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Multilayer Adsorption of Alcohols from Benzene/n-Heptane Mixtures on Silica Gel

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An equation for multilayer adsorption from multicomponent liquid mixtures on solid surfaces[1] has been examined. For this purpose experimental adsorption data for four alcohols from benzene/n-heptane mixture on silica gel have been measured. Average number of the adsorbed layers, heterogeneity parameter and capacity of the surface phase have been evaluated by using the equation mentioned above.

(Keywords: Adsorption from ternary liquid mixtures; Adsorption of alcohols on silica gel; Multilayer liquid adsorption)

Mehrschichten-Adsorption von Alkoholen aus Benzol/n-Heptan-Mischung an Silica Gel

Eine Gleichung für Mehrschichten-Adsorption an festen Oberflächen[1] aus Mehrkomponentenlösungen wurde getestet. Zu diesem Zweck wurden experimentelle Daten für die Adsorption von vier Alkoholen aus Benzol/n-Heptan-Mischung an Silica Gel herangezogen. Der Mittelwert für die Anzahl der Adsorptionsschichten, der Heterogenitätsparameter und die Kapazität der Oberflächenphase wurde aus dieser Gleichung berechnet.

Introduction

In the preceeding paper[1] theory of the multilayer adsorption from multicomponent liquid mixtures on energetically homogeneous and heterogeneous solid surfaces has been formulated. This formulation is an extension of earlier theoretical studies[2–5] concerning the monolayer adsorption from multicomponent liquid mixtures on solid surfaces. According to the paper[1], the mole fractions of components in the

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surface phase for ternary liquid mixture "1 + 2 + 3" and solid surface showing quasi-*Gauss*ian energy distribution may be expressed as follows:

$$y_1 = \frac{x_{13}}{rz} \frac{(L_{13}^{(1)} z)^m}{1 + (L_{13}^{(1)} z)^m} + \frac{1}{r} \sum_{k=2}^{r} \frac{L_{13}^{(k)} x_{13}}{1 + L_{13}^{(k)} x_{13} + L_{23}^{(k)} x_{23}} \tag{1}$$

$$y_2 = \frac{L_{21}^{(1)} x_{23}}{rz} \frac{(L_{13}^{(1)} z)^m}{1 + (L_{13}^{(1)} z)^m} + \frac{1}{r} \sum_{k=2}^{r} \frac{L_{23}^{(k)} x_{23}}{1 + L_{13}^{(k)} x_{13} + L_{23}^{(k)} x_{23}} \tag{2}$$

$$y_3 = \frac{1}{r} \frac{1}{1 + (L_{13}^{(1)} z)^m} + \frac{1}{r} \sum_{k=2}^{r} \frac{1}{1 + L_{13}^{(k)} x_{13} + L_{23}^{(k)} x_{23}} \tag{3}$$

where

$$z = x_{13} + L_{21}^{(1)} x_{23} \tag{4}$$

$$L_{i3}^{(k)} = \prod_{l=k}^{r} K_{i3}^{(l)} \; ; \; i = 1,\, 2 \tag{5}$$

$$L_{i3}^{(r)} = K_{i3}^{(r)} \; ; \; i = 1,\, 2 \tag{6}$$

$$L_{ij}^{(k)} = L_{i3}^{(k)} / L_{j3}^{(k)} ; \; i \neq j \text{ and } i, j = 1,\, 2 \tag{7}$$

and

$$x_{ij} = x_i / x_j \text{ for } i, j = 1,\, 2,\, 3 \text{ and } i \neq j \tag{8}$$

x_i and y_i are mole fractions of the i-th component in the bulk and surface phases, respectively, $K_{i3}^{(k)}$ is the equilibrium constant describing the exchange of a molecule of the i-th component from the $(k + 1)$-layer with a molecule of the 3-rd component from the k-th adsorbed layer, r is the total number of adsorbed layers and m is the heterogeneity parameter characterizing shape of the quasi-*Gauss*ian energy distribution.

The first terms in Eqs. (1)-(3) describe the monolayer adsorption of the i-th component, whereas, the other terms in these expressions describe the total adsorption of the i-th component in the second and higher adsorbed layers. Eqs. (1)-(3) have been derived by assuming that the 1-st and 2-nd components show similar interactions with the adsorbent surface and they differ from the 3-rd component.

