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Thermodynamics of adsorption from solutions: non-electrolyte systems[☆]

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Abstract

The concept of global activity coefficients is developed in terms of adsorption at the liquid/solid interface. These coefficients evaluated from the excess adsorption data characterize non-ideality of the surface phase resulting from differences in molecular interactions which are additionally perturbed by heterogeneity of the solid. A method for separating a non-ideality of the adsorbed phase caused by intermolecular forces from that generated by surface heterogeneity is presented. It is shown theoretically that the global activity coefficients plotted as functions of the bulk or surface phase composition are characteristic for a given adsorption system and are useful for assessing adsorbent heterogeneity effects. The results presented are also helpful for evaluating the surface phase capacity which is a very important quantity in the study of adsorption from solutions on solids.

Keywords: Activity coefficients; Adsorption; Surface heterogeneity

1. Introduction

The problem of the surface activity coefficients is very important in liquid/solid adsorption, especially in adsorption from solutions of non-electrolytes on heterogeneous solid surfaces [1]. However, the following question arises here: what is the physical meaning of the "surface activity coefficients"? It is known that these coeffi-

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cients provide information about interactions in the surface phase and for this reason they may differ from the bulk activity coefficients. This difference may be explained by the influence of the solid surface which additionally perturbs intermolecular interactions in the surface region. However, these coefficients, evaluated for many experimental systems by means of literature methods, have maxima, minima, or sections with constant values which cannot be explained in terms of existing thermodynamic theories [2]. Consequently, the second question arising here: why the surface activity coefficients differ from those anticipated from the known thermodynamic considerations.

Several authors, e.g. Everett [3], and Zettlemoyer and Micale [4] have suggested that heterogeneity of the solid can be a main source of imperfection of the surface phase. For this reason it is important to assess the influence of the surface phase heterogeneity on the process in question and desirable to distinguish the influence of non-ideal behaviour arising from intermolecular forces from that generated by surface heterogeneity of the solid. This was partially achieved by Dabrowski [5] and Dabrowski et al. [6–8] who explained the activity coefficients in terms of the mole fraction of a given component in the entire surface phase formed on a random heterogeneous surface. In this paper, the concept of global activity coefficients is reexamined and used for characterizing the experimental systems. These coefficients characterize both non-ideality of the surface phase caused by differences in molecular interactions, and non-ideality of this phase generated by surface heterogeneity of the solid. Our approach corresponding to the so-called NBP adsorption model (both non-ideal phases) is suitable for characterizing all types of excess adsorption isotherms. The global activity coefficients characterize the total deviation of a real adsorption system from the reference adsorption system, which consists of an ideal surface phase formed on an energetically homogeneous solid surface thermodynamic equilibrium with an ideal bulk phase. So, this deviation takes into account adsorbate–adsorbate interactions in both phases and non-ideality effects of the surface phase associated with the energetic heterogeneity of the solid surface.

It is shown that the ratio of the surface activity coefficients caused by the adsorbent heterogeneity may be evaluated for each isotherm equation involving random distribution of adsorption sites on heterogeneous surfaces and that this is useful for estimating the global surface heterogeneity of any adsorbent with respect to the liquid mixture of adsorbates (or eluents in liquid/solid chromatography with respect to the mixed mobile phases). Several model studies and analyses of real systems were carried out to show the advantages of our approach for evaluating the surface heterogeneity from the experimental data.

Our results can be useful for evaluating the value of the surface phase capacity, which is an important quantity in the study of adsorption from solutions. This quantity is very significant for calculating all thermodynamic functions which characterize competetive adsorption at the liquid/solid interface.

2. Theoretical

Let us consider the liquid adsorption from a binary liquid mixture "1 + 2" consisting of molecules of equal sizes on heterogeneous solid surfaces, assuming a continuous distribution of the difference of adsorption energies of both components, $E_{12} = E_1 - E_2$. A fundamental equation dealing with this process has the following form [1, 2]

$$x_1^s(x_1^l) = \int_\Delta \frac{K_{12}X_{12}}{1 + K_{12}X_{12}} F(E_{12})\,\mathrm{d}E_{12} \tag{1}$$

where x_1^s denotes the total mole fraction of the first component in the whole surface region and x_1^l is the bulk mole fraction of this component. The interval of possible changes in E_{12} is marked by Δ and usually $\Delta = (-\infty, +\infty)$ [9]. $F(E_{12})$ is the differential distribution function of adsorption sites with regard to the value E_{12}; the constant K_{12} is defined as [9]

$$K_{12} = K^0(T)\exp\left(\frac{E_{12}}{RT}\right) \tag{2}$$

where $K^0(T)$ is a temperature-dependent constant. The general form of the variable X_{12} is considered in terms of the models of both the adsorption system and of those accepted for a heterogeneous surface of the solid.

The present investigations on adsorption at the solid/liquid interface allow us to distinguish the four models of adsorption systems:

1. NBP-na model: non-ideal behaviour in both bulk and adsorbed phases, where the adsorbed phase is non-autonomous.
2. NBP-a model: non-ideal behaviour in both bulk and adsorbed phases, with an autonomous surface phase.
3. IAP model: non-ideal bulk phase and ideal adsorbed phase.
4. IBP model: both phases ideal.

