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Theoretical Studies on the Adsorption from Non-Ideal Binary Liquid Mixtures on Heterogeneous Surfaces Involving Difference in Molecular Sizes of Components

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An equation for the phenomenon of competetive adsorption from binary liquid mixtures onto solids has been derived using the kinetic approach. In this equation the difference of the molecular sizes, the non-ideality of both bulk surface phases, and the energetic heterogeneity of the solid surface have been taken into account.

(Keywords: Adsorption from non-ideal solutions; Adsorption on heterogeneous surfaces)

Theoretische Untersuchungen zur Adsorption aus nichtidealen binären Lösungsmittelgemischen an heterogene Oberflächen fester Körper unter Berücksichtigung der Unterschiede in den molekularen Größen der Komponenten

Auf Grund kinetischer Erwägungen wurde eine Gleichung, die die Konkurrenzadsorption aus binären Lösungsmittelgemischen an den Oberflächen fester Körper beschreibt, aufgestellt. In der Gleichung wurde der Größenunterschied der Teilchen, die Nichtidealität der Lösung in der Volumen- und Oberflächenphase, sowie die energetische Heterogenität der Oberfläche des festen Körpers berücksichtigt.

Introduction

Competetive adsorption from liquid mixtures onto solids is of fundamentally practical interest. The phenomenon is ultimate for petroleum oil recovery, effluent purification and, in general, for the theory of colloidal stability. Despite of these facts only little theoretical progress has been made in this subject in the recent years owing to the complexity of the problem. Expecially theoretical studies of liquid adsorption onto solids, involving heterogeneity of the adsorbent surface, non-ideality of the bulk and adsorbed phases, and the difference of

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the molecular sizes of adsorbate molecules, reveal great difficulties[1]. The majority of papers on adsorption from solutions of non-electrolytes onto solids presume identical molecular sizes for the components[2]. Moreover, either adsorption from non-ideal solutions on homogeneous surfaces[2,3] or adsorption from ideal solutions on heterogeneous surfaces[4,5] is usually considered.

Recently *Dąbrowski* et al.[6–10] and *Rudziński* et al.[11] have published a series of papers, in which they have given exhaustive theoretical and numerical studies of the combined effects of surface heterogeneity, intermolecular interactions in both surface and bulk phases, and mutual interactions between molecules in the adsorbed and bulk phases.

The simplest equation of the isotherm for monolayer adsorption from liquid mixtures containing molecules of different sizes was firstly formulated in terms of classical thermodynamics by *Schuchowitzky*[12] and later this equation was used by *Everett*[13]. Another equation for monolayer adsorption from mixtures consisting of non-equal-size species was derived on the basis of a mass balance by *Elton*[14], *Schay* and *Nagy*[15] and *Everett*[13]. However, the concept of the monolayer adsorbed phase is not likely to be valid when the ratio of the areas occupied by two molecules is very different from unity. This concept may be also used for non-spherical molecules when this ratio becomes large; then an additional assumption must be made about the orientation of the molecules with respect to the adsorbent surface. To avoid these difficulties *Hansen* and *Fackler*[16] have developed an equation of the isotherm in terms of potential theory of adsorption, which breaks away completely from the concept of monolayer surface phase. *Everett*[13,17] made the first quantitative attempt to describe the adsorption from solutions containing molecules of different molecular sizes. He applied the *Flory-Huggins* statistics for athermal and non-athermal mixtures in contact with a plane homogeneous surface. In these theories either the all adsorbed molecules are assumed to lie parallel to the surface in the monolayer or all are oriented perpendicular to the surface.

Quite recently, *Chan* et al.[18] studied numerically a competitive adsorption process using the hard sphere model for liquid mixture of molecules of different sizes and taking into account the adsorbate—adsorbate and adsorbate—adsorbent interactions. Their theory is less usefull to characterize real liquid/solid adsorption systems and concerns homogeneous adsorbent only.

It seems that until now a quantitative theoretical description involving the combined effects of surface heterogeneity, intermolecular interactions in both surface and bulk phases and molecular sizes of the adsorbate molecules in liquid adsorption on solids is still unknown.

In this paper a general equation for the adsorption isotherm is derived using the kinetic approach. In this equation the difference of molecular sizes of molecules, non-ideality of both bulk and surface phases, and energetic heterogeneity of real solid surface are taken into account. On the basis of this equation and assuming the simple statistical model for non-athermal solutions model studies are carried out. In these studies the influence of the above factors on the shape of excess adsorptions isotherms and deviations of adsorption systems from ideal behaviour is discussed. Although our general formulation is rested on the controversial assumption of the monolayer surface phase with paralell orientation of all adsorbing species to the solid plane, it should provide more reliable informations about the nature of the adsorption process at solid/liquid interface.

