Interaction of montmorillonite and benzothiazole derivatives

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The sorption of benzothiazole cations and its derivatives by montmorillonite has an ion-exchange mechanism and is inversely proportional to the molecular mass of sorbate. The reaction is accompanied by change of water content, both the water adsorbed on surface and bonded in interlamellar space.

Сорбция катионов бензотиазола и его производных на монтморильоните протекает по механизму ионного обмена и обратно пропорциональна молекулярной массе сорбируемого вещества. Реакция сопровождается изменением содержания воды как адсорбированной на поверхности, так и связанной в межслойном пространстве.

Based on the study of organoclays as products of clay mineral reactions with organic compounds, these can be classified into three main groups [1]:

1. Organoclays containing in interlamellar space complexes with organic molecules as ligands and exchangeable cations as central atoms.
2. Organoclays in which the silicate layers are solvated by organic molecules whereas the exchangeable cations of clays are located in the interlamellar space.
3. Organoclays in which the exchangeable positions are occupied by organic cations.

The formation reactions of group 1 and 3 organoclays take place mainly in the interlamellar space of sorbent, while in the case of group 2 clays the substrate reacts predominantly on their surface. The sorbent—sorbate reaction mechanism in the group 1 and 2 has a nature of a molecular sorption whereas the group 3 clays are formed by ion-exchange reactions [2—5].

The organoclays exhibit characteristic properties resulting from the chemical nature of interaction between clay minerals and organic molecules or cations.

A study of such interactions helps us to solve complicated processes proceeding in soil systems which have been provoked by use of fertilizers and insecticides.

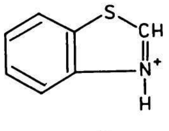
Experimental

The montmorillonite was isolated as a fine fraction (<2 μm) by sedimentation of 4 % water suspension of Jelšový Potok bentonite. The Ca, Mg, Na, Co, and Cu forms of montmorillonite were prepared from its natural form by multiple treatment with 0.1 mol dm^{-3} solution of corresponding chloride. The exchangeable cations were estimated complexometrically or by flame photometry [6]. The concentrations of sorbate solutions used in preparations of organomontmorillonites were 0.1—0.01 mol dm^{-3}. The sorbent was dried to constant mass at 110 °C and the sorbent to sorbate ratio was 1 g:50 cm^3. The solid and liquid phases were kept in contact for 24 h at room temperature. As sorbates, solutions of new benzothiazole derivatives [7—10] having positive effect on sugar content increase in sugar beet and moderate antifungal effect were used [10].

The carbon, hydrogen, and nitrogen estimations were made on Hewlett—Packard CHN-analyzer. The interlayer distance values were found using vertical Philips goniometer (conditions: 35 kV, 20 mA, Cu lamp and Ni filter). The IR spectra in KBr disks were measured on Perkin—Elmer 598 spectrophotometer. The water content in organomontmorillonites was calculated from TG curves registered on Derivatograph MOM. The sorption and desorption of water vapour by starting form as well as by organomontmorillonites were performed at 25 °C above sulfuric acid solutions with defined water vapour tension.

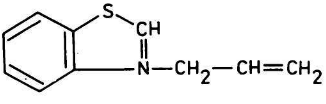
Results and discussion

In Figs. 1 and 2 there are shown the isotherms of sorption of three benzothiazole derivatives by the natural (Ca, Mg) and prepared Ca, Mg, Na, Co, and Cu forms of montmorillonite: benzothiazolium sulfate having cation BTS$^+$



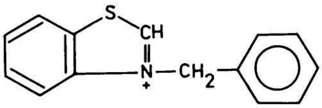
I

3-(2-propene)benzothiazolium bromide containing cation PBT$^+$



II

and 3-benzylbenzothiazolium bromide containing BBT^+ cation



III

These cations have molecular masses 136.2 (*I*), 176.3 (*II*), and 224.1 (*III*), respectively.

