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Adsorption from Solutions of Nonelectrolytes on Heterogeneous Solid Surfaces: A Four-Parameter Equation for the Excess Adsorption Isotherm

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A four-parameter single-solute adsorption isotherm equation is generalized to the adsorption of binary liquid mixtures of nonelectrolytes. This equation comprises all isotherms being a simple extension of the *Everett* isotherm to liquid adsorption on heterogeneous solid surfaces. The benzene—cyclohexane excess adsorption data on silica gel are studied by using this new equation.

(Keywords: Adsorption from liquid mixtures; Adsorption from solutions on solids; Four-parameter generalized Everett equation; Benzene—cyclohexane adsorption on silica gel)

Adsorption aus Lösungen von Nichtelektrolyten an heterogenen festen Oberflächen: Eine Vierparametergleichung für die Excess-Adsorptions-Isotherme

Es wird eine Vierparameter-Isothermengleichung für binäre Lösungen von Nichtelektrolyten diskutiert. Diese Gleichung umfaßt alle Isothermen vom Typ der einfachen Erweiterung der *Everett*-Isotherme für Flüssig-Adsorption auf heterogenen festen Oberflächen. Die Daten für die Adsorption von Benzol—Cyclohexan werden mittels dieser neuen Gleichung behandelt.

Introduction

Although a significant progress has been made during the last few years in elaborating the adsorption from solutions on heterogeneous solid surfaces, the further studies of heterogeneity effects in liquid adsorption are still desirable [1—3]. The problems, such as: evaluation of the energy distribution functions from the experimental excess adsorption isotherms, correlation between heterogeneity parameters obtained from gas and liquid adsorption data, prediction of the total adsorption from a mixture by means of the parameters characterizing simple adsorption systems and derivation of new isotherms equations involving surface heterogeneity, may be studied in future utilizing the recent achievements in gas adsorption on heterogeneous surfaces[1,4—7]. An attempt of an unified description of gas and liquid adsorption on heterogeneous surfaces has been presented by *Jaroniec*[1], who discussed the procedures of extension of the single-gas adsorption isotherm equations to those describing adsorption from gas and liquid mixtures.

In this paper we shall extend a four-parameter single-solute adsorption isotherm equation to liquid adsorption. This equation has been discussed by *Marczewski* and *Jaroniec*[8]; it defines the relative surface coverage θ as a function of concentration c:

$$\theta(c) = \left[\frac{(\bar{K}c)^{n'}}{1+(\bar{K}c)^{n'}}\right]^{m'/n'} \tag{1}$$

The heterogeneity parameters m' and n' determine the width of the quasi-*Gaussian* energy distribution, whereas the constant $\bar{K}$ determines its position on the energy axis. This constant is connected with the adsorption energy for which the energy distribution reaches the maximum. Equation (1) will be generalized to liquid adsorption according to the procedure described in the review[1]. The generalized form of Eq. (1) comprises all overall isotherm equations reducible to *Everett*'s equation. The experimental data of adsorption of benzene from cyclohexane on silica gel will be applied to examine the generalized form of Eq. (1). Also, the theoretical excess adsorption isotherms, calculated according to this equation, will be discussed.

Theory

The starting point of our consideration is the general expression for the equilibrium constant $K_{12,l}$ describing the phase-exchange reaction between molecules of 1st and 2nd components on the l-th type of adsorption sites[9]:

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

where

$$\beta_{12,l} = \frac{f^s_{1,l}}{f^l_1}\left(\frac{f^l_2}{f^s_{2,l}}\right)^r \tag{3}$$

The equilibrium constant $K_{12,l}$, expressed by means of the activities in the bulk phase (a_1^l, a_2^l) and the activities of both components on the l-the type of adsorption sites ($a_{1,l}^s$, $a_{2,l}^s$), describes the phase-exchange reaction on the l-th type of adsorption sites for binary liquid mixtures containing molecules of different molecular sizes ($r \neq 1$). The mole fractions of both components in the bulk (x_1^l, x_2^l) and surface ($x_{1,l}^s$, $x_{2,l}^s$) phases fulfil the evident conditions:

