

Liquid adsorption and immersional wetting on hydrophilic/hydrophobic solid surfaces

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Abstract - The preferential adsorption on adsorbents with different surface hydrophobicity (hydrophobic layer silicates) can be properly described by the thermodynamic data of the adsorbed layer. When the components in a binary liquid mixture are very different in polarity, as they are in methanol-benzene mixtures, the polarity of the surface can be characterized through the shape of the excess isotherms and the azeotropic composition. The free energy $\Delta_{21}G = f(x_1)$ calculated from the excess isotherms, gives information about the decrease in free energy due to the displacement. The displacement enthalpy isotherms $\Delta_{21}H = f(x_1)$ can be determined with flow microcalorimetry and the thermodynamic description of the adsorption layer is complete. The combination of displacement free energy and enthalpy with adsorption excess amounts gives a new way to determine the volume of the adsorbed layer. The combination also gives data to determination of the molar ($\Delta_{21}g$, $\Delta_{21}h$) thermodynamic data, which describe the polarity of a surface in a certain liquid mixture.

INTRODUCTION

Silicate surfaces are usually hydrophilic against water because inorganic counter ions compensate the negative charges created by isomorphous substitutions in the silicate layer structure. By exchanging these counter ions by cationic surfactants the surface can be made hydrophobic. Suitable cations are, for instance, alkylammonium ions or alkyipyridinium ions.

Surface excess adsorption isotherms from binary liquid mixtures respond sensitively to the degree of hydrophobicity of the adsorbent [1-6]. The composition of the adsorption phase changes with the character of the surface. Preceding studies with montmorillonite as adsorbent revealed the mutual influence of the liquid molecules and the long chain organic cations onto the surface structure of the adsorption layer(4-6).

By combination of adsorption excess and enthalpy isotherms of wetting, this work is aimed at the structural changes occurring in the adsorption layer in response to changes of the liquid composition. In the case of organophilic montmorillonites the structural changes of the adsorption layer can be detected by X-ray diffraction studies.

Our aim is, therefore, to establish correlations between the adsorption excess isotherms and the enthalpy isotherms, and to calculate the dependence of the enthalpy of wetting on the composition of the liquid mixture. The results provide useful information not only about the structure of the adsorption layer, but also the colloidal stability of dispersed systems in organic medium.

1. THEORETICAL RELATIONS

1.1. The volume and the composition of the surface layer

For the adsorption of binary liquid mixtures, the adsorption excess amount $n_1^{\sigma(n)}$ on the solid surface is given by definition [1-3]:

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

in which n^0 is the total amount of the liquid mixture, x_1^0 is the mole fraction of the first component before adsorption and x_1 in the equilibrium bulk phase.

If only physical adsorption occurs the material balance from of the adsorption the Ostwald- de Izaguirre equation is obtained:

$$n_1^s \sigma(n) = n^0 \Delta x_1 = n_1^s x_2 - n_2^s x_1 = n_1^s - n^s = n^s (x_1^s - x_1) \quad (2)$$

which establishes a correlation between the adsorption excess amount, the material content $n^s = n_1^s + n_2^s$ and the composition $x_1^s = n_1^s/n^s$ of the interfacial layer. According to the adsorption layer model the volume of the interfacial layer [V^s] is given by the next equation.

$$V^s = n_1^s V_{m,1} + n_2^s V_{m,2} \quad (3)$$

$V_{m,1}$ and $V_{m,2}$ are the molar volumes of the materials in the adsorption layer and, by first approximation, can be considered identical with the molar volume in the liquid state. This model ("adsorption space filling model") is essentially analogous to the pore filling model and implies the condition that the thickness of the adsorption layer should be constant in an certain composition range. From the knowledge of the adsorption volume V^s , and the specific surface A^s , the thickness of the layer $t = V^s/A^s$, can be calculated [4-6]. Equation (3) can be transformed into

$$V^s = (n_1^s + r n_2^s) V_{m,1} \quad (4)$$

where $r = V_{m,2}/V_{m,1}$ is the ratio of the molar volumes of the components. Introducing the volume fraction of the adsorption layer:

$$\Phi_1^s = \frac{n_1^s V_{m,1}}{V^s} \quad \text{and} \quad \Phi_2^s = \frac{n_2^s V_{m,2}}{V^s} \quad (5)$$

from Equations (2)-(5) we obtain the relationship

$$\Phi_1^s = \frac{x_1^s}{x_1^s + r x_2^s} = \Phi_1 + \frac{n_1^s \sigma(n) V_{m,2}}{V^s (x_1 + r x_2)} \quad (6)$$

in which $\Phi_1 = x_1/(x_1 + r x_2)$ is the volume fraction of the bulk phase. The volume fraction of the adsorption layer can be calculated from the excess isotherm and V^s .

There are several methods for calculating the adsorption capacity of the pure component $V_{1,0}^s$. One is the well-known Everett-Schay function [7,8]:

$$\frac{x_1 x_2}{n_1^s \sigma(n)} = \frac{V_{m,1}}{V_{1,0}^s} \left[\frac{r}{S-1} \cdot \frac{S-r}{S-1} \right] x_1 \quad (7)$$

which can preferentially be applied for the determination of $V_{1,0}^s$ in the case of U-shaped excess isotherms.

Another is the Schay-Nagy graphical extrapolation, in which n_1^s and n_2^s can be calculated from the middle linear section of the S-shaped excess isotherms [2,8]. The value of V^s is obtained from Eq.(4).

