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Competitive Adsorption from Multicomponent Non-electrolytic Liquid Mixtures on Heterogeneous Solid Surfaces

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Summary. A simple model for competitive adsorption from multicomponent non-electrolytic liquid mixtures on energetically heterogeneous solid surfaces is discussed in terms of statistical thermodynamics. Integral equations are derived for the fundamental thermodynamic quantities that characterize competitive adsorption at the liquid-solid interface. Extensive model studies are presented in order to illustrate the influence of adsorbent heterogeneity on the behaviour of these thermodynamic quantities.

Keywords. Adsorbent heterogeneity; Adsorption at the liquid-solid interface; Adsorption from multicomponent solutions; Thermodynamic functions of adsorption.

Thermodynamic der Konkurrenzadsorption von flüssigen Multikomponenten-Mischungen von Nichtelektrolyten an heterogenen Oberflächen von Festkörpern

Zusammenfassung. Die Konkurrenzadsorption von Multikomponenten-Mischungen von Nichtelektrolyten an energetisch heterogenen Festkörpern wird im Rahmen der Statistischen Thermodynamik beschrieben. Die Integralgleichungen für fundamentale thermodynamische Größen, die Konkurrenzadsorption an der Festkörper – Flüssigkeit Phasengrenze charakterisieren, sind ausgeführt. Es wurden extensive Modelluntersuchungen zur Illustration des Einflußes der Heterogenität der Adsorbenten auf das Verhalten dieser thermodynamischen Größen durchgeführt.

Introduction

Adsorption is a very important phenomenon which occurs at different interfaces. This process is widely spread in natural systems and it is also utilized in various technological processes. Practical applications of adsorption stimulate experimental as well as theoretical studies of this phenomenon. Because of the complicated character of adsorption, especially for the multicomponent liquid–solid systems, the investigations in this field are not satisfactorily advanced. Most studies were devoted to the description of adsorption equilibria in simple systems [1–7], e.g., adsorption from binary solutions on homogeneous and heterogeneous surfaces. Theory of adsorption from multicomponent liquid mixtures on solids is still insufficiently elaborated.

In this paper a simple model for competitive adsorption from multicomponent solutions of non-electrolytes is discussed in terms of statistical thermodynamics. Theoretical description of this model is presented for energetically homogeneous as well as heterogeneous solid surfaces. The current paper is a continuation of an earlier work [8]. In addition to Ref. [8] the current work presents expressions for the basic thermodynamic functions and illustrates extensively their dependence on the energetic heterogeneity of adsorbent.

Theory

Adsorption on Homogeneous Solids

Let us formulate the basic assumptions of the model:

(1) cell model of the surface phase with one molecule in each cell,
(2) the square-well potential for representing the adsorbate-surface interaction,
(3) ideality of the surface phase,
(4) equality of molecular sizes for all solution components,
(5) constancy of the total number of adsorbed molecules,
(6) limitation of the surface phase thickness to one adsorbed layer.

The canonical partition function for the above adsorption model with the n-component surface phase has the following form [8]:

$$Q=\frac{B!}{\left(\prod_{i=1}^{n-1} N_i!\right)\left(B-\sum_{i=1}^{n-1} N_i\right)!}\left[\prod_{i=1}^{n-1} q_i^{N_i}\right] q_n^{\left(B-\sum_{i=1}^{n-1} N_i\right)}, \tag{1}$$

where

$$q_i = J_i(T)\exp(\varepsilon_i/kT) \quad i=1,2,\ldots,n. \tag{2}$$

Here B is the total number of molecules in the surface phase, N_i is the number of molecules of the i-th component, ε_i is the adsorption energy of the i-th component, $J_i(T)$ is the partition function of an isolated molecule of this component, k is the Boltzmann constant and T is the absolute temperature.

It was shown elsewhere [3] that the competitive adsorption of liquid mixtures on solid surfaces can be characterized by the difference of the chemical potentials of the i-th and n-th components in the surface phase; this difference is associated with the canonical partition function Q as follows [8, 9]:

$$\mu_{in}^s=\mu_i^s-\mu_n^s=-kT\left(\frac{\partial \ln Q}{\partial N_i}\right)_{B,T,N_{j\neq i}}=kT\ln\frac{N_i}{\left(B-\sum_{i=1}^{n-1}\right)q_{in}}$$

$$=kT\ln\frac{x_i^s}{\left(1-\sum_{i=1}^{n-1} x_i^s\right)q_{in}} \quad i=1,2,\ldots,n-1, \tag{3}$$

where

$$q_{in} = q_i/q_n = J_i(T)/J_n(T)\exp\left(\frac{\varepsilon_i - \varepsilon_n}{kT}\right) = J_{in}(T)\exp\left(\frac{\varepsilon_{in}}{kT}\right), \tag{4}$$

and

$$x_i^s = N_i/B \quad \sum_{i=1}^{n} x_i^s = 1. \tag{5}$$

Here μ_i^s denotes the chemical potential of the i-th component in the surface phase, and x_i^s denotes its mole fraction in the surface phase. At the adsorption equilibrium the difference of the chemical potentials of the i-th and n-th components in the surface phase is equal to the difference of their chemical potentials in the bulk phase:

$$\mu_{in}^s = \mu_{in} = \mu_i - \mu_n = \mu_{in}^0 + kT\ln(x_{in}f_{in}), \tag{6}$$

where

$$\mu_{in}^0 = \mu_i^0 - \mu_n^0, \quad x_{in} = x_i/x_n, \quad f_{in} = f_i/f_n. \tag{7}$$

Here μ_i^0 is the standard chemical potential of the i-th component, x_i and f_i are its mole fraction and activity coefficient in the bulk phase, respectively.

Eqs. (3) and (6) lead to the well-known form of adsorption isotherm [7, 11]:

$$x_i^s = \frac{K_{in}x_{in}f_{in}}{1 + \sum_{j=1}^{n-1} K_{jn}x_{jn}f_{jn}}, \tag{8}$$

where the equilibrium constant K_{in} is equal to:

$$K_{in} = q_{in}\exp(\mu_{in}^0/kT) = J_{in}(T)\exp(\mu_{in}^0/kT)\exp(\varepsilon_{in}/kT). \tag{9}$$

The thermodynamic functions that characterize the localized adsorption of liquid mixtures on energetically homogeneous solids can be calculated by using the general relationships between the canonical partition function and the thermodynamic quantities [10, 11]. These relationships applied to the canonical partition function [viz., Eq. (1)] give the following expressions:

Helmholtz free energy

$$\Delta A_n = -kT\ln Q = BkT\left[\sum_{i=1}^{n} x_i^s\ln x_i^s - \sum_{i=1}^{n} x_i^s\ln q_i\right]; \tag{10}$$

