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ADSORPTION FROM TERNARY LIQUID MIXTURES ON SILICA GEL AND ALUMINIUM OXIDE

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Abstract

Formation of mixed adsorbed layers was tested for ternary liquid mixtures containing methanol or acetone and the binary solvent benzene+*n*-heptane. The specific excess adsorption isotherms from the liquid phase were measured on silica gel, silanized silica gel and aluminium oxide. The experimental adsorption data are discussed on the basis of the changes in the mixed solvent composition.

Keywords: adsorption, aluminium oxide, silica gel, ternary mixtures

Introduction

Adsorption at a solid/liquid interface is a complicated process depending on many factors. The competition of liquid mixture components for the adsorbent surface and the intermolecular interactions in both the liquid and the surface phase play the main role. Theories of adsorption from solution have been developed in several forms [1–3]. Usually, binary liquid mixtures were taken into account. Some attempts at a theoretical description of adsorption on solids from multicomponent mixtures over the whole concentration range have also been proposed [4–7]. Some of these treatment involve the prediction of adsorption from multicomponent mixtures by using parameters characterizing the corresponding binary solutions [4, 5].

The main problem in the interpretation of adsorption data is to estimate the surface phase capacity and the composition of the surface phase. The adsorption isotherms for liquid mixtures represent the specific surface excess of a given component against its concentration in the bulk solution at equilibrium. The surface layer capacity is not evident in the excess isotherm. Thus, many attempts have been proposed to resolve these isotherms into the individual adsorption isotherms representing the real amounts of liquid components against the bulk solution concentration. The results obtained by using different isotherm equations depend on the assumed model of adsorption and may differ considerably.

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Recently, we proposed a new approach to the interpretation of adsorption data giving information concerning the competition of liquid components for the solid surface and also the formation of mixed surface layers [8–11]. Measurements were made for systems with a ternary liquid phase containing appropriate selected components. The two remaining components constitute a mixed solvent of constant initial composition. Analysis of the changes in mixed solvent composition after equilibration permits conclusions concerning the surface phase structure.

The present work is an attempt to study the solid/liquid interface between ternary solutions of strongly polar components (methanol and acetone) with a mixed solvent (benzene+*n*-heptane) and three types of solids, i.e. silica gel, silanized silica gel and aluminium oxide.

Experimental

Silica gel Si-100, silanized silica gel Si-60H (RP-2) and aluminium oxide Al_2O_3-60H from Merck (Germany) were used as the adsorbents. The specific surface areas a_s of these adsorbents were determined via the low-temperature adsorption/desorption isotherms of nitrogen at 77 K. Nitrogen adsorption/desorption was measured volumetrically with automated Sorptomatic 1800 apparatus, Carlo Erba (Italy). The surface areas were calculated from the linear form of the BET equation, assuming the cross-sectional area of the nitrogen molecule to be 16.2 Å^2. The measured surface areas for the investigated adsorbents were: Si-100, $a_{s_{BET}}=320$ m^{2}g^{-1}; Si-60H (silanized), $a_{s_{BET}}=318$ m^{2}g^{-1}; Al_2O_3-60H, $a_{s_{BET}}=152$ m^{2}g^{-1}.

Additionally, the desorption isotherms were used to estimate the mean pore radius (R_p) and pore volume (V_p). The values for Si-100, Si-60H (RP-2) and Al_2O_3-60H were: $R_p=66$ Å, $V_p=0.98$ cm^{3}g^{-1}, $R_p=47$ Å, $V_p=0.74$ cm^{3}g^{-1} and $R_p=21$ Å, $V_p=0.20$ cm^{3}g^{-1}, respectively.

Moreover, the silanol groups on the surface of bonded silica (silanized) were determined by using high-performance liquid chromatographic instrumentation. The method is based on complete exchange of the silanol protons with deuterium [11]. The same methods served for determination of the surface silanols on the non-bonded, fully hydroxylated silica gel. The estimated concentrations of hydroxyl groups were 7.8 and 3.4 μmol m^{-2} for silica Si-100 and Si-60H (silanized), respectively.