1.2. Immersional wetting in binary liquids

The heat of immersion can be calculated for the adsorption layer model. When the adsorbent is immersed in the liquid mixture, an adsorption layer $n^s = n_1^s + n_2^s$ is formed on the surface. The total enthalpy of wetting is given, according to Everett [7,9]:

$$\Delta_w H_t = n^s x_1^s \Delta_a h_1 + n^s x_2^s \Delta_a h_2 + H^{se}(x_1^s) + \Delta H^e(x_1) \quad (8)$$

in which $\Delta H^e(x_1) = H^e(x_1) - H^e(x_1^0)$ is a mixing therm, i.e. the change in the enthalpy of mixing in bulk phase. For a given liquid mixture, where $\Delta x_1 = x_1^0 - x_1$, is known the function $\Delta H^e(x_1)$ can be calculated from the enthalpies of mixing found in literature. The function $\Delta_w H_t = f(x_1)$ should be corrected by function $\Delta H^e = f(x_1)$. In adsorption of ideal or almost ideal liquid mixtures, this correction is not necessary ($\Delta H^e=0$). After the correction, introducing the volume fractions Φ_1^s and Φ_2^s , Eq.(8) will be

$$\Delta_w H = \Delta_w H_t - \Delta H^e = \Phi_1^s n^s \Delta_a h_1 + \Phi_2^s n^s \Delta_a h_2 + H^{se}(\Phi_1^s) \quad (9)$$

The therm $\Delta_a h_i = h_i^s - h_i$ ($i=1,2$) is the change of enthalpy due to adsorption of the components i which will further be

called molar enthalpy of adsorption. The $n^s_{i,0}$ ($i=1,2$) is the adsorption capacity in the pure liquid. In Eq.(9) $n^s_{2,0}\Delta_a h_2 = \Delta_w H_2^0$ is the wetting enthalpy in the pure second component. After further transformations,

$$\Delta_{21}H = \Delta_w H - \Delta_w H_2^0 = \Phi_1^s n^s_{1,0}(\Delta_a h_1 - \Delta_a h_2/r) + H^{se}(\Phi_1^s) \tag{10}$$

which is related to the calculation of $\Delta_{21}H$ displacement enthalpy. The enthalpy change due to the adsorption displacement can be measured in a flow microcalorimeter.

If the adsorption layer shows ideal behaviour, $H^{se}=0$, the surface layer composition Φ_1^s calculated from the calorimetric data [10]:

$$\Phi_{1,cal}^s = \frac{\Delta_w H - \Delta_w H_2^0}{\Delta_w H_1^0 - \Delta_w H_2^0} = \frac{\Delta_{21}H}{\Delta_w H_1^0 - \Delta_w H_2^0} \tag{11}$$

In systems with U-shaped excess isotherms, where the function $\Delta_w H = f(x_1)$ increases monotonously, Φ_1^s is calculated according to Eq. (9) (Fig. 1A).

In systems with S-shaped excess isotherms, the function $\Delta_w H = f(\Phi_1)$ has a backward section for $\Phi_1 > \Phi_1^a$, and Eq. (9) is not suitable for the calculation of Φ_1^s . For this purpose, the enthalpy isotherm of immersional wetting has to be divided into two sections at the azeotropic composition (x_1^a), and the calculations have to be made for the regions separately [11-14].

The first section ranges from $\Phi_1 = 0$ to $\Phi_1 = \Phi_1^a$ and the formula proposed is

$$\Phi_{1,cal}^s = \frac{(\Delta_w H - \Delta_w H_2^0)\Phi_1^a}{\Delta_w H^a - \Delta_w H_2^0} \tag{12}$$

which is a version of Eq.(11) using U-shaped excess isotherms. In Eq.(12) the heat of wetting $\Delta_w H^a$, related to the azeotropic point, is obtained from the function $\Delta_w H(\Phi_1)$ at Φ_1^a (Fig. 1B).

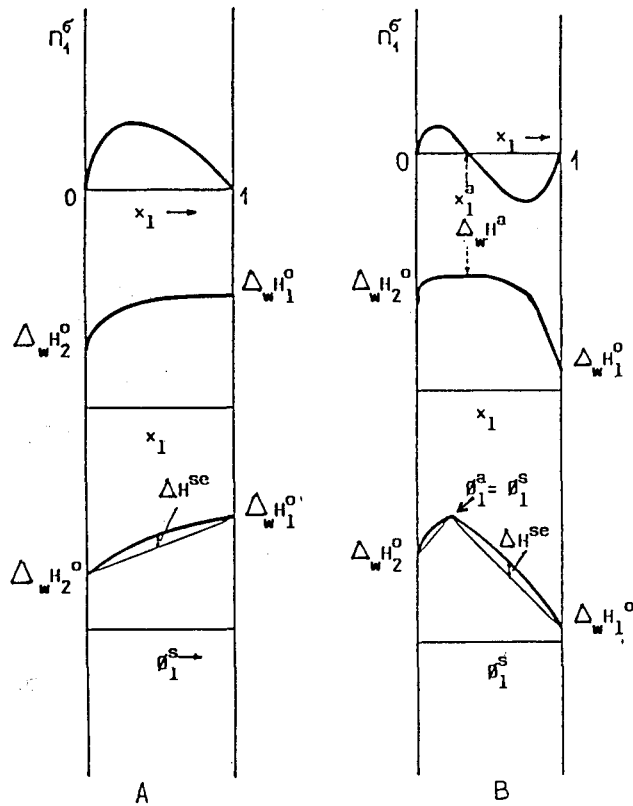


Fig. 1. Correlation between the adsorption excess ($n_1 \sigma(n)$) and the enthalpy of wetting ($\Delta_w H$) isotherms. A: U-shaped excess isotherm, B: S-shaped excess isotherm.

The second range is from $\Phi_1 = \Phi_1^a$ to $\Phi_1 = 1$. In this case the following equation can be used:

$$\Phi_{1,\text{cal}}^s = \Phi_1^a + \frac{(\Delta_w H - \Delta_w H_2^0)(1 - \Phi_1^a)}{\Delta_w H_1^0 - \Delta_w H_1^a} \quad (13)$$

If the values of $\Phi_{1,\text{cal}}^s$ calculated from Eq.(12) and (13) are identical to the composition of the interfacial layer Φ_1^s , then $H^{se}=0$, i.e. the adsorption layer, behaves ideally.