In this paper Eq. (3) has been examined by using experimental data of the excess adsorption for alcohols adsorbed from benzene/n-heptane mixture on silica gel. Further, the subscript 1 will be used for n-heptane, 2 - for benzene and 3 - for a given alcohol.

Theoretical

Adsorption data are frequently measured for $x_{12} = const$[6]. At this condition the variable $L_{13}^{(1)} z$ is equal to:

$$L_{13}^{(1)} z = a\, x_{13} \tag{9}$$

where

$$a = L_{13}^{(1)} + L_{23}^{(1)} x_{21} \tag{10}$$

However, the variable

$$L_{13}^{(k)} x_{13} + L_{23}^{(k)} x_{23}$$

may be expressed as follows:

$$L_{13}^{(k)} x_{13} + L_{23}^{(k)} x_{23} = x_{13} (L_{13}^{(k)} + L_{23}^{(k)} x_{21}) = b^{(k)} x_{13} \tag{11}$$

Assuming that the equilibrium constants $L_{i3}^{(k)}$ for the second and higher layers are equal, i.e.,

$$L_{i3}^{(2)} = L_{i3}^{(3)} = \ldots = L_{i3}^{(r)} = L_{i3} \text{ for } i = 1, 2 \tag{12}$$

we obtain the following relationship:

$$b^{(2)} = b^{(3)} = \ldots = b^{(r)} = b \tag{13}$$

According to Eqs. (10), (11) and (13) the quantities a and b may be treated as parameters of Eq. (3). This equation may be rewritten in the following form:

$$y_3 = \frac{1}{r} \frac{1}{1 + (a\, x_{13})^m} + \frac{r - 1}{r(1 + b\, x_{13})} \tag{14}$$

Relationship between the adsorption excess of the 3-rd component n_3^e, and Eq. (14) is the following:

$$n_3^e = n^s \left[\frac{1}{r[1 + (a\, x_{13})^m]} + \frac{r - 1}{r(1 + b\, x_{13})} - x_3 \right] \tag{15}$$

where n^s is the capacity of adsorbed layers.

Eq. (15) contains five parameters: n^s, r, m, a and b, which may be evaluated from the experimental dependence of n_3^e upon x_3.

Numerical Procedure

The parameters n^s, r, m, a and b of Eq. (15), may be evaluated by calculating minimum of the following function:

$$F = \sum_{p=1}^{P} [n_{3,p}^{e(\exp)} - n_{3,p}^{e(\text{calc})} (n^s, r, m, a, b)]^2 \tag{16}$$

with respect to the parameters n^s, r, m, a, b, where P is the total number of experimental points, and $n_{3,p}^{e(\mathrm{exp})}$ and $n_{3,p}^{e(\mathrm{calc})}$ are the p-th experimental and calculated values of n_3^e, respectively. The value $n_{3,p}^{e(\mathrm{calc})}$ may be calculated according to Eq. (15). Minimum of the function F may be evaluated by using algorithm MINUITS available from CERN Computer Centre Program Library. The main steps of this algorithm are following:

1. Initial estimation of the parameters n^s, r, m, a and b by using the simplex method.
2. Exact evaluation of the parameters n^s, r, m, a and b, estimated in the first step, by means of the algorithm of coupled gradients. For the purpose of shortening of calculation time the gradient of the function F has been evaluated by applying the analytical equations for the partial derivatives.

Calculations have been performed for successive values of r, i.e., $2, 3, 4, \ldots$.

Experimental

The experimental excess isotherms have been measured for ethanol, propanol, *n*-butanol and *n*-pentanol adsorbed from benzene/*n*-heptane mixture on silica gel at 298 K. The adsorbates were obtained from POCh, Gliwice, Poland. The silica gel (0.2 to 0.5 mm fraction) was from E. Merck, Darmstadt, G.F.R., and its *BET* surface area, determined by nitrogen adsorption, was equal to 290 m^2/g.

The surface excess was calculated by Eq. (3) given in the paper of *Minka* and *Myers*[7]. A ternary solution of known amount and composition was prepared for each experimental point. The solutions for a given set of experimental points were prepared in such way that $x_{21} = 0.333$, 1.0 and 3.0. The amounts of liquid and adsorbent were measured gravimetrically. Equilibrium was obtained by shaking the flask with the adsorbent and liquid mixture in a water bath for 15 to 20 h at 298 K ± 0.1. Compositions of ternary solutions were measured with a gas chromatograph. Other details concerning the measurements are described in the papers[6,8].

