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INTERACTIONS OF BENZOTRAZOLE WITH Co-MONOIONIC FORMS OF MONTMORILLONITE

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ABSTRACT: The mode of interaction of benzotriazole with Co-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. The extent and mechanism of retention were determined by using XRD, elemental analysis and IR spectroscopy. Obtained results indicated that there is a cation-exchange reaction (when benzotriazolium cation is intercalated) in the acid solution. In the neutral solution benzotriazole is coordinated to Co^{2+} - cation as neutral molecule and in the basic solution as benzotriazole anion.

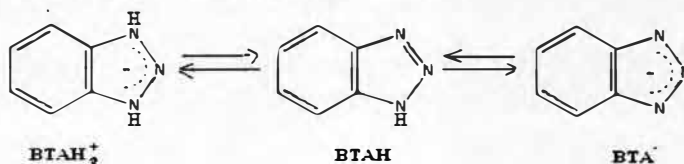
KEY WORDS: Co(II)-montmorillonite, benzotriazole, X-ray diffraction analysis, IR-spektroskopy

1. INTRODUCTION

Interactions of numerous heterocyclic compounds containing one benzene ring in their structure with clay minerals were studied rather rarely [1]. It is known that these compounds represent important chemical agents. Unfortunately, many of them exhibit pronounced carcinogenic effects [2] and they behave as dangerous water and/or soil pollutants. Therefore, it is necessary to try to solve the problem of their immobilization (fixation) by using suitable solid host substrate with appropriate adsorption abilities. Precisely mineral montmorillonite could be used as one of the suitable host exhibiting desirable properties.

Montmorillonite belongs to the group of expanding layer silicates (known as smectites), having the layers formed by two tetrahedral sheets linked with an octahedral one. Negative charge of the layers is balanced by hydrated exhalable cations (e.g. Co^{2+}). Polar organic molecules (e.g. benzotriazole) are able replace water molecules which occupy the interlayer space in the montmorillonite [3-6].

Benzotriazole is one of the most effective corrosion inhibitors for staining and tarnishing of many metals and it can be incorporated into lacquers, polishes and fluids as cleaning solutions and detergents [7]. The schematic structure of benzotriazole (BTAH) and next benzotriazole species (BTAH_2^+ and BTA^-) studied in this work is given in formula:



We have recently studied interactions of benzimidazole with Ni-exchanged montmorillonite [7,8]. The aim of this work was to determine the possibility of intercalate and the type of interactions of

Co(II) with benzotriazole in the interlayer space of montmorillonite (at various pH values of appropriate aqueous solutions of BTAH).

2. EXPERIMENT

2.1 Synthesis

Montmorillonite from Jelšový potok (Slovakia) with a composition:

$\text{Ca}_{0,48}(\text{Si}_{7,59}\text{Al}_{0,41})\text{Al}_{3,06}\text{Fe}_{0,34}\text{Mg}_{0,63}\text{O}_{20}(\text{OH})_4$ [9,10] has been used as a carrier for intercalated Co(II) complexes.

The $< \mu\text{m}$ fractions were obtained by sedimentation. The cation exchange capacity (CEC), determined according to the method [11] was 0.98 mmol.g^{-1} (Co-MMT).

Benzotriazole (BTAH) was supplied by Merck and the other chemicals of analytical grade were purchased from Lachema.

The Co(II)-exchanged montmorillonite (Co-MMT) was prepared as immersion (five times) of 1g of Ca-MMT in 100 cm^3 water solution with a concentration of 0.1 mol.dm^{-3} of CoCl_2 at room temperature. The excess salt was removed by washing with deionised water until the Cl^- tests were negative. The interlayer spacing of Co-montmorillonite was 1.4 nm.

The reaction of benzotriazole with Co(II)-montmorillonite was performed by suspending 1g Co-clay in 100 cm^3 of aqueous solution of benzotriazole with a concentration of 0.06 mol.dm^{-3} . The appropriate pH value was adjusted with aqueous solution of HCl or NaOH. Suspensions were stirred at room temperature for 48 h. Solids were separated from the solution by filtering, washed with 200 cm^3 of water and dried at 50°C . The amount of Co(II), which was released from Co(II)-montmorillonite in the reaction with benzotriazole, was determined by complexometric titration.

2.2 Characterization

Powder diffraction data was collected on a Philips PW 1050 X-ray diffractometer in the range of $4\text{-}20^\circ 2\theta$ by using CuK_α radiation.

