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An Isotherm Equation for Adsorption from Binary Liquid Mixtures on Solids Involving Surface Heterogeneity and Differences in Molecular Sizes of Components and its Numerical Verification

Andrzej Dąbrowski

Institute of Chemistry, MCS University, PL-20031 Lublin, Poland

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An equation derived previously[14] for adsorption from binary liquid mixtures composed of molecules of different sizes on heterogeneous solids has been reexamined. Verification of this equation by means of numerical simulation showed its applicability for describing the liquid adsorption onto weakly and strongly heterogeneous surfaces.

(Keywords: Adsorption from solutions; Adsorption on heterogeneous surfaces)

Eine Isothermen-Gleichung für die Adsorption aus binären flüssigen Gemischen an heterogenen Oberflächen fester Körper unter Berücksichtigung der Differenzen in den Molekülgrößen der Komponenten und ihre numerische Verifikation

Es wurde die früher[14] abgeleitete Isothermen-Gleichung der Adsorption aus binären flüssigen Gemischen an heterogenen Oberflächen fester Körper abermals untersucht. Durch Computersimulation wurde gezeigt, daß diese Gleichung den obengenannten Prozeß, der sich sowohl an schwach wie auch an stark heterogenen Oberflächen vollzieht, gut beschreibt.

Introduction

The importance of surface heterogeneity in liquid adsorption onto solids has been widely studied in the recent years and several papers have been published on this subject[1—12]. Review[13] deals with both monolayer as well as multilayer models of the adsorbed phase and presents a first comprehensive survey of the achievements in this field. Simultaneously, review[13] reveals little progress concerning a theoretical description of the adsorption on real solid surfaces from solutions consisting of molecules of different molecular sizes. On the other hand, the majority adsorption systems of a great practical importance include such type of solutions.

In the previous paper of this series[14] an equation for the adsorption isotherm has been proposed on the basis of the kinetic treatment of liquid adsorption. Moreover, in this equation, which was formulated in terms of the monolayer model of surface phase, the difference of molecular sizes of admolecules and energetic heterogeneity of the solid was taken into account. The influence of the above factors and also interactions between molecules on the shape of the excess adsorption isotherms and deviations of the adsorption systems from ideal behaviour has been discussed.

Quite recently *Rudziński* et al.[15], by extending the condensation approximation (CA) method which was firstly adopted to the theory of liquid adsorption on heterogeneous surfaces by *Ościk* et al.[16,17] and *Dąbrowski* et al.[2], were able to derive an analytical equation like the mathematical form of the equation proposed in [14]. In contrast to the equation proposed in [14] *Rudziński*'s isotherm cannot be, in any way, rearranged into the well known *Everett* equation describing liquid adsorption process onto homogeneous surfaces[18]. This statement is connected with the fact that the CA method gives reasonable results for adsorption on very strongly heterogeneous surfaces only[2,12] and then *Rudziński*'s expression may be useful. However, the comparison of the above mentioned two equations will be subject of a future publication[19]. The present paper reexamines our general equation derived previously[14] and proves its applicability for describing the liquid adsorption onto weakly and strongly heterogeneous solids. To this end a computer simulation approach was used. For simplicity, our considerations deal with the IBP model (ideal behaviour in both adsorbed and bulk phases) of adsorption system. According to Ref.[14] in such case the kind of topography of adsorption sites is meaningless. Since the adsorption from solutions consisting of species of different molecular sizes is studied, the volume fractions of components in both phases will be handled, instead of the mole fractions.

Method

General Considerations

One of the most fundamental equations dealing with the liquid adsorption on heterogeneous surfaces, characterized by a continuous energy distribution, has the following form[13]:

$$\Phi_1^s = \int_{\Omega} \varphi_1^s(\varepsilon_{12}, \Phi_1^l)\,\chi(\varepsilon_{12})\,d\,\varepsilon_{12} \tag{1}$$

where ε_{12} is the difference of the adsorption energies of both components; Φ_1^s denotes the average of the volume fractions of the component 1, φ_1^s, reffering to the homogeneous surface patches having the difference of adsorption energies equal to ε_{12} and Ω is the interval of possible changes in ε_{12}; however, Φ_1^l is the volume fraction of the component 1 in the bulk phase.

To solve Eq. (1) the known method of *Stieltjes* transform is usually applied[13].

