

ANNALES
UNIVERSITATIS MARIAE CURIE-SKŁODOWSKA
LUBLIN—POLONIA

VOL. XXXVIII, 9

SECTIO AA

1983

Institut Chemii UMCS
Zakład Chemii Teoretycznej
Kierownik: prof. dr hab. Władysław Rudziński

Andrzej DĄBROWSKI

Effects of Surface Heterogeneity in Adsorption from Non-ideal Binary Liquid Mixtures on Solids

Wpływ heterogeniczności adsorbentu na proces adsorpcji z nieidealnych dwuskładnikowych roztworów nieelektrolitów na powierzchniach ciał stałych

Влияние гетерогенности адсорбента на процесс адсорбции из бинарных неидеальных растворов неэлектролитов на поверхностях твердых тел

INTRODUCTION

The influence of surface heterogeneity on the mechanism of the adsorption process at solid/liquid interface has been intensively studied during last decade [1-13]. Recently, a comprehensive survey of various approaches to liquid adsorption onto heterogeneous adsorbents has been given by Dąbrowski et al. [14]. In the cited papers both monolayer as well as multilayer models of adsorbed phase formation on heterogeneous solids were discussed. However, the monograph [14] pointed out inadequate investigations dealing with the role of surface heterogeneity of the adsorbent

when a liquid mixture is non-ideal in both bulk and surface phases. The recent papers of Dąbrowski et al. [3] and Dąbrowski [8-11] do not explain this problem satisfactorily. On the other hand, Everett [15], Zettlemoyer [16] and Hansen [17] suggested that the heterogeneity of the surface can play a dominant role as a source of imperfection in the adsorbed region. Simultaneously, ought to expect that (except for the adsorption onto extremely strongly heterogeneous surfaces where a dominant role of the factor in question is beyond doubt proved [3, 11, 18]) an influence of the non-ideality of the bulk and (or) surface phases on the mechanism of adsorption at solid/liquid interface is like to that arising from surface heterogeneity of the adsorbent used. Hence, from theoretical view point a double possibility to explain of deviations of experimental results from simplest form of Everett's equation (this equation reflects so-called ideal behaviour of adsorption system) appears: 1. either in terms of so-called surface activity coefficients, or 2. in terms of surface heterogeneity effects. Fortunately, bulk activity coefficients are independent on the adsorption experiment and, in view of it, a role of interactions at free solution in liquid adsorption can be easily established. The determination separately of an influence of intermolecular interactions among admolecules and surface heterogeneity of the solid on imperfection of the adsorbed phase is more complicated.

To look for a solution of the above problem, so-called Langmuir-Freundlich (LF) equation will be handled by us. Previously this type of isotherm has been introduced in liquid ad-

sorption by means of kinetic approach by J a r o n i e c [19], however, D a b r o w s k i et al. [2] explained it on the basis of both the Stieltjes transform and condensation approximation method [20]. It has been shown [3] that (LF) equation describes the monolayer adsorption from solutions consisting of molecules of equal sizes and this one corresponds to the symmetrical quasi-gaussian energy distribution.

In this paper on the basis of (LF) equation and assuming the simple statistical model for regular solutions, analytical expressions for isosteric heats of adsorption are derived. Next, the combined effects of surface heterogeneity and non-ideality of both bulk and surface phases as well as interactions among molecules belonging to those on the excess adsorption isotherms and isosteric heats of adsorption, are studied numerically. Besides, criteria for the formation of S-shaped excess isotherms are established. Next, the problem of surface activity coefficients is widely discussed. In terms of (LF) isotherm, the suitable equations are proposed with the aim to separate an influence of heterogeneity effects and intermolecular interactions between admolecules on the imperfection of the adsorbed phase. Above-mentioned equations are studied theoretically and some literature experimental data are applied to their verification. It is proved that experimental results explained previously in terms of negative deviations of adsorbed solution from Raoult's law can be explained in terms of a more realistic assumption respecting surface heterogeneity of the solid. Moreover, by means of suitable experimental data a temperature dependence of the heterogeneity parameter appearing in (LF) equation is discussed too.

Regardless of the fact that the crude assumptions underlying (LF) equation (i.e., monolayer model of surface phase and symmetrical quasi-gaussian energy distribution corresponding to it) expression in question seems to be one of the most popular and useful equations used for characterizing many simple adsorption systems [3-5, 21-24]. Hence, we believe that our considerations such as below can provide valuable information about the nature of the adsorption process at solid/liquid interface.

GENERAL CONSIDERATIONS

One of the most fundamental equations dealing with the liquid adsorption on heterogeneous solid surfaces, characterized by a continuous energy distribution has the following form [14]:

$$x_{1,t}^s(x_1^l) = \int_{\Delta} x_{1,1}^s(x_1^l, \epsilon_{12}) \lambda(\epsilon_{12}) d\epsilon_{12} \quad (1)$$

where $x_{1,t}^s$ denotes the total (average) mole fraction of the 1st component in the whole surface region, $x_{1,1}^s$ is an analogous local value referred to the homogeneous surface patch with the difference of adsorption energies of both components $\epsilon_{12} = \epsilon_1 - \epsilon_2$, but Δ denotes the interval of possible changes in ϵ_{12} and usually $\Delta = (-\infty, +\infty)$ [3], $\lambda(\epsilon_{12})$ is the differential distribution function of adsorption sites with regard to the value ϵ_{12} .

The distribution functions appearing in eq. (1) fulfill the normalization condition:

$$\int_{-\infty}^{+\infty} \lambda(\epsilon_{12}) d\epsilon_{12} = 1 \quad (2)$$

Equation (1) may be solved analytically by means of the Stieltjes transform method [3] or by using the condensation approximation approach [8, 25]. As the kernel of integral equation in question, i.e., as the local adsorption isotherm, the famous Everett's expression is introduced and then eq. (1) may be rewritten in the following form:

$$x_{1,t}^s(x_1^l) = \int_{-\infty}^{+\infty} K_{12} X_{12,1} (1 + K_{12} X_{12,1})^{-1} \lambda(\epsilon_{12})^d \epsilon_{12} \quad (3)$$

where the constant K_{12} is defined as follows [14]:

$$K_{12} = K^0(T) \exp(\epsilon_{12}/RT) \quad (4)$$

Above, $K^0(T)$ denotes the temperature dependent constant; it is common practice in the theory of adsorption from solutions to admit that $K^0(T) \approx 1$ [14].

The general form of the local variable $X_{12,1}$ corresponds to a model supposed for heterogeneous surface as well as to a model supposed for adsorption system. The current state of theory of liquid adsorption on solids allows us to distinguish four models of adsorption systems:

1. NBP-na model; non-ideal behaviour in both bulk and adsorbed phases, where the adsorbed phase is nonautonomous, i.e., this phase interacts with bulk one,
2. NBP-a model with an autonomous surface phase,
3. IAP model; non-ideal bulk phase and ideal adsorbed phase,
4. IBP model; both phases ideal.

Recently, Everett and Podolil [26] have been introduced a model with ideal bulk phase and non-ideal adsorbed phase; the suitable abbreviations dealing with this model are following: NAP-na and NAP-a.

For IAP and IBP models the variable $X_{12,1}$ is independent on a model of heterogeneous surface; it means that in this case the type of topography of adsorption sites is meaningless [14]. On the contrary, both NBP and NAP models require an additional assumption towards the type of heterogeneous surface which influences the behaviour of admolecules showing differentiated mutual interactions. Hence, for NBP and NAP models also the patchwise surface, the variable $X_{12,1}$ has the following form:

$$x_{12,1}^s = \begin{cases} \gamma_{21,1}^s(x_{1,1}^s, x_1^1) a_{12}^1 & , \text{ for NBP-na model} \\ \gamma_{21,1}^s(x_{1,1}^s) a_{12}^1 & , \text{ for NBP-a model} \\ \gamma_{21,1}^s(x_{1,1}^s, x_1^1) x_{12}^1 & , \text{ for NAP-na model, where } \gamma_1^1=1 \\ & \text{or at least } \gamma_{12}^1=1 \\ \gamma_{21,1}^s(x_{1,1}^s) x_{12}^1 & , \text{ for NAP-a model, where } \gamma_1^1=1 \\ & \text{or at least } \gamma_{12}^1=1 \end{cases}$$

where $\gamma_{21,1}^s = \gamma_{2,1}^s / \gamma_{1,1}^s$ and $\gamma_{i,1}^s$ ($i=1,2$) is the local surface activity coefficient; $\gamma_{12}^1 = \gamma_1^1 / \gamma_2^1$ and γ_i^1 ($i=1,2$) denotes the bulk activity coefficients, $x_{12}^1 = x_1^1 / x_2^1$ and $a_{12}^1 = a_1^1 / a_2^1$, where $a_i^1 = x_i^1 \gamma_i^1$ ($i=1,2$) is the activity of the i -th component in the bulk phase.

