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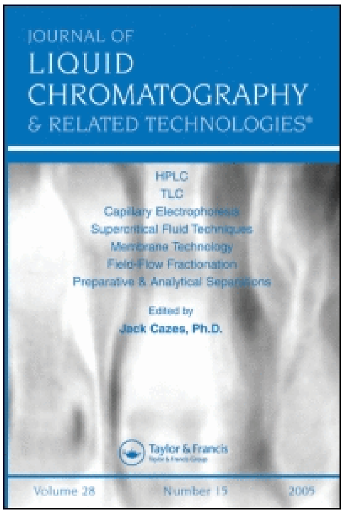

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CHARACTERIZATION OF LIQUID-SOLID ADSORPTION SYSTEMS BY USING TLC DATA

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ABSTRACT

The thin-layer chromatography (TLC) method is used to measure the excess adsorption isotherms for different binary liquid mixtures on silica gel. These isotherms are interpreted by means of the Langmuir-Freundlich equation, which involves the adsorbent heterogeneity and the difference in the molecular sizes of the components. This equation makes possible the evaluation of the surface phase capacity, equilibrium constant and heterogeneity parameter, which characterize liquid-solid adsorption systems.

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INTRODUCTION

Sandwich thin-layer chromatography (STLC), introduced by Soczewiński (1), was recently used to determine surface phase capacity (2) and excess adsorption isotherms (3). It has been shown in the papers (2,3) that the STLC method is very useful to evaluate quickly the fundamental data characterizing liquid-solid adsorption systems. Classical measurements of the excess adsorption data are time-consuming in comparison to the method proposed by Markowski et al. (2,3). Of course, the accuracy of the excess adsorption data measured by the STLC method (3) is smaller than that of the data obtained by the classical methods (4-6), but it is frequently sufficient to evaluate the parameters characterizing liquid-solid adsorption systems.

In this paper we will show the utility of the STLC method for a quick characterization of liquid-solid adsorption systems. Using the STLC method, the excess adsorption isotherms are measured for several binary liquid mixtures on silica gel. These isotherms are interpreted by means of the Langmuir-Freundlich equation in order to determine the surface phase capacity, equilibrium constant and heterogeneity parameter. These quantities are usually used to characterize the adsorption properties of liquid-solid systems.

EXPERIMENTAL

The experimental procedure was quite analogous to that described in the previous papers (2,3). Its outline is the following: the TLC measurements were carried out using the sandwich tank (1), in which a glass distributor delivers the solvent from a glass capillary siphon and a small container (ca 5 cm^3) across the whole width of the layer. The plates, 5 x 20 cm, coated with 0.5 mm (nominal thickness) layers of adsorbent, were prepared and activated in the usual way. The adsorbent Silica Gel G 60 (E. Merck, Darmstadt, F.R.G.) of specific surface area 500 m^2/g was used to prepare the TLC plates. A Quickfit (Jobling) spreader was used. The slurry was prepared by mixing 40 g of silica gel with 100 cm^3 of water. In all cases, the development distance was 16.5 ± 0.1 cm. The width of the adsorbent layer was 4.8 cm. Dyes were spotted at a distance of 1.5 cm from the edge of the layer. The following dyes were used to localize the solvent demixing front: azulene, azobenzene, HPTLC test mixture (E. Merck) and HPLC test mixture (E. Merck). Solutions were prepared by weighing the solvents in the container. All solvents used were dried over silica gel.

RESULTS AND DISCUSSION

Calculation of the excess adsorption isotherms from STLC data

Calculation of the excess adsorption isotherms from the STLC data was performed according to the procedure described in the previous paper (3). It follows from the theoretical considerations presented in Ref. (3) that the adsorption excess $n_1^{\sigma(n)}$ (expressed usually in mmole/g) may be connected with the R_{Fd}-value, which is obtained from the STLC measurements (3). The relationship between $n_1^{\sigma(n)}$ and R_{Fd} may be written as follows:

$$n_1^{\sigma(n)} = \frac{V_o \, \bar{v} \, c_1^{\ell}}{m_a \, v_2} \cdot \left(\frac{1 - R_{Fd}}{R_{Fd}} \right) \tag{1}$$