The liquids, of puriss grade from Merck (Germany) and POCH (Poland), were dried over molecular sieves and silica gel before experiments, and were then used without further purification. The ternary solutions were prepared gravimetrically by mixing an appropriate amount of polar component 1 with the binary solvent (2+3). The ratio of the mole fractions of the third and second components, x_3^0/x_2^0, was constant and equal to 1. Adsorption from solutions was measured by the static, immersional method. For each composition, two flask containing the same mixture were prepared. A known quantity of silica (about 4 g) was added to the weighed amount of mixture (about 8 g) in one of the two flasks. The system consisting of mixture and adsorbent was shaken for 8 h. the temperature was controlled to 298±0.1 K. After equilibration, the supernatant solution was centrifuged and then analysed on an HP5890 gas chromatograph from Hewlett-Packard. The initial mixtures served for detector calibration.

Results and discussion

The specific surface excess of the preferentially adsorbed component 1 is expressed in the following form:

$$n_1^{\sigma(n)} = \frac{n^0 (x_1^0 - x_1^l)}{m} \tag{1}$$

where n^0 is the total number of moles of liquid components in contact with m grams of the adsorbent, while x_1^0 and x_1^l are the mole fractions of the first component in the initial and equilibrium solutions, respectively.

Specific surface excess isotherms were determined for five system:

I [methanol (1)+benzene (2)+*n*-heptane (3)]/silica gel Si-100
II [methanol (1)+benzene (2)+*n*-heptane (3)]/silanized silica gel Si-60H/RP-2
III [methanol (1)+benzene (2)+*n*-heptane (3)]/Al_2O_3-60H
IV [acetone (1)+benzene (2)+*n*-heptane (3)]/silica gel Si-100
V [acetone (1)+benzene (2)+*n*-heptane (3)]/silanized silica gel Si-60H/RP-2

The results in the form of the specific excess adsorption isotherms $n_1^{\sigma(n)}=f(x_1^l)$ are shown in Figs 1 and 2. Methanol and acetone are the components preferentially adsorbed over the whole composition range. The results confirm the higher affinity of the adsorbents for polar components than for benzene or *n*-heptane, independently of whether the adsorbent surface is of a polar character (silica, alumina) or is partially nonpolar (silanized silica gel). In this latter case, about 50% of the surface silanol groups are eliminated by the reaction with silanized reagent. As may be expected, on this part of the surface the preferential adsorption of polar components is questionable. However, the resulting excess adsorption of methanol and acetone on silanized silica gel is positive. The shapes of the isotherms are similar and follow a type II or III isotherm in the Schay-Nagy classification [12].

The Gibbs diagram (Fig. 3) illustrates schematically the concentrations of the liquid components for the ternary mixtures used in our experiments. The solid line represents points of different concentrations of component 1 at a constant value of x_3^0/x_2^0, i.e. the initial composition of the liquid phase. At the adsorption equilibrium, due to adsorption, the ratio x_3^l/x_2^l and the composition of the ternary mixtures is represented by a broken line. The deviation of the value of x_3^l/x_2^l from that of x_3^0/x_2^0 is highest at a small concentration of component 1 in the bulk solution. Thus, the specific surface excess isotherms in Figs 1 and 2 show the dependences $n_1^{\sigma(n)}=f(x_1^l)$ along line a'.

