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Displacement processes on hydrophilic/hydrophobic surfaces in 1-propanol-water mixtures

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Abstract: Selective adsorption of 1-propanol-water mixtures was investigated on adsorbents of various surface character. The enthalpy of displacement of 1-propanol by water was studied on graphitized PRINTEX-80, K-60 silicagel, and n-alkylammonium vermiculites. The free enthalpy and entropy isotherms of displacement were derived. The adsorption between the silicate layers of hydrophobic vermiculites was followed by x-ray measurements, and thermodynamic functions were calculated for the structural changes in the adsorption layers. Formation of alcohol-water clusters on the surfaces plays an important role.

Key words: Adsorption – solid–liquid interface – enthalpy of displacement – layer silicates

Introduction

Adsorption of methanol-water mixtures on organophilic vermiculites shows very unusual adsorption isotherms with two maxima [1]. The adsorption behavior can be compared with that on adsorbents with both apolar and polar surfaces (carbon black and silica). The adsorption volume increases in two steps in parallel with the interlamellar expansion.

The question may arise if the unusual form of the isotherm is typical of alcohol–water mixtures or is restricted to a particular alcohol, i.e., methanol. As in our previous paper, thermodynamic functions are derived from displacement measurements. The layer separation measured by x-ray diffraction provides the geometric data which are required to evaluate the structure of the adsorption layer.

Theoretical part

Adsorption from binary mixture is described by specific excess quantities [2–4]. The reduced surface excess of component i is $n_i^{\sigma(n)} = n^0 \Delta x_i / m$. When n^0 moles of the liquid mixture are brought into contact with the mass m of the solid, adsorption changes the molar fraction of component i by Δx_i. At constant temperature the surface tension σ of the solid/liquid interface is related to the adsorption excess by the Gibbs equation [2–4]:

$$d\sigma = n_1^{\sigma(2)} \, d\mu_1 \, , \tag{1}$$

where μ_1 is the chemical potential of component 1, which remains constant in the whole system under equilibrium conditions; $n_1^{\sigma(2)}$ is the relative excess of component 1 related to component 2. The relation between the relative and reduced material excesses is [2]:

$$n_1^{\sigma(2)} = n_1^{\sigma(n)} / x_2 \, . \tag{2}$$

From the excess isotherm and the bulk activities of the components the surface excess free enthalpy, $\Delta_{21}G$, is calculated [1, 5]:

$$\Delta_{21}G = \sigma - \sigma_2^0 = -\int_0^1 \frac{n_1^{\sigma(n)}}{x_2 x_1 \gamma_1} d(x_1\gamma_1) \, . \tag{3}$$

In (3) γ_1 is the activity coefficient of component 1, and σ_2^0 is the surface tension between the solid interface and the pure component 2. The integration of Eq. (3) over the entire composition range gives the difference of the free enthalpy of immersion in the pure components 1 and 2. For the system 1-propanol(1)-water(2) the activity coefficients were calculated by the Renon three-parameter equation [6]:

$$\ln \gamma_i = x_j^2 \left[\frac{\tau_{ij} g_{ij}^2}{(x_i + x_j g_{ij})^2} + \frac{\tau_{ji} g_{ji}}{(x_j + x_i g_{ji})^2} \right] \tag{4}$$

$$g_{12} = \exp(-\alpha\tau_{12});\ g_{21} = \exp(-\alpha\tau_{21}) ,$$

where $i = 1, 2; j = 2, 1$ and $i \neq j$. The parameters are $\tau_{12} = 2.129$, $\tau_{21} = 0.535$, and $\alpha = 0.389$. The integral enthalpy of displacement, $\Delta_{21}H$, is expressed as a function of the amounts adsorbed and the molar enthalpies [1]:

$$\Delta_d H = \Delta n_1^s h_1^s + \Delta n_2^s h_2^s + \Delta H^{se} + \Delta H^e + \Delta H_{\text{mix}} \tag{5a}$$

$$\sum_{x_1=0}^{1} (\Delta_d H - \Delta H_{\text{mix}}) = \Delta_{21} H , \tag{5b}$$

