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ADSORPTION OF LIQUID MIXTURES ON HYDROPHILIC AND ORGANOPHILIC KAOLINITE

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ABSTRACT

Results relating to selective sorption from methanol-benzene mixtures show that methanol is adsorbed preferentially on the original polar kaolinite and that an excess isotherm of type II is obtained. If the surface of the kaolinite is modified by alcohol treatment or is covered to various extents by HDP cations, excess isotherms of type IV results. The extent of surface modification can be characterized by the azeotropic composition of adsorption, x_1^a.

INTRODUCTION

Since kaolinite is a non-swelling clay mineral, molecules adsorbed on its surface can be bound only on the external surface, but cannot penetrate between the layers. To determine the specific surface areas of kaolinites, nitrogen and water vapour are used. Examinations of adsorption from solutions reveals that kaolinite with a polar surface primarily adsorbs polar molecules. However, if its surface is modified, the adsorption of apolar molecules may become favoured. The study of selective liquid adsorption on the surface of kaolinite means essentially determination of the adsorption excess isotherms for binary mixtures. Conclusions can be drawn from the adsorption excess isotherm with regard to the mosaic structure and surface heterogeneity of the mineral in the case of a given liquid mixture. From the value of the adsorption capacity, the specific surface of the adsorbent can be determined. In the knowledge of the adsorption capacities of liquid mixtures, it can be decided whether the disaggregation of kaolinite takes place when various liquid-pairs are applied.

The aim of the present work was to determine the adsorption properties of hydrophilic kaolinite in various liquid mixtures and, in addition, to study the mosaic structure and the surface heterogeneity of kaolinite with a modified (organophilic) surface.

MATERIALS AND METHODS

The $d \leqq 2\,\mu m$ fine fraction of kaolinite was separated from Sedlec (Zettlitz) kaolin by peptization with sodium carbonate and sedimentation. The alkaline kaolin suspension was then dialyzed to pH 6.5 to remove the excess electrolyte from the sample. The suspension was next evaporated, and the residue was dried at 378 K and sieved through a 200 mesh. The resulting kaolinite gave characteristic reflexions on X-ray diffraction examination and proved to be adequately pure for adsorption measurements.

Organophilic products were produced by ion exchange with hexadecylpyridinium chloride. On the action of the cationic tenside the suspension coagulated rapidly.

The hexadecylpyridinium kaolinite (HDP kaolinite) was dried and, in order to separate the excess tenside, extracted with methanol for 50 hours. By this procedure HDP kaolinite was produced with three different organophilicities, i. e. 2.4, 3.6 and 4.8 mequ/100 g.

The adsorption of liquid mixtures was examined in benzene — n-heptane and methanol — benzene at 298±0.5 K. The concentration change resulted by selective liquid sorption was determined with a Zeiss liquid-interferometer. The specific excess adsorption of the mixtures (n_1^σ) was calculated from the following equation:

$$n_1^\sigma = \frac{N_o}{m}(x_{1,0}-x_1) = n_o \Delta x_1$$

where N_0 is the total amount of the liquid mixture (in mmole), m is the mass of the adsorbent, $x_{1,0}$ is the mole fraction of component 1 before adsorption and x_1 is the equilibrium fraction in the homogeneous liquid phase.

The specific surface areas of the adsorbents were determined on the basis of the B. E. T. equation, by nitrogen-adsorption, too.

RESULTS AND DISCUSSION

The type I excess isotherms $n_1^\sigma = f(x_1)$ determined on kaolinite and its organophilic derivatives in benzene (1)-n-heptane (2) mixtures are demonstrated in *Fig. 1*. Adsorption capacities were determined with the aid of the linear individual isotherm method from the function $n_1^\sigma/x_2 = f(x_1)$ (1). Equivalent specific surface areas obtained from the adsorption capacities agree very well with the B. E. T. surface areas (Table 1) There is no essential difference between the original kaolinite and the organophilic

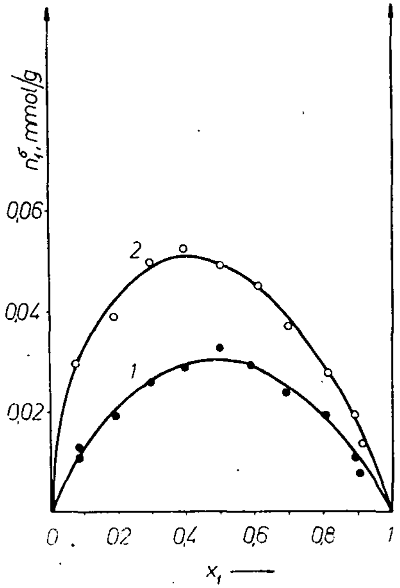

Fig. 1. Benzene(1)—n-heptane(2) excess isotherms on kaolinites. 1. original, 2. HDP-kaolinite III

