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A Simple Method for Determining the Multilayer Effects in Adsorption of Alcohols on Silica Gel

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The excess adsorption isotherms of *n*-pentanol, pentan-2-ol and 2-methylbutan-2-ol from binary and ternary solutions in benzene and *n*-heptane were measured. Experimental adsorption data are discussed in terms of a multilayer model of the surface phase. The main assumption of this model is that the surface layers being near the solid surface contain the molecules of the preferentially adsorbed component only. The phase-exchange reaction of molecules between bulk phase and last surface layer has been taken into account.

On the basis of this theory it has been established for the investigated systems that the surface phase contains three molecular layers. Simultaneously appropriate surface phase capacities were determined.

(Keywords: Multilayer liquid adsorption; Adsorption of alcohols; Ternary liquid mixtures)

Eine einfache Untersuchungsmethode für Mehrschicht-Effekte bei der Adsorption von Alkoholen an Kieselgel

Die Adsorptionsisothermen binärer und ternärer flüssiger Mischungen von *n*-Pentanol, 2-Pentanol oder 2-Methyl-2-butanol in Benzol und/oder *n*-Heptan wurden bezüglich Kieselgel gemessen. Die experimentellen Daten der Adsorption wurden mittels des Mehrschichts-Modells der Oberflächenphase diskutiert. Die Hauptvoraussetzung dieses Modells ist die Annahme, daß die Oberflächenschichten, die sich in der Nähe des Kieselgels befinden, nur Moleküle der bevorzugt adsorbierten Komponente enthalten. Es wurde auch die Phasen-Austauschreaktion von Molekülen zwischen Phaseninnerem und der letzten Oberflächenschicht in Betracht gezogen.

Auf der Basis dieser Theorie wurde für die untersuchten Systeme festgestellt, daß die Oberflächenphase aus drei Molekülschichten besteht. Außerdem wurden die ermittelten Volumina der Oberflächenphase berechnet.

Introduction

The studies of adsorption phenomena of liquid mixtures on solid surfaces under static conditions offer important information which may be used for explaining the retention mechanism of solutes under chromatographic conditions. For polar solvents, especially those which are able to interact with the silica gel surface by hydrogen bonding, the formation of multilayer surface structure was demonstrated[1—4]. In many cases it is reasonable to assume that the surface layer is of two molecular thickness[1,5]. The composition of multilayer surface structure depends strongly on the chemical character of components of the liquid mixture. According to *Toth*'s studies[6,7] if the adsorbent surface shows a polarity similar to one component of the liquid mixture, this component is preferentially adsorbed in the first layer and the second component of different polarity is accumulated in the next layer (negative adsorption of first component in the second layer is observed). Our earlier investigations indicate bilayer adsorption of ester molecules from *n*-heptane solutions and positive/negative bilayer adsorption in the case of benzene solutions i.e. positive adsorption in the first layer and negative adsorption in the second layer[3].

In the present paper the investigations concerning adsorption of isomeric amyl alcohols from binary and ternary mixtures in benzene and *n*-heptane on silica gel surface are presented. An attempt has been made to describe the structure of the adsorbed layers.

Materials and Methods

Silica gel (0.2–0.5 mm fraction) from Merck (GFR) was used as the adsorbent. The specific surface area of the silica gel was determined by the *B.E.T.* method using nitrogen adsorption data at 78 K. Assuming molecular size of one nitrogen molecule equal to 0.162 nm^2, the specific surface area of the silica was evaluated to be about 300 m^2 g^{-1}.

Benzene, *n*-heptane, *n*-amyl alcohol from POCH (Gliwice, Poland) and *sec.*-amyl, *tert.*-amyl alcohols from Fluka (GFR) were dried over silica gel and were used without further purification.

