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# Adsorption of 1-butanol from water on modified silicate surfaces

I. Regdon, Z. Király, I. Dékány, and G. Lagaly[1])

Department of Colloid Chemistry, Attila József University, Szeged, Hungary
[1]) Institute of Inorganic Chemistry, University Kiel, Kiel, FRG

*Abstract*: The structure and the sorption properties of partially hydrophobized silicates (dodecylammonium and dodecyldiammonium vermiculites) have been investigated in aqueous solutions of 1-butanol. The alcohol is preferentially adsorbed on the surface. The interlayer composition is calculated from adsorption and x-ray diffraction data. In air-dried state the organic cations lie flat on the interlamellar surface. In aqueous butanol solutions, the basal spacing of dodecylammonium vermiculite gradually increases with the extent of butanol adsorption because the chains increasingly point away from the surface. The basal spacing of dodecyldiammonium vermiculite is virtually independent on the interlayer composition because the expansion of the interlayer space is sterically restricted and a relatively rigid structure is formed. The enthalpy of the displacement of water by 1-butanol has been determined by flow sorption microcalorimetry. The displacement process is endothermic.

*Key words*: Adsorption from solution – alkylammonium ions – clay minerals – enthalpy of displacement – solid/liquid interface – surface modification – vermiculite

## Introduction

In our previous studies on hydrophobized montmorillonites and vermiculites, attention was focused on the adsorption and immersional wetting properties in completely miscible liquids [1–6]. Stul et al. reported adsorption data and basal spacings of several organo-montmorillonites in dilute aqueous solutions of 1-butanol, 1-hexanol, and 1-octanol [7–9]. Only a few papers have been published that combine adsorption and calorimetric data when the liquid components have a limited mutual solubility [10–12]. In this paper, aqueous solutions of 1-butanol have been selected as the liquid medium to get some insight into the sorption and wetting properties of partially miscible liquids on hydrophobized silicates. The silicate is vermiculite and it is modified by exchanging dodecylammonium ($DDAm^+$) and dodecyldiammonium ($DD(Am)_2^{2+}$) cations for the inorganic interlayer cations. When these vermiculites are dispersed in the binary liquid mixtures, the liquids penetrate between the layer and the basal spacing increases. The basal spacing is calculated from the (OOl)-reflections in the x-ray powder diagram. The distance between the layers derived from the basal spacing gives quantitative information about the liquid volume between two neighboring silicate layers and also on the possible orientation of the alkyl chains of the organic cations. Combination of the basal spacings with adsorption data reveals the exact interlayer composition.

## Theoretical background

### *X-ray diffraction*

The volume of the alkyl chains per formula unit ($[Si,Al]_4O_{10}$) of the silicate framework is

$$V_{alk} = 0.205[0.127(n_{C-C} + n_{C-N}) + 0.28]\xi \quad (nm^3/[Si, Al]_4O_{10}) \qquad (1a)$$

for alkylammonium vermiculites and

$$V_{\text{alk}} = 0.205[0.127(n_{\text{C-C}} + n_{\text{C-N}})]\xi/2 \quad (\text{nm}^3/[\text{Si, Al}]_4\text{O}_{10}) \tag{1b}$$

for alkyldiammonium vermiculites. The product in the bracket gives the length of the alkyl chains anchored at the surface. $n_{\text{C-C}}$ and $n_{\text{C-N}}$ denote the number of carbon–carbon and carbon–nitrogen bonds. The cross-sectional area of a normal aliphatic hydrocarbon chain is taken as 0.205 nm$^2$. The charge per formula unit (layer charge) $\xi = 0.71$ 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:

$$V_{\text{int}} = 0.495(d_{\text{L}} - 0.94)/2 \quad (\text{nm}^3/[\text{Si, Al}]_4\text{O}_{10}) \,. \tag{2}$$

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

*Adsorption excess isotherms*

The molar reduced excess amount of component 1 per unit mass of the solid ($n_1^{\sigma(n)}$) is [14]:

$$n_1^{\sigma(n)} = n^0(x_1^0 - x_1)/m = n^0 \Delta x_1/m \,, \tag{3}$$

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 [14]:

$$n_1^{\sigma(n)} = n_1^s x_2 - n_2^s x_1 = n_1^s - n^s x_1 = n^s(x_1^s - x_1) \,, \tag{4}$$

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 $n_1^s$ [14].