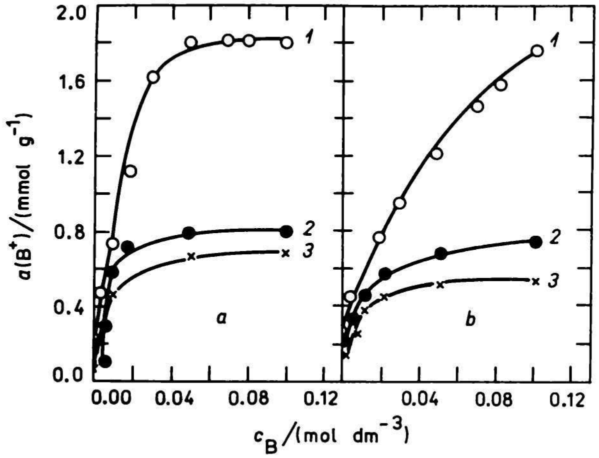


Fig. 1. a) Isotherms of sorption of BTS^+ (*1*), PBT^+ (*2*), and BBT^+ (*3*) by Ca, Mg-montmorillonite. *b*) Isotherms of sorption of BTS^+ (*1*), PBT^+ (*2*), and BBT^+ (*3*) by Mg-montmorillonite.

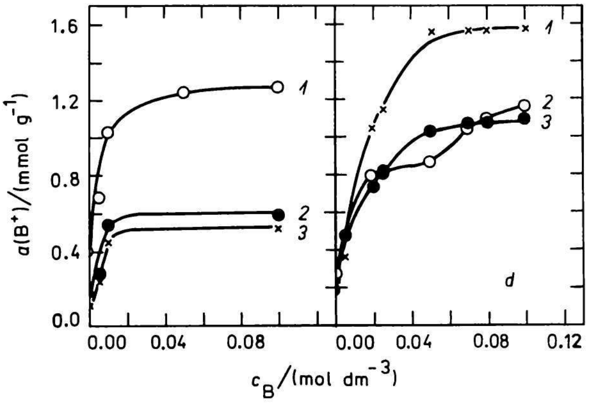


Fig. 2. c) Isotherms of sorption of BTS^+ (*1*), PBT^+ (*2*), and BBT^+ (*3*) by Ca-montmorillonite. *d*) Isotherms of sorption of BTS^+ by Na-montmorillonite (*1*), Co-montmorillonite (*2*), and Cu-montmorillonite (*3*).

As follows from the isotherms, the amount of bonded organic cation is in the same parent form of montmorillonite inversely proportional to its relative molecular mass. The sorption is not influenced by the sorbate and it increases in dependence on the nature of exchangeable cation in the following order: Cu^{2+}, Co^{2+}, Ca^{2+}, Na^{+}, and Mg^{2+}

We have found that the sorption has an ion-exchange character and the ion-exchange equilibrium

$$M^{n+}\text{-montmorillonite} + B^{+} \rightleftarrows B^{+}\text{-montmorillonite} + M^{n+} \qquad (A)$$

is influenced by the relative molecular mass of sorbate. At the same sorbate concentration in solution, the lower the molecular mass, the greater the equilibrium shift to the formation of organomontmorillonite. This fact is illustrated by Fig. 3.

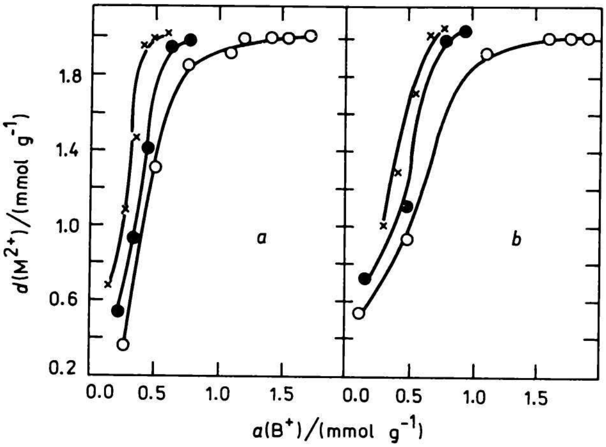


Fig. 3. Desorption of Mg^{2+} (*a*) and Ca^{2+} (*b*) cations from Mg- and Ca,Mg-montmorillonite at sorption of BTS^{+} (○), PBT^{+} (●), and BBT^{+} (×).

The d_{001} interlayer distance values indicate an entry of organic cation into the interlamellar space of montmorillonite. In the BTS^{+}—montmorillonite systems they were in the range 1.66—1.69 nm, in the PBT^{+}—montmorillonites in the range 1.49—1.50 nm and in the BBT^{+} systems they changed from 1.62 nm to 1.64 nm. These values were obtained at maximal sorption independently on the nature of exchangeable cation and so they indicate a perpendicular orientation of benzene ring to the montmorillonite surface [11].

