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ORIGINAL CONTRIBUTION

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A new way for calculating the adsorption capacity from surface excess isotherms

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Abstract Adsorption of *n*-butanol and water from butanol–water mixtures is studied on adsorbents of different hydrophobicity (activated carbon and hydrophobized montmorillonites). The shape of the adsorption isotherms of the hydrophobized clay minerals does not indicate preferential adsorption of butanol. Therefore, the adsorption capacity cannot be determined on the basis of the Langmuir isotherm.
A new equation for determining the adsorption capacity is derived by combining the free enthalpy of adsorption with the adsorption excess amount. Both collections of data are obtained from the surface excess isotherm. The reliability of the adsorption capacity is checked by X-ray diffraction measurements.

Key words Adsorption – *n*-butanol – clay minerals – adsorption capacity – surface polarity – alkylammonium montmorillonite – hexadecylpyridinium montmorillonite

Introduction

Determination of adsorption excess amounts from diluted solution often yields isotherms which cannot be described by the Langmuir model. Therefore, neither the adsorption capacity nor parameters characterizing the solid/liquid interaction are available. We introduced in our earlier studies relationships which allow calculation of the adsorption capacity and enthalpy by combining adsorption isotherms and microcalorimetric measurements [1–4]. However, microcalorimetric measurements are often cumbersome, difficult to perform and to reproduce [4–6]. Flow calorimetric measurements cannot be carried out with highly dispersed adsorbents or swelling and disaggregating materials like several clay minerals and their hydrophobic derivatives [4]. We consider it necessary to introduce a new method to calculate the adsorption capacity solely by analyzing the adsorption isotherm. The free energy of adsorption is calculated from the isotherm on the basis of the Gibbs equation and is combined with the adsorption excess amount. The method is illustrated by the adsorption of butanol–water on carbon and hydrophobized montmorillonites.

Theoretical background

The reduced specific adsorption excess $n_1^{\sigma(n)}$ for adsorption from liquid mixtures on solids is given by the Ostwald–de Izaguirre equation [7, 8]

$$n_1^{\sigma(n)} = n_1^{s} - n^{s} x_1 = n^{s}(x_1^{s} - x_1) \; . \qquad (1)$$

The component i adsorbed on the surface occupy the volume

$$V^{s} = n_1^{s} V_{m,1} + n_2^{s} V_{m,2} \; , \qquad (2)$$

where n_i^{s} and $V_{m,i}$ are the amount and the partial molar volume of the component in the adsorption layer. The adsorption capacity of the pure component 1 is

$$n_{1,0}^{s} = n_1^{s} + r n_2^{s} = n^{s} x_1^{s} + r n^{s} x_2^{s} \; , \qquad (3)$$

where $r = V_{m,2}/V_{m,1} = n^s_{1,0}/n^s_{2,0}$; x_i and x^s_i are the molar fractions of component i in the liquid mixture at equilibrium and in the adsorption layer. Rearrangement of Eq. (3) leads to

$$n^s = \frac{n^s_{1,0}}{x^s_1 + r x^s_2} \; . \tag{4}$$

The separation factor of adsorption is defined as

$$S = \frac{x^s_1 x_2}{x^s_2 x_1} = \frac{n^s_1 x_2}{n^s_2 x_1} \; . \tag{5}$$

Replacing x^s_1 and x^s_2 in eq. (4) by S gives

$$n^s = n^s_{1,0} \frac{S x_1 + x_2}{S x_1 + r x_2} \; . \tag{6}$$

When Eq. (6) is introduced into Eq. (1),

$$\frac{n^{\sigma(n)}}{n^s_{1,0}} = \frac{(S-1) x_1 x_2}{(S-r) x_1 + r} \; . \tag{7}$$

The adsorption capacity $n^s_{1,0}$ of the pure component is determined from the linear relationship between $x_1 x_2 / n_1^{\sigma(n)}$ and x_1 (Everett–Schay method [9–12]):

$$\frac{x_1 x_2}{n_1^{\sigma(n)}} = \frac{1}{n^s_{1,0}} \left[\frac{r}{S-1} + \frac{S-r}{S-1} \right] x_1 \; , \tag{8}$$

where S is constant for ideal adsorption from ideal solutions [13, 14]. The constancy of the separation factor in many other cases may result from compensation effects.