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

The interlayer composition can be expressed by the volume fractions

$$\phi_i^s = V_i^s/(V_1^s + V_2^s) = V_i^s/(V_{\text{int}} - V_{\text{alk}}) \,, \tag{5}$$

where $V_i^s$ denotes the volume of component $i$ ($i = 1$, solute; $i = 2$, solvent) in the interlamellar space. If the silicate is hydrophobized, the volume fractions in the interlamellar space may also be related to the ternary system:

$$\phi_j^{s,x} = V_j^s/(V_1^s + V_2^s + V_3^s) = V_j^s/V_{\text{int}} \,, \tag{6}$$

where the alkyl chains are considered as the third component ($j = 3$).

In the case of dilute solutions and for preferential adsorption of the solute, the volume of the adsorbed solute is approximately

$$V_1^s = n_1^s V_{\text{m},1} \approx n_1^{\sigma(n)} V_{\text{m},1} \,, \tag{7}$$

where $V_{\text{m},1}$ is the molar volume of the solute. Since $V_3^s = V_{\text{alk}}$ is known (Eq. (1a, b)), $\phi_i^s$ and $\phi_j^{s,x}$ can be calculated from the adsorption data and the basal spacing.

*Flow sorption microcalorimetry*

The enthalpy change for an adsorption–displacement process at the solid/binary liquid interface ($\Delta_d H$) is the difference between the final and initial enthalpy of the system. The driving force of the displacement process is the establishment of a new equilibrium between the bulk and the surface layer when the bulk composition is changed [6, 10, 11, 15]. Formally, the enthalpy of displacement is expressed as a function of the amounts adsorbed and the molar enthalpies [6, 15]:

$$\Delta_d H = \Delta n_1^s h_1^s + \Delta n_2^s h_2^s + \Delta H^{\text{se}} + \Delta H^{\text{e}} + \Delta H_{\text{mix}} \,, \tag{8}$$

where $\Delta n_i^s$ is the decrease or increase of the amount of the $i$-th component in the adsorption layer during the displacement, $h_i^s$ is the molar enthalpy of the pure component $i$ in the layer, $\Delta H^{\text{se}}$ and $\Delta H^{\text{e}}$ are the excess enthalpies of the adsorption layer and bulk solution due to deviation from the ideal behavior. The term $\Delta H_{\text{mix}}$ is attributed to the mixing of the replaced solution with the replacing solution (non-plug flow). It is measured in a separate experiment [6, 15].

The integral enthalpy of displacement is obtained by summation of the values $\Delta_d H - \Delta H_{\text{mix}}$ (from Eq. (8)) over the desired composition range

$$\Delta_{21} H = \sum_{x_1=0}^{x_1} (\Delta_d H - \Delta H_{\text{mix}}) \,. \tag{9}$$

$\Delta H_{\text{mix}}$ was found to be negligible for dilute aqueous solutions of 1-butanol, provided small concentration steps are chosen [16].

## Materials and methods

### *Organo-vermiculites*

Vermiculite from South-Africa (cation exchange capacity: 1.97 mmol $g^{-1}$; specific surface area (basal planes only) from crystal geometry: 788 $m^2 g^{-1}$) was rendered organophilic by exchanging dodecylammonium and dodecyldiammonium ions for the inorganic interlayer cations (67 °C, 1 month, 0.1 M surfactant in 1.5-fold excess related to the CEC, pH = 4.5). The organo-derivatives were washed several times with alcohol-water mixtures = 1:1. This purification procedure was followed by Soxhlet-extraction in a mixture of *i*-propanol-water = 1:1 for 48 h. The vermiculites were dried in a vacuum dessicator overnight at 67 °C before use.

### *Aqueous butanol solutions*

Double distilled water was saturated with 1-butanol (Reanal, Hungary) in a thermostatted separating funnel at 25 ± 0.05 °C. After equilibration the aqueous phase was diluted with water to the desired butanol concentration. Saturation corresponds to a molar fraction $x_{\text{sat}} = 0.01880$ at 25 °C. The experimental results are presented on a relative concentration scale: $x_{1,r} = x_1/x_{\text{sat}}$. The volume fractions $\phi_{1,r}$ are also expressed as relative values.

### *Adsorption measurements*

Volumes of 6 $cm^3$ of butanol(1)-water(2) solutions were brought into contact with about 0.5 g of vermiculite. After equilibration (2 days, 25 ± 0.1 °C) the change in the composition of the bulk liquid phase ($\Delta x_1$) was analyzed with a Zeiss liquid interferometer.