Unfortunately, this method cannot be employed in the case of adsorption on heterogeneous surfaces with solutions composed of molecules having different sizes, because the local isotherm φ_1^s has the form of a complex function[18].

Let us suppose now, according to [14] that a heterogeneous surface of the solid consists of M adsorption sites distributed among N surface patches, where additionally $M = \sum_{k=1}^{N} M_k$ and M_k is the number of adsorption sites of the k-th type. Then, instead of Eq. (1) we can write:

$$\Phi_1^s = \sum_{k=1}^{N} f_K \varphi_{1,k}^s \tag{2}$$

where $f_k = M_k/M$ denotes the fraction of adsorption sites distributed on the k-th homogeneous patch and connected with the value $\varepsilon_{12,k}$. The constant, which governs the equilibrium state on this patch has the following form[14, 18]:

$$K_k = \left(\frac{\varphi_{1,k}^s}{\Phi_1^l}\right)^r \left(\frac{\Phi_2^l}{\varphi_{2,k}^s}\right) \tag{3}$$

where $\Phi_2^l = 1 - \Phi_1^l$ and $\varphi_{2,k}^s = 1 - \varphi_{1,k}^s$. However,

$$K_k = \exp(\varepsilon_{12,k}/RT) \tag{4}$$

and

$$\varepsilon_{12,k} = r\,\varepsilon_{1,k} - \varepsilon_{2,k} \tag{5}$$

Parameter $\varepsilon_{i,k}$ $(i = 1, 2)$ denotes an adsorption energy of the component i on the k-th patch. The symbol r appearing in Eq. (3) is the ratio of the cross-sectional areas of 2-nd and 1-st components, i. e., $r = w_2^s/w_1^s$.

Basing on Eq. (2) and using the kinetic approach described in [14] the following equation for the liquid adsorption on real solid surfaces has been obtained:

$$\bar{K} = \exp(\bar{\varepsilon}_{12}/RT) = \frac{(\Phi_1^s)^{r/c}}{(\Phi_2^s)^{1/c}} \frac{\Phi_2^l}{(\Phi_1^l)^r} \tag{6}$$

where $\bar{K}$ and $\bar{\varepsilon}_{12}$ appear as some averages of the constants K_k and energies $\varepsilon_{12,k}$ respectively referring to the whole heterogeneous solid surface[14], however, c denotes the heterogeneity parameter. This parameter may be expressed as follows[5]:

$$c = 1/(c_1 + 1) \tag{7}$$

where $c_1 \geqslant 0$ is a free parameter. So, $c \in (0, 1\rangle$ and it characterizes the shape of a *Gauss*ian-like distribution[14]. For $c = 1$ Eq. (6) produces the well-known *Everett*'s equation dealing with adsorption on homogeneous surfaces from solutions composed of molecules having different sizes[18], but for $r = 1$ Eq. (6) may be rearranged to give the exact, analytical solution of Eq. (1)[2].

Theory

Let suppose now the following, typical *Gauss*ian distribution of the variable $\varepsilon_{12} = r\,\varepsilon_1 - \varepsilon_2$:

$$\chi(\varepsilon_{12}) = \frac{1}{\Delta\sqrt{2\pi}} \exp\left[-\frac{(\varepsilon_{12}-\varepsilon_{12}^{\circ})^2}{2\Delta^2}\right] \tag{8}$$

where Δ is the parameter characterizing the width of the distribution in question, but ε_{12}° corresponds to the value of ε_{12} for which the function $\chi(\varepsilon_{12})$ reaches a maximum. When the parameter Δ tends to zero, the function $\chi(\varepsilon_{12})$ becomes the *Dirac* delta distribution $\delta(\varepsilon_{12}-\varepsilon_{12}^{\circ})$. In this instance we have to deal with a homogeneous surface characterized by the adsorption energy $\varepsilon_{12} = \varepsilon_{12}^{\circ}$. Function $\chi(\varepsilon_{12})$ expressed by Eq. (8) fulfils the normalization condition:

$$\int_{-\infty}^{+\infty} \chi(\varepsilon_{12})\,\mathrm{d}\varepsilon_{12} = 1 \tag{9}$$

