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ORIGINAL CONTRIBUTION

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Adsorption of nitrobenzene and *n*-pentanol from aqueous solution on hydrophilic and hydrophobic clay minerals

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Abstract The sorption of nitrobenzene and *n*-pentanol from dilute aqueous solution on swelling clay minerals and their organophilized derivatives (organo clays) was studied. Adsorption excess isotherms were obtained by the immersion method. The basal spacings of the clay minerals were determined by X-ray diffraction measurements. By combining these two independent methods, composition and structure of the interlamellar space could be calculated. On the hydrophilic surface of montmorillonite negative adsorption of the organic component was observed at low molar fractions of nitrobenzene or pentanol, i.e., water was preferentially adsorbed. On organophilized montmorillonite and vermiculite adsorption of nitrobenzene and pentanol was positive over the whole range of liquid composition. The amount of interlamellar alkyl chains which is determined by the surface charge of clay mineral inversely affected the adsorption of both solutes.

Key words Adsorption of organic substances – clay minerals – intercalation – surfactant

Introduction

The adsorption of inorganic and organic components from dilute solutions has been the subject of many publications. Practical applications, the range of which has considerably widened in the past few years (environmental protection, sewage purification, tertiary oil recovery, separation technologies, etc.) necessitate a more detailed investigations in this field.

Adsorption of organic components from aqueous solutions on clay minerals has been studied for a few cases only [1–3]. More attention has been given to the sorption processes on the so-called organoclays [4–7]. Recently, environmental research has become concerned with the sorption of organic pollutants on soil minerals (especially on clay minerals) and on their hydrophobized derivatives [8, 9].

An interesting field of adsorption experiments is the adsorption from binary solutions. Typical features of these processes were calculated by Dékány, Lagaly and coworkers [10–18]. Adsorption studies with binary liquid mixtures of toxic components are required to understand the adsorption properties of clay minerals used for environmental protection. As examples, we report the adsorption of aqueous solutions of *n*-pentanol and nitrobenzene on sodium and calcium montmorillonite, hexadecylpyridinium montmorillonite and octadecylammonium vermiculite.

Theoretical part

Adsorption excess isotherms

The molar reduced excess amount of component 1 per unit mass of the solid ($n_1^{\sigma(n)}$) is [10, 11]:

$$n_1^{\sigma(n)} = n^0(x_1^0 - x_1)/m = n^0 \Delta x_1/m \quad (1)$$

where n^0 is the total number of moles of the liquid, x_1^0 and x_1 are the initial and equilibrium molar fractions of component 1, and m is the mass of the adsorbent. For the adsorption of binary liquid mixtures, the Ostwald-de-Izaguirre equation relates the adsorption excess amount and the real amount adsorbed [10, 11]:

$$n_1^{\sigma(n)} = n_1^s x_2 - n_2^s x_1 = n_1^s - n^s x_1 = n^s(x_1^s - x_1) \qquad (2)$$

where $n^s = n_1^s + n_2^s$ is the material content of the adsorption layer and $x_1^s = (1 - x_2^s) = n_1^s/n^s$ is the molar fraction of component 1 in this layer. For preferential adsorption of solute (1) over solvent (2) in diluted solutions, the excess amount $n_1^{\sigma(n)}$ is approximately equal to the real amount adsorbed n_1^s [10, 11].

In the case of dilute solutions and for preferential adsorption of the solute, the volume of the adsorbed solute is approximately [12–14]:

$$V_1^s = n_1^s V_{m,1} \approx n_1^{\sigma(n)} V_{m,1} \, , \qquad (3)$$

where $V_{m,1}$ is the molar volume of the solute.

In the case of swelling layer silicates (e.g., vermiculites and montmorillonites) the internal surface area is large compared to the external surface area (factor ≥ 10 for powderd vermiculites). It is reasonable to relate the adsorbed phase to the free interlamellar space.

The interlayer composition can be expressed by the volume fractions:

$$\phi_1^s = V_1^s/(V_1^s + V_2^s) = V_1^s/(V_{\mathrm{int}} - V_{\mathrm{alk}}) \, , \qquad (4)$$

where V_i^s denotes the volume of component i ($i = 1$, solute; $i = 2$, solvent) in the interlamellar space.