It follows from the foregoing considerations that for patchwise surface equation (1) cannot be solved analytically with respect to $x_{1,1}^s$. However, if the more realistic random distribution of adsorption sites is introduced, the surface activity coefficient $\gamma_{i,1}^s$ ($i=1,2$) appear to be function of the composition of the entire adsorbed region and, with respect to model of adsorption system used, eventually the composition of the bulk phase. Consequently, the variable $x_{12,1}$ corresponding to

the random surface is independent on ξ_{12} and may be expressed as follows:

$$x_{12, l=x_{12}}^s \left\{ \begin{array}{ll} \gamma_{21}^s(x_1^s, t, x_1^l) a_{12}^l & , \text{ for NBP-na model} \\ \gamma_{21}^s(x_1^s, t) a_{12}^l & , \text{ for NBP-a model} \\ \gamma_{21}^s(x_1^s, t, x_1^l) x_{12}^l & , \text{ for NAP-na model} \\ \gamma_{21}^s(x_1^s, t) x_{12}^l & , \text{ for NAP-a model} \\ a_{12}^l & , \text{ for IAP model} \\ x_{12}^l & , \text{ for IBP model} \end{array} \right. \quad (6)$$

To take advantage of above-mentioned models with non-ideal adsorbed phase, an assumption concerning a solution structure is frequently introduced. In this and the simple, statistical model of regular solution is applied usually [5, 11, 15, 26]. Following by Everett [15], the activity coefficients in the regular bulk and adsorbed phases are determined as follows:

$$\gamma_i^l = \exp \left[\hat{q}^l (1-x_i^l)^2 \right] \quad (7)$$

$$\gamma_i^s = \exp \left[lq^s (1-x_{i,t}^s)^2 + m\hat{q}^l (1-x_i^l)^2 \right] \quad (8)$$

where $\hat{q}^l = q^l/RT$, $\hat{q}^s = q^s/RT$; the parameters q^l and q^s are responsible for molecular interactions in the bulk and surface phase, respectively, but $\hat{q}^l, \hat{q}^s \in (-\infty, 2)$. The constants of regular solution: l and m have their usual meaning and $l+2m=1$ [15].

Equation (8) is valid by assuming that interaction between molecules in the adsorbed phase equals that in the bulk phase. Taking eqs. (7), (8) and (6) into considerations, we obtain the following expressions for the variable X_{12} :

$$x_{12}^1 = \left\{ \begin{array}{l} \exp[1\hat{q}^S(2x_1^S, t^{-1}) + m\hat{q}^1(2x_1^1 - 1)] \cdot \exp[\hat{q}^1(1 - 2x_1^1)] x_{12}^1, \quad \text{for} \\ \text{NBP-na model on random surfaces} \\ \exp[1\hat{q}^S(2x_1^S, t^{-1})] \exp[\hat{q}^1(1 - 2x_1^1)] x_{12}^1, \quad \text{for NBP-a model} \\ \text{on random surface} \\ \exp[1\hat{q}^S(2x_1^S, t^{-1}) + m\hat{q}^1(2x_1^1 - 1)] x_{12}^1, \quad \text{for NAP-na model} \\ \text{on random surfaces} \\ \exp[1\hat{q}^S(2x_1^S, t^{-1})] x_{12}^1, \quad \text{for NAP-a model on random} \\ \text{surfaces} \\ \exp[\hat{q}^1(1 - 2x_1^1)] x_{12}^1, \quad \text{for IAP model} \\ x_{12}^1, \quad \text{for IBP model.} \end{array} \right. \quad (9)$$

Equation (9) will be handled by us during model studies of liquid adsorption onto heterogeneous solid surfaces.

THE LF EQUATION AND ITS APPLICATION TO THEORETICAL STUDIES OF ADSORPTION PROCESS AT SOLID/LIQUID INTERFACE

To solve analytically eq. (2) with respect to $x_{1,t}^S$, taking the local functions (6) or (9) into account, various distributions $\lambda(\varepsilon_{12})$ can be admitted [14]. However, the most popular and effective distribution appears to be quasi-gaussian one. This function has the following form [3]:

$$\lambda(\varepsilon_{12}) = (\pi RT)^{-1} \frac{\sin(\pi c) \exp(c \tilde{\varepsilon}_{12})}{1 + 2\cos(\pi c) \exp(\tilde{\varepsilon}_{12} c) + \exp(\tilde{\varepsilon}_{12} 2c)} \quad (10)$$

where

$$\tilde{\varepsilon}_{12} = (\varepsilon_0 - \varepsilon_{12}) / RT \quad (11)$$

The value of ε_0 corresponds to such value of ε_{12} for which the function (10) reaches a maximum. The heterogeneity parameter c determines the shape of the distribution (10) and $c \in (0, 1)$. In

the case of homogeneous surface, the parameter $c=1$ and the distribution (10) becomes the δ -Dirac function for which we have:

$$\int_{-\infty}^{+\infty} \lambda(\xi_{12}) d\xi_{12} = \int_{-\infty}^{+\infty} \delta(\xi_0 - \xi_{12}) = 1 \quad (12)$$

Combining eqs. (3) and (10) one gets, by means of Stieltjes transform method, the above-mentioned Langmuir-Freundlich equation:

$$x_{1,t}^s(x_1^1) = (K_{12} x_{12})^c / [1 + (K_{12} x_{12})^c] \quad (13)$$

where the variable x_{12} is given by equations(6) or(9) and the constant K_{12} is defined as follows [4]:

$$K_{12} \simeq K^0(T) \exp(\xi_0/RT) \quad (14)$$

However, the parameter c is temperature dependent [27]:

$$c = c(T) = c_0 RT \quad (15)$$

where the temperature-independent constant c_0 is characteristic for a given adsorbent. On the basis of eqs. (9) and (13) we can obtain the following expression for NBP-na adsorption model on random surfaces:

$$c \ln K_{12} = \ln[(x_{1,t}^s/x_{2,t}^s)/(x_1^1/x_2^1)^c] + c \hat{q}^1(1-m)(2x_1^1-1) + c \hat{q}^s(1-2x_{1,t}^s) \quad (16)$$

where $\ln K_{12} \simeq \xi_0/RT$.

An expression analogous to eq. (16) but valid for homogeneous surfaces was derived previously by Everett [15]. Equation (16) enables us to evaluate the isosteric heat of adsorption Q^{st} by using the following formula [28]:

$$Q^{st}(x_1^1, T) = RT^2 \left(\frac{\partial \ln x_{12}^1}{\partial T} \right)_{x_{1,t}^s} = (RT^2/x_1^1 x_2^1) \left(\frac{\partial x_1^1}{\partial T} \right)_{x_{1,t}^s} \quad (17)$$

Bearing in mind eqs. (16) and (17), also applying rules of differentiation of the complex functions, we can get the expression for Q^{st} , which corresponds to the most general NBP-na model of adsorption system:

$$Q^{st}(x_1^1, T; m, l, c) = (RT/x_1^1 x_2^1) (-F_T/F_{x_1^1}) \quad (18)$$

where

$$F_T = \exp(-\xi_1) (x_{12,t}^s)^{-c} [\xi_1 - (1/c) \ln x_{12,t}^s] + x_{12}^1 X \exp(X) \quad (19)$$

$$F_{x_1^1} = [2x_{12}^1 (1-m) \hat{q}^1 - (1-x_1^1)^{-2}] \quad (20)$$

$$X = [\hat{q}^1 (1-n) (1-2x_1^1) - 1 \hat{q}^s (1-2x_{1,t}^s)] \quad (21)$$

$$\xi_1^* = \xi_0 / RT \quad (22)$$

The expressions for Q^{st} , corresponding to all other adsorption models, can be developed from eqs. (16) and (18)-(22). As an instance, for the simplest IBP model of adsorption system, eqs. (16), (18)-(21) become:

$$Q^{st} = \xi_0 - (1/c_0) \ln x_{12,t}^s$$

Equations (16) and (18)-(22) give the possibility to study numerically the combined effects of the surface heterogeneity, intermolecular interactions in both surface and bulk phases as well as mutual interactions between species belonging to these phases on the shape of the excess adsorption isotherms and the isosteric heats of adsorption. The theoretical adsorption isotherms can be calculated by means of the following equation:

$$n_{1,t}^e(x_1^1) = n_t^s(x_{1,t}^s - x_1^1) \quad (23)$$

where n_t^s is the surface phase capacity on the whole heterogeneous surface. All model calculations presented below were carried out for $n_t^s=1$.

Besides, eq. (16) gives a possibility of obtaining criteria for the formation of S-shaped excess isotherms, i.e., an interval of values of \bar{K}_{12} over which an adsorption azeotrope may be observed can be specified. Bearing in mind that at the azeotrope point $x_{1,t}^S = x_1^1$, and supposing NBP-na model with $\hat{q}^1 = \hat{q}^S = \hat{q}$, $m=0,25$, $l=0,5$, the following relationship from equation (16) may be developed:

$$\bar{K}_{12}^x = x_1^1 \quad 1-c \exp c\hat{q}m \quad 2x_1^1-1 \quad (24)$$

where $\bar{K}_{12} = (\bar{K}_{12}^x)^c$. Hence, for a given value of \hat{q} , an adsorption azeotrope is observed in the interval of \bar{K}_{12}^x given by:

$$\bar{K}_{12}^x \in <0, \infty) \quad (25)$$

Let us compare this result with that arising from homogeneous approach presented by Everett [15]. For $c:1$ eq. (24) becomes to:

$$K_{12} = \exp[mq (2x_1^1 - 1)] \quad (26)$$

from which Everett's condition results [15]:

$$K_{12} \in <\exp(-m\hat{q}), \exp(+m\hat{q})> \quad (27)$$

Hence, for the most tightly filled spatial lattice ($l \neq 0,5$, $m=0,25$) a surface azeotrope is observed over the following, limited range of values of K_{12} :

$$K_{12} \in <0.606, 1.648> \quad (28)$$

Nevertheless, as far as an adsorption on heterogeneous surfaces is considered, the relation (25) is in force.

