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CHARACTERIZATION OF SOLID-LIQUID ADSORPTION SYSTEMS BY USING GAUSSIAN ENERGY DISTRIBUTION

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ABSTRACT

Theoretical foundations of the isotherm equations derived for adsorption from binary liquid mixtures composed of molecules of different sizes on heterogeneous surfaces characterized by Gaussian energy distribution are discussed. On the basis of numerical simulation studies the correlation between adsorption parameters of the equations in question and the parameters of the Gaussian energy distribution are established. These studies allow characterization of the Gaussian-type adsorbents on the basis of excess adsorption data.

INTRODUCTION

In the last years great interest has been shown in the physical adsorption of liquid mixtures on heterogeneous solid surfaces [1-4] ; the two last surveys [3,4] are fully devoted to adsorption of liquid mixtures on solids. The main effort in this area has been to study the role of energetic heterogeneity of the adsorbent surface and non-ideality of the bulk and surface solutions in the adsorption process. These studies have usually been carried out by assuming equality of the molecular sizes of the components forming the liquid mixture.

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In comparison, theoretical studies of adsorption from liquid mixtures on energetically heterogeneous surfaces involving differences in molecular sizes of the components, are fewer [5-8]. Jaroniec [5] and Dąbrowski [6] proposed a simple expression for the adsorption isotherms of binary liquid mixtures of non-electrolytes for random topography of surface sites by assuming a Gaussian-like energy distribution. Their expression involves also differences in molecular sizes of components forming the liquid mixture. An alternative expression has been developed by Rudziński et al. [8], who applied the condensation approximation method [9-10] for its derivation.

The isotherm equations corresponding to Gaussian-like energy distributions play an important role in liquid adsorption on solid surfaces, because these distributions are characteristic for many adsorption systems [10-13].

The purpose of the present work is to give the theoretical foundations for the expression proposed by Jaroniec [5] and Dąbrowski [6], by using the numerical simulation method [7], and to study the correlation of its parameters with those representing Gaussian energy distribution. These numerical simulation studies provide an easy interpretation of the experimental adsorption data by means of the expression in question; it is illustrated by using several excess adsorption isotherms available from the literature. Moreover, comparative studies concerning both isotherm equations [6,8] are presented.

THE ISOTHERM EQUATIONS FOR QUASI-GAUSSIAN ENERGY DISTRIBUTION

Let us consider the adsorption from binary liquid mixtures containing components of different molecular sizes. Then the equilibrium constant describing the phase-exchange reaction

occuring on the l-th type of adsorption sites, may be expressed as follows [14] :

$$K_{12,l} = \left(\frac{\Phi^s_{1,l}}{\Phi^l_1}\right)^r \left(\frac{\Phi^l_2}{\Phi^s_{2,l}}\right) \tag{1}$$

where

$$K_{12,l} = \exp\left[\frac{(r\varepsilon_{1,l} - \varepsilon_{2,l})}{RT}\right] = \exp\left[\frac{\varepsilon_l}{RT}\right] \tag{2}$$

$$\varepsilon_l = r\varepsilon_{1,l} - \varepsilon_{2,l} \quad \text{and} \quad r = w^s_2/w^s_1 \tag{3}$$

In the above, Φ^l_i denotes the volume fraction of the i-th component in the bulk phase, $\Phi^s_{i,l}$ denotes the volume fraction of the i-th component adsorbed on the l-th type of adsorption site, $\varepsilon_{i,l}$ is the adsorption energy of the i-th component on the l-th type of adsorption sites, r is the ratio of the cross-sectional area of a molecule of the second component to that referring to the first component.

The equilibrium constant $K_{12,l}$ given by eqn. (1) is defined by assuming the pre-exponential factor is equal to unity. This assumption is frequently used in adsorption, especially for liquid mixtures showing small deviations from ideality [1,4]. In the case of heterogeneous surfaces, the volume fraction Φ^s_1 referring to the entire surface is equal to:

$$\Phi^s_1 = \sum_{l=1}^{L} f_l \Phi^s_{1,l} \tag{4}$$

where f_l is the ratio of the number of adsorption sites of the l-th type to the total number of adsorption sites. Application of eqns. (1) and (4) for describing the experimental adsorption data is very difficult because it requires calculation of L

parameters $K_{12,l}$, and L parameters f_l and r. Therefore, Dąbrowski [6] approximated these equations by the following expression:

$$\bar{K}_{12} = \left[\frac{(\Phi_1^s)^{1/c}}{\Phi_1^l}\right]^r \left[\frac{\Phi_2^l}{(\Phi_2^s)^{1/c}}\right] \tag{5}$$

where $\bar{K}_{12}$ is the constant obtained by averaging the constant $K_{12,l}$ for $l = 1,2,\ldots,L$, c is the heterogeneity parameter characterizing the shape of the energy distribution which can change from zero to unity. For c = 1 (homogeneous surface) eqn. (5) becomes eqn. (1), which has been discussed by Everett [14]. However, for r = 1 (identical molecular sizes of both components) eqn. (5) reduces to the so-called Langmuir-Freundlich equation, which was considered by Dąbrowski et al. [10,11]. It is:

$$\bar{K}_{12} = \left(\frac{x_1^s}{x_2^s}\right)^{1/c} \left(\frac{x_2^l}{x_1^l}\right) \tag{6}$$

where x_i^s and x_i^l are mole fractions of the i-th component in the surface and bulk phases, respectively. Equation (6) corresponds to quasi-Gaussian energy distribution [10]. It is suggested that eqn. (5) should relate a Gaussian-like energy distribution too. This conclusion will be proved by numerical simulation.

Jaroniec [5] proposed an analogous expression to eqn. (5), but he used the mole fractions instead of the volume fractions. According to the studies of several authors [4] the equilibrium constant K_{12} may be defined by means of the volume fractions or mole fractions in the case of r changing from 0.7 to 1.2. However, for liquid mixtures showing great differences in the molecular sizes of both components, the volume fractions are recommended for defining the phase-exchange equilibrium constant.