Infrared spectra were measured in KBr pellets on a Nicolet 750 Magna spectrometer in the $400\text{-}4000 \text{ cm}^{-1}$ range.

3. RESULTS AND DISCUSSION

Analytical characteristics of prepared samples, together with their interlayer distances and colours of samples are summarized in Table 1 and infrared spectra are given in Table 2.

Tab. 1: The concentration (c), the values of benzotriazole reaction solutions, the number of released Co^{2+} ions ($\text{Co}^{2+}_{\text{rel}}$), interlayer space (d_{001}) and colours of samples

Sample	c [mol.dm^{-3}]	pH	$\text{Co}^{2+}_{\text{desorb.}}$ [mmol.g^{-1}]	d_{001} [nm]	Colors
Co-MMT	–	–	–	1.47	pink
Co-BTAH 1	0.02	2.03	0.33	1.42	light-pink
Co-BTAH 2	0.02	5.79	–	1.48	orange
Co-BTAH 3	0.02	11.97	–	1.27	brown

Tab. 2: The IR wavenumbers (cm^{-1}) of Co(II)-montmorillonite treated with benzotriazole

Assignment	$\tilde{\nu}$ [cm^{-1}]		
	Co-BTAH 1	Co-BTAH 2	Co-BTAH 3
δ (CH)	747	748	744
δ (CH)	779	791	781
δ (N-N)	1259	1257	-
δ (N-N)	-	1275	1279
δ (CH)	-	1446	1446
δ (CH)	-	-	1489
δ (N=N)	-	1575	1575
ν (C=C)	1635	1636	-
δ (H-O-H)			1637
$\text{HN}^+ \equiv$	1836	1836	-
$\text{HN}^+ \equiv$	1932	1936	-
ν (NH)	3171	3171	-

As a result of mutual interactions of compounds in montmorillonite, the interlayer distances d_{001} of individual samples with benzotriazole changed (Table 1) in comparison to Co-MMT. After interactions, the basal spacing decreased and we assume that observed changes were due to intercalation of benzotriazole into the interlayer's space of montmorillonite.

Various ways in which benzotriazole forms bonds in the interlayer space of the Co(II)-montmorillonite can be deduced from IR spectra of the prepared samples. When the reaction of Co(II)-exchanged montmorillonite with benzotriazole solution was performed in acid medium ($\text{pH} = 2.03$), an ionic exchange of Co^{2+} for benzotriazole cation BTAH_2^+ took place. This is shown by the fact that according to the analysis ($\text{Co}^{2+}_{\text{rel}} = 0.33 \text{ mmol.g}^{-1}$) this sample practically contains no Co^{2+} ions (Table 1). The IR spectrum obtained from benzotriazolium-montmorillonite Co-BTAH 1 shows bands at 1836 cm^{-1} and 1932 cm^{-1} ($\text{NH}^+ = \text{cation}$) and 3171 cm^{-1} (ν (N-H)), where they are typical for benzotriazolium cation (Table 2) [1].

The IR spectrum of sample Co-BTAH 2, obtained from nearly neutral solution ($\text{pH} = 5.99$) illustrates, especially bands corresponding δ (N-H) and δ (CN) vibrations in the 1500 cm^{-1} (Table 2), that ligand proton remains bounded by the nitrogen atom on the benzotriazole. Thus, benzotriazole is coordinated to Co-(II) in the interlayer space of montmorillonite. But bands at 1836 cm^{-1} and 1936 cm^{-1} in sample Co-BTAH 2 also indicate the presence of benzotriazolium ions.

The IR spectrum of the sample Co-BTAH 3 in which the reaction of Co(II)-montmorillonite with benzotriazole was performed in basic solution ($\text{pH} = 11.97$) illustrates (in agreement of literature [12]), that benzotriazole anions BTA^- may be formed. This conclusion is supported by the absence of the bands in the region $1800\text{-}2000 \text{ cm}^{-1}$ (Table 2) corresponding to the $\text{NH}^+ = \text{cations}$.

4. CONCLUSIONS

X-ray powder diffraction and infrared spectra showed, that benzotriazole was successfully intercalated into interlayer spaces of Co(II)-montmorillonite. Formation of different types of interaction of benzotriazole to Co(II) in the silicate interlayers (BTAH, BTAH₂⁺, BTA⁻) is expressively influenced by the reaction's conditions. Obtained result is also important from environmental aspects.

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