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SHORT COMMUNICATION

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Nanolayer liquid density on hydrophobic surfaces

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Abstract The excess volumes of dispersions of hydrophobic silica particles and hydrophobized layer silicates were studied in ethanol–cyclohexane mixtures.

A plot of the excess volume vs. composition $[V^\sigma = f(x_1)]$ indicates that the components, ethanol and cyclohexane, on hydrophobic SiO_2 are ordered to a considerable extent. The excess volumes which are positive in the pure solvent, i.e. without dispersed particles, take on negative values over the entire composition range. On the other hand, excess volumes for layer silicates the surface of which had been modified by long ($n_c = 18$) alkyl chains were calculated by a combination of adsorption isotherms with X-ray diffraction data and were positive in the entire composition range.

It is established that the density of the adsorption layer on the solid/liquid interface in colloid dispersions significantly differs from that of the bulk phase. The differences depend on the surface structure of the adsorbent.

Key words Liquid density – hydrophobic surfaces – ethanol – cyclohexane – densitometry – excess volumes – dispersions

Introduction

Changes in molar mixing excess volumes are a measure of the deviation of mixtures from ideality. The reason is a change in the environment of the molecules which – as a consequence of modifications of the intermolecular forces – brings about composition-dependent changes in the extensive thermodynamic properties of the mixture. The volume of a mixture is not equal to the sum of the volumes of the individual pure components: either contraction or expansion takes place.

Findenegg et al. were the first to determine excess values on the solid/liquid interface of pure liquids [1–3]. They studied the structure of monocarboxylic acids and hexadecanol on the liquid/Graphon interface by immersion experiments. The liquid structure in the interfacial layer differed from that in the bulk phase since the density of the packing of the molecules on the solid surface was different [1]. This conception was supported by measurements of the surface excess mass of the adsorbed liquid. The surface excess mass of pure liquids can be determined by pycnometry [1, 2]

$$m^\sigma = m_{\text{liq.}} - \rho^0_{\text{liq.}} V_{\text{liq.}} \,, \qquad (1)$$

where $m_{\text{liq.}}$ is the mass of the liquid in the pycnometer and $V_{\text{liq.}}$ is its volume which is equal to the difference of the total volume of the pycnometer and the volume of solid material, while $\rho^0_{\text{liq.}}$ is the density of the liquid bulk phase at the given temperature, determined in a separate experiment.

When graphite was immersed in an organic solvent (propane), excess volumes were determined as a result of the effect of adsorption forces. Findenegg et al. measured the [2–4] excess volumes of various pure liquids on the graphite/liquid interface. For the homologues series of

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long-chain paraffins, primary aliphatic alcohols and carboxylic acids, these authors showed that excess values exhibit a significant dependence on temperature in the vicinity of the freezing-point which was attributed to the alignment (structuring) of carbon chains within the interfacial layer [2–4].

Schay [4] discussed that at least two effects have to be taken into consideration for the description of the adsorption of liquids on solid surfaces: (i) a change in structure (density), caused (in the case of mixtures and pure liquids) by the interaction with the solid surface (lyosorption), (ii) a change in the composition of the interfacial layer, brought about by adsorption.

In several studies on the thermodynamic properties of aqueous solutions of organic compounds (e.g. ethylene glycol, urea, formamide, acetone, etc.), densities and excess volumes were reported [5–8]. Typically, the molar excess volumes of aqueous solutions are negative. Contraction observed in aqueous solutions of hydrated polar compounds (e.g. urea) is usually less extensive than that in aqueous solutions of compounds containing both polar and nonpolar groups (e.g. alcohols).

Excess volumes of solutions of *n*-butylamine in C_3–C_6-alcohols were found to be negative over the entire composition range [9]. The same result was obtained for the aqueous solutions of C_1–C_4-alcohols [10]. However, positive molar excess volumes were measured in mixtures of benzene with various cyclic and aliphatic hydrocarbons [11] and in binary mixtures of propylene carbonate and cyclic hydrocarbons [12]. Binary mixtures of 2-butoxyethanol and *n*-hexane or *n*-heptane, furthermore acryl esters, highly important polymer building blocks, and organic solvents were systematically investigated by Sastry et al. [13–15]. The excess volumes of 2-butoxyethanol mixed with *n*-hexane, *n*-heptane or the mixture of hexane and heptane were positive over the entire composition range.