When the adsorption excess isotherm, $n_1^{\sigma(n)} = f(x_1)$, and the activity coefficients (γ_i, $i = 1, 2$) of the bulk liquid phase are known, the free enthalpy of adsorption at the solid–liquid interface, $\Delta_{21}G$, is determined by the Gibbs equation [15–18]:

$$\Delta_{21} G = -RT \int_0^{x_1} \frac{n_1^{\sigma(n)}}{(1 - x_1) x_1} \left(1 + \frac{\mathrm{d} \ln \gamma_1}{\mathrm{d} \ln x_1} \right) \mathrm{d} x_1 \; , \tag{9}$$

where γ_1 is the activity coefficient of the solute. The term of the activity coefficient in the bracket vanishes for ideal or ideally diluted solutions (like *n*-butanol in water).

The material transfer in the adsorption layer is $\Delta n^s_1 = -r \Delta n^s_2$. The free enthalpy of adsorption, $\Delta_d G$, is connected with the molar free enthalpies, g^s_i, and the amount n^s_i:

$$\Delta_d G = \Delta n^s_1 g^s_1 + \Delta n^s_2 g^s_2 \; . \tag{10}$$

The sum of $\Delta_d G$ in the whole composition range ($x_1 = 0$ to $x_1 \to 1$) is:

$$\sum_{x_1 = 0}^{x_1} \Delta_d G = \Delta_{21} G = n^s_1 (g^s_1 - g^s_1 / r) \; . \tag{11}$$

Introducing $n^s_1 = n_1^{\sigma(n)} + n^s x_1$ (Eq. (1)) into Eq. (11) and dividing by the adsorption excess $n_1^{\sigma(n)}$ leads to [20]

$$\frac{\Delta_{21} G}{n_1^{\sigma(n)}} = g^s_1 - g^s_2/r + n^s (g^s_1 - g^s_2/r) \frac{x_1}{n_1^{\sigma(n)}} = \Delta_{21} g + n^s \Delta_{21} g \frac{x_1}{n_1^{\sigma(n)}} \; . \tag{12}$$

Linear representation of Eq. (12) gives $\Delta_{21} g = g^s_1 - g^s_2/r$ (from the intercept) and the adsorbed amount n^s (from the slope).

The volume of the alkyl chains per formula unit $(\mathrm{Si, Al})_4\mathrm{O}_{10}$ of the alkylammonium montmorillonite is [19]:

$$V_{\mathrm{alk}} = 0.205 [0.127 (n_{\mathrm{C-C}} + n_{\mathrm{C-N}}) + 0.28] \zeta \quad (\mathrm{nm}^3/(\mathrm{Si, Al})_4\mathrm{O}_{10}) \; . \tag{13a}$$

The product in the bracket 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 the unbranched hydrocarbon chain is taken as 0.205 nm^2 and the length of the NH_3^+ group is 0.28 nm. The charge per formula unit of montmorillonite was $\zeta = 0.32$.

The volume of an hexadecylpyridinium ion is $V_{\mathrm{HDP}} = 0.5919$ nm^3. Per formula unit $(\mathrm{Si, Al})_4\mathrm{O}_{10}$ the hexadecylpyridinium ions occupy a volume

$$V_{\mathrm{alk}} = 0.32 \, \sigma V_{\mathrm{HDP}} \; . \tag{13b}$$

The ratio of the amount of hexadecylpyridinium ions to the total exchange capacity was $\sigma = 0.24$ and 1.0 for the partially and totally exchanged hexadecylpyridinium montmorillonite.