Fig. 1 shows the normalized functions of the energy distribution relating to Eq. (8), evaluated for $\varepsilon_{12}^{\circ} = 0$ and different values of Δ. For comparative purposes, all functions presented in this graph have been drawn on an identical scale. It follows from Fig. 1 that the function $\chi(\varepsilon_{12})$ corresponding to $\Delta = 0.25$ (curve a) approximates the *Dirac* delta distribution and there is an inconsiderable interval of changes $\varepsilon_{12}\langle -0.65\,\text{kcal}, +0.65\,\text{kcal}\rangle$. So, we can state that in this case the function $\chi(\varepsilon_{12})$ characterizes a nearly homogeneous surface of the solid. However, the function corresponding to $\Delta = 2$ (curve d) is extended through a wide range of $\varepsilon_{12}\langle -5.5\,\text{kcal}, +5.5\,\text{kcal}\rangle$ and characterizes a highly energetically heterogeneous surface. Bearing in mind Eq. (2) we have to replace the continuous distribution (8) by the discreet one. Recently, it has been proved by *Czarniecki* and *Jaroniec*[20] that such replacement is a sufficient rigorous approximation, in case that an interval of significant changes of the variable ε_{12} is taken into account. For the discreet distribution the normalization condition (9) may be rewritten in the following form:

$$\sum_{k=1}^{N} f_k = 1 \tag{10}$$

with

$$f_k = \chi(\varepsilon_{12,k}) / \sum_{k=1}^{N} \chi(\varepsilon_{12,k}) \tag{11}$$

One must stress that the meaning of the parameter f_k given by Eq. (11) is equivalent to that appearing in Eq. (2).

With a view to our further considerations, in Fig. 2 the function (8) evaluated for $\Delta = 1$ and $\varepsilon_{12}^{\circ} = 0$ is presented. For this instance the interval of significant quantities of ε_{12} is: $\langle -3.2\,\text{kcal}, +3.2\,\text{kcal}\rangle$ and that was divided into sixteen mutually-equal subintervals, i. e., the upper index appearing in the sum (10) is equal to $N = 17$.

To demonstrate the utility of Eq. (6) the numerical calculations have been performed according to the scheme described below.

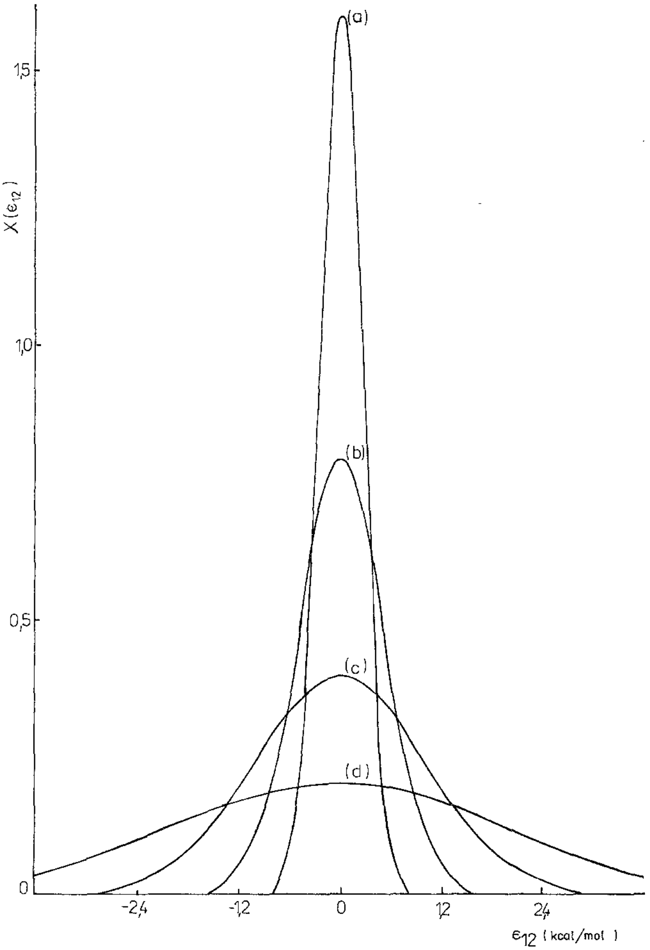

Fig. 1. Normalized distribution functions (8) calculated for various values of Δ and $\varepsilon_{12}^{\circ} = 0$: $\Delta = 0.25$ (*a*); $\Delta = 0.5$ (*b*); $\Delta = 1$ (*c*); $\Delta = 2$ (*d*)

1. The calculation of the volume fractions Φ_1^l and $\Phi_2^l = 1 - \Phi_1^l$ by means of the following relation[14]:

$$\Phi_1^l = \frac{x_1^l}{x_1^l + r(1 - x_1^l)} \qquad (12)$$

for given values of r_1 and x_1^l where $r_1 = r^{-1}$.