$$x_1^l + x_2^l = 1; \quad x_{1,l}^s + x_{2,l}^s = 1 \tag{4}$$

For $r \neq 1$ Eq. (2) cannot be solved analytically with respect to the mole fraction of the 1st component on the l-st type of adsorption sites, $x_{1,l}^s$. Therefore, further considerations will be presented for binary liquid mixtures of molecules occupying identical surface areas ($r = 1$). The above assumption is frequently used in the theory of adsorption from solutions[1,9]. Since our further considerations will concern the liquid adsorption with nonideal both phases on heterogeneous surfaces, we must introduce an assumption about the topography of adsorption sites onto surface. The analytical expressions for the overall mole fraction x_1^s may be obtained only for heterogeneous surfaces showing random distribution of adsorption sites[1]. Then, we can assume that the activity coefficients of both components defined for the l-th type of adsorption sites are independent on the type of adsorption sites and characterize nonideality of the whole surface phase. It means that for heterogeneous surfaces of random distribution of adsorption sites the overall activity coefficients of both components, f_1^s and f_2^s, dependent on the overall mole fraction x_1^s, should be used[10]. Taking into account the above considerations we can rewrite Eq. (2) for $r = 1$ and the l-th type of adsorption sites distributed randomly onto surface in the following way:

$$K_{12,l} = \frac{x_{1,l}^s x_2^l}{x_1^l x_{2,l}^s} \beta_{12} \tag{5}$$

where

$$\beta_{12} = \frac{f_1^s(x_1^l, x_1^s) f_2^l(x_1^l)}{f_1^l(x_1^l) f_2^s(x_1^l, x_1^s)} \quad \text{for } r = 1 \tag{6}$$

Defining

$$\beta_{21} = 1/\beta_{12} \tag{7}$$

we can express $x_{1,l}^s$ as follows:

$$x_{1,l}^s = \frac{K_{12,l}\beta_{21} x_1^l/x_2^l}{1 + K_{12,l}\beta_{21} x_1^l/x_2^l} \tag{8}$$

Using Eq. (8) for describing the local isotherm, which appears in the integral equation defining the overall mole fraction of the 1st component in the surface phase[1], and solving this integral for the energy distribution discussed in [8], we obtain an analogous isotherm equation to Eq. (1):

$$x_1^s = \left[\frac{(\bar{K}_{12}\,\beta_{21}\,x_1^l/x_2^l)^n}{1+(\bar{K}_{12}\,\beta_{21}\,x_1^l/x_2^l)^n}\right]^{m/n} \tag{9}$$

The energy distribution corresponding to Eq. (9) has a quasi-*Gauss*ian shape; the heterogeneity parameters m and n determine its width[8]. These parameters may vary from zero to unity. For $m = n$ this energy distribution is symmetrical, however, for $m \neq n$ it is asymmetrical. If $m > n$ the distribution is widened to the left-hand side, whereas, for $m < n$ it is widened to the right-hand side. For special sets of the heterogeneity parameters m and n Eq. (9) reduces to the isotherm equations discussed in [10]:

$$x_1^s = \frac{(\bar{K}_{12}\,\beta_{21}\,x_1^l/x_2^l)^m}{1+(\bar{K}_{12}\,\beta_{21}\,x_1^l/x_2^l)^m} \quad \text{for } n = m \tag{10}$$

$$x_1^s = \left[\frac{\bar{K}_{12}\,\beta_{21}\,x_1^l/x_2^l}{1+\bar{K}_{12}\,\beta_{21}\,x_1^l/x_2^l}\right]^m \quad \text{for } n = 1 \tag{11}$$

$$x_1^s = \frac{\bar{K}_{12}\,\beta_{21}\,x_1^l/x_2^l}{[1+(\bar{K}_{12}\,\beta_{21}\,x_1^l/x_2^l)^n]^{1/n}} \quad \text{for } m = 1 \tag{12}$$

Eqs. (10)–(12) may be more simplified by assuming ideality of the surface phase ($f_1^s = f_2^s = 1$) or ideality of both phases ($\beta_{21} = 1$). For ideal both phases Eqs. (10)–(12) become:

$$x_1^s = \frac{(\bar{K}_{12}\,x_1^l/x_2^l)^m}{1+(\bar{K}_{12}\,x_1^l/x_2^l)^m} \quad \text{for } n = m \tag{13}$$

$$x_1^s = \left[\frac{\bar{K}_{12}\,x_1^l/x_2^l}{1+\bar{K}_{12}\,x_1^l/x_2^l}\right]^m \quad \text{for } n = 1 \tag{14}$$

$$x_1^s = \frac{\bar{K}_{12}\,x_1^l/x_2^l}{[1+(\bar{K}_{12}\,x_1^l/x_2^l)^n]^{1/n}} \quad \text{for } m = 1 \tag{15}$$

Eq. (13), known as *Langmuir-Freundlich*-type (*LF*) isotherm, was widely discussed by *Dąbrowski* et al.[11] and applied to describe the experimental adsorption data from binary liquid mixtures on solids[12–14]. Similarly Eq. (15) was discussed theoretically by *Patrykiejew* et al.[15];

it is known as *Tóth*-type (T) isotherm. However, Eq. (14) is analogous to the generalized *Freundlich* (GF) isotherm known in the gas adsorption[1]. The special forms of Eqs. (13)–(15) were also used to represent the single-solute data of adsorption from dilute aqueous solutions on activated carbons[16,17].