Recently, Rudziński et al. [8] used eqn. (1) as the local adsorption isotherm in the integral equation, which usually is applied to represent the overall adsorption isotherm on energetically heterogeneous surfaces. Solving this integral equation for a Gaussian-like energy distribution by means of the condensation approximation method [9,10], Rudziński et al. [8] obtained the following expression:

$$K_{12}^{*} = \left(\frac{\Phi_1^s}{\Phi_2^s}\right)^{1/c} \frac{\Phi_2^1}{\Phi_1^1}^{r} \tag{7}$$

where

$$K_{12}^{*} = \bar{K}_{12} \cdot 2^{r-1} \tag{8}$$

For r = 1 eqn.(7) reduces to the same expression as eqn. (5); i.e., it becomes eqn. (6). However, for c = 1 and r ≠ 1 eqn. (7) does not reduce to eqn. (1), which describes the adsorption from binary liquid mixtures on a homogeneous solid surface. According to the Rudziński et al. [8] explanation, eqn. (7) has been derived for strongly heterogeneous surfaces and its transformation at c = 1 to the equation for homogeneous surfaces is impossible. On the other hand, the overall adsorption isotherm equations derived by means of the condensation approximation method for r = 1 (identical molecular sizes of both components) correctly predict the behaviour characteristic for homogeneous surfaces (c = 1) [9]. Therefore, it is surprising that the application of the condensation approximation method in the case of r ≠ 1 leads to the isotherm eqn. (7), which is not reducible to eqn. (1) at c = 1. In the authors' opinion this problem needs further theoretical studies (see Appendix).

NUMERICAL METHOD OF VERIFICATION OF THE ISOTHERM EQUATIONS

The exact energy distribution function corresponding to the isotherm eqn. (6) is a Gaussian-like distribution. Equations (5) and (7) have been obtained by extending eqn. (6), in which the parameter characterizing differences in molecular sizes of the components, has been introduced. Thus, the energy distribution functions corresponding to eqns. (5) and (7) also show quasi-Gaussian shape. For the purpose of verification of the isotherm eqns. (5) and (7) and evaluation of their applicability regions, we performed the following numerical studies: the theoretical adsorptions isotherms have been calculated for Gaussian distributions of different width, and next these isotherms have been approximated by eqns. (5) and (7) to calculate the parameters $\bar{K}_{12}$, K^{*}_{12}, c, c^{*} and r. The details of this procedure as follows: the continuous Gaussian distribution $F(\varepsilon)$ of the width Δ and the average value ε_0, i.e.,

$$F(\varepsilon) = \frac{1}{\Delta\sqrt{2\pi}} \exp\left[-\frac{(\varepsilon-\varepsilon_0)^2}{2\Delta^2}\right]; \quad \varepsilon = r\,\varepsilon_1 - \varepsilon_2 \tag{9}$$

is first approximated by a discrete distribution of the following type:

$$F_d(\varepsilon) = \sum_{l=1}^{L} f_l \delta(\varepsilon - \varepsilon_l) \tag{10}$$

where $\delta(\varepsilon - \varepsilon_l)$ is the Dirac delta function defined as follows:

$$\delta(\varepsilon - \varepsilon_l) = \begin{cases} 0 \text{ for } \varepsilon \neq \varepsilon_l \\ 1 \text{ for } \varepsilon = \varepsilon_l \end{cases} \tag{11}$$

and

$$f_l = F(\varepsilon_l) \Big/ \sum_{k=1}^{L} F(\varepsilon_k) \tag{12}$$

The values f_l fulfil the following normalization condition:

$$\sum_{l=1}^{L} f_l = 1 \tag{13}$$

The interval of ε , in which the Gaussian distribution reaches values giving significant contribution to the overall adsorption isotherm, is divided into L parts. The number L is dependent on the width of the energy interval. The numerical simulation studies of Czarniecki and Jaroniec [15] showed that the continuous distribution may be well approximated by the discrete distribution given by eqn. (10); already for small integers L, the main features of the continuous distribution are reproduced by the discrete function.

The next step of the numerical procedure is calculation of the overall volume fraction of the first component in the surface phase, Φ_1^s , according to eqn. (4) for a given discrete distribution; i.e., eqn. (10). The values f_l for $l = 1,2,\ldots,L$, appearing in eqn. (4), are calculated according to eqn. (12), however, the volume fractions $\Phi_{1,l}^s$ are obtained by solving eqn. (1) for given values of r and $K_{12,l}$. The equilibrium constants $K_{12,l}$ for $l = 1,2,\ldots,L$ are evaluated by means of eqn. (2) for the values ε_l corresponding to the values f_l.

The theoretical adsorption isotherms $\Phi_1^s(\Phi_1^l)$, calculated for Gaussian distributions of different width, are approximated by the linear forms of eqns. (5) and (7). They are:

$$\ln \frac{1 - \Phi_1^s}{(\Phi_1^s)^r} = -c \ln \bar{K}_{12} + c \ln \frac{1 - \Phi_1^l}{(\Phi_1^l)^r} \tag{14}$$

relating to eqn. (5) and

$$\ln \frac{1 - \Phi_1^s}{\Phi_1^s} = -c^* \ln K_{12}^* + c^* \ln \frac{1 - \Phi_1^l}{(\Phi_1^l)^r} \tag{15}$$

corresponding to eqn.(7).

The parameters c and c^* characterize the width of the energy distribution and may be compared with the parameter Δ . These numerical studies make it possible to plot the dependences Δ vs. c and Δ vs. c^*. These dependences are obtained by approximating the theoretical adsorption isotherms calculated for Gaussian distributions of different values of Δ by the linear eqns. (14) and (15). Knowing such dependences, we can find the width Δ of the Gaussian distribution by means of the parameters c and c^*, which may be easily evaluated from the adsorption data.