For the IAP and IBP models, the variable X_{12} is not dependent on a model of the heterogeneous surface, but both NBP models require an additional assumption. If the random distribution of adsorption sites for liquid adsorption on solids is assumed to be more realistic, the aforementioned variable X_{12} is not dependent on E_{12} and may be expressed as follows

$$X_{12} = \begin{cases} f_{21}^s(x_1^s, x_1^l)a_{12}^l, & \text{NBP-na model} \\ f_{21}^s(x_1^s)a_{12}^l, & \text{NBP-a model} \\ a_{12}^l, & \text{where } f_i^s = 1 \text{ or at least } f_{21}^s = 1\text{, IAP model} \\ x_{12}^l, & \text{where } f_i^l = 1, f_i^s = 1 \text{ or at least } f_{12}^l/f_{12}^s = 1\text{, IBP model} \end{cases} \tag{3}$$

where $f_{21}^s = f_2^s/f_1^s, f_{12}^l = f_1^l/f_2^l, a_{12}^l = a_1^l/a_2^l$ and $a_i^l = x_i^l f_i^l$, for $i = 1, 2$.

In expression (3), the symbols f_i^l and f_i^s ($i = 1, 2$) denote the bulk and surface activity coefficients, and a_i^l is the bulk activity of the ith component.

In view of subsequent considerations it is desirable to assume that the bulk and surface phases are regular. Taking into account the definitions of the activity coefficients formulated by Everett [3] we may rewrite the functions X_{12} given by Eq. (3) as follows

$$X_{12} = \begin{cases} \exp[l\hat{q}^{s}(2x_1^{s} - 1) + m'\hat{q}^{l}(2x_1^{l} - 1)]\exp[\hat{q}^{l}(1 - 2x_1^{l})]\,x_{12}^{l}, \\ \quad \text{for NBP-na model on random surfaces} \\ \exp[l\hat{q}^{s}(2x_1^{s} - 1)]\exp[\hat{q}^{l}(1 - 2x_{12}^{l})]\,x_{12}^{l}, \\ \quad \text{for NBP-a model } (m' = 0) \text{ on random surfaces} \\ \exp[\hat{q}^{l}(1 - 2x_1^{l})x_{12}^{l}, \quad \text{for IAP model} \\ x_{12}^{l}, \quad \text{for IBP model} \end{cases} \tag{4}$$

In the above equations, $\hat{q}^l$ and $\hat{q}^s$ characterize the deviations from Raoult's law and, for completely miscible components, change in the interval $< +2, -\infty)$. The lattice parameters l and m' denote the fractions of the closest neighbours of an adsorbed molecule in the surface phase and the adjacent bulk plane, and $l + 2m' = 1$ [3].

Combining Eq. (1) with the definite analytical forms of the distribution functions $F(E_{12})$ [1], using Stieltje's transform method [9], the following equation describing liquid adsorption on random heterogeneous solid surfaces can be obtained

$$x_1^s = \left[\frac{(\bar{K}_{12}X_{12})^n}{1 + (\bar{K}_{12}X_{12})^n}\right]^{m/n} \tag{5}$$

where $\bar{K}_{12}$ is the average equilibrium constant referring to the entire surface of the solid connected with the characteristic energy E_0 which determines the position of the function $F(E_{12})$ on the energy axis. The parameters n and m are the heterogeneity parameters within the interval $(0, 1>$ determining the width and asymmetry of the one-peak distribution functions. Eq. (5) reduces to three simpler expressions, namely the generalized Freundlich equation (GF) for $n = 1$, the Langmuir–Freundlich equation (LF) for $n = m$, and the Toth equation (T) for $m = 1$. The curves illustrating the distribution functions $F(E_{12})$ corresponding to these equations are presented in Fig. 1.

The physical meaning of the heterogeneity parameters n and m refers to their influence on the shape of these curves [1]. From a physical point of view, these parameters have to be greater than zero. The LF equation corresponds to a symmetrical quasi-Gaussian

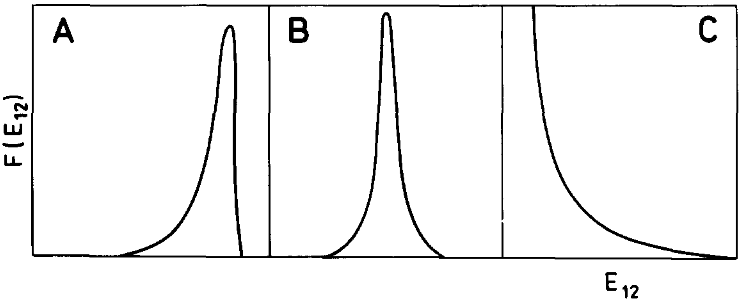

Fig. 1. Schematic diagram illustrating the distribution functions $F(E_{12})$, which correspond to Eq. (5) for $m = 1$ (A), $m = n$ (B) and $n = 1$ (C)

function $F(E_{12})$ and tends to zero for the smallest and the greatest values of E_{12}. For increasing values of $n = m$, the function $F(E_{12})$ becomes narrower, but for $n = m = 1$ it becomes the Dirac δ-function which is characteristic for energetically homogeneous surfaces. The distribution function relating to the T equation is an asymmetrical quasi-Gaussian function with a broadening at the left-hand side. The smaller the heterogeneity parameter n values, the larger the broadening and asymmetry. The energy distribution function for the GF equation is a decreasing exponential function which tends asymptotically to zero for E_{12} tending to infinity. When the heterogeneity parameter m decreases towards zero, the suitable functions $F(E_{12})$ move towards the energy axis.

The function $F(E_{12})$ is generally accepted for characterizing adsorbent heterogeneity for adsorption at the liquid/solid interface.

