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**INTERACTION OF BENTONITE WITH
DODECYL-BENZYL-DIMETHYLAMMONIUM
BROMIDE AND N-[1-(ETHOXYCARBONYL)PENTA-
DECYL]TRIMETHYLAMMONIUM BROMIDE**

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Interaction of bentonites with tetrasubstituted ammonium cations of surface-active compounds were studied both by classic heating and in microwave field. The intercalation of the layered silicate which is contained in the bentonite proceeds as an ion exchange, and the interlayer distance increases during this process. Products of the reactions were characterized by gravimetry, DTA, DTG, IR, and X-ray diffraction.

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Introduction

The interaction between surfactants and clay minerals is of great importance for environmental, waste disposal, and technical research [1]. Bentonites are of a great commercial value, and notwithstanding the variable content of montmorillonite, research works into these natural layered materials could lead to their practical exploitation especially for purification of wastewater and contaminated groundwater containing quaternary ammonium salts [2]. Due to the weakly coupled layered structure of aluminosilicate, the interlayer cations can be easily ion-exchanged with a variety of inorganic and organic cations [3]. Bentonite pellets modified with a quaternary amine compounds were used to remove oil from produced water [4]. Reactions of bentonite with water solutions of dodecyl-benzyl-dimethylammonium bromide (SEPTONEX, herein-after called SP) and N-[1-(ethoxycarbonyl)pentadecyl]-trimethylammonium bromide (AJATINE, herein after called AJ) were studied as models of interactions of bentonite with cationic tensides. In contrast to synthetic layered silicates and montmorillonite, bentonites have low crystallinity and contain sizable amounts of quartz and other impurities and considerable contents of water, therefore it is very difficult to interpret the results of measurements. By means of Poirier adsorption isotherms in the clay-water systems [5] it should be possible to distinguish water associated with cation, that adsorbed on external and internal surfaces and pore water. Other authors [6] showed that, at the greater water content, pore water becomes predominant and the individual contributions of adsorbed and pore water are difficult to distinguish.

It has been shown [7] that microwave field could accelerate some reactions, particularly the reaction rate of solid state reactions could be increased in order of magnitude. A high water content in clay minerals leads to a clear difference in the morphological features of the microwave-dried and oven-dried samples [8]. The microwave-dried samples had a distinctly higher surface area compared with oven-dried samples. Microwave irradiation has been used to synthesize Al-intercalated montmorillonites with high surface area [9]. Evidence has been found for the considerable mobility of magnesium (II) ion within the lapponite lattice during microwave heating [10]. The experiments with microwave field were formerly carried out in commercial microwave ovens.

Experimental

Two different samples of bentonites were used for this study. Bentonite Clair was a material only slightly yellowish with about 13% wt. of total water; after drying at 90 °C for 24 hrs the water content decreased to 3%. Bentonite Keramost Special 750 was dark yellow, rather brownish with about 17% of water, which content decreased only to 12% after the same drying process. Both types of bentonite were

boiled 30 min. with hydrochloric acid (2 mol l^{-1}), then washed and dried before using for intercalation reactions. Bentonite Keramost turned to a lighter hue during this process, and iron(III) cations were partially released to the hydrochloric acid solution.

SP and AJ were commercial products, SP was available as a crystalline substance, AJ as a water solution of 0.26 mol l^{-1} .

Interaction of 25 ml of water solution of SP or AJ, respectively (0.2 mol l^{-1}) with 2.000 g bentonite was carried out either by refluxing at a boiling point of reaction mixture (45 min.) or by a 5 minute action of microwave field (frequency of $2450 \pm 30 \text{ MHz}$, with a total generator output of 800 W, out of which 30 – 50 W is absorbed by the reaction mixture) in a specially constructed device (Radana, Czech Rep.) at the atmospheric pressure. The product of the interaction of bentonite with SP was the same when 0.02 mol l^{-1} solution was used. Solid phases obtained after finishing the reaction were filtered, washed with water and air-dried for 24 hrs at $90 \text{ }^\circ\text{C}$.

The course of reactions was followed by means of powder diffraction with an X-ray diffractometer HZG-4 (Freiberger Präzisionsmechanik, Germany). The diffraction angles were measured from 2° to 50° (2θ). The diffraction line positions were corrected using known lines for the quartz present in bentonite. Also interaction of the bentonite (Clair) and crystalline SP in the triturated mixtures (1 : 3) was examined with the X-ray diffractometer. The methods of measurement and verification were described in our previous work [11].