To compare the representations of the adsorption data by eqns. (14) and (15), we calculated the excess adsorption isotherms by using the parameters c, $\bar{K}_{12}$, c^*, K_{12}^* and r. These isotherms were calculated by means of the following relationship [6]:

$$n_1^e = \frac{n_{1,0}^s (x_1^s - x_1^l)}{r + x_1^s (1 - r)} \tag{16}$$

where $n_{1,0}^s$ denotes the surface phase capacity with respect to the first component and it was assumed to be unity, and x_1^s, x_1^l are the mole fractions connected with the volume fractions Φ_1^s and Φ_1^l as follows:

$$x_1^l = \frac{r\ \Phi_1^l}{r\ \Phi_1^l + (1 - \Phi_1^l)} \tag{17}$$

$$x_1^s = \frac{r\ \Phi_1^s}{r\ \Phi_1^s + (1 - \Phi_1^s)} \tag{18}$$

However, the sum of square deviations (SD) was evaluated with regard to the excess adsorption isotherm:

$$SD = \sum_{j=1}^{J} (n_{1,j}^{e,G} - n_{1,j}^{e,c})^2 \qquad (19)$$

where J denotes the number of points in the excess adsorption isotherm, $n_{1,j}^{e,G}$, which has been calculated for Gaussian distribution; however, $n_{1,j}^{e,c}$ is the excess isotherm calculated by using the parameters c, $\bar{K}_{12}$ and r. The analogous sum of square deviations to that expressed by eqn. (19) SD^* may be evaluated by means of the parameters c^*, K_{12}^* and r.

RESULTS OF NUMERICAL STUDIES AND DISCUSSION

First of all, we present the numerical studies concerning eqn. (5). According to the numerical procedure described in the previous section, the theoretical adsorption isotherms have been calculated for r changing from 0.6 to 1.4 and different Gaussian distributions characterized by Δ = 0.25, 0.5, 1.0, 1.5, 2.5, 3.0, 3.5, 4.0 and ε_o = 0, 0.5, 1.0 and 2.0. The most extensive numerical studies have been performed for Gaussian distributions with ε_o = 0 and different values of Δ. In the case of ε_o = 0 and Δ = 0 (homogeneous surface) the average constant $\bar{K}_{12}$ is equal to unity (cf., eqn. (2)) and then the excess adsorption is equal to zero over the whole concentration region. However, for heterogeneous surfaces(Δ greater than zero) the adsorption excess is different from zero even for $\bar{K}_{12}$ = 1 [10]. Therefore, the numerical studies performed for Gaussian distributions with ε_o = 0 and $\Delta > 0$ are the most interesting because they show the influence of the energetic heterogeneity of the adsorbent surface, which is characterized by Δ, on the parameters appearing in eqn (5).

To evaluate the parameters c and $\bar{K}_{12}$, the adsorption istotherms Φ_1^s (Φ_1^l), calculated for Gaussian distributions of different values of Δ and ε_o, have been approximated by eqn. (14). Fig. 1B illustrates the method of numerical studies of eqn.(5).

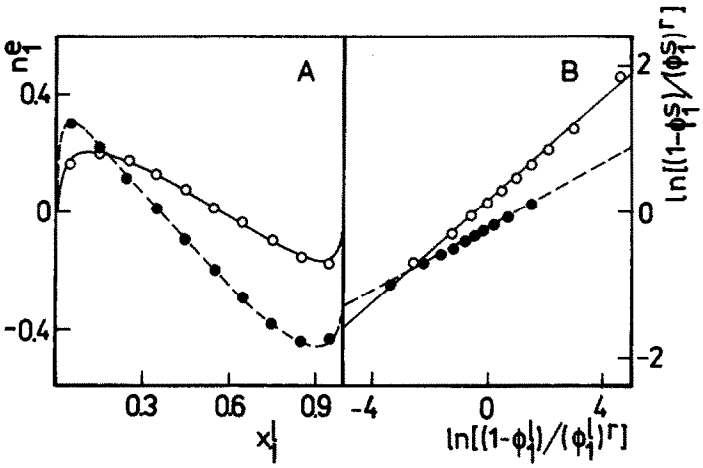

Fig. 1. Excess adsorption isotherms calculated according to eqs. (5) and (16-18) (lines in Fig. 1A) fitting the isotherms simulated for Gaussian energy distribution (circles) and their linear representations plotted according to eqn. (14) (lines in Fig.1B); the white circles refer to r = 1.4 and the black circles refer to r = 0.6. The adsorption parameters refering to the curves shown in this Fig. are summarized in Table I

The simulated adsorption data, denoted by means of the circles, have been calculated according to the procedure described in the previous section for r = 0.6, (dashed line with filled circles), r = 1.4 (solid line with open circles) and Gaussian distribution with $\varepsilon_o = 0$ and $\Delta = 2.5$. It follows from Fig. 1B that the linear eqn. (14) gives a good representation of such data and the parameters c and $\bar{K}_{12}$ may be easily evaluated. Using these parameters, the theoretical excess adsorption isotherms have been calculated by means of eqns. (16-18) and (5) and they are displayed in Fig. 1A. Moreover, the theoretical curves are compared with the excess adsorption isotherms simulated numer-

Table I. Adsorption Parameters of Eqns. (14) and (15) Calculated for Different Values of ε_o, Δ and r

ε_o	Δ	r	c	c^*	$\bar{K}_{12}$	K^*_{12}	SD	SD^*	No.of Fig.
0	2.5	0.6	0.219		2.419		0.0005		1
		1.4	0.351		0.631		0.0008		
0	0.25	0.6	0.978	1.161	1.009	0.692	0.00009	0.0043	8A
		1.4	0.988	0.804	0.988	1.462	0.000004	0.0022	
0	2	0.6	0.268	0.349	1.827	0.673	0.0004	0.0001	8B
		1.4	0.422	0.346	0.715	1.455	0.0005	0.0002	
0	1.5	0.6	0.434	0.522	1.355	0.684	0.001	0.0001	9
1	0.5	1.4	0.919	0.808	5.139	7.561	0.00005	0.0011	10

ically for Gaussian distribution (circles). This comparison and the linear representation of the adsorption data by means of eqn. (14) show that the adsorption data simulated for distribution (9) and different values of r may be well approximated by eqn. (14), which is a linear form of the examined eqn. (5).