2. The calculation of the equilibrium constants K_k, according to Eq. (4) describing the adsorption onto homogeneous patches connected with the energies $\varepsilon_{12,k}$, estimated for a given distribution function $\chi(\varepsilon_{12})$ (see also Fig. 2).

3. The calculation of the volume fraction Φ_1^s by means of Eq. (2). To this end the fraction of adsorption sites distributed onto the k-th homogeneous patch

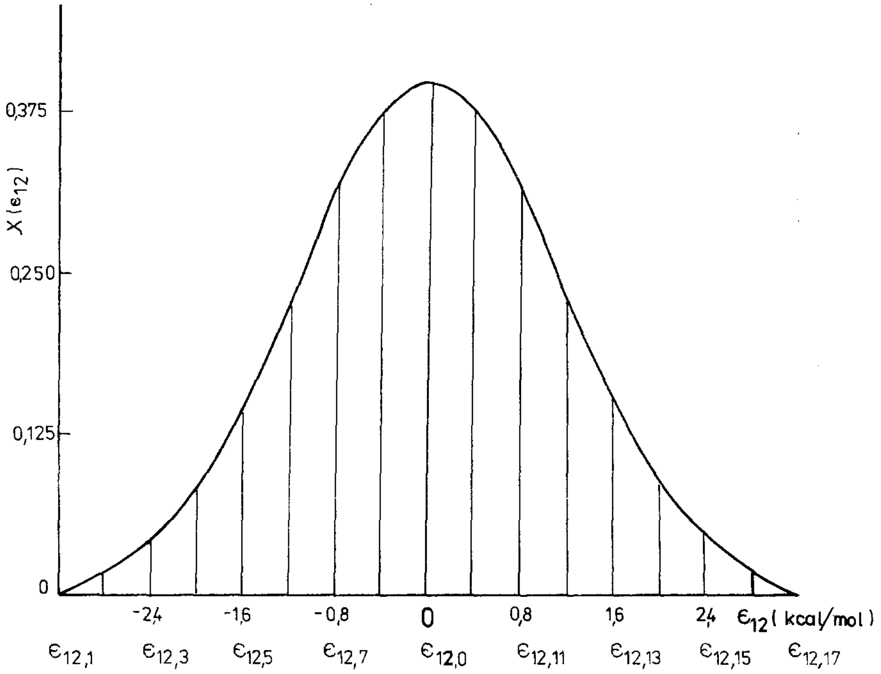

Fig. 2. Schema illustrating the numerical procedure used for verification of Eq. (6)

characterized by the energy $\varepsilon_{12,k}$, was obtained according to Eq. (11). However, the volume fraction $\varphi^s_{1,k}$ corresponding to the adsorption on this same, homogeneous k-th patch, was evaluated by means of the numerical solution of Eq. (3), where respective values K_k evaluated according to Eq. (4) were used.

4. The recalculation of the volume fractions Φ^s_1 to the mole fractions X^s_1 using the expression[14]:

$$X^s_1 = \frac{r\Phi^s_1}{r\Phi^s_1 + (1 - \Phi^s_1)} \tag{13}$$

and finally, the calculation of the excess isotherm $N^e_1 = N^e_1(x^l_1)$ describing the adsorption process on the heterogeneous surface, according to the following formula[14]:

$$N^e_1 = \frac{X^s_1 - x^l_1}{r + X^s_1(1 - r)} \tag{14}$$

The simulated isotherms $\Phi^s_1 = \Phi^s_1(\Phi^l_1)$ and $N^e_1 = N^e_1(x^l_1)$ will be treated by us as "experimental ones".