In the above, $n_1^{\sigma(n)}$ is the reduced surface excess of the first component adsorbed from the binary liquid mixture (1 + 2) on a solid surface (5,6); R_{Fd} is the ratio of the distances of the fronts of the two zones from the origin of the system (the composition of the mobile phase in the back zone corresponds to its initial composition, whereas the mobile phase in the front zone contains only pure diluent "2") (3); V_o denotes one bed volume, which is the interstitial volume accessible to the solvent in the thin layer of the adsorbent on the plate; c_1^{ℓ} is the concentration of the first component in the solution; $\bar{v}$ and v_2 are the average molar volume of the solution (3) and the molar volume of the second component, respectively; and m_a is the mass of adsorbent on the plate along the development distance. To calculate the adsorption excess $n_1^{\sigma(n)}$ according to equation 1 it is thus sufficient to determine the following values: the bed volume V_o of the adsorbent layer on the development distance and the position of the demixing front, R_{Fd}. All assumptions limiting the use of equation 1 were discussed in the previous paper (3).

Table 1 presents the organic compounds which were used to make different binary liquid mixtures applied in the STLC

TABLE 1

Adsorption parameters characterizing the excess isotherms for different binary liquid mixtures on Silica Gel G 60

Component "1" + Component "2"	$n^s_{1,o}$ (mmole/g)	r	$\bar{K}_{12}$	m
Acetonyloacetone + Cyclohexane	3.40	0.89	9.50	0.76
Acetonyloacetone + n-Heptane	5.15	1.25	9.54	0.70
Acetonyloacetone + Benzene	6.65	0.98	1.61	0.72
N,N-dimethylaminoethanol + Benzene	4.40	0.94	5.64	0.55
Ethyl cyanoacetate + Benzene	4.15	0.93	2.76	0.65
Diethyl malonate + Benzene	3.00	0.66	1.72	0.67
Dioxane + Benzene	4.50	1.31	3.44	0.57
Diethylamine + Benzene	2.30	1.19	22.9	0.55
Isopropylalcohol + Benzene	4.30	1.24	13.0	0.42
Ethyl acetoacetate + Benzene	2.25	0.79	3.98	0.64
Isopropyl ether + Benzene	1.70	0.85	3.95	0.57
Methyl isobutyl ketone + Benzene	2.80	0.86	2.60	0.71
Isobutyl ketone + Benzene	3.25	0.62	1.20	0.74
Morpholine + Methylene chloride	3.95	0.69	2.84	0.47

measurements. For one composition of the solution, one value of $n_1^{\sigma(n)}$ is obtained. To measure the excess adsorption isotherm $n_1^{\sigma(n)}$ vs. x_1^{ℓ} (the mole fraction of the first component in the mobile phase), we carried out the STLC measurements for different compositions of the solution.

Interpretation of the excess adsorption isotherms by means of the Langmuir-Freundlich equation

The excess adsorption data $n_1^{\sigma(n)}$ vs. x_1^{ℓ} measured for different binary liquid mixtures (see Table 1) were analyzed by means of the Langmuir-Freundlich equation additionally involving a difference in molecular sizes of the components; it is (7):

$$\bar{K}_{12} = \frac{\left(x_{1,t}^{s}\right)^{r/m}\left(1 - x_1^{\ell}\right)}{\left(x_1^{\ell}\right)^{r}\left(1 - x_{1,t}^{s}\right)^{1/m}} \tag{2}$$

where $x_{1,t}^{s}$ is the mole fraction of the first component in the surface phase formed on an energetically heterogeneous surface; x_1^{ℓ} is the mole fraction of the first component in the mobile phase; r is the ratio of molecular sizes of the second and first components; m is the heterogeneity parameter characterizing the width of the quasi-Gaussian energy distribution (7,8); and $\bar{K}_{12}$ is the constant obtained by averaging the equilibrium constants K_{12} referring to different types of adsorption sites (7). Equation 2 may be rewritten in the following linear form:

$$\ell n \frac{(1 - x^s_{1,t})}{\left(x^s_{1,t}\right)^r} = m \ \ell n \ \bar{K}_{12} + m \ \ell n \frac{(1 - x^\ell_1)}{\left(x^\ell_1\right)^r} \qquad (3)$$

The mole fraction $x^s_{1,t}$ is connected with the adsorption excess $n_1^{\sigma(n)}$ as follows (7):

$$n_1^{\sigma(n)} = \frac{n^s_{1,o} \ (x^s_{1,t} - x^\ell_1)}{r + x^s_{1,t} \ (1 - r)} \qquad (4)$$

where $n^s_{1,o}$ is the surface phase capacity with respect to the first component.