Since $V_i^s = V_{\mathrm{alk}}$ is known (see below, Eq. (5)), ϕ_1^s and ϕ_{alk} can be calculated from the adsorption data and the basal spacing.

The interlayer volume

The volume of the alkyl chains per formula unit ($[\mathrm{Si, Al}]_4\mathrm{O}_{10}$) of the silicate framework is

$$V_{\mathrm{alk}} = 0.205[0.127(n_{\mathrm{C-C}} + n_{\mathrm{C-N}}) + 0.28]\xi \quad (\mathrm{nm}^3/[\mathrm{Si, Al}]_4\mathrm{O}_{10}) \qquad (5)$$

for alkylammonium vermiculites. The product in brackets gives the length of the alkyl chains anchored at the surface. $n_{\mathrm{C-C}}$ and $n_{\mathrm{C-N}}$ denote the number of carbon–carbon and carbon–nitrogen bonds. The cross-sectional area of *all-trans* aliphatic hydrocarbon chain is taken as 0.205 nm^2. The charge per formula unit (layer charge, $\xi = 0.71$ for vermiculite and 0.32 for montmorillonite) was calculated from the concentration of grafted alkyl chains determined by thermogravimetric analysis.

The interlamellar volume between two opposite layers (per formula unit) is obtained from the basal spacing (d_L):

$$V_{\mathrm{int}} = 0.495(d_L - 0.94)/2 \quad (\mathrm{nm}^3/[\mathrm{Si, Al}]_4\mathrm{O}_{10}] \, . \qquad (6)$$

The thickness of the silicate layer is 0.94 nm and the surface area of two $[\mathrm{Si, Al}]_4\mathrm{O}_{10}$ units (equivalent with the unit cell) is 0.495 nm^2. The "free" interlayer volume is $V_{\mathrm{int}} - V_{\mathrm{alk}}$.

Materials and methods

Materials

Binary liquid mixtures

Two systems of partially miscible liquids were prepared:

1) *n*-pentanol(1) – water(2)
2) nitrobenzene(1) – water(2).

To prepare a saturated solution of *n*-pentanol (Reanal, Hungary) in water, the components were mixed, shaken and allowed to stand in a separating funnel, thermostated at 25 ± 0.1 °C (saturation time 48 h). The lower phase rich in water was then separated and serially diluted for use in adsorption measurements.

Aqueous solutions of nitrobenzene were prepared from nitrobenzene (Carlo Erba, Italy) and distilled water. The saturated solution was prepared by mechanical shaking in dark bottles at 20 ± 0.5 °C (saturation time 24 h). The upper, less dense aqueous phase was used for serial dilution.

Adsorbents

The two series of dilute solutions were examined on four kinds of adsorbents: *n*-hexadecylpyridinium montmorillonite (HDP-montmorillonite); *n*-octadecylammonium vermiculite (C_{18}-vermiculite); Na-montmorillonite; Ca-montmorillonite.

The raw vermiculite originating from South Africa was converted to Li-vermiculite (exchanged by 1 M LiCl solution), which was then used for the preparation of the organo complex with octadecylammonium chloride solutions for 1 month. 0.05 M octadecylammonium chloride in 20% (v/v) ethanol–water mixture was added to Li-vermiculite at 50 °C. The amount of cationic surfactant was twice the equivalent data. After washing the organophilic product with 1:1 ethanol–water mixture and in a Soxhlet extractor for 5 days, the cation exchange capacity of vermiculite was 1.97 meq/g, determined by thermoanalysis.

The fine fraction of montmorillonite ($d \leq 2\ \mu$m) was obtained from Ca-montmorillonite (Süd-Chemie AG, Germany) by peptization and ion exchange with sodium chloride. The cation exchange capacity of the sample was 0.851 meq/g, determined by thermoanalytic experiments.

