Monatshefte für Chemie 112, 59—71 (1981)

Monatshefte für Chemie

Statistical Thermodynamics of Adsorption from Multicomponent Liquid Mixtures on Heterogeneous Solid Surfaces

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(Received 30 November 1979. Accepted 29 February 1980)

The statistical thermodynamics of adsorption from multicomponent liquid mixtures on heterogeneous solid surfaces is discussed by assuming the cell adsorption model and ideal adsorbed phase.

Two integral representations for the adsorption isotherm are proposed: one based on n-dimensional energy distribution function (i.e., each adsorption site is characterized by adsorption energies of all components), and the other based on distribution of differences of adsorption energies of n-1 components in relation to adsorption energy of the chosen component (i.e., each adsorption site is characterized by n-1 differences of adsorption energies of the components in relation to adsorption energy of the chosen component).

The expressions for differential adsorption heat for adsorption from binary liquid mixtures have been derived from both integral equations.

(Keywords: Adsorption from solutions; Adsorption on heterogeneous surface; Statistical thermodynamics)

Statistische Thermodynamik der Adsorption aus flüssigen Mehrkomponentenmischungen auf heterogenen festen Oberflächen

Die statistische Thermodynamik der Adsorption von aus mehreren Komponenten bestehenden flüssigen Mischungen auf heterogenen festen Oberflächen wird für das Modell der Zellenadsorption bei ideal adsorbierter Phase diskutiert.

Zwei Integraldarstellungen der Adsorptionsisotherme werden vorgeschlagen: eine auf eine n-dimensionale Verteilungsfunktion der Energie gestützte (das heißt, jede Adsorptionsstelle wird durch Adsorptionsenergien von allen Komponenten charakterisiert); die andere basiert auf der Verteilung der Unterschiede von Adsorptionsenergien der n—1-Komponenten in bezug auf die Adsorptionsenergie der ausgewählten Komponente (das heißt, jede Adsorptionsstelle wird durch n—1-Unterschiede charakterisiert. Formeln für differentiale Adsorptionswärmen für die Adsorption aus binären flüssigen Mischungen sind von beiden Integral-Gleichungen abgeleitet worden.

0026-9247/81/0112/0059/$ 02.60

Introduction

In the majority of the theoretical papers concerning adsorption from liquid mixtures, homogeneity of the adsorbent surface has been assumed. Also the classical[1–5] and statistical[6–9] thermodynamics of adsorption from solution was formulated for homogeneous adsorbentes.

Numerous experimental[10,11] and theoretical[12–18] studies have shown that heterogeneity effects play an important role in adsorption from liquid mixtures. *Delmas* and *Patterson*[19], *Siŝkova* and *Erdös*[20,21] saw in the surface heterogeneity of the adsorbent a source of imperfection of surface phase. They suggested that the change of the sign of the excess adsorption isotherm should be associated with surface heterogeneity. Theoretical description of adsorption from binary liquid mixtures on heterogeneous surface, presented in the papers[12–18], bases on an integral equation for the excess or individual adsorption isotherm which was similar to the fundamental integral equation used in the theory of gas adsorption.

In this paper, the integral equation will be discussed in detail in terms of the statistical thermodynamics. Also, the differential heat for adsorption of binary mixtures on heterogeneous surfaces will be derived. The starting point of these considerations is the paper of *Sircar* and *Myers*[7], which deals with statistical thermodynamics of adsorption from liquid mixtures on homogeneous surfaces. Similarly as *Sircar* and *Myers*[7] we assume the cell model for adsorption of binary liquid mixtures on solids and ideality of the adsorbed phase.