where h_i^s is the molar enthalpy, Δn_i^s is the change of the amount of the pure component i in the adsorption layer during the displacement, ΔH^{se} and ΔH^e are the excess enthalpies of the adsorption layer and bulk solution due to deviation from the ideal behavior. The excess enthalpy function $\Delta_{21}H^e = f(x_1)$ was constructed as described in earlier publications [7, 8]. The entropy of displacement was calculated from $T\Delta_{21}S = \Delta_{21}H - \Delta_{21}G$. The equilibrium constant of the adsorption exchange process, K', was calculated as in the previous paper [1]:

$$K' = \frac{(x_1^s)^r x_2 \gamma_2}{(x_1 \gamma_1)^r x_2^s} \tag{6a}$$

$$x_1^s = \frac{r n_1^{\sigma(n)} + x_1 V^s / V_{m,1}}{V^s / V_{m,1} + n_1^{\sigma(n)}(r-1)} . \tag{6b}$$

In these equations x_1^s and $V_{m,1}$ are the molar fraction and the molar volume of component 1. V^s is the adsorption volume; r is the ratio of the molar volumes, $r = V_{m,2}/V_{m,1}$.

The interlayer volume V_{int} of organophilic vermiculites was determined from the basal spacings d_L. The volume occupied by the alkyl chains, V_{alk}, was obtained from geometrical considerations and the amount of alkylammonium ions bound ξ (= layer charge) [1,9]:

$$V_{\text{int}} = 0.495(d_L - 0.94)/2 \tag{7}$$

$$V_{\text{alk}} = 0.205(0.127 n_c + 0.28)\xi . \tag{8}$$

The volume V_{uc}^s occupied by the adsorbed molecules is calculated from the composition of the adsorption layer [1]:

$$V_{uc}^s = M(n_1^s V_{m,1} + n_2^s V_{m,2})/N_A . \tag{9}$$

$V_{m,1}$ and $V_{m,2}$ are the partial molar volumes of propanol and water, respectively, M is the mass of the $(\text{Si,Al})_4\text{O}_{10}$ organo clay unit, and N_A is the Avogadro number.

Experimental

Materials

a) Silica K-60 (Kieselgel K-60, Merck) was boiled with methanol for 24 h at 330 K; the specific BET surface area is $a_{\text{BET}}^s = 435\ \text{m}^2\text{g}^{-1}$.

b) Graphitized carbon black (Printex-80, Sigri Electrographit GmbH) was extracted with a 1:1 methanol-water mixture for 48 h; $a_{\text{BET}}^s = 113\ \text{m}^2\text{g}^{-1}$.

c) n-Alkylammonium vermiculites (South Africa) with $n_c = 12$ and 18 carbon atoms in the alkyl chain: sodium vermiculite was dispersed in 0.1 M n-alkylammonium chloride solution and stored in a thermostat at 328 K for 1 month. The tenside, at a 20% surplus of the cationic exchange capacity, was added to the sodium clay at pH = 4.5. The alkylammonium derivative was extracted with a 1:1 isopropanol-water mixture for 48 h. The density of organic cations on the vermiculite surface was calculated from the weight loss in the DTA/TG diagram. The amount of alkylammonium ions is $\xi = 0.71$ ions/$(\text{Si,Al})_4\text{O}_{10}$ unit for both derivatives. The total geometrical surface area of vermiculite is calculated from the dimension and the molecular mass of the unit cell [1]: $a_t = 788\ \text{m}^2\ \text{g}^{-1}$.

The adsorbents were dried in a vacuum oven at 383 K (a, b) or at 333 K (c) and 1 Pa before the adsorption measurements. 1-propanol of p.a. purity was stored over 4-Å molecular sieve. The water was freshly twice-distilled.

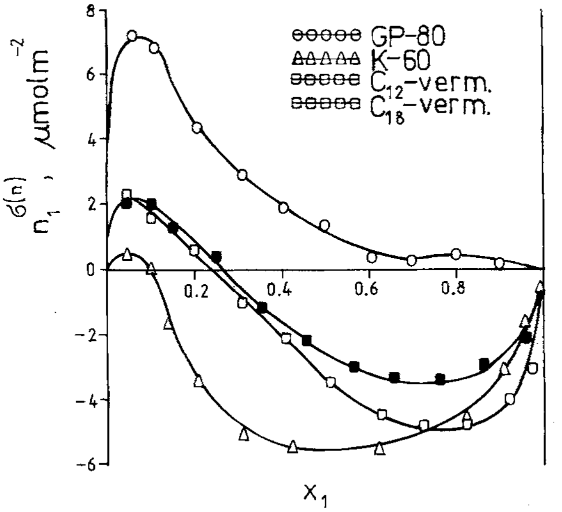

Fig. 1. Adsorption excess isotherms for 1-propanol(1)-water(2) mixtures on GP-80 graphite, K-60 silicagel, dodecyl- and octadecylammonium vermiculite. X_1 is the molar fraction of propanol.