Theory

Let the adsorption system consist of a binary liquid mixture $1 + 2$ (adsorbate) and insoluble solid (adsorbent). We assume for simplicity that the solid is unperturbed by the presence of liquid molecules on its surface. The following assumptions are made for the derivation of the equation for the adsorption isotherm:

(a) adsorption is supposed to be monolayer one,

(b) the cross-sectional areas of the molecules are not equal,

(c) the both bulk and surface phases are non-ideal and interact with each other,

(d) the adsorbent surface is energetically heterogeneous and consists of M adsorption sites distributed onto N surface patches; moreover, $M = \sum_{k=1}^{N} M_k$ where M_k denotes the number of adsorption sites of the k-th type,

(e) the square-well potential for adsorbate-adsorbent interactions is applied.

The above assumptions (a) and (b) should be discussed in some detail. It is known that for mixtures of molecules of strongly different sizes the definition of thickness of the adsorbed phase is difficult[2]. In view of this fact, the so-called parallel-layer model, in which all adsorbed molecules lie in the layer adjacent to the surface, is usually assumed[13,17]. According to the assumption (b) the volume fractions of components in both phases will be handled by us instead of the mole fractions frequently used in the theory of adsorption from solutions.

In the case of liquid adsorption the monolayer is always complete. For each surface patch the process of competitive adsorption may be represented by the following exchange reaction[2]:

$$\frac{w^{\theta}}{w_1^s}(1)^l + \frac{w^{\theta}}{w_2^s}(2)^s \rightleftharpoons \frac{w^{\theta}}{w_1^s}(1)^s + \frac{w^{\theta}}{w_2^s}(2)^l \qquad (1)$$

where (1) and (2) denote molecules of the 1st and 2nd component in the bulk (l) and surface (s) phases, respectively; $w_i^s (i = 1, 2)$ is the cross-sectional area of a molecule of the i-th component, w^{θ} is the standard area per molecule (w^0 may be chosen as the unit of area per molecule). Equation (1) may be expressed in the alternative form:

$$r\,(1)^l + (2)^s \rightleftarrows r\,(1)^s + (2)^l \tag{2}$$

where $r = w_2^s/w_1^s$.

Let the symbols $x_{1,k}^s$ and $\varphi_{1,k}^s$ denote the mole and volume fractions of component 1, respectively, onto the k-th surface patch; then:

$$\varphi_{1,k}^s = \frac{x_{1,k}^s}{x_{1,k}^s + r\,(1 - x_{1,k}^s)} \tag{3}$$

and

$$\varphi_{2,k}^s = 1 - \varphi_{1,k}^s \tag{4}$$

Analogously, for the bulk phase we have:

$$\Phi_1^l = \frac{x_1^l}{x_1^l + r\,(1 - x_1^l)} \tag{5}$$

and

$$\Phi_2^l = 1 - \Phi_1^l \tag{6}$$

where x_1^l and Φ_1^l denote the mole and volume fractions of the component 1 in this phase.

The volume fraction of the component 1 in the whole monolayer, Φ_1^s, is defined by:

$$\Phi_1^s = \sum_{k=1}^{N} f_k \cdot \varphi_{1,k}^s \tag{7}$$

where $f_k = M_k/M$ denotes the relative number of adsorption sites of the k-th type.

The rate of phase-exchange reaction (2) onto the k-th surface patch may be expressed as follows[5]:

$$\frac{\mathrm{d}\,\varphi_{1,k}^s}{\mathrm{d}t} = K_k^a(\Phi_1^l\gamma_1^l)^r\,(\varphi_{2,k}^s\gamma_{2,k}^s) - K_k^d(\Phi_2^l\gamma_2^l)\,(\varphi_{1,k}^s\gamma_{1,k}^s)^r \tag{8}$$

In the above K_k^a and K_k^d denote the rate constants for the adsorption and desorption on the k-th surface patch, respectively; $\Phi_i^l (i = 1, 2)$ is the equilibrium volume fraction of the i-th component; $\gamma_i^l (i = 1, 2)$ is the activity coefficient corresponding to the volume fraction Φ_i^l, and $\gamma_{i,k}^s (i = 1, 2)$ is the suitable defined surface activity coefficient.

For the rate constants K_k^a and K_k^d we can write[5,16]:

$$K_k^a = k^a \exp[-(r\,\mathrm{E}_{1,k}^{\mathrm{a}} - E_{2,k}^a)/RT] = k^a \exp[-{}_r\mathrm{E}_{12,k}^{\mathrm{a}}/RT] \tag{9}$$

and

$$K_k^d = k^d \exp[-({}_r\mathrm{E}_{1,k}^{\mathrm{d}} - E_{2,k}^d)/RT] = k^d \exp[-{}_r\mathrm{E}_{12,k}^{\mathrm{d}}/RT] \quad (10)$$

where $E_{i,k}^a (i = 1, 2)$ is the activation energy of adsorption for component i on the k-th surface patch; $E_{i,k}^d (i = 1, 2)$ is the activation energy of desorption.