Energy

$$\Delta E_n = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{B,N_i} = BkT^2\left[\sum_{i=1}^{n} x_i^s\frac{\partial \ln J_i(T)}{\partial T}\right] - B\sum_{i=1}^{n} x_i^s\varepsilon_i; \tag{11}$$

Entropy

$$\Delta S_n = kT\left(\frac{\partial \ln Q}{\partial T}\right)_{B,N_i} + k\ln Q = \Delta S_n^{nc} + \Delta S_n^c; \tag{12}$$

Non-configurational entropy

$$\Delta S_n^{nc} = Bk\left[T\sum_{i=1}^{n} x_i^s\frac{\partial \ln J_i(T)}{\partial T} + \sum_{i=1}^{n} x_i^s\ln J_i(T)\right]; \tag{13}$$

Configurational entropy

$$\Delta S^{c}_{n} = k\ln\frac{B!}{\left(\prod_{i=1}^{n-1} N_i!\right)\left(B-\sum_{i=1}^{n-1} N_i\right)!} = -kB\sum_{i=1}^{n} x^{s}_{i}\ln x^{s}_{i}. \tag{14}$$

Adsorption on Heterogeneous Solids

Let us assume that B_r denotes the number of adsorption sites with adsorption energies $\varepsilon_r = (\varepsilon_{1r_1}, \varepsilon_{2r_2}, \ldots, \varepsilon_{nr_n})$. The components of vector $\boldsymbol{r} = (r_1, r_2, \ldots, r_n)$ characterize a given surface patch. The total number of molecules adsorbed on sites characterized by the energies ε_r is $\sum_{i=1}^{n} N_{ir} = B_r$, where N_{ir} is the number of molecules of the i-th component adsorbed on the sites of the $\boldsymbol{r}$-th type. The total number of molecules of the i-th component adsorbed over the whole surface phase on the sites $B = \sum_r B_r$ is equal to $N_i = \sum_r N_{ir}$. Let us assume additionally, that the numbers N_{ir} are the large numbers for which Stirling's approximation may be used. Thus, for a given number of molecules $N = \sum_{i=1}^{n} N_i$ and for a given their distribution N_{ir} on the sites B_r the canonical partition function can be expressed as follows [8]:

$$Q_{N_{1r}N_{2r}\ldots N_{nr}} = \prod_r \frac{B_r!}{\left(\prod_{i=1}^{n-1} N_{ir}!\right)\left(B_r-\sum_{i=1}^{n-1} N_{ir}\right)!}\cdot\left[\prod_{i=1}^{n-1} q_{ir_i}^{N_{ir}}\right] q_{nr_n}^{\left(B_r-\sum_{i=1}^{n-1} N_{ir}\right)}, \tag{15}$$

where

$$q_{ir_i} = J_{ir_i}(T)\exp(\varepsilon_{ir_i}/kT). \tag{16}$$

The total partition function Q for the surface phase is the sum of the functions given by Eq. (15):

$$Q = \sum_r Q_{N_{1r}N_{2r}\ldots N_{nr}}. \tag{17}$$

After replacing this sum by its maximum term, the logarithm of the canonical partition function Q may be approximated as follows:

$$\ln Q = \sum_r\left[B_r\ln B_r - \sum_{i=1}^{n} N_{ir}\ln N_{ir} + \sum_{i=1}^{n} N_{ir}\ln q_{ir_i}\right]. \tag{18}$$

At the adsorption equilibrium (cf., Eq. (6)] on the sites of the $\boldsymbol{r}$-th type we obtain:

$$\mu^{s}_{inr} = -kT\left(\frac{\partial\ln Q}{\partial N_{ir}}\right)_{B_r,T,N_{jr}(j\neq i)} = kT\ln\frac{N_{ir}q_{nr_n}}{\left(B_r-\sum_{j=1}^{n-1} N_{jr}\right)q_{ir_i}}$$

$$= \mu_{in} = \mu^{0}_{in} + kT\ln(x_{in}f_{in}). \tag{19}$$

Thus, the mole fraction of the i-th component adsorbed on the r-th sites is equal to:

$$x_{ir}^{s}=\frac{N_{ir}}{B_{r}}=\frac{K_{inr}x_{in}f_{in}}{1+\sum\limits_{j=1}^{n-1}K_{jnr}x_{jn}f_{jn}},\tag{20}$$

where

$$K_{inr}=\frac{q_{ir_i}}{q_{nr_n}}\exp\left(\frac{\mu_{in}^{0}}{kT}\right)=\frac{J_{ir_i}(T)}{J_{nr_n}(T)}\exp\left(\frac{\mu_{in}^{0}}{kT}\right)\exp\left(\frac{\varepsilon_{ir_i}-\varepsilon_{ir_n}}{kT}\right).\tag{21}$$

Consequently, the total mole fraction of the i-th component is given by:

$$x_{i,t}^{s}=\frac{N_{i}}{B}=\sum_{r}\frac{B_{r}}{B}x_{ir}^{s}=\sum_{r}g_{r}x_{ir}^{s},\tag{22}$$

where $g_r = B_r/B$ is the fraction of the r-th type of adsorption sites. Replacing the discrete distribution of adsorption energies by a continuous one we get:

$$x_{i,t}^{s}=\int\limits_{\Delta n}x_{i}^{s}(x,\varepsilon)F(\varepsilon)\mathrm{d}\varepsilon,\tag{23}$$

where Δn is the n-dimensional integration range, $x=(x_1,x_2,\ldots,x_n)$, however, $F(\varepsilon)$ is the n-dimensional distribution function of adsorption energies.

Taking into account the competitive character of adsorption from solutions, the global integral Eq. (23) may be expressed in terms of the differences of adsorption energies for the i-th component and the n-th reference component [12]:

$$\begin{aligned}x_{i,t}^{s}=\int\limits_{\Delta n^{*}}&x_{i}^{s}(x_{1n},x_{2n},\ldots,x_{n-1,n},\varepsilon_{1n},\varepsilon_{2n},\ldots,\varepsilon_{n-1,n})\\&\cdot F^{*}(\varepsilon_{1n},\varepsilon_{2n},\ldots,\varepsilon_{n-1,n})\mathrm{d}\varepsilon_{1n}\mathrm{d}\varepsilon_{2n}\cdots\mathrm{d}\varepsilon_{n-1,n}.\end{aligned}\tag{24}$$

Above, Δn^{*} is the $(n-1)$-dimensional integration range, $\varepsilon_{in}=\varepsilon_i-\varepsilon_n$, and

$$F^{*}(\varepsilon_{1n},\varepsilon_{2n},\ldots,\varepsilon_{n-1,n})=\int\limits_{\Delta n}F(\varepsilon_{1n}+\varepsilon_{n},\varepsilon_{2n}+\varepsilon_{n},\ldots,\varepsilon_{n-1,n}+\varepsilon_{n},\varepsilon_{n})\mathrm{d}\varepsilon_{n}.$$