Relations analogous to (24), but valid for IAP and IBP models of adsorption systems are following:

$$\bar{K}_{12}^x = (x_1^1)^{1-c} \exp[c\hat{q}^1 (2x_1^1-1)(m-1)], \text{ for IAP model} \quad (29)$$

and

$$\bar{K}_{12}^x = (x_1^1)^{(1-c)}, \text{ for IBP model} \quad (30)$$

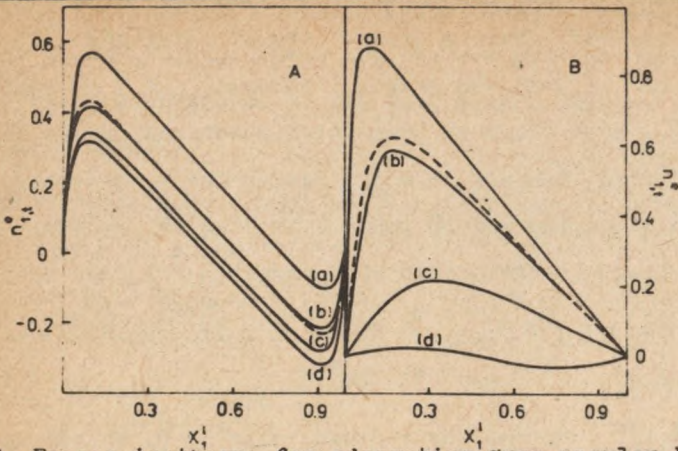


Fig. 1. Excess isotherms for adsorption from regular binary solutions calculated according to eqs. (16) and (25) by using: $c=0.2$ (A) and $c=1$ (B), $\hat{q}^1=\hat{q}^S=1$, $m=0.25$, $l=0.5$. Curves (a) - (d) denote the situation when $\ln \bar{K}_{12}$ runs the values: 5, 2, 0.6, 0, respectively. In both parts of the figure the dashed lines correspond to $\ln \bar{K}_{12}=2$ and $m=0$ (autonomous surface phase)

Concluding above results we can state that, in contrast to adsorption on homogeneous surface, the so-called S-shaped isotherms may be expected on heterogeneous surface even for a significant difference between adsorption energies of both components. Such deduction is confirmed by the model studies presented in Fig. 1, where the theoretical excess adsorption isotherms, corresponding to NBP-na model with $\hat{q}^1=\hat{q}^S=1$, evaluated by means of eqs. (16) and (24) for $c=0.2$ (A) and $c=1$ (B), are showed. In both parts curves (a) - (d) denote the situation when $\ln \bar{K}_{12}$ runs the values: 5, 2, 0.6 and 0. In diagram A ($c=0.2$, strongly heterogeneous surface) all isotherms are S-shaped, irrespective to value of \bar{K}_{12} , which varies from $\bar{K}_{12}=148.4$ (curve a) to $\bar{K}_{12}=1$ (curve d). On the contrary, in diagram B ($c=1$, homogeneous surface) all curves are U-shaped except curve (d) for which $\bar{K}_{12}=1$. Here, an adsorption azeotrope is observed as a consequence

of non-ideality of the both phases. What is more, the interaction between molecules in the adsorbed and bulk phases is taken here into account and the neglect of that is revealed for $\ln \bar{K}_{12}=2$. In both parts of Fig. 1 curves (b) denote the situation when $m=0.25$ (NBP-na model) but dashed lines correspond to $m=0$ (NBP-a model). It follows from Fig 1A that the influence of m is negligible during adsorption onto heterogeneous surfaces. On the other hand, this effect announces a bigger ascendancy when homogeneity of solid is admitted.

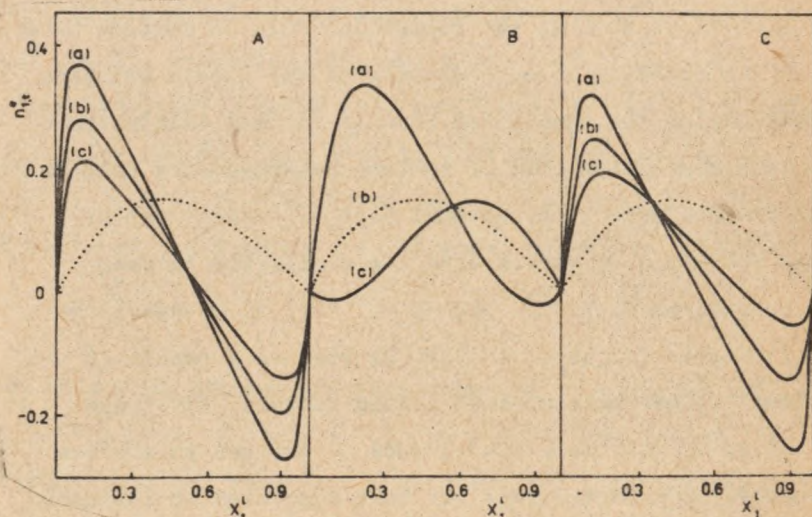


Fig. 2. Excess isotherms for adsorption from regular binary solutions calculated according to eqs. (16) and (23) by using: $\ln \bar{K}_{12}=0.6$, $m=0.25$, $l=0.5$. Other adsorption parameters are following: (A) $c=0.3$, and $\hat{q}^1=2$, $\hat{q}^S=1$ (a); $\hat{q}^1=\hat{q}^S=0$ (b); $\hat{q}^1=-2$, $\hat{q}^S=-1$ (c); (B) $c=1$ and $\hat{q}^1=2$, $\hat{q}^S=1$ (a); $\hat{q}^1=\hat{q}^S=0$ (b); $\hat{q}^1=-2$, $\hat{q}^S=-1$ (c); (C) $\hat{q}^1=\hat{q}^S=0$ and $c=0.2$ (a); $c=0.4$ (b), $c=0.6$ (c). In all parts of the figure the IAS model behaviour ($\hat{q}^1=\hat{q}^S=0$, $c=1$) is denoted by dotted lines

The next Fig. 2 shows in parts A and B an influence of the interaction parameters in the bulk and surface phases on the

course of the excess adsorption isotherms assuming heterogeneity (2A, $c=0.3$) and homogeneity (2B, $c=1$) of the adsorbent surface. Moreover, in the part C of Fig. 2, the effect of surface heterogeneity on the excess adsorption isotherm corresponding to IBP model is shown. All presented here calculations were carried out for $\ln \bar{K}_{12}=0.6$, i.e., for $\bar{K}_{12}=1.82$. For comparative purposes in all parts of Fig. 2, the dotted lines represent results corresponding to so-called IAS model (ideal adsorption system) for which $\bar{q}^1=\bar{q}^s=0$ and $c=1$. Figure 2 constitutes confirmations of the earlier suggestions towards the dominating role of surface heterogeneity in the relation to non-ideality of the liquid solution in the controlling the adsorption process in real solid/liquid systems. This dominating role of surface heterogeneity will be explained in more detail in the next part of present paper.

It is worthwhile to stress here the similarity between curves presented in parts A and C of Fig. 2. However, the S-shaped isotherms displayed in Fig. 2A vary as a result of interactions between molecules of liquid mixture, but these showed in Fig. 2C vary as a consequence of changes in surface heterogeneity. This fact points out that sometimes an influence of surface heterogeneity on the adsorption process at solid/liquid interface may be similar to that of the interactions in the liquid mixture.

We will return to this problem in the section dealing with the problem of surface activity coefficients. In the next Fig. 3 the isosteric heats of adsorption, Q^{st} vs $x_{1,t}^s$, calculated according to eqs. (18) - (21) are presented. Part A displays the influence of an alternation of the heterogeneity parameter c on the heats in question. The curves (a) - (d) correspond to the alternation in c from $c=0.4$ (curve a) to $c=1$ (curve d), but

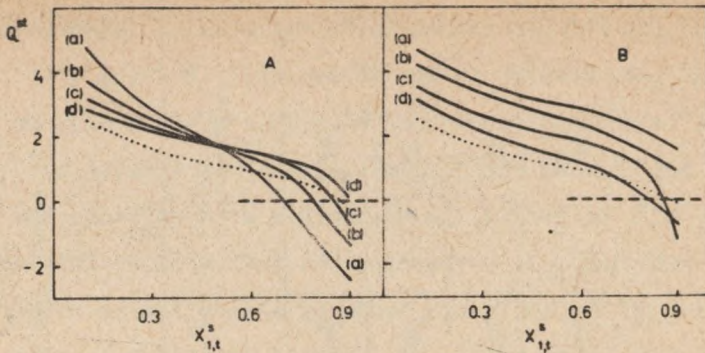


Fig. 3. Isosteric heats of adsorption for adsorption from regular binary solutions calculated according to eqs. (18) - (22) by using: $m=0.25$, $l=0.5$; (A) $\ln \bar{K}_{12}=2$, $\hat{q}^1=1$, $\hat{q}^s=0.5$ and curves (a) - (d) are for: $c=0.4$ (a), $c=0.6$ (b), $c=0.8$ (c), $c=1$ (d); (B) $c=0.7$ and curves (a) - (d) are for: $\hat{q}^1=1.5$, $\hat{q}^s=1$ and $\ln \bar{K}_{12}=4$ (a) and $\ln \bar{K}_{12}=2$ (c), $\hat{q}^1=0.5$, $\hat{q}^s=0.5$ and $\ln \bar{K}_{12}=4$ (b) and $\ln \bar{K}_{12}=2$ (d). In both parts of the figures the IAS model behaviour ($\hat{q}^1=\hat{q}^s=0$, $c=1$) for $\bar{K}_{12}=2$ is denoted by dotted lines

other adsorption parameters were supposed as follows: $\ln \bar{K}_{12}=2$ ($K_{12}=7.38$), $\hat{q}^1=1$, $\hat{q}^s=0.5$, $l=0.5$ and $m=0.25$. The dotted line represents the IAS behaviour ($\hat{q}^1=\hat{q}^s=0$, $c=1$). It appears from Fig. 3A that the isosteric heats of adsorption from solutions are decreasing functions of $x_{1,t}^s$, however these functions alter more rapidly in the case of high heterogeneity (curve a) than for homogeneous surface of solid (curve d). It can be seen, that curve d is approximately parallel to dotted line reflecting IAS behaviour. It can point out that, in contrast to influence of the surface heterogeneity, the shape of functions Q^{st} vs $x_{1,t}^s$ is slightly dependent on the values of interaction parameters \hat{q}^1 and \hat{q}^s . Such deduction is strongly confirmed by the shape and course of the theoretical functions Q^{st} vs $x_{1,t}^s$ presented in Fig. 3B. All functions showed here were evaluated for $c=0.7$.