Results and Discussion

Adsorption from Binary Liquid Mixtures on Solid Surfaces

The canonical partition function for two-component adsorbed phase on a homogeneous surface may be written as follows[7]:

$$Q = \frac{M!}{N_1!\,(M - N_1)!}\, q_1^{N_1} q_2^{M-N_1} \tag{1}$$

where

$$q_k = J_k(T) \exp\left(\frac{E_k}{k_B T}\right) \tag{2}$$

and

$$M = N_1 + N_2 = const \tag{3}$$

In the above equations M is constant and it denotes the total number of molecules in the adsorbed phase; N_k is the number of molecules of the k-th component in the adsorbed phase; E_k and J_k are adsorption energy and partition function of the isolated adsorbed molecule of the k-th component, respectively; k_B is the *Boltzman* constant, and T is the absolute temperature. Eq. (1) refers to liquid mixtures composed from molecules of equal sizes.

At equilibrium the difference of chemical potentials in the adsorbed phase is equal to the difference of chemical potentials in the bulk phase. Taking into account this condition and calculating from Eq. (1) the difference of chemical potentials in the adsorbed phase, we obtain

$$x_1^s = \frac{K_{12}\,a_{12}}{1 + K_{12}\,a_{12}} \tag{4}$$

where

$$K_{12} = q_{12} \exp\left(\frac{\mu_{12}^{\circ}}{k_B T}\right) = A_{12} \exp\left(\frac{E_{12}}{k_B T}\right) \tag{5}$$

and

$$A_{12} = J_{12} \exp\left(\frac{\mu_{12}^{\circ}}{k_B T}\right) \tag{6}$$

In the above $a_{12} = a_1/a_2$ is the ratio of activities a_1 and a_2, x_i^s is the mole fraction of the i-th component in the adsorbed phase, $q_{12} = q_1/q_2$, $J_{12} = J_1/J_2$ and μ_{12}° is the difference of the standard chemical potentials in the bulk solution. If the activity coefficients $f_k = 1$ $(k = 1, 2)$, Eq. (4) assumes the well-known form:

$$x_1^s = \frac{K_{12}x_{12}}{1 + K_{12}\,x_{12}} \tag{7}$$

where $x_{12} = x_1/x_2$ is the ratio of mole fractions of both components in the bulk phase.

In the general theory of adsorption of binary mixtures on heterogeneous surface, each adsorption site is unambiguously characterized by two energies: $E_{1,ij}$ and $E_{2,ij}$[22].

Let $M_{ij} = M_{1,ij} + M_{2,ij}$ denote the number of the sites having the adsorption energies $E_{1,ij}$ and $E_{2,ij}$, and $\sum\limits_{ij} M_{ij} = \mathrm{N}_1 + \mathrm{N}_2 = \mathrm{M}$ is number of molecules in the adsorbed phase, which assumed to be constant. Moreover $N_{1,ij}$ and $N_{2,ij}$ are assumed to be large numbers. For any distribution $N_{1,ij}$, $N_{2,ij}$ among M_{ij} we have[23, 24]

$$Q_{N_{1,ij}N_{2,ij}} = \\ = \prod_{ij} \frac{M_{ij}!}{N_{1,ij}!\,(M_{ij} - N_{1,ij})!}\, q_{1,i}^{N_{1,ij}}\, q_{2,j}^{M_{ij}-N_{1,ij}} \tag{8}$$

where

$$q_{k,r} = J_k(T) \exp\left(\frac{E_{k,r}}{k_B T}\right) \tag{9}$$

for $k = 1, 2$ and $r = i, j$, respectively.

The total partition function Q is the sum of the partition functions $Q_{N_{1,ij}N_{2,ij}}$. Replacing this sum by the maximum term[23], we can express the difference of chemical potentials of both components $\mu^s_{12,ij}$ for molecules occuping adsorption sites M_{ij} as follows:

$$\frac{\mu^s_{12,ij}}{k_B T} = -\left(\frac{\partial \ln Q}{\partial N_{1,ij}}\right)_{M_{ij},\, T} = \ln \frac{N_{1,ij}\, q_{2,j}}{(M_{ij} - N_{1,ij})\, q_{1,i}} \tag{10}$$