### *Flow sorption microcalorimetry*

The integral enthalpy of displacement was determined in a LKB-2107 flow sorption microcalorimeter at 25 ± 0.02 °C. The flow rate of the butanol solutions was about 24 $cm^3 h^{-1}$.

### *X-ray diffractometry*

The basal spacing of the vermiculites in contact with the butanol/water mixtures were measured with a Philips PW-1830 x-ray diffractometer (Cu$K\alpha$ radiation, $1° \leq 2\theta \leq 10°$).

## Results and discussion

The surface modification by cation exchange renders the hydrophilic vermiculite hydrophobic. The adsorption excess isotherms of butanol(1)-water(2) on dodecylammonium ($DDAm^+$) and dodecyldiammonium ($DD(Am)_2^{2+}$) vermiculite are shown in Fig. 1. The initial slope of the isotherm for $DD(Am)_2^{2+}$-vermiculite is significantly smaller than for $DDAm^+$-vermiculite, indicating a lower adsorption affinity for butanol. The equilibrium diagrams of the adsorption (given in

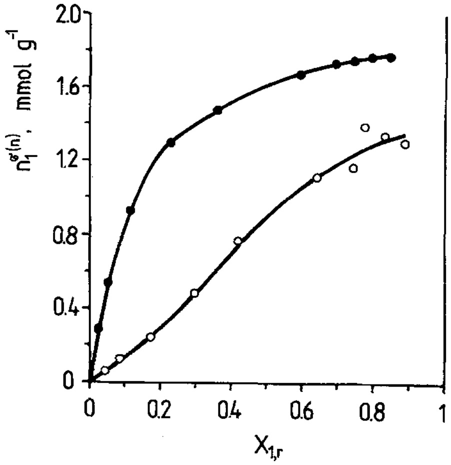

Fig. 1. Adsorption excess isotherms of 1-butanol(1) from water(2) on (●) dodecylammonium vermiculite and (○) dodecyldiammonium vermiculite at 25 °C

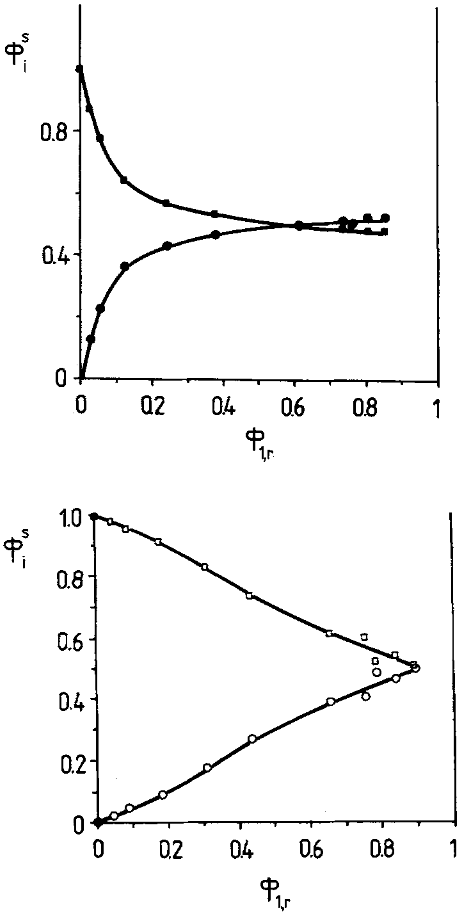

Fig. 2. Composition of the interlamellar space of the organo-vermiculites in butanol(1)-water(2), represented by $\phi_i^s = f(\phi_{1,r})$
2a) DDAm$^+$-vermiculite: butanol (●), water (■);
2b) DD(AM)$_2^{2+}$-vermiculite: butanol (○), water (□)