The hydrophobic derivative of montmorillonite was prepared by a 48-h ion exchange reaction at 65 °C with an amount of 0.1 M aqueous solution of hexadecylpyridinium chloride corresponding to 1.5 times the cation exchange capacity.

The hexadecylpyridinium montmorillonite was washed with an ethanol–water mixture and subsequently extracted by a 1 : 1 mixture of isopropanol and water for 48 h in a Soxhlet apparatus. The samples were finally dried and ground.

Determination of adsorption excess isotherms

Adsorption excess isotherms were determined by the immersion method. Known volumes (6–9 cm^3) of the binary solutions were added to 0.1–0.5 g of the adsorbents. The dispersions were stored at 25 ± 0.5 °C with occasional shaking. Solutions containing nitrobenzene were stored in the dark in order to prevent photodegradation. After equilibration the samples were centrifuged and the concentration of the supernatant and the original solution was determined by a Zeiss liquid interferometer. The $n_1^{\sigma(n)}$ excess amounts were presented as the function of the relative equilibrium mole fraction $x_{1,r}$ ($x_{r,r} = x_1/x_{1,\mathrm{sat}}$), where $x_{1,\mathrm{sat}}$ is the saturation concentration calculated from solubility data [15].

XRD investigations

X-ray diffraction measurements were carried out in a Philips x-ray diffractometer (PW 1830 generator, PW 1820 goniometer), with CuK-α radiation ($\lambda = 1.5418$ Å) at $2\Theta = 1$–10°. In order to prevent the evaporation of the liquids, the adsorbent in contact with the equilibrium solution was coated by a Mylar foil. The basal spacing (d_L) was calculated from the (0 0 1) reflexion.

Results and discussion

Hydrophobic clay minerals

Adsorption excess isotherms of *n*-pentanol–water and nitrobenzene–water on hexadecylpyridinium montmorillonite and octadecylammonium vermiculite are presented in Figs. 1a and b. Adsorption of the solutes is positive in the entire range of composition ($x_{1,r} = 0$–1), i.e., the adsorption of *n*-pentanol and nitrobenzene is preferential. The adsorption excess of nitrobenzene increases steeply at $x_{1,r} = 0.3$–0.4 and then reaches saturation. The adsorption of *n*-pentanol continuously increases with concentration in the whole range.

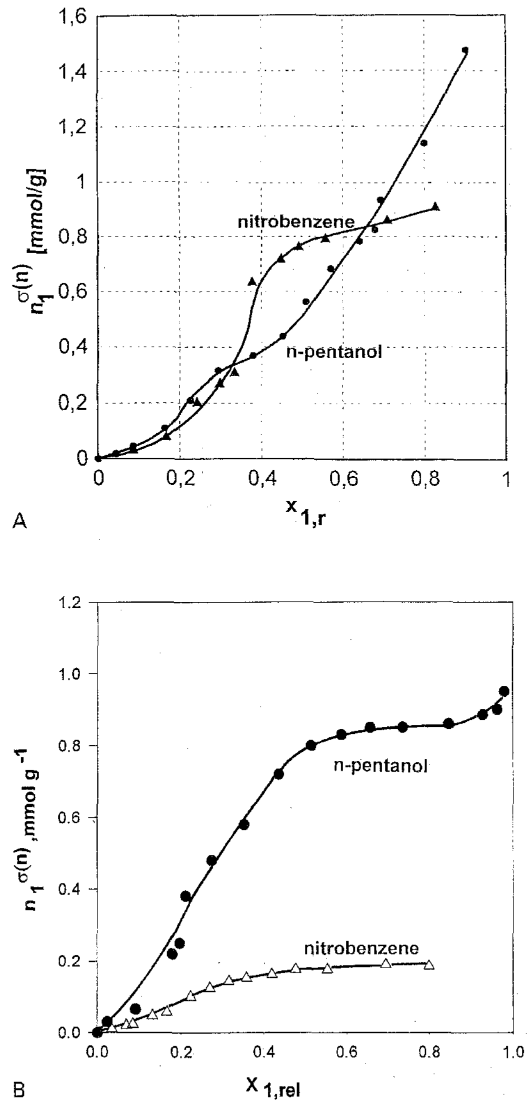


Fig. 1A Adsorption excess isotherms of *n*-pentanol and nitrobenzene from water on hexadecylpyridinium montmorillonite at 25 °C ($x_{1,r}$ = relative molar fraction of pentanol or nitrobenzene); **B** Adsorption excess isotherms of *n*-pentanol and nitrobenzene from water on octadecylammonium vermiculite at 25 °C ($x_{1,r}$ = molar fraction of pentanol or nitrobenzene)