5. The approximation of the experimental function $\Phi^s_1 = \Phi^s_1(\Phi^l_1)$ using the linear form of Eq. (6):

$$\ln\frac{1 - \Phi^s_1}{(\Phi^s_1)^r} = c\ln(\bar{K})^{-1} + c\ln\frac{1 - \Phi^l_1}{(\Phi^l_1)^r} \tag{15}$$

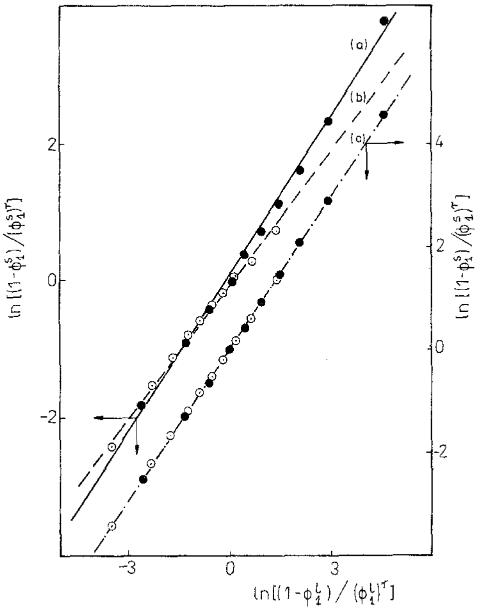

Fig. 3. Linear dependence, Eq. (15), examined for the simulated experimental data obtained by means of Eq. (2) for $\varepsilon_{12}^{\circ} = 0$; other adsorption parameters are equal to: $\Delta = 1$, $r_1 = 1.4$ [solid line (*a*) with filled circles]; $\Delta = 1$, $r_1 = 0.6$ [dashed line (*b*) with open circles]; $\Delta = 0.25$, $r_1 = 1.4$ [filled circles and line (*c*)]; $\Delta = 0.25$, $r_1 = 0.6$ [open circles and line (*c*)]

6. The evaluation of theoretical excess isotherms using Eqs. (6), (12)–(15). To solve Eq. (6), the parameters c and $\bar{K}$ obtained on the basis of Eq. (15) were applied.

7. The calculation of the sum of square deviations (SD) defined by the following equation:

$$\mathrm{SD} = \sum_{i=1}^{I} [N_{1i}^{e,exp} - N_{1i}^{e,theor}]^2 \qquad (16)$$

where I denotes the total number of the experimental points, but $N_{1i}^{e,exp}$ and $N_{1i}^{e,theor}$ denote experimental and theoretical values of the excess isotherms, respectively.

While performing the above described numerical calculations it was admitted that x_1^l runs through the following values: $\{0.05, 0.15, \ldots, 0.95\}$, i. e., the upper index I in Eq. (16) is: $I = 10$. Simultaneously, the parameter $r_1 = r^{-1}$ runs through the values: $\{0.6, 0.7, \ldots, 1.4\}$. Other parameters necessary to carry out our model studies were admitted as follows: $N = 17$ [see Eq. (2)] and $RT = 0.6$ kcal/mol [see Eq. (4)].