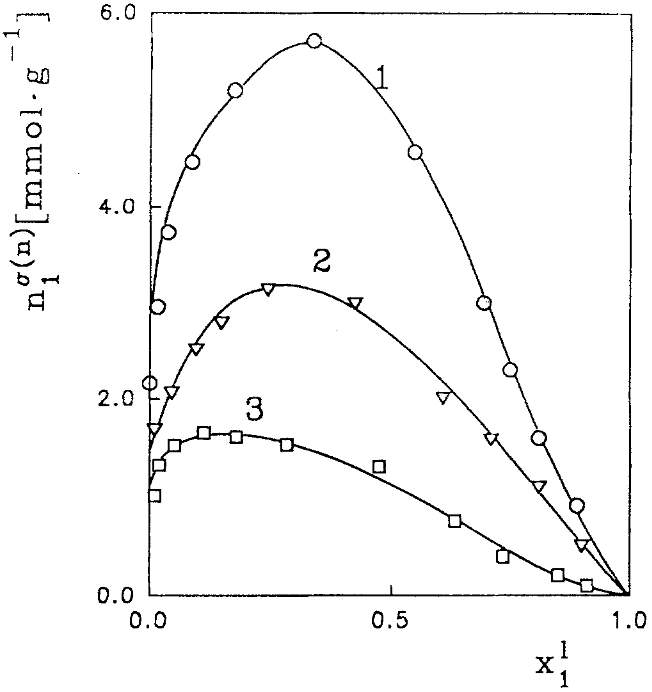

Fig. 1 Experimental surface excess isotherms for the system [methanol (1)+benzene (2)+*n*-heptane (3)] as a function of x_1^l at 298 K for $x_3^0/x_2^0=1$ on silica gel Si-100 (1), silanized silica gel Si-60H (2) and Al_2O_3-60H (3)

The very high adsorption of methanol and acetone suggests the formation of multilayer surface structures.

The surface excess of the *i*-th component from an *n*-component liquid mixture may be written in terms of the adsorbed phase mole fraction of this component, $x_{i(n)}^s$:

$$n_i^{\sigma(n)} = n^s\,(x_{i\,(n)}^s - x_i^l) \tag{2}$$

where n^s is the total number of moles in the surface phase, while $x_{i(n)}^s$ and x_i^l are the mole fractions of the *i*-th component in the surface and bulk phase, respectively. Then,

$$\sum_{i=1}^{n} n_i^{\sigma(n)} = 0 \quad \text{and} \quad \sum_{i=1}^{n} x_{i\,(n)}^{s} = 1$$

for $n = (1, 2, \ldots, n)$. The mole fraction of the i-th component in the surface phase is a function of the bulk phase composition. The analytical form of this function depends on the assumed surface model.

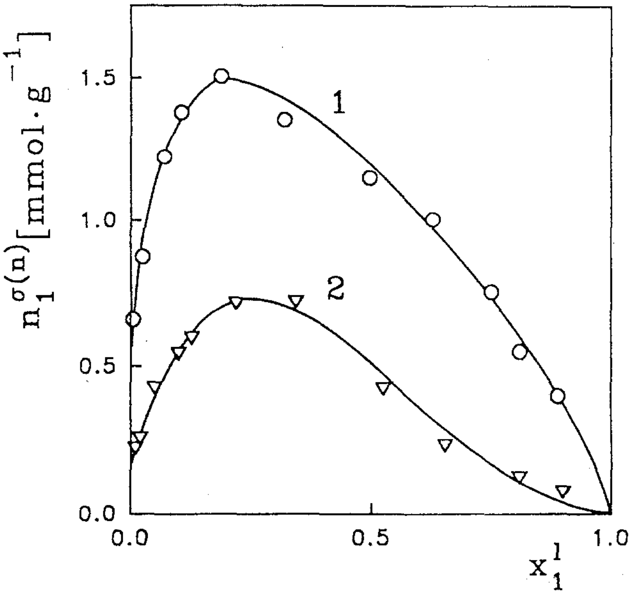

Fig. 2 Experimental surface excess isotherms for the system [acetone (1)+benzene (2)+n-heptane (3)] as a function of x_1^1 at 298 K for $x_3^0/x_2^0=1$ on silica gel Si-100 (1) and silanized silica gel Si-60H (2)

Generally, for an energetically homogeneous adsorbent surface, the mole fraction $\chi_{i(n)}^{s}$ may be expressed as follows [5]:

$$x_{i\,(n)}^{s} = \frac{K_{in}x_{in}}{1 + \sum_{j=1}^{m} K_{jn}x_{jn}} \tag{3}$$

for $i = 1, 2, \ldots, m = n-1$, where

$$x_{in} = x_i^1 | x_n^1$$

and

$$K_{in} = \frac{K_i}{K_n} = \exp - \frac{\varepsilon_{in}}{RT} \tag{4}$$

where ε_{in} is the difference between the adsorption energies of the i-th and n-th components. Additionally, the following assumptions are made in Eq. (3): the molecular sizes of all components are identical, the total number of molecules in the surface phase is constant, and both phases, surface and bulk, are ideal. Calculation of the mole fractions $x^s_{i(n)}$ requires a knowledge of n^s.