Thus, the equilibrium state is governed by the equlibrium constant, which may be expressed as follows:

$$K = (\bar{K}^a/\bar{K}^d) = \frac{(\Phi_2^l \gamma_2^l)\left[\sum_{k=1}^{N} f_k \left(\frac{K_k^d}{\bar{K}^d}\right)(\varphi_{1,k}^s \gamma_{1,k}^s)^r\right]}{(\Phi_1^l \gamma_1^l)^r \left[\sum_{k=1}^{N} f_k \left(\frac{K_k^a}{\bar{K}^a}\right)(\varphi_{2,k}^s \gamma_{2,k}^s)\right]} \quad (12)$$

where

$$\bar{K}^a = k^a \exp(-{}_r\bar{E}_{12}^a/RT) \quad (13)$$

$$\bar{K}^d = k^d \exp(-{}_r\bar{E}_{12}^d/RT) \quad (14)$$

In the above ${}_r\bar{E}_{12}^a$ and ${}_r\bar{E}_{12}^d$ are some complex type of average values of ${}_rE_{12}^a$ and ${}_rE_{12}^d$.

In the case of a continuous distribution of the different kinds of adsorption sites Eq. (12) becomes:

$$K = \frac{(\Phi_2^l \gamma_2^l)\left[\int_{\Delta^d} \left(\frac{K^d}{\bar{K}^d}\right)(\varphi_1^s \gamma_1^s)^r \chi^d({}_rE_{12}^d)\, \mathrm{d}\, {}_rE_{12}^d\right]}{(\Phi_1^l \gamma_1^l)^r \left[\int_{\Delta^a} \left(\frac{K^a}{\bar{K}^a}\right)(\varphi_2^s \gamma_2^s)\, \chi^a({}_rE_{12}^a)\, \mathrm{d}\, {}_rE_{12}^a\right]} \quad (15)$$

where $\chi^d({}_rE_{12}^a)$ and $\chi^d({}_rE_{12}^d)$ are the differential distribution functions of adsorption sites with regard to the values ${}_rE_{12}^a$ and and ${}_rE_{12}^d$, respectively; Δ^a and Δ^d denote the intervals of possible changes in ${}_rE_{12}^a$ and ${}_rE_{12}^d$.

It is known that the activity coefficients $\gamma_{i,k}^s (i = 1, 2)$ are some functions of the surface phase composition[2]. For heterogeneous adsorbents with a patchwise distribution of adsorbtion sites those coefficients depend on the volume fraction $\varphi_{i,k}^s (i = 1, 2)$ which refers to the k-th patch. When we handle heterogeneous surfaces with a random distribution of adsorbtion sites the activity coefficients $\gamma_{i,k}^s$ appear as a function of the composition of the solution contained in the whole monolayer. When this phase is an ideal one the topography of adsorption sites onto the surface is not important.

Let us suppose now an adsorbent surface with a random distribution of adsorption sites. Applying to Eq. (12) an approximation developed first by *Kemp* and *Wojciechowski*[5,19] we can get the following expression:

$$K = \bar{K}^a/\bar{K}^d = \frac{(\Phi_2^l \gamma_2^l)(\gamma_1^s)^r (\Phi_1^s)^{r/c}}{(\Phi_1^l \gamma_1^l)^r \gamma_2^s (\Phi_2^s)^{1/c}} \tag{16}$$

where c is the heterogeneity parameter characterizing the shape of the quasi-*Gauss*ian distribution and $c \in \langle 0, 1 \rangle$[6]. Equation (16) may be considered as a general equation for liquid adsorption on real solid surfaces.

Let us consider the three special cases of Eq. (16).

1. The parameter c is equal to unity, i.e., the solid surface is homogeneous, so that Eq. (16) leads to:

$$K = \left(\frac{\Phi_1^s \gamma_1^s}{\Phi_1^l \gamma_1^l}\right)^r \left(\frac{\Phi_2^l \gamma_2^l}{\Phi_2^s \gamma_2^s}\right) \tag{17}$$

According to Eqs. (12-14), the equilibrium constant K is now given by:

$$K = k_{12} \exp\left[-(rE_1 - E_2)/RT\right] \tag{18}$$

where $k_{12} = k^a/k^d$ and $E_i = E_i^a - E_i^d\,(i = 1,2)$ is an adsorption energy of the component i.

Eq. (17) has been first introduced by *Schuchowitzky*[12] and later by *Everett*[13,17], who examined the experimental adsorption data for non-athermal and athermal solutions. An analogous expression to Eq. (17) was derived in terms of a potential theory of adsorption by *Hansen* and *Fackler*[16].

On the condition that $\gamma_i^s = 1$ $(i = 1,2)$, i.e. the surface phase is an ideal one, Eq. (17) assumes the following linear form:

$$\ln \frac{\Phi_2^l \gamma_2^l}{(1 - \Phi_1^s)} = \ln K + r \ln \frac{\Phi_1^l \gamma_1^l}{\Phi_1^s} \tag{19}$$

It should be remembered that the bulk activity coefficients γ_i^l $(i = 1,2)$ may be evaluated by a separate method because they characterize the bulk solution only.

