Application of a Bilayer Adsorption Model for Explaining the Adsorption of Esters from *n*-Heptane and Benzene on Silica Gel

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The adsorption isotherms of methyl, ethyl, *n*-propyl and *n*-butyl acetates from benzene and *n*-heptane on silica gel have been measured at 298 K. A bilayer model of surface phase has been used to interpret these experimental data. It has been shown that the chain length of the hydrocarbon part of the ester and the solvent affinity to the adsorbent influence the structure of the surface phase. Moreover, this structure is also determined by energetic heterogeneity of the adsorbent surface.

(Keywords: Adsorption of esters of acetic acid on silica gel; Bilayer liquid adsorption; Heterogeneity effects in bilayer liquid adsorption)

Die Anwendung eines Zweischicht-Adsorptionsmodells zum Verständnis der Adsorption von Estern aus n-Heptan- und Benzollösungen auf Kieselgel

Es wurden die Adsorptionsisothermen der Methyl-, Ethyl-, *n*-Propyl und *n*-Butylacetate in Benzol und *n*-Heptanlösungen auf Kieselgel bei 298 K gemessen. Zur Interpretation der experimentellen Daten ist ein Zweischicht-Modell für die Oberflächenphase benutzt worden. Es wurde gezeigt, daß die Länge der Esterkohlenwasserstoffkette und die Aktivität des Lösungsmittels Einfluß auf die Struktur der Oberflächenform haben. Außerdem ist diese Struktur durch energetische Inhomogenität der Adsorbensoberfläche bestimmt.

Introduction

The structure of surface phase in adsorption at a liquid/solid interface is dependent on the affinity of the components to the adsorbent surface. The differences in affinities of saturated and aroma-

tic hydrocarbons with respect to the silica surface may influence the adsorption selectivity of monofunctional organic compounds and their orientation on the adsorbent surface[1-6]. Interesting results were obtained for the organic compounds containing carbonyl groups adsorbed from various solvents. The influence of fatty acids association in the bulk phase on the adsorption on silica gel have been discussed in literature[4,5]. Earlier we have stated that thickness of the surface phase of ketones is greater for n-heptane solutions than for benzene solutions[6]. The investigations on adsorption of C_6, C_{10} and C_{14} esters from benzene and CCl_4 on silica gel had shown that the surface phase is a monolayer and the structure of this layer depends strongly on the solvent character[1-3]. This paper presents the experimental studies of adsorption of several binary solutions (ester + hydrocarbon) on silica gel. For interpretation of these data we shall use the bilayer adsorption model discussed in Ref.[7].

Experimental

The excess adsorption isotherms of methyl, ethyl, n-propyl and n-butyl acetates from n-heptane and benzene on silica gel were measured at 298 K.

The silica gel (0.2-0.5 mm fraction) for column chromatography from Merck (GFR) was used as the adsorbent. The specific surface area of the silica was determined by the *BET* method using nitrogen adsorption data at 78 K. Assuming that one molecule of nitrogen occupies the surface area equal to 0.162 nm² the specific surface area of the silica was calculated to be 320 m² g⁻¹.

Benzene and n-heptane (puriss. grade) from POCh (Gliwice, Poland) were dried over silica gel and were used immediately in adsorption measurements without further purification. Methyl acetate from Reachim (USSR), ethyl, n-propyl and n-butyl acetates from Fluka A.G. (GFR) were above 99% pure. They were stored over silica gel in dry nitrogen atmosphere.

The adsorption isotherms were measured by using a static method in a wide concentration range of solutions. Portions (about 10 cm³) of binary solutions, prepared gravimetrically, were added to the glass ampoules containing the adsorbent about 4 g. The silica gel was dried before adsorption at 453 K for 24 h. The sealed ampoules were placed in a bath with controlled temperature which was equal to 298 ± 0.1 K. All solutions were frequently stirred. After equilibration the solution concentrations were analyzed by gas-liquid chromatography.

Results and Discussion

The excess adsorption isotherms $n_1^e = f(x_1^l)$ were calculated from the relationship:

$$n_1^e = n^0 (x_1^0 - x_1^l)/w \tag{1}$$

where n^0 is the total number of moles of both components being in contact with w grams of the adsorbent, x_1^0 and x_1^l are the mole fractions of 1st component in the initial and equilibrium solutions, respectively.