The relations presented above were adopted for ternary mixtures (component 1+mixed solvent (2+3)), assuming the constancy of the mole fractions of the two components, $x^l_3/x^l_2 = r = \text{const}$.

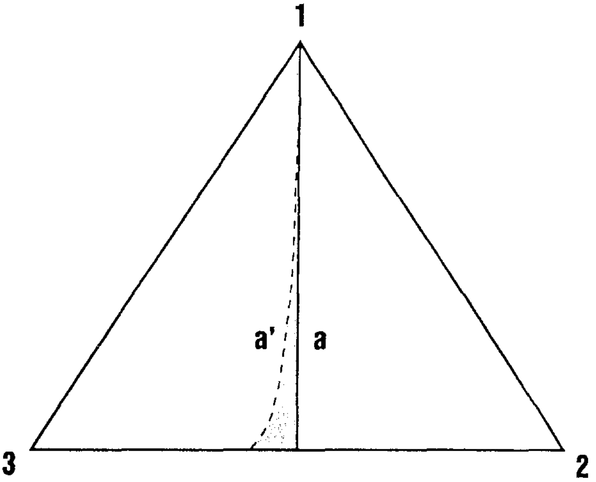

Fig. 3 Gibbs diagram illustrating the compositions of the ternary mixtures used in the experiments, a – initial compositions, a' – equilibrium compositions, 1 – methanol/acetone, 2 – benzene, 3 – n-heptane

From Eqs. 1 and 3, after some transformations, one can obtain for $n=3$ [10]:

$$\frac{x^l_1(1-x^l_1)}{n_1^{\sigma(n)}} = \frac{1}{n^s}\left(\frac{1}{K^*-1} + x^l_1\right) \tag{5}$$

where

$$K^* = \frac{(r+1)K_{13}}{1+rK_{23}} \tag{6}$$

Equation (6) is a special case of the general equation describing adsorption from multicomponent liquid mixtures given in [6].

The parameters n^s may be determined from the dependence of the left-hand side of Eq. (5) on x^l_1. This procedure is identical with Everett's method for determining n^s in the case of adsorption from binary solutions [13]. Theoretically, if the assumptions of the adsorption model corresponding to Eq. (5) are fulfilled, the dependence of the left-hand side of Eq. (5) on χ_1^l should give a straight line with slope $1/n^s$. For different values of r, these lines should be parallel.

Figure 4a,b shows plots of Eq. (5) for the investigated systems. The range of the least squares fit is shown by the solid lines. The linearity is good in most cases for x_1^l<0.5. calculated values of n^s are given in Table 1. For exclusive adsorption of component 1, one can assume that the surface phase contains only molecules of this component. In that case, the n^s values represent the real ad-