On octadecylammonium vermiculite (Fig. 1b) the adsorption of the organic component is also preferential in the entire concentration range and reaches saturation at higher concentrations. Adsorption excesses are lower on vermiculite than on montmorillonite. The reason is the

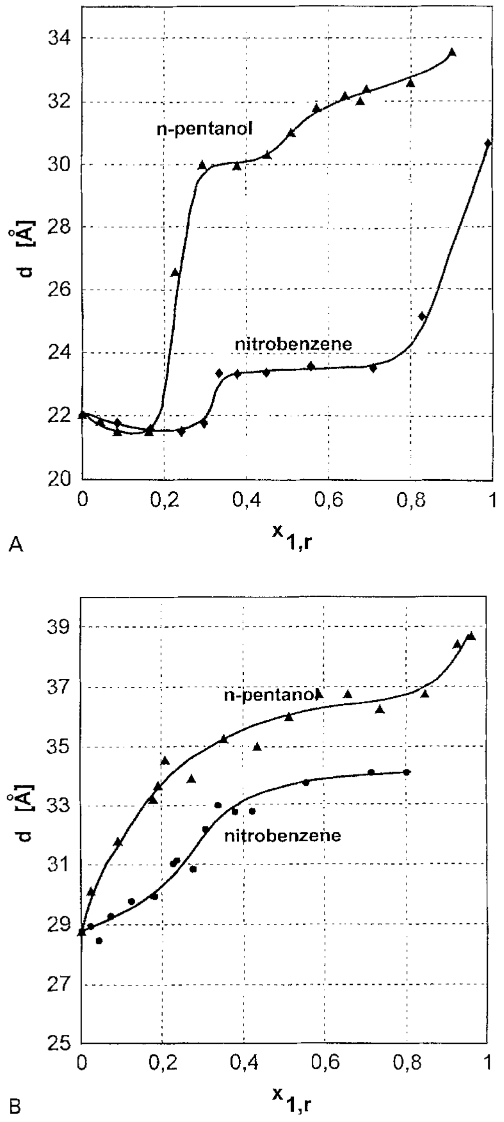


Fig. 2A Basal spacings of hexadecylpyridinium montmorillonite in aqueous solutions of *n*-pentanol and nitrobenzene at 25 °C; **B** Basal spacings of octadecylammonium vermiculite in aqueous solutions of *n*-pentanol and nitrobenzene at 25 °C

higher alkyl chain density on the surface of vermiculite. There is less space available for adsorption of *n*-pentanol or nitrobenzene. The saturation character of the isotherms is also a consequence of the high alkyl chain density. The amount of the organic component in the interlayer space cannot increase beyond a saturation level. In the case of *n*-pentanol–water and HDP-montmorillonite with smaller alkyl chain volume sufficient space remains accessible for pentanol.

Figures 2a and b show the basal spacings as a function of equilibrium composition. The basal spacing of the dried adsorbents and in the pure organic solvents are reported in Table 1.

A steep increase in basal spacing of HDP-montmorillonite (Fig. 2a) was observed at $x_{1,r} = 0.8$ for nitrobenzene and at about $x_{1,r} = 0.25$ for pentanol. Due to the smaller adsorption excess, the increase of the basal spacing is smaller in the nitrobenzene–water system than in *n*-pentanol–water. In all cases the changes of the basal spacing with $x_{1,r}$ are not exactly parallel with the adsorption isotherms.