Eqs. (13)–(15) may be considered as special cases of Eq. (9) with $\beta_{21} = 1$ (ideal both phases), i.e.,

$$x_1^s = \left[\frac{(\bar{K}_{12}\, x_1^l / x_2^l)^n}{1 + (\bar{K}_{12}\, x_1^l / x_2^l)^n}\right]^{m/n} \tag{16}$$

Fig. 1 presents the extensive model calculations illustrating the properties of the excess adsorption isotherm generated by Eq. (16). The excess

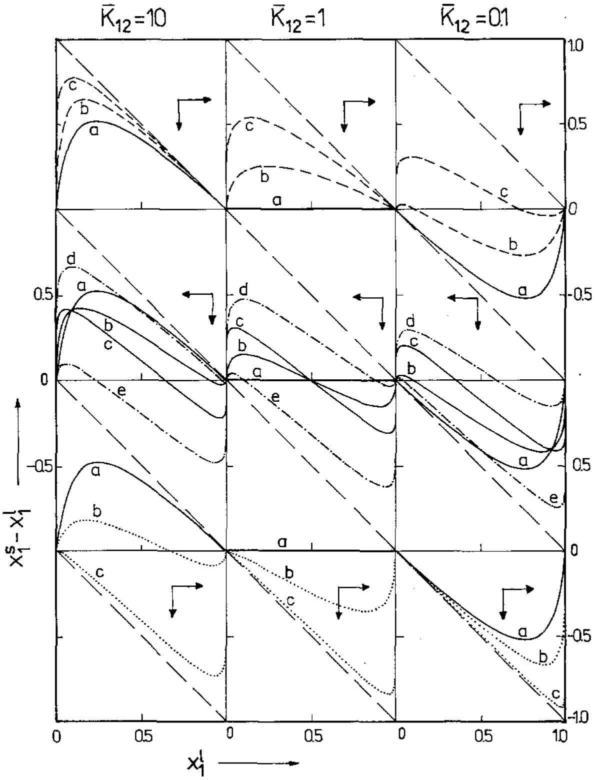

Fig. 1. Theoretical excess adsorption isotherms calculated according to Eq. (17) for parameters summarized in Table 1

adsorption isotherms, presented in this figure, were calculated according to the following expression:

$$x_1^s - x_1^l = \left[\frac{(\bar{K}_{12} x_1^l / x_2^l)^n}{1 + (\bar{K}_{12} x_1^l / x_2^l)^n} \right]^{m/n} - x_1^l \tag{17}$$

for different values of $\bar{K}_{12}$, m and n. The solid lines denote the excess adsorption isotherms calculated according to Eq. (17) for $m = n$ [in other words, the mole fraction x_1^s has been expressed by the *LF* isotherm Eq. (13)], the dashed lines were calculated according to Eq. (17) with $n = 1$ [i.e., x_1^s has been expressed by the *GF* Eq. (14)] and the dotted lines were plotted according to Eq. (17) with $m = 1$ [i.e., x_1^s has been expressed by the *Tóth* Eq. (15)]. The dashed-dotted lines denote the excess isotherms calculated according to Eq. (17) for $n \neq m$ and $m, n \in (0, 1)$. The values of parameters m and n used in the calculation of the excess adsorption isotherms shown in Fig. 1 are summarized in Table 1. The dependence of the excess adsorption isotherm Eq. (17) upon the heterogeneity parameters m and n is clearly presented in Fig. 1 for $\bar{K}_{12} = 1$ and different values of m and n. The excess adsorption isotherm calculated according to Eq. (17) for $m = n = 1$ and $\bar{K}_{12} = 1$ is equal to zero in the whole concentration region. It is evident that for homogeneous solid surfaces ($m = n = 1$) and $\bar{K}_{12} = 1$ Eq. (17) predicts a zero value for $x_1^s - x_1^l$. However, for heterogeneous surfaces (m and n vary from unity to zero) the adsorption excess is different from zero even for $\bar{K}_{12} = 1$. For an energy distribution widened to the right-hand side, i.e., higher values of differences of adsorption energies of both components ($m < n$ and $n = 1$), the excess adsorption isotherms of type II are obtained (dashed lines). An increase in the adsorption excess of the 1st component is due to a decrease in the value of the heterogeneity parameter m; then the widening of the distribution function increases.