At equilibrium, i.e., when $\mu^s_{12,ij} = \mu_{12}$, we obtain

$$x^s_{1,ij} = \frac{K_{12,ij}\, a_{12}}{1 + K_{12,ij}\, a_{12}} \tag{11}$$

where

$$x^s_{1,ij} = N_{1,ij}/N_{2,ij} \tag{12}$$

and

$$K_{12,ij} = (q_{1,i}/q_{2,j}) \exp\left(\frac{\overset{\circ}{\mu}_{12}}{k_B T}\right) =$$

$$= A_{12} \exp\left(\frac{E_{1,i} - E_{2,j}}{k_B T}\right) = A_{12} \exp\left(\frac{E_{12,ij}}{k_B T}\right) \tag{13}$$

For the whole adsorbent surface we get

$$x^s_{1,\mathrm{t}} = N_1/M = \sum_{ij} N_{1,ij}/M = \sum_{ij} g_{ij}\, x^s_{1,ij} \tag{14}$$

where

$$g_{ij} = M_{ij}/M \tag{15}$$

and $x^s_{1,t} + x^s_{2,t} = 1$.

Generalized Integral Equation in Adsorption from Binary Liquid Mixtures

If the distribution of the adsorption sites is such that the sumation (14) can be replaced by integration, we obtain

$$x^s_{1,t} = \iint_{\Delta_{12}} x^s_1(a_{12}, E_{12})\, G_{12}(E_1, E_2)\, \mathrm{d}E_1\, \mathrm{d}E_2 \tag{16}$$

where $M\, G_{12}(E_1, E_2)\, \mathrm{d}E_1\, \mathrm{d}E_2$ denotes the number of sites with values of adsorption energies from two-dimensional region $(E_1, E_1 + \mathrm{d}E_1)$ ×

$\times$ $(E_2, E_2 + \mathrm{d}E_2)$ i.e., G_{12} is two-dimensional energy distribution normalized to unity:

$$\iint_{\Delta_{12}} G_{12}(E_1, E_2)\,\mathrm{d}E_1\,\mathrm{d}E_2 = 1 \tag{17}$$

Δ_{12} is the two-dimensional integration region.

Eq. (16) may be presented in a more general form

$$x^s_{1,t}(a_1, a_2) = $$

$$= \iint_{\Delta_{12}} x^s_1(a_1, a_2, E_1, E_2)\; G_{12}\;(E_1, E_2)\,\mathrm{d}E_1\;\mathrm{d}E_2 \tag{18}$$

where $x^s_1(a_1, a_2, E_1, E_2)$ is the individual isotherm describing adsorption of binary liquid mixtures on adsorption sites having energies E_1 and E_2. Eq. (18) can be used to describe the adsorption of binary liquid mixtures on heterogeneous surfaces which have arbitrarily distributed adsorption sites on the surface (patchwise or randomly), if for x^s_1 and adsorption isotherm derived for homogeneous surface without interactions between molecules in the adsorbed phase is assumed.

The excess adsorption isotherm for the whole surface $n^e_{1,t}$ is also expressed in integral form, because both terms of this quantity are additive ones. Thus

$$n^e_{1,t} = \iint_{\Delta_{12}} n^e_1 G_{12}\,\mathrm{d}E_1\,\mathrm{d}E_2 = \iint_{\Delta_{12}} (x^s_1 - x_1)\,G_{12}\,\mathrm{d}E_1\,\mathrm{d}E_2 = x^s_{1,t} - x_1 \tag{19}$$

Integral Representation of the Adsorption Isotherm Without Interactions in the Adsorbed Phase

Adsorption from binary liquid mixtures on heterogeneous surfaces, neglecting the interactions between molecules in the adsorbed phase, may be described by a slightly different integral equation.