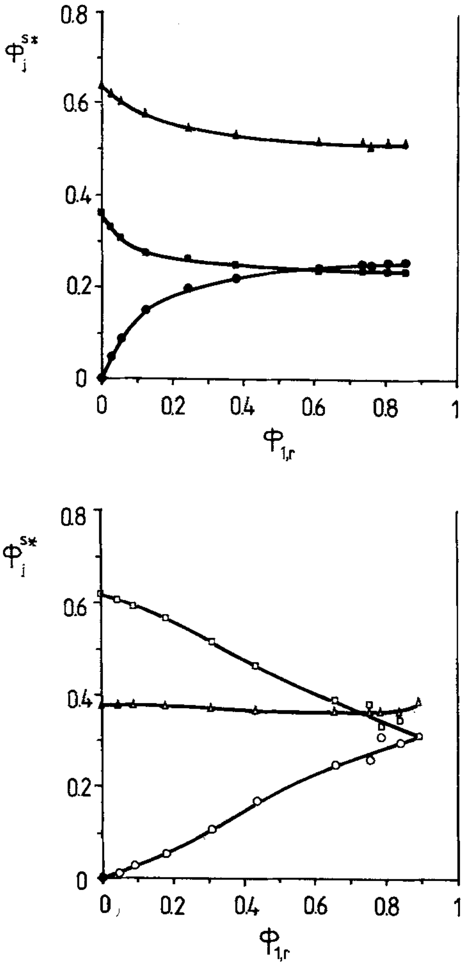

Fig. 3. Composition of the interlamellar space of the organo-vermiculites in butanol(1)-water(2) represented by $\phi_j^{s,x} = f(\phi_{1,r})$
3a) DDAm$^+$-vermiculite: butanol (●), water (■), dodecyl chains (▲); 3b) DD(Am)$_2^{2+}$-vermiculite: butanol (○), water (□), dodecyl chains (△)

Fig. 2 as $\phi_i^s$ vs. $\phi_{1,r}$ and in Fig. 3 as $\phi_j^{s,x}$ vs. $\phi_{1,r}$) also show that the accumulation of butanol on DD(Am)$_2^{2+}$-vermiculite is less preferred compared to the DDAm$^+$-derivative. When the saturation volume fraction is approached ($\phi_{1,r} \rightarrow 1$), the volume fractions of water and butanol become equal ($\phi_1^s \approx \phi_2^s \approx 0.5$) for both vermiculites (Figs. 2a, b). A more realistic picture of the interlayer composition is obtained if the dodecyl chains are considered as the third component in the interlayer space (Figs. 3a, b). The interlamellar space is filled with a considerable amount of dodecyl chains, especially for DDAm$^+$-vermiculite. Also remarkable is the high water content in both vermiculites. Comparing Figs. 2 and 3, it should be noted that the relation $\phi_1^s/\phi_2^s = \phi_1^{s,x}/\phi_2^{s,x}$ immediately follows from combination of Eqs. (5) and (6).

After drying (vacuum desiccator, 70 °C, overnight) the basal spacing was 2.03 nm for DDAm$^+$ and 1.53 nm for DD(Am)$_2^{2+}$ vermiculite (Table 1, Fig. 4). The alkyl chains lie flat onto the silicate surface and form a monolayer of DD(Am)$_2^{2+}$ ions and an interstratification of bilayers and pseudo-trimolecular layers for DDAm$^+$ ions [24] (only the bilayer arrangement is shown in Fig. 6). The calculated basal spacing for the DD(Am)$_2^{2+}$ vermiculite is 1.34 nm (Figs. 5, 6).

Table 1. Experimental and calculated basal spacings ($d_L$/nm) for DDAm$^+$-vermiculite and DD(Am)$_2^{2+}$-vermiculite in dried state and dispersed in water, butanol and saturated solution.

| Organocomplex | Dried | Flat-lying chains (calc.) | Paraffin-type structure 56° (calc.) | Dispersed in pure water | Dispersed in saturated solution ($x_{1,r} = 1$) | Dispersed in pure butanol |
|---|---|---|---|---|---|---|
| DDAm$^+$-vermiculite | 2.03 | 1.77–2.20* | 2.41 | 2.78 | 3.24 | 3.28 |
| DD(Am)$_2^{2+}$-vermiculite | 1.53 | 1.34 | 2.38 | 2.37 | 2.44 | 2.36 |

*) depending on the degree of interstratification

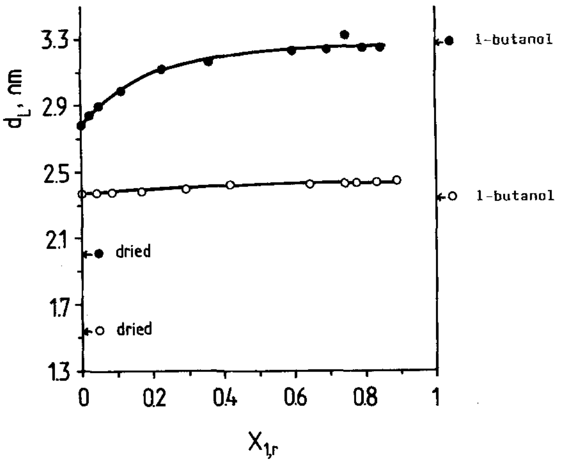

Fig. 4. Basal spacings of the organo vermiculites in aqueous solutions of butanol at 25 °C
(●) dodecylammonium-vermiculite, (○) dodecyldiammonium-vermiculite

The interlamellar expansion of both vermiculites dispersed in water is considerable. In water-butanol solutions the spacing of DD(Am)$_2^{2+}$-vermiculite remains constant, whereas it increases for the other vermiculite from 2.78 to 3.28 nm.