Let us now assume that the adsorption process on a heterogeneous surface of a random distribution of adsorption sites is described by the Everett-type equation [3]

$$\bar{K}_{12} = \frac{x_1^{\mathrm{s}} f_1^{\mathrm{s}}}{x_1^{\mathrm{l}} f_1^{\mathrm{l}}} \frac{x_2^{\mathrm{l}} f_2^{\mathrm{l}}}{x_2^{\mathrm{s}} f_2^{\mathrm{s}}} \tag{6}$$

It is clear that the activity coefficient f_i^{s} $(i = 1, 2)$ reflects the non-ideality of the surface phase caused by differences in molecular interactions and the non-ideality of this phase generated by the adsorbent heterogeneity. Thus, this coefficient is the global surface activity coefficient and according to the considerations presented in Ref. [5] is expressed as follows

$$f_i^{\mathrm{s}} = f_{i,\mathrm{int}}^{\mathrm{s}} f_{i,\mathrm{h}}^{\mathrm{s}}, \quad i = 1, 2 \tag{7}$$

where $f_{i,\mathrm{int}}^{\mathrm{s}}$ and $f_{i,\mathrm{h}}^{\mathrm{s}}$ denote the factors responsible for intermolecular interactions in the surface phase and non-ideality arising from the surface heterogeneity, respectively.

By means of Eqs. (6) and (7) one can obtain the following adsorption isotherm

$$x_1^{\mathrm{s}} = \frac{\bar{K}_{12} \beta_{12} x_{12}^{\mathrm{l}} f_{21,\mathrm{h}}^{\mathrm{s}}}{1 + \bar{K}_{12} \beta_{12} x_{12}^{\mathrm{l}} f_{21,\mathrm{h}}^{\mathrm{s}}} \tag{8}$$

where $\beta_{12} = f_{12}^{\mathrm{l}} / f_{12,\mathrm{int}}^{\mathrm{s}}$, $f_{12}^{q} = f_1^{q} / f_2^{q}$, $f_{21}^{q} = (f_{12}^{q})^{-1}$, and $x_{12}^{q} = x_1^{q} / x_2^{q}$ $(q = \mathrm{l}, \mathrm{s})$.

The corresponding reduced surface excess of the first component is given by the expression

$$n_1^{\sigma(n)} = n^{\mathrm{s}} (x_1^{\mathrm{s}} - x_1^{\mathrm{l}}) \tag{9}$$

where n^{s} is the so-called surface phase capacity on the whole heterogeneous surface. The extensive quantities in this equation refer to the mass unit.

From Eq. (8) we have

$$f_{12,\mathrm{h}}^{\mathrm{s}} = \bar{K}_{12} x_{12}^{\mathrm{l}} (\beta_{12} / x_{12}^{\mathrm{s}}) \tag{10}$$

and

$$\ln f_{12,\mathrm{h}}^{\mathrm{s}} = \ln \bar{K}_{12} + \ln x_{12}^{\mathrm{l}} + \ln \beta_{12} - \ln x_{12}^{\mathrm{s}} \tag{11}$$

We also have

$$\ln f^{s}_{12} = \ln f^{s}_{12,\mathrm{h}} + \ln f^{s}_{12,\mathrm{int}} \tag{12}$$

It follows from Eq. (11) that the $\bar{K}_{12}$ value does not change the shape of the curve $\ln f^{s}_{12,\mathrm{h}}$ vs. x^{l}_{1}, but only its position with respect to the x^{l}_{1} axis.

However, we can prove that function (11) is dependent on the heterogeneity parameters n and m only. In order to achieve this aim we rewrite Eq. (5) as follows [5]

$$x^{s}_{1} = \left[\frac{(\bar{K}_{12}\beta_{12}x^{l}_{12})^{n}}{1+(\bar{K}_{12}\beta_{12}x^{l}_{12})^{n}}\right]^{m/n} \tag{13}$$

By using Eq. (13) we can write

$$\bar{K}_{12}\beta_{12}x^{l}_{12} = \left[\frac{(x^{s}_{1})^{n/m}}{1-(x^{s}_{1})^{n/m}}\right]^{1/n} \tag{14}$$

Combining Eqs. (10) and (14) one gets the expression

$$\ln f^{s}_{12,\mathrm{h}} = \frac{1}{n}\ln\left[\frac{(x^{s}_{1})^{n/m}}{1-(x^{s}_{1})^{n/m}}\right] - \ln x^{s}_{12} \tag{15}$$

It is clear that the mole fraction x^{s}_{1} is a function of the bulk concentration x^{l}_{1} and for this reason $\ln f^{s}_{12,\mathrm{h}}$ vs. x^{l}_{1} depends only on the heterogeneity parameters n and m. So, this function may be helpful for characterizing experimental systems dealing with adsorption at the liquid/solid interface.