The plots n_1^e vs. x_1^l are presented in Figs. 1 and 2, in which circles denote the experimental points. These experimental plots were approximated by the following equations[7]:

$$x_1^s = \frac{0.5 \, (K_{12} \, x_1^l)^m}{(x_2^l)^m + (K_{12} \, x_1^l)^m} + \frac{0.5 \, K_{12}^{(2)} x_1^l}{x_2^l + K_{12}^{(2)} x_1^l} \tag{2}$$

and

$$n_1^e = n^s \, (x_1^s - x_1^l) \tag{3}$$

In the above formulae x_i^s and x_i^l are the mole fractions of the i-th component in the surface and bulk phases, respectively, n^s is the surface phase capacity, $K_{12}^{(2)}$ is the equilibrium constant describing the exchange of molecules of both components between the 2nd adsorbed layer and the bulk solution, K_{12} is the equilibrium constant describing the exchange of molecules of both components between the 1st adsorbed layer and the bulk solution, and m is the heterogeneity parameter characterizing the width of the quasi-*Gaussian* energy distribution. Eq. (2) has been derived for the following assumptions[7]:

both phases are ideal,
the surface phase is bilayer,
molecular sizes of both components are identical,
the energetic heterogeneity of the adsorbent is characterized by a quasi-*Gaussian* distribution and it influences the formation of the 1st layer only,
the total number of molecules contained in each adsorbed layer are identical and they are constant during the adsorption process,
the energy of a given molecule being in the 2nd layer is independent on the identity of the molecule adsorbed beneath it in the 1st layer.

Table 1 contains the parameters n^s, K_{12}, $K_{12}^{(2)}$ and m characterizing the adsorption systems investigated. These parameters have been calculated by using an analogous numerical algorithm as in the previous paper[8] concerning the adsorption of alcohols from benzene and n-heptane on silica gel. Moreover, in Tab. 1 values of the sum square deviations are summarized. They have been calculated according to equation (4):

$$S = \sum_{j=1}^{J} \, [n_{1, \, exp}^e \, (x_{1j}^l) - n_{1, \, cal}^e \, (x_{1j}; \, n^s, \, K_{12}, \, K_{12}^{(2)}, \, m)]^2 \tag{4}$$

where the subscripts "exp" and "cal" refer to the experimental and calculated values of n_1^e, respectively, the subscript "j" refers to the i-th experimental point and J is the total number of experimental points.

Table 1. *Information concerning the adsorption system investigated*

Mixture	n^s (mmol g^{-1})	K_{12}	$K_{12}^{(2)}$	m	S
Methyl acetate + n-heptane	4.48	105.0	3.48	0.435	0.458
Ethyl acetate + n-heptane	3.20	164.4	3.68	0.407	0.011
n-Propyl acetate + n-heptane	2.85	451.5	2.40	0.420	0.002
n-Butyl acetate + n-heptane	2.62	628.6	1.02	0.573	0.002
Methyl acetate + benzene	3.28	35.2	0.94	0.720	0.005
Ethyl acetate + benzene	2.80	42.2	0.65	0.543	0.002
n-Propyl acetate + benzene	1.38	287.1	0.42	0.964	0.004
n-Butyl acetate + benzene	1.08	298.7	0.31	1.170	0.005