We published numerous adsorption and calorimetric studies on hydrophilic and hydrophobic solid surfaces immersed in binary mixtures. In this paper we report the determination of excess volumes and excess volume isotherms for ethanol/cyclohexane mixtures via densitometry. Changes in specific excess volumes associated with the adsorption of the liquid components on surfaces of various polarity (hydrophobic SiO_2 and hydrophobized layer silicates) were analyzed.

Theoretical background

The molar excess volume (V^σ_{mix}) in binary mixtures is calculated according [9–15]:

$$V^\sigma_{\text{mix}} = \frac{x_1 M_1 + x_2 M_2}{\rho_\ell} - \left(\frac{x_1 M_1}{\rho_1^0} + \frac{x_2 M_2}{\rho_2^0}\right) , \quad (2)$$

where ρ_i^0 is the density of pure components, ρ_ℓ is the density of the mixtures at a composition x_i (at the given temperature) and M_i is the molar mass of the given component in the binary mixture ($i = 1, 2$).

When studying solid/liquid interactions of dispersions in binary mixtures, the excess volume per unit mass of adsorbent (V^σ) may be determined by two different methods.

Vibration densitometry

For calculating the excess volume by this method, densities of pure liquids, mixtures and dispersions have to be determined. The excess volume (V^σ) is the difference of the total volume of the system (V_{disp}) and the sum of the volumes of the components

$$V^\sigma = V_{\text{disp}} - \left(V_\ell + \frac{m_s}{\rho_s}\right) , \quad (3)$$

where m_s and ρ_s are the mass and the density of the adsorbent, respectively, and V_ℓ is the volume of the liquid. The equation may be formulated in the following way to separate measurable mass and density values:

$$V^\sigma = \frac{m_1 + m_2 + m_s}{\rho_{\text{disp}}} - \left(V_\ell + \frac{m_s}{\rho_s}\right) , \quad (4)$$

where m_i is the mass of the ith component and ρ_{disp} is the density of the dispersion.

The volume V_ℓ of the mixture of density ρ_ℓ is added to the mass m_s of adsorbent, to yield the mass m_{disp} of the dispersion. When this mass is divided by the measured density of the dispersion (ρ_{disp}), the volume of the dispersion V_{disp} is obtained. Thus, Eq. (4) can be formulated in the following way:

$$V^\sigma = \frac{m_{\text{disp}}}{\rho_{\text{disp}}} - \left(V_\ell + \frac{m_s}{\rho_s}\right) = \frac{\rho_\ell V_\ell + m_s}{\rho_{\text{disp}}} - \left(V_\ell + \frac{m_s}{\rho_s}\right) . \quad (5)$$

Equations (4) and (5) reveal that the magnitude of V^σ is determined exclusively by the value of ρ_{disp} which is measured by vibration densitometry. All other data are known.

Pycnometry

The excess volume expressed as the difference of the volume of the pycnometer (V_{pyc}) and the volumes of the components combined is given by the following equation:

$$V^\sigma = V_{\text{pyc}} - \left(\frac{m_\ell}{\rho_\ell} + \frac{m_s}{\rho_s}\right) . \quad (6)$$

In other words, the mass of the liquid (or mixture) determining the value of V^σ is now calculated from $m_\ell = m_{\mathrm{disp}} - (m_{\mathrm{pyc}} + m_{\mathrm{s}})$.

The density of each solid material has to be determined in separate measurements by He pycnometry. Equation (6) is identical with Eq. (5) since the volume of the dispersion filling the pycnometer is $V_{\mathrm{pyc}} = V_{\mathrm{disp}} = m_{\mathrm{disp}}/\rho_{\mathrm{disp}}$, and the density of the dispersion can be factored out in the following way: $\rho_{\mathrm{disp}} = m_{\mathrm{disp}}/V_{\mathrm{pyc}}$.