For several experimental systems we can assume ideality of the bulk phase, i.e. we can assume the IBP model of adsorption system. Then the term $\ln \beta_{12}$ in Eq. (11) cancels out giving the expression

$$\ln f^{s}_{12,\mathrm{h}} = \ln \bar{K}_{12} + \ln x^{l}_{12} - \ln x^{s}_{12} \tag{16}$$

However, we can estimate this term using independent thermodynamic data for non-ideal bulk solutions. The procedure used then is the following: estimation of the surface phase capacity, n^{s}, using one of the literature methods [10]; by assuming that $f^{l}_{i,\mathrm{int}}(x^{l}_{1}) = f^{s}_{i,\mathrm{int}}(x^{s}_{1})$, calculation of the function $\ln f^{s}_{12,\mathrm{int}}$ vs. x^{l}_{1}; the latter operation is connected with recalculation of the function $\ln f^{s}_{12,\mathrm{int}}$ vs. x^{s}_{1} to the function $\ln f^{s}_{12,\mathrm{int}}$ vs. x^{l}_{1} by means of the individual isotherm, $x^{s}_{1}(x^{l}_{1}) = (n^{\sigma(n)}_{1}/n^{s}) + x^{l}_{1}$. In consequence, the function $\ln f^{s}_{12,\mathrm{h}}$ vs. x^{l}_{1} may be obtained from the excess adsorption isotherm and used for characterizing the experimental systems. Let us compare Eq. (13) with Everett's equation dealing with an ideal adsorption system (IAS behaviour) [3]

$$x^{s}_{1} = \frac{\bar{K}_{12}x^{l}_{12}}{[1+\bar{K}_{12}x^{l}_{12}]} \tag{17}$$

We can state now that all deviations of any experimental system from IAS behaviour are produced by non-ideality of the bulk and surface phases, but the latter factor is generated by both molecular interactions in the surface solution and surface heterogeneity of the solids.

3. Model investigations

The model investigations require defining the molecular structure of the adsorbing solution. A regular lattice model of the liquid mixture was used. To describe liquid adsorption on a heterogeneous surface corresponding to the NBP-a model, Eq. (5) was applied for calculating the term x^{s}_{12} appearing in expression (11). The term $\beta_{12} = f^{1}_{12}/f^{s}_{12,\mathrm{int}}$ was evaluated by using suitable definitions for the bulk and surface activity coefficients assuming the value of $l = 0.5$ [3]

$$f^{1}_{12} = \exp[\hat{q}^{1}(1 - 2x^{1}_{1})] \tag{18}$$

$$f^{s}_{12,\mathrm{int}} = \exp[l\hat{q}^{s}(1 - 2x^{s}_{1})] \tag{19}$$

Introducing the autonomous surface phase is justified for the adsorption process occurring on heterogeneous surface of solids [1]. The functions $\ln f^{s}_{12,\mathrm{int}}$ vs. x^{1}_{1} were obtained by means of Eqs. (19) and (5). For $n = m = 1$ (homogeneous surface) and $\bar{K}_{12} = 1$, the adsorption excess $n^{\sigma(n)}_{1}$ vs. x^{1}_{1} is equal to zero in the whole concentration region. In the case of a heterogeneous surface ($n \neq 1$, $m \neq 1$), even for $\bar{K}_{12} = 1$, the adsorption excess is different from zero. The model investigations with $\bar{K}_{12} = 1$ are interesting because the quantities calculated for this assumption reflect mainly adsorbent heterogeneity. Figs. 2–4 present the functions $\ln f^{s}_{12}$ vs. x^{1}_{1}, $\ln f^{s}_{12,\mathrm{int}}$ vs. x^{1}_{1}, and $\ln f^{s}_{12,h}$ vs. x^{1}_{1}, respectively. These functions were calculated for $\bar{K}_{12} = 1$ and for this reason we can observe here the influence of surface heterogeneity and molecular interactions in both phases. It can be seen from our figures that the curves plotted for the LF equation ($n = m$) intersect the x^{1}_{1} axis at $x^{1}_{1} = 0.5$, and, except for the functions $\ln f^{s}_{12,\mathrm{int}}$ vs. x^{1}_{1}, are practically increasing functions of x^{1}_{1}. However, the curves relating to the GF equation ($n = 1$) lie below the x^{1}_{1} axis, whereas those relating to the Toth equation ($m = 1$) lie above it. The model results presented in Figs. 2–4 provide information about the type of energy distribution function, which characterizes adsorbent heterogeneity.

Comparing the course of $\ln f^{s}_{12,\mathrm{h}}$ vs. x^{1}_{1} and $\ln f^{s}_{12,\mathrm{int}}$ vs. x^{1}_{1}, it can be stated that: for positive deviations of liquid mixtures from Raoult's law, the contributions of $\ln f^{s}_{12,\mathrm{h}}$ and $\ln f^{s}_{12,\mathrm{int}}$ to $\ln f^{s}_{12}$ compensate each other, i.e. the functions have opposite signs; for negative deviations from Raoult's law, these contributions sum up, i.e. the function signs are the same.

In Fig 5. the functions $\ln f^{s}_{12,\mathrm{h}}$ vs. x^{s}_{1} calculated for $\bar{K}_{12} = 10$ (A, B, D) and $\bar{K}_{12} = 1$ (D, E, F) are presented. It follows from this figure that the change in $\bar{K}_{12}$ does not change the shape of the curves, but causes a parallel translation in relation to the x^{1}_{1} axis by $\ln \bar{K}_{12}$. In Fig. 6, the functions $\ln f^{s}_{12,\mathrm{h}}$ vs. x^{1}_{1} calculated for $\bar{K}_{12} = 1$, fixed parameters n and m, and various values of $\hat{q}^{1}$ and $\hat{q}^{s}$ are shown. It follows from this figure that for strongly heterogeneous surfaces of the solids the influence of the molecular interactions in the bulk and surface phases is negligible. Moreover, the aforementioned conclusions dealing with the utility of the functions $\ln f^{s}_{12,\mathrm{h}}$ vs. x^{1}_{1} for estimating the adsorbent heterogeneity are confirmed.