The solid lines in Figs. 1 and 2 represent the theoretical adsorption isotherms calculated according to Eqs. (1) and (2) for the parameters summarized in Table 1. It follows from these figures that Eqs. (1) and (2) give a good representation of the above experimental data. Fig. 1 shows that the esters are preferentially adsorbed onto silica gel from n-heptane solutions in the whole concentration range. The ester molecules are adsorbed on the silica gel surface by a hydrogen bonding interactions between the carbonyl group of the ester and free surface silanol groups[3]. The dashed and dotted lines represent the adsorption excesses of the 1st component (ester) in the first and second layer, respectively. Fig. 1 shows that adsorption of methyl, ethyl and n-propyl acetates is of the bilayer type. The values of $K_{12}^{(2)}$ for these systems are considerably smaller than the K_{12} values. It means that the existence of a third layer seems most unlikely. It should be noted that with increasing hydrocarbon chain length the adsorption of ester in the second layer becomes smaller and smaller and for n-butyl acetate/n-heptane system it is practically monolayer [$K_{12}^{(2)} \simeq 1$]. According to the results obtained for the adsorption of C$_6$, C$_{10}$ and C$_{14}$ esters from dilute solutions in CCl$_4$[1-3] the ester adsorption limits are set by the availability of the isolated surface silanol groups. These results indicate that the alkyl chains of the above mentioned esters are not lying on the surface and they can screen the carbonyl groups. These chains form a layer of aliphatic hydrocarbon chains which separate the carbonyl groups bonded with the surface silanols from the bulk solution. In the case of smaller ester molecules the carbonyl group is easily reached for the ester molecules from the bulk phase. Thus, these molecules can form the second layer. This suggestion is confirmed by results presented in Fig. 1 were we observe a decrease of adsorption in the second layer for successive esters.
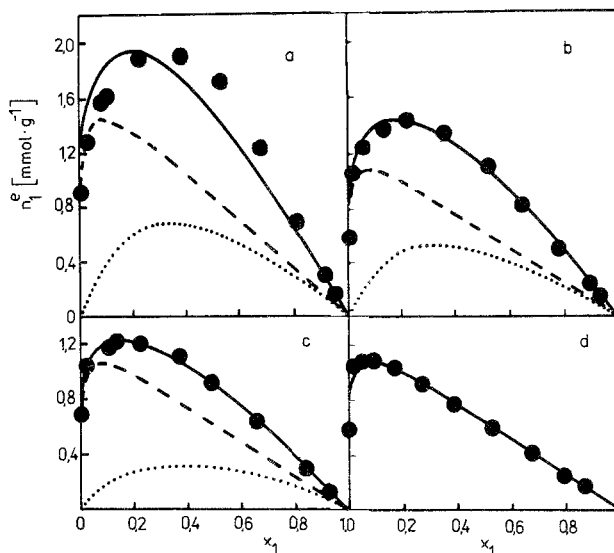
Fig. 1. Excess adsorption isotherms of the esters from n-heptane solutions on silica gel at 298 K; a methyl acetate; b ethyl acetate; c n-propyl acetate; d n-butyl acetate. Circles represent the experimental points. The solid lines represent the theoretical total adsorption isotherms, the dashed and dotted lines denote the surface adsorption excesses of the ester in the 1st and 2nd layer respectively

Another behaviour of ester molecules on the surface is observed in the case of benzene solutions. It follows from Fig. 2 that adsorption of the esters decrease with an increase of the alkyl chain length. Moreover, the negative excess adsorption of the esters in the second adsorbed layer is observed. This negative adsorption increases gradually from methyl acetate to n-butyl acetate. The shape of adsorption isotherms, which are concave at higher equilibrium concentrations indicates the presence of both components of liquid mixture in the surface phase. In Ref.[1] the authors suggest that the adsorption process of esters from benzene is determined by the significant interactions of aliphatic hydrocarbon chains with benzene molecules; this fact is the cause of formation of mixed surface phase. In contradiction to adsorption of esters from n-heptane, were the majority of silanols is bonded to the carbonyl groups of ester molecules, in the case of adsorption from benzene solutions the surface silanols may be occupied by the carbonyl groups or benzene molecules. Thus, in the ester adsorption from benzene the interactions between the alkyl chains of esters and benzene molecules (solvation) and competitive interactions of carbonyl groups
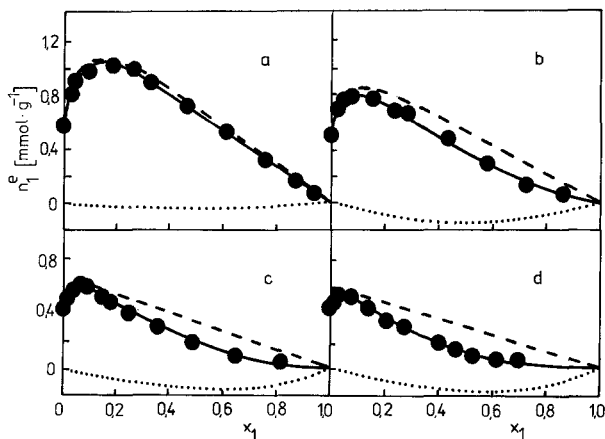
Fig. 2. Excess adsorption isotherms of the esters from benzene solutions on silica gel at 298 K. Labelling as in Fig. 1

of esters and solvent molecules with the surface silanols influence mainly the formation of the surface phase. The final result of these interactions may be the bilayer surface phase, in which the first adsorbed layer contains mainly the ester molecules, whereas, the second layer contains mainly benzene molecules. The above suggestion is confirmed by the results presented in Fig. 2. For instance, in the case of methyl acetate adsorption from benzene where the solvation effects are smaller we observe practically the monolayer adsorption [the constant $K_{12}^{(2)} \simeq 1$].