Both curves (a) and (b) correspond to NBP-na model of adsorption system with $\ln \bar{K}_{12}=4$, however in the former case $\hat{q}^1=1.5$, $\hat{q}^s=1$ (curve a), but in the last case $\hat{q}^1=\hat{q}^s=0.5$ (curve b). Analogous calculations, but carried out for $\ln \bar{K}_{12}=2$ are represented by curves (c) and (d). As in Fig. 3A the dotted line reflects the IAS behaviour with $\ln \bar{K}_{12}=2$. Obviously, the influence of interactions parameters on the isosteric heats of adsorption is rather greater if the less value of K_{12} is assumed. Identical conclusion towards the influence of interactions parameters on the isosteric heats of adsorption from solutions were obtained on the experimental grounds by Kiselev and Pavlova [29].

SURFACE ACTIVITY COEFFICIENTS RELATING TO THE (LF) EQUATION

Let us now consider the problem of surface activity coefficients in the light of Langmuir-Freundlich equation. First, we shall attempt to take advantage of the full form of eq. (16) for description of adsorption of benzene from cyclohexane on fourth various adsorbents (see Table 1). The liquid mixture in question may be treated as a near-regular solution [30] and the bulk interaction parameter is equal to: $\hat{q}^1=0.5$ [31]. Let us suppose that the parameters \hat{q}^1 and \hat{q}^s appearing in eq. (16) are proportional to each other. Then

$$\hat{q}^s/\hat{q}^1 = n \quad (31)$$

Combining eqs. (16) and (31) we obtain the following expression ($l=0.5$, $m=0.25$):

$$x_{1,t}^s = \left\{ 1 + \bar{K}_{12}^x (x_{12}^1)^{-c} \exp \left[0.25cn\hat{q}^1 (1-2x_{1,t}^s) - c\hat{q}^1 0.75 (1-2x_1^1) \right] \right\}^{-1} \quad (32)$$

where, according to (24):

$$x_{1,t}^s = (n_{1,t}^e/n_t^s) + x_1^1 \quad (33)$$

Table 1. Adsorption parameters of Langmuir-Freundlich equation (32) for adsorption of benzene from cyclohexane on various adsorbents

Adsorbent	Temp. [K]	q^1 [31]	n_t^s [4]	n	c	$K_{12}^{**} (K_{12})^c$	$q^s = n \cdot q^1$	ref. to adsorption system
spheron	293	0.55	0.48	0.76	0.827	6.05	0.418	[32]
charcoal	293	0.55	3.02	1.27	0.794	5.66	0.698	[32]
boehmit	293	0.55	1.56	0.96	0.998	6.83	0.528	[33]
graphit	293	0.55	1.07	0.38	0.921	1.217	0.209	[32]

Equation (32) is the four-parameter one with the following unknowns: n_t^s , \bar{K}_{12} , n and c . To reduce their number, the parameter n_t^s corresponding to system in question has been taken from the paper by Dąbrowski and Jaronic [4] where systems from Table 1 were investigated by means of IAP model corresponding to (LF) equation (13). The results of our analysis are given in Table 1. It appears from this Table that, except adsorption on charcoal, the parameter n is less from unity, i.e., the interactions between admolecules are less from those in the bulk phase. Such result is in agreement with earlier studies presented by Ash et al. [30] and coincides with the suggestions of several authors [14]. However, for adsorption on charcoal the molecular interactions in the surface phase appear to be greater than those in the bulk phase ($n=1.27$), but the parameter c has the least of all value among values of c characterizing other adsorption systems placed in Table 1. Concluding above results we can state that heterogeneity of the solid may either decrease or sometimes increase a non-ideality of the adsorbed region.

Equation (32) has not the simple form and its application seems to be little encouraging. Besides, this equation does not give a possibility to study an influence of both surface heterogeneity and interactions in the adsorbed phase on the non-ideality of the adsorbed solution. This question is very important in liquid adsorption at all because, as it follows from foregoing model studies, either surface heterogeneity or non-ideality of the adsorbed solution may lead to S-Shaped excess adsorption isotherms. What is more, some adsorption systems may be quite formally interpreted both in terms of the non-ideality of the

liquid mixture as well as in terms of heterogeneity of the adsorbent surface (see Fig. 2). Because the bulk activity coefficients are independent on the adsorption experiment it would be desirable to give a way of separating of a non-ideal behaviour in the surface region arising from intermolecular interactions between adsorbed molecules from that due to the surface heterogeneity of solid.

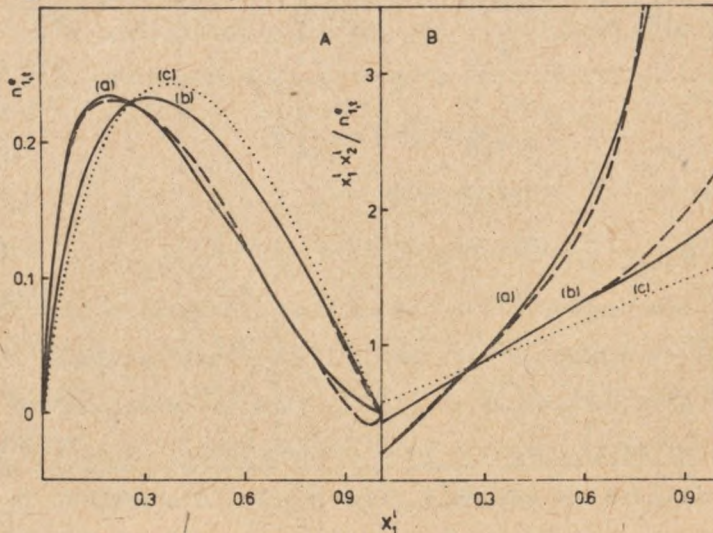


Fig. 4. Excess adsorption isotherms (A) and corresponding to them functions (34) evaluated for NAP-na model with $c=1$ (solid lines) and for IBP model with $c \neq 1$ (dashed lines). Other adsorption parameters are equal to: $\bar{K}_{12}=2.718$ $\hat{q}^1=0$, $\hat{q}^S=-2$, $c=1$ (solid line a); $\hat{q}^1=\hat{q}^S=0.5$, $c=1$ (solid line b); $\hat{q}^1=\hat{q}^S=0$, $c=0.9$ (dashed line b). In both parts of the figure the IAS model behaviour ($\hat{q}^1=\hat{q}^S=0$, $c=1$) is denoted by dotted lines (c).

At first, we shall discuss the results of the model studies presented in Fig. 4. In part A the solid lines present the excess adsorption isotherms calculated according to eqs. (16)

and (23) in terms of NAP-na model of adsorption system assuming the following sets of adsorption parameters: $n_{1,t}^S=1$, $\bar{K}_{12}=2.718$, $\hat{q}^1=0$ and $\hat{q}^S=-2$, $c=1$ (curve a) and $\hat{q}^S=-0.5$, $c=1$ (curve b); the corresponding dashed lines show the excess obtained for IBP model of adsorption system for which $c=0.7$, $\hat{q}^S=0$ (dashed line a) and $c=0.9$, $\hat{q}^S=0$ (dashed line b). The dotted line (c) presents the excess adsorption isotherm referring to IAS behaviour ($c=1$, $\hat{q}^1=\hat{q}^S=0$). In part B of Fig. 4 the following functions, corresponding to the isotherms from diagram 3A, are displayed [15]:

$$x_1^1 x_2^1 / n_{1,t}^e = f(x_1^1), \text{ lines (a) and (b)} \quad (34)$$

in comparison to the linear dependence

$$x_1^1 x_2^1 / n_{1,IAS}^e = f(x_1^1), \text{ dotted line (c)} \quad (35)$$

where $n_{1,IAS}^e$ denotes the excess adsorption isotherms calculated for IAS model of adsorption system. The important conclusion may be drawn from both parts of Fig. 4, namely: deviations of adsorption systems in question from IAS behaviour, generated by the non-ideality of the adsorbed phase may be interpreted, in a good approximation, by means of a surface heterogeneity of the solid.

To better explain the above problem, the following numerical operations were carried out:

1. excess adsorption isotherms were tabulated according to eq. (16) in terms of various, homogeneous models of adsorption systems, assuming: $\bar{K}_{12}=2.718$, $n_{1,t}^S=1$, $c=1$, $m=0.25$, $l=0.5$, and subsequently,

2. these isotherms were approximated by the following linear form of eq. (13), corresponding to the heterogeneous IBP model of adsorption system ($\hat{q}^1=\hat{q}^S=0$, $c \neq 1$):

$$\ln \left[(1-x_{1,t}^S) / x_{1,t}^S \right] = c \ln \left[(1-x_1^1) / x_1^1 \right] - c \ln \bar{K}_{12} \quad (36)$$

Table 2. Adsorption parameters of eq. (13) reflecting the behaviour of various models of adsorption systems

Model supposed for adsorption system with: $K_{12}=2.718, c=1,$ $l=0.5, m=0.25$	\hat{q}^l	\hat{q}^s	Adsorption parameters of eq. 13 evaluated for IBP model of adsorption system	
			c	\bar{K}_{12}
NAP-a	0	-0.5	0.917	2.718
NAP-a	0	-1.0	0.841	2.717
NAP-a	0	-1.5	0.776	2.708
NAP-a	0	-2.0	0.715	2.707
IAP	0.5	0	0.853	3.234
IAP	1.0	0	0.705	4.133
NBP-na	0.5	0.5	0.924	3.252
NBP-na	1.0	0.5	0.774	4.187
NBP-na	-1.0	2.0	1.781	2.135
NBP-na	0.5	-0.5	1.179	3.219

Hence, the parameters c and \bar{K}_{12} were obtained and ones are given in Table 2. Results presented in Table 2 confirm strongly the conclusions obtained on the basis of diagrams presented in Fig. 4. Namely, there is a formal possibility to interpret the deviations of any adsorption system from IAS behaviour in terms of:

1. non-ideality of one or both phases of adsorption system under condition that $c=1$ (homogeneous surface of solid), .
2. effects of the surface heterogeneity of the solid, under condition that $\hat{q}^l = \hat{q}^s = 0$ (IBP behaviour).

