an approximate contraction correction and finally subtracting 0.95 nm (the thickness of a silicate sheet). The results are shown in Table I.

It is obvious that the CTOL values do not correlate in a simple way with the z dimensions (Table II) representing the height of the guest molecule. Accordingly a tilted, rather than an upright arrangement can be suggested for the larger species (ABT, EBT and BBT). Taking into account the size characteristics of the cations (Table II) and the CTOL values, the tilting angle between the silicate sheet and the plane of the benzene ring of the mentioned compounds seems to be 55–60°. The suggestion of a tilted position may be favoured by the suggested repelling action of the sulphur atom (from the heterocyclic ring) towards the surface oxygens of the MMT structure.

The arrangement of the smaller cations (BT and MBT) is difficult to deduce. E.g. there is no clear evidence for a flat arrangement of non-substituted BT compounds in the form of a double-layer as far as the results of the adsorption measurements are concerned (no indication on stepwise adsorption, the equilibrium retention at full saturation is lower than expected for a complete two layer formation). Nevertheless, the CTOL value (0.82 nm) is close to double both the y (3.70 nm) and z (4.94 nm) values.

4. Conclusions

The insertion of benzothiazolium compounds into montmorillonite interlayers proceeds on the basis of a cation exchange mechanism. The chemical, rather than steric characteristics of N -substituted BT^+ cations control the extent of retention at full saturation. It is suggested that the position of the guest molecules in MMT interlayers is changing during adsorption from a flat to a tilted arrangement. There are, however, differences between non-substituted and N -substituted compounds. The preference for the tilted arrangement is supported by the repelling action of the sulphur atom (present in guest molecules) towards the surface oxygens of the MMT structure. But additional studies are needed to explain the role of the residual interlayer water in the guest–host interactions.

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