The above conclusion results from extensive numerical studies performed for different values of r changing from 0.6 to 1.4 and Gaussian distributions of different values of Δ and ε_o. Consequently, eqn. (5) may be treated as an isotherm equation corresponding to Gaussian-like distribution.

The parameters c and $\bar{K}_{12}$ depend on the value of r. Figs. 2 and 3 show the dependences $\bar{K}_{12}$ vs. r and c vs. r for $\varepsilon_o = 0$ and different values of Δ. For small values of Δ these

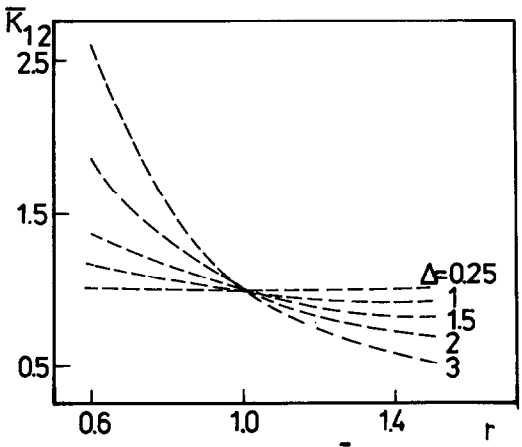

Fig. 2. The dependence $\bar{K}_{12}$ vs. r plotted for different values of Δ; the values of $\bar{K}_{12}$ were calculated from the adsorption isotherms simulated for Gaussian energy distributions with $\varepsilon_o = 0$ and Δ= 0.25, 1, 1.5, 2 and 3 by means of eqn. (14).

parameters change insignificantly for r changing from 0.6 to 1.4. However, for greater values of Δ (wide Gaussian distributions) these parameters are more sensitive on changes in r. It means that for values of r considerably differing from unity, eqn. (5)

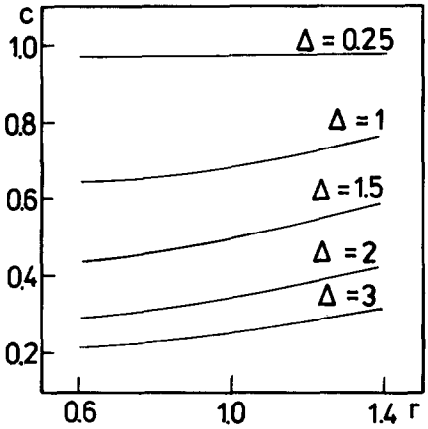

Fig. 3. The dependence c vs. r plotted for different values of Δ ; the values of c were calculated from the adsorption isotherms simulated for Gaussian energy distributions with $\varepsilon_o = 0$ and Δ = 0.25, 1, 1.5, 2 and 3 by means of eqn. (14).

can give a poor representation of the liquid adsorption data. The applicability region of this equation is for values of r close to unity; i.e., a good approximation for r changing from 0.6 to 1.4. In this region the effects connected with orientation of molecules in the surface phase are smaller. However, for r considerably differing from unity, another theoretical equation for liquid adsorption should be used; this equation should take into account the shape of the adsorbed molecules and their orientation in the surface phase [16].

Figures 2 and 3 illustrate the dependence of the parameters c and $\bar{K}_{12}$ on the parameter r. From a practical viewpoint the dependences Δ vs. c and ln $\bar{K}_{12}$ vs. ln K_o, [where the constant $K_o = \exp(\varepsilon_o/RT)$] are more useful because they make possible prediction of the Gaussian energy distribution by means of the parameters c and $\bar{K}_{12}$. Fig. 4 show the dependence Δ vs. c for $\varepsilon_o = 0$ and r = 0.6, 1.0 and 1.4. It follows from this Figure

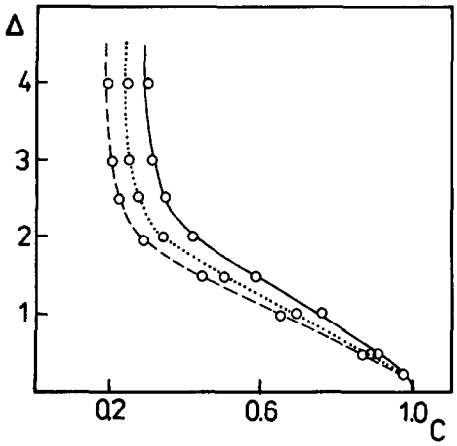

Fig. 4. The dependence Δ vs. c plotted for ε_0 = 0 and r = 1.4 (solid line), 1.0 (dotted line) and 0.6 (dashed line).

that values of the parameters c obtained from the adsorption isotherms simulated for different Gaussian distributions are smaller than unity, as in the case of the Langmuir-Freundlich isotherm equation [10,11], which has been derived on the basis of the integral equation. For values of c greater than 0.6 and tending to unity, the dependence Δ vs. c plotted for different values of r are similar. In this region we can easily evaluate the parameter Δ, characterizing the width of the Gaussian distribution, knowing the value of c [it may be determined from adsorption data by means of eqn. (14)].

Fortunately, real adsorption systems are usually characterized by values of c in the range (0.6 - 1) [11,13]. Fig. 4 shows that evaluation of the value of Δ corresponding to c in the region of the smaller values of c is difficult, but this region of c is only slightly interesting from a practical viewpoint. The dependence Δ vs. c may be insignificantly changed by ε_0 (see Fig. 5).