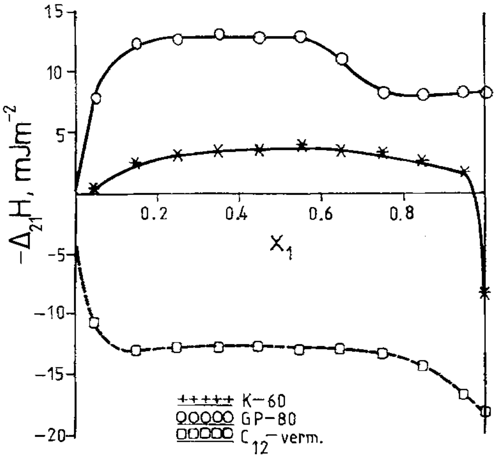

Fig. 2. Integral enthalpy of displacement isotherms in 1-propanol(1)-water(2) mixtures.

Methods

The excess isotherms were determined at 298 ± 0.5 K. The composition of the liquid mixtures before and after adsorption was measured with a liquid interferometer (Zeiss, Jena).

The net heat effect which accompanies the displacement process between the bulk and surface layer was recorded in a flow microcalorimeter (LKB 2107) at 298 ± 0.01 K.

The basal spacings of dodecyl- and octadecylammonium vermiculite in 1-propanol-water mixtures were measured by an x-ray diffractometer (Philips PW 1820/PW 1830).

Results and discussion

The adsorption excess isotherms for 1-propanol(1)-water(2) on different adsorbents are shown in Fig. 1. The U-shaped isotherm results from the preferential adsorption of propanol on graphitized Printex-80. As compared with the isotherm of methanol-water on the same adsorbent [1], 1-propanol is more strongly adsorbed than methanol. Since the adsorption arises mainly from dispersion forces between alkyl groups of the alcohol and the graphite surface, this result was expected. A secondary shallow maximum occurs at a molar fraction of propanol $x_1 = 0.8$. Similar results were reported by Hansen and Craig [10], Everett and Fletcher [11]. For ethanol-water on graphon the secondary maximum appeared above $T = 328.15$ K. Presumably, the secondary maximum results from the strong structure-forming effect of alcohol/water mixtures. This is supported by the integral enthalpy of displacement $\Delta_{21}H = f(x_1)$ on GP-80, directly measured by flow microcalorimetry (Fig. 2). $\Delta_{21}H$ reveals an exothermic displacement process between $x_1 = 0$ and $x_1 = 0.2$. An endothermic part follows an athermal region (at $x_1 = 0.6$–0.8). This endothermic effect corresponds to the secondary maximum of the excess isotherm.

The adsorption excess of 1-propanol from water on K-60 silica gel is positive below $x_1 = 0.1$, and becomes negative above this value (Fig. 1).

The displacement enthalpy corresponding to the positive excess of water on K-60 changes only slightly and becomes endothermic between $x_1 = 0.95$–1.0 (Fig. 2).

The isotherms for GP-80 and K-60 do not contain a linear section, so the Schay extrapolation [4] cannot be used to calculate the adsorption capacity. Assuming a quasi-ideal adsorption layer, Eq. (10) can be used to calculate the adsorption volume [1] (Fig. 3) which is found to be constant between $x_1 = 0.4$–1.0 (Table 1):

$$\frac{\Delta_{21}Gx_1}{\phi_1 n_1^{\sigma(n)}} = \frac{V^s \Delta_{21}g^s}{V_{m,1}} \frac{x_1}{n_1^{\sigma(n)}} + r\Delta_{21}g^s \,. \tag{10}$$

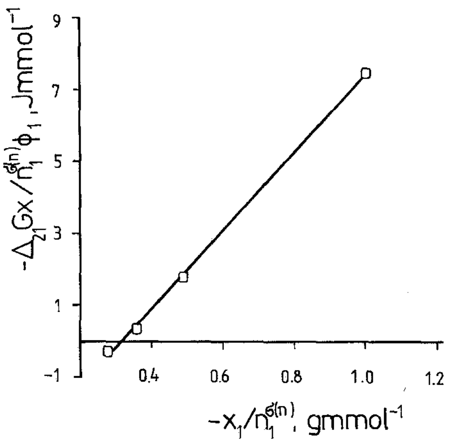

Fig. 3. Combined free enthalpy-adsorption excess functions calculated from Eq. (14) in ref. [1], where $Y = G$.