To reduce the number of free parameters appearing in equations 3 and 4, we evaluated the parameter r by using the molecular sizes calculated according to Snyder's method (9). The molecular size of an organic compound may be expressed as the sum of areas of the groups forming the molecule. Snyder (9) tabulated the area values for different groups and his data provides a general basis for calculating the molecular size for any compound of interest. Table 1 contains the values of r for binary liquid mixtures used in the STLC measurements, which have been calculated by applying Snyder's method (9) for evaluating the molecular sizes of the components.

The parameters $n^s_{1,o}$, $\bar{K}_{12}$ and m were obtained from the excess adsorption data $n_1^{\sigma(n)}$ vs. x^ℓ_1 by means of equations 3 and 4. A numerical procedure applied to this end appears to be analogous to that used in Ref. (8) where the Langmuir-Freundlich isotherm (i.e., equation 3 with r = 1) was utilized. A short outline of this procedure follows: using an arbitrary, physically realistic value of $n^s_{1,o}$ we recalculated the data $n_1^{\sigma(n)}$ vs. x_1^ℓ on the set of data $x^s_{1,t}$ vs. x_1^ℓ and next the data $x^s_{1,t}$ vs. x_1^ℓ were approximated by the linear equation 3 to evaluate the parameters m and $\overline{K}_{12}$. The calculations were carried out for different values of $n^s_{1,o}$ to draw the dependence of the standard deviation SD on $n^s_{1,o}$; the standard deviation was calculated with regard to the values of the adsorption excess $n_1^{\sigma(n)}$ (7,8). Parts C in Figures 1 and 2 show the dependence of SD on $n^s_{1,o}$ for two selected adsorption systems. In all cases, the curve SD vs. $n^s_{1,o}$ shows a distinct minimum, which enables us to determine the best-fit value of $n^s_{1,o}$. Knowing the best-fit value of $n^s_{1,o}$, we have automatically the best-fit values of m and $\overline{K}_{12}$ corresponding to the above value of $n^s_{1,o}$.

Table 1 contains the best-fit values of $n^s_{1,o}$, m and $\overline{K}_{12}$ for all systems studied. For the purpose of illustration, Figures 1 and 2 present the experimental excess adsorption isotherms (circles) in comparison to the theoretical curves calculated according to equations 2 and 4 (the solid lines in part A of Figures 1 and 2) and their linear representations plotted according to equation 3 (part B of Figures 1 and 2) for two selected systems from Table 1. It follows from Figures 1 and 2 that