The same type of the adsorption isotherms is obtained for energy distributions widened to the left-hand side ($n < m$ and $m = 1$) but they are negative (dotted lines). In this case an increase in the adsorption excess of the 1st component is due to an increase in the value of n; then the widening of the distribution function decreases. However, a decrease in the value of n causes an increase in the adsorption excess of the 2nd component.

The excess isotherms corresponding to the symmetrical energy distribution ($m = n$) intersect the axis x_1^l at the point 0.5 (solid lines). In the case of a symmetrical distribution ($m = n$) the behaviour of the excess isotherms in the concentration region before the intersection point is similar as in the case of isotherms calculated for $m < n$ and $n = 1$, however, in the region after the intersection point these isotherms

Table 1. *Values of the parameters m and n used in calculations of the excess adsorption isotherms according to Eq. (17) shown in Fig. 1*

Line	Code of curve	m	n
solid	a	1.0	1.0
	b	0.5	0.5
	c	0.2	0.2
dashed	b	0.5	1.0
	c	0.2	1.0
dotted	b	1.0	0.5
	c	1.0	0.2
dashed-dotted	d	0.2	0.5
	e	0.5	0.2

behave analogously as those calculated for $n < m$ and $m = 1$. Thus, the type of the energy distribution function influences strongly the behaviour of the excess isotherms.

Fig. 1 also presents the excess isotherms calculated according to Eq. (17) for $\bar{K}_{12} = 10$, 0.1 and different values of m and n. In the case of $m = n = 1$ the adsorption excess calculated for $\bar{K}_{12} = 10$ is positive in the whole concentration region, however, for $\bar{K}_{12} = 0.1$ is negative and at each concentration its absolute value is equal to that corresponding to the value $\bar{K}_{12}$. For m and n smaller than unity this correlation is not observed; it is connected with the fact that the adsorption excess for $\bar{K}_{12} = 1$ and $m, n \in (0, 1)$ is different from zero. However, a correlation is observed between the excess adsorption isotherms of the 1st component calculated for $\bar{K}_{12} = 10$, $n = 1$ and $\bar{K}_{12} = 0.1$, $m = 1$; the first isotherms are positive in the whole concentration region and they correspond to the energy distribution widened to right-hand side, whereas the second isotherms show similar shape but they are negative (they relate to the distributions widened to the left-hand side). Thus, the excess isotherms of the 1st component for $\bar{K}_{12} = 10$, $m \in (0, 1)$ and $n = 1$ are quite analogous to those of the 2nd component for $\bar{K}_{12} = 0.1$, $n \in (0, 1)$ and $m = 1$.

Results and Discussion

The experimental data for the adsorption of benzene from cyclohexane on silica gel, measured by *Goworek*[18], were used to examine the four-parameter isotherm Eq. (16). Two samples of silica gel, type 60 and 100, were taken from Merck (Darmstadt, FRG). The excess adsorption data of benzene from cyclohexane on these samples were interpreted by means of Eq. (16). For the purpose of comparison we also described these data by means of the *Dubinin-Radushkevich* isotherm equation[1]:

$$x^s = \exp\left[-B_0\left(RT \ln \frac{x_{12}}{x_{12}^0}\right)^2\right]; \quad x_{12} = x_1^l/x_2^l \tag{18}$$

where B_0 and x_{12}^0 are parameters.

The adsorption parameters $\bar{K}_{12}$, m, n, and B_0, x_{12}^0 have been evaluated as follows: for a given value of the surface phase capacity n^s, the real adsorption of the 1st component a_1 was calculated from the experimental adsorption excess n_1^e by means of the expression[9]:

$$a_1 = n^s x_1^s = n_1^e + n^s x_1^l \tag{19}$$

Next, the dependence $\varphi = \partial \ln a_1/\partial \ln x_{12}$ vs. $\ln x_{12}$ was plotted for adsorption isotherms measured on silica gel 60 and 100. For Eq. (18) this dependence is linear and its parameters may be used to determine B_0 and x_{12}^0. The parameters m and n may be also evaluated by means of the φ-function using the procedure described in our previous paper[8].