The sorption of organic cation caused changes in the content of water in interlamellar space and sorbed on the montmorillonite surface. These changed water amounts were calculated on the basis of mass loss on the TG curves in the temperature interval ⟨20 °C; 150 °C⟩. In this way we have found that at certain content of bonded sorbate, the water amount—bonded sorbate amount curve exhibits a minimum (Figs. 4 and 5) which corresponds with the first maximum of release of exchangeable cation.

The mentioned relations observed in all examined systems allow us to suppose that the surface of montmorillonite is dehydrated maximally if the inorganic cation is substituted "equivalently" by the organic cation while the negative charge of

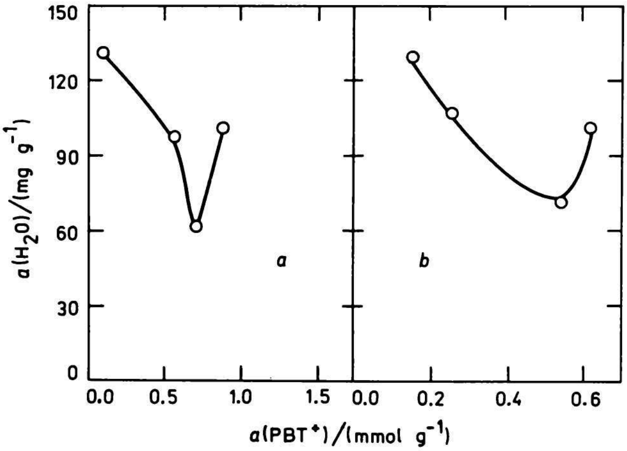


Fig. 4. Dependence of bonded water amount on sorbate amount in the system: *a*) Ca,Mg-montmorillonite—PBT^+; *b*) Ca-montmorillonite—PBT^+

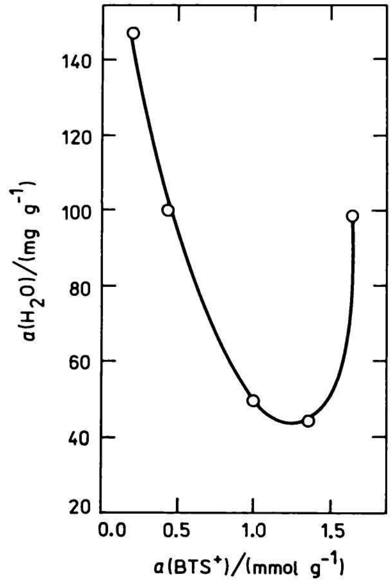


Fig. 5. Dependence of bonded water amount on sorbed BTS^+ amount in Ca,Mg-montmorillonite.

montmorillonite surface is so completely compensated by the positive part of organic sorbent. However, as the capacity of montmorillonite is reached and the organic cation is sorbed on its surface, the cation forms *via* —NH^+ functional groups hydrogen bonds with water molecules, in which way the water content in samples increases.

These our considerations are supported by the results we obtained from the isotherms of sorption and desorption of water vapour by organomontmorillonites. We have calculated the average sizes of the surface area available for water molecules using the BET equation. In Table 1 there are shown the values calculated for BTS^+ sorbate.

Table 1

Sizes of average specific surfaces

$c(BTS^+)/(mol\ dm^{-3})$	$s/(m^2\ g^{-1})$ Ca-montmorillonite—BTS^+	$s/(m^2\ g^{-1})$ Ca,Mg-montmorillonite—BTS^+
0.10	46.5	19.0
0.08	30.5	13.5
0.07	30.0	29.5
0.05	55.0	29.5
0.025	52.0	30.5
0.020	50.5	66.5
0.005	53.5	80.5
0.001	182.0	82.5
0.000	513.5	425.0

The IR spectra show all characteristic absorption bands of benzothiazole [12] with maxima at $\tilde{\nu}/cm^{-1}$: 715, 755, 800, 820, 1415, 1505, 1581, and 1610. The N—H stretching vibrations are shifted towards higher wavenumbers — 2840 cm^{-1} and 2920 cm^{-1} compared with 2460 cm^{-1} and 2560 cm^{-1} in the benzothiazole.

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