Combination of adsorption and X-ray diffraction data

In the case of clay minerals, the specific excess volume may also be determined by a combination of adsorption excess isotherms and X-ray diffraction data since the interlamellar liquid volume can be calculated from the basal spacing d_{L} [16, 17]. Knowing (i) the individual adsorption isotherms, i.e. the number of moles (n_i^{s}) of the components in the interfacial layer – which may be determined by the Schay–Nagy extrapolation method [17] – and (ii) the molar masses of the liquid components (M_i), the mass of the adsorbed liquid (m^{s}) is:

$$m^{\mathrm{s}} = n_1^{\mathrm{s}} M_1 + n_2^{\mathrm{s}} M_2 \; . \tag{7}$$

When the function x_1^{s} vs. x_1 is calculated from the adsorption excess isotherm $n_1^{\sigma(\mathrm{n})} = f(x_1)$ [18], the density of the mixtures $[\rho_\ell^{\mathrm{s}}(x_1^{\mathrm{s}})]$ corresponding to various compositions of the adsorption layer (x_1^{s}) may be read from the density functions of the mixtures. Division of the masses calculated according to Eq. (7) by these densities yields the volume that would be occupied by the mixture with the composition of x_1^{s}, when the adsorbent were not present. Thus, the calculated volume of the adsorption layer is $V^{\mathrm{s}} = m^{\mathrm{s}}/\rho_\ell^{\mathrm{s}}(x_1^{\mathrm{s}})$.

The volume of the liquid present in the interlamellar space is equal to the interlamellar free volume ($V_{\mathrm{int}} - V_{\mathrm{alk}}$). The interlamellar volume V_{int} is calculated from

$$V_{\mathrm{int}} = A_{\mathrm{u.c.}}(d_{\mathrm{L}} - 0.94)/2 \; , \quad \mathrm{nm}^3/(\mathrm{Si, Al})_4\mathrm{O}_{10} \; , \tag{8}$$

where $A_{\mathrm{u.c.}}$ is the surface of two opposite $(\mathrm{Si, Al})_4\mathrm{O}_{10}$ units (unit cells) and V_{alk} is the fraction of the interlamellar volume filled by alkyl chains [16]

$$V_{\mathrm{alk}} = 0.205[0.127(n_{\mathrm{C-C}} + n_{\mathrm{C-N}}) + 0.28]\zeta \; , \quad \mathrm{nm}^3/(\mathrm{Si, Al})_4\mathrm{O}_{10} \; . \tag{9}$$

The cross-sectional area of the alkyl chain is 0.205 nm^2, $n_{\mathrm{C-C}}$ and $n_{\mathrm{C-N}}$ are the numbers of chemical bonds in the molecule, 0.28 nm is the radius of the methyl endgroup. The surface charge density of vermiculite, $\zeta = 0.355$ (eq/$(\mathrm{Si, Al})_4\mathrm{O}_{10}$), is calculated from thermogravimetric measurements [16].

Since the interfacial volume V^{s} is calculated from the excess isotherm using the Schay–Nagy extrapolation method, this value may be directly compared with the interlamellar free liquid volume

$$\Delta V = [V^{\mathrm{s}} - (V_{\mathrm{int}} - V_{\mathrm{alk}})]/m_{\mathrm{s}} \; , \quad \mathrm{cm}^3/\mathrm{g} \; . \tag{10}$$