The interlamellar volume between two silicate layers (per formula unit = half unit cell) is obtained from the basal spacing

$$V_{\mathrm{int}} = 0.495 (d_{\mathrm{L}} - 0.94)/2 \quad (\mathrm{nm}^3/[\mathrm{Si, Al}]_4\mathrm{O}_{10}) \; . \tag{14}$$

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

Materials and methods

Carbon F-400 (Chemviron, New Jersey U.S.A.)

Carbon F-400 is a porous, hydrophobic adsorbent. The specific BET surface area ($a^s = 835\ \mathrm{m^2\,g^{-1}}$) was determined by N_2 adsorption at 77 K (automatic gas sorptometer, Gemini 2375, Micromeritics).

Organophilic montmorillonites

Organic derivatives of montmorillonite were prepared from aqueous solutions of the cationic surfactants hexadecylpyridinium chloride, dodecyl- and octadecylammonium chloride (Fluka AG). The aqueous dispersion of montmorillonite ($5\,\mathrm{g\,l^{-1}}$) was treated with the aqueous surfactant solution for 24 h. The dispersions coagulated rapidly. After filtration and washing with water the solids were dried at 363 K, ground and passed through a 60 mm sieve.

Two types of hexadecylpyridinium montmorillonite were prepared. A partially exchanged sample, (sodium, hexadecylpyridinium) montmorillonite, was prepared by reacting 2000 ml of the montmorillonite dispersion ($5\,\mathrm{g\,l^{-1}}$) with 40 ml of 0.05 M hexadecylpyridinium chloride solution. The fully exchanged sample was obtained from 2000 ml of the montmorillonite dispersion and 130 ml of the 0.1 M hexadecylpyridinium chloride solution.

The alkylammonium montmorillonites (completely exchanged samples) were prepared from 2000 ml of the dispersion and 130 ml of 0.1 M solution of dodecyl- and octadecylammonium chloride.

The montmorillonite was a Schwaiba bentonite from Bayern, Germany. The $d < 2$ mm fraction of the bentonite was separated by sedimentation from 0.5 w/v aqueous suspension. The cation exchange capacity (from carbon content of the alkylammonium derivatives) was $0.85\,\mathrm{meq\,g^{-1}}$.

Butanol–water solutions

n-butanol of p.a. purity (Reanal, Hungary) was used without further purification. Twice distilled water was saturated with butanol in a special separating funnel maintained at 298 ± 0.1 K. Solutions were prepared by diluting the water-rich lower phase. The saturation molar fraction of 1-butanol in water was $x_1^{\mathrm{sat}} = 1.877 \times 10^{-2}$ at 298 K [20–22].

Adsorption experiments

The adsorption excess isotherms were measured at 298 ± 0.5 K. The change of the liquid composition by adsorption ($\Delta x_i = x_i^0 - x_i$) was determined with a Zeiss liquid interferometer. The excess amount of adsorption, $n_1^{\sigma(n)}$, was plotted versus $x_{1,r} = x_1/x_1^{\mathrm{sat}}$, the relative molar fraction of *n*-butanol in water.

X-ray diffraction

The basal spacing (d_L values) of the organophilic montmorillonites was determined from the basal reflections in the powder diagram (diffractometer Philips PW 1830, Cu K_α) The powder diffraction goniometer was used to study dried materials and dispersions. In the latter case the dispersion was covered by a piece of Mylar foil (25 μm) to prevent evaporation of the liquids. The experimental results were reproduced within 0.02 nm.