The basal spacing of the diammonium derivative corresponds to an all-trans conformation of the dodecyldiammonium ions with the chains tilted at an angle of 56° to the silicate layer. The calculated basal spacing (Fig. 5) is 2.38 nm, in good agreement with the experimental data ranging from 2.37 to 2.44 nm. The bridging of the layers by the bifunctional cation impedes a further expansion of the interlayer space and the spacing remains constant with increasing butanol concentration. As this steric restriction is absent for the DDAm$^+$-vermiculite, the distance between the silicate layers changes with the interlamellar liquid composition. The basal spacing for the dodecylammonium ion tilted at an angle of 56° (all trans orientation) is 2.41 nm (Fig. 6). The experimental spacings increase from 2.78 to 3.24 nm with increasing adsorption of butanol. Insertion of increasing amounts of butanol, therefore, causes a further expansion of the interlayer space (Fig. 6).

The enthalpy of displacement of water by butanol, $\Delta_{21}H = f(x_{1,r})$, (Fig. 7) reveals an increasing endothermic effect for DD(Am)$_2^{2+}$-vermiculite over the whole concentration range. For DDAm$^+$-vermiculite the enthalpy is less endothermic and

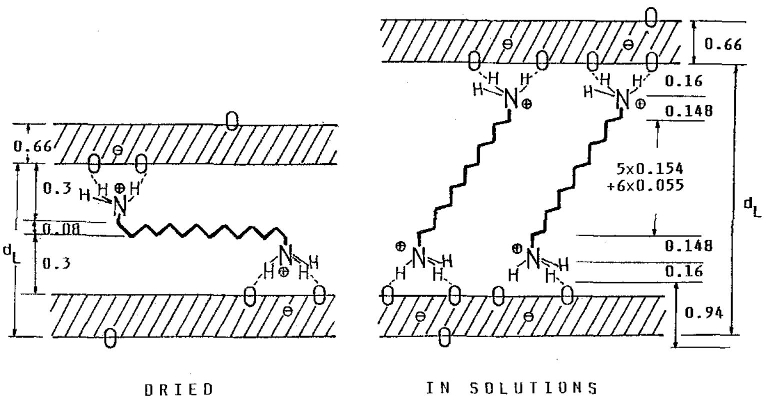

Fig. 5. Orientation of the alkyldiammonium chains between the silicate layers in dried state and in water or diluted aqueous solutions of butanol.