Obviously, during interpretation most of adsorption systems of practical interest both these factors should be taken into account. Moreover, it appears from Table 2 that supposition about unrealistic values of parameters \hat{q}^1 and \hat{q}^S leads to unphysical values of parameters c , which appear to be greater from unity. One must stress, that in the light of the results presented in Table 2 and those showed in Fig. 4, the equilibrium of the NAP-na model with $c=1$ and IBP model with $c \neq 1$ is without controversy. Similar conclusion has been obtained earlier in terms of two patch heterogeneous model of the surface by O u and M y e r s [34]. The above results will be desirable for discussion literature adsorption data interpreted previously by using a little realistic NAP-na model of adsorption system (see following).

Let us pass now to a more general considerations dealing with the possibility of separation a non-ideality of the surface region caused by intermolecular forces from that generated by surface heterogeneity of the solid. In order to do it we shall take advantage of results of the osmotic theory of adsorption of gas mixtures onto solid surfaces [35]. Followed by this theory the surface activity coefficient γ_i^S ($i=1,2$) characterizing a non-ideality of the adsorbed solution is generated by two main factors:

1. lateral interactions in the surface region, and
2. heterogeneity of the adsorbent surface.

For purposes of adsorption from solutions, the former factor should be extended over all interactions in the adsorption space, i.e., over lateral interactions between adsorbed molecules and interactions between molecules belonging to the adjacent bulk and surface phases, too.

Let us suppose now, as previously, the random distribution of adsorption sites onto solid. Then, the surface activity coefficient γ_i^s may be represented as follows [35]:

$$\gamma_i^s = \gamma_{i,h}^s \cdot \gamma_{i,int}^s \quad \text{for } i=1,2 \quad (37)$$

where $\gamma_{i,h}^s$ is the factor responsible for non-ideality of the whole adsorption region, which is generated by the heterogeneity of the adsorbent surface, but $\gamma_{i,int}^s$ denotes the factor responsible for non-ideality of adsorption space caused by the intermolecular interactions. The osmotic theory of adsorption gives the following expression for $\gamma_{i,h}^s$ [35]:

$$\gamma_{i,h}^s = (x_{i,t}^s)^{[(1/c)-1]} \quad \text{for } x_{i,t}^s \in (0,1) \text{ and } i=1,2 \quad (38)$$

Keeping in mind the above considerations, the variable x_{12} corresponding to homogeneous adsorbent surface has, for the NBP-na model, the following form (see eq. 6):

$$x_{12} = a_{12}^1 \cdot \gamma_{21,int}^s \quad (39)$$

However, an analogous variable, but referring to adsorption on heterogeneous surfaces may be expressed as follows:

$$x_{12,h} = a_{12}^1 \cdot \gamma_{21}^s \quad (40)$$

where, according to eqs. (37) and (38):

$$\gamma_{21}^s = \gamma_{21,h}^s \cdot \gamma_{21,int}^s \quad (41)$$

but

$$\gamma_{21,h}^s = [(1-x_{1,t}^s)/x_{1,t}^s]^{[(1/c)-1]} \quad \text{for } x_{1,t}^s \in (0,1) \quad (42)$$

Obviously, for $c=1$ (homogeneous surface) $x_{12,h} = x_{12}$.

Let us suppose, that adsorption process onto heterogeneous surfaces is described by the Everett-type equation [15]:

$$x_{1,t}^s = K_{12} a_{12}^1 \gamma_{21}^s / [1 + K_{12} a_{12}^1 \gamma_{21}^s] \quad (43)$$

This equation has the identical mathematical form as equation relating to adsorption on homogeneous surfaces. However, eq. (43) combined with eqs. (41) and (42) leads to the Langmuir-Freundlich isotherms (13), which has here the following form:

$$x_{1,t}^s = (\bar{K}_{12} a_{12}^1 \gamma_{21,int}^s)^c / [1 + (\bar{K}_{12} a_{12}^1 \gamma_{21,int}^s)]^c \quad (44)$$

Hence, it is evident that all deviations of any adsorption system from IAS behaviour predicted by simple form of Everett's equation:

$$x_1^s = K_{12} x_{12}^1 / (1 + K_{12} x_{12}^1) \quad (45)$$

are produced due to:

1. non-ideality of the bulk phase,
2. non-ideality of the adsorbed phase,

but this least factor may be generated by:

1. intermolecular interactions in the adsorbed region, and
2. surface heterogeneity of the adsorbent.

Using eq. (43) we lose a possibility to assess an influence of surface heterogeneity on the non-ideality of the adsorbed phase and surface activity coefficients corresponding to eq. (43) do not give reliable informations about interactions in the surface region, because they implicitly include the surface heterogeneity effects.

Obviously, a separation γ_i^s between $\gamma_{i,h}^s$ and $\gamma_{i,int}^s$ is difficult in general, however, such procedure is possible in some simple cases (see following).

At present, we can explain on the basis of foregoing considerations the similarities arising between NAP model with $c=1$ and IBP model with $c \neq 1$ (see Fig. 4). For simplicity, the NAP-a model of adsorption system will be handled by us for which, according to eq. (8) we can get ($m=0$):

$$\Delta_i^s = \Delta_{i,int}^s = \exp \left[0.5 \hat{q}^s (1 - x_{i,t}^s)^2 \right] \quad \left. \vphantom{\Delta_i^s} \right\} \text{for NAP-a model with } c=1 \quad (46)$$

$$\Delta_{21}^s = \Delta_{21,int}^s = \exp \left[0.5 \hat{q}^s (2x_{1,t}^s - 1) \right] \quad (47)$$

However, for IBP model the following relationship is true:

$$\Delta_i^s = \Delta_{i,h}^s = (x_{i,t}^s)^{\left[(1/c) - 1 \right]} \quad \left. \vphantom{\Delta_i^s} \right\} \text{for IBP model with } c \neq 1 \quad (48)$$

$$\Delta_{21}^s = \Delta_{21,h}^s = (x_{21,t}^s)^{\left[(1/c) - 1 \right]} \quad (49)$$

Table 3. Values of parameters $\Delta_{1,h}^s$, $\Delta_{1,int}^s$ and $\Delta_{21,h}^s$, $\Delta_{21,int}^s$ evaluated according to eqs. (46)-(49) for NAP-a model with $c=1$ and for IBP model with $c=0.9$

$x_{1,t}^s$	NAP-a model with $c=1$ and $\hat{q}^s = -0.5$		IBP model with $c=0.9$	
	$\Delta_{1,int}^s$	$\Delta_{21,int}^s$	$\Delta_{1,h}^s$	$\Delta_{21,h}^s$
0.1	0.817	1.221	0.774	1.276
0.2	0.852	1.162	0.836	1.166
0.3	0.884	1.105	0.875	1.098
0.4	0.913	1.051	0.903	1.046
0.5	0.939	1	0.926	1
0.6	0.961	0.951	0.945	0.956
0.7	0.978	0.904	0.961	0.910
0.8	0.990	0.860	0.976	0.857
0.9	0.997	0.818	0.988	0.783

It appears from eq. (43) that the above parameter Δ_{21}^s influence the shape of excess adsorption isotherms for NAP and IBP models of adsorption systems.

In the Table 3 the values Δ_{21}^s evaluated according to eqs. (47) for $\hat{q}^s = -0.5$ and (49) for $c=0.9$ and $x_{1,t}^s = 0.1, 0.2 \dots 0.9$ are listed. It can be seen that these values are practically