The excess adsorption isotherms of *n*-amyl, *sec.*-amyl and *tert.*-amyl alcohols from binary and ternary mixtures in benzene and *n*-heptane on silica gel were measured at 298 K by using a method described in Ref.[3]. The data for adsorption of *n*-amyl alcohol from benzene were taken from Ref.[2].

Results and Discussion

The excess adsorption isotherms, $n_1^e = \mathrm{f}(x_1^l)$, were calculated according to the relation:

$$n_1^e = n^0 (x_1^0 - x_1^l)/m \qquad (1)$$

where n^0 is the total number of moles of the liquid components being in contact with m grams of the adsorbent, x_1^0 and x_1^l are the mole fractions of 1-st component in the initial and equilibrium solutions, respectively. The plots n_1^e vs. x_1^l are presented in Figs. 1, 2, and 3. The curves 1 and 5 in all figures correspond to binary systems of alcohols with *n*-heptane and benzene, respectively. However, the curves 2, 3, and 4 correspond to ternary systems : amyl alcohol + benzene + *n*-heptane at the ratio of mole fractions of benzene to *n*-heptane 1 : 3, 1 : 1, and 3 : 1, respectively. Experimental points for these systems are shown in the *Gibbs* triangulars. Moreover, in the *Gibbs* triangulars the approximate lines representing the same surface excess are shown. The shape of our isotherms suggests that already at low concentrations of alcohol in bulk solution the maximum

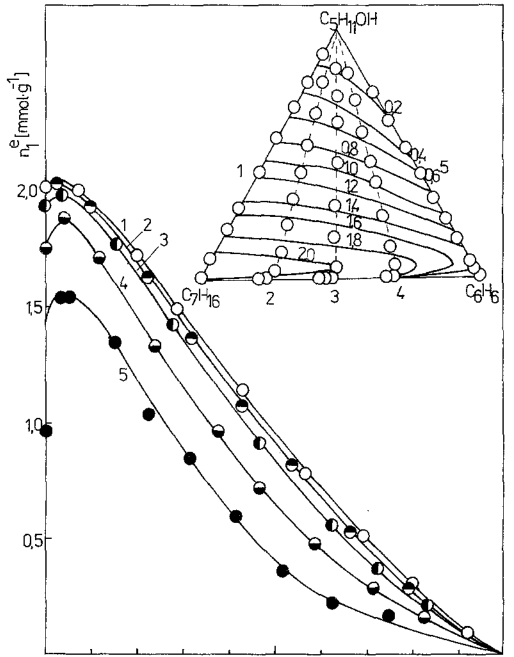

Fig. 1. Excess adsorption isotherms of *n*-amyl alcohol on silica gel at 298 K. Curves *1* and *5*: binary solutions of alcohol in *n*-heptane and benzene, respectively. Curves *2, 3,* and *4* ternary solutions, alcohol + benzene + *n*-heptane at the ratio of mole fractions of benzene to *n*-heptane $x_{C_6H_6}/x_{C_7H_{16}} \simeq 1:3;\ 1:1,$ and $3:1$, respectively. Gibbs triangular: circles represent experimental points, solid lines correspond to the same surface excess (surface excess amounts in mmoles per gram of adsorbent), dashed lines 2, 3, and 4 correspond to the ratios of mole fractions of benzene and *n*-heptane $x_{C_6H_6}/x_{C_7H_{16}} \simeq 1:3;\ 1:1,$ and $3:1$, respectively