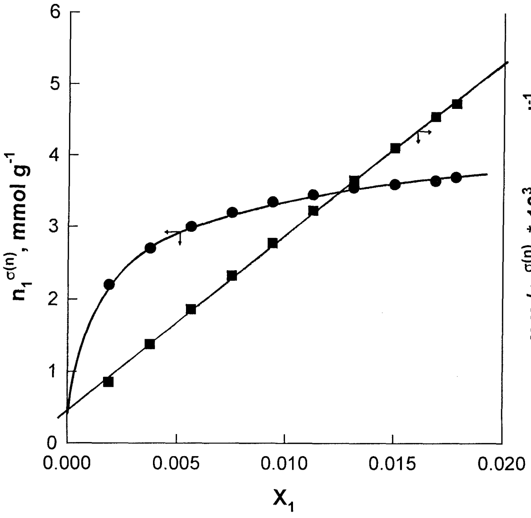

Fig. 1 Adsorption excess isotherm (●) of butanol–water on carbon (Chemviron F400). (■) $x_1x_2/n_1^{\sigma(n)} = f(x_1)$ (Everett–Schay representation)

Results and discussion

The adsorption excess isotherm recorded in butanol–water on activated carbon and its reciprocal Langmuir representation are shown in Fig. 1. Butanol is preferentially adsorbed on the hydrophobic, microporous material. The adsorption capacity is obtained from the Everett–Schay representation (Eq. (8)). In Fig. 2 the free enthalpy of adsorption, $\Delta_{21}G$ (Eq. (9)), is plotted versus $x_{1,r}$. The function $\Delta_{21}G/n_1^{\sigma(n)}$ (Eq. (12)) is almost linear for $x_{1,r}/n_1^{\sigma(n)} = 0.1$–$0.25$ (Fig. 3). Linear extrapolation gives $\Delta_{21}g = -3.56\,\mathrm{J\,mmol^{-1}}$ and $n^s = 3.21\,\mathrm{mmol\,g^{-1}}$ (Table 1). The adsorption capacity calculated by the Everett–Schay procedure (Eq. (8)) is $n^s = 3.98\,\mathrm{mmol\,g^{-1}}$.

The adsorption isotherms of *n*-butanol–water on dodecyl- and octadecylammonium montmorillonite are concave (Fig. 4) and cannot be evaluated by Eq. (8). Both samples adsorb practically the same amounts of butanol, indicating that the length of the alkyl chain hardly affects $n_1^{\sigma(n)}$. However, adsorption of butanol on dodecylammonium montmorillonite is associated with a smaller change of $-\Delta_{21}G$ compared with the octadecylammonium derivative (Fig. 5). Also, the increase of $-\Delta_{21}G/$

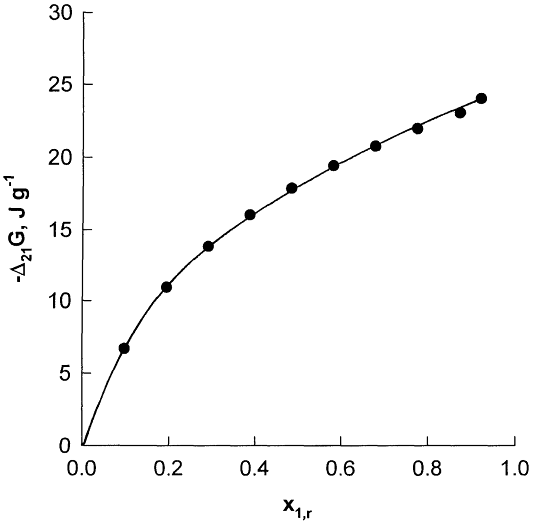

Fig. 2 Free enthalpy of adsorption of butanol–water on carbon (Chemviron F400), calculated by Eq. (9)

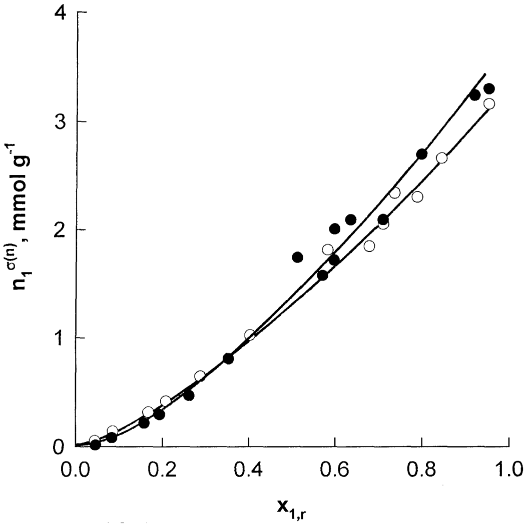

Fig. 4 Adsorption excess isotherms of butanol–water on (●) dodecyl- and (○) octadecylammonium montmorillonite