Therefore, the first step in evaluation of the parameters of Gaussian distribution is the estimation of ε_0 and knowing it we

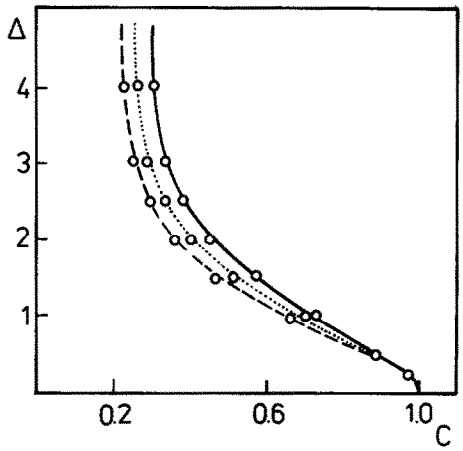

Fig. 5. The dependence Δ vs. c plotted for ε_o = 0.5 and r = 1.4 (solid line), 1.0 (dotted line) and 0.6 (dashed line).

can evaluate the parameter Δ . Fig. 6 shows the dependence ln $\bar{K}_{12}$ vs. ln K_o for two different values of Δ and r. In the case of the small values of Δ (narrow Gaussian distribution), this dependence is practically not perturbed by r, however, for greater values of Δ the influence of r on its course is visible. Never-

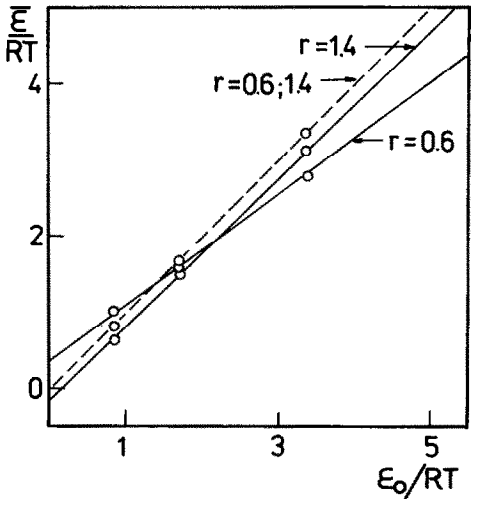

Fig. 6. The dependence ($\bar{\varepsilon}$/RT) vs. (ε_o/RT) plotted for two values of r = 0.6 and 1.4 (they are shown in the Fig.) and Δ = 0.25 (dashed line) and 1.5 (solid lines).

theless, this effect is not great and all curves are close to each other. Thus evaluating the parameter $\bar{K}_{12}$ from adsorption data by means of eqn. (14) and taking into account the dependence $\ln \bar{K}_{12}$ vs. $\ln K_0$ obtained from the model studies, we can estimate with a good approximation the parameter K_0, which gives automatically the value $\varepsilon_0 = RT \ln K_0$, being the average value of Gaussian distribution. Knowing the value ε_0, we can estimate the parameter Δ on the basis of the dependence Δ vs. c (see Fig. 4 and 5) plotted for a given value of ε_0. The parameters ε_0 and Δ define the Gaussian distribution (9) corresponding to the adsorption isotherm analysed by means of eqn. (14).

In our numerical procedure for evaluating the Gaussian energy distribution from liquid adsorption data, the volume fractions of components are used. If we apply the mole fractions instead of the volume fractions, the numerical calculations become simpler.

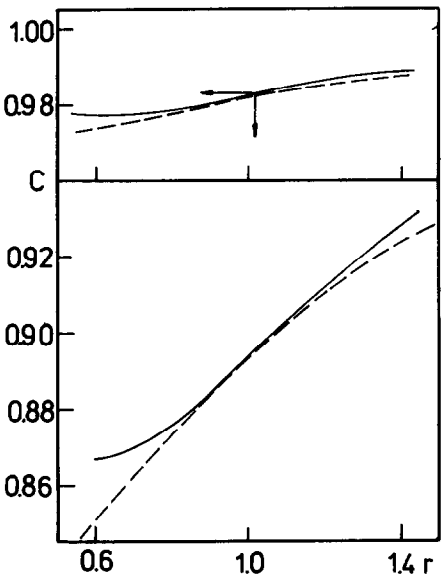

Fig. 7. The dependence c vs. r for $\Delta = 0.25$ (the upper part of the Fig.) and $\Delta = 0.5$ (the lower part of the Fig.). The solid lines refer to the volume fractions, whereas the dashed lines refer to the mole fractions.

The model studies presented in Fig. 7 show that for the narrow Gaussian distributions(Δ smaller than 0.5) application of the mole fractions or volume fractions of components in the calculations does not influence significantly the values of the adsorption parameters. Even for wider Gaussian distributions, this effect is not significant in the region of r changing from 0.8 to 1.2. It means that in this region of r we can use the mole fractions of components instead of their volume fractions;however, in the case of narrow energy distribution, this simplification may be used in a wider region of r than that given above.

Summing up the model studies dealing with the isotherm eqn. (5), we can state that the theoretical adsorption isotherms calculated for Gaussian distributions are well approximated by eqn. (14), which is a linear form of eqn. (5). The best-fit parameters obtained by means of eqn. (14) are simultaneously the best-fit parameters for the excess adsorption data, because the theoretical lines calculated according to eqn. (14) and the theoretical excess isotherms calculated by means of eqns. (5) and (16-18) coincide well with the experimental points (see Fig. 1). Eqn. (5) gives the best representation of the adsorption isotherms calculated for the narrow Gaussian distributions. It is also useful for describing the adsorption isotherms relating to the wider Gaussian distribution. Although eqn. (5) was proposed on the basis of a kinetic adsorption model [5-7], our studies showed that it corresponds to the Gaussian-like energy distribution. However, in the case of r = 1 (identical molecular sizes of both components) eqn. (5) becomes the so-called Langmuir-Freundlich isotherm for which the Gaussian-like energy distribution has been exactly found [10].

The evaluation of energy distribution for the adsorption systems with $r \neq 1$ is easy when the dependences Δ vs. c and

ln $\bar{K}_{12}$ vs. ln K_o are known. These dependences make possible the evaluation of the parameters Δ and ε_o, defining the Gaussian distribution on the basis of the parameters c and $\bar{K}_{12}$ obtained from the adsorption isotherm.

Now, we will present the model studies dealing with eqn. (15) in comparison to those obtained for eqn. (14). For the purpose of illustration, Fig. 8 presents the linear approximations according to eqns. (14) and (15) of the adsorption isotherms calculated $\varepsilon_o = 0$, r = 0.6, 1.4 and Δ = 0.25 (Fig. 8A) and 2.0 (Fig. 8B).