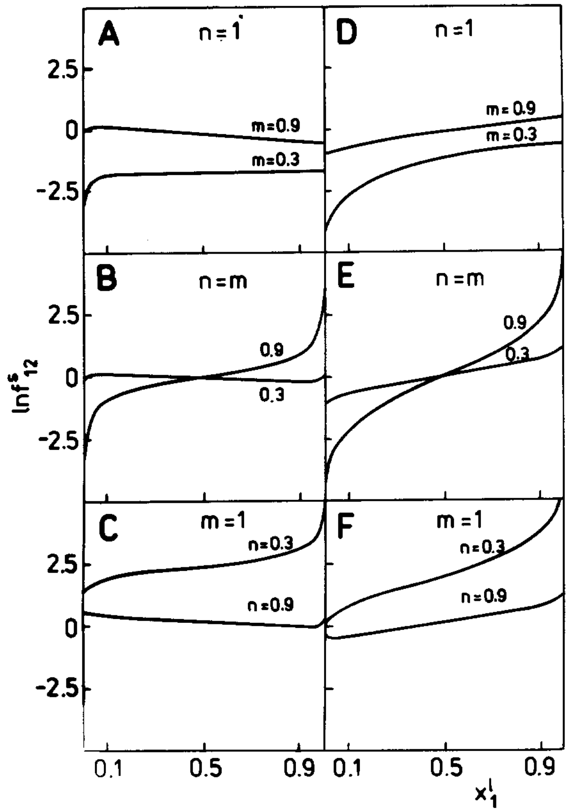

Fig. 2. Functions ln f^s_{12} vs. x_1^l plotted for the NBP-a model of adsorption system calculated for $\bar{K}_{12} = 1$ and various values of n and m: A, B, C, $\hat{q}^l = \hat{q}^s = 1$; D, E, F, $\hat{q}^l = \hat{q}^s = -1$.

4. Experimental revision

In order to explain the foregoing considerations, Eqs. (11) and (12) were applied for analysing the experimental adsorption isotherms taken form the literature. Information concerning these systems is included in Table 1. Table 2 contains the values $\bar{K}_{12}$ and n^s evaluated by the classical Everett method [17]. Although this method affords only approximate values of $\bar{K}_{12}$ for heterogeneous adsorbents, this accuracy is sufficient to evaluate ln$f^s_{12,h}$, since these values do not change the nature of the function ln $f^s_{12,h}$ vs. x_1^l, but only move its position with respect to the x_1^l axis. All experimental systems from Table 1 were analysed by means of Eqs. (11) and (12) assuming the non-ideality of the bulk solutions.

Fig. 7 presents the dependences ln $f^s_{12,h}$ vs. x_1^l calculated according to Eq. (11) for the system containing benzene (1) + n-heptane (2) on silica gel with the changing parameter of surface phase capacity n^s. This figure provides information on the influence of the n^s values on the function in question. The value of $n^s = 2.02$ mmol g^{-1} obtained

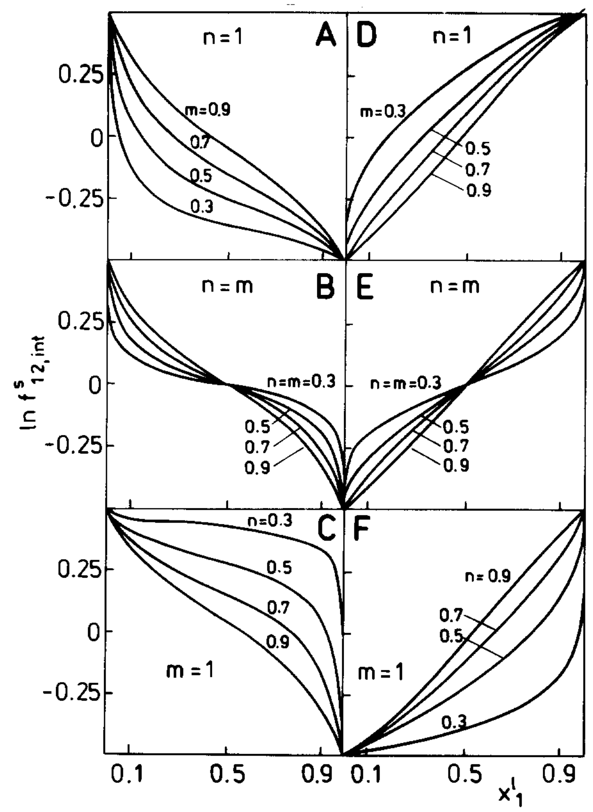

Fig. 3. Functions $\ln f^s_{12,\text{int}}$ vs. x^l_1 plotted for the NBP-a model of adsorption system calculated for $\bar{K}_{12} = 1$ and various values of n and m: Parts A, B, C, $\hat{q}^l = \hat{q}^s = 1$; D, E, F, $\hat{q}^l = \hat{q}^s = -1$.

using the Everett method gives the function $\ln f^s_{12,\text{h}}$ vs. x^l_1 which falls out from the model calculations presented in Fig. 4. However, the value $n^s = 2.40$ mmol g^{-1} assures the best linearity of Everett's equation and may be introduced as the corrected value of n^s. Table 2 includes the values of n^s numerically corrected by means of Eq. (11) for all systems investigated. We can see in this table that the corrected values of surface phase capacities are generally larger than those obtained in terms of the linear Everett method. In the case of the system aminobenzene(1) + ethanol(2) on charcoal, the corrected capacity is larger by up to a factor of 3 than the parameter n^s obtained by means of this traditional approach.