In this case the local adsorption isotherms (14) or (17) are functions of the difference of adsorption energies E_{12}. Let $H\,(E_{12})$ be distribution function normalized to unity:

$$\int_{\Omega} H\,(E_{12})\,\mathrm{d}E_{12} = 1 \tag{20}$$

where Ω is the range of possible variation of E_{12}. Then, adsorption isotherms $x^s_{1,t}$ and $n^e_{1,t}$ may be expressed by:

$$x^s_{1,t}(a_{12}) = \int_{\Omega} x^s_1(a_{12}, E_{12})\,H(E_{12})\,\mathrm{d}E_{12} \tag{21}$$

or

$$n^e_{1,t}(a_{12}) = \int_{\Omega} n^e_1(a_{12}, E_{12})\, H(E_{12})\, \mathrm{d}E_{12} \tag{22}$$

In the papers[12–18], Eqs. (21) and (22) are used to derive the analytical equations for adsorption isotherms of binary liquid mixtures by using different distributions. In these papers Eq. (4) was applied for the local adsorption isotherm. Numerical studies of Eqs. (21) and (22) showed that these equations described the experimental data considerably better than equations suitable for homogeneous surfaces.

Eqs. (21) and (22) can be obtained from suitable Eqs. (18) and (19). For this purpose let us consider the following transformation of the variables E_1 and E_2:

$$E_2 = E_2 \text{ and } E_{12} = E_1 - E_2 \tag{23}$$

Then, from Eq. (18) we obtain

$$x^s_{1,t}(a_{12}) = \int_{\Omega} x^s_1(a_{12}, E_{12}) \left[\int_{\Delta_2} G_{12}(E_2, E_{12} + E_2)\, \mathrm{d}E_2\right] \mathrm{d}E_{12} \tag{24}$$

where Δ_2 is one-dimensional integration region for E_2.

Defining the distribution function $H(E_{12})$ by the following expression

$$H(E_{12}) = \int_{\Delta_2} G_{12}(E_2, E_{12} + E_2)\, \mathrm{d}E_2 \tag{25}$$

we obtain Eq. (21). In a similar way Eq. (22) may be derived.

Differential Adsorption Heat for Binary Liquid Mixtures

According to *Kiselev* and *Pavlova*[1] the following definition may be written for differential adsorption heats of binary liquid mixtures:

$$q^{dif}_{12} = -\left[\frac{\partial \ln x_{12}}{\partial (1/k_B T)}\right]_{x^s_1} \tag{26}$$

for the local adsorption heat, and

$$Q^{dif}_{12} = -\left[\frac{\partial \ln x_{12}}{\partial (1/k_B T)}\right]_{x^s_{1,t}} \tag{27}$$

for overall adsorption heat.

To calculate Q^{dif}_{12} we propose the modification of *Van Dongen*'s method for adsorption from liquid mixtures[25].

Differentiating Eq. (21) with respect to $(1/k_B T)$ at constant $x^s_{1,t}$, we obtain

$$\int\limits_{\Omega} \left[\frac{\partial x^s_1}{\partial (1/k_B T)}\right]_{x^s_{1,t}} H(E_{12})\,\mathrm{d}E_{12} = 0 \tag{28}$$

The local isotherm x^s_1, expressed by Eq. (7), is the function x_{12}, E_{12} and T. Then

$$\begin{aligned} \mathrm{d}x^s_1 = \left[\frac{\partial x^s_1}{\partial \ln x_{12}}\right]_T \mathrm{d}\ln x_{12} + \\ + \left[\frac{\partial x^s_1}{\partial (1/k_B T)}\right]_{x_{12}} \mathrm{d}(1/k_B T) \end{aligned} \tag{29}$$

For $x^s_1 = \text{const}$, from Eq. (29) we obtain

$$q^{dif}_{12} = \left[\frac{\partial x^s_1}{\partial (1/k_B T)}\right]_{x_{12}} \Bigg/ \left[\frac{\partial x^s_1}{\partial \ln x_{12}}\right]_T \tag{30}$$

However, for $x^s_{1,t} = \mathit{const}$ from Eq. (29) we have

$$\begin{aligned} \left[\frac{\partial x^s_1}{(1/k_B T)}\right]_{x^s_{1,t}} &= -\left[\frac{\partial x^s_1}{\partial \ln x_{12}}\right]_T Q^{dif}_{12} + \left[\frac{\partial x^s_1}{\partial (1/K_B T)}\right]_{x_{12}} = \\ &= (q^{dif}_{12} - Q^{dif}_{12}) \left[\frac{\partial x^s_1}{\partial \ln x_{12}}\right]_T \end{aligned} \tag{31}$$