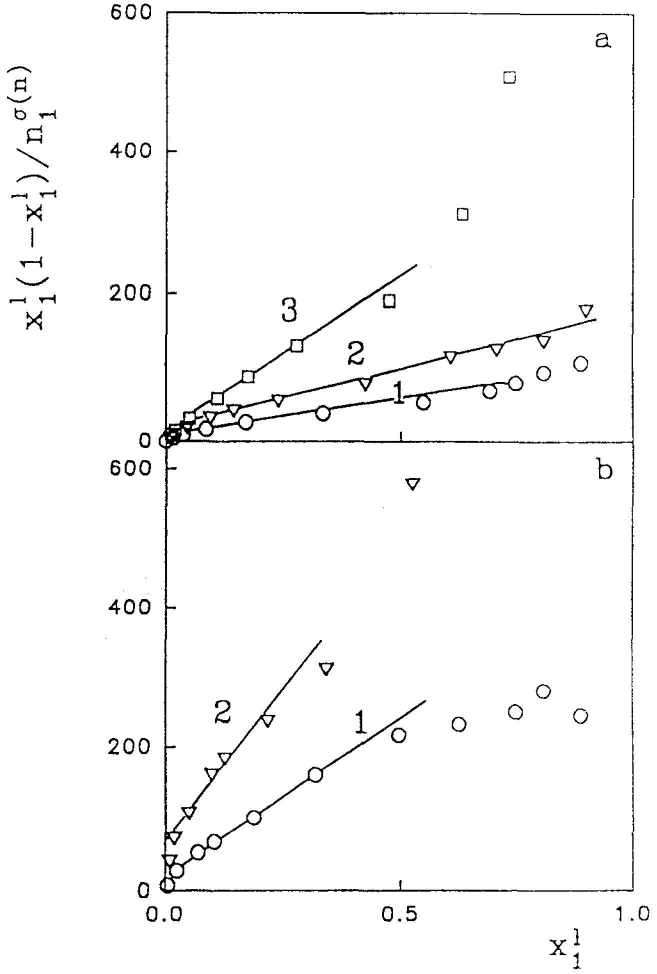

Fig. 4 Experimental results plotted according to Eq. (5); a) [methanol (1)+benzene (2)+n-heptane (3)] system: 1 – Si-100; 2 – Si-60H, 3 – Al_2O_3-60H; b) [acetone (1)+benzene (2)+n-heptane (3)] system: 1 – Si-100; 2 – Si-60H

sorption of component 1, $n^s = n_1^s$. If the appropriate n_1^s values are taken into account, the number of molecular layers t may be calculated from the relation:

$$t = \frac{n_1^s a_1 N}{S_{BET}} \tag{7}$$

where a_1 is the molecular area occupied by component 1 in the interface, and N is Avogadro's number.

Calculations were performed by using molecular areas of methanol and acetone equal to 0.20 and 0.36 nm^2/molecule, respectively. The molecular areas were estimated via the empirical equation of McClellan and Harnsberger [14]. The results suggest that the adsorbed phase for a prevailing number of the systems is of a multilayer character (Table 1, column IV). The experimental results for the [acetone (1)+benzene (2)+n-heptane (3)]/Si-60H system are consistent with the monolayer model of the adsorbed phase.

Table 1 Information concerning the adsorption systems investigated

Mixture	Adsorbent	n^s / mmol g^{-1}	t
Methanol(1) + benzene(2) + n-heptane(3)	SiO_2	11.4	4.3
Methanol(1) + benzene(2) + n-heptane(3)	SiO_2–RP2	6.71	2.5
Methanol(1) + benzene(2) + n-heptane(3)	Al_2O_3	2.27	1.8
Acetone(1) + benzene(2) + n-heptane(3)	SiO_2	2.29	1.5
Acetone(1) + benzene(2) + n-heptane(3)	SiO_2–RP2	1.24	0.9

The values of t should be considered with some approximation, due to the idealized assumptions introduced during their calculation, and also the uncertainty in the values of the molecular areas of the liquid components. In fact, the orientation of these molecules in the adsorbed phase is difficult to predict unambiguously. Particular care should be taken in the case of t values for the systems showing the presence of mixed surface layers involving very dissimilar molecules.

With the breakdown of the monolayer model for silica gel Si-100, Si-60H silanized and aluminium oxide Al_2O_3-60H, it is possible to examine whether the adsorbed phase contains t layers of uniform composition. The composition of the adsorbed phase may be tested on the basis of adsorption data for benzene and n-heptane, i.e. for components which form the mixed solvent of constant (equimolar) initial composition. We shall now analyze the changes in concentration of components 2 and 3 during the preferential adsorption of component 1.