A critical discussion of the various methods for determining the surface phase capacity from the excess adsorption data has been published by Dabrowski and Jaroniec [10]. According to the thermodynamic considerations they presented, all linear methods for evaluating the surface phase capacity (including the Everett method) can give only the minimal value of the surface capacity and frequently this value is inconsistent from a thermodynamic point of view. In particular, the linear methods

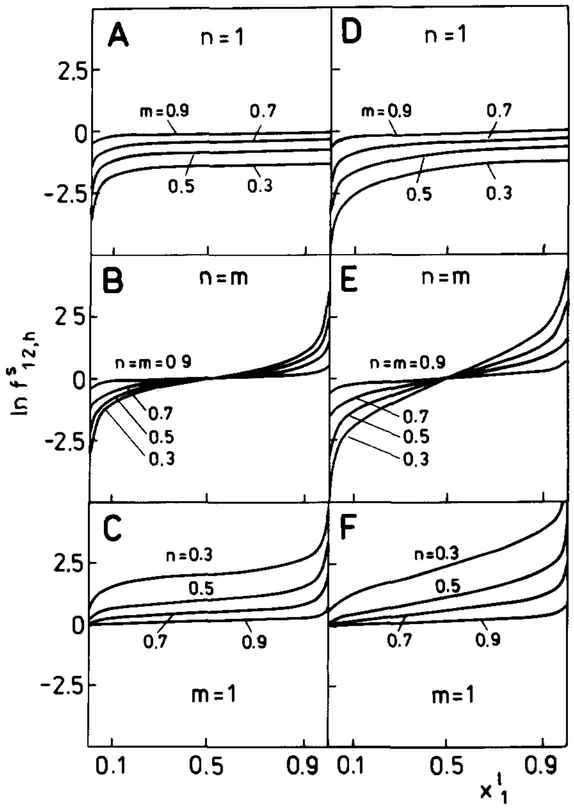

Fig. 4. Functions ln $f^s_{12,h}$ vs. x^l_1 plotted for the NBP-a model of adsorption system for $\bar{K}_{12} = 1$ and various values of n and m: A, B, C, $\hat{q}^l = \hat{q}^s = 1$; D, E, F, $\hat{q}^l = \hat{q}^s = -1$.

cannot provide a basis for the monolayer character of the surface phase. So, the n^s values obtained in terms of the Everett method should be carefully analysed with respect to their physical reality. This is probably why our thermodynamic approach gives significantly larger corrected values of surface phase capacity for some experimental systems.

It follows from Fig. 7 that $\ln f^s_{12,h}$ vs. x^l_1 is greater than zero in the whole concentration region and is approximated by the model functions presented in Fig. 4C. This result suggests that the distribution function characterizing the heterogeneity of silica gel with respect to the benzene (1) + *n*-heptane (2) liquid mixture may correspond to Toth's equation, i.e. the distribution is directed towards lower values of E_{12}. An identical conclusion can be drawn from the results presented for the system in question in Fig. 8. The liquid mixture consisting of benzene (1) + *n*-heptane (2) shows a certain bulk non-ideality and Fig. 8 shows that the surface phase is slightly non-ideal in the whole concentration range. As follows from Fig. 8, the curve $\ln f^s_{12,h}$ vs. x^l_1 has significant values, which is evidence for strong surface heterogeneity of silica gel. At the

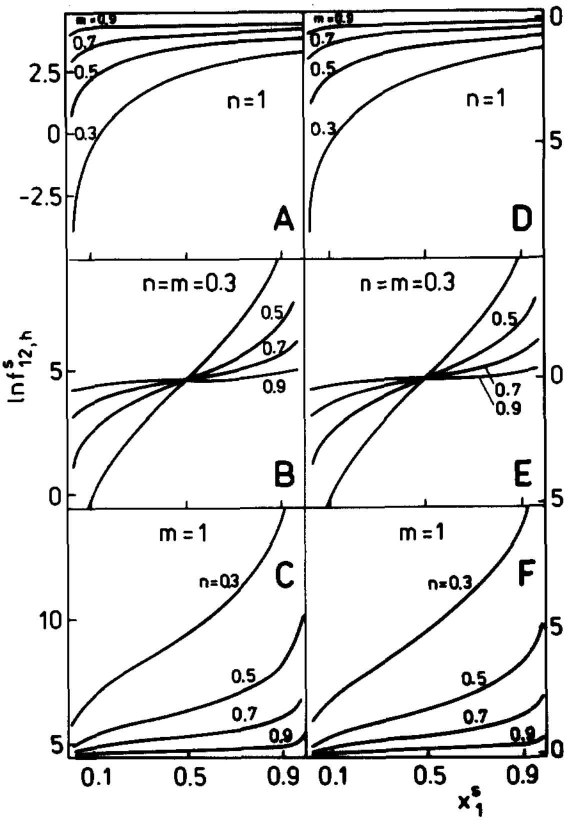

Fig. 5. Functions $\ln f^s_{12,h}$ vs. x^s_1 plotted for the NPB-a model of adsorption system assuming $\hat{q}^l = \hat{q}^s = 1$ and various values of n and m: A, B, C, $\bar{K}_{12} = 10$; D, E, F, $\bar{K}_{12} = 1$

same time, due to the opposite signs of $\ln f^s_{12,h}$ vs. x^l_1 and $\ln f^s_{12,int}$ vs. x^l_1, the global surface non-ideality represented by the function $\ln f^s_{12}$ vs. x^l_1 is smaller than that generated by the surface heterogeneity of the solid.