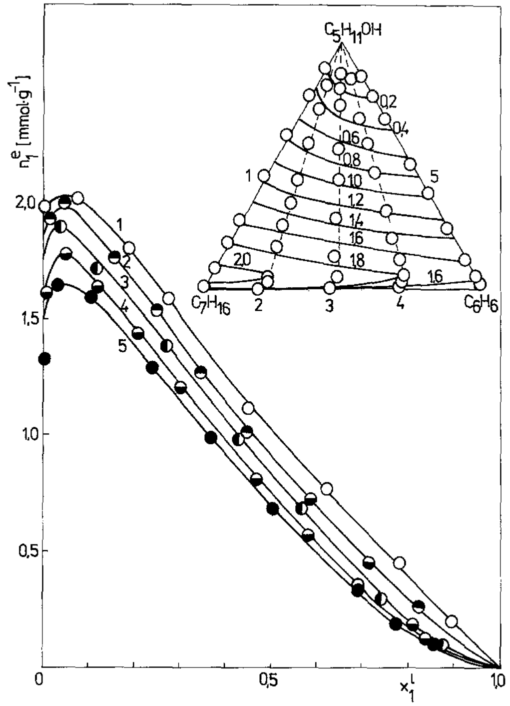

Fig. 2. Excess adsorption isotherms of *sec.*-amyl alcohol on silica gel at 298 K (labelling as in Fig. 1)

thickness of the surface layer is reached. A quantitative interpretation of the experimental data may be made in terms of the formulation presented in Refs.[8,9]. In the case of an adsorption system, in which the 1-st component is strongly adsorbed in comparison to the other components of the liquid mixture (e.g., adsorption of alcohol on silica gel from apolar and weakly polar solvents), we can assume that surface layers being near the adsorbent surface contain the alcohol molecules only. However, the last surface layer contains also the molecules of the other components. The mole fraction of 1-st component in the whole surface phase x_1^s can be defined as follows:

$$x_1^s = \frac{r-1}{r} + \frac{1}{r} y_1^{(r)} \qquad (2)$$

where r is the number of the surface layers.

The mole fraction of 1-st component in the r-th surface layer may be expressed by an *Everett*-type equation[8]:

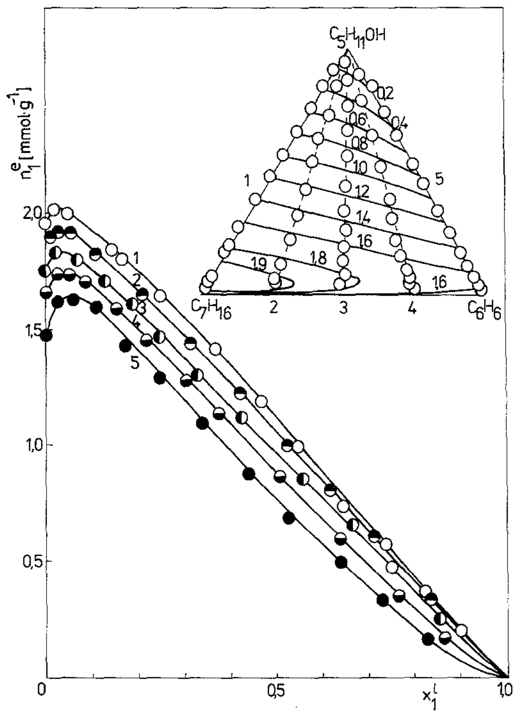

Fig. 3. Excess adsorption isotherms of *tert.*-amyl alcohol on silica gel at 298 K (labeling as in Fig. 1)

$$y_1^{(r)} = \frac{K_{12}^{(r)} x_1^l}{x_2^l + K_{12}^{(r)} x_1^l} \tag{3}$$

where x_1^l and x_2^l are the mole fractions of the 1-st and 2-nd component in the bulk phase, and $K_{12}^{(r)}$ is the equilibrium constant describing the phase exchange reaction of molecules between the bulk phase and the last surface layer.

After differentiation of Eq. (2) with respect to x_1^l we obtain:

$$\frac{\partial x_1^s}{\partial x_1^l} = \frac{1}{r} \frac{K_{12}^{(r)}}{[1 + (K_{12}^{(r)} - 1) x_1^l]^2} \tag{4}$$

On the other hand, taking into account the relationship between x_1^s and the adsorption excess of the 1-st component n_1^e:

$$x_1^s = \frac{n_1^e}{n^s} + x_1^l \tag{5}$$

we have

$$\frac{\partial x_1^s}{\partial x_1^l} = \frac{1}{n^s}\frac{\partial n_1^e}{\partial x_1^l} + 1 \tag{6}$$

where n^s is the total number of moles of both components in the surface phase, which is independent of the bulk phase composition because identical molecular sizes of components have been assumed.