The orientation of the interlamellar alkyl chains can be deduced on the basis of refs. [16–18]. If, on C_{18}-vermiculite, the length of the alkyl chain (l) is 25.6 Å and its angle of inclination is 55°, then basal spacing (d_L) equals $9.4 + l \times \sin 55°$, that is 30.4 Å and 51.4 Å for a single (Fig. 6a) and double layer, respectively. A monolayer of perpendicular chains gives a theoretical spacing of 34.1 Å. For HDP-montmorillonite, the length of the C_{16}-chain is $l = 23.1$ Å, its angle of inclination – due to the planar orientation of the pyridine ring – is 35°. The calculated values of d_L are $9.6 + l \times \sin 35°$, that is 22.8 and 36.1 Å for single and double layers of alkyl chains. It is evident from the data in Table 1 and Figs. 2a and b that the interlamellar adsorption of water and organic molecules in vermiculite causes a continuous expansion of the interlayer space but the fully expanded bilayer structure is not attained, the structure may be described as expanded monolayer for water–pentanol (Fig. 6b). The maximal basal spacing for water–nitrobenzene corresponds to monolayers of perpendicular chains. The strong increase of basal spacings of hexadecylpyridinium montmorillonite reveals the transition into compressed bilayer structures (Fig. 6c). These structures were discussed by Lagaly and Witter [16].

Hydrophilic clay minerals

The adsorption of organic components is negative on the first section of the adsorption excess isotherm of hydrophilic montmorillonites (Figs. 3a and b), i.e., water is preferably adsorbed. The isotherms reach an azeotropic point ($n_1^{\sigma(n)} = 0$ i.e., $x_1^s = x_1$) at relative molar fractions of approximately 0.9 for *n*-pentanol–water/Na-montmorillonite, 0.55 for *n*-pentanol–water/Ca montmorillonite and 0.45 for nitrobenzene–water/Ca-montmorillonite. The adsorption of pentanol or nitrobenzene at higher molar fractions is then positive. The reason is the distinct surface hydrophilicity of the clay minerals due to the hydration of the interlayer cations. Only higher concentrations of *n*-pentanol can displace water from the interlayer space.

The basal spacing in Na-montmorillonite is indefinite because the crystals delaminate completely. Even small amounts of nitrobenzene and *n*-pentanol reduce the

Table 1 Basal spacings of clays and their organo complexes in dry state and in suspension of organic pollutants

Adsorbent	d_L (Å) dry	d_L (Å) in water	d_L (Å) in *n*-pentanol	d_L (Å) in nitrobenzene
C_{18}-verm.	27.70	28.76	36.88	33.43
HDPmontm.	17.67	22.03	29.60	46.20
Na-montm.	12.34	14.26	13.41	14.79
Ca-montm.	14.34	19.01	18.17	15.01