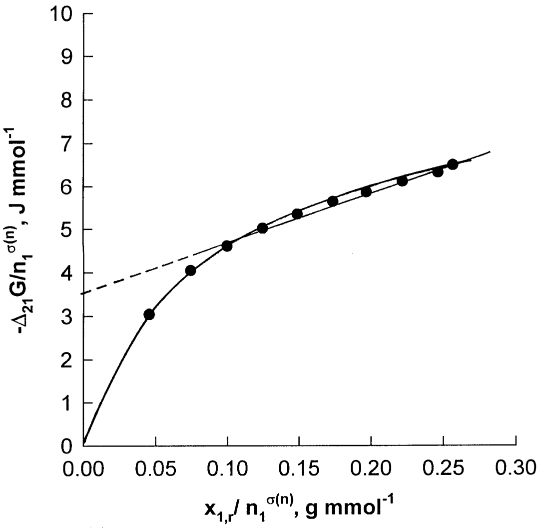

Fig. 3 Combination of adsorption excess and free enthalpy data (Eq. (12)) on carbon (Chemviron F400) in butanol–water

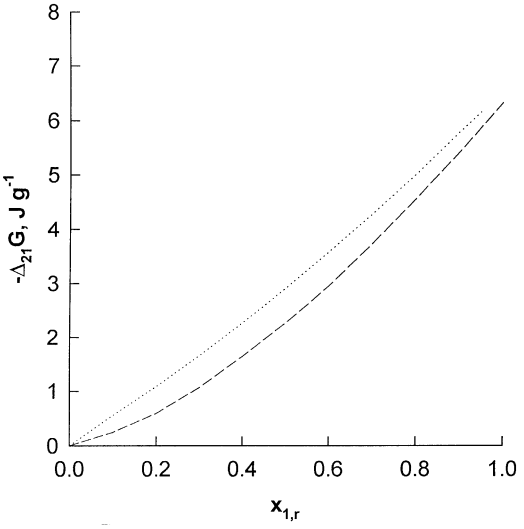

Fig. 5 Free enthalpy of adsorption of butanol–water on (●) dodecylammonium and (○) octadecylammonium montmorillonite

$n_1^{\sigma(n)}$ with $x_1/n_1^{\sigma(n)}$ (Fig. 6) is different for both adsorbents and reveals the different hydrophobicity of these materials. The value of the molar-free enthalpy of adsorption is $\Delta_{21}g = -1.12\ \mathrm{J\,mmol^{-1}}$ for dodecylammonium montmorillonite and $-1.68\ \mathrm{J\,mmol^{-1}}$ for the octadecylammonium derivative. The adsorbed amounts n^s (calculated from Eq. (12)) are also different (1.01 and 1.94 mmol g^{-1} for dodecyl and octadecylammonium montmorillonite). The volume V^s of the adsorbed phase is calculated from n^s by assuming that only butanol is adsorbed. This value is compared with $V_{\mathrm{int}} - V_{\mathrm{alk}}$ in Fig. 7. Agreement is found as long as the alkylammonium montmorillonite does not swell strongly in butanol–water. When $x_{1,r}$ exceeds 0.3 (dodecylammonium montmorillonite) or 0.5 (octadecylammonium montmorillonite), water is also taken up and the interlayer space is largely expanded.