Results and Discussion

The experimental adsorption excesses for alcohol (3) and benzene (2) are plotted in Figs. 1-4 (circles). The adsorption excesses for alcohols were utilized to calculate the parameters n^s, r and m. These parameters have been evaluated by using the numerical procedure described above for each set of experimental points. It follows from Figs. 1-4 that change of the composition of benzene and *n*-heptane in the bulk phase ($x_{21} = 0.333$, 1.0 and 3.0) influences insignificantly on the adsorption excesses of alcohols. Therefore, in Table 1 the average parameters r, n^s

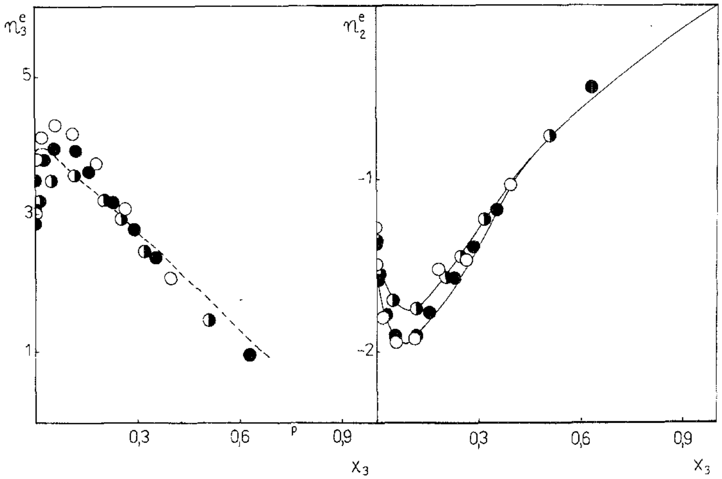

Fig. 1. Experimental adsorption excesses (circles) for ethanol (n_3^e) and benzene (n_2^e) on silica gel at 298 K plotted for $x_{21} = 0.333$ (◑), 1.0 (●) and 3.0 (○). Ternary bulk phase: ethanol (3) + benzene (2) + n-heptane (1). The dashed line denotes n_3^e obtained from Eq. (15) for $x_{21} = 1$ and the solid lines denote n_2^e obtained from analogous equation to Eq. (15)

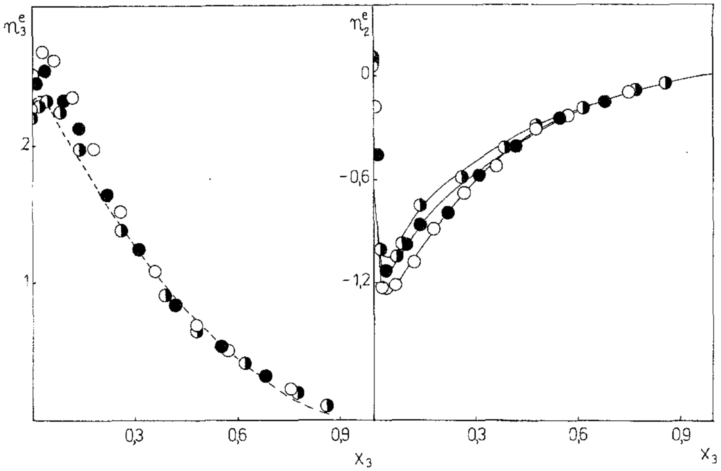

Fig. 2. Experimental adsorption excesses (circles) for propanol (n_3^e) and benzene (n_2^e) on silica gel at 298 K plotted for $x_{21} = 0.333$ (◑), 1.0 (●) and 3.0 (○). Ternary bulk phase propanol (3) + benzene (2) + n-heptane (1). The dashed line denotes n_3^e obtained from Eq. (15) for $x_{21} = 3.0$ and the solid lines denote n_2^e obtained from analogous equation to Eq. (15)