2. Assuming in Eq. (16) the identity of the molecular sizes of two components we have $[r = 1,\ \Phi_i^l \equiv x_i^l,\ \Phi_i^s \equiv X_i^s$, for $(i = 1,2)]$:

$$K = \left(\frac{X_1^s}{X_2^s}\right)^{\frac{1}{c}} \cdot \frac{x_2^l}{x_1^l} \cdot \beta \tag{20}$$

and

$$\beta = (f_1^s/f_2^s)/(f_1^l/f_2^l) \tag{21}$$

where the symbols f_i^l, f_i^s $(i = 1,2)$ denote the bulk and surface activity coefficients, which are corresponding to the equlibrium mole fractions x_i^l and $X_i^s (i = 1, 2)$, respectively.

According to Eqs. (12–14) the equlibrium constant K is here defined as follows $(r = 1)$:

$$K = \bar{k}_{12} \exp [-\overline{(E_1 - E_2)}/RT] = \bar{k}_{12} \exp [-\bar{E}_{12}/RT] \tag{22}$$

Eqs. (20) and (22) have been obtained by *Dąbrowski* et al.[6,7] for the liquid adsorption on heterogeneous surfaces with random topography of adsorption sites using the method of *Stieltjes* transformation.

Assuming the model of regular solution for the surface phase and non-ideality of the bulk phase, Eq. (20) may be rearranged to give:

$$\ln \frac{x_1^l f_1^l}{x_2^l f_2^l} = \ln K^* + \alpha X_1^s + \frac{1}{c} \ln \frac{X_1^s}{1 - X_1^s} \tag{23}$$

where

$$K^* = (K)^{-1} \exp (q^s/RT) \text{ and } \alpha = -2q/RT$$

Parameter q^s denotes the interaction energy between adsorbed molecules. This parameter is assumed to be constant for the whole heterogeneous surface with random distribution of adsorbtion sites. Eq. (23) has been used by *Dąbrowski* and *Jaroniec*[8] for studying the adsorption from non-ideal liquid mixtures. When the surface phase is an ideal one, i.e., $q^s = 0$, then Eq. (23) reduces to:

$$\ln \frac{x_1^l f_1^l}{x_2^l f_2^l} = \frac{1}{K} + \frac{1}{c} \ln \frac{X_1^s}{1 - X_1^s} \tag{24}$$

This expression has been extensively examined in several papers dealing with the liquid adsorption on heterogeneous surfaces[7,20,21].

3. Let us assume that $r \neq 1$, $c \neq 1$ and the surface phase is an ideal one: then Eq. (16) may be rearranged to give:

$$\ln \frac{\Phi_2^s}{(\Phi_1^s)^r} = c \ln K + c \ln \frac{\Phi_2^l \gamma_2^l}{(\Phi_1^l \gamma_1^l)^r} \tag{25}$$

It seems that this equation should be useful for studying the liquid adsorption expecially from dilute solutions.

Numerical Studies of Adsorption from Non-Athermal Solutions

Let us consider the monolayer adsorption model from non-athermal liquid mixtures onto heterogeneous surfaces with random distribution of adsorption sites. In the above model all adsorbed molecules are assumed to lie parallel to the solid surface. According to *Everett*'s considerations[13] the activity coefficients for non-athermal bulk and adsorbed phases may be determined as follows:

$$\gamma_i^l = \exp\left[\hat{q}^l\left(1 - \Phi_i^l\right)^2\right] \text{ for } i = 1, 2 \tag{26}$$

and

$$\gamma_i^s = \exp\left[l\hat{q}^s\left(1 - \Phi_i^s\right)^2 + m\hat{q}^l\left(1 - \Phi_i^l\right)^2\right] \text{ for } i = 1, 2 \tag{27}$$

where

$$\hat{q}^l = q^l/RT \text{ and } \hat{q}^s = q^s/RT.$$

In the Eqs. (26 and 27) the parameters l, m, q^l and q^s have their well-known meaning[13]. Equation (27) is valid for the assumption that interactions between molecules from adsorbed and bulk phases are equal to those in the bulk phase.

Combining Eqs. (17), (26) and (27) one gets for non-athermal solutions the following relation:

$$\ln \frac{\left(\Phi_1^s\right)^r \left(\Phi_2^l\right)^c}{\left(\Phi_1^l\right)^{rc} \left(\Phi_2^s\right)} + cr\hat{q}^l(1 - m)\left(2\Phi_1^l - 1\right) + crl\hat{q}^s\left(1 - 2\Phi_1^s\right) = \ln K_c \tag{28}$$

where $K_c = (K)^c$.

Putting $m = 0$ into the above Eq. (28) we neglect the interactions between molecules in the adsorbed and bulk phases[6].