Another method for determination of the adsorption capacity is the combination $n_1^s = n_1^{\sigma(n)} + n^s x_1$ (Eq.(2)) with Eqs.(8,9). If $H^{se}=0$, we obtain [12]:

$$\frac{\Delta_w H - \Delta_w H_2^0}{n_1^{\sigma(n)}} = \Delta_a h_1 - \Delta_a h_2/r + n^s(\Delta_a h_1 - \Delta_a h_2/r) \frac{x_1}{n_1^{\sigma(n)}} \quad (14)$$

This equation is also a linear function, the intercept of which is $b = \Delta_a h_1 - \Delta_a h_2/r$, and the slope $S = n^s (\Delta_a h_1 - \Delta_a h_2/r)$. The adsorption capacity is $n^s = S/b$. Eq.(14) was first applied by Woodbury and Noll for the study of the adsorption of diluted solutions via flow microcalorimetric measurements [15]. According to our studies on the adsorption of binary liquid mixtures, Eq.(14) can well be used for the determination of n^s in a relatively wide concentration range [14].

In S-shaped excess isotherms, the value of the adsorption azeotropic composition x_1^a is known. As, at the azeotropic point, $x_1^a = x_1^s = n_1^s/n^s$ the value V^s can also be determined from Eq.(4):

$$V^s = [n^s x_1^a + r n^s (1 - x_1^a)] V_{m,1} \quad (15)$$

The differential molar enthalpy of wetting ($\Delta_{d,w}h$) can be calculated by differentiating Equation (8) in relation to ($n_1^s = n^s x_1^s$).

$$\Delta_{d,w}h = \left[\frac{d(\Delta_w H - \Delta_w H_2^0)}{dn_1^s} \right]_{T,A^s} = \Delta_a h_1 - \Delta_a h_2/r + \left(\frac{dH^{se}}{dn_1^s} \right)_{T,A^s} \quad (16)$$

Assuming that the adsorption layer is ideal, $\Delta_{d,w}h = \Delta_a h_1 - \Delta_a h_1/r$ the difference between the adsorption enthalpies of the two components is constant. This difference can also be determined from Eq.(14). The validity of both Eqs.(14) and (16) can be checked by experimental data.

1.3. Free energy of wetting in binary liquids

The free energy change can be calculated in analogy to Eq. (10):

$$\Delta_{21}G = \Delta_w G - \Delta_w G_2^0 = \Phi_1^s n^s_{1,0} (\Delta_a g_1 - \Delta_a g_2/r) + G^{se}(\Phi_1^s) \quad (17)$$

In Eq. (17) $\Delta G^e(\Phi_1)$ is neglected because the Gibbs equation contains only quantities characteristic of the adsorbed layer, which means that mixing in the bulk does not affect data related to the adsorbed layer.

Free energy of wetting is the isothermic reversible work done when an S/L interface forms and is calculated from the Gibbs equation [2,16-18]:

$$\Delta_{21}G = \sigma - \sigma_2^0 = -RT \int_{a_1=0}^{a_1} \frac{n_1^{\sigma(n)}}{x_2^{a_1}} da_1 \quad (18)$$

where σ_2^0 is the S/L interfacial energy in pure component 2 and σ is at $a_1 = x_1 f_1$ in the mixture, respectively.

The Redlich-Kister equation is very reliable for calculating the activity coefficients for the bulk phase of the two components [19]:

$$\ln f_1 = x_2^2 \left\{ \sum_{j=1}^N \alpha_j [(2j-1) \cdot x_1 - x_2] \cdot (x_1 - x_2)^{j-2} \right\} \quad (19)$$

$$\ln f_2 = x_1^2 \left\{ \sum_{j=1}^N \alpha_j [x_1 - (2j-1) \cdot x_2] \cdot (x_1 - x_2)^{j-2} \right\} \quad (20)$$

After determination of the liquid -vapour equilibrium data, the activities can be calculated ($a_i = f_i x_i$) [20-23]. Combining Eqs.(17) and (6) gives (21) if, in a certain concentration range of the adsorption layer, $G^{se} = 0$. This assumption can be justified with Eq.(17) because $\Delta_{21}G = f(\Phi^{s_1})$ gives a linear function in a wide concentration range:

$$\frac{\Delta_{21}Gx_1}{n_1\sigma(n)\Phi_1} = r(\Delta_a g_1 - \Delta_a g_2/r) + n^{s_{1,0}}(\Delta_a g_1 - \Delta_a g_2/r) \frac{x_1}{n\sigma(n)_1} \quad (21)$$

Equation (21) gives a straight line provided the adsorbed layer can be taken as ideal, i.e., $\Delta G^{se} \cong 0$. For displacement enthalpies, similarly,

$$\frac{\Delta_{21}Hx_1}{n_1\sigma(n)\Phi_1} = r(\Delta_a h_1 - \Delta_a h_2/r) + n^{s_{1,0}}(\Delta_a h_1 - \Delta_a h_2/r) \frac{x_1}{n_1\sigma(h)} \quad (22)$$

Applying Eqs. (21) and (22) together, provides several data as:

- (a) adsorption capacity ($n^{s_{1,0}}$ and $V^{s_{1,0}} = n^{s_{1,0}} \cdot V_{m,1}$)
- (b) molar free energy of displacement ($\Delta_{21}g = \Delta_a g_1 - \Delta_a h_2/r$)
- (c) molar enthalpy of displacement ($\Delta_{21}h = \Delta_a h_1 - \Delta_a h_2/r$)
- (d) molar entropy of displacement ($\Delta_{21}s = \Delta_a s_1 - \Delta_a s/r$).