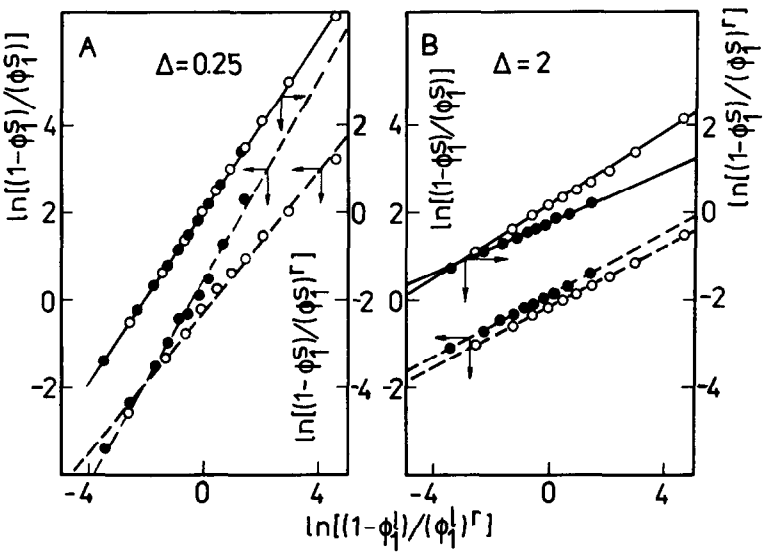

Fig. 8. Linear representations of the adsorption isotherms simulated for r = 0.6 (black circles), 1.4 (white circles) and Gaussian energy distributions with $\varepsilon_o = 0$ and Δ = 0.25 (part A), 2.0 (part B) plotted according to eqns. (14) (solid lines) and (15) (dashed lines). The parameters are summarized in Table I.

Both linear relationships, i.e., eqns. (14) and (15), give a good representation of the adsorption data in question. An advantage of eqn. (14) is the slight dependence of the adsorption parameters c and $\bar{K}_{12}$ on the value of r in the case of narrow Gaussian

distribution; e.g., for Δ = 0.25 the points of the adsorption isotherms relating to r = 0.6 and 1.4 lie on this same straight line (see Fig. 8A). Fig. 9 and 10 presents analogous linear dependences as those shown in Fig. 8, but refer to other values of Δ and ε_o. The values of the parameters c, $\bar{K}_{12}$, eqn. [(14)] and

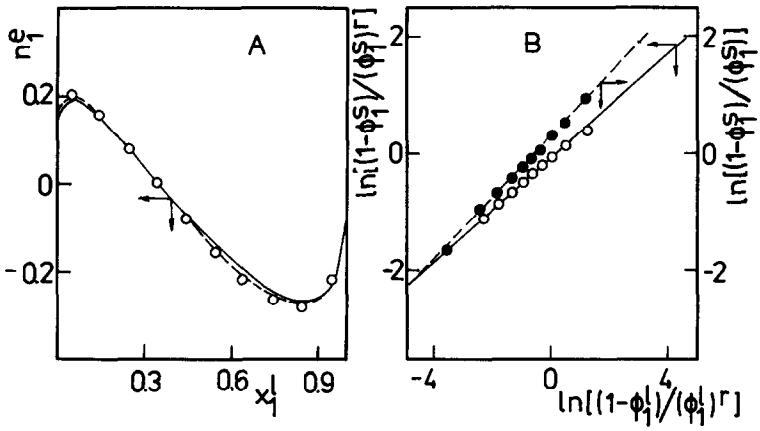

Fig. 9. Excess adsorption isotherms (part A) and their linear representations (part B); the solid lines refer to eqn. (5), whereas the dashed lines refer to eqn. (7). Circles denote the adsorption data simulated for Gaussian energy distribution with ε_o = 0 and Δ = 1.5. The parameters are given in Table I.

c^*, K_{12}^* [eqn. (15)] corresponding to the linear dependences showed in Figs. 8-10, are listed in Table I.

Additionally, Figs. 9 and 10 present the excess adsorption isotherms calculated by means of the parameters c, K_{12} and c^*, K_{12}^* obtained from the linear dependences (14) (the solid lines) and (15) (the dashed lines) compared to the excess isotherms (circles) simulated for Gaussian distributions. Table I contains also the standard deviations corresponding to eqns. (14) (SD) and (15) (SD^*). Both linear eqns. (14) and (15) give a good representation of the adsorption isotherms in question and make possible evaluation of the parameters c, K_{12}, and c^*, K_{12}^*. However, while

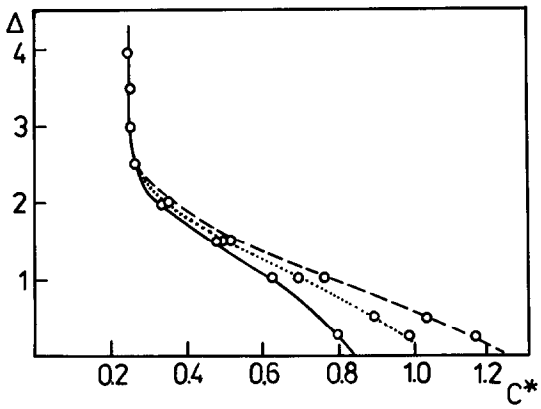

Fig. 10. The excess adsorption isotherms (part A) and their linear representations (part B); the solid lines refer to eqn. (5), whereas the dashed lines refer to eqn. (7). Circles denote the adsorption data simulated for Gaussian energy distribution with ε_o = 1.0 and Δ = 0.5. The parameters are given in Table I.

the linear dependence (14) gives distinctly better values of SD for narrow Gaussian distributions, the parameters SD and SD* [eqn. (15)] have comparable values for wider distributions (see Table I).