Equation (28) allows us to carry out the model investigations, the purpose of which is to show how the differences in the molecular sizes of the adsorbed species, surface heterogeneity and non-ideality of both bulk and adsorbed solutions controls the type and range of the excess adsorption isotherms. An alternative method, which is likely to be useful in the investigation of deviations of any adsorption system from ideal behaviour is comparison of the function:

$$\frac{x_1^l x_2^l}{N_1^e} = f\left(x_1^l\right) \tag{29}$$

with the linear dependence:

$$\frac{x_1^l x_2^l}{n{*}_1^e} = f\left(x_1^l\right) \tag{30}$$

In the above N_1^e is the excess adsorption isotherm which describes the adsorption process from non-athermal solutions onto heterogeneous surfaces and $n{*}_1^e$ is the excess adsorption isotherm calculated for so-called IAS model (ideal adsorption system) for which $r = 1$, $c = 1$, $\hat{q}^l = 0$ and $\hat{q}^s = 0$.

In our investigations, to calculated the function N_1^e, we shall take advantage of the knwon *Everett*'s formula[13]:

$$X_1^s - x_1^l = N_1^e \left[\frac{x_1^l + r x_2^l}{(n_{1,0}^s/m) + (r-1) N_1^e} \right] \tag{31}$$

where, as previously, X_1^s denotes the total mole fraction of component 1 in the whole surface phase which can accomodate $(n_{1,0}^s/m) = a_s/w_1^s$ moles of this component per gram of solid. Here a_s is the specific surface area of the adsorbent. To study the influence of differences in molecular sizes of components on the adsorption process we assume that the surface phase capacity with respect to the 1st component is equal to unity, i.e., $(n_{1,0}^s/m) = 1$. Thus, putting $(n_{1,0}^s/m) = 1$ into Eq. (31) we obtain the following expression for N_1^e:

$$N_1^e = \frac{X_1^s - x_1^l}{r + X_1^s(1-r)} \tag{32}$$

Equation (32) for $r = 1$, i.e., when $(n_{1,0}^s/m) = (n_{2,0}^s/m) = (n^s/m) = 1$, becomes:

$$N_1^e = X_1^s - x_1^l \tag{33}$$

or assuming the homogeneity of the adsorbent surface:

$$n_1^e = x_1^s - x_1^l \tag{34}$$

where x_1^s is the mole fraction of the component 1 onto the homogeneous solid surface.

Our model calculations have been performed using the following numerical calculations:

(1) the calculation of the volume fractions Φ_1^l and Φ_2^l by means of Eq. (5) for given values r and x_1^l,

(2) the calculation of the volume fractions Φ_1^s and $\Phi_2^s = 1 - \Phi_1^s$ by means of Eq. (28) for a given but varying sets of parameters K_c, c, $\hat{q}^l$, $\hat{q}^s$ and r,

(3) the calculation of the mole fraction X_1^s and $X_2^s = 1 - X_1^s$ using the expression:

$$X_1^s = \frac{r\Phi_1^s}{r\Phi_1^s + (1-\Phi_1^s)} \tag{35}$$

(4) the calculation of the excess isotherm N_1^e according to Eq. (32) and finally, the calculation of the function (29).

The parameters l and m were taken for the close-packed cubic lattice, $l = 0.5$ and $m = 0.25$. Moreover, the quantities $\hat{q}^l$ and $\hat{q}^s$, as a measure of deviations from *Raoult*'s law may vary, in the case of completely miscible components from $\hat{q}^l$, $\hat{q}^s < 0$ (negative deviations from ideality) to $\hat{q}^l = 2$, $\hat{q}^s = 2$ (strong, positive deviations from ideality). Particular values of $\hat{q}^l$ and $\hat{q}^s$ will be given in the discussion of illustrative numerical studies.

The model calculations are carried out for the following models of adsorption systems:

(1) the NBP model (non-ideal behaviour in both adsorbed and bulk phases),

(2) the IAP model (ideal behaviour in both adsorbed and bulk phases),

(3) the IBP model (ideal behaviour in both adsorbed and bulk phases).

The last two models for $r = 1$ and $c = 1$ are most often used in the theory of adsorption from solutions on solids[2,3].

With the aim of a better explanation of the influence of various parameters on the adsorption process in Figs. 1–3 the excess isotherms and the corresponding linear functions (30), refering to the IAS model, are presented.

Fig. 1 shows the excess adsorption isotherms (A) and corresponding to them functions (29) (B). All calculations presented in this figure have been carried out for the most popular IBP adsorption model, assuming various sets of paramters r and c. The value of equilibrium constant K_c is equal to 2. It appears from Fig. 1 that the IBP model is very sensitive one on a change of values of these parameters r and c. For example, when $c = 1$ and r varies from $r = 1$ [curve (c)] to $r = 1.4$ [curve (e)] a decrease of the adsorption of component 1 is observed; it is clear that bigger species are less strongly adsorbed on the solid surface. On the other hand, a change in the heterogeneity parameter c from $c = 1$ to $c = 0.8$ [see curves (c) and (b) as well as curves (e) and (d)] causes an alternation in the range and magnitude of the adsorption. Additionally, for $r = 0.5$ and $c = 0.8$ [curve (a)] the effect of change in the surface heterogeneity is strong and the excess isotherms go from type I [curves (c) and (e)] through nearly type II [curves (b) and (d)] to type III [curve (a)] in *Schay-Nagy* classification[15]. The very same influence of the surface heterogeneity on the adsorption excess was observed and explained in details in Ref.[10].