1.4. Interlayer swelling and disaggregation in binary liquids

Adsorbents susceptible to swelling or disaggregation in pure liquids or mixtures do not maintain their definite surface structure, which is characteristic in the dried state. When such an adsorbent is immersed in a liquid, internal surface areas become accessible and the material is disaggregated (Fig.2.). In case of layered materials such as 2/1 layer silicates, the internal surface areas (inter-layer-spaces) also become accessible, but the adsorbent is not disaggregated completely [24-27]. The stacks of layers remain together and the wetting liquid is present between the layers. These structural changes can be detected by X-ray diffraction and the layer separation can be determined [4-6,27].

Before wetting, the enthalpy of the adsorbent is $mh^s = A^{s_{dry}}h^s$. In the equilibrium state after wetting and swelling and disaggregation the enthalpy is changed to $A^{s_{wet}}h^s + \Delta_{sw}H$. The surface of the wetted and disaggregated adsorbent is $A^{s_{wet}}$, $A^{s_{wet}} > A^{s_{dry}}$. The enthalpy of swelling is $\Delta_{sw}H$ and h^s is the surface enthalpy of the adsorbent e.g. in unit of Jm^{-2} . Considering these effects in Eqs. (8)-(10), the next Eq. becomes:

$$\Delta_w H = \Phi^{s_1} \Delta_w H^{\circ}_1 + (1 - \Phi^{s_1}) \Delta_w H^{\circ}_2 + H^{se}(\Phi^{s_1}) + h^s(A^{s_{wet}} - A^{s_{dry}}) + \Delta_{sw}H \quad (23)$$

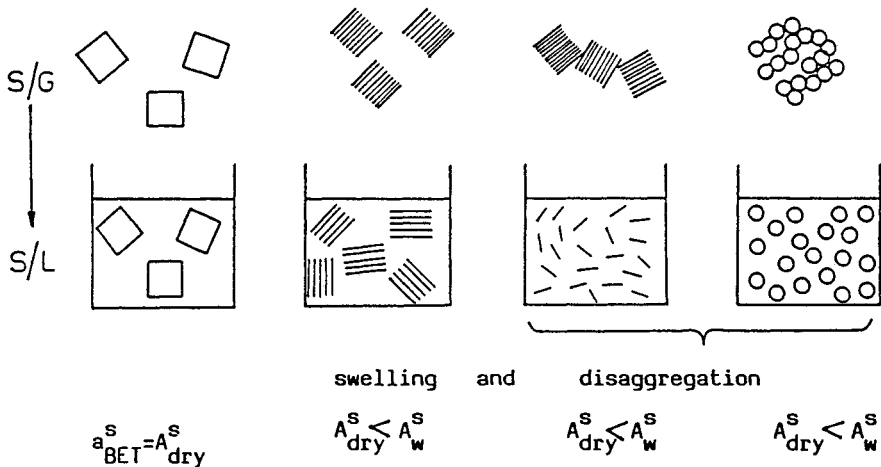


Fig.2. The immersional wetting process in different types of adsorbent

For layered materials, this statement can be checked by X-ray diffraction. However these measurements indicate the interlayer separation (basal spacing d_L) to depend on the composition of the liquid mixture Φ_1 . Therefore, the part of enthalpy related to swelling $\Delta_{sw}H$ depends also on the composition of the bulk phase. The function $\Delta_{sw}H = f(\Phi_1)$ in Eq.(23) can only be determined if the adsorption and microcalorimetric studies are in the same liquid mixture on non-swelling adsorbents having almost identical surface properties. Comparison of Eqs. (8-10) and (23) gives the relationship

$$\Delta_w H = \Delta_w H_{id} + H^{se}(\Phi_1^s) + \Delta_{sw} H \quad (24)$$

$\Delta_w H_{id}$ can be computed separately. In non-swelling adsorbents the difference $\Delta_w H - \Delta_w H_{id}$ gives the function $H^{se}(\Phi_1^s)$. The enthalpy of swelling can then be calculated to

$$\Delta_{sw} H = \Delta_w H - \Delta_w H_{id} - H^{se}(\Phi_1^s) \quad (25)$$

as a function of the bulk phase composition.

2. MATERIALS AND METHODS

The adsorption experiments were performed with organophilic derivatives of two clay minerals, the non-swelling illite and the swelling montmorillonite. Preparation of the organophilic derivatives has been described in previous publications [14,26,27]. The following materials were used (Table 1):

Illite, Montmorillonite: natural layer silicate, $d < 2\mu m$, separated by peptization and sedimentation, purified by dialysis, pretreated with methanol.

Surfactant-clay organocomplexes: purified clay made organophilic through treating with cationic surfactants to different extent (4-6,14,26,27):

Hexadecylpyridinium-illites (HDP-illite)

Hexadecylpyridinium-montmorillonites (HDP-mont.)

Octadecylpyridinium-montmorillonite (ODP-mont.)

Dimethyldihexadecylammonium-montmorillonite (DMDH-mont.)

The organic cation content (organophilicity) is given in Table I.

Table 1. Results of the analysis of the adsorption excess isotherms and S/L thermodynamic potential functions in methanol(1)-benzene(2) mixtures

Adsorbent	organic cation mmol/g	$V_{1,0}^s \cdot 10^2$ (cm ³ /g) S.N.	$V_{1,0}^s \cdot 10^2$ (cm ³ /g) Eq.(14)	$V_{1,0}^s \cdot 10^2$ (cm ³ /g) Eq.(21)	$V_{1,0}^s \cdot 10^2$ (cm ³ /g) Eq.(22)	$-\Delta_{21}^s$ kJ/mol Eq.(21)	$-\Delta_{21}^h$ kJ/mol Eq.(22)	$-T\Delta_{21}^s$ kJ/mol
Na-illite	0.000	3.37	3.37	3.30	3.00	2.50	13.65	11.15
HDP-illite 1	0.097	5.03	4.62	4.60	3.67	2.82	4.32	1.50
HDP-illite 2	0.139	5.23	5.07	4.25	4.75	2.18	3.21	1.03
HDP-illite 3	0.233	5.17	5.18	5.50	5.52	1.98	2.27	0.29
Na-montm.	0.000	8.60	8.51	8.07	8.50	10.50	21.50	11.00
HDP-montm.1	0.555	18.52	-	17.60	-	5.56	-	-
HDP-montm.2	0.851	23.10	-	22.51	-	4.2	-	-
HDP-montm.	0.820	22.65	-	24.70	-	4.6	-	-
DMDH-montm.	0.824	20.61	-	23.55	-	3.8	-	-

S.N. : Schay-Nagy extrapolation method.