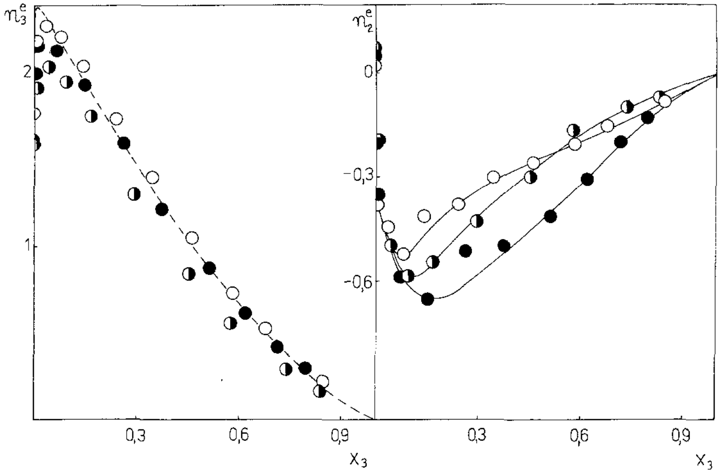

Fig. 3. Experimental adsorption excesses (circles) for *n*-butanol (n_3^e) and benzene (n_2^e) on silica gel at 298 K plotted for $x_{21} = 0.333$ (◑), 1.0 (●) and 3.0 (○). Ternary bulk phase: *n*-butanol (3) + benzene (2) + *n*-heptane (1). The dashed line denotes n_3^e obtained from Eq. (15) for $x_{21} = 1/3$ and the solid lines denote n_2^e obtained from analogous equation to Eq. (15)

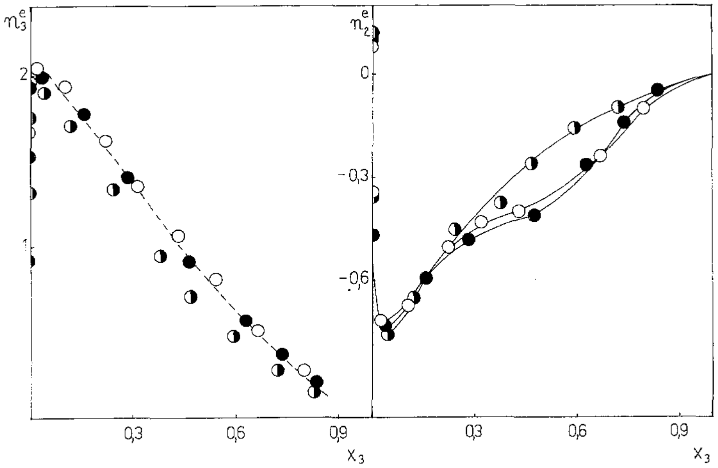

Fig. 4. Experimental adsorption excesses (circles) for *n*-pentanol (n_3^e) and benzene (n_2^e) on silica gel at 298 K plotted for $x_{21} = 0.333$ (◑), 1.0 (●) and 3.0 (○). Ternary bulk phase: *n*-pentanol (3) + benzene (2) + *n*-heptane (1). The dashed line denotes n_3^e obtained from Eq. (15) for $x_{21} = 1$ and the solid lines denote n_2^e obtained from analogous equation to Eq. (15)

and *m* are summarized. These parameters are compared with those evaluated by *Ościk* et al.[9] from the excess isotherms of alcohols adsorbed from benzene or *n*-heptane on silica gel. The parameters *r* and n^s, taken from the paper[8], were calculated by using the modified *Everett*'s test for evaluating the number of adsorbed layers. The agreement of the parameters *r* and n^s evaluated from adsorption of ternary and suitable binary liquid mixtures is satisfactory. For the adsorption of the systems investigated, the parameter *m* is about 0.3, n^s changes from 5.5 to 4.9, and *r* is equal to 4 for ethanol and gradually decreases to 2. It follows from theoretical considerations[10] that the parameter *m* belongs to the interval (0,1) and for $m = 1$ Eqs. (1)-(3) become the expressions for energetically homogeneous solid surfaces. The value $m = 0.3$ obtained for adsorption systems investigated, is small; it means that effects of energetic heterogeneity are great.

Table 1. *Parameters characterizing adsorption of alcohols from benzene/n-heptane mixtures on silica gel at 298 K*

Alcohol	r	n^s	m	r^{b}	$n^{s\,\mathrm{b}}$	r^{h}	$n^{s\,\mathrm{h}}$
Ethanol	4	5.2	0.31	3	7.1	4-5	9.2
Propanol	3	5.5	0.28	3	5.2	4	4.8
n-Butanol	2	4.3	0.50	3	4.5	2-3	3.9
n-Pentanol	2	4.9	0.30	2-3	3.2	1-2	3.8

Code: b — parameters *r* and n^s characterizing adsorption of alcohol from benzene mixtures, taken from Ref.[9]. h — parameters *r* and n^s characterizing adsorption of alcohol from *n*-heptane mixtures, taken from Ref.[9].

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