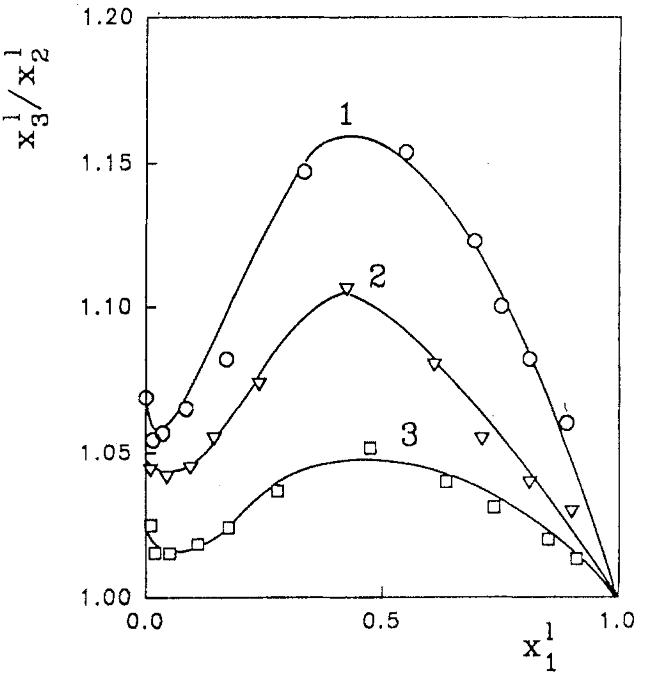

Fig. 5 x_3^l/x_2^l as a function of x_1^l for the system [methanol (1)+benzene (2)+*n*-heptane (3)]: 1 – Si-100; 2 – Si-60H; 3 – Al_2O_3-60H

Figure 5 shows the dependences of the ratio of the mole fractions of *n*-heptane to benzene x_3^l/x_2^l on x_1^l in the equilibrium solution for ternary mixtures containing methanol. As mentioned earlier, the initial ratio $x_3^0/x_2^0=1$. It appears that, for all the investigated systems, the values of x_3^l/x_2^l are higher than x_3^0/x_2^0. This suggests the stronger adsorption of benzene than that of *n*-heptane. At small values of x_1^l, the values of x_3^l/x_2^l are very high and rapidly decrease as the concentration of component 1 increases. At a very low concentration of component 1, only part of the surface is covered by its molecules. The remaining part is occupied by benzene. The decrease in x_3^l/x_2^l illustrates the displacement process, i.e. the process in which alcohol molecules displace benzene from the interface. Because of the very weak adsorption of *n*-heptane, it can be assumed that, even at very low concentrations of component 1 in the bulk solution, *n*-heptane is completely removed from the surface phase. Thus, in the competition process for the adsorbent surface, practically only molecules of alcohol and benzene take part. At higher concentrations of component 1, the values of x_3^l/x_2^l are similar but not identical to the initial value $x_3^0/x_2^0=1$. The equality of x_3^l/x_2^l and x_3^0/x_2^0 would mean that the surface phase is of uniform composition and contains only molecules of component 1 or, rather improbable, the two components of the mixed solvent are adsorbed similarly. The values of $x_3^l/x_2^l>1$ indicate that, on the preferential adsorption of methanol, benzene is also present in the surface phase. Although the constancy of r may be assumed only within higher concentration ranges, the linearity of the plots in Fig. 4 is satisfactory at lower concentrations of component 1. This may be a result of some compensation of the factors connected with the deviations of the bulk and surface phases from ideal behaviour, associated with interactions of the adsorbed molecules, molecular size differences, orientation effects and the surface heterogeneity of the solids. Equation (6) has not been applied previously to systems in which exclusive preferential adsorption of one component occurs. It should be noted that Everett's equation for binary mixtures, analogous in form to Eq. (5), is widely used for the analysis of excess adsorption data for nonideal systems, giving good straight lines (see e.g. [15]).

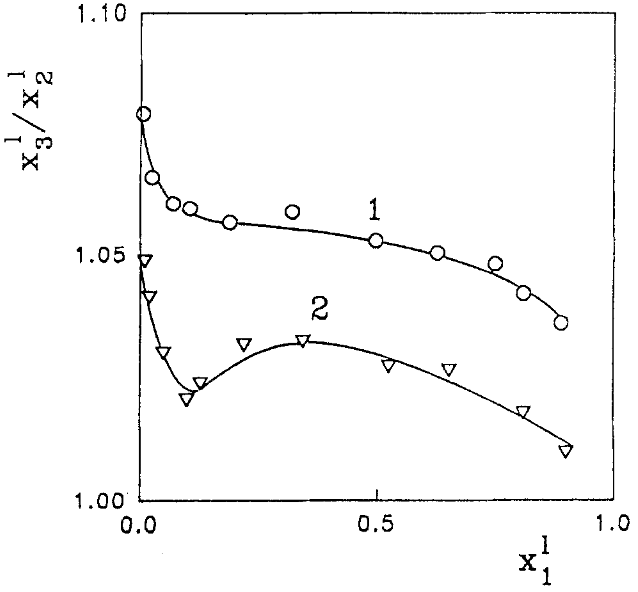

Fig. 6 x_3^1/x_2^1 as a function of x_1^1 for the system [acetone (1)+benzene (2)+n-heptane (3)]: 1 – Si-100; 2 – Si-60H