Fig. 11 shows the dependence Δ vs. c^* calculated according to eqn. (15) for r = 0.6, 1.0, 1.4 and ε_o = 0. This dependence is

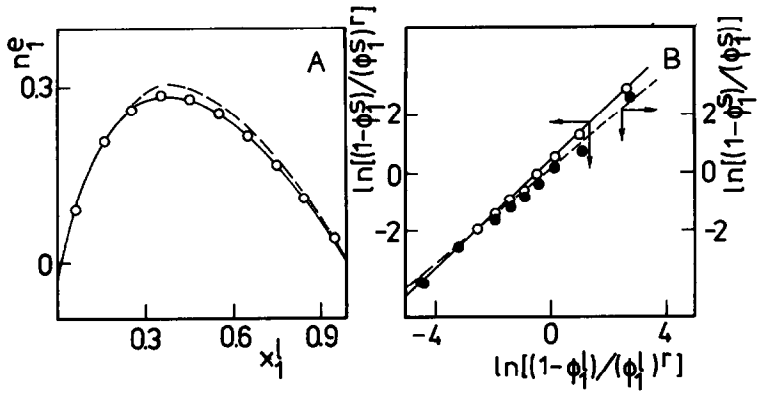

Fig. 11. The dependence Δ vs. c^* plotted for ε_o = 0 and r = 0.6 (dashed line), 1.0 (dotted line) and 1.4 (solid line).

different from that presented in Fig. 4 for the values of c obtained by means of eqn. (14). In contrast to eqn. (14), which leads to a good correlation between Δ and c in the region of c-values closer to unity, in this region eqn. (15) predicts the curves Δ vs. c^* to be strongly dependent on the value of r. However, for r smaller than unity, eqn. (15) predicts values of c^* greater than unity, which are unrealistic from a physical viewpoint [4,10]. Although, in the region of low values of c^* the curves Δ vs. c^* refering to different values of r coincide, estimation of Δ by means of the parameter c^* is rather difficult because these curves become parallel to the Δ - axis. The best region of the values of c^* for estimating Δ lie between 0.3 and 0.5.

Generally speaking, eqn. (14) is more suitable for describing the adsorption data on weakly heterogeneous surfaces (e.g., for c changing from 0.6 to 1), whereas eqn. (15) gives better results for strongly heterogeneous surfaces (e.g., for c^* changing from 0.3 to 0.5).

APPLICATION TO THE EXPERIMENTAL ADSORPTION DATA

Equation (5) and its linear form, eqn. (14), approximate the excess adsorption data for moderate heterogeneous surfaces better than eqns. (7) and (15). Therefore, the excess adsorption data available from the literature (see Table II) were analysed by means of eqn. (14). However, for our purposes this equation has been used in a form written in terms of the mole fractions ($r \in (0.6, 1.4)$), taking into account the non-ideality of the bulk phase. In such a case, eqns. (5) and (14) may be rewritten as follows:

$$\bar{K}_{12} = \left[\frac{(x_1^s)^{1/c}}{(x_1^l \gamma_1^l)}\right]^r \left[\frac{(x_2^l \gamma_2^l)}{(x_2^s)^{1/c}}\right] \tag{20}$$

and

$$\ln \frac{(1 - x_1^s)}{(x_1^s)^r} = c \ln \bar{K}_{12} + c \ln \frac{(1 - x_1^l)\gamma_2^l}{(x_1^l \gamma_1^l)^r} \tag{21}$$

where the symbol γ_i^l (i = 1,2) denotes the activity coefficient of the i-th component in the bulk phase.

Table II contains the parameters c and $\bar{K}_{12}$ for several adsorption systems, obtained on the basis of eqn. (21). The parameter r has been calculated as the ratio of the literature values of $n_{1,0}^s$ and $n_{2,0}^s$ ($r = n_{1,0}^s/n_{2,0}^s$), where $n_{i,o}^s$ (i = 1,2) denotes the total number of moles of the i-th pure component in the surface phase. The parameters $n_{i,o}^s$ (i = 1,2) were evaluated by means of single-gas adsorption data, measured on this same adsorbent and at this same temperature as liquid adsorption data. So, we can believe that possible errors regarding the values of r are probably negligible.

While the literature values of $n_{1,0}^s$ and $n_{2,0}^s$ were applied only to evaluate the relative value of r, more exact values of $n_{1,0}^s$ and the parameters c and $\bar{K}_{12}$ were obtained from the excess adsorption data by means of eqns. (20),(21) and (16). A numerical procedure applied to this end appears to be analogous to that used by us in paper [11] where the Langmuir-Freundlich isotherm [i.e., eqn. (20) with r = 1] was utilized. For comparative purposes, Table II contains (in parentheses) the values of c, $n^s = n_{1,0}^s = n_{2,0}^s$ and SD refering to the Langmuir-Freundlich

Table II. Adsorption Parameters for Different Binary Liquid Mixtures on Solids Calculated According to Eqns. (21) and (16)

Liquid mixture (1+2)	Adsorbent	Temp. (K)	$r^a = n^s_{1,0}/n^s_{2,0}$	$n^s_{1,0}$ [b]	c [b]	$\bar{K}_{12}$	SD [b]	Ref. to ads. system	Ref. to bulk activity coefficients
benzene + cyclohexane	boehmite	293	1.15	1.50 (1.56)	0.990 (0.980)	3.98	0.0037 (0.0212)	17	18
chloroform + benzene	boehmite	293	1.12	1.52 (1.60)	1.01 (0.967)	4.29	0.0013 (0.0118)	17	19
benzene + cyclohexane	graphite	293	1.20	1.05 (1.07)	0.941 (0.984)	1.82	0.0004 (0.0080)	18	18
benzene + cyclohexane	spheron	293	1.29	2.90 (3.02)	0.728 (0.839)	9.98	0.0031 (0.0109)	18	18
chloroform + carbon tetrachloride	charcoal	293	1.31	1.58 (1.64)	0.795 (0.922)	13.81	0.0098 (0.032)	18	18
ethylene dichloride + benzene	charcoal	293	1.14	2.90 (2.30)	0.662 (0.592)	0.69	0.0068 (0.0324)	18	$\gamma^1_1 = \gamma^1_2$
chloroform + acetone	charcoal	293	0.92	1.78 (1.82)	0.619 (0.611)	2.31	0.0132 (0.0322)	18	18
methyl acetate + benzene	charcoal	293	1.17	4.42 (3.62)	0.886 (0.835)	0.54	0.0196 (0.0370)	18	18

[a] $r = n^s_{1,0}/n^s_{2,0}$ was calculated by means of the literature values of $n^s_{i,0}$ (i = 1,2) measured on the basis of single gas adsorption data; ref. to $n^s_{i,0}$ as to adsorption system

[b] the values in parentheses were calculated previously under the assumption r = 1 [11]

isotherm; these parameters are taken from our previous paper [11]. Figs. 12 - 14 show the linear dependences, eqn. (21) (part B), the excess adsorption isotherms (part A) and the standard deviations SD as a function of $n^s_{1,0}$ (part C) for the selected systems from Table II.