The thermodynamic functions that characterize adsorption from a n-component solution on an energetically heterogeneous surface may be expressed as follows:

$$\Delta A_{n}=BkT\int\limits_{\Delta n}\left[\frac{1}{kT}\sum_{i=1}^{n-1}(x_{i}^{s}\mu_{in})+\ln\left(1-\sum_{i=1}^{n-1}x_{i}^{s}\right)-\ln q_{n}\right]F(\varepsilon)\mathrm{d}\varepsilon;\tag{25}$$

$$\Delta E_{n}=BkT^{2}\int\limits_{\Delta n}\left[\sum_{i=1}^{n}x_{i}^{s}\frac{\partial\ln J_{i}(T)}{\partial T}-\sum_{i=1}^{n}x_{i}^{s}\frac{\varepsilon_{i}}{kT^{2}}\right]F(\varepsilon)\mathrm{d}\varepsilon;\tag{26}$$

$$\Delta S_{n}^{nc}=BkT\int\limits_{\Delta n}\left[\sum_{i=1}^{n}x_{i}^{s}\frac{\partial\ln J_{i}(T)}{\partial T}-\sum_{i=1}^{n}x_{i}^{s}\ln J_{i}(T)\right]F(\varepsilon)\mathrm{d}\varepsilon;\tag{27}$$

$$\Delta S_{n}^{c}=-Bk\int\limits_{\Delta n}\sum_{i=1}^{n}x_{i}^{s}\ln x_{i}^{s}F(\varepsilon)\mathrm{d}\varepsilon.\tag{28}$$

Results and Discussion

In order to analyse the effect of various parameters and adsorbent heterogeneity on changes in the thermodynamic functions that characterize adsorption from solutions, extensive model investigations were performed. These studies were made for two special cases of adsorption systems – from binary and ternary liquid mixtures.

First, let us discuss the results of model calculations performed for binary solutions. To perform the calculations, Eqs. (25)–(28) were presented as sums of the terms linearly-dependent on the mole composition of the surface phase (e.g., $x^s_{1,t}$) and the terms nonlinearly-dependent on this composition:

$$\frac{\Delta A_2}{BkT} = -\left\{x^s_{1,t}\left[\ln J_1(T) + \frac{\bar{\varepsilon}_1}{kT}\right] + (1 - x^s_{1,t})\left[\ln J_2(T) + \frac{\bar{\varepsilon}_2}{kT}\right]\right\}$$
$$-\iint_{\Delta 2}\left[x^s_1\left(\frac{\varepsilon_1 - \bar{\varepsilon}_1}{kT}\right) + (1 - x^s_1)\left(\frac{\varepsilon_2 - \bar{\varepsilon}_2}{kT}\right) - x^s_1 \ln x^s_1 - x^s_2 \ln x^s_2\right]F(\varepsilon_1, \varepsilon_2)\mathrm{d}\varepsilon_1 \mathrm{d}\varepsilon_2; \quad (29)$$

$$\frac{\Delta E_2}{BkT} = -\left\{x^s_{1,t}\left[\frac{\bar{\varepsilon}_1}{kT} - \frac{\partial \ln J_1(T)}{\partial \ln(T)}\right] + (1 - x^s_{1,t})\left[\frac{\bar{\varepsilon}_2}{kT} - \frac{\partial \ln J_2(T)}{\partial \ln(T)}\right]\right\}$$
$$-\iint_{\Delta 2}\left[x^s_1\left(\frac{\varepsilon_1 - \bar{\varepsilon}_1}{kT}\right) + (1 - x^s_1)\left(\frac{\varepsilon_2 - \bar{\varepsilon}_2}{kT}\right)\right]F(\varepsilon_1, \varepsilon_2)\mathrm{d}\varepsilon_1 \mathrm{d}\varepsilon_2; \quad (30)$$

$$\frac{T\Delta S^{nc}_2}{BkT} = \left\{x^s_{1,t}\left[\ln J_1(T) + \frac{\partial \ln J_1(T)}{\partial \ln(T)}\right] + (1 - x^s_{1,t})\left[\ln J_2(T) - \frac{\partial \ln J_2(T)}{\partial \ln(T)}\right]\right\}; \quad (31)$$

$$\frac{T\Delta S^c_2}{BkT} = -\iint_{\Delta 2}\left[x^s_1 \ln x^s_1 + (1 - x^s_1)\ln(1 - x^s_1)\right]F(\varepsilon_1, \varepsilon_2)\mathrm{d}\varepsilon_1 \mathrm{d}\varepsilon_2. \quad (32)$$

In order to simplify analysis of the functions given by Eqs. (29)–(32) the linear correlation between adsorption energies for the 1-st and 2-nd components was assumed; i.e.,

$$\frac{\varepsilon_2}{kT} = a + b\left(\frac{\varepsilon_1}{kT}\right). \quad (33)$$

This assumption transforms a bivariate integration in Eqs. (29)–(32) to an integration that depends only on ε_1.

The model calculations were performed for four types of the distribution function of adsorption energy $F(\varepsilon_1)$: square-shaped, symmetrical triangle-shaped, triangle-shaped widened to the right-side, and triangle-shaped widened to the left-side. Besides, it was assumed that all interactions in the system are similar so we can assume that $f_{12} = 1$.

As it results from Eqs. (29)–(32) the quantities $\ln J_i(T)$, $\partial \ln J_i(T)/\partial \ln T$ $(i = 1, 2)$ influence only terms of the thermodynamic functions which depend linearly on $x^s_{1,t}$, however, $J_{12}(T)$ and μ^0_{12}/kT affect the shape of the isotherm $x^s_{1,t}(x^s_1)$. The values of these quantities do not change the behaviour of the terms nonlinearly dependent on $x^s_{1,t}$.

In Fig. 1 the effect of the quantities $\ln J_i(T)$, $\partial \ln J_i(T)/\partial \ln T$ $(i = 1, 2)$, μ^0_{12}/kT and $\bar{\varepsilon}_{12} = \bar{\varepsilon}_1 - \bar{\varepsilon}_2$ on the thermodynamic functions (29)–(32) is presented for a given square-shaped energy distribution function. These quantities have no influence on the dependence of configurational entropy vs. $x^s_{1,t}$ (Eq. 32). For the other thermodynamic functions, it is observed that the terms linearly-dependent on $x^s_{1,t}$