The solids obtained were also characterized by means of IR spectroscopy in KBr pellets in the region of $4000 - 500 \text{ cm}^{-1}$ (Biorad, FTS 40, U.S.A.). DT and TG analyses were carried out in air within $20 - 600 \text{ }^\circ\text{C}$ at a heating rate $5 \text{ }^\circ\text{C min}^{-1}$, the weight of samples was 100 mg (derivatograph MOM, Hungary).

The experiment designed to replace the intercalated tetrasubstituted cation by hydronium was carried out by boiling the intercalate with an excess of hydrochloric acid solution (2 mol l^{-1}) 5 hrs or in microwave field 10 min.. The released cation was determined by means of titration with tetraphenylborate with the help an ion-selective electrode [12].

Results

Both bentonites contained rather small amount of the layered aluminosilicate of low crystallinity besides a high content of quartz and further impurities. The only one sharp and distinct line in diffractograms could be used in some cases for the determination of the interlayer distance. The quality of the diffractograms was improved after intercalation.

Reaction conditions and data characterizing the intercalates are presented in Table I. The reactions carried out in the microwave field proceeded very easy and

Tab. I Reaction conditions and product characterization for the reactions of bentonite with tetrasubstituted ammonium cations

Starting material	Guest	Reaction conditions	Product characterization		
			d_l , nm	TG, %	GA, %
bentonite (Clair)			1.257	10 (100 °C) 13 total (600 °C)	
bentonite (Clair) dried			1.244	3 total (600 °C)	
bentonite (Clair) dried	SP	0.2 mol l ⁻¹ , reflux 45 min	3.465	32 total (600 °C)	28.1
bentonite (Clair) dried	SP	0.2 mol l ⁻¹ , 7 days, room temp.	3.430	31 total (600 °C)	27.5
bentonite (Clair) dried	SP	0.2 mol l ⁻¹ , MW, 5 min.	3.465	31.8 total (600 °C)	28.5
bentonite (Clair) dried	SP	Clair/SP _(S) = 1/3 MW, 10 min.	3.625		
bentonite KERAMOST			1.530	7 (100 °C) 16 (600 °C)	
bentonite,dried KERAMOST			1.389	12 total (600 °C)	
bentonite,dried KERAMOST	SP	0.2 mol l ⁻¹ , reflux 45 min.	3.750	40 total (600 °C)	29.9
bentonite,dried KERAMOST	SP	0.2 mol l ⁻¹ , MW 5 min	3.798	42 total (600 °C)	31.5
Bentonite (Clair)	AJ	0.2 mol l ⁻¹ , reflux 45 min.	3.181	29 total (600 °C)	20.4
Bentonite (Clair) dried	AJ	0.2 mol l ⁻¹ , reflux 45 min.	3.038	23 total (600 °C)	12.6
Bentonite (Clair) dried	AJ	0.2 mol l ⁻¹ , MW 5 min	3.302	26 total (600 °C)	15.1

more quickly in comparison with the classic heating (see reaction times). The intercalates were characterized by means of the interlayer distance (d_l) determined from the powder diffractograms. The decrease in weight of the intercalated material, which was determined from the results of thermogravimetric analyses, is denoted TG in Table I. The gravimetric determination of the weight increase after intercalation reaction which was calculated as a difference between the starting