However, the non-ideality associated with the interactions in the bulk and surface phase is similar. The curves $\ln f^s_{12,int}$ vs. x^l_1 lie closer to the $\ln f^s_{12,int}$ curves (see also Figs. 9 and 10). The global non-ideality of the surface solution under consideration is greater in comparison to that observed in the bulk phase and is due to the energetic heterogeneity of the adsorbed surface. In Fig. 9, the functions $\ln f^s_{12,h}$, $\ln f^s_{12}$, $\ln f^s_{12,int}$ and $\ln f^s_{12}$ vs. x^l_1 for adsorption of methyl acetate (1) + 1,2-dichloroethane (2) on boehmite are presented. In this case, the non-ideality of the surface region caused by the adsorbent heterogeneity is smaller than that in Fig. 8.

Comparison of the presented functions with the model studies shows that a symmetrical quasi-Gaussian distribution should represent the adsorbent heterogeneity of the boehmite. Earlier studies [18] show that this adsorption system is well described by the Langmuir–Freundlich equation with $n = 0.93$.

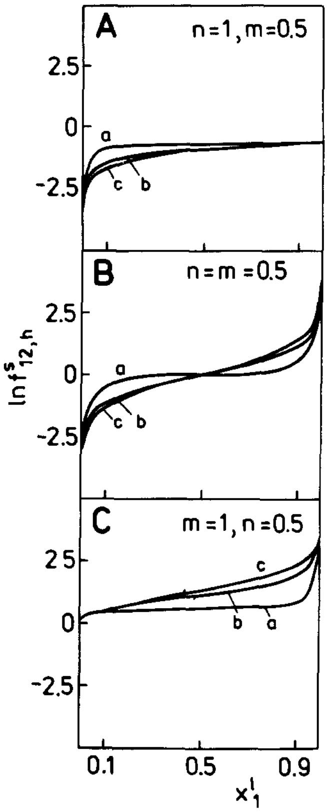

Fig. 6. Functions $\ln f^s_{12,h}$ vs. x^l_1 calculated for $\bar{K}_{12} = 1$, fixed parameters of n and m, and various values of $\hat{q}^l$ and $\hat{q}^s$: A, $\hat{q}^l = \hat{q}^s = 2$; B, $\hat{q}^l = \hat{q}^s = 0$; C, $\hat{q}^l = \hat{q}^s = -2$.

Fig. 10 presents the functions $\ln f^s_{12,h}$, $\ln f^s_{12,\mathrm{int}}$ and $\ln f^l_{12}$ vs. x^l_1 for adsorption of butylamine (1) from benzene (2) on charcoal. In this case the liquid mixture is almost ideal and the surface phase is similar. However, the charcoal surface is strongly heterogeneous with respect to the adsorbing solution and the distribution function characterizing this heterogeneity with respect to the liquid mixture may correspond to Toth's isotherm.

5. Conclusions

The concept of global surface activity coefficients developed in this paper leads to a simple method for estimating heterogeneity effects in adsorption from solutions on solids. The functions $\ln f^s_{12,h}$ vs. x^l_1 may be evaluated from the excess adsorption isotherms and may give some information about the heterogeneity effects of the adsorbents. However, the functions $\ln f^s_{12,\mathrm{int}}$ vs. x^l_1 may be distinguished from the

Table 1
Essential information on the adsorption systems studied by means of Eqs. (11) and (12)

No. of adsorption system	Liquid mixture 1st component	Liquid mixture 2nd component	Adsorbent	Temp./K	Ref. to adsorption system	Ref. to the bulk activity coefficient
1	Benzene	*n*-Heptane	Silica gel	298	[11]	[16]
2	Benzene	*n*-Heptane	Silica gel	303	[12]	[12]
3	Benzene	Cyclohexane	Silica gel	273	[13]	[16]
4	Benzene	Cyclohexane	Silica gel	303	[13]	[16]
5	Benzene	Cyclohexane	Silica gel	333	[13]	[16]
6	Benzene	Cyclohexane	Silica gel	303	[12]	[12]
7	Benzene	1,2-Dichloroethane	Active carbon	303	[12]	[12]
8	Chloroform	Carbon tetrachloride	Charcoal	293	[14]	[14]
9	Trichloroethane	Butyl chloride	Charcoal	293	[14]	[14]
10	Butylamine	Benzene	Charcoal	193	[14]	[14]
11	Trichloromethane	Carbon tetrachloride	Charcoal	293	[14]	[14]
12	Aminobenzene	Ethanol	Charcoal	293	[14]	[14]
13	Benzene	Cyclohexane	Boehmite	293	[15]	[15]
14	Methyl acetate	Benzene	Boehmite	293	[15]	[15]
15	Methyl acetate	1,2-Dichloroethane	Boehmite	293	[15]	[14]
16	Chloroform	Benzene	Boehmite	293	[15]	[15]

Table 2
Values of the average equilibrium constant $\bar{K}_{12}$ and the surface phase capacity n^s for the adsorption systems summarized in Table 1