Similar shapes of the curves $x_3^1/x_2^1 = f(x_1^1)$ may be observed for the mixtures containing acetone (Fig. 6). On aluminium oxide, measurement of the adsorption of acetone is impossible, due to the condensation of acetone molecules in the presence of the basic adsorbent surface. The absolute values of x_3^1/x_2^1 for various adsorbents in Figs 4 and 5 are difficult to compare because they depend on the extent of adsorption on a given solid sample.

The results presented in Figs 5 and 6 become comparable when expressed in terms of the changes in concentration of components 3 and 2 in the bulk solution, i.e. $\Delta x_3^1/\Delta x_2^1$ *vs.* x_1^1, where $\Delta x_i^1=(x_i^0-x_i^1)$.

In fact, the ratio $\Delta x_3^1/\Delta x_2^1$ represents the ratio of the surface excesses $n_3^{\sigma(n)}/n_2^{\sigma(n)}$ at a given x_1^1. Appropriate relationships are shown in Figs 7 and 8. The

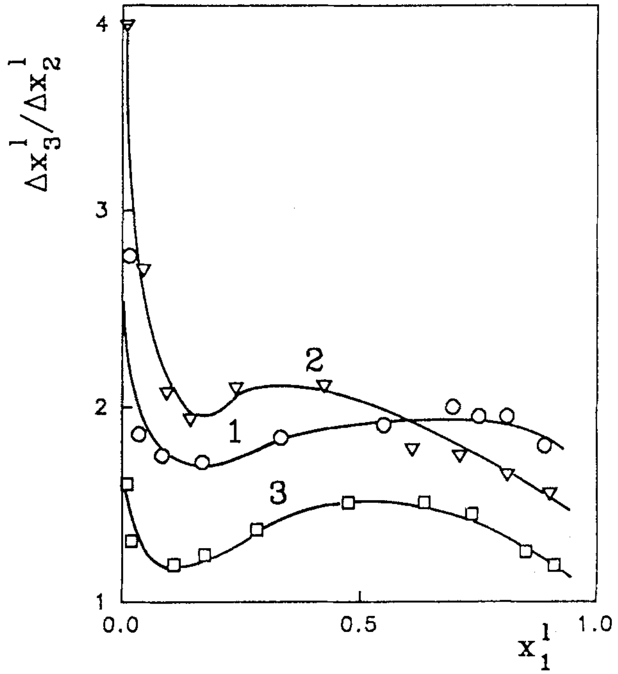

Fig. 7 $\Delta x_3^1/\Delta x_2^1$ as a function of x_1^1 for the system [methanol (1)+benzene (2)+*n*-heptane (3)]: 1 – Si-100; 2 – Si-60H, 3 – Al_2O_3-60H

values of $\Delta x_3^1/\Delta x_2^1$ for the methanol system are seen to be higher than 1. In the case of a uniform surface phase containing only component 1, the value of $\Delta x_3^1/\Delta x_2^1$ should be equal to $x_3^0/x_2^0=1$.

The shape of the curves at lower concentrations of component 1 is most interesting. The widths of the segments corresponding to the displacement process are different and depend on the character of the adsorbent surface. In the case of silanized silica gel, the range of the competition is wider in comparison with fully hydroxylated silica gel for both methanol and acetone. For aluminium oxide, the values of $\Delta x_3^1/\Delta x_2^1$ are relatively low and approach 1 at $x_1^1=0.1$. This may suggest that at this concentration of methanol in the bulk solution the surface is covered with a monolayer of methanol. The increase in the value of $\Delta x_3^1/\Delta x_2^1$ for $x_1^1>0.1$ is probably connected with the adsorption of benzene on the closely packed polar molecules of alcohol.