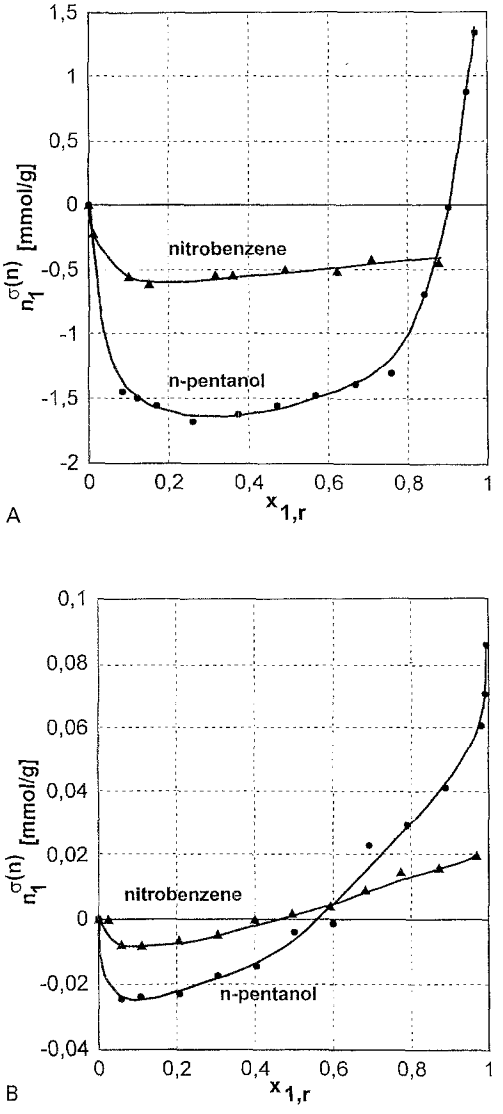


Fig. 3A Adsorption excess isotherms of *n*-pentanol and nitrobenzene from water on Na-montmorillonite at 25 °C; **B** Adsorption excess isotherms of *n*-pentanol and nitrobenzene from water on Ca-montmorillonite at 25 °C

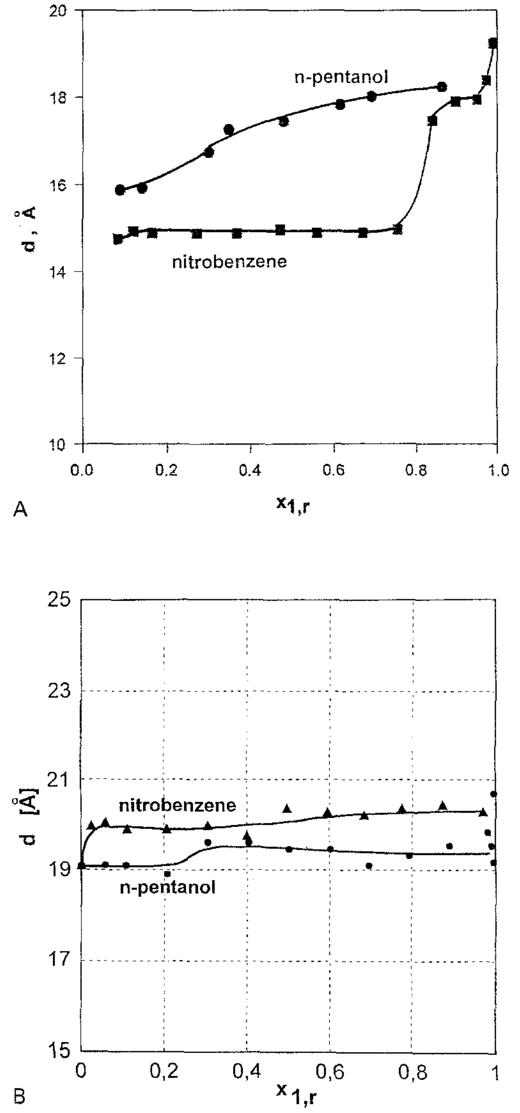


Fig. 4A Basal spacings of Na-montmorillonite in aqueous solutions of *n*-pentanol and nitrobenzene at 25 °C; **B** Basal spacings of Ca-montmorillonite in aqueous solutions of *n*-pentanol and nitrobenzene at 25 °C

spacing to about 15 Å. The basal spacing in nitrobenzene–water (about 15 Å) remains almost unchanged up to a composition of $x_{1,r} \approx 0.8$ then increases to 19 Å. The basal spacing of Na-montmorilonite in pentanol–water increases slightly but continuously with the equilibrium concentration.

Ca-montmorillonite shows a nearly constant basal spacing of 19–20 Å which corresponds to four water layers (Figs. 4a, b). The strong interaction energy between the calcium ions and the silicate layers impedes penetration of the organic components into the interlayer space.

Interlamellar composition and structure

Aqueous solutions of *n*-pentanol and nitrobenzene are very diluted, and for this reason the adsorption excess of the alcohol, $n_1^{\sigma(n)}$, may be taken as equal to the amount of material actually present in the interfacial layer. The volume of solute in the interlamellar space is calculated on the basis of Eq. (3). The interlamellar space is filled by alkyl chains and the adsorbed components of the solution:

$$V_{\mathrm{int}} \geq V_{\mathrm{alk}} + V_1^s + V_2^s \, . \tag{7}$$

The symbol $\geq$ indicates that in addition to the adsorbed components and the alkyl chains, the interlayer space may contain a certain volume of the so-called "bulk-like" liquid (V^b) of the same composition as in the equilibrium solution [17, 18]. The molecules of this liquid do not belong to the adsorption phase. V^b may be dependent on the composition of the equilibrium solution. Thus