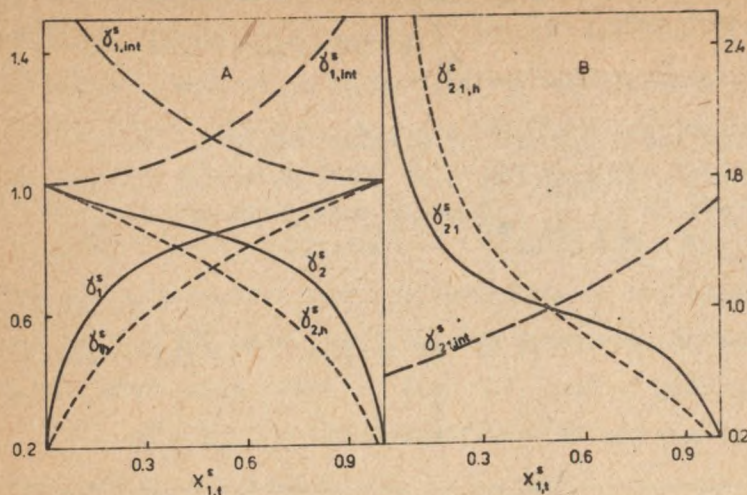


Fig. 5. Surface activity coefficients γ_i^S vs $x_{1,t}^S$ (A) and corresponding to them functions γ_{21}^S vs $x_{1,t}^S$ calculated according to eqs. (46)-(49) for $c=0.7$, $\hat{q}^S=1$

equal in the whole range of $x_{1,t}^S$, thus in the whole range of x_1^1 . In view of the small values of excess adsorption isotherms for $x_{1,t}^S$ (and x_1^1) approaching to unity, the differences between suitable functions (34) in the region of high values of x_1^1 are observed in Fig. 4. In the Table 3 the values of γ_1^S both for NAP-a model with $c=1$, $\hat{q}^S=-0.5$ and IBP model with $c=0.9$ are listed, too. It follows from Table 3 that the contribution to the coefficient $\gamma_1^S = \gamma_{1,h}^S \cdot \gamma_{1,int}^S$ from $\gamma_{1,h}^S$ is like, for $\hat{q}^S < 0$, to that arising from $\gamma_{1,int}^S$. One of possible consequences of this fact is presented in Fig. 5, where the model studies carried out on the basis of eqs. (37), (41) and (46) - (49) for $c=0.7$ and $\hat{q}^S=+1$ (positive deviations from ideality) are displayed. Part A in Fig. 5 presents the following functions: $\gamma_{i,h}^S$ vs $x_{1,t}^S$, $\gamma_{i,int}^S$ vs $x_{1,t}^S$ and $\gamma_i^S = \gamma_{i,h}^S \gamma_{i,int}^S$ vs $x_{1,t}^S$. Irrespective of the fact that $\hat{q}^S=1$, the surface activity coefficient γ_i^S is less

from unity in the whole concentration interval. It means, that due to surface heterogeneity, an adsorbed region is characterized by the surface activity coefficients γ_i^s suitable for liquid mixture showing negative deviations from ideality. In part B of Fig. 5, the functions γ_{21}^s vs $x_{1,t}^s$, $\gamma_{21,h}^s$ vs $x_{1,t}^s$ and $\gamma_{21,int}^s$ vs $x_{1,t}^s$ are shown. It follows from diagram B that over concentration interval $x_{1,t}^s \in (0, 0.5)$ the influence of $\gamma_{21,h}^s$ on the shape of excess adsorption isotherms is greater than that arising from the factor $\gamma_{21,int}^s$; however, for $x_{1,t}^s \in (0.5, 1)$ the situation is inversed. Such conclusion is strongly supported by the results given in Table 3.

Let us now consider the utilization of eqs. (37), (41) and (46) - (49) to characterize two literature experimental systems. In order to do it the parameters n_t^s , c and \hat{q}^s have to be obtained on the basis of (IF) equation. In the paper [5] Dąbrowski and Jaroniec have been applied eq. (13) in the form corresponding to NEM- α model of adsorption system, for which the bulk phase was admitted to be non-ideal (but not regular) and the surface phase was supposed to be regular one with the autonomous surface phase. Supposition about the autonomous surface phase. Supposition about the autonomous character of surface phase seems to be reasonable in the light of model studies presented in Fig. 1.

First, we shall discuss the results of our analysis carried out for the system: pyridine (1) + ethyl alcohol (2) on charcoal at 293K investigated experimentally by the Blackburn et al. [32]. Above system is characterized by the following set of adsorption parameters [5]: $n_t^s = 3.56 \text{ mmol/g}$, $c = 0.84$, $\hat{q}^s = 0.915$ and $\hat{q}^1 = 0$ [32]. The surface mole fraction appearing in eqs. (46) -

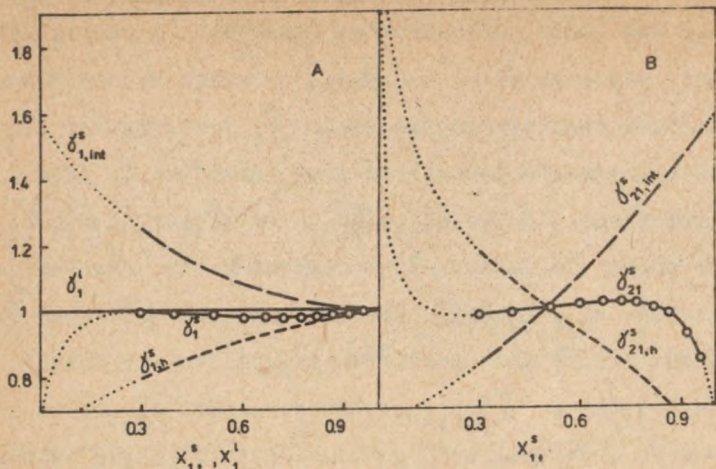


Fig. 6. Surface activity coefficients for the experimental system: pyridine (1) + ethyl alcohol (2) on charcoal at 293K [32]. Contributions to the surface activity coefficient γ_1^s (solid line with circles) (A) and to corresponding to it parameter γ_{21}^s (solid line with circles) (B) from the interactions in the adsorbed phase (strongly dashed curves) and surface heterogeneity effects (dashed curves). In the diagram (A) the bulk activity coefficients are represented by solid line without circles. In both parts of the figure the dotted lines calculated according to the equations representing γ_1^s , $\gamma_{1,h}^s$, $\gamma_{1,int}^s$ and γ_{21}^s , $\gamma_{21,h}^s$, $\gamma_{21,int}^s$ by using: $c=0.04$ and $\bar{q}^s=0.915$ [5]

-(49) has been obtained according to eq. (33). to avoid the overlapping of the functions γ_1^s vs $x_{1,t}^s$ and γ_2^s vs $x_{1,t}^s$, in Fig. 6A the former one is presented only. The solid line parallel to concentration axis, with ordinate equal to unity, presents the bulk activity coefficients: $\gamma_i^1 = 1$ ($i=1,2$), but the solid line with circles experimental points shows the function $\gamma_1^s = \gamma_1^s(x_{1,t}^s)$. It can be seen that the experimental results

do not cover the low $x_{1,t}^S$ region and the dotted lines in Fig. 6 present the courses of suitable functions evaluated by means of eqs. (46)-(49) for lower values of $x_{1,t}^S$. In spite of the fact that the solution is ideal in the bulk phase, the function $\gamma_{1,int}^S$ vs $x_{1,t}^S$ points out an existence of lateral interactions between admolecules caused probably by the mainly chemical unhomogeneity of the charcoal surface. However, due to course the function $\gamma_{1,h}^S$ vs $x_{1,t}^S$ (see also Fig. 5), the total activity coefficient: $\gamma_1^S = \gamma_{1,h}^S \cdot \gamma_{1,int}^S$ is approximately equals to unity over the whole concentration region, except the lower values of $x_{1,t}^S$.

In the part B of Fig. 6, the function γ_{21}^S vs $x_{1,t}^S$ is shown, too. In the next Fig. 7 the results of analogous analysis for the system: n-heptane (1)+cyclohexane (2) on tin-oxide gel at 300K are presented. This system was investigated experimentally by Madan et al. [36] and is characterized by the following set of adsorption parameters [5]: $n_t^S = 0.69 \text{ mmol/g}$, $c = 0.93$ and $\hat{q}^S = 0.83\theta$. In Fig. 7A the both functions γ_i^S ($i=1,2$) vs $x_{1,t}^S$ are showed. The solid line without circles presents the bulk activity coefficients suitable for system in question [37]. It follows from Fig. 7A that, in contrast to the results presented in Fig. 6A, the interactions in the bulk liquid are greater than those in the adsorbed phase. However, due to the surface heterogeneity, the function γ_1^S vs $x_{1,t}^S$ goes below the function $\gamma_{1,int}^S$ vs $x_{1,t}^S$ and is greater from unity. In Fig. 7B the function γ_{21}^S vs $x_{1,t}^S$ is presented and this one has different course from that showed in Fig. 6B. It follows from Figs. 6B and 7B that the dominating role of the surface heterogeneity on the shape of excess adsorption isotherms deals with the lower values of $x_{1,t}^S$ but in the

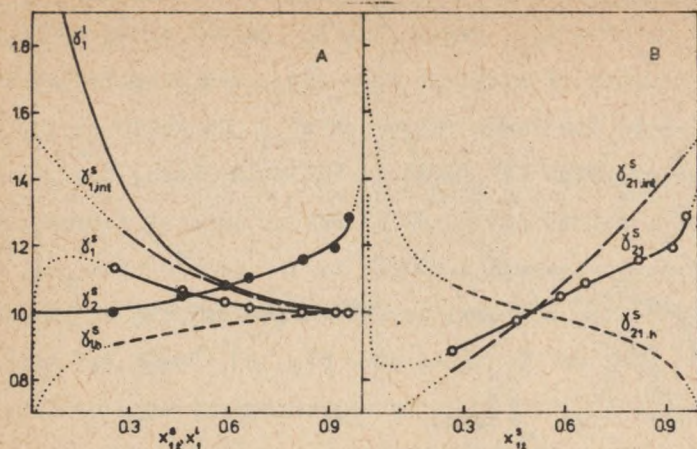


Fig. 7. Surface activity coefficients for the experimental system: n-heptane (1)+cyclohexane (2) on tin-oxide gel at 300K [36]. Contributions to the surface activity coefficients γ_1^s (solid line with white circles) and γ_2^s (solid line with black circles) (A) and to corresponding parameter γ_{21}^s (solid line with white circles) (B) from the interactions in the adsorbed phase strongly dashed curves and surface heterogeneity effects (dashed curves). In the diagram A the bulk activity coefficient γ_1^l is represented by the solid line without circles. In both parts of the figure the dotted lines calculated according to the equations representing γ_i^s , $\gamma_{i,h}^s$, $\gamma_{i,int}^s$ ($i=1,2$) and γ_{21}^s , $\gamma_{21,h}^s$, $\gamma_{21,int}^s$ by using: $c=0.93$, $\hat{q}^s = 0.838$ [5]

region of higher mole fractions, the dominating role of lateral interactions between admolecules is observed.