In the case of densitometry $m_\ell = V_\ell \rho_\ell$ is calculated from the values of the volumes and densities. In the case of pycnometry, the mass of the liquid m_ℓ is calculated from the difference of the volume of the pycnometer and that of the solid adsorbent: $m_\ell = (V_{\mathrm{pyc}} - m_{\mathrm{s}}/\rho_{\mathrm{s}})\rho_\ell$. This liquid mass is added to the adsorbent of the mass m_{s}. When the S/L adsorption equilibrium is established, the total liquid volume of the interfacial layer changes by the excess volume V^σ, $V_{\mathrm{tot}} = V_\ell - V^\sigma$. Since the liquid mass m_ℓ is constant, the so-called average (perturbed) liquid density (ρ_ℓ^*) may be formulated

$$\rho_\ell^* = \frac{m_\ell}{V_\ell - V^\sigma} \; . \tag{11}$$

Results and discussion

Adsorption excess isotherms measured on the surface of R 972 silica and for octadecylammonium vermiculite are shown in Fig. 1a [19]. Since the surface of the adsorbents is hydrophobic, sign reversal of $n_1^{\sigma(\mathrm{n})}$ was observed on both excess isotherms. The equilibrium diagram $[x_1^{\mathrm{s}} = f(x_1)]$ supports the conclusion that the interfacial layer is enriched in ethanol on both adsorbents up to the azeotropic composition x_1^{a}, while at $x_1 > x_1^{\mathrm{a}}$ enrichment in cyclohexane takes place.

The density of the ethanol(1)–cyclohexane(2) mixtures measured at 25 ± 0.05 °C is presented in Fig. 2a as a function of the composition. The reproducibility of density measurements was $\pm 1 \times 10^{-5}$ g cm^{-3}. Molar excess volumes calculated according to Eq. (2) as a function of the composition are shown in Fig. 2b. Excess values are positive over the entire composition range, indicating that mixing of ethanol and cyclohexane is accompanied by an expansion [20].

Densities of dispersions as a function of mixture composition are displayed in Fig. 3. The densities of R 972 dispersions were measured directly in a vibration densitometer (DMA 58, Anton Paar Comp.) while densities of dispersions of the hydrophobic clay mineral derivative were determined by pycnometry. Significant changes in the density of the aerosil dispersion are only observed in mixtures rich in ethanol while the curve for octadecylammonium vermiculite has a minimum.

Specific excess volume (V^σ/m_{s}) on hydrophobized silica (R 972) and octadecylammonium vermiculite are

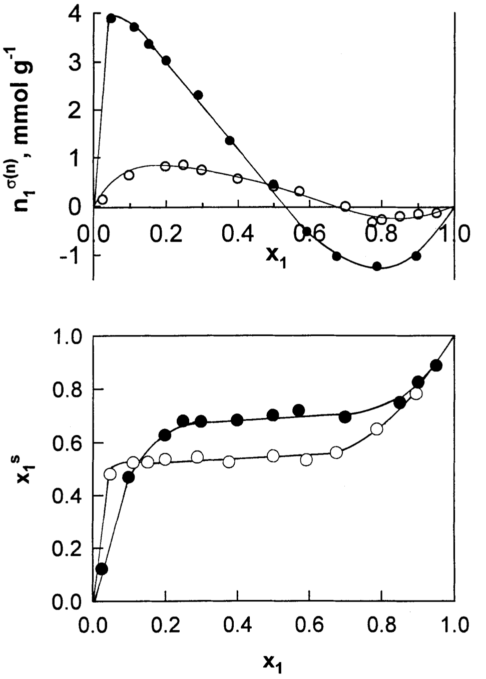

Fig. 1 Adsorption from ethanol(1)–cyclohexane(2) mixtures on hydrophobic silica (○) and octadecylammonium vermiculite (●)