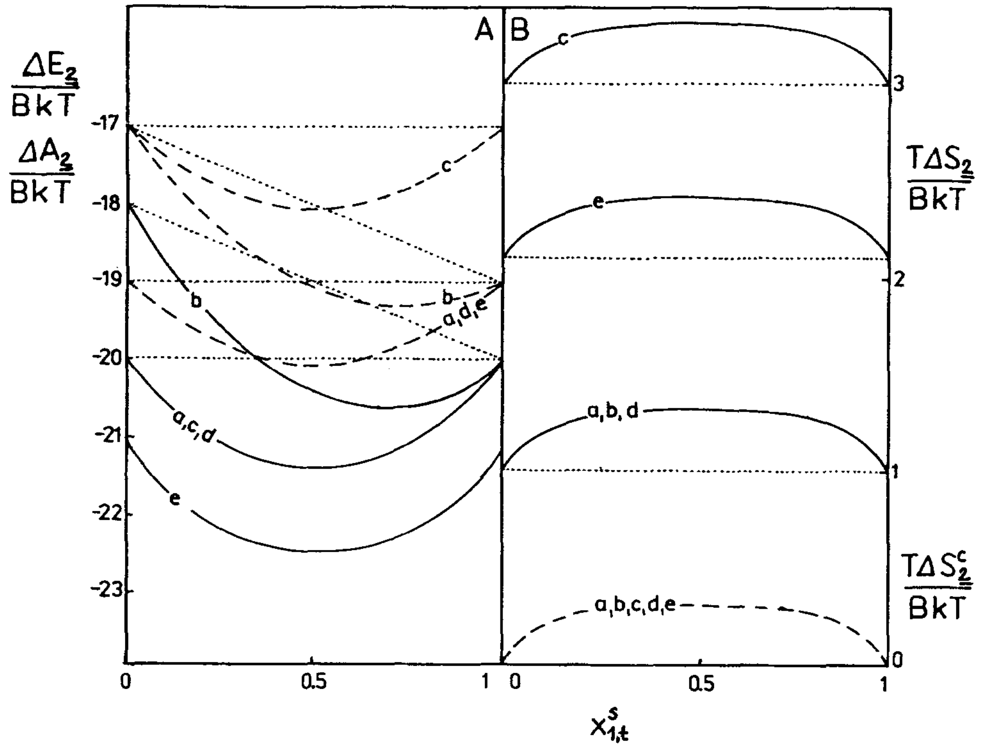

Fig. 1. Effect of the parameters: J_1, J_2, $\partial \ln J_1/\partial \ln T$, $\partial \ln J_2/\ln T$, μ^0_{12}/kT on the behavior of the thermodynamic functions (29)–(32) $\Delta A_2/BkT$ (solid line) and $\Delta E_2/BkT$ (dashed line) (part A) and $T\Delta S_2/BkT$ (solid line) and $T\Delta S^c_2/BkT$ (dashed line) (part B) for a square-shaped energy distribution. The following parameter values were assumed: $\varepsilon_1/kT \in \langle 10, 30\rangle$ for all curves; $J_1 = J_2 = 1$, $\partial \ln J_1/\partial \ln T = \partial \ln J_2/\partial \ln T = 1$, $\mu^0_{12}/kT = 0$, $\varepsilon_2/kT = 10 + 0.5(\varepsilon_1/kT)$, ($\bar{\varepsilon}_1 = \bar{\varepsilon}_2 = 20\,kT$, $\bar{\varepsilon}_{12} = 0$, $\sigma_1 = 5.77$, $\sigma_2 = 2.89 = \sigma_{12}$) (curves a); $\varepsilon_2/kT = 8 + 0.5(\varepsilon_1/kT)(\bar{\varepsilon}_2 = 18\,kT$, $\bar{\varepsilon}_{12} = 2\,kT)$ and the other parameters are as for the curves a (curves b); $\partial \ln J_1/\partial \ln T = \partial \ln J_2/\ln T = 3$ and the other parameters are as for the curves a (curves c); $\mu^0_{12}/kT = 1$ and the other parameters are as for the curves a (curves d); $J_1 = J_2 = 3$ and the other parameters are as for the curves a (curves e). The symbol σ denotes the dispersion of reduced adsorption energy $E = \varepsilon/kT$. The behavior of the linear terms of functions (29)–(32) is marked by dotted lines

change with changing these quantities. An increase in the mean energy difference $\bar{\varepsilon}_{12}$ at a constant $\bar{\varepsilon}_1$ causes a change in the functions $\Delta A/BkT$ and $\Delta E/BkT$ (cf., the curves a and b in Fig. 1). This change may be expressed as follows:

$$h(x^s_{1,t}, \bar{\varepsilon}_{12})_{\bar{\varepsilon}_1} = h(x^s_{1,t}, \bar{\varepsilon}_{12} = 0)_{\bar{\varepsilon}_1} + (1 - x^s_{1,t})\frac{\bar{\varepsilon}_{12}}{kT}, \qquad (34)$$

where

$$h = \Delta A/BkT \quad \text{or} \quad \Delta E/BkT.$$

This effect is not observed for the entropy $T\Delta S/BkT$ (Eqs. 31, 32).

The change in the parameters $J_1(T)$ and $J_2(T)$ influences the linear terms of the functions $\Delta A/BkT$ and $T\Delta S/BkT$ (Eqs. 29, 31, 32); consequently, the dependencies analogous to Eq. (34) are observed (the curves a and c in Fig. 1).

A similar effect is observed for the functions $\Delta E/BkT$ and $T\Delta S/BkT$ (Eqs. 30–32) with a change in the $\partial \ln J_i(T)/\partial \ln T$ ($i = 1, 2$) values (cf., the curves a and e in Fig. 1); however, a change in μ^0_{12}/kT does not cause any changes in the behavior of all thermodynamic functions investigated (cf., the curves a and d in Fig. 1).

In further model investigations the effect of the type of energy distribution function on the behavior of the thermodynamic functions was studied. In these calculations it was assumed for simplicity that:

$$J_1(T) = J_2(T) = 1, \quad \frac{\partial \ln J_1(T)}{\partial \ln T} = \frac{\partial \ln J_2(T)}{\partial \ln T} = 1, \quad \frac{\mu^0_{12}}{kT} = 0.$$

Figure 2 illustrates the influence of the surface heterogeneity on the thermodynamic functions (29)–(32) for a square-shaped energy distribution function. For comparison the functions calculated under the assumption of adsorbent homogeneity are also drawn in Fig. 2. It is easy to see that a heterogeneity increase causes a distinct decrease in the values of the non-linear terms for all thermodynamic functions (29)–(32). Additionally, it ought to be remarked that the behavior of the thermodynamic functions calculated for a homogeneous system is the same as that obtained under the assumption $\bar{\varepsilon}_{12} = const$ (the surface homogeneous with regard to the component exchange).