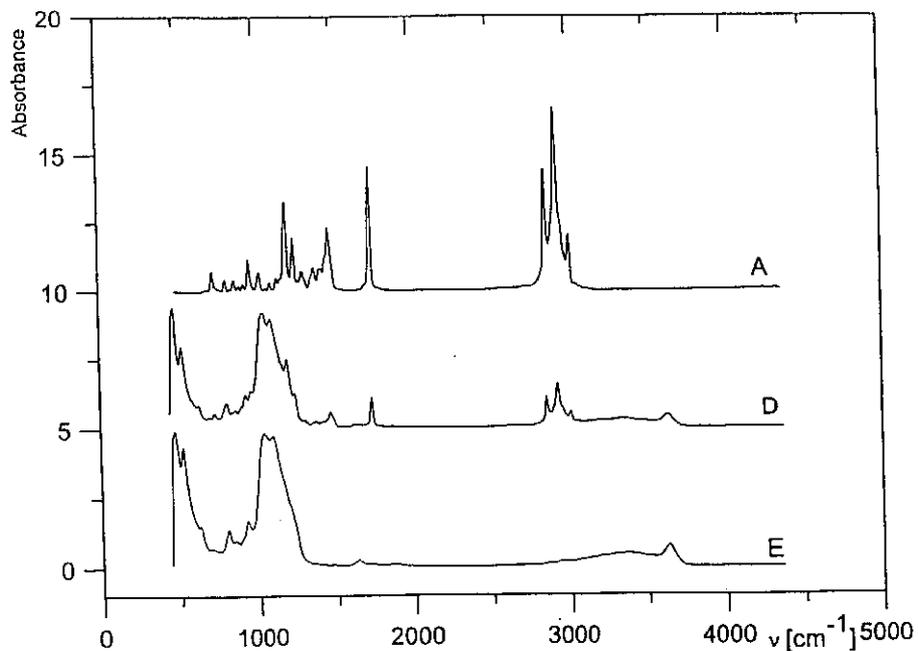


Fig. 1. IR spectra of SP (A), intercalate of bentonite with SP (D), and bentonite Clair (E)

amount of the dried bentonite and the amount of the obtained washed and dried material, is presented in Table I in the column denoted GA. Both values in the columns TG and GA have been converted to the weight per cent of the intercalated cation in the intercalated material. The experiments last mentioned were repeated at least three times for every reaction system. The values presented in the column (GA) are then arithmetic averages of the experimental results the difference of which was less than 3% in all the cases. The values obtained from the experiments with SP showed minor variances while experiments with AJ were less reproducible probably due to ability of AJ to steam-distil.

Figure 1 shows IR spectra of SP, bentonite (Clair) and a spectrum of the intercalate obtained from the above given components (0.2M SP) in microwave field. The comparison of these spectra shows that the spectra of tetrasubstituted ammonium cation are the same whether its counter-ion is simple bromide (in SP) or the negative charge of the layer in the intercalate.

Figure 2 shows five diffractograms namely of the crystalline SP (A), the freshly triturated mixture of SP and bentonite (B), the triturated mixture of SP and bentonite after 2 days at the 60 °C (C), the same mixture after 10 min. in microwave field (D), and the bentonite (E). It is clear that microwave field accelerates the reaction in orders and the intercalate obtained has a proper crystallinity. Two main lines of quartz contained in bentonite are marked Q.

Attempts to determine the content of the cation intercalated after releasing it from the intercalate by substitution for hydronium (by reaction of the intercalate with hydrochloric acid) were not successful. The experiments repeated several times were not reproducible and the tetrasubstituted cation was released only partially (30 – 50 % wt. with regard to the content of this cation found by gravimetry or by TG).

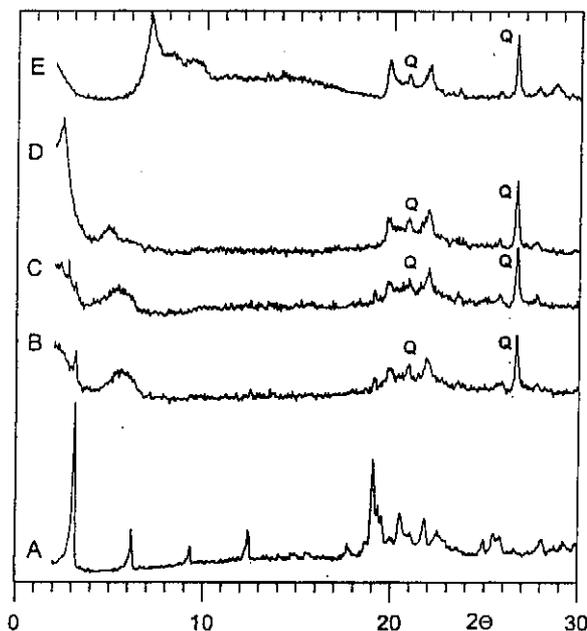


Fig. 2. X-ray diffractograms of the crystalline SP (A), the freshly triturated mixture of SP and bentonite (B), the triturated mixture of SP and bentonite after 2 days at 60 °C, the diffractogram of the same mixture after 10 min. in microwave field (D), and the diffractogram of bentonite (E)

Discussion

Starting Materials

Both bentonites were boiled with hydrochloric acid before using for intercalation reactions. The colour of bentonite KERAMOST turned to light tint only very slightly during this process. The dark yellow colour of the last named original material gave evidence for the presence of cations of transition metals, especially iron(III). The present metal cations are hydrated and this fact might cause a higher water content (12%) in bentonite KERAMOST after drying in comparison with bentonite Clair

(3%), see Table I. This chemically bonded water is released gradually at temperature higher than 100 °C. The interlayer distance increases not only with the increased amount of the intercalated tetrasubstituted cations present in the interlayer space but also with the water content in these two starting materials.