The effect of hydrophobization of montmorillonite by different amounts of hexadecylpyridinium ions on butanol adsorption is shown in Fig. 8. At a low coverage (0.20 meq g^{-1}), butanol is negatively adsorbed at $x_{1,r} < 0.62$ because large amounts of sodium ions (0.65 meq g^{-1}) are in exchange positions at the surface. At $x_{1,r} > 0.6$, $n_1^{\sigma(n)}$

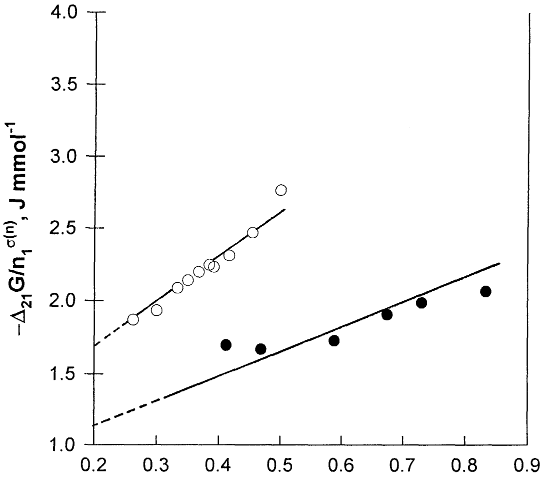

Fig. 6 Combination of adsorption excess and free enthalpy data (Eq. (12)): (●) dodecyl- and (○) octadecylammonium montmorillonite in butanol–water

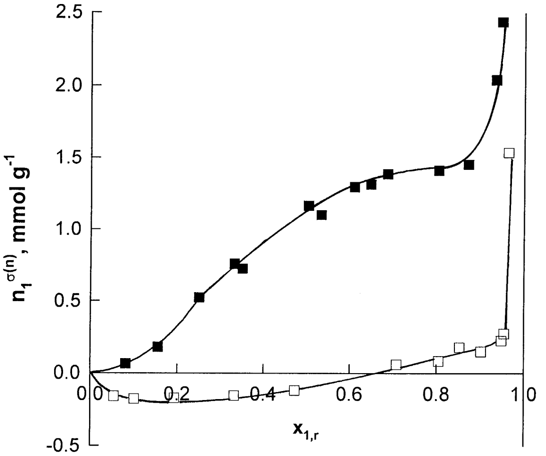

Fig. 8 Adsorption excess isotherms of butanol–water on (□) (sodium, hexadecylpyridinium) montmorillonite and (■) hexadecylpyridinium montmorillonite

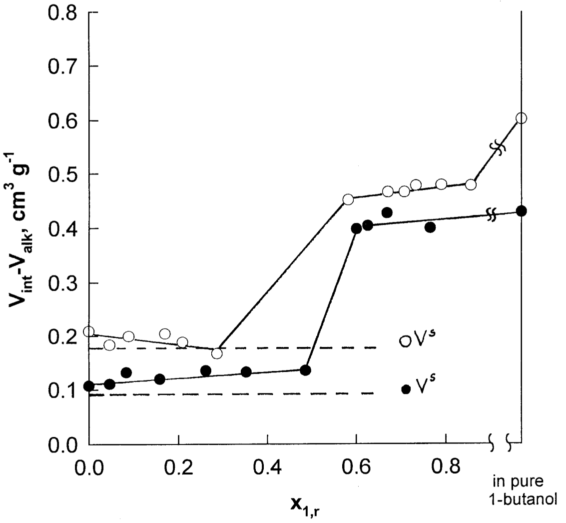

Fig. 7 Free interlamellar volume (Eqs. (13, 14)): (●) dodecyl- and (○) octadecylammonium montmorillonite in butanol–water

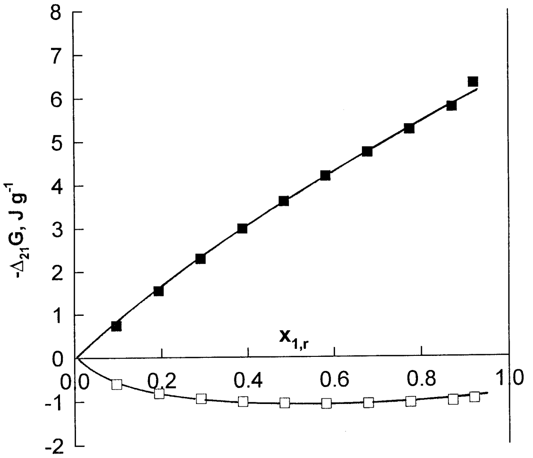

Fig. 9 Free energy of adsorption of butanol–water on (□) (sodium, hexadecylpyridinium) montmorillonite and (■) hexadecylpyridinium montmorillonite