Combination of Eqs. (4) and (6) gives:

$$\frac{\partial n_1^e}{\partial x_1^l} + n^s = \frac{n^s K_{12}^{(r)}}{r[1 + (K_{12}^{(r)} - 1)x_1^l]^2} \tag{7}$$

Eq. (7) may be transformed to the following linear form:

$$h(x_1^l) = \left(\frac{\partial n_1^e}{\partial x_1^l} + n^s\right)^{-1/2} = \left(\frac{r}{n^s K_{12}^{(r)}}\right)^{1/2} [1 + (K_{12}^{(r)} - 1)x_1^l] \tag{8}$$

Having the excess adsorption isotherm $n_1^e(x_1^l)$ we can calculate the function $h(x_1^l) = (\partial n_1^e/\partial x_1^l + n^s)^{-1/2}$. This function has a positive slope for $K_{12}^{(r)} > 1$ (positive adsorption excess in the r-th layer) and a negative slope for $K_{12}^{(r)} < 1$ (negative adsorption excess in the r-th layer). Such behaviour of the adsorption excess in the r-th layer results from the assumption of the *Everett*-type equation (3) for describing the adsorption in the layer in question.

Evaluation of the function $h(x_1^l)$ from the experimental excess adsorption isotherms is possible when the surface phase capacity n^s is known. The relationship (8) is especially convenient for analyzing the decreasing part of the excess adsorption isotherm because in this concentration range the derivative $\partial n_1^e/\partial x_1^l$ is negative, however, $-\partial n_1^e/\partial x_1^l$ assumes a positive value. Thus, evaluating the gratest value of $-\partial n_1^e/\partial x_1^l$ from decreasing part of the isotherm we obtain information that n^s should be greater than this value[10]. Next, we can plot the relationship (8) for successive values of n^s up to the moment of obtaining the linear dependence $h(x_1^l)$ vs. x_1^l. Using the slope and ordinate of this dependence we can calculate the parameters $K_{12}^{(r)}$ and r. It should be pointed out that applicability of Eq. (8) is restricted by the same factors as those concerning *Everett* equation.

For the illustrative purposes we present in Fig. 4 the function $h(x_1^l)$ plotted for different values of n^s for the decreasing part of the excess adsorption isotherm of *sec.*-amyl alcohol from benzene on silica gel. It follows from this figure that assumption of n^s equal to 2.8 mmol g^{-1} gives a good linearity of the function $h(x_1^l)$. Moreover, this function is a little sensitive to changes in the n^s value for higher concentrations of the 1-st component. Fig. 5 shows an example of dependence $\partial n_1^e/\partial x_1^l$ vs. x_1^l and

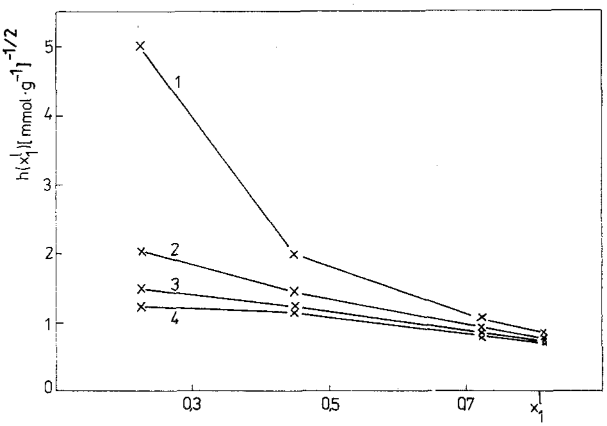

Fig. 4. Dependence of $h(x_1^l)$ against x_1^l plotted according to Eq. (8) at different n^s values for *sec.*-amyl alcohol + benzene system. Curves *1, 2, 3,* and *4* correspond to n^s values equal to: 2.4; 2.6; 2.8, and 3.0 mmol g^{-1}, respectively

