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Multilayer Effects in Adsorption of Alcohols from Benzene and *n*-Heptane on Silica Gel

Short Communication

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Experimental data for the title systems are compared with calculations based on theoretical adsorption parameters.

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Mehrschichteffekte bei der Adsorption von Alkoholen aus Benzol und n-Heptan auf Silicagel (Kurze Mitteilung)

Für die im Titel genannten Systeme werden experimentelle Daten mit Berechnungen verglichen, die auf theoretischen Parametern basieren.

In a previous paper[1] the multilayer adsorption from multicomponent liquid mixtures on solid surfaces has been discussed theoretically. According to this paper the equation for multilayer adsorption isotherm for binary liquid mixtures and solid surfaces showing quasi-*Gauss*ian energy distribution may be expressed as follows:

$$y_1 = \frac{1}{r}\frac{(L_{12}^{(1)} a_1)^m}{a_2{}^m + (L_{12}^{(1)} a_1)^m} + \frac{1}{r}\sum_{k=2}^{r}\frac{L_{12}^{(k)} a_1}{a_2 + L_{12}^{(k)} a_1} \tag{1}$$

where

$$L_{12}^{(k)} = \sum_{l=k}^{r} K_{12}^{(l)};\ L_{12}^{(r)} = K_{12}^{(r)} \tag{2}$$

and

$$a_i = f_i x_i \text{ for } i = 1,\ 2. \tag{3}$$

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In the above y_i and x_i are mole fractions of the i-th component in the surface and bulk phases, respectively, a_i and f_i are activity and activity coefficient of the i-th component in the bulk phase, r is the total number of adsorbed layers, m is the heterogeneity parameter connected with the width of the quasi-*Gauss*ian energy distribution and $K_{12}^{(k)}$ is the equilibrium constant describing the exchange of a molecule of the 1-st component from the $(k+1)$-th adsorbed layer with a molecule of the 2-nd component from the k-th adsorbed layer. However, the constant $L_{12}^{(r)} = K_{12}^{(r)}$ describes the exchange reaction of molecules of 1-st and 2-nd components between the r-th adsorbed layer and the bulk solution. The adsorption excess of 1-st component is equal to:

$$n_1^e = n^s (y_1 - x_1) \tag{4}$$

where n^s is the surface phase capacity.

Equations (1) and (4) have been applied to determine the thickness of the surface phase formed in adsorption process of aliphatic alcohols from benzene and n-heptane on silica gel. The silica gel of the specific surface area equal to 292 m^2/g was used as the adsorbent. The excess adsorption isotherms $n_1^e(x_1)$ were measured by using the method described in Ref.[2]. For this purpose of evaluation of adsorption parameters from the excess adsorption isotherms the algorithm MINUITS available from CERN computer Centre Program Library was applied. Moreover, we assumed that the ratio of $L_{12}^{(k)}$ and $L_{12}^{(k-1)}$ is constant, i.e.,

$$L_{12}^{(k)}/L_{12}^{(k-1)} = 1/q = const. \text{ for } k = 2, 3, \ldots, r \tag{5}$$

Equations (5) and (2) give:

$$L_{12}^{(k)} = K_{12}^{(r)} q^{r-k} \tag{6}$$

and

$$K_{12}^{(k)} = q \text{ for } k = 2, 3, \ldots, r - 1 \tag{7}$$

The values of r and n^s for all adsorption systems studied are summarized in Table 1. For the purpose of comparison we summarized in Table 1 the numbers of adsorbed layers r_b obtained from the method based on the material balance between the bulk and surface phases[2]. The last column of this table contains the n^s-values calculated by means of the DR equation[3].