becomes positive because butanol is adsorbed in the interlayer space. When all sodium ions on the surface are exchanged by hexadecylpyridinium ions, butanol is positively adsorbed in the entire concentration range. At high molar fractions of butanol, $n_1^{\sigma(n)}$ is distinctly smaller than for the dodecyl- and octadecylammonium samples.

The free enthalpy $\Delta_{21}G$ calculated from the isotherms by Eq. (9) (Fig. 9) also displays the different surface hydrophobicity of the hexadecylpyridinium derivatives. $\Delta_{21}G/n_1^{\sigma(n)}$ for (sodium, hexadecylpyridinium) montmorillonite (Fig. 10(a)) changes differently from the other derivatives (Figs. 6 and 10(b)). When only 0.20 meq g^{-1} hexadecylpyridinium ions are bound, $\Delta_{21}g = -3.56\ \mathrm{J\,mmol^{-1}}$ is identical with the value for carbon ($\Delta_{21}g = -3.56\ \mathrm{J\,mmol^{-1}}$, Table 1). This montmorillonite does not swell largely in butanol-water; the basal spacing only varies between 1.46 and 1.80 nm. The sample behaves as a microporous adsorbent. The thickness of the liquid layer in the

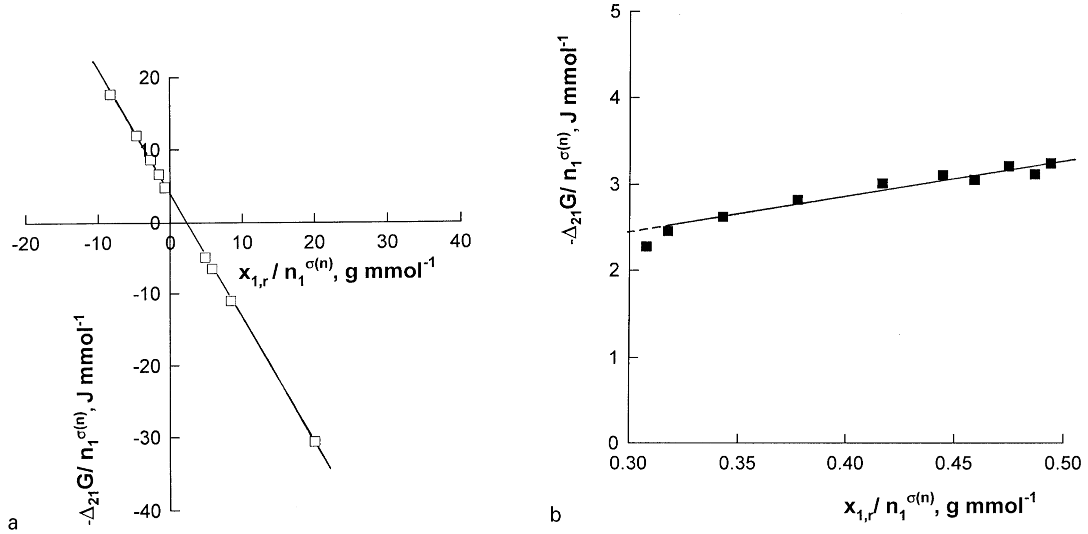

Fig. 10 (a) Combination of adsorption excess and free energy data (Eq. (12)) for (sodium, hexadecylpyridinium) montmorillonite in butanol–water. (b) Combination of adsorption excess and free energy data (Eq. (12)) for hexadecylpyridinium montmorillonite in butanol–water