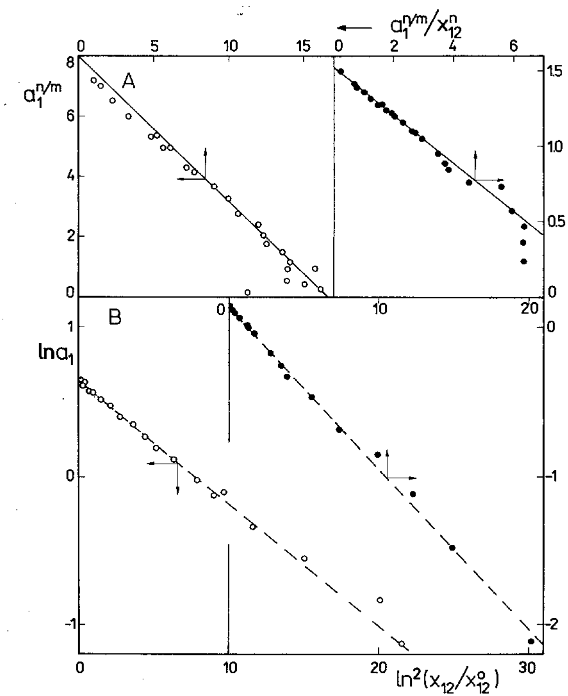

Fig. 2. Linear dependences (20) (*A*) and (21) (*B*) for benzene—cyclohexane adsorption on silica gels 60 (white circles) and 100 (black circles) at 298 K

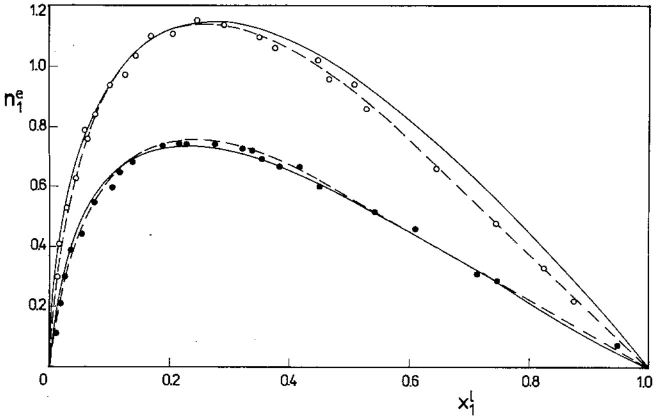

Fig. 3. Experimental excess adsorption isotherms for benzene—cyclohexane on silica gels 60 (white circles) and 100 (black circles) in comparison to the theoretical ones calculated according to Eqs. (16) and (22) (solid lines) and Eqs. (18) and (22) (dashed lines) for the parameters summarized in Table 2

Taking into account the parameters m, n, and x_{12}^0 we plotted in Fig. 2 the benzene—cyclohexane adsorption data according to the following linear equations:

$$a_1{}^{n/m} = (n^s)^{n/m} - (\bar{K}_{12})^{-n} \left[a_1{}^{n/m}/(x_{12}{}^n)\right] \tag{20}$$

$$\ln a_1 = \ln n^s - B_0 \left(RT \ln \frac{x_{12}}{x_{12}^0} \right)^2 \tag{21}$$

These dependences give an information about the exactness of evaluation of m, n, and x_{12}^0 and make it possible to determine the exact values of n^s, $\bar{K}_{12}$, and B_0. The adsorption parameters are summarized in Table 2. However, Fig. 3 presents the experimental excess adsorption isotherms (circles) in comparison to the theoretical ones calculated

Table 2. *Adsorption parameters for benzene—cyclohexane data on silica gels 60 and 100 at temperature 298 K*

Type of gel	Equation (16)				Equation (18)		
	n^s mmol/g	$\bar{K}_{12}$	m	n	n^s mmol/g	$\ln x_{12}^0$	$B_0\,(RT)^2$
60	3.2	21	0.56	1.0	1.89	0.3	0.082
100	1.8	14	1.0	0.7	1.13	—0.2	0.106

according to Eq. (16) (solid lines) and Eq. (18) (dashed lines) by using the relationship[9]:

$$n_1^e = n^s (x_1^s - x_1^l) \tag{22}$$

and adsorption parameters summarized in Table 2. Both equations give a good representation of benzene—cyclohexane adsorption data on silica gel, although in the case of Eq. (16) the approximation is slightly better. This result is reasonable because both isotherm equations correspond to quasi-*Gauss*ian energy distribution[1].

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