Analysing the model calculations, one can see that only a distribution function of the energy differences for both solution components controls the behavior of the terms of the thermodynamic functions which depend non-linearity on $x^s_{1,t}$. Thus, it is suitable to present the dependencies (29)–(32) in a form depending on the energy

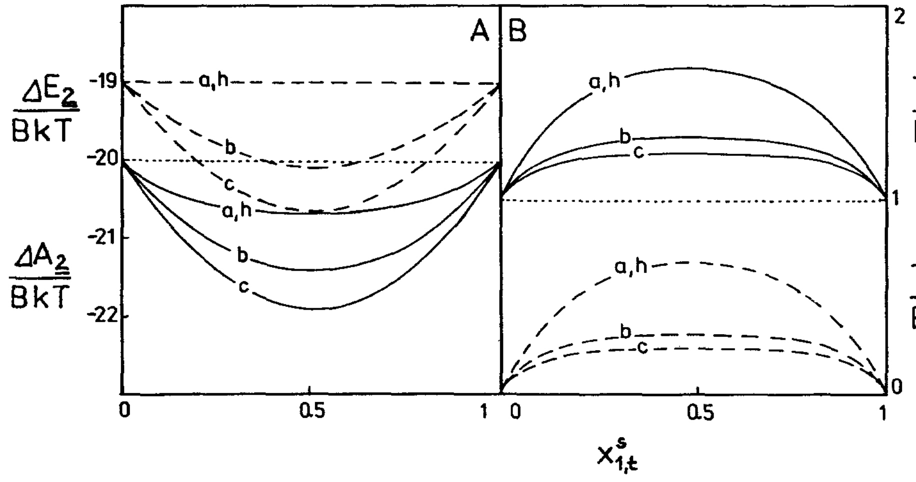

Fig. 2. Effect of the parameters of a square-shaped energy distribution function on the behavior of thermodynamic functions (29)–(32) $\Delta A_2/BkT$ (solid line) and $\Delta E_2/BkT$ (dashed line) (part A) and $T\Delta S_2/BkT$ (solid line) and $T\Delta S^c_2/BkT$ (dashed line) (part B). The following parameter values were assumed: $J_1 = J_2 = 1$, $\partial \ln J_1/\partial \ln T = \partial \ln J_2/\partial \ln T = 1$, $\mu^0_{12} = 0$, $\varepsilon_1/kT \in \langle 10, 30 \rangle$ for all curves; $\varepsilon_2/kT = \varepsilon_1/kT$ ($\bar{\varepsilon}_1/kT = \bar{\varepsilon}_2/kT = 20, \bar{\varepsilon}_{12} = 0, \sigma_1 = \sigma_2 = 5.77, \sigma_{12} = 0$) (curves a); $\varepsilon_2/kT = 10 + 0.5(\varepsilon_1/kT)$ ($\bar{\varepsilon}_1/kT = \bar{\varepsilon}_2/kT = 20$, $\bar{\varepsilon}_{12} = 0$, $\sigma_1 = 5.77$, $\sigma_2 = 2.89$, $\sigma_{12} = 2.89$) (curves b); $\varepsilon_2/kT = 14 + 0.3(\varepsilon_1/kT)$ ($\bar{\varepsilon}_1 = \bar{\varepsilon}_2 = 20\,kT$, $\bar{\varepsilon}_{12} = 0$, $\sigma_1 = 5.77$, $\sigma_2 = 1.73$, $\sigma_{12} = 4.04$ (curves c). For comparison the respective functions for a homogeneous surface are also presented: $\varepsilon_1/kT = \varepsilon_2/kT = 20$ ($\varepsilon_{12} = 0$, $\sigma_{12} = 0$) (curves h). The behavior of the linear terms of functions (29)–(32) is marked by dotted lines

difference ε_{12}. With regard to the following equality:

$$\iint\limits_{\Delta 2}\left[x_1^s\left(\frac{\varepsilon_1-\bar{\varepsilon}_1}{kT}\right)+(1-x_1^s)\left(\frac{\varepsilon_2-\bar{\varepsilon}_2}{kT}\right)\right]F(\varepsilon_1,\varepsilon_2)\mathrm{d}\varepsilon_1\mathrm{d}\varepsilon_2$$
$$=\iint\limits_{\Delta 2}\left[\frac{\varepsilon_{12}-\bar{\varepsilon}_{12}}{kT}\right]x_1^s F(\varepsilon_1,\varepsilon_2)\mathrm{d}\varepsilon_1\mathrm{d}\varepsilon_2. \tag{35}$$

Eqations (29)–(32) may be rewritten as follows:

$$\frac{\Delta A_2}{BkT}=-\left\{x_{1,t}^s\left[\ln J_1(T)+\frac{\bar{\varepsilon}_1}{kT}\right]+(1-x_{1,t}^s)\left[\ln J_2(T)+\frac{\bar{\varepsilon}_2}{kT}\right]\right\}$$
$$-\int\limits_{\Delta 2^*}\left[\frac{\varepsilon_{12}-\bar{\varepsilon}_{12}}{kT}\right]x_1^s(\varepsilon_{12})F^*(\varepsilon_{12})\mathrm{d}\varepsilon_{12}$$
$$+\int\limits_{\Delta 2^*}[x_1^s\ln x_1^s+(1-x_1^s)\ln(1-x_1^s)]F^*(\varepsilon_{12})\mathrm{d}\varepsilon_{12}; \tag{36}$$

$$\frac{\Delta E_2}{BkT}=-\left\{x_{1,t}^s\left[\frac{\bar{\varepsilon}_1}{kT}-\frac{\partial\ln J_1(T)}{\partial\ln(T)}\right]+(1-x_{1,t}^s)\left[\frac{\bar{\varepsilon}_2}{kT}-\frac{\partial\ln J_2(T)}{\partial\ln(T)}\right]\right\}$$
$$-\int\limits_{\Delta 2^*}\left[\frac{\varepsilon_{12}-\bar{\varepsilon}_{12}}{kT}\right]x_1^s(\varepsilon_{12})F^*(\varepsilon_{12})\mathrm{d}\varepsilon_{12}; \tag{37}$$

$$\frac{T\Delta S_2^{nc}}{BkT}=\left\{x_{1,t}^s\left[\ln J_1(T)+\frac{\partial\ln J_1(T)}{\partial\ln(T)}\right]+(1-x_{1,t}^s)\left[\ln J_2(T)-\frac{\partial\ln J_2(T)}{\partial\ln(T)}\right]\right\}; \tag{38}$$

$$\frac{T\Delta S_2^{c}}{BkT}=-\int\limits_{\Delta 2^*}[x_1^s\ln x_1^s+(1-x_1^s)\ln(1-x_1^s)]F^*(\varepsilon_{12})\mathrm{d}\varepsilon_{12}. \tag{39}$$