$$V_{\mathrm{int}} = V_{\mathrm{alk}} + V_1^s + V_2^s + V^b \, . \tag{8}$$

Division of this equation by V_{int} yields the composition of the interlamellar space expressed in volume fractions:

$$\Phi_{\mathrm{alk}} + \Phi_1^s + \Phi_2^s + \Phi^b = 1 \, . \tag{9}$$

For diluted solutions, the terms Φ_2^s and Φ^b can be combined to $\Phi_2^{s,b}$. For preferential adsorption of component 1 (nitrobenzene or pentanol on the organic derivatives) the bulk-like liquid is composed mainly of component 2 (water). Thus Eq. (9) becomes:

$$\Phi_{\mathrm{alk}} + \Phi_1^s + \Phi_2^{s,b} = 1 \, . \tag{10}$$

As Φ_{alk} and Φ_1^s are known, $\Phi_2^{s,b}$ and therefore, $V_2^{s,b}$ and $n_2^{s,b}$ can be calculated:

$$\Phi_2^{s,b} V_{\mathrm{int}} = V_2^{s,b} = n_2^{s,b} V_{\mathrm{m},2} \, .$$

This gives important information on the interlamellar adsorption of water. It is evident from Figs. 5a–c how significantly the interfacial layer is enriched in *n*-pentanol (or nitrobenzene): the volume fraction Φ_1 of the bulk phase is by one, or in the case of the nitrobenzene–water even by more than two orders of magnitude lower.

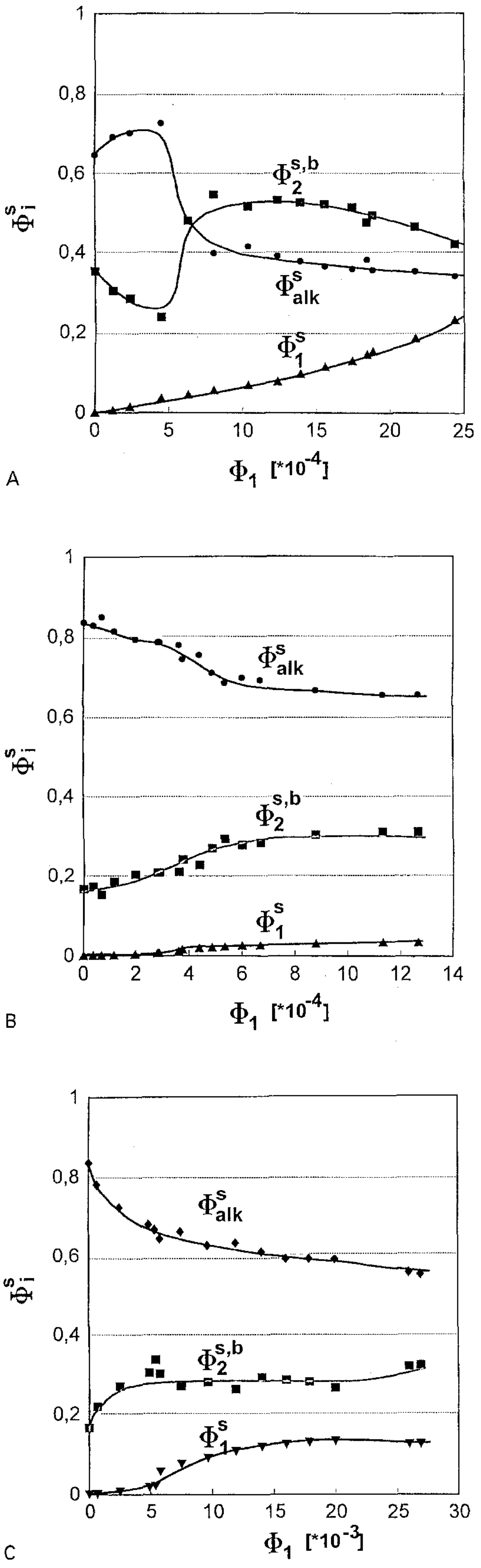
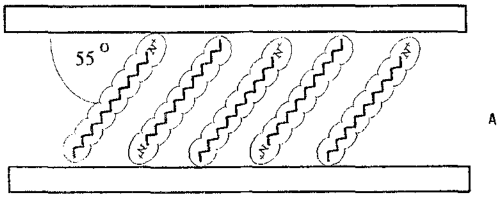
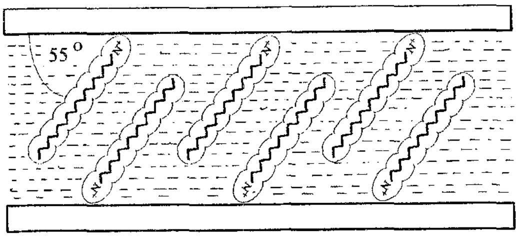