No. of adsorption system	Average equilibrium constant $\bar{K}_{12}$	Surface phase capacity according to Everett method n^s/(mmol g^{-1})	Surface phase capacity corrected by means of Eq. (11) n^s/(mmol g^{-1})
1	166.77	2.02	2.40
2	14.77	2.90	3.90
3	18.85	3.36	4.30
4	17.02	3.05	3.90
5	12.58	2.56	3.60
6	29.66	2.57	3.30
7	148.92	0.78	1.00
8	19.06	1.27	1.70
9	9.83	1.74	2.50
10	73.19	1.57	1.80
11	11.21	0.61	1.00
12	1.00	0.65	2.00
13	107.34	0.77	1.20
14	23.10	1.27	2.10
15	20.94	1.30	1.90
16	5.04	1.33	2.10

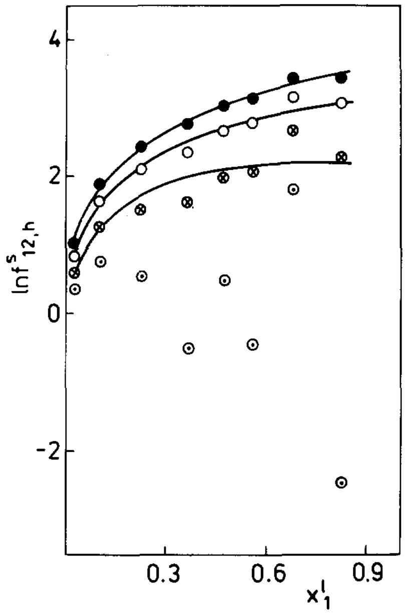

Fig. 7. Functions ln $f^s_{12,h}$ vs. x^l_1 for adsorption of benzene (1) + *n*-heptane (2) on silica gel at 297 K for $\bar{K}_{12}$ = 166.80 and various values of n^s: ●, n^s = 2.60 mmol g^{-1}; ○, n^s = 2.40 mmol g^{-1}; ⊗, n^s = 2.20 mmol g^{-1}; ⊙, n^s = 2.02 mmol g^{-1}.

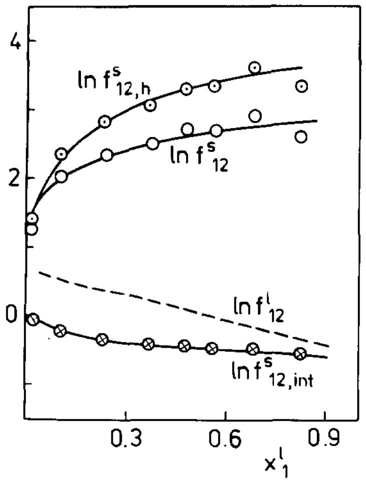

Fig. 8. Functions ln $f^s_{12,h}$, ln f^s_{12}, ln $f^s_{12,int}$ and ln f^l_{12} vs. x^l_1 for adsorption of benzene (1) + *n*-heptane (2) on silica gel at 297 K for $\bar{K}_{12}$ = 166.80 and n^s = 2.40 mmol g^{-1}.

global activity coefficients to give information about molecular interactions in the surface phase. If the above functions have opposite signs over the whole concentration range, then the compensation effects mean that the global non-ideality of the surface phase may be smaller than the non-ideality generated by the surface heterogeneity of

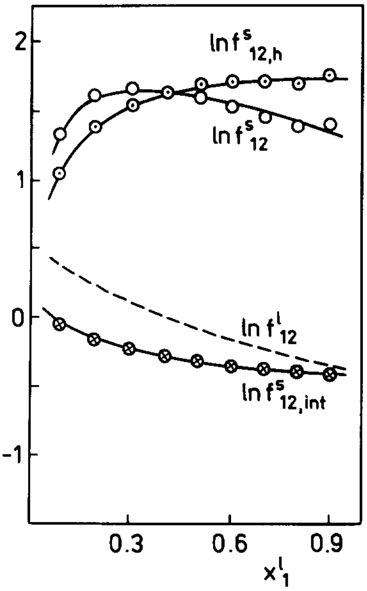

Fig. 9. Functions $\ln f^s_{12,h}$, $\ln f^s_{12}$, $\ln f^s_{12,int}$ and $\ln f^l_{12}$ vs. x^l_1 for adsorption of methyl acetate (1) + 1,2-dichloroethane (2) on boehmite at 293 K for $\bar{K}_{12} = 20.94$ and $n^s = 1.90$ mmol g^{-1}.

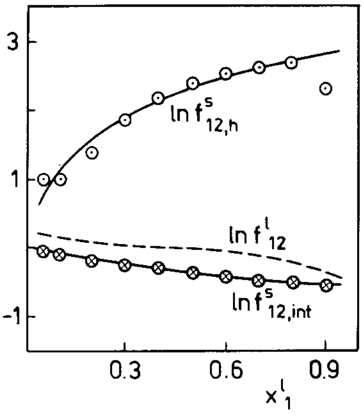

Fig. 10. Functions $\ln f^s_{12,h}$, $\ln f^s_{12,int}$ and $\ln f^l_1$ vs. x^l_1 for adsorption of butylamine (1) + benzene (2) on charcoal at 293 K for $\bar{K}_{12} = 73.19$ and $n^s = 1.80$ mmol g^{-1}.

the solid. The presented results can also be helpful for accepting the values of the surface phase capacity which characterize the sorption properties of the adsorbents and are very important for calculating thermodynamic functions which characterize competitive adsorption at the liquid/solid interface.

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