The adsorption excess isotherms were determined in methanol-benzene mixtures [4-6]. The enthalpies of wetting were determined with batch method in the pure liquids and mixtures. The liquid/solid ratio was so large that the condition $x_1^\circ = x_1$ was fulfilled, which is necessary for the application of Eqs. (9)-(14) and (22)-(25). The exothermic and endothermic heat effects are reported in detail in [27]. The X-ray diffraction measurements were also carried out in pure liquids and liquid mixtures [4-6,27]. The organic liquids were dried over a Merck molecular sieve immediately before use. The accuracy of the measurements has been discussed in previous papers [4,6,27].

3. RESULTS AND DISCUSSION

3.1. Non-swelling illite and HDP-illites

The adsorption capacities V^S for U- and S-shaped excess isotherms were calculated by the Schay-Nagy extrapolation and the adsorption space filling model by Eqs. (2-7).

Figures 3 and 4 show the excess isotherms and surface layer compositions determined for illite and for three gradually organophilized HDP-illites in methanol(1)-benzene(2) mixtures. These adsorption equilibrium functions (Eq. (6)) indicate the composition of the adsorption layers Φ_1^S as a function of the composition of the bulk phase Φ_1 in volume fractions. The amount of methanol in the adsorption layer decreases with increasing coverage by hexadecylpyridinium cations.

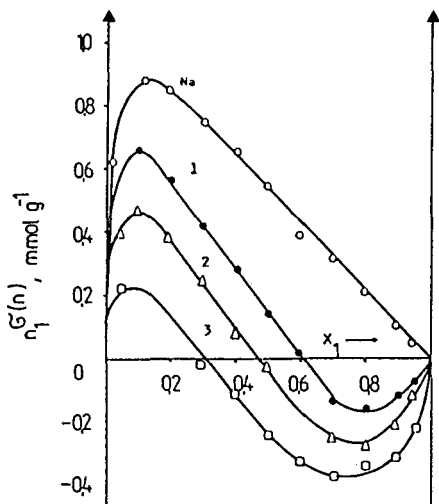


Fig.3. Adsorption excess isotherm on Na-illite and on HDP-illite derivatives in methanol(1)-benzene(2) mixtures. Na: sodium-illite, 1, 2, 3, HDP-illites organocomplexes

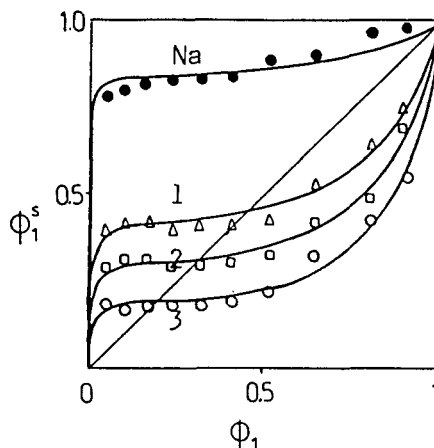


Fig.4 Volume fraction of methanol in the adsorption layer in methanol (1)-benzene(2) mixtures. Na: sodium-illite, 1, 2, 3, HDP-illites organocomplexes

The excess free energy functions, given by integration of the excess isotherms, Eq. (18) reflect the extent of hydrophobization (Fig. 5). Methanol displaces benzene with a maximum change in free energy on Na-illite. The displacement process results in smaller free energy changes on HDP-treated surfaces: the functions show plateau-like maxima at the azeotropic compositions. The free energy function for the sample with maximum hydrophobicity changes sign, which means that the displacement of benzene by methanol is not favoured. Illites and their organophilic derivatives can be dispersed well in methanol-benzene mixtures, therefore their wetting properties can be studied with batch microcalorimetry. Thus, the solid-liquid interaction can be studied only with immersion techniques. The displacement enthalpy can be given as $\Delta_{21}H = \Delta_w H - \Delta_w H^0_2$; its integral isotherm is plotted in Figure 6.

The immersion wetting enthalpy is appreciable on Na-illite. The majority of heat evolution is due to the preferential adsorption of methanol. The enthalpy change decreases upon hydrophobization and it becomes endothermic even in $x_1 > 0.5$

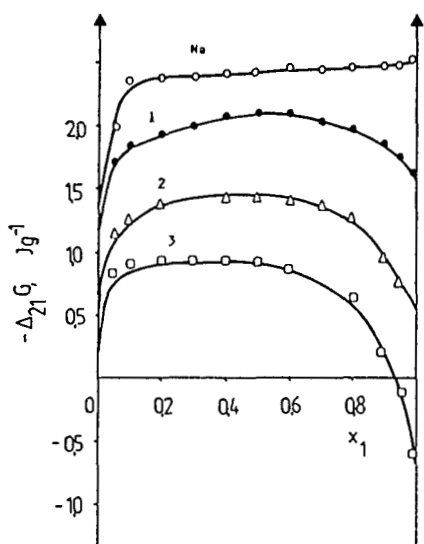


Fig. 5 Free energy of wetting on illites derivatives in methanol(1)-benzene(2) mixtures. Notation as in Fig. 3