In Fig. 3 the effect of the energy distribution type on the behavior of the thermodynamic terms dependent non-linearly on $x_{1,t}^s$ is presented. The calculations were performed for two types of symmetrical distributions (square-shaped and symmetrical triangle-shaped) and for two types of asymmetrical functions (triangle-shaped widened to right and left sides) with various widths. These curves were compared with the courses of the respective functions obtained under the assumption of constancy of the energy differences. For a symmetrical distribution function $F^*(\varepsilon_{12})$ the curves symmetrical with respect to the point $x_{1,t}^s=0.5$ are obtained. With an increase in the distribution width (dispersion), the variability range of the function values is increased; see Fig. 3A for $\Delta A_2/BkT$, Fig. 3B for $\Delta E_2/BkT$ and Fig. 3C for $T\Delta S_2^c/BkT$. In the case of an asymmetrical distribution function $F^*(\varepsilon_{12})$, the curves of the thermodynamic functions are asymmetrical with respect to the point $x_{1,t}^s=0.5$. For the function widened to right-side the maximum of function $T\Delta S_2^c/BkT$ (Fig. 3C) is observed over the range of $x^s>0.75$; however for $\Delta E_2/BkT$ (Fig. 3B) and $\Delta A_2/BkT$ (Fig. 3A) the minimum is found over the range $x_{1,t}^s<0.5$. For the function widened to left-side, the extreme of $T\Delta S_2^c/BkT$ is shifted to the range $x_{1,t}^s<0.5$, whereas the extremes of $\Delta E_2/BkT$ and $\Delta A_2/BkT$ are shifted to the range $x_{1,t}^s>0.5$. With an increase in the distribution width, the behavior of the non-linear terms of all functions is similar to that observed for the symmetrical distributions.

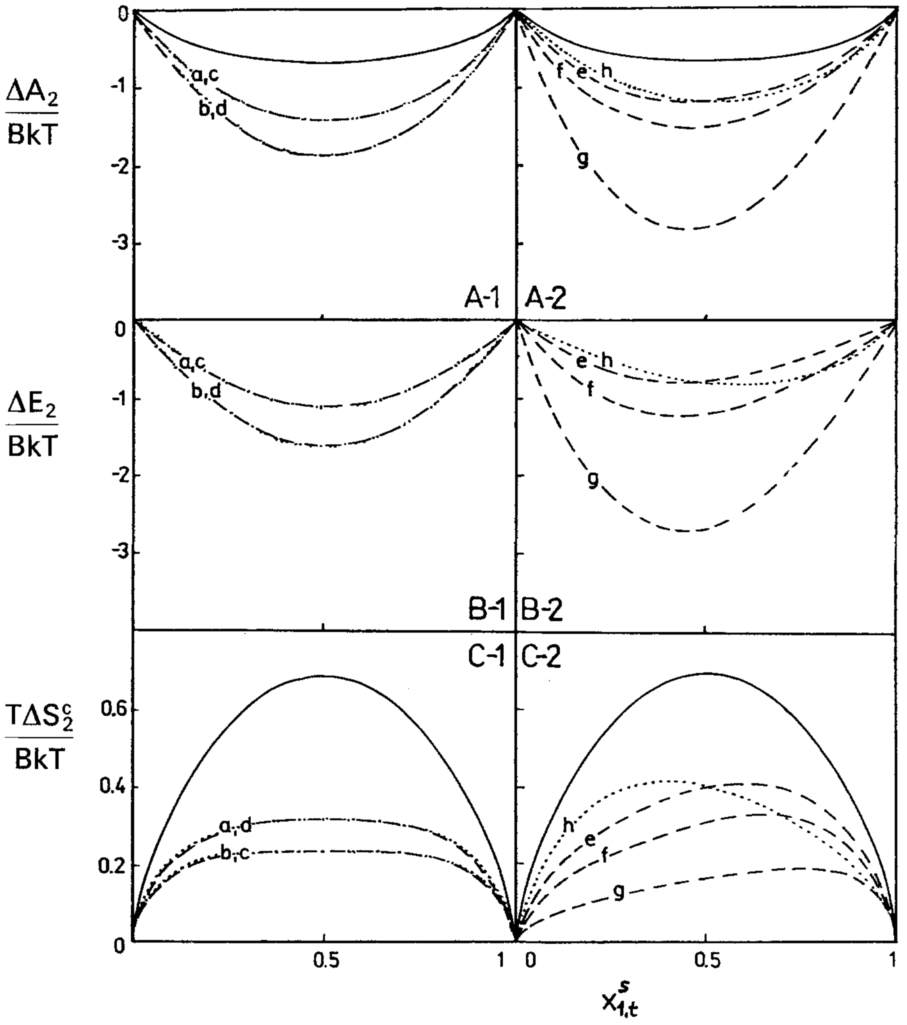

Fig. 3. Effect of type of adsorbent heterogeneity on the behavior of the non-linearly dependent terms for $\Delta A_2/BkT$ (**A**), $\Delta E_2/BkT$ (**B**) and $T\Delta S_2/BkT$ (**C**). Panels A-1, B-1 and C-1 present the results for the square-shaped distribution (---) [$(\varepsilon_{12max} - \varepsilon_{12min})/kT = 10$ and $\sigma_{12} = 2.89$ (*curve a*) and $(\varepsilon_{12max} - \varepsilon_{12min})/kT = 14$ and $\sigma_{12} = 4.04$ (*curve b*)], and for the symmetrical triangle-shaped distribution (···) [$(\varepsilon_{12max} - \varepsilon_{12min})/kT = 10$ and $\sigma_{12} = 2.04$ (*curve c*) and $(\varepsilon_{12max} - \varepsilon_{12min})/kT = 14$ and $\sigma_{12} = 2.86$ (*curve d*)]. The panels A-2, B-2 and C-2 show the results for the triangle-shaped distribution widened to right-side (---) [$(\varepsilon_{12max} - \varepsilon_{12min})/kT = 10$ and $\sigma_{12} = 2.36$ (*curve e*) and $(\varepsilon_{12max} - \varepsilon_{12min})/kT = 14$ and $\sigma_{12} = 3.30$ (*curve f*) and $(\varepsilon_{12max} - \varepsilon_{12min})/kT = 28$ and $\sigma_{12} = 6.60$ (*curve g*)], and for the triangle-shaped distribution widened to left-side (···)[$(\varepsilon_{12max} - \varepsilon_{12min})/kT = 10$ and $\sigma_{12} = 2.36$ (*curve h*)]. The solid lines denote the suitable curves obtained under the assumption of the constancy of the energy difference $\varepsilon_{12} = 0$)

Next, the effect of adsorbent heterogeneity on adsorption was also investigated for the adsorption from ternary solutions. The considerations were performed for the square-shaped energy distribution, and for two types of mutual dependencies between ε_{13} and ε_{23} (the third component is the reference substance).