Intercalation Process

The layered aluminosilates, which contained water in the interlayer space, were probably delaminated in the microwave field; therefore the crystallinity of the materials obtained after intercalation and reassociation improved and the reaction rate of these intercalation processes was increased in orders. The most conclusive evidence of the effect of microwave field on the reactions was the finding of the reaction products in the triturated mixtures of the solid SP and bentonite after short exposition to microwave radiation (Fig. 2).

The products of intercalation of SP are the same after intercalations with 0.2 and 0.02 mol l⁻¹ solutions. The intercalates of SP from solutions less concentrated were obtained only in microwave field. These last mentioned reactions were not interpreted quantitatively. Only very weak lines of intercalate were found after intercalation reaction with diluted (0.02 mol l⁻¹) solutions of AJ by microwave heating.

Most of experiments with microwave field were formerly carried out in commercial microwave oven so that authors could not determine the part of generator output absorbed in the reaction mixture. The device used for our experiments with an exactly defined microwave field could, in the future, help to elucidate the effect of microwave field on the acceleration of reactions. These experiments should be carried out with exactly defined starting materials. Also the effect of water molecules intercalated between the layers of aluminosilicates (as one of the water molecules adsorbed with an assistance of microwave field) is to be studied later.

Interaction between the Intercalated Tetrasubstituted Ammonium Cation and the Negative Layers of Aluminosilicate

The cations are probably held between the layers only by electrostatic forces because the IR spectrum of crystalline N-[1-(ethoxykarbonyl)pentadecyl]trimethylammonium bromide, (SP) does not show any difference from the spectra of the intercalate of SP and bentonite obtained in microwave field (Fig. 1). This means that bentonite serves as an ion exchanger, however, the hydronium ion cannot be used for regeneration.

Very large intercalated cations fundamentally increase the interlayer distances

(Table I). Values marked d_i indicate not only the amount of intercalated cation and its packing between the layers but in our case also the amount and packing of water molecules which remained in bentonite after drying at the temperature below 100 °C. These water molecules are expected to remain in the interlayer space during the ion exchange. It is possible to state that the highest values of the interlayer distance d_i in the intercalates obtained in microwave field are connected with the highest content of tetrasubstituted ammonium cation. The greater interlayer distances for intercalates of SP (in comparison with AJ) are certainly connected with the presence of higher amount of the intercalated cation between the layers of the aluminosilicate. It is not clear whether the lower content of AJ in the intercalates is connected with a smaller ability of the cation of this compound to replace small metal cations of bentonite or with experimental difficulties during the intercalation process (AJ distills with steam). A more effective course of the intercalation reaction (i.e. a higher content of the cation of AJ in the intercalate) for non-dried bentonite could be explained by the larger interlayer distance in the starting non dried material. This fact supports the idea that the less effective course of intercalation of AJ is given by the smaller ability of the cation of AJ to intercalate.

The drying process of bentonites can be followed by the DTA and DTG. The values in the column TG show how the pore water and the water chemically bonded, which remain in non-intercalated bentonite after drying, are gradually released at temperature higher than 100 °C. The total weight decrease (column TG) corresponds sufficiently to the sum of the amount of the cation (GA) and chemically bonded water which is released above 100 °C. A higher content of water which is gradually released from bentonite KERAMOST could be explained either by the presence of hydrated cations of transition metals (impurities) or by the presence of water chemically bonded (hydrogen bond) to oxygen atoms on the surface of bentonite.

Conclusion

Intercalation reactions of large tetrasubstituted ammonium cations with layered aluminosilicate present in bentonite proceed via ion-exchange, and the amount of the intercalated cation in the product of the reaction with SP corresponds to about 29 % wt. The products obtained by the interaction of bentonites with AJ contained about 20 % wt. The intercalation process is strongly accelerated by microwave heating.

The study of the interaction of bentonites with tetrasubstituted ammonium cations should serve for a further research of potential exploitation of these natural materials for sewage treatment.

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