Substitution of Eq. (31) to (28) leads to the following expression

$$Q^{dif}_{12} = \frac{\displaystyle\int\limits_{\Omega} q^{dif}_{12}(E_{12}, x_{12}, T) \left[\frac{\partial x^s_1}{\partial \ln x_{12}}\right]_T H(E_{12})\,\mathrm{d}E_{12}}{\displaystyle\int\limits_{\Omega} \left[\frac{\partial x^s_1}{\partial \ln x_{12}}\right]_T H(E_{12})\,\mathrm{d}E_{12}} \tag{32}$$

Calculation of q^{dif}_{12} for the adsorption isotherm (4) leads to the expression

$$q^{dif}_{12} = \left[\frac{\partial K_{12}}{\partial (1/k_B T)}\right]_{x^s_1} = -k_B T^2 \frac{\partial \ln A_{12}}{\partial T} + E_{12} \tag{33}$$

Assuming temperature independence of A_{12} (A_{12} is often assumed to be unity), Eq. (33) is reduced to a very simple form:

$$q_{12}^{dif} = E_{12} \tag{34}$$

Applying a similar method to that presented above it is possible to express the adsorption heat Q_{12}^{dif} by means of G_{12}:

$$Q_{12}^{dif} = \frac{\iint\limits_{\Delta_{12}} q_{12}^{dif} \left[\frac{\partial x_1^s}{\partial \ln x_{12}}\right]_T G_{12}(E_1, E_2)\, \mathrm{d}E_1\, \mathrm{d}E_2}{\iint\limits_{\Delta_{12}} \left[\frac{\partial x_1^s}{\partial \ln x_{12}}\right]_T G_{12}(E_1, E_2)\, \mathrm{d}E_1\, \mathrm{d}E_2} \tag{35}$$

It is easy to prove that Eq. (32) is a special case of Eq. (35).

Adsorption from n-Component Liquid Mixtures on Solid Surfaces

Most papers on adsorption from liquid mixtures concern binary solutions. Mainly the studies of *Griazev* and *Kiselev*[26], *Ościk*[27–31] and *Minka* and *Myers*[32] concern the adsorption from multicomponent liquid mixtures on homogeneous surfaces, especially the adsorption from ternary liquid mixtures. These theoretical results were next used to interpret the experimental data obtained by liquid chromatography[33].

In this section, the results obtained for adsorption from binary liquid mixtures will be generalized for adsorption from n-component liquid mixtures on homogeneous and heterogeneous solid surfaces.

In the case of adsorption from n-component liquid mixtures on homogeneous surface the canonical partition function may be expressed in the form:

$$Q = \frac{M!}{\left(\prod\limits_{l=1}^{n-1} N_l!\right)\left(m - \sum\limits_{l=1}^{n-1} N_l\right)!} \left[\prod_{l=1}^{n-1} q_l^{N_l}\right] q_n{}^{M - \sum\limits_{l=1}^{n-1} N_l} \tag{36}$$

where

$$M = \sum_{l=1}^{n} N_l = const \tag{37}$$

The difference of chemical potentials μ_k^s is equal to

$$\mu_k^s - \mu_n^s = \mu_{kn}^s = -k_B T \left(\frac{\partial \ln Q}{\partial N_k} \right)_{M,T,N_{l \neq k}} =$$

$$= k_B T \ln \frac{N_k q_n}{\left(M - \sum_{l=1}^{n-1} N_l \right) q_k}; \text{ for } k = 1, 2, \ldots, n-1 \tag{38}$$

At equilibrium, the difference of chemical potentials for the k-th and n-th components is equal to difference of chemical potentials of these components in the bulk phase.