Let us pass to Fig. 1 B showing the influence of parameters r and c on the deviations of the IBP adsorption model from ideal behaviour. This last one is attributed to the IAS model and is denoted by the solid line (c). The diagrams presented in Fig. 1 B prove that even a small variations in the parameters r and c cause a drastic deviation of a given system from the IAS model. For example, the comparison of the curves (c) and (b) points distinctly to a great and characteristic influence of the heterogeneity on the course of the functions (29), especially for high

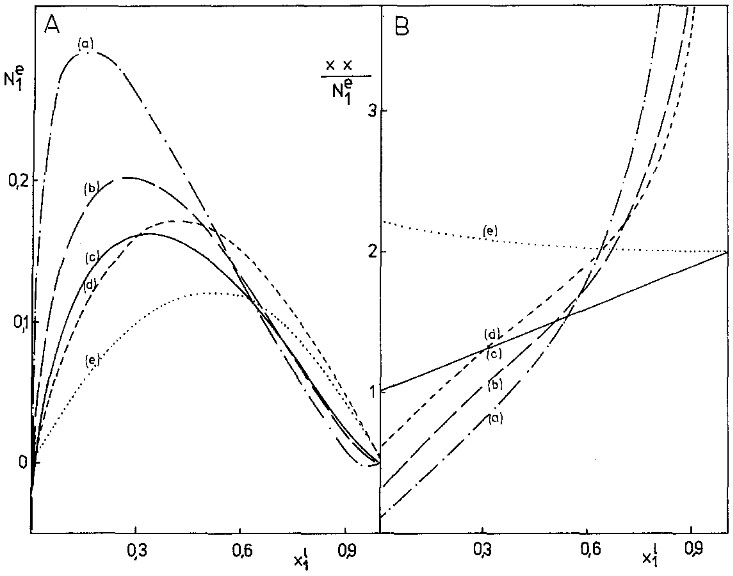

Fig. 1. Excess adsorption isotherms (A) and corresponding functions (29) (B), evaluated for the IBP model ($\hat{q}^l = \hat{q}^s = 0$) and $K_c = 2$; other adsorption parameters are equal to: $r = 0.5, c = 0.8$ (a); $r = 1.0, c = 0.8$ (b); $r = 1.0, c = 1.0$ (c); $r = 1.4$, $c = 0.8$ (d); $r = 1.4$, $c = 1.0$ (e)

values of x_1^l. Such effects are often observed in experiments[23]. Moreover, the courses of curves (a), (b) and (d) seem to be especially interesting because a comparison of them leads to the conclusion that the ratio of the areas occupied by two molecules may increase for $r < 1$ [see curves (a) and (b)] or decrease when $r > 1$ [see curves (b) and (d)] the effects of surface heterogeneity. This conclusion is strongly confirmed by the shape and course of the corresponding excess isotherms in Fig. 1 A. A very important result may be drawn from Fig. 1 B, which is connected with the most popular methods of the determination of the surface phase capacity, the so-called *Everett* method[22] ($r = 1$) or the generalized *Everett* method[24] ($r \neq 1$). This parameter is determined frequently from the first, usually linear part of function (29). However, careful attention must be applied for such a procedure. For example, when $r = 1$, we can find on the basis of curves (c) and (b) in Fig. 1 B, that the parameter $(n^s/m) = 1$ [curve (c)] and $(n^s/m) = 0.26$ [curve (b)]. The last value breakes away completely from unity, which was supposed by us in the model calculations.

Fig. 2 shows the functions (29) calculated for the three different adsorption models: IBP model (A); IAP model, $\hat{q}^l = 1, \hat{q}^s = 0$ (B); NBP model, $\hat{q}^l = \hat{q}^s = 1$ (C). The purpose of these calculations was to study the influence of the various sets of r and c on the deviations of the above adsorption models from ideal behaviour (IAS model denoted by solid lines). The diagrams presented in Fig. 2 A prove completely the results obtained from Fig. 1 B. Moreover, from Figs. 2 B and 2 C an important conclusion can be drawn that IAP model deviates much stronger from IAS behaviour than the NBP model. Prevously this result was found experimentally by *Coltharp*[25]. Finally, comparing the curves (c) and (d) in Figs. 2 B and 2 C we can find that a positive deviation of the liquid mixture from ideality increases the influence of surface heterogeneity on the deviations of any adsorption system from ideal behaviour. A negative deviation from *Raoult*'s law brings an opposite influence[10].