Finally, we can explain a reason for which the S-shaped isotherms are produced by (LF) equation on strongly heterogeneous surfaces, irrespective of values admitted for \bar{K}_{12} and other adsorption parameters (see Figs. 1 and 2). In Table 4 the values of function $\gamma_{21,h}^s$ vs c , obtained according to eq. (42).

Table 4. Values of $\Delta_{21,h}^s$ vs c evaluated according to eq. (49) for $x_{1,t}^s=0.1$ and for $x_{1,t}^s=0.95$

c	$\Delta_{21,h}^s = \Delta_{21,h}^s(c)$ for	
	$x_{1,t}^s = 0.1$	$x_{1,t}^s = 0.95$
0.9	1.29	0,72
0.8	1.73	0.48
0.7	2.56	0.28
0.6	4.33	0.14
0.5	8.99	0.05
0.4	26.99	0.01
0.3	168.40	$1.04 \cdot 10^{-3}$
0.2	6555.11	$7.80 \cdot 10^{-6}$
0.1	$3.87 \cdot 10^8$	$3.23 \cdot 10^{-12}$

for $x_{1,t}^s=0.1$ and $x_{1,t}^s=0.95$ are given. It appears from Table 4 that the difference between $\Delta_{21,h}^s$ at $x_{1,t}^s=0.1$ and $x_{1,t}^s=0.95$ is insignificant, but for $c=0.1$ this difference is immense. Hence, bearing in mind eqs. (33) and (43) we can state that the excess isotherm is greater from zero for low values of $x_{1,t}^s$ (thus x_1^1) and less from zero for higher values of $x_{1,t}^s$ (thus x_1^1). Due to this fact an adsorption azeotrope appears on strongly heterogeneous surface of solid.

APPLICATION OF THE LF EQUATION FOR DESCRIBING EXPERIMENTAL
DATA MEASURED AT VARIOUS TEMPERATURES

Recently Everett and Podoll [26] have analysed the excess adsorption isotherms measured for adsorption of benzene from mixture with 1,2-dichloroethane on Graphon at four temperatures: 273K, 298K, 313K and 323 K. All experimental isotherms are S-shaped and they show a temperature-dependent

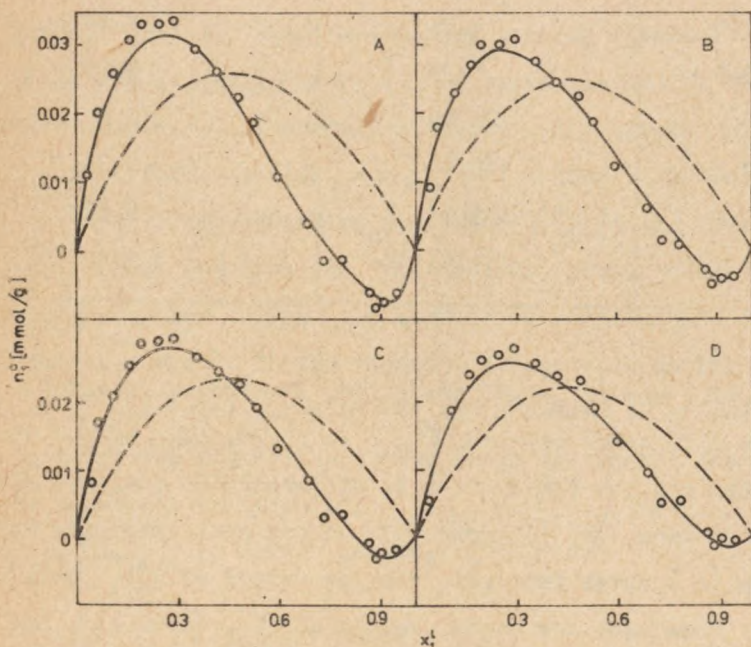


Fig. 8. Adsorption of benzene 1 from 1,2-dichloroethane 2 on Graphon at 273K A , 298K B , 313K C and 323K D 26 . Experimental excess adsorption isotherms circles in comparison to the theoretical curves solid lines calculated according to eq. 51 . In all parts of the figure the dashed lines present the theoretical isotherms calculated according to eq. 51 with $c=1$ by means of the parameters \bar{K}_{12} and n_t^E from Table 5

reversal of preferential adsorption from benzene component 1 to 1,2-dichloroethane (component 2) at high benzene mole fractions (see circles in Fig. 8). It is known, that the liquid mixture under considerations is near-ideal (shows inconsiderable

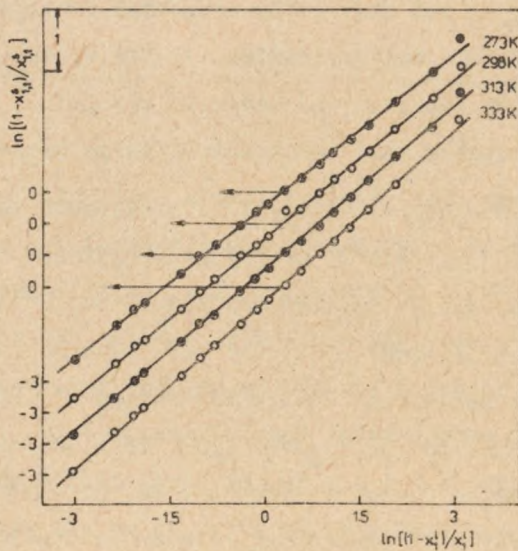


Fig. 9. Adsorption of benzene 1 from 1,2-dichloroethane 2 on Graphon at various temperatures 26, linear dependence calculated according to eq. 36. Circles denote experimental points

positive deviations from Raoult's law [38]). On the other hand, if follows from above presented considerations that no possibility exists to interpret S-shaped isotherms in terms of IBP model of adsorption system with $c=1$ (homogeneous surface). For this reason, to explain experimental results by means of homogeneous approach, Everett and Podolil [26] admitted the NAP-na model of adsorption system with large negative deviations from ideality in the regular adsorbed phase. Such same model has been utilized by Li and Ku [39] to explain experimental results dealing with the adsorption of some bulk near-ideal liquid mixtures on silica gel surface. Such approach was severely criticized by Sircar [12] who stated that admission of large deviations from ideality in the adsorbed phase is little realistic in view of the fact that the bulk solutions are nearly ideal and show certain positive deviations from Raoult's law. On the other hand, the formal equipose between NAP model with $c=1$ and IBP model with $c \neq 1$ has been proved and explained by us. For this reason we will try to explain experimental results measured by Everett and Podolil [26] by means of IBP model of adsorption system, assuming $c \neq 1$. In order to do it, eq. (36) has been utilized and results of our numerical analysis are given in Table 5. During our calculations the values of $x_{1,t}^S$ appearing in eq. (36) were evaluated on the basis of eq. (33) where the parameter n_t^S was estimated as follows:

$$n_t^S = a_s / \bar{a}_1^0 = 0.363 \text{ mmol/g} \quad (50)$$

Above, the specific surface area of the Graphon, a_s , was assessed by the authors of the experimental data and $a_s = 84 \text{ m}^2/\text{g}$ [26], but \bar{a}_1^0 denotes an arithmetic average of the cross-sectional

Table 5. Adsorption parameters of eq. (36) evaluated for adsorption of benzene (1) from 1,2-dichloroethane (2) on Graphon at various temperatures

T [K]	\bar{K}_{12}	c	$\ln \bar{K}_{12}$	1/T [K ⁻¹]
273	1.294	0.823	0.258	3.66 10 ⁻³
298	1.281	0.859	0.248	3.36 10 ⁻³
313	1.276	0.878	0.243	3.19 10 ⁻³
333	1.271	0.905	0.239	3.00 10 ⁻³

areas of the components of liquid solution and, following by Everett and Podoll, $\bar{a}_1^0 = 2.315 \cdot 10^2 \text{ m}^2/\text{mmol}$.

Figures 8 and 9 show the results of our analysis carried out by means of eqs. (33) and (36). Parts A, B, C and D of Fig. 8 present experimental excess adsorption isotherms (circles) measured at 273K, 298K, 313K and 323K, respectively with comparison to the theoretical curves solid lines calculated by assuming the best-fit parameters from Table 5, by means of the following formula [4]:

$$n_{1,t}^e = n_t^s \left[(\bar{K}_{12} x_{12}^1)^c (1 - x_1^1) - x_1^1 \right] / 1 + (\bar{K}_{12} x_{12}^1)^c \quad (51)$$

However, in Fig. 9 the linear dependences calculated according to eqs. (33) and (36) with comparison to experimental points (circles) are presented. It appears from Figs. 8 and 9 that the experimental data in question, measured at various temperatures, can be described relatively well by the (LF) equation corresponding to IBP model with $c \neq 1$. The dashed line in each part of Fig. 8 shows the corresponding homogeneous surface excess isotherms evaluated according to eq. (51) with $c=1$ and using the same

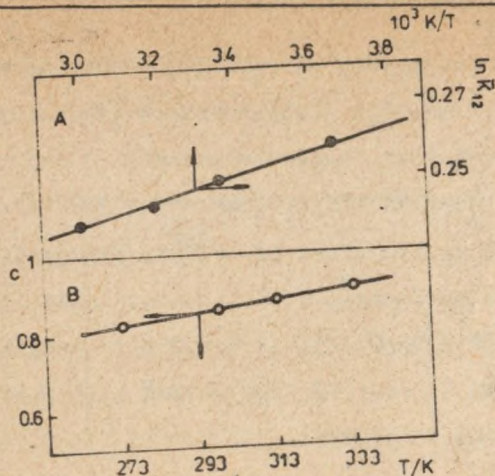


Fig. 10. $\ln \bar{K}_{12}$ vs $(1/T)$ (A) (solid line with black circles) and c vs T (B) (solid line with white circles) for adsorption of benzene (1) from 1,2-dichloroethane (2) on Graphon at various temperatures [26]. Values of suitable parameters are given in

Table 5

values of \bar{K}_{12} from Table 5. In Fig 8A considerable influence of inappreciable surface heterogeneity of Graphon (see Table 5) on the shape of excess isotherms is observed. This fact is connected with the small values of \bar{K}_{12} corresponding to systems in question. It follows from Table 5 that both heterogeneity parameter c as well as the constant \bar{K}_{12} are temperature-dependent. In part B of Fig. 10 the variation of c with T is shown; the relation is linear and from the slope of this line the parameter c_0 can be easily evaluated. On the basis of eq. (15) we can write:

$$c_0 = (1/R) (dc/dT) \quad (52)$$

and it has been found that $c_0 = 1.75 \cdot 10^{-4}$ mol/J.