Results and Discussion

In Fig. 3 the linear dependences, $\ln[(1-\Phi_1^s)/(\Phi_1^s)^r]$ vs. $\ln[(1-\Phi_1^l)/(\Phi_1^l)^r]$ evaluated according to Eq. (15) for $\varepsilon_{12}^{\circ} = 0$ and $\Delta = 0.25$ (straight line c) and $\Delta = 1$ (straight lines a and b) are presented. For both values of Δ, the experimental points were obtained by means of Eq. (2) for $r_1 = 0.6$ (open circles) and $r_1 = 1.4$ (filled circles). It follows from Fig. 3 that Eq. (15), being the linear form of the examined expression (6), gives a good representation of the simulated adsorption data both for $\Delta = 0.25$ (a small surface heterogeneity) and for $\Delta = 1$ (a considerable surface heterogeneity) and for $\Delta = 1$ (a considerable surface heterogeneity) (see also Fig. 1). However, in the former case the parameter c, determined directly by the slope of the straight lines, appears to be practically independent upon the difference in the molecular sizes of both components ($c = 0.997$ for $r_1 = 0.6$, and $c = 0.998$ for $r_1 = 1.4$), but in the last case this parameter is slightly dependent on r ($c = 0.643$ for $r_1 = 0.6$ and $c = 0.775$ for $r_1 = 1.4$). In other words, for adsorption onto heterogeneous surfaces, from solutions composed of molecules having different sizes, the parameter r modifies the true value of the heterogeneity parameter c. At first sight it is a rather surprising conclusion, because irrespective of changes in r, the parameter c characterizing via $\Delta = \text{const.}$ the shape of the *Gaussian* distribution should be constant, too. However, such result is in accordance with the model studies performed on the basis of Eq. (6) and presented in Ref.[14] (see Fig. 1, Ref.[14]). Therefore careful attention has to be applied using Eq. (6) for describing experimental adsorption data and suitable corrections in relation to the parameter c must be taken into account (see below). On the other hand, when adsorption takes place on slightly heterogeneous surfaces, then the influence of r onto c may be neglected[21]. It is interesting that the equilibrium constant $\bar{K}$, similar to c, is practically independent on r when c tends to unity e. g., $\Delta = 0.25$, $c \simeq 1$, $\bar{K} = 1.008$ for $r_1 = 0.6$ and $\bar{K} = 0.996$ for $r_1 = 1.4$. However, the differences in $\bar{K}$ increase simultaneously with r when the parameter Δ increases. Above deductions are strongly supported by the results showed in Fig. 4. In the part B of this figure the linear dependence (15) applied for describing experimental points simulated by means of Eq. (2) for $\Delta = 2$ are showed, but in part A the suitable experimental and theoretical excess adsorption isotherms are compared. The labeling is as in Fig. 3, but here the dotted line with crossed circles denotes the situation when $r = 1$. The parameters c, $\bar{K}$ and SD corresponding to results presented in Figs. 3–4 are summarized in Table 1. It follows from Table 1 that irrespective to changes in Δ, the values of $\bar{K}$ for $r_1 = 1$ correspond to $\varepsilon^{\circ}_{12} = 0$ for which the function (8) reaches a maximum, i. e., $\bar{K} \simeq 1$. We shall illustrate it as follows. For $r_1 = 1$, Eq. (6) may be rearranged to give:

$$\ln \bar{K} = [\overline{(\varepsilon_1 - \varepsilon_2)}/RT] = [\bar{\varepsilon}^{*}_{12}/RT] \qquad (17)$$

Because the distribution function (8) is symmetric, the value of $\bar{\varepsilon}^{*}_{12}$ is the average difference of adsorption energies of both components for which

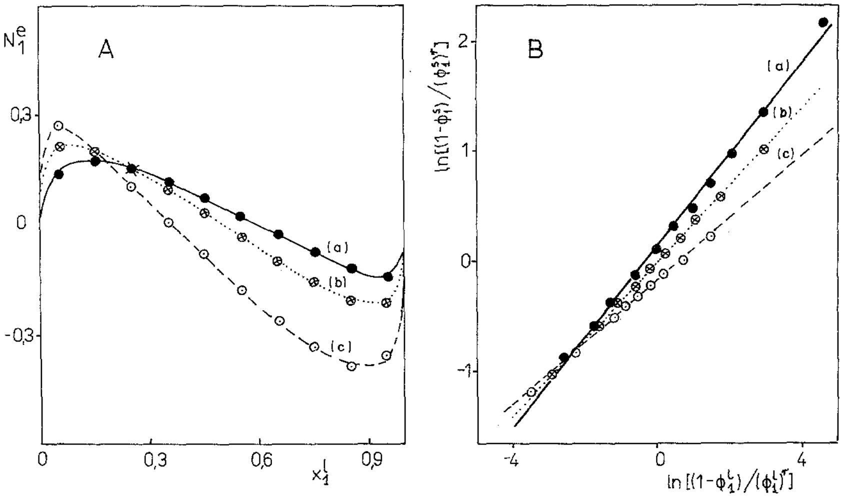

Fig. 4. Simulated excess adsorption isotherms (*A*) and corresponding functions (15) (*B*) evaluated for $\varepsilon_{12}^\circ = 0$ and $\Delta = 2$. Circles denote the experimental points, but the lines denote theoretical functions; other adsorption parameters are equal to: $r_1 = 1.4$ [solid line (*a*) with filled circles]; $r_1 = 1$ [dotted line (*b*) with crossed circles]; $r_1 = 0.6$ [dashed line (*c*) with open circles]

Table 1. *Adsorption parameters of Eq. (6) calculated for $\varepsilon_{12}^\circ = 0$ and $\Delta = 0.25, 1, 2$*