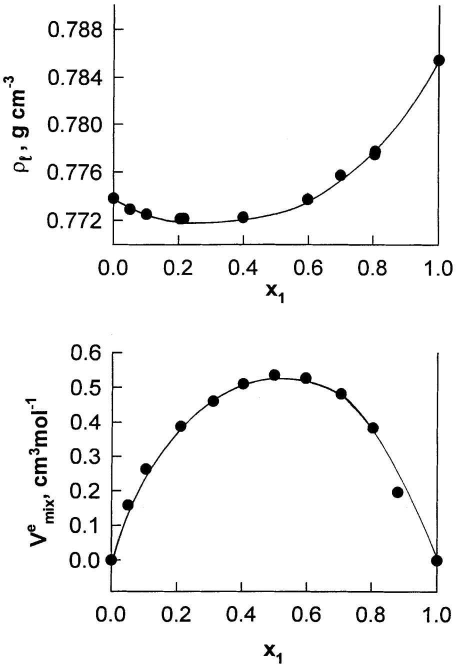

Fig. 2 Density of the mixtures and the excess volume ethanol(1)–cyclohexane(2)

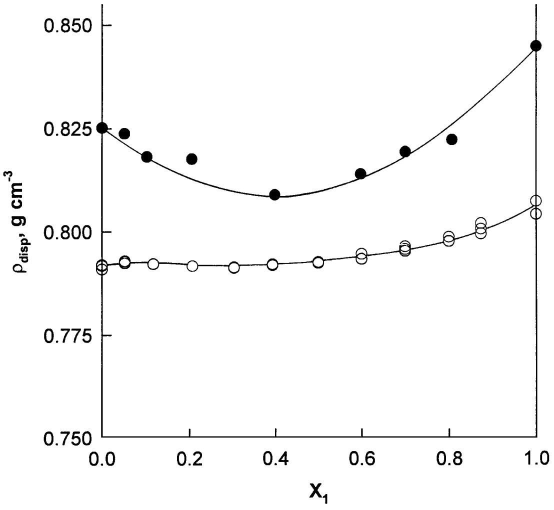

Fig. 3 Density of the silica (○) and octadecylammonium vermiculite (●) dispersions in ethanol(1)–cyclohexane(2)

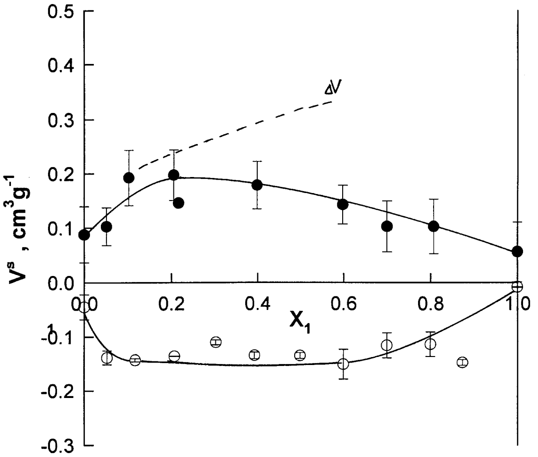

Fig. 4 The excess volume of silica (calculated by Eq. (5), ○) and of octadecylammonium vermiculite (calculated by Eq. (6), ●) and the volume change calculated Eq. (10) (- - - -)

shown in Fig. 4. Ethanol and cyclohexane are so strongly adsorbed on the methylated surface of aerosil R 972 that the specific surface excess volumes are negative in the pure liquids and over the entire mixture composition. The specific excess volumes of octadecylammonium vermiculite (calculated by Eq. (6) from pycnometric measurements) are positive over the entire composition range, and their absolute values are higher than those obtained for hydrophobic silica. This indicates that, due to solvation of the long alkyl chains attached to the layers of vermiculite, the liquid structure formed in the ethanol–cyclohexane mixtures breaks down. Information on this process is obtained from the adsorption excess isotherm (Fig. 1) and X-ray data (Fig. 5). The basal spacing of for octadecylammonium vermiculite in the dried state is $d_L = 1.72$ nm.