Table 1. Analysis of adsorption excess isotherms in 1-propanol(1)-water(2) liquid mixtures

Adsorbent	a^s_{BET} m^2 g^{-1}	a^s_{graph} m^2 g^{-1}	V^s_{graph}# cm^3 g^{-1}	V^s Eq. (10) cm^3 g^{-1}	K' Eq. (6)
GP-80	113	–	–	0.062**	1.20
C_{12}-verm.	788*	801	0.390	0.389	0.83
C_{18}-verm.	788*	838	0.427	0.396	0.88
K-60	435	–	–	0.091***	0.53

Schay-Nagy graphical extrapolation [4]
* The total geometric surface area, calculated from the dimension of the unit cell
** between $x_1 = 0.4 - 1.0$
*** between $x_1 = 0.2 - 0.8$

The isotherms of the alkylammonium vermiculites (Fig. 1) are of type IV (Schay-Nagy classification [4]) and can be evaluated graphically. The calculated surface areas (a^s_{graph}) and adsorption volumes (V^s_{graph}) are shown in Table 1.

The basal spacing (d_L) of the alkylammonium vermiculites changes in a characteristic way with x_1 (Fig. 4). The basal spacing of the vermiculites in the propanol-water mixtures is distinctly higher than in the pure liquids (Fig. 4, Table 2). The spacing of C_{12}- and C_{18}-vermiculites in pure water is considerably smaller than reported before [12], probably because of the lower packing density of the alkylammonium ions. The basal spacing of dodecylammonium vermiculite in pure liquids indicates monolayers of alkylammonium ions. It is difficult to decide whether the spacings in the mixtures are caused by bilayers of tilted and/or denting chains [12–14].

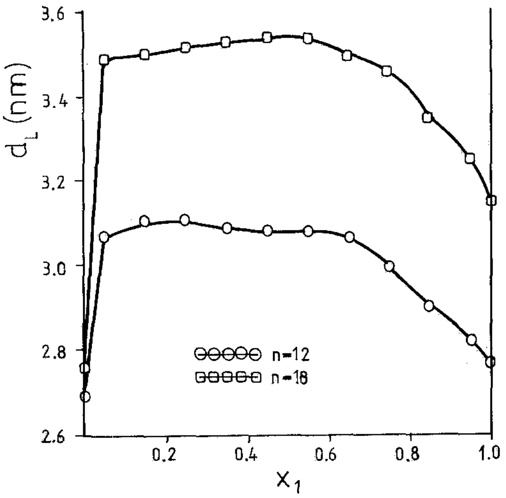

Fig. 4. Basal spacings of dodecyl- and octadecylammonium vermiculites in 1-propanol(1)-water(2) mixtures.

In agreement with adsorption and calorimetric measurements the basal spacing and, therefore, the interlamellar volume (Figs. 4 and 5) are nearly constant for $x_1 = 0.1$–0.6. The interlamellar free volume ($V_{\mathrm{int}} - V_{\mathrm{alk}}$), which changes in the same way as the basal spacing, is the same for dodecyl- and octadecylammonium vermiculite. The adsorption volume V^s_{uc} determined from Eq. (9) on

Table 2. The distances between the silicate layers of dodecyl- and octadecylammonium vermiculite

Adsorbent	Length# nm	$d_L - 0.94$## in water nm	$d_L - 0.94$ $x_1 = 0.5$ nm	$d_L - 0.94$ in propanol nm
C_{12}-verm.	1.80	1.71	2.16	1.81
C_{18}-verm.	2.57	1.81	2.56	2.21

alkyl chain length = $0.127\, n_c + 0.28$
The thickness of a silicate layer is 0.94 nm.