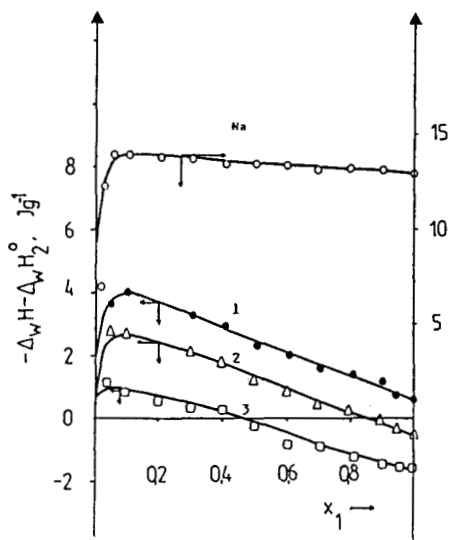


Fig. 6 Immerstonal wetting enthalpy isotherms on illites derivatives. Notation as in Fig. 3

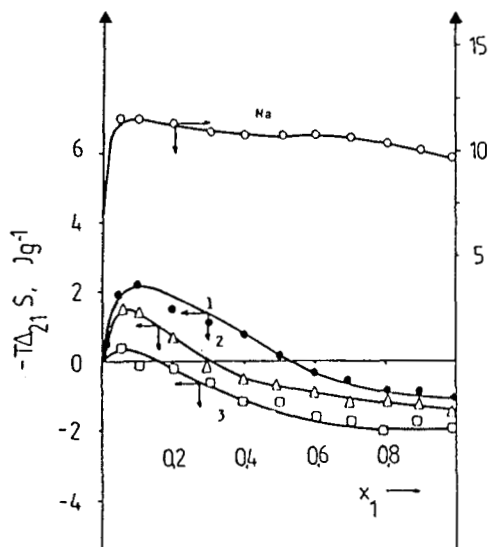


Fig. 7 Entropy of wetting functions on illite derivatives in methanol(1)-benzene(2) mixtures. Notation as in Fig. 3

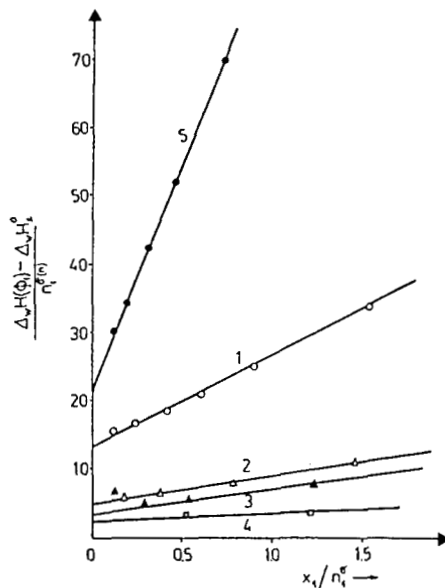


Fig. 8 Determination of the adsorption capacity from Eq. (14). 1: Na-illite, 2, 3, 4: HDP-illites, 5: Na-montm. in methanol (1)-benzene(2) mixtures. Notation as in Fig. 3

compositions. As a consequence, $T\Delta_{21}S$ entropy functions show that displacement must proceed with entropy increase on the hydrophobic samples. There is a decrease in entropy when methanol adsorbs on the hydrophilic illite (see Fig. 7).

The application of Eq. (14) is more favourable, since it enlightens the difference between the molar adsorption enthalpies of the components (Fig. 8, lines 1-4). Eq. (14) can well be used for illite. A good agreement with the adsorption capacities calculated by previous methods is also obtained for the organophilic derivatives. (Table 1.)

The linearized free energy and enthalpy functions for HDP-illites can be seen in Figs. 9. and 10. respectively. The parameters of Eqs. (21) and (22) give the adsorption capacities, the molar wetting energy changes ($\Delta_{21}g$), and the molar wetting enthalpy changes ($\Delta_{21}h$). These data show that the change in molar wetting data decrease with increasing hydrophobicity. (Table 1).

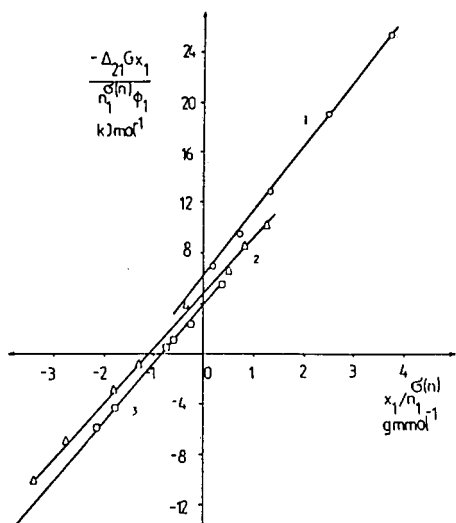


Fig.9 Linear free energy functions on illite derivatives
Notation as in Fig.3

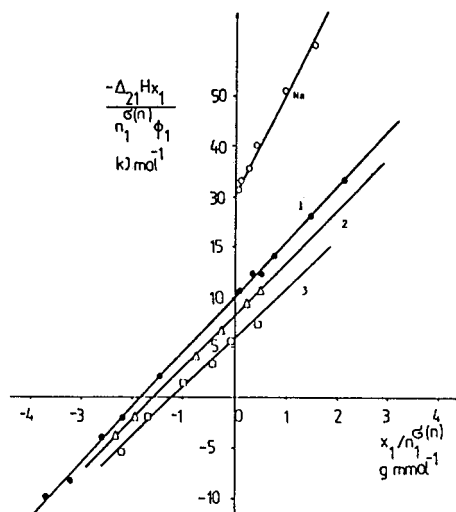


Fig.10 Linear enthalpy of wetting functions on Na: sodium-montm., 1,2,3; HDP-illites in methanol(1)-benzene(2). Notation as in Fig.3

3.2. The swelling montmorillonite and its hydrophobic derivatives

The function $\Psi_1^s = f(\Phi_1)$ derived from the excess isotherm in methanol-benzene mixtures are the same, as on HDP-illite derivatives. The excess isotherm for Na-montmorillonite is U-shaped; methanol is preferentially adsorbed on the surface (4,14). The preferential adsorption of methanol and, correspondingly, the constant thickness of the adsorption layer, are verified by X-ray diffraction measurements. The basal spacing d_L is 16.2Å in concentration range $x_1 = 0.1-1.0$ (Fig. 11.A). The methanol layer between the two silicate layers is $16.2-9.4 = 6.8$ Å thick.