Fig. 5A Composition of the interlamellar space of the hexadecylpyridinium montmorillonite in *n*-pentanol(1)–water(2), represented by $\Phi_i^s = f(\Phi_1)$; **B** Composition of the interlamellar space of the octadecylammonium vermiculite in nitrobenzene(1)–water(2), represented by $\Phi_i^s = f(\Phi_1)$; **C** Composition of the interlamellar space of the octadecylammonium vermiculite in *n*-pentanol(1)–water(2), represented by $\Phi_i^s = f(\Phi_1)$



In water



In aqueous solutions of n-pentanol

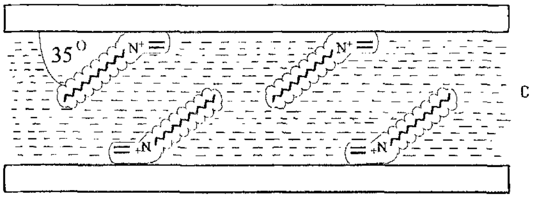


Fig. 6A Orientation of octadecyl chains in vermiculite (idealized structure, calculated basal spacing 30.4 Å, observed in water about 29 Å); **B** Expanded monolayer structure in octadecylammonium vermiculite (maximum basal spacings observed in *n*-pentanol–water: 39 Å, in nitrobenzene–water: 34 Å); **C** Compressed bilayer structure in hexadecylpyridinium montmorillonite (maximum basal spacings observed in *n*-pentanol–water: 33 Å, in nitrobenzene–water: 31 Å)

Summary

The excess isotherms for *n*-pentanol–water and nitrobenzene–water are similar for both adsorbents even if the volume fractions of nitrobenzene in water are smaller by a factor of 20. Positive adsorption of nitrobenzene and *n*-pentanol is observed in both organic derivatives in the whole range of composition (up to $x_{1,r} = 1$). On montmorillonite water was preferentially adsorbed at the initial region of the isotherm. Only at higher relative molar fractions of the organic component adsorption of the dissolved material becomes positive. The saturation type isotherms of octadecylammonium vermiculite, a material with a high surface charge density exhibits smaller excesses than those of hexadecylpyridinium montmorillonite with a lower surface charge density. Na-montmorillonite shows a strongly preferential adsorption of water. The surface excess values for Ca-montmorillonite are significantly smaller. The isotherms of *n*-pentanol–water display larger excesses than those for nitrobenzene–water, which is a consequence of the considerably different solubilities.

The results of x-ray diffraction measurements are in good agreement with those of adsorption experiments: whenever a region of the isotherm indicates an increase in the excess of the organic component, an increase in basal spacing is also observed. An exception is Ca-montmorillonite where the divalent cations held the spacing at 19–20 Å.

The interlamellar composition, expressed in molar fractions, is calculated from the adsorption excesses and basal spacings. A higher amount of interlamellar alkyl chains decreases the adsorption of organic molecules. The higher densities of alkyl chains reduces the expansibility of the layers by the adsorbed liquids (11 Å for hexadecylpyridinium montmorillonite and 9 Å for octadecylammonium vermiculite in *n*-pentanol).

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