Eq. (38) gives the following expressions for x_k^s:

$$x_k^s = \frac{K_{kn} a_{kn}}{1 + \sum_{l=1}^{n-1} K_{ln} a_{ln}} \text{ for } k = 1, 2, \ldots, n-1 \tag{39}$$

and

$$x_k^s = \frac{K_{kn} x_{kn}}{1 + \sum_{l=1}^{n} K_{ln} x_{ln}} \text{ for } k = 1, 2, \ldots, n-1 \tag{40}$$

where

$$x_k^s = N_k / M \text{ and } K_{kn} = (q_k / q_n) \exp \left(\frac{\overset{\circ}{\mu}_{kn}}{k_B T} \right) \tag{41}$$

Eqs. (39) and (40) determine the mole fraction of the k-th component in the n-component adsorbed phase. The excess of the k-th component in the adsorbed phase may be calculated by means of the well-known relation[32]:

$$n_k^e = x_k^s - x_k \text{ for } k = 1, 2, \ldots, n-1 \tag{42}$$

In the case of adsorption from n-component liquid mixtures on heterogeneous surfaces the canonical partition function assumes the following form:

$$Q_{N_{1,\mathrm{i}} N_{2,\mathrm{i}} \ldots N_{n,\mathrm{i}}} = \prod_{\mathrm{i}} \frac{M_{\mathrm{i}}!}{\left(\prod_{l=1}^{n-1} N_{l,\mathrm{i}}! \right) \left(M_{\mathrm{i}} - \sum_{l=1}^{n-1} N_{l,\mathrm{i}} \right)!}$$

$$\left[\prod_{l=1}^{n-1} q_{l,i_l}^{N_{l,\mathrm{i}}} \right] q_{n,i_n}^{M - \sum_{l=1}^{n-1} N_{l,\mathrm{i}}} \tag{43}$$

where the vector $\mathfrak{i} = (i_1, i_2, \ldots, i_n)$ characterizes an adsorption site having adsorption energies $\mathfrak{E}_\mathfrak{i} = (E_{1'i_1}, E_{2,i_2}, \ldots, E_{n,i_n})$; $M_\mathfrak{i} = \sum_{l=1}^{n} N_{l,\mathfrak{i}}$ is the total number of adsorption sites characterized by vector $\mathfrak{i}$; $N_{l,\mathfrak{i}}$ is the number of molecules of the l-th component adsorbed on the adsorption sites of the adsorption sites of the $\mathfrak{i}$-th kind; $M = \sum_\mathfrak{i} M_\mathfrak{i}$ is the total number of the adsorption sites on the whole surface and $N_l = \sum_\mathfrak{i} N_{l,\mathfrak{i}}$ is the number of molecules of the l-th component adsorbed on the whole surface.

Let $\mu^s_{k,\mathfrak{i}}$ denote the chemical potential for the k-th component on the adsorption sites of the $\mathfrak{i}$-th kind. Thus, the difference of chemical potentials $\mu^s_{k,\mathfrak{i}}$ and $\mu^s_{n,\mathfrak{i}}$ is given by:

$$\mu^s_{k,\mathfrak{i}} - \mu^s_{n,\mathfrak{i}} = -k_BT\left[\frac{\partial \ln Q}{\partial N_{k,\mathfrak{i}}}\right]_{T,M_\mathfrak{i},N_{l,\mathfrak{i}(l\neq k)}} = k_BT \ln \frac{N_{k,i}q_{n,i_n}}{\left(M_\mathfrak{i} - \sum_{l=1}^{n-1} N_{l,\mathfrak{i}}\right) q_{k,i_k}} \tag{44}$$

At equilibrium, the expression for x^s_k, is analogous to that in (39):

$$x^s_{k,\mathfrak{i}} = \frac{K_{kn,\mathfrak{i}}a_{kn}}{1 + \sum_{l=1}^{n-1} K_{ln,\mathfrak{i}}a_{ln}} \quad \text{for } k = 1, 2, \ldots, n-1 \tag{45}$$

where

$$K_{kn,\mathfrak{i}} = (q^s_{k,i_k}/q^s_{n,i_n}) \exp\left(\frac{\overset{\circ}{\mu}_{kn}}{k_BT}\right) \tag{46}$$