Table 1 Combination of adsorption excess and free energy data

	$-\Delta_{21}\,g$ [J mmol^{-1}] Eq. (12)	n^s [mmol g^{-1}] Eq. (12)	V^s [cm^3 g^{-1}] Eq. (2)
Carbon	3.56	3.21*	0.295
Dodecylammonium-montmorillonite	1.12	1.01	0.093
Octadecylammonium-montmorillonite	1.68	1.94	0.179
(Sodium, hexadecylpyridinium) montmorillonite	3.56	0.48	0.044
Hexadecylpyridinium montmorillonite	2.44	1.66	0.153

* $n^s_{1,0}$ calculated from $x_1x_2/n_1^{\sigma(n)} = \mathrm{f}(x_1)$ (Everett–Schay representation, Eq. (8)): 3.98 mmol g^{-1}.

interlamellar space (d_L — 0.96 nm), varying within 0.50 and 0.84 nm, indeed, corresponds to the size of micropores. The value of $-\Delta_{21}g$ for the fully exchanged hexadecylpyridinium montmorillonite is distinctly lower than that of the partially exchanged sample and carbon. It is better comparable to the small values of $-\Delta_{21}g$ for the alkylammonium derivatives (Table 1). The smaller values are typical of swelling systems because energy is required to rearrange the chains in the interlayer space [23].

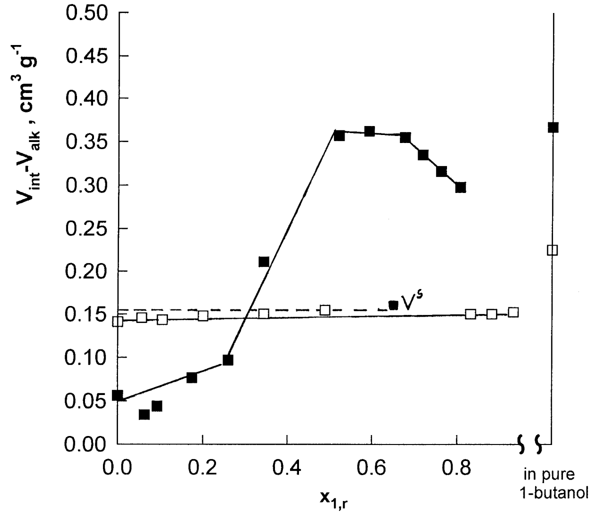

Fig. 11 Free interlamellar volume (Eqs. (13, 14)): (□) (sodium, hexadecylpyridinium) and (■) hexadecylpyridinium montmorillonite in butanol–water

The adsorbed amount on hexadecylpyridinium montmorillonite, $n^s = 1.66$, gives $V^s = 0.153\,\mathrm{cm}^3\,\mathrm{g}^{-1}$ (assuming only butanol to be adsorbed) which is larger than $V_{\mathrm{int}} - V_{\mathrm{alk}}$ at $x_{1,r} < 0.3$ but much smaller for $x_{1,r} > 0.3$ (Fig. 11). In the adsorption layer the volume fraction of butanol (1) and water (2) is [19]: $\Phi^s_1 = 0.49$, $\Phi^s_2 = 0.51$ at $x_{1,r} = 0.25$ and $\Phi^s_1 = 0.22$, $\Phi^s_2 = 0.78$ at $x_{1,r} = 0.50$. The steep increase of $V_{\mathrm{int}} - V_{\mathrm{alk}}$ at $x_{1,r} < 0.3$ again indicates the uptake of larger amounts of water together with butanol. The problem of V^s being larger than $V_{\mathrm{int}} - V_{\mathrm{alk}}$ is discussed in [24].

Conclusion

In the case of non-preferential adsorption from diluted solutions the adsorption capacity and the solid/liquid interaction cannot be deduced from of the surface excess isotherms. Rather, realistic values of the amounts adsorbed are obtained by combining free enthalpy of adsorption data and adsorption excess amounts (Eq. (12)) which both are calculated from the surface excess isotherms. Equation (12) also reveals differences in the surface polarity.

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