TABLE 1

Results of analysis of excess isotherms

Adsorbent	HDP cation meq./100 g	$n^s_{1.0}$ mmole g^{-1}	a_s, equ. $m^2\ g^{-1}$	x_1^a	Isotherm type	a_s (B. E. T.) $m^2\ g^{-1}$
liquid mixture: benzene(1) — n-heptane(2)						
kaolinite	0	0.10	18	—	I	16.2
kaolinite (treated with methanol)	0	0.12	21	—	I	21.2
HDP kaolinite III	4.8	0.16	28	—	I	24.2
liquid mixture: methanol(1) — benzene(2)						
kaolinite	0	1.05	100	—	II	16.0
kaolinite (treated with methanol)	0	1.70	162	0.59	IV	21.2
HDP kaolinite I	2.4	1.77	168	0.52	IV	—
HDP kaolinite II	3.6	1.83	174	0.46	IV	—
HDP kaolinite III	4.8	2.07	179	0.40	IV	24.2

products. On this basis the conclusion is that the adsorption of benzene from benzene — n-heptane mixtures takes place on the external surface.

The excess isotherm determined for methanol(1)-benzene(2) mixtures belongs to type II, which indicates that methanol is preferentially adsorbed on the polar surface *(Fig. 2)*. If kaolin is pre-treated with methanol in a Soxhlet-extractor for 50 hours, the course of the excess isotherm changes and an isotherm of type IV results. This change indicates that the interfacial adsorption phase the adsorption of benzene is appreciable beside that of methanol. To explain the phenomenon it must be considered that the Si-OH groups on the edges of the kaolinite layers and the Al-OH groups of the basal planes are capable of esterification during the 50-hour methanol treatment (2). Such a chemisorption effect might result in "loosening" of the compact hydrogen-bonded structure of the kaolinite and might make the layers stip on top one an other. This is indicated by the adsorption capacities, since the adsorption capacity increases compared to the dialyzed kaolinite (Table 1). The adsorption capacities of these liquid mixtures are essentially greater than in the case of a benzene — n-heptane mixture-pair. Accordingly, it can be concluded that kaolinite is capable of partial disaggregation in methanol — benzene mixtures, due to the strong adsorption of the methanol. This disaggregation is of only a slight extent, since the specific surface area derived from the excess isotherms by the SCHAY—NAGY graphical extrapolation method (3,4) is 100—160 m^2/g, i. e. 10—15% of the total basal surface area (1070 m^2/g).

The course of the excess isotherms determined on the HDP kaolinites with the three different organophilicities indicate clearly the influence of the surface modification due to the cationic tenside *(Fig. 3)*. If the surface is previously covered with HDP cations, the adsorption of the benzene becomes increasingly favoured, which means that the azeotropic composition of adsorption (x_1^a) shifts towards smaller mole fractions. Thus, methanol molecules adsorb on the free polar surface on organophilic kaolinite, while benzene is bound on a hydrophobic surface covered with HDP cations.

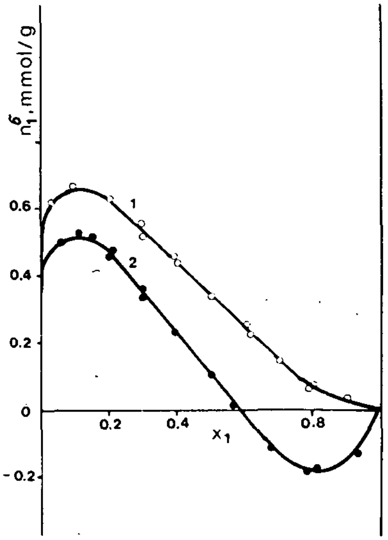

Fig. 2. Methanol(1) — benzene(2) excess isotherms on kaolinites. 1. original, 2. kaolinite treated with methanol

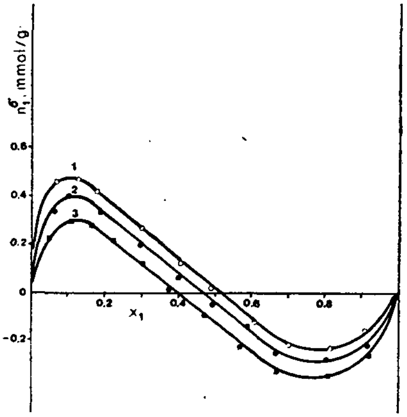

Fig. 3. Methanol(1) — benzene(2) excess isotherms on organophilic kaolinites. 1. HDP-kaolinite I, 2. HDP-kaolinite II, 3. HDP-kaolinite III

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