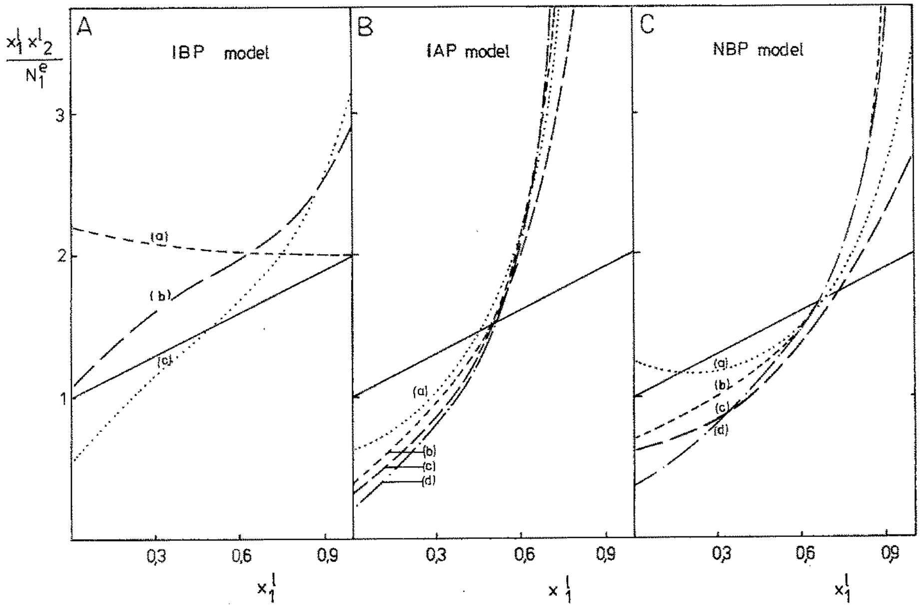

Fig. 2. Functions (29) corresponding to different adsorption models assuming $K_c = 2$. (*A*) IBP model: $r = 1.4, c = 1.0$ (*a*); $r = 1.4, c = 0.9$ (*b*); $r = 1.0, c = 0.9$ (*c*). (*B*) IAP model with $\hat{q}^l = 1, \hat{q}^s = 0$: $r = 1.0, c = 1.0$ (*a*); $r = 1.4, c = 0.9$ (*b*); $r = 1.0, c = 1.0$ (*c*); $r = 1.0, c = 0.9$ (*d*). (*C*) NBP model with $\hat{q}^l = \hat{q}^s = 1$: $r = 1.4, c = 1.0$ (*a*); $r = 1.4, c = 0.9$ (*b*); $r = 1.0, c = 1.0$ (*c*); $r = 1.0, c = 0.9$ (*d*). The IAS model behaviour is denoted by solid lines

Next, Fig. 3 A shows the dependence of N_1^e upon the value of r and Fig. 3 B shows the corresponding function (29). The model calculations have been made for the adsorption parameters: $\hat{q}^l = \hat{q}^s = 0$ (IBP model), $c = 0.9$, $K_c = 2$. The parameter r runs through the values 0.8, 1, 1.4, 1.8. An ideal behaviour is represented by the solid line (c). It can be

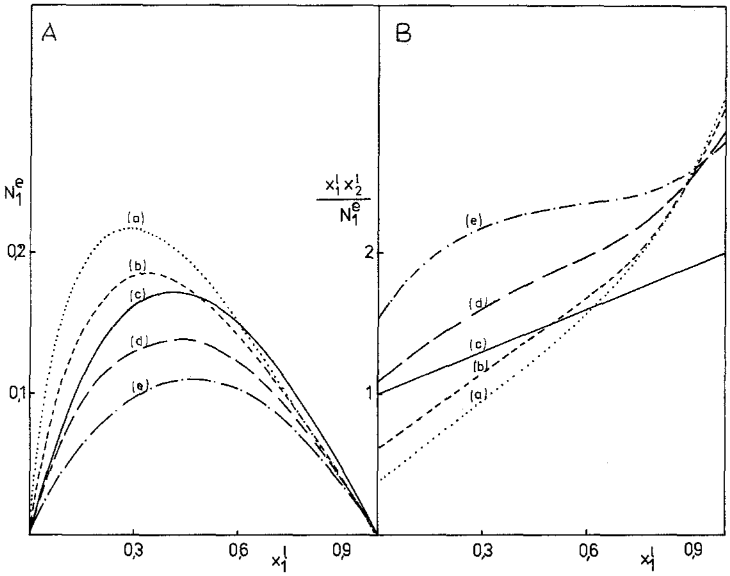

Fig. 3. Excess adsorption isotherms (A) and corresponding to them functions (29) (B) evaluated for the IBP model ($\hat{q}^l = \hat{q}^s = 0$) and $K_c = 2$, $c = 0.9$. Curves (a)-(e) are for $r = 0.8$, 1.0, 1.0 (and $c = 1.0$), 1.4, 1.8

found that at a constant heterogeneity parameter a variation in r does not change the sign of the excess adsorption isotherm, although the magnitude of adsorption of component 1 is changed very distinctly. In addition, earlier conclusions concerning *Everett*'s method for the estimation of the surface phase capacity are confirmed.