For the adsorption of methanol on silica gel Si-100, the surface phase has multilayer thickness ($t \cong 4$). The surfaces of silica gel and aluminium oxide are strongly polar, and full coverage with methanol (first layer) is attained at low concentrations of alcohol in the bulk solution. Thus, as may be expected, the composition of the further surface layers is determined mainly by the adsorbate-adsorbate interactions. Our results indicate the different structures of the adsorbed phase for silica gel and aluminium oxide. A more uniform composition

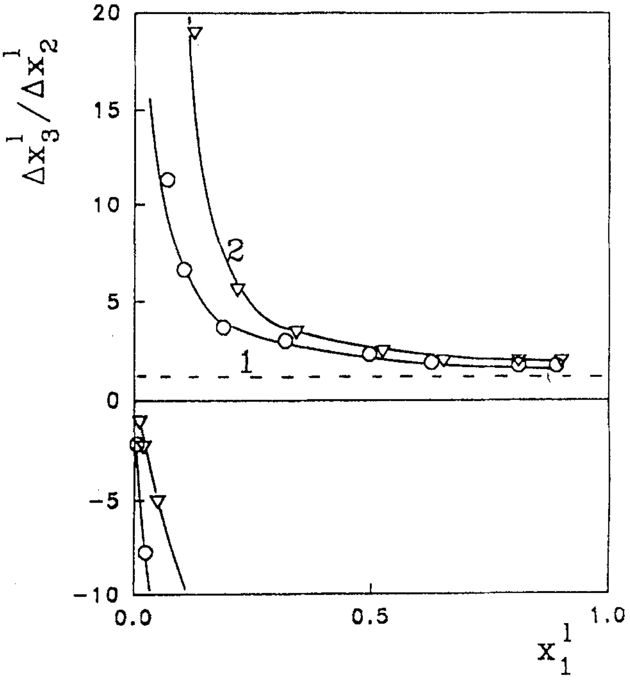

Fig. 8 $\Delta x_3^1/\Delta x_2^1$ as a function of x_1^1 for the system [acetone (1)+benzene (2)+*n*-heptane (3)]: 1 – Si-100; 2 – Si-60H

occurs for Al_2O_3-60H (monolayer/bilayer adsorption), and a mixed composition (methanol+benzene) for Si-100 (multilayer adsorption). In this latter case, the structure and composition of the surface phase are influenced not only by competition, but particularly by other factors such as solvation and/or complexation processes. With regard to the multilayer adsorption of methanol, it can be assumed that benzene molecules are accommodated in a matrix of interstitially bonded alcohol molecules.

Similar behaviour of the liquid components is observed for acetone systems. However, the competition of benzene and acetone for the silica surface is so strong that at lower concentrations ($x_1^1<0.1$) the surface excesses of both acetone and benzene are positive (positive Δx_1^1 and Δx_2^1 values). Thus, in Figs 6 and 7 the ratios $\Delta x_3^1/\Delta x_2^1$ for $x_1^1<0.1$ are negative (Δx_3^1 is negative in the whole concentration range). Above $x_1^1=0.1$, the values of $\Delta x_3^1/\Delta x_2^1$ decrease in accordance with the adsorption mechanism described above.

Similarly, as in the case of the methanol system, the segment of the curve corresponding to the displacement process is extended for silanized silica gel. Moreover, the values of $\Delta x_3^1/\Delta x_2^1$ are higher than those for the methanol system. This indicates that the dual character of the silanized silica surface increases the adsorption of benzene. As a result, the formation of a mixed surface layer in contact with the adsorbent surface within the whole composition range should be assumed. However, in the case of silica Si-100 too the ratio $\Delta x_3^1/\Delta x_2^1$ does not reach the initial value of $x_3^0/x_2^0=1$. This effect may be explained in terms of the complexing tendency of acetone with benzene [16]. It is very probable that the mixed acetone–benzene complexes are present in the surface phase in the whole concentration range.

To summarize, it can be stated that analysis of the composition of the mixed solvent during the adsorption of a specifically adsorbed component gives valuable information concerning the structure of the surface phase. The approach does not require model assumptions. The results of applying this procedure to the present data indicate that the adsorbed phases exhibit a mixed character.

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