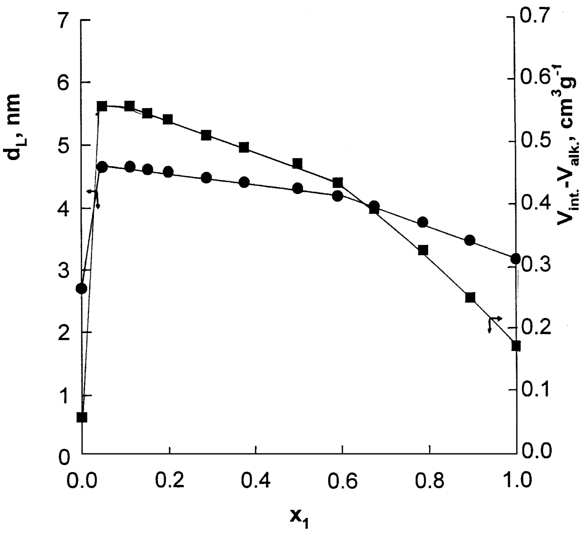

Fig. 5 Basal spacings of octadecylammonium vermiculite and the free interlamellar volume in ethanol(1)–cyclohexane(2)

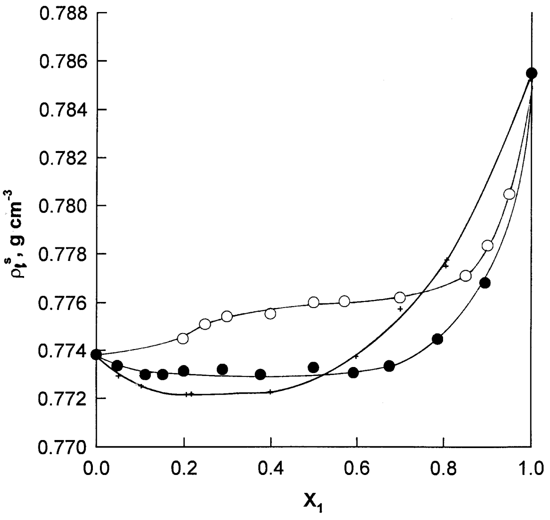

Fig. 6 Density of liquid in the interfacial layer: hydrophobic silica (○) and the octadecylammonium vermiculite (●). The points (+) are the density of ethanol–cyclohexane mixtures

When dispersed in pure liquids, it expands in ethanol to $d_L = 3.13$ nm, in cyclohexane to $d_L = 2.70$ nm. At low molar fractions of ethanol ($x_1 < 0.6$) neighboring layers move apart significantly and the basal spacing ($d_L = 4.7$–4.3 nm) considerably exceeds that in pure liquids. As the ratio of ethanol within the mixture is increased, the interlamellar distance is reduced.

The expansion of the clay mineral layers covered by the alkyl chains is due to a selective adsorption of ethanol. Within the range of $x_1 = 0.05$–0.4, this process promotes disintegration of the clusters formed in ethanol–cyclohexane and the volume occupied by the same amount of liquid increases. When the layers approach (decreasing basal spacings, Fig. 5), the process is reversed and specific excess volume decreases. The decrease of the excess volume (Fig. 4) is parallel to that of basal spacing (Fig. 5).

Changes of the specific excess volume for octadecylammonium vermiculite calculated by Eq. (10), on the basis of $n_1^{\sigma(n)}$ vs. x_1 and $V_{int} - V_{alk}$ vs. x_1 (Fig. 5), are also displayed in Fig. 4. For $x_1 < 0.5$, the pycnometrical data are in good agreement with those calculated by a combination of adsorption and X-ray diffraction data. The reason for deviations in the initial and terminal regions is that the constant ($n^s = n_1^s + n_2^s = 8.98$ mmol g^{-1}) determined by the Schay–Nagy extrapolation method is not constant at all molar fractions x_1. Deviations can also occur because adsorbed amounts (n_i^s) as well as the adsorption volume itself (V^s) are dependent on the composition [21].