First, the case of lack of correlation between these energies was analyzed. Thus, When ln J and its derivative equal to unity, Eqs. (29), (30), (32) may be reformulated as follows:

$$\frac{\Delta A_3}{BkT} = -\left[\sum_{i=1}^{3} x_{i,t}^{s}\frac{\bar{\varepsilon}_i}{kT}\right] - \int_{\Delta 3^*}\sum_{i=1}^{2} x_i^s\left(\frac{\varepsilon_{i3}-\bar{\varepsilon}_{i3}}{kT}\right)F^*(\varepsilon_{13})F^*(\varepsilon_{23})\mathrm{d}\varepsilon_{13}\mathrm{d}\varepsilon_{23}$$

$$+\int_{\Delta 3^*}\sum_{i=1}^{3} x_i^s \ln x_i^s F^*(\varepsilon_{13})F^*(\varepsilon_{23})\mathrm{d}\varepsilon_{13}\mathrm{d}\varepsilon_{23}; \tag{40}$$

$$\frac{\Delta E_3}{BkT} = -\left[\sum_{i=1}^{3} x_{i,t}^{s}\left(\frac{\bar{\varepsilon}_i}{kT}-1\right)\right] - \int_{\Delta 3^*}\sum_{i=1}^{2} x_i^s\left(\frac{\varepsilon_{i3}-\bar{\varepsilon}_{i3}}{kT}\right)F^*(\varepsilon_{13})F^*(\varepsilon_{23})\mathrm{d}\varepsilon_{13}\mathrm{d}\varepsilon_{23}; \tag{41}$$

$$\frac{T\Delta S_3^c}{BkT} = -\int_{\Delta 3^*}\sum_{i=1}^{3} x_i^s \ln x_i^s F^*(\varepsilon_{13})F^*(\varepsilon_{23})\mathrm{d}\varepsilon_{13}\mathrm{d}\varepsilon_{23}. \tag{42}$$

At the second stage a linear correlation between ε_{13} and ε_{23} was regarded:

$$\frac{\varepsilon_{13}}{kT} = a + b\left(\frac{\varepsilon_{23}}{kT}\right).$$

Then, the dependencies (29), (30), (32) have the following form:

$$\frac{\Delta A_3}{BkT} = -\left[\sum_{i=1}^{3} x_{i,t}^{s}\frac{\bar{\varepsilon}_i}{kT}\right] - \int_{\Delta 2^*}\sum_{i=1}^{2} x_i^s\left(\frac{\varepsilon_{i3}-\bar{\varepsilon}_{i3}}{kT}\right)F^*(\varepsilon_{23})$$

$$+\int_{\Delta 2^*}\sum_{i=1}^{3} x_i^s \ln x_i^s F^*(\varepsilon_{23})\mathrm{d}\varepsilon_{23}; \tag{43}$$

$$\frac{\Delta E_3}{BkT} = -\left[\sum_{i=1}^{3} x_{i,t}^{s}\left(\frac{\bar{\varepsilon}_i}{kT}-1\right)\right] - \int_{\Delta 2^*}\sum_{i=1}^{2} x_i^s\left(\frac{\varepsilon_{i3}-\bar{\varepsilon}_{i3}}{kT}\right)F^*(\varepsilon_{23})\mathrm{d}\varepsilon_{23}; \tag{44}$$

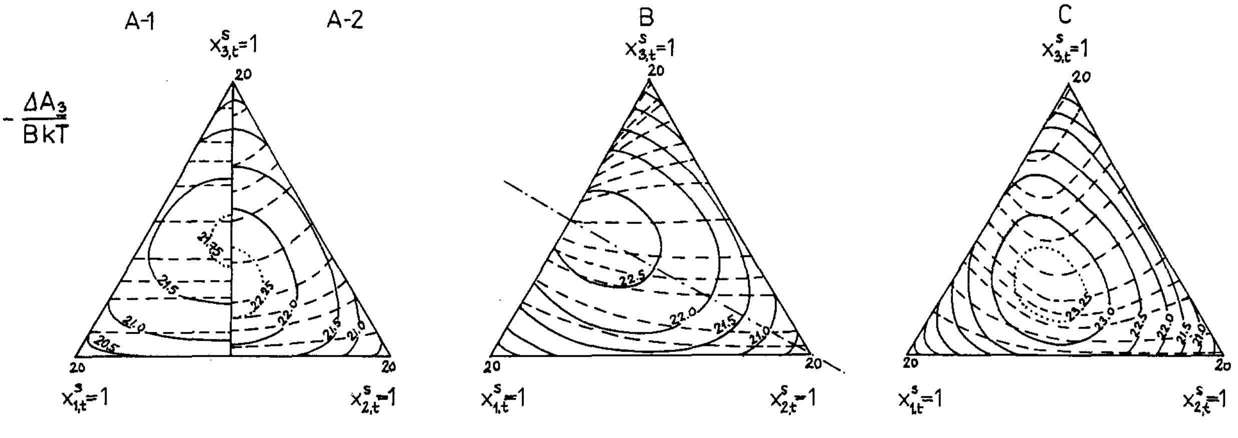

Fig. 4. Dependence of the configurational entropy on the composition of the surface phase for a ternary liquid system with changing composition (——), and with the given values of x_3 and changing values of x_{12} (---). The calculations were performed for a square-shaped distribution of the energy differences. Part **A**: $\varepsilon_{13}/kT \in \langle -5, 5\rangle$, $\varepsilon_{23}/kT \in \langle -5, 5\rangle$ and ε_{13}/kT and ε_{23}/kT correlated linearly (A-1) and ε_{13}/kT and ε_{23}/kT uncorrelated (A-2). Part **B**: $\varepsilon_{13}/kT \in \langle -10, 10\rangle$, $\varepsilon_{23}/kT \in \langle -5, 5\rangle$ and ε_{13}/kT and ε_{23}/kT correlated linearly. Part **C**: $\varepsilon_{13}/kT \in \langle -10, 10\rangle$, $\varepsilon_{23}/kT \in \langle -5, 5\rangle$ and ε_{13}/kT and ε_{23}/kT uncorrelated

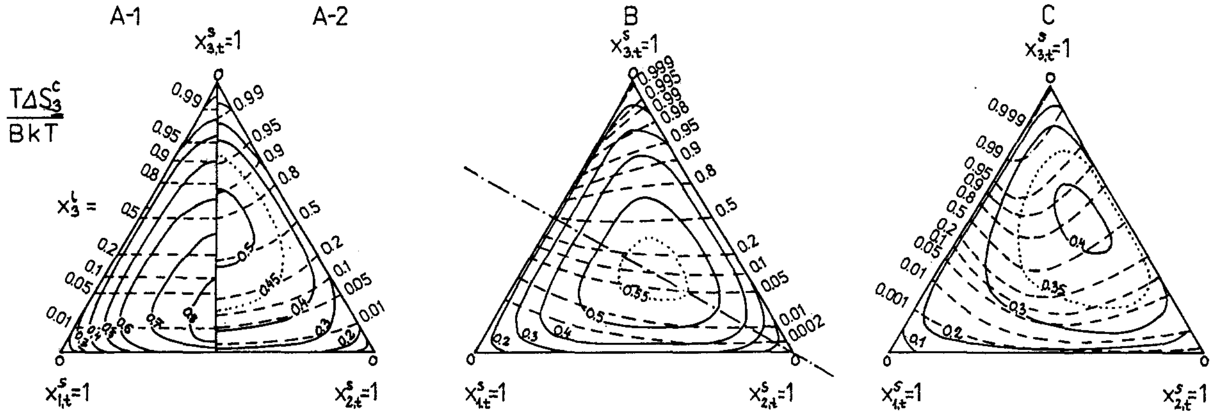

Fig. 5. Dependence of the energy on the composition of the surface phase for a ternary liquid system with changing composition (——), and with the given values of x_3 and changing values of x_{12} (---). The legend is the same as in Fig. 4