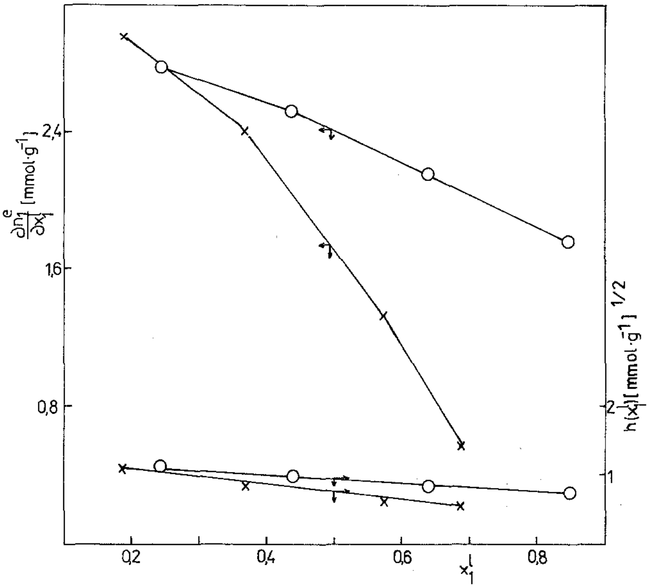

Fig. 5. Dependence of $\partial n_1^e/\partial x_1^l$ vs. x_1^l and $h(x_1^l)$ vs. x_1^l for the best-fit n^s value: *n*-amyl alcohol + benzene system (x), *n*-amyl alcohol + *n*-heptane system (o)

$h(x_1^l)$ vs. x_1^l for adsorption of *n*-amyl alcohol from binary mixtures in benzene and *n*-heptane on silica gel. This figure presents the function $h(x_1^l)$ for the best-fit value of n^s. The numerical values of n^s, $K_{12}^{(r)}$ and r for all investigated systems are summarized in Table 1.

Table 1. *Informations concerning the systems investigated*

Mixture	$-(\partial n_1^e/\partial x_1^l)$ [mmol g^{-1}]	n^s [mmol g^{-1}]	$K_{12}^{(r)}$	r
n-Amyl alcohol + benzene	2.96	3.80	0.15	1.0
n-Amyl alcohol + *n*-heptane	2.76	3.60	0.47	2.6
sec.-Amyl alcohol + benzene	2.36	2.80	0.33	3.0
sec.-Amyl alcohol + *n*-heptane	2.43	3.00	0.66	3.1
tert.-Amyl alcohol + benzene	2.35	3.20	0.44	2.4
tert.-Amyl alcohol + *n*-heptane	2.35	3.10	1.10	2.7

According to Ref.[11] we have the molecular areas a_i equal to 0.43, 0.57 and 0.48 nm^2 for benzene, *n*-heptane and amyl alcohol, respectively. Thus, for the systems investigated in the present paper we may assume that the molecular sizes of the mixture components are approximately equal.

The values of $K_{12}^{(r)}$ summarized in Table 1 are smaller than unity for the preveailing number of systems; it means that the adsorption excess in the last surface layer is negative. This negative adsorption decreases from *n*-amyl to *tert.*-amyl alcohol and becomes positive in the case of the *tert.*-amyl alcohol—*n*-heptane system. In other words, it depends on the alkyl chain length of alcohol molecules. The strong interactions of hydroxyl groups of alcohol with silanol groups of the silica surface and interactions between the alkyl chains of alcohols and benzene molecules cause that the final result is the threelayer surface phase, in which the third layer contains practically molecules of the solvent. This effect is smaller for *n*-heptane solutions of amyl alcohols in comparison to benzene solutions.