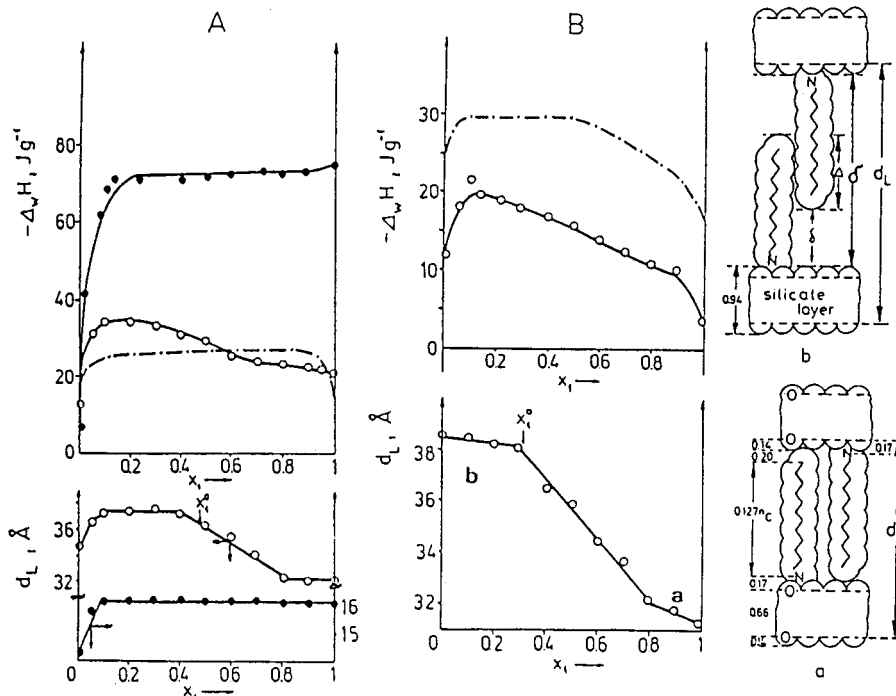


Fig.11. Enthalpy of wetting isotherm ($\Delta_w H$) and basal spacing (d_L) with schematic interlayer structure. A: (o) Na-montm. experimental data, (---) calculated $\Delta_w H_{id}$ using Eq.(11), (o) HDP-montm-1. exp. data, (-.-.-) calc. using Eq.(12,13). B: HDP-montm. (o) exp. data, (-.-.-) calc. data of $\Delta_w H_{id}$ from Eqs.(12,13).

As organophilic montmorillonites give S-shaped excess isotherms from Eqs.(12) and (13) cannot to calculate $\Delta_w H_{id}$. The reason for this is that the three fixed points ($\Delta_w H_1^0$, $\Delta_w H_2^0$ and $\Delta_w H^a$) necessary for the calculation, simply a change of the enthalpy $\Delta_{sw}H$ due to swelling. This enthalpy change measured in non-swelling illite was subtracted from the heat of immersion measured in swelling montmorillonite. This is given by the difference of enthalpies $\Delta_{sw}H$ in the wetting of organophilic montmorillonites and illites of identical surface structure (14,26,27).

Having determined these data, the enthalpy function $\Delta_w H_{id}=f(x_1)$ can now be determined by Eqs. (12) and(13). The deviation between measured and calculated data is -8.0 J/g for $x_1 = 0-0.3$, and 3.5 J/g for $x_1 = 0.6-1.0$. In this Na-HDP-montmorillonite the swelling is not really significant (see that function $d_L = f(x_1)$ in Fig.11.A), consequently the deviation in Fig.11.A is equally determined by the surface excess enthalpy H^{se} and the enthalpy of swelling $\Delta_{sw}H$ according to Eq.(24). In the quantitatively exchanged HDP-montmorillonite, the deviation is more significant (Fig.11.B), i.e. the measured heat effects $\Delta_w H$ are considerably smaller than the calculated values. The change of the extent of swelling is significantly larger and decreases the heat of immersion.

The enthalpy of swelling $\Delta_{sw}H$ for the liquid mixtures was calculated by Eq.(25). Fortunately, the molar excess enthalpy functions $h^{se}=f(\Phi_1^s)$ determined for the organophilic illites are available and, with adsorption capacity n^s , the above function can be calculated for the organophilic montmorillonites that have greater adsorption capacity, but a similar surface mosaic structure. The enthalpies of swelling, calculated according to Eq.(25) as a function of the bulk phase composition, are presented in Fig.12. These endothermic enthalpy changes are in two linear section with the basal spacing d_L (Fig.13).