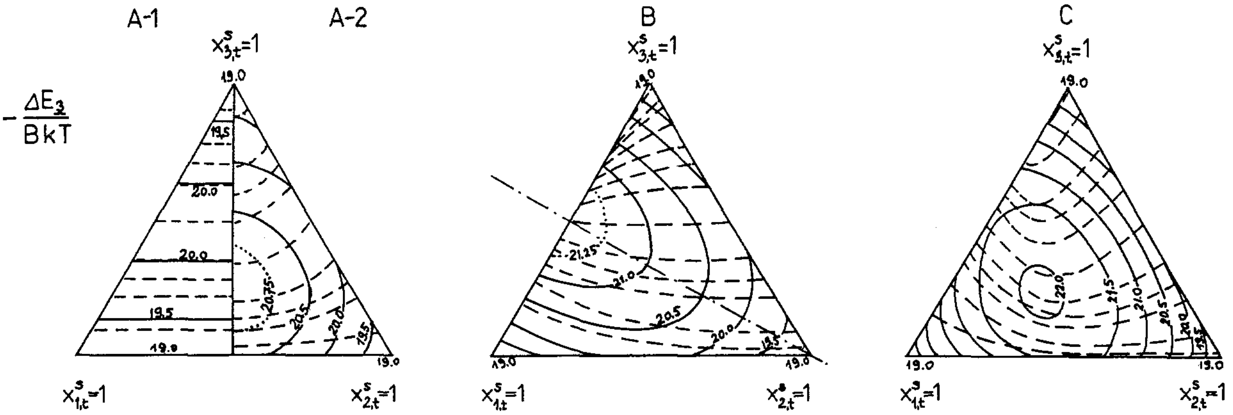

Fig. 6. The dependence of the Helmholtz free energy on the composition of the surface phase for a ternary liquid system with changing composition (——) and with the given values of x_3 and changing values of x_{12} (---). The legend is the same as in Fig. 4

$$\frac{T\Delta S_3^c}{BkT} = -\int_{\Delta 2^*} \sum_{i=1}^{3} x_i^s \ln x_i^s F^*(\varepsilon_{23}) \mathrm{d}\varepsilon_{23}. \qquad (45)$$

Figures 4–6 present the dependencies of the thermodynamic functions (43)–(45) versus the composition of the surface phase for various square-shaped energy distribution and under the assumptions of:

(i) a linear correlation between the energy differences,
(ii) the lack of such correlation.

The calculations were performed for model systems corresponding to the following energy distribution functions: $E_{13}, E_{23} \in \langle -5, 5 \rangle$, and E_{13} and E_{23} are correlated linearly (parts A-1 of Figs. 4–6); $E_{13}, E_{23} \in \langle -5, 5 \rangle$, and E_{13} and E_{23} are not correlated (parts A-2 of Figs. 4–6); $E_{13} \in \langle -10, 10 \rangle$, $E_{23} \in \langle -5, 5 \rangle$, and E_{13} and E_{23} are correlated linearly (parts B of Figs. 4–6); $E_{13} \in \langle -10, 10 \rangle$, $E_{23} \in \langle -5, 5 \rangle$, and E_{13} and E_{23} are not correlated (parts C of Figs. 4–6). The solid lines in Figs. 4–6 represent the changes in the thermodynamic functions for a ternary system with changing composition; however, the dashed lines were obtained by assuming constant values x_3 and changing x_{12}.

Figure 4 presents the changes in the configurational entropy $T\Delta S_3^c/BkT$ under the assumptions given above. In the part A the properties of this function are shown for two above mentioned mutual dependencies between the energy differences. As it might be expected, in the case of the linear correlation between E_{13} and E_{23}, the adsorption system shows greater energetic homogeneity in comparison to the system for which such correlation does not exist. It ought to be remarked that with regard to a symmetry of these dependencies with respect to the exchange of 1-st and 2-nd components, the whole Gibbs triangle may be reconstructed by using its half part. In Fig. 4B the configurational entropy changes are presented for the linearly correlated energy differences. The system is symmetrical with respect to the exchange of 1-st and 3-rd components (the dispersions in the energy differences are identical for the pairs of components 13 and 23); however, Fig. 4C shows the same dependencies as Fig. 4B, but for the uncorrelated energy differences. Similarly as for the system presented in Fig. 4A, a decrease in the configurational entropy in comparison to that shown in Fig. 4B denotes that the energetic heterogeneity is greater for this system.

Analogous dependencies illustrating the changes in the energy $\Delta E_3/BkT$ are presented in Fig. 5. Comparing the curves drawn for the distributions with identical dispersions (Fig. 5A), one can state that the system with a linear correlation between E_{13} and E_{23} is characterized by the deeper minimum energy values in comparison to the system showing a lack of such correlation. Moreover, in the case of the linearly correlated energy differences E_{13} and E_{23} a constancy of the energy function is observed for a constant value of x_3; as a result from Eq. (44) the dispersions of E_{13} and E_{23} are identical. In Figs. 5B and 5C, the energy functions are compared for the systems with the correlated and uncorrelated values of E_{13} and E_{23}, and for the energy distributions with different dispersions. In both cases, the extrema are achieved at the different solution compositions. Similarly as in Fig. 5A, the system for which the energy differences are linearly correlated is characterized by the flattered energy function.

A similar behavior to that shown in Fig. 5 is observed for the Helmholtz free energy $\Delta A_3/BkT$ plotted against the composition of ternary surface phase (Fig. 6). The character of the changes in $\Delta A_3/BkT$ is analogous for all cases considered except the system with identical dispersions for the linearly correlated energy differences (Figs. 5A-1 and 6A-1). Under such assumptions, the energy function is constant for constant values of x_3 (Fig. 5A-1), however, the Helmholtz free energy shows different behavior (Fig. 6A-1). It results from the fact that the Helmholtz free energy function has an additional entropy term in comparison to the energy function (Eqs. 43, 44). This term is responsible for the non-linear changes in the Helmholtz free energy at constant values of x_3.

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