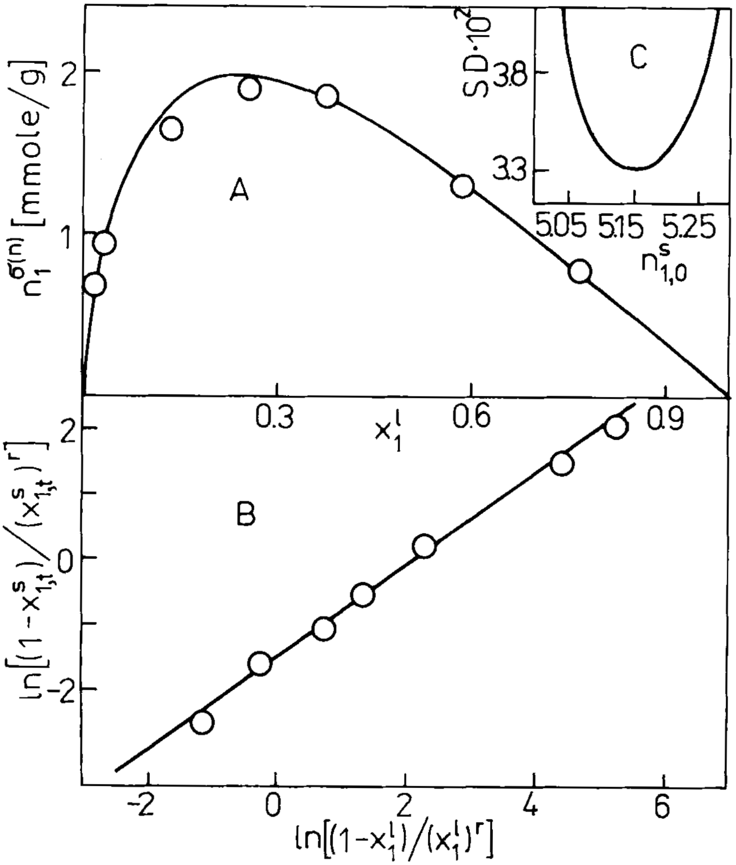

FIGURE 1. Excess adsorption isotherm (part A), its linear representation according to equation 3 (part B) and dependence SD vs. $n_{1,o}^s$ (part C) for adsorption of acetonyloacetone from n-heptane on silica gel G 60. Parameters referring to this system are given in Table 1.

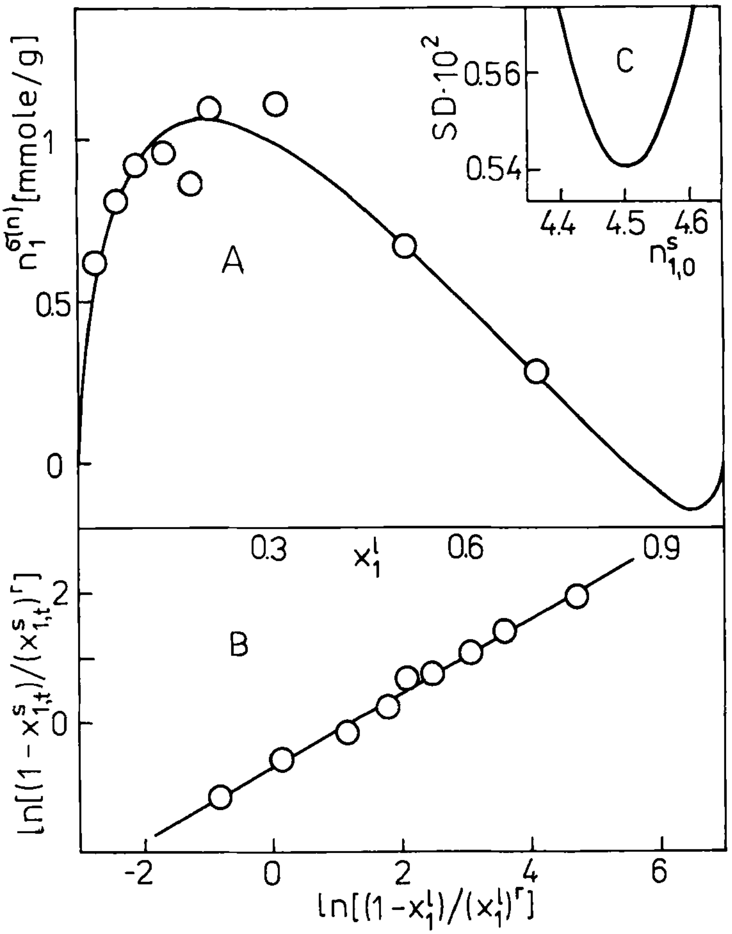

FIGURE 2. The dependences as in Figure 1 for adsorption of dioxane from benzene on silica gel G 60. Adsorption parameters referring to this system are given in Table 1.

equations 2 and 4 give a good representation of the excess adsorption data obtained from the STLC measurements. The parameters m, $\overline{K}_{12}$ and $n^s_{1,o}$ characterize adsorption properties of the system: binary liquid mixture - solid surface. These parameters are also useful to describe the TLC data of different solutes chromatographed in binary mobile phases. It has been shown in several works [see references in the review (10)] that the solute retention quantities are dependent on the compositions of the surface and mobile phases. To evaluate the surface phase compositions we should earlier determine the excess adsorption isotherm characterizing the eluent-adsorbent system, which enables us to calculate the surface phase compositions relating to different mobile phase compositions.

The possibility of evaluation of the excess adsorption data from the STLC measurements considerably simplifies characterization of the eluent-adsorbent systems. This procedure of characterization of the liquid-solid adsorption systems seems to be promising because both the solute retention data as well as the excess adsorption data for the eluent-adsorbent system are obtained by using the simple and quick STLC method.

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