Fig. 4 shows the excess adsorption isotherms evaluated for different sets of adsorption parameters which are summarized in Table 1. Fig. 4 C displays the dependence of N_1^e upon the value of c in terms of the NBP model ($\hat{q}^l = \hat{q}^s = 1$). The calculations have been made for $K_c = 2$ and $r = 1.4$, when c assumes the values 0.1 (a) and (a′), 0.5 (b) and (b′), 1.0 (c) and (c′). The interaction between molecules in the adsorbed and bulk phases is either taken into account [$m = 0.25$, curves (a), (b) and (c)] or neglected [$m = 0$, curves (a′), (b′) and (c′)]. It appears from Fig. 1 C that

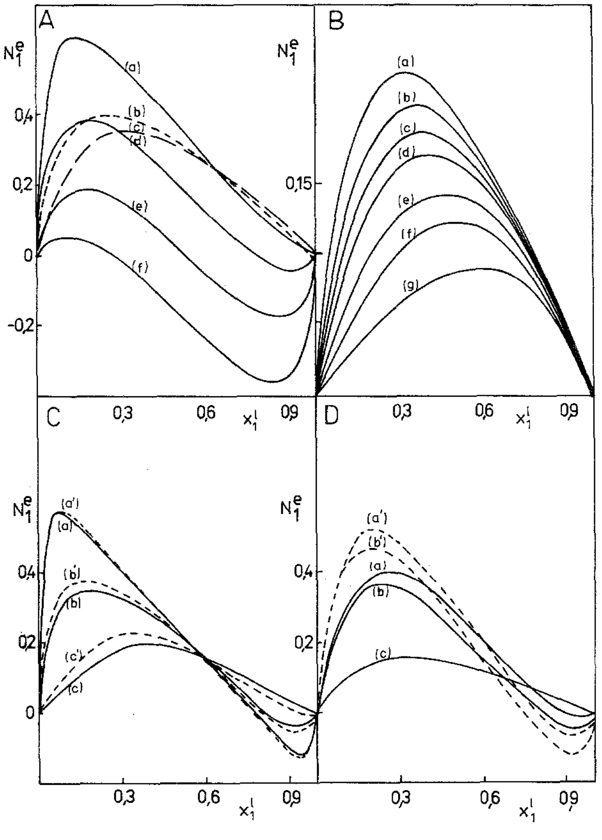

Fig. 4. Excess adsorption isotherms evaluated for various sets of adsorption parameters; the parameters are summarized in Table 1

the excess adsorption isotherms on a strongly heterogeneous surface have S-shape [$c = 0.1$, curves (a) and (a')] and the influence of m is very small. However, on a homogeneous surface [$c = 1.0$, curves (c) and (c')] the excess isotherms are U-shape and a bigger influence of interaction between both phases is observed.

Fig. 4 D shows the dependence of N_1^e upon the values of $\hat{q}^l$ and $\hat{q}^s$ (see Table 1) when $m = 0$ [dotted curves (a') and (b')] as well as $m = 0.25$ [solid curves (a) and (b)]. In this case $c = 0.8$ and for this reason the influence of the parameter m is relatively great. Moreover, Figs. 4 C and 4 D confirm the earlier conclusion that the positive deviations of liquid mixture from *Raoult*'s law increase the influence of the surface hetero-

Table 1. *The values of adsorption parameters used in the calculation of the excess adsorption isotherms shown in Fig. 4*

Figure	Curve	K_c	$\hat{q}^l$	$\hat{q}^s$	r	c	m
A	a)	5	2	2	1.1	0.8	0.25
	(b)	5	0	0		0.8	
	(c)	5	0	0		1.0	
	(d)	2	2	1		0.8	
	(e)	1	2	1		0.8	
	(f)	0.5	2	1		0.8	
B	(a)	2	0	0	0.7	1	0.25
	(b)				0.8		
	(c)				0.9		
	(d)				1.0		
	(e)				1.2		
	(f)				1.4		
	(g)				1.8		
C	(a′)	2	1	1	1.4	0.1	0.0
	(a)					0.1	0.25
	(b′)					0.5	0.0
	(b)					0.5	0.25
	(c′)					1.0	0.25
	(c)					1.0	0.25
D	(a′)	2	2	2	1.4	0.8	0.0
	(a)		2	2			0.25
	(b′)		2	1			0.0
	(b)		2	1			0.25
	(c)		0	0			0.25

geneity on the type, range, and magnitude of adsorption from solutions.

We hope that conclusions drawn on the basis of our model may be useful for systematic experimental studies of adsorption from non-ideal solutions on real solid surfaces.

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