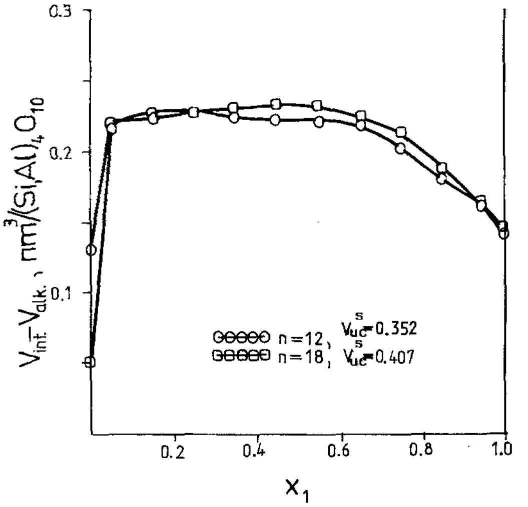

Fig. 5. The free interlayer volume ($V_{int} - V_{alk}$) of dodecyl- and octadecylammonium vermiculites in 1-propanol(1)-water(2) mixtures. V^s_{uc} represents the volume (in nm^3/unit) calculated from adsorption isotherms.

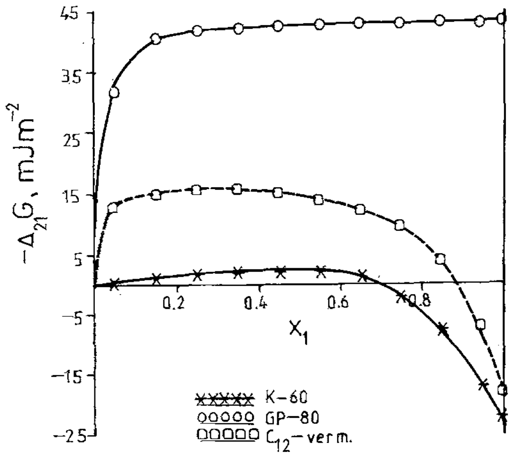

Fig. 6. Surface excess free enthalpy in 1-propanol(1)-water(2) mixtures as a function of the bulk composition.

the basis of the adsorption pore filling model [15] is distinctly larger than the interlamellar free volume (Fig. 5).

The change of the surface excess free enthalpy, $\Delta_{21}G$ (Fig. 6) is in accordance with the adsorption isotherms (Fig. 1). The preferential adsorption of propanol on GP-80 is accompanied by a significant decrease of $\Delta_{21}G$ up to $x_1 = 0.2$. Above $x_1 = 0.2$ $\Delta_{21}G$ is practically constant. For silicagel $\Delta_{21}G$ hardly changes between $x_1 = 0$–0.7, and becomes endothermic at higher propanol concentrations. This is due to the unfavorable displacement of water by propanol on the hydrophilic silica surface. Interpreting the thermodynamic functions for dodecylammonium vermiculite/propanol-water, one has to take into consideration the change of the basal spacing between $x_1 = 0$–0.15 and $x_1 = 0.65$–1.0 (Fig. 4). In this case, a term *fdh* has to be included in Eq. (1) (Eq. (34) in ref. [16]), which considers the interlamellar forces between the silicate layers changing with the layer separation:

$$-d\sigma = \frac{1}{2} f dh + \sum_{i=2}^{i=c} \Gamma_i^{(1)} d\mu_i \,. \qquad (11)$$

Presently, no direct data are available for *fdh*. They may be obtained by compression studies. The influence of *fdh* on the free enthalpy seems to be negligible, since the basal spacing of dodecylammonium vermiculite is high and changes with the composition by only 0.4 nm. This is supported by the thermodynamic functions in Figs. 2, 6, 7 and the equilibrium constant K'. The functions $\Delta_{21}G$ and $T\Delta_{21}S$ of C_{12}-vermiculite are lying between the corresponding functions for K-60 and GP-80, indicating that the surface energy of dodecylammonium vermiculite is between silica and graphite. K' describes the selectivity of adsorption, and thus is related to the surface polarity. The values of K' for both alkylammonium