The error of the determination of specific excess volume is quite large (0.7–52.1%), depending on mixture composition). Aggregation of the hydrophobic silica particles in the dispersion, interferes with the vibration densitometry measurements. In the case of octadecylammonium vermiculite the pycnometrical determinations involve large errors. In accordance with the sign of specific excess volumes, the densities of mixtures constituting part of the hydrophobic silica dispersions are somewhat higher than those of the mixtures without adsorbent, while relatively large decreases in density are observed in vermiculite dispersions. The difference between the absolute values is related to the significantly different specific surface areas between aerosil R 972 (128 m^2 g^{-1}), and octadecylammonium vermiculite (788 m^2 g^{-1}). The result is that ethanol–cyclohexane clusters are condensed by the surfacial methyl groups of the hydrophobic aerosil, but disintegrated by vermiculite layers with the alkyl chains attached. The densities of the mixtures corresponding to the composition of the adsorption layer (x_1^s) are represented as a function of composition in Fig. 6.

Conclusion

Molar excess volumes of ethanol(1)–cyclohexane(2) mixtures are positive over the entire composition range, indicating that intermolecular interactions are less significant in mixtures than in pure liquids.

The present study is an investigation of the effect of solid hydrophobic materials of various surface characteristics on the structure of liquid mixtures. Silica modified by grafted methyl groups (R 972) promotes the development of clusters in binary mixtures thus condensing the liquid phase: the density of the liquid phase constituting part of a dispersion, therefore, increases compared to the pure liquids. In contrast, the liquid structure is weakened on hydrophobic vermiculite with the layers modified by octadecyl chains and the density of the adsorbed decreases.

The equilibrium diagram calculated on the basis of the adsorption isotherm (Fig. 1b) indicates accumulation of ethanol on the surface of both adsorbents. Since the density of ethanol (0.78548) is higher than that of cyclohexane (0.77382), the enrichment of ethanol in the adsorption layer increases the density compared with the corresponding pure liquid mixture. Thus, up to compositions of $x_1 = x_1^a = 0.68$ for octadecylammonium vermiculite and $x_1 = x_1^a = 0.50$ for hydrophobic aerosil, the preferential adsorption of ethanol ($x_1^a > x_1$) necessarily results in a density of the adsorption layer exceeding that of the bulk phase. This is demonstrated by the density functions shown in Fig. 6 where the density of the bulk phase is also given. Thus, even if the perturbation effect of the adsorption force field on the liquid components is disregarded, i.e. the ideal case is considered, the density of the adsorption layer is still increased by the selective liquid adsorption up to the azeotropic composition. In the case of octadecylammonium vermiculite this increase in density is overcompensated by the structure-breaking effect of alkyl chains in the interlamellar space, resulting in a decrease of ρ_ℓ and the positive sign of the excess volumes V^σ.

List of symbols

$A_{\mathrm{u.c.}}$	the surface area of two $[\mathrm{Si, Al}]_4\mathrm{O}_{10}$ units (= unit cell) is 0.495 nm^2
M_i	relative molar mass of component *i*
m_i	mass of component *i*
m_ℓ	mass of liquid
m_{s}	mass of adsorbent
m^{s}	mass of adsorbed liquid
m_{disp}	mass of suspension
m^σ	surface excess mass
n_i^{s}	amount of adsorbed component *i*
ρ_i^0	density of liquid component *i*
ρ_ℓ	density of bulk phase
$\rho_\ell^{\mathrm{s}}(x_1^{\mathrm{s}})$	density of interfacial layer
ρ_ℓ^*	perturbed density of liquid phase in the disperse system
ρ_{s}	density of adsorbent
ρ_{disp}	density of dispersion
x_1^{a}	azeotropic composition of component (1)
x_1^{s}	molar ratio of component (1) in the interfacial layer
V_{alk}	volume of alkyl chains per formula unit of the silicate framework
V_{int}	volume of interlamellar space (interlamellar volume)
$V_{\mathrm{int}} - V_{\mathrm{alk}}$	the "free" interlamellar volume
V_ℓ	volume of liquid
$V_{\mathrm{m},i}$	partial molar volume of component *i*
$V_{\mathrm{m},i}^{\mathrm{s}}$	partial molar volume of component *i* in the interfacial layer
V_{mix}^σ	excess volume of liquid mixtures
V_{pyc}	volume of pycnometer
V_{disp}	volume of dispersion

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