Δ	$r_1 = r^{-1}$	c	$\bar{K}$	SD	No. of figures
	0.6	0.978	1.009	0.00009	
0.25	1.0	0.983	1.001	0.000006	3
	1.4	0.988	0.998	0.00004	
	0.6	0.643	1.141	0.0002	
1	1.0	0.679	1.001	0.00001	3
	1.4	0.775	0.935	0.0004	
	0.6	0.286	1.821	0.0004	
2	1.0	0.345	1.000	0.00003	4
	1.4	0.422	0.715	0.0005	

the *Gauss*ian distribution reaches a maximum, i.e., $\bar{\varepsilon}_{12}^* = \varepsilon_{12}^\circ = 0$ and $\bar{K} \simeq 1$. Moreover, such a result indicates the accuracy of the procedure dealing with the substitution of the integral (1) by the sum (2).

Let us notice that Eq. (6) for $c = 1$ and $r = 1$ becomes the simple form of *Everett*'s equation[22] which for $\bar{K} = K = 1$ predicts a zero value for the adsorption excesses in the whole concentration interval. As follows from

Fig. 4 and Refs.[2,11], during the liquid adsorption onto heterogeneous surfaces the excesses are different from zero even for $\bar{K} = 1$ and $r = 1$. This same inference is kept during the adsorption onto homogeneous surfaces when $c \simeq 1$ but $r \neq 1$[19].

Summing up the results obtained, we can state that our examined Eq. (6) gives good representation of experimental data in the wide range of changes in surface heterogeneity of solids, however the parameter c obtained by means of this formula depends on r when Δ increases. The true value of c many be reckoned by using the diagrams Δ vs. c similar to that presented in Fig. 5. This figure confirms our previous statements[14] in relation to Eq. (6), namely:

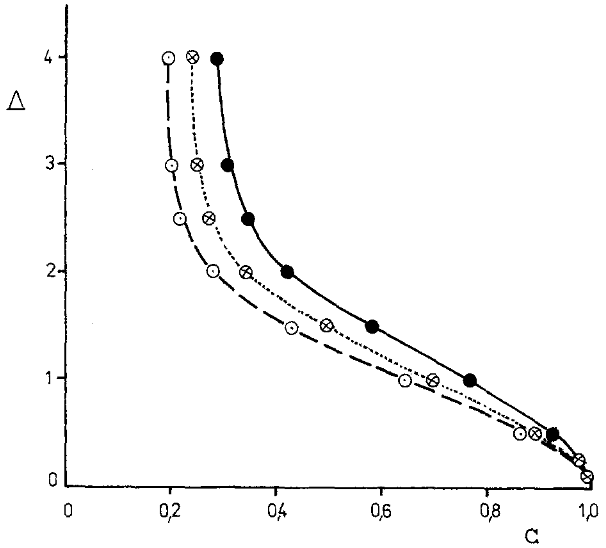

Fig. 5. Dependence Δ vs. c, obtained by means of Eqs. (2) and (15) for $\varepsilon_{12}^{\circ} = 0$; other adsorption parameters are equal to: $r_1 = 1.4$ (solid line with filled circles); $r_1 = 1$ (dotted line with crossed circles); $r_1 = 0.6$ (dashed line with open circles)

1. the equation in question corresponds to a *Gaussian* distribution of the variable ε_{12},
2. equation (6) predicts that the heterogeneity parameter $c = c(\Delta) \in (0, 1\rangle$
3. for $c = 1$ the parameter $\Delta = 0$ and distribution (8) becomes equal to the *Dirac* delta function.

Simultaneously, it appears from Fig. 5, that Eq. (6) gives in sufficient results for $\Delta > 2.5$ for which $c < 0.3$, because the diagram Δ vs. c is little sensitive on alternation in Δ. Fortunately, parameters c characterizing most of the experimental systems are greater than $c = 0.5$ (Refs.[3,23]).

To evaluate the distribution function (8) characterizing any experimental system, a knowledge of the parameter ε_{12}° is necessary. The procedure to solve this problem and an application of Eq. (6) for analysing real experimental systems and some other problems dealing with liquid adsorption from solutions composed of molecules having different sizes will be the subject of a further communication[19].

Note added in proof:

Model calculations presented in Refs.[14, 19] were carried out for $r_1 = r^{-1}$.

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