For the mixture *n*-amyl alcohol + benzene we observe some inconsistency between the values of n^s, $K_{12}^{(r)}$ and r (see Table 1). It means that the assumed model of the surface phase cannot be used for describing this system. Adsorption of normal alcohols from benzene was discussed in papers[2,4]. Two different approaches lead to the conclusion that benzene is present even in the first adsorbed layer. Different adsorption mechanisms of normal and chain branched amyl alcohols may be connected either with different solvation of alkyl chains of both types of molecules or with higher competition of benzene and *n*-amyl alcohol clusters for silica

Table 2. *The equilibrium adsorption data for the n-amyl alcohol (1) + benzene (2) + n-heptane (3) system at* $x_{C_6H_6}/x_{C_7H_{16}} \simeq 1:1$

x_1^l	x_2^l	n_1^e [mmol g^{-1}]	n_2^e [mmol g^{-1}]
0.007	0.468	1.942	—0.465
0.042	0.463	1.992	—0.736
0.164	0.401	1.783	—0.588
0.288	0.343	1.419	—0.485
0.474	0.261	0.916	—0.413
0.633	0.182	0.569	—0.268
0.738	0.131	0.376	—0.182
0.842	0.079	0.214	—0.093

Table 3. *The equilibrium adsorption data for the sec.-amyl alcohol (1) + benzene (2) + n-heptane (3) system at* $X_{C_6H_6}/x_{C_7H_{16}} \simeq 1:1$

x_1^l	x_2^l	n_1^e -[mmol g^{-1}]	n_2^e [mmol g^{-1}]
0.041	0.464	1.902	—0.707
0.126	0.418	1.727	—0.563
0.278	0.345	1.370	—0.453
0.432	0.278	0.972	—0.403
0.573	0.207	0.680	—0.236
0.744	0.127	0.299	—0.145
0.814	0.093	0.177	—0.085
0.878	0.060	0.099	—0.041

Table 4. *The equilibrium adsorption data for the tert.-amyl alcohol (1) + benzene (2) + n-heptane (3) system at* $x_{C_6H_6}/x_{C_7H_{16}} \simeq 1:1$

x_1^l	x_2^l	n_1^e [mmol g^{-1}]	n_2^e [mmol g^{-1}]
0.006	0.478	1.741	0.179
0.025	0.477	1.821	—0.377
0.074	0.468	1.797	—0.470
0.130	0.432	1.706	—0.407
0.191	0.399	1.605	—0.363
0.255	0.378	1.463	—0.310
0.336	0.334	1.291	—0.274
0.428	0.288	1.118	—0.250
0.564	0.224	0.857	—0.202
0.670	0.172	0.651	—0.177
0.761	0.123	0.471	—0.155
0.868	0.064	0.242	—0.094

surface (*n*-amyl alcohol may be adsorbed in associated form which is little probable for *sec.*-amyl and *tert.*-amyl alcohol).

Different structures of the surface phase of the investigated alcohol isomers are confirmed by a different shape of excess adsorption isotherms. It is easy to observe that in the case of *n*-amyl alcohol the adsorption isotherms are much more concave in comparison to *sec.* and *tert.*-amyl alcohol. Moreover, in the case of ternary solutions the extent of *n*-amyl alcohol adsorption depends relatively more strongly on benzene concentration in the bulk solution.

Experimental data for ternary mixtures confirm the existence of mixed surface layers which contain mainly alcohol and benzene molecules forming multilayer surface structures. As an illustration the adsorption data of the investigated alcohol isomers and benzene for chosen ratios of mole fractions of benzene to *n*-heptane, $x_{C_6H_6}/x_{C_7H_{16}} \simeq 1$, are summarized in Tables 2, 3, and 4. The negative surface excess of benzene is smaller than the surface excess of *n*-heptane in the whole concentration range of solutions.

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