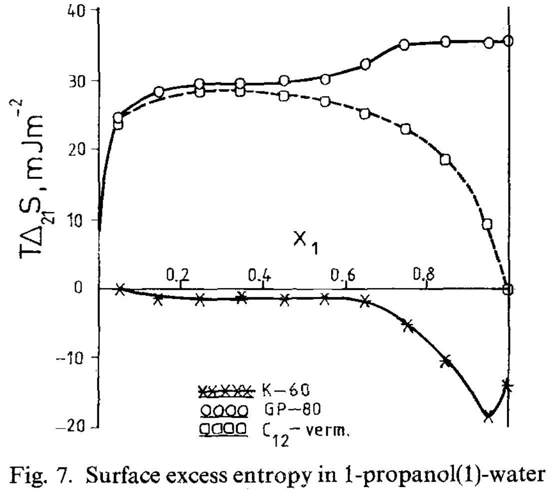

Fig. 7. Surface excess entropy in 1-propanol(1)-water(2) mixtures as a function of the bulk composition.

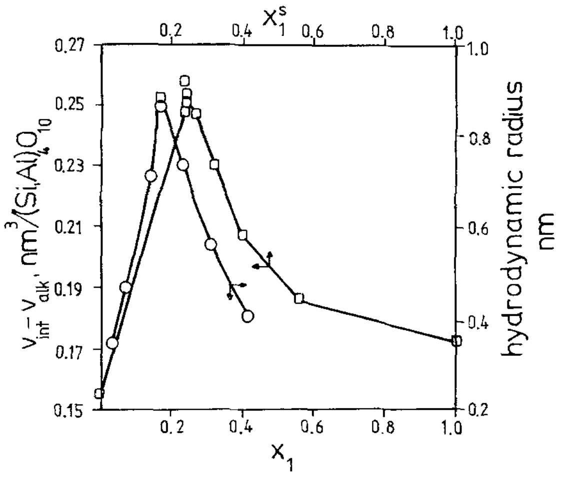

Fig. 8. The free liquid volume, $V_{int} - V_{alk}$, as a function of the surface composition (x_1^s) and the hydrodynamic radius of clusters formed in 1-propanol(1)-water(2) mixtures versus the bulk composition x_1.

vermiculites are identical, and are also between the K' values for GP-80 and K-60 (Table 1). The changes of $\Delta_{21}H$ and $\Delta_{21}G$ at $x_1 < 0.1$ and $x_1 > 0.6$ are related to the swelling and deswelling processes.

When the molecules of the liquid mixture, as in case of propanol/water, are strongly associating, the structuring influence of the surface, especially of a complex surface like that of an organophilic vermiculite, has to compete with the self-association of the liquid molecules. Großmann and Ebert [17] studied the structure of 1-propanol/water. They found a strong cluster formation around $x_1 = 0.17$. The clusters appear to be rather stable, their hydrodynamic radius is $a = 0.8$ nm, and the apparent molecular mass is $M_{app} = 400$ g mol^{-1}. In Fig. 8 are shown the free interlamellar volume of dodecylammonium vermiculite as a function of the surface composition, x_1^s, together with the hydrodynamic radius as a function of the bulk composition x_1. The coincidence is striking; the slopes of the two functions are nearly identical. Under the influence of the vermiculite surface grafted with long alkyl chains the maximum of $(V_{int} - V_{alk})$ is shifted to $x_i^s = 0.24$. This surface concentration remains constant in a wide range of the bulk composition ($0.2 < x_1 < 0.8$) and indicates a stable interlamellar structure.

Summary

Adsorption of propanol from water was studied on graphite GP-80, silicagel K-60, dodecyl- and octadecylammonium vermiculite. The adsorption of alcohol on graphite is preferential in the entire composition range, on K-60 only between a molar fraction of propanol < 0.1. The isotherms for the alkylammonium vermiculites are of type IV (sigmoid; Schay-Nagy classification) with an azeotropic point at $x_1 = 0.25$–0.3. The surface energy of C_{12}-vermiculite is intermediate between that of silica and graphite, as revealed by the thermodynamical functions $\Delta_{21}G$ and $T\Delta_{21}S$ and the equilibrium constant K' for the adsorption exchange process. The adsorption volume calculated from the adsorption data is distinctly larger than the free interlayer volume derived from the basal spacing. The difference changes with the chain length of the alkylammonium ions. The propanol/water mixture forms strong clusters at $x_1 = 0.17$. Under the influence of the vermiculite surface covered with dodecylammonium ions the molar fraction of propanol of the interlamellar clusters is shifted to the slightly higher value $x_1^s = 0.24$.

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