In Fig. 1 *a* the excess adsorption isotherms for butanol and ethanol from benzene and n-heptane are shown. The circles denote experimental points, however, the lines represents the theoretical adsorption isotherms. Fig. 1 *b* and 1 *c* show the adsorption excesses for 1-st adsorbed layer (the curves denoted by 1) and higher adsorbed layers

Table 1. *Parameters r and n^s characterizing the adsorption of aliphatic alcohols from benzene and n-heptane on silica gel at 298 K.* The values of r_b and n^s_{DR} are taken from Ref.[2]. In the case of nonideal solutions the activity coefficients are taken from Ref.[7]

Alcohol	Solvent	Bulk solution	r	n^s mmol/g	r_b	n^s_{DR} mmol/g
Methanol	Benzene	nonideal	4	9.11	4-5	9.20
Ethanol	Benzene	nonideal	3	5.03	3	5.05
n-Propanol	Benzene	nonideal	2	3.20	3	4.30
n-Propanol	Benzene	ideal	3	3.20	3	5.20
n-Butanol	Benzene	ideal	2	3.01	3	4.50
Ethanol	*n*-Heptane	ideal	4	5.47	4-5	6.10
n-Propanol	*n*-Heptane	ideal	3	3.10	4	4.80
n-Butanol	*n*-Heptane	ideal	3	3.02	2-3	3.90

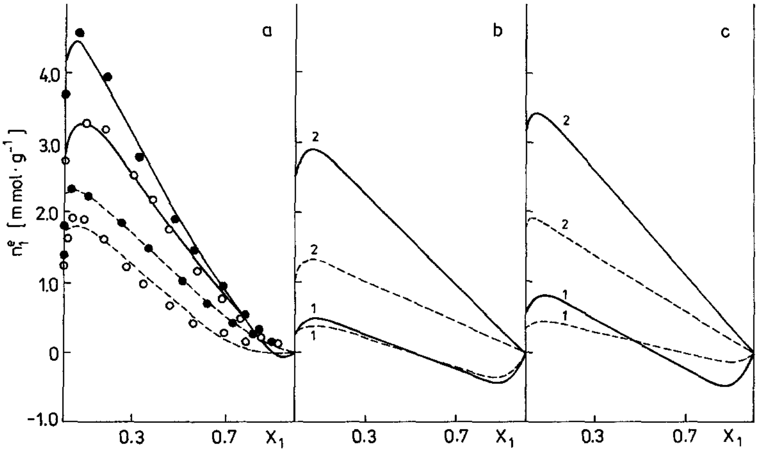

Fig. 1. The adsorption excesses for ethanol and butanol from benzene and *n*-heptane on silica gel at 298 K. The total excess isotherms are presented in part *a*; solid lines refer to the adsorption of ethanol from benzene (○) and *n*-heptane (●), whereas the dashed lines refer to adsorption of butanol from benzene (○) and *n*-heptane (●). Parts *b* and *c* present the adsorption excesses of ethanol (the solid lines) and butanol (the dashed lines) from benzene (b) and *n*-heptane (c) for the 1-st adsorption layer (the curves with the number 1) and higher adsorption layers (the curves with the number 2)

(the curves denoted by 2). The similar courses of adsorption excesses have been observed for methanol and propanol solutions.

It follows from Table 1 that thicknesses of the surface phase obtained by using different methods are similar and the values of r change from 2 to 4. Moreover, equations (1) and (4) give a good representation of the adsorption data of alcohols from benzene and n-heptane on silica gel. The adsorption excesses for the 1-st adsorbed layer belong to the IV-th type of adsorption isotherms[4]; it means that the 1-st adsorbed layer consists of both components of the liquid mixture in a large concentration range. An analogous effect has been observed by *Matayo* and *Wightman* for similar adsorption systems[5].

It is probable that in the case of multilayer adsorption of alcohols the azeotropic character of the excess adsorption isotherm for the 1-st adsorbed layer is connected with the concavity of the total excess adsorption isotherm at higher equilibrium concentrations[6]. Although the above results give an important information about the adsorption mechanism, they are still insufficient for determining the structure of the surface phase. Therefore, this problem requires further experimental studies.

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