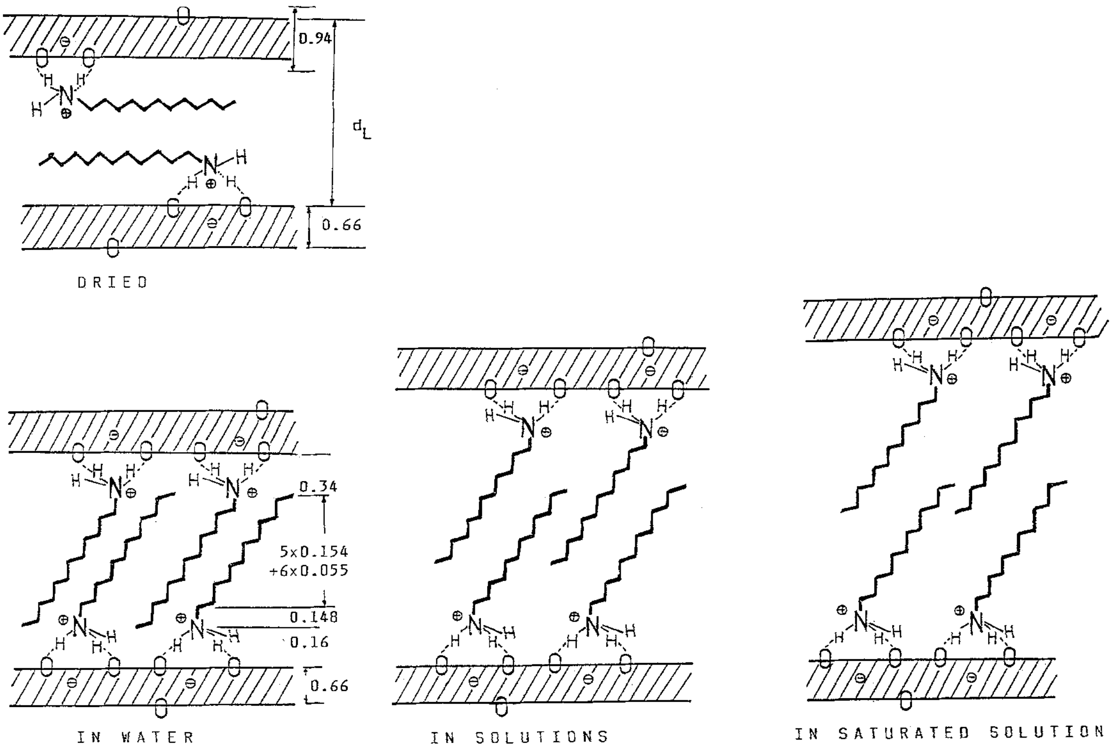

Fig. 6. Orientation of the alkylammonium chains between the silicate layers in dried state and in diluted aqueous solutions with increasing concentration of butanol. (In the dried state, only the bilayer arrangement is shown.)

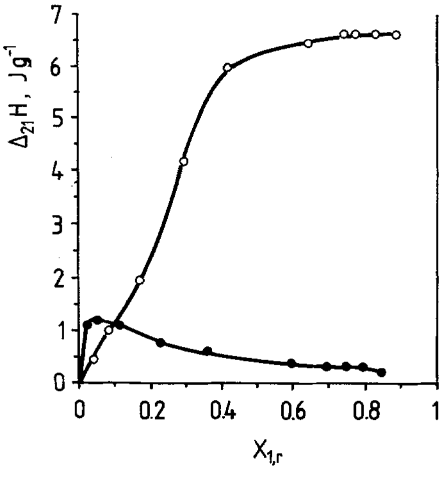

Fig. 7. Integral enthalpy of displacement for the organo-vermiculite in butanol(1)-water(2) at 25°C
(●) dodecylammonium-vermiculite, (○) dodecyldiammonium-vermiculite

shows a slight maximum. In both cases, the enthalpy isotherms are endothermic in spite of the positive adsorption of butanol from water. This surprising observation is in accordance with the positive temperature dependence of the adsorption of some alcohols from dilute aqueous solutions on organo-montmorillonites [7,9].

The displacement process for the two systems under discussion is rather complex and needs further analysis which will be discussed in more detail in a subsequent paper. It can be anticipated that there is a close relationship between the displacement process and the transfer of butanol from water to hydrocarbon media [17,18] (this transfer is strongly endothermic: $\sim +31$ kJ mol$^{-1}$ at infinite dilution of the alcohol) and/or the transfer of butanol from water to micellar systems [19,23]. Liquid structuring (formation of an ordered liquid crystalline phase) and interlamellar expansion may contribute decisively to the enthalpy change of the overall displacement process, making the interpretation of thermal data rather complicated.

## Summary

The structure of the DD(Am)$_2^{2+}$-vermiculite dispersed in aqueous solutions of 1-butanol is not

seriously affected by the solution composition, while a considerable expansion of the $DDAm^+$-vermiculite occurs with increasing concentration of butanol. The adsorption excess isotherms and the enthalpies of displacement reveal that adsorption of butanol by the $DD(Am)_2^{2+}$-vermiculite is less preferential than on $DDAm^+$-vermiculite. The cause is the presence of the diammonium ions which hold together the neighboring silicate layers and do not allow an expansion beyond the monolayer structure (Fig. 5). The interlamellar structure and the interlamellar volume of the $DDAm^+$-derivative change with the composition of the solution. The interlamellar adsorption of butanol from water is strongly preferential and the enhanced accumulation of the alcohol molecules around the alkyl chains gradually increases the basal spacing.

The displacement of water by butanol in the interlamellar space is predominantly an endothermic process. The enthalpy of displacement is more endothermic for $DD(Am)_2^{2+}$ than for $DDAm^+$-vermiculite.

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Authors' address:

Prof. Dr. I. Dékány
Department of Colloid Chemistry
Attila József University
H-6720 Szeged, Hungary