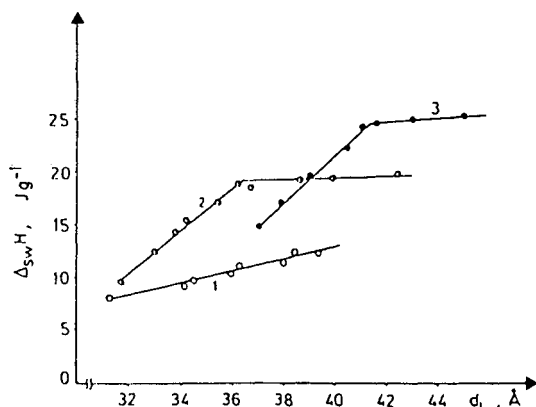


Fig. 12 Enthalpy of swelling as function of basal distances on organophilic montmorillonites in methanol(1)-benzene(2) mixtures

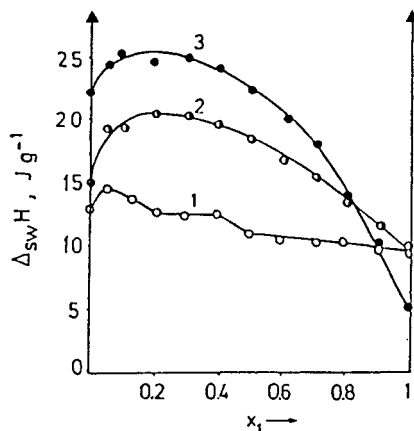


Fig.13 Enthalpy of swelling on organophilic montmorillonites in methanol(1)-benzene(2) mixtures calculated from Eq. (25)

4. CONCLUSIONS

The results obtained from the combination of adsorption and immersional wetting studies on hydrophobic illites, establish that the function $\Phi_1^s = f(\Phi_1)$ essentially determines the enthalpy of wetting isotherms. The calculations are valid only for ideal behaviour of the adsorption layer, but the differences between $\Delta_w H$ (measured) and $\Delta_w H_{id}$ (calculated) provide information about the excess enthalpy of the adsorption layer. The layer on the surface of the illite and its organophilic derivatives is of ideal behaviour in a relatively wide concentration range i.e. $\Delta_w H > \Delta H^{se}$, and therefore the equations proposed for the ideal adsorption layer can well be used to determine, for instance, the adsorption capacity V^s . Among the different equations Eqs.(14,21,22) especially important, since it allows the determination of $n^s_{1,0}$ or V^s and the difference of the free energies

and enthalpies of adsorption (Δ_{21g} , Δ_{21h}), a thermodynamic quantity related to surface hydrophobicity. An analysis of the enthalpy isotherms requires "cutting" the system at the azeotropic point (x_1^a , Φ_1^a). One explanation may be that two adsorption regions of different energies occur at the surface, and the long hydrophobic alkyl chains attached at the surface. The intention was to determine the enthalpy of swelling $\Delta_{sw}H$ using the adsorption and wetting data obtained for the non-swelling organophilic illites. Since both clay minerals have a similar surface structure, the difference between the enthalpies of wetting on the two systems - taking into consideration the necessary correction $H^{se} = f(\Phi_1^s)$ in the liquid mixtures- gives the endothermic enthalpy change related to swelling (5-24 J/g), as a function of the bulk composition and interlayer distance (Figs.12. and 13.).

REFERENCES

1. IUPAC Manual Appendix II. Part I. , Pure Appl. Chem. 31. 579. (1973)
2. Schay G, in Proc. Int. Symposium on Surface Area Determination (Ed.: D.H. Everett) Butterworths, London, p.273. (1970)
3. Kipling J.J., Adsorption from Solution of Non-Electrolytes, Academic Press, New York London, p.54. (1965)
4. Dékány I., Szántó F., Weiss A., Lagaly G., Ber. Bunsenges. Phys.Chem. 89. 62. (1985)
5. Dékány I., Szántó F., Weiss A., Lagaly G., Ber. Bunsenges. Phys.Chem. 90. 422. (1986)
6. Dékány I., Szántó F., Weiss A., Lagaly G., Ber. Bunsenges. Phys.Chem. 90. 427. (1986)
7. Everett D.H., Trans Faraday Soc. 60. 1803. (1964)
8. Schay G., Nagy L. G., J. Coll.Interf. Sci., 38. 302. (1972)
9. Everett D.H., Trans. Faraday Soc.,61. 2478. (1965)
10. Sircar S., J. Chem. Soc. Faraday Trans. I., 79. 2058. (1983)
11. Dékány I., Zsednai Á., László Kr., Nagy L.G., Coll. Surf. 19. 47. (1986)
12. Dékány I., Zsednai Á., Király Z., László Kr., Nagy L. G., Coll. Surf., 23. 41. (1987)
13. Dékány I., Ábraham I., Nagy L.G., László Kr., Coll. Surf., 23, 57. (1987)
14. Dékány I., Szántó F., Nagy L.G., Coll. Polymer Sci., 266, 82. (1988).
15. Woodbury Jr. G.W., Noll L.A., Coll. Surf., 8.1.(1983)
16. Nagy L. G. Schay G. Acta Chim.Hung. 39. 365 (1963)
17. Rudzinski W., Zajac I., Hsu C.C., J. Coll. Interf. Sci., 103. 528. (1985)
18. Rudzinski W., Zajac I., Dékány I., Szántó F., J. Coll. Interf. Sci., 112. 473. (1986)
19. Redlich O., Kister A. T., Ind. Eng. Chem. 40.341.(1948)
20. Hála E., Pick J., Fried V., Vilim O., Vapour-Liquid Equilibrium, Ch.4. Pergamon, London, 1958.
21. Scatchard G., Ticknor L.B., J. Amer. Chem. Soc., 74. 3724. (1952)
22. Miller G.A. Lee C.S., J.Phys. Chem. 77. 2441. (1973)
23. Király Z., Dékány I., Coll.Surf., 34. 1. (1988)
24. Dékány I., Szántó F., Nagy L. G., Coll. Polymer Sci., 256. 150. (1978)
25. Dékány I., Szántó F., Nagy L.G., Progr. Coll. Polymer Sci., 65. 125. (1978)
26. Dékány I., Szántó F., Nagy L. G., J.Coll. Interf.Sci., 103. 321. (1985)
27. Dékány I., Szántó F., Nagy L.G., J. Coll.Interf. Sci., 109. 376. (1986)