Now, we shall discuss the parameters K_{12} and $K_{12}^{(2)}$. It follows from Tab. 1 that the values of K_{12} increase with increasing hydrocarbon chain length. To explain this fact we shall analyse the constant K_{12}. According to Ref.[7] it is equal to:

$$K_{12} = \alpha \exp (E_1 - E_2)/RT \tag{5}$$

where α is the pre-exponential entropy factor, E_1 and E_2 are the adsorption energies of ester and solvent, respectively. Let us assume that the adsorption energies for successive ester molecules change additively with respect to the number of carbon atoms in alkyl chain, i. e.[9],

$$E_1 = E_1^0 + n E_1^{'} \tag{6}$$

where E_1^0 represents adsorption energy of the head group of a given ester (CH_3—COO—) on silica gel surface, n is the number of carbon

atoms in alkyl chain and E_1' is the adsorption energy refering to the methylenic group (CH_2—). Eqs. (5) and (6) give:

$$\ln K_{12} = A_1 + n\,(E_1'/RT) \tag{7}$$

where $A_1 = \ln \alpha + (E_1^0 - E_2)/RT$.

Eq. (7) shows that $\ln K_{12}$ is a linear function of n. In Fig. 3 these linear functions are presented for the adsorption systems studied. From the slope of the plots $\ln K_{12}$ vs. n we may calculate E_1'. The intercept on
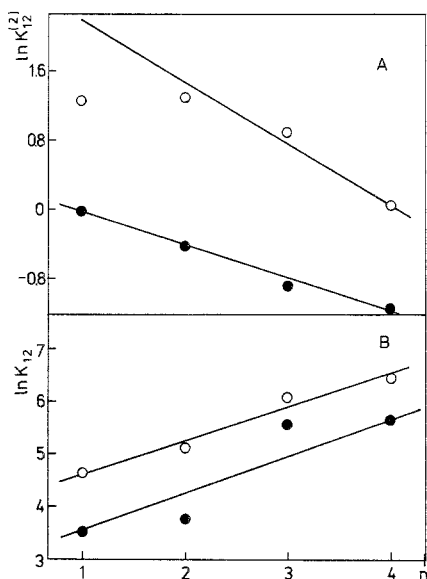

Fig. 3. The experimental dependences $\ln K_{12}$ vs. n and $\ln K_{12}^{(2)}$ vs. n for the adsorption systems studied. The white circles refer to ester/n-heptane solutions, whereas, the black circles refer to ester/benzene solutions

the $\ln K_{12}$ axis at $n = 0$ gives the value of parameter A_1 which represents the difference of adsorption energies of the ester head group and the solvent molecule.

A similar dependence to Eq. (7) may be written for the constant $K_{12}^{(2)}$, i.e.,

$$\ln K_{12}^{(2)} = A_2 + n\,(E_1''/RT) \tag{8}$$

where E_1'' is the analogous energy to E_1' for the molecules contained in the second layer and A_2 is analogous to A_1 and refers to the second layer.

Fig. 3 b shows the dependence of $\ln K_{12}^{(2)}$ vs. n. It follows from Fig. 3 that the best-fit values of K_{12} and $K_{12}^{(2)}$ fulfil the linear relationships (7) and (8) with a good approximation. The plots in Fig. 3 show that E'_1 is similar for adsorption of esters from benzene and n-heptane solutions and it is equal to $\sim 1.5 \, \text{kJ mol}^{-1}$. The parameters E''_1 calculated in a similar way for the second layer are equal to: $-0.91 \, \text{kJ mol}^{-1}$ for benzene solutions and $-1.76 \, \text{kJ mol}^{-1}$ for n-heptane solutions.

From the intercepts in Fig. 3 values of parameter $A'_1 = A_1 \cdot RT$ are obtained: $7.15 \, \text{kJ mol}^{-1}$ and $9.86 \, \text{kJ mol}^{-1}$ for benzene and n-heptane solutions, respectively. The values of $A'_2 = A_2 \cdot RT$, similarly obtained as A_1, are equal to $0.96 \, \text{kJ mol}^{-1}$ and $7.30 \, \text{kJ mol}^{-1}$ for benzene and n-heptane solutions, respectively.

The greater value of A'_1 for n-heptane solutions is in agreement with the observation described earlier that the aromatic molecules of benzene are stronger adsorbed on silica gel surface than n-heptane molecules.

It should be pointed out that the above presented energy values are not precise and they may be used for a qualitative description of adsorption process only.

Summing up our considerations we may conclude that Eq. (1) describing the bilayer model of surface phase is useful for the interpretation of ester adsorption from the hydrocarbon solvents on silica gel.

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