In contrast to the parameter c , the parameter c_0 is temperature-independent and this one characterizes the surface heterogeneity of the Graphon.

In part A of Fig. 10 the graph $\ln \bar{k}_{12}$ vs $(1/T)$ is plotted and this appears to be a linear, too. Taking eq. (4) into account we can write:

$$\ln \bar{k}_{12} = \ln k^{\circ}(T) + \xi_0/RT \quad (53)$$

Hence, the slope of the straight line in Fig 10A directly determines the parameter $\ln k^{\circ}(T)$ and $\ln k^{\circ}(T) = 0.144$, i.e., $K^{\circ}(T) = 1.154$. In view of this fact that $K^{\circ}(T)$ is slightly different from unity, the intersection point of the straight line with ordinate is approximately equal to:

$$\left[\frac{\partial \ln \bar{k}_{12}}{\partial (T)^{-1}} \right] \approx \xi_0/R \quad (54)$$

where it has been found that $\xi_0 \approx 0.214$ KJ/mol = 0.057 kcal/mol. Introducing the above evaluated parameter ξ_0 to eq. (10), the distribution function characterizing the adsorption systems in question may be easily evaluated. In view of the temperature dependence of the parameter c , these functions will have a slightly different shape, but their maximum corresponds to the fixed value of $\xi_0 \approx 0.241$ KJ/mol.

Table 6. Adsorption parameters of eq. (36) for experimental systems investigated at 293K on silica gel by Li and Ku [39]

Liquid mixture	c	\bar{k}_{12}	n_t^s a) (mmol/g)
Toluene (1) + Chlorobenzene (2)	0.856	1.39	2.06
Toluene (1) + Bromobenzene (2)	0.898	1.52	2.06
Benzene (1) + Toluene (2)	0.917	1.53	2.16
Benzene (1) + Chlorobenzene (2)	0.973	2.15	2.16
Chlorobenzene 1 + Bromobenzene (2)	0.982	1.14	2.06

a) Obtained by using eq. 50 by means of parameters a_s and \bar{a}_i° from the paper [39].

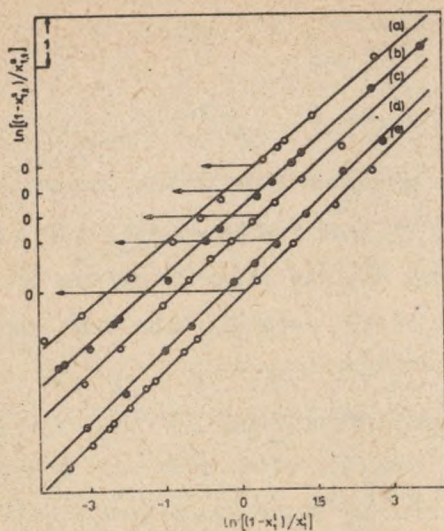


Fig. 11. Linear dependences calculated according to eq. (36) for adsorption systems from Table 6 [39:] (a) toluene (1) + chlorobenzene (2), (b) toluene (1) + bromobenzene (2), (c) benzene (1) + toluene (2), (d) benzene (1) + chlorobenzene (2), (e) chlorobenzene + bromobenzene (2). Circles denote experimental points.

Concluding foregoing considerations we can state that little realistic NAP model with $\bar{q}^S < 0$, used in previous analysis of adsorption of benzene from solutions in 1,2-dichloroethane on Graphon at various temperatures can be explained in terms of more realistic IBP model of adsorption on a heterogeneous surface. This remark is in force also towards experimental systems investigated by Li and Ku [39]. The results of numerical analysis dealing with their data are given in Table 6, but in Fig. 11 the linear dependences plotted according to eq. (36) by means of parameters from this table are presented, too.

REFERENCES

1. Rudziński, W., J. Ościk and A. Dąbrowski: Chem. Phys. Lett. 20, 5 (1973).
2. Ościk, J., A. Dąbrowski, M. Jaroniec and W. Rudziński: J. Colloid Interface Sci., 56, 403 (1976).
3. Dąbrowski, A., J. Ościk, - W. Rudziński and M. Jaroniec: J. Colloid Interface Sci. 69, 287 (1979).
4. Dąbrowski, A., M. Jaroniec: J. Colloid Interface Sci. 73 475 (1980).
5. Dąbrowski A., M. Jaroniec: J. Colloid Interface Sci. 77, 571 (1980).
6. Dąbrowski A., M. Jaroniec: Acta Chim. Hung. 99, 255 (1979).
7. Dąbrowski, A., M. Jaroniec: Acta Chim. Hung. 104, 183 (1980).
8. Dąbrowski, A., *Chemica Scripta*, in press.
9. Dąbrowski, A., and Jaroniec, M., *Materials Chemistry and Physics*, in press.
10. Dąbrowski, A., *Monatsh. Chem.*, in press.
11. Dąbrowski, A., *Monatsh. Chem.* 114, 875 (1983).
12. Sircar, S.: J. Chem. Soc., Faraday Trans. 1, 79, 2085 (1983).
13. Jaroniec, M., A. W. Marczewski: *Monatsh. Chem.* 115, 541 (1984).
14. Dąbrowski, A., M. Jaroniec and J. Ościk: *Colloid and Surface Science*, E. Matijevic, ed., New-York, Wiley-Interscience 14 (1985).
15. Everett, D. H.: *Trans. Faraday Soc.* 61, 2478 (1965).
16. Zettlemyer, A.C., F. J. Micale: *Croat. Chem. Acta* 42, 247 (1970).
17. Hansen, R. S., U. H. Mai: *J. Phys. Chem.* 61, 573 (1957).
18. Coltharp, M. T., N. Hackerman: *J. Colloid Interface Sci.* 43 176 (1973), 43, 185 (1973).

19. Jaroniec M.: *CJ. Catal. Hokkaido Univ.* 26, 155 (1978).
20. Cerofolinie, G. F.: *Surf. Sci.* 24, 391 (1971).
21. Dąbrowski A., M. Jaroniec: *Z. phys. Chemie, Leipzig* 261 359 (1980).
22. Ościk, J., J. Goworek and A. Dąbrowski: *Z. phys. Chemie, Leipzig* 262, 11 (1981).
23. Goworek, J., J. Ościk and A. Dąbrowski: *Pol. J. Chem.* 55 197 (1981).
24. Rudziński, W., J. Narkiewicz-Michałek, R. Scholner, W. Herden and W. D. Einicke: *Acta Chim. Hung.* 113, 207 (1983).
25. Ościk, J., A. Dąbrowski, M. Jaroniec and S. Sokołowski: *J. Catal. Hokkaido Univ.* 23, 91 (1976).
26. Everett, D. H., T. Podoll: *J. Colloid Interface Sci.* 82 14 (1981).
27. Misra, D. N.: *Indian J. Pure and Appl. Phys.* 9, 358 (1971).
28. Ościk, J., Adsorption, PWN-Horwood, Warszawa and Chichester 1982.
29. Kiselev, A. V., L. Pavlova: *Neftkhimiya* 2, 861 (1962).
30. Ash, S.G., R. Bown and D. H. Everett; *J. Chem. Soc. Faraday Trans 1*, 1, 123 (1975).
31. Nagy, L. G. and G. Schay: *Acta Chim. Hung.* : 39, 365 (1963).
32. Blackburn, A., J. J. Kipling and D. A. Tester: *J. Chem. Soc.* 2373 (1957).
33. Kipling, J. J. and D. B. Peakall: *J. Chem. Soc.* 1956 4828.
34. Ou, J.D., A.L. Myers: *AICHE Pap.*, 1982 .
35. Dubinin, M., T. S. Yakubov, M. Jaroniec and V. V. Serpinsky: *Pol. J. Chem.* 54, 1721 (1980).
36. Madan, R.L., N.K. Sandle and J. S. Tygai: *Curr. Sci.* 44 879 (1975).

37. Smith, V. C., R.L. Robinson: J. Chem. Eng. Data 15, 391 (1970).
38. Sieg, L., J. L. Crutzen and W. Jost: Z.phys. Chem. A198 263 (1951).
39. L., P., T. Ku: Sci. Sinica 12, 1384 (1979).

STRESZCZENIE

Stosując model monowarstwowej fazy powierzchniowej opisano proces adsorpcji z dwuskładnikowych roztworów nieelektrolitów na energetycznie niejednorodnych powierzchniach adsorbentów stałych. W opisie uwzględniono nieidealność fazy powierzchniowej i objętościowej oraz oddziaływania pomiędzy cząsteczkami należącymi do tych faz.

Резюме

Используя модель монослоя для адсорбционной фазы, описано процесс адсорбции из бинарных растворов неэлектролитов на энергетически гетерогенных твердых адсорбентах. Это описание учитывает неидеальность адсорбированной и блочной фазы и взаимодействие между молекулами этих фаз.