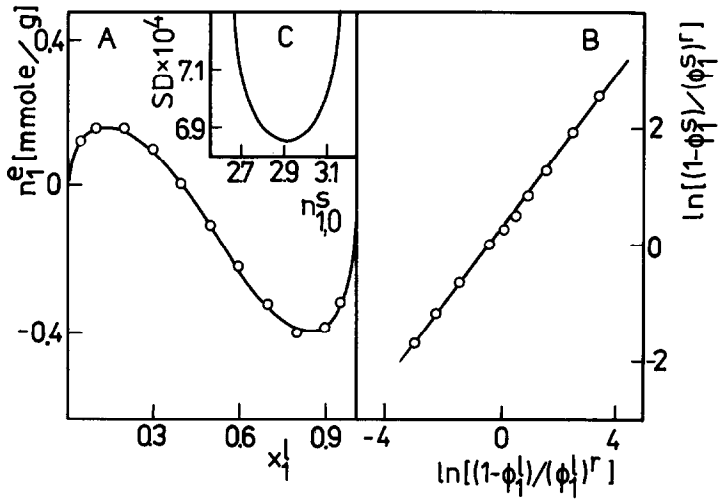

Fig. 12. Excess adsorption isotherm (part A), its linear representation (part B) and dependence SD vs. $n^s_{1,0}$ (part C) for adsorption of ethylene dichloride from benzene on charcoal at 293 K. Information and parameters refering to this system are given in Table II.

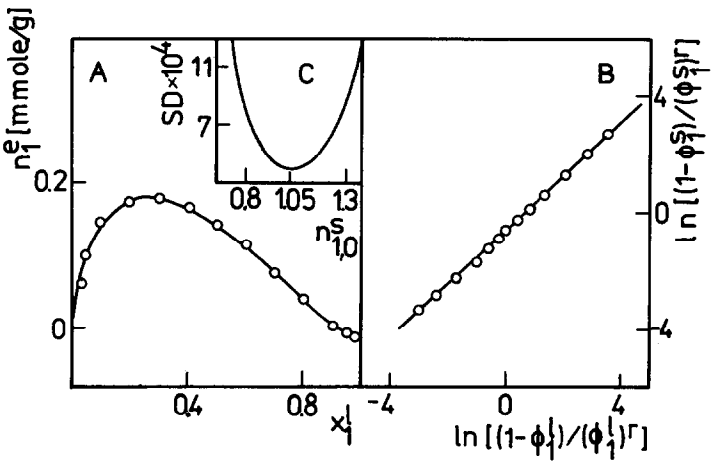

Fig. 13. The dependences as in Fig. 12 for adsorption of benzene from cyclohexane on graphite at 293 K; other details in Table II.

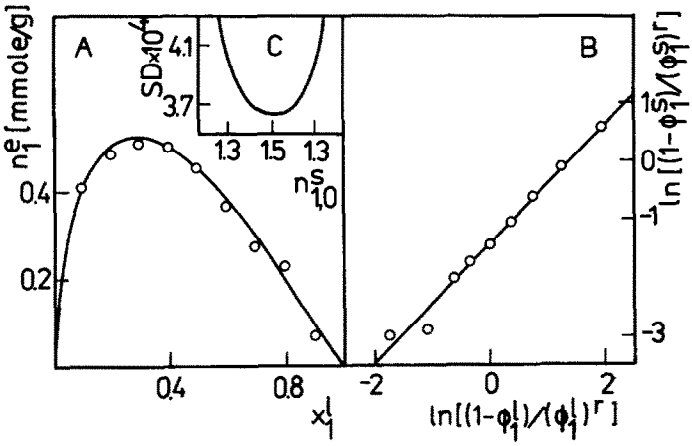

Fig. 14. The dependences as in Fig. 12 for adsorption of benzene from cyclohexane on boehmite at 293 K; other details in Table II.

From Table II and Figs. 12 - 14 the following conclusions can be drawn:

(i) the parameters c and $\bar{K}_{12}$ corresponding to the optimized parameter $n_{1,0}^s$ predict very well the excess adsorption,

(ii) the dependence SD <u>vs.</u> $n_{1,0}^s$ shows a distinct minimum and it may be used to determine the parameter $n_{1,0}^s$,

(iii) eqn. (20) gives a better description of the adsorption systems than its special form, <u>i.e.</u>, eqn. (20) with r = 1.

The parameters Δ and ε_o relating to the values of c and RT ln $\bar{K}_{12}$, may be evaluated on the basis of Figs. 4 - 6; they define the Gaussian distribution characteristic for a given system. In that case we can state that eqn. (20) [or eqn. (5)] may be used to characterize the experimental adsorption systems containing liquid mixtures composed of molecules of different sizes and heterogeneous adsorbents of Gaussian-type distribution.

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APPENDIX

Raising eqn. (5) to the power $r' = 1/r$ and taking into account the definition: $\bar{K}_{21} = (\bar{K}_{12})^{-r'}$, we obtain the expression for $\bar{K}_{21}$, which analogous to that defining the constant $\bar{K}_{12}$. Another situation is observed in the case of eqn. (7). Application of the same transformation to eqn. (7) as in the case of eqn. (5) gives an expression differing from the equation obtained by using the local equilibrium constant $K_{21,l}$ and the condensation approximation method. This inconsistency is a disadvantage of eqn. (7).