As n-dimensional vector $\mathfrak{E}$ determines an adsorption site, energy distribution characterizing the global adsorbent heterogeneity should be n-dimensional function, i.e., $G_\mathfrak{n}(\mathfrak{E})$. Then, the mole fraction of the k-th component calculated with regard to the whole adsorbent surface is given by:

$$x^s_{k,t} = \int_{\Delta_\mathfrak{n}} x^s_k(\mathfrak{a}, \mathfrak{E})\, G_\mathfrak{n}(\mathfrak{E})\, d\mathfrak{E} \tag{47}$$

where x_k^s is the local adsorption isotherm, Δ_n is the n-dimensional integration region and $\mathfrak{a} = (a_1, a_2, \ldots, a_n)$. For x_k^s Eq. (45) may be assumed.

The adsorption from solution has competitive character, i.e., differences between adsorption energies play an important role in this process. Because the adsorption isotherm $x_k^s(\mathfrak{a}, \mathfrak{E})$ is the function of the n-1 variables E_{kn} $(k = 1, 2, \ldots, n—1)$; introducing a new distribution function

$$H(E_{1n}, E_{2n}, \ldots E_{n-1n}) = \int_{\Delta_n} G_n(E_n, E_{1n} + E_n,\ E_{2n} + E_n, \ldots) \mathrm{d}E_n \tag{48}$$

we obtain

$$x_{k,t}^s = \int_{\Delta^*} x_k^s(a_{1n}, a_{2n}, \ldots, a_{n-1n}, E_{1n}, E_{2n}, \ldots, E_{n-1n}) \times \\ \times H(E_{1n}, E_{2n}, \ldots, E_{n-1n}) \,\mathrm{d}E_{1n}\, \mathrm{d}E_{2n} \ldots \mathrm{d}E_{n-1n} \tag{49}$$

The symbol Δ_n denotes the region of possible variations of $\mathfrak{E}$ whereas Δ^*_n is the $(n—1)$-dimensional integration region.

Generalizing the above considerations it can be stated that we characterize heterogeneity of the adsorbent surface in the case of adsorption from solutions by means of energy differences of the particular components with respect to the chosen component (e.g. n-th component) bringing, purely formally, the description method of adsorption from $(n—1)$-component gas mixture.

Conclusions

Both, excess and individual adsorption isotherms from ideal and slightly nonideal multicomponent liquid mixtures on heterogeneous surfaces may be represented by means of multiple integrals. This form of adsorption isotherm is a general one and it may be used for different models of heterogeneous surfaces if the interactions between molecules adsorbed are neglected, or for patchwise heterogeneous surfaces if the interactions in the adsorbed phase are taken into account. The heterogeneity of the adsorbent surface is characterized by an n-dimensional energy distribution.

The alternative equation describing the adsorption from multicomponent liquid mixtures on heterogeneous surfaces is based on the distribution function of the differences of adsorption energies. In the method surface heterogeneity is characterized with respect to the differences of adsorption energies.

Therefore, the local adsorption isotherm should be the function of the differences of adsorption energies only. This condition is satisfied by the most popular equations, which are used in the theory of liquid mixture adsorption on homogeneous surfaces[7].

Starting from the canonical partition function for completely filled adsorption phase on heterogeneous surface (8), the integral adsorption isotherms (18) and (19), and differential adsorption heat (32) are obtained. Using the well-known definition of thermodynamic functions by means of the canonical partition function the *Helmholtz* free energy and entropy for adsorption of multicomponent liquid mixtures on heterogeneous surfaces can be easily obtained.

Acknowledgment

This research was supported by Polish Academy of Sciences, project No. 03.10.6.03.03.

References

[1] *A. V. Kiselev* and *L. F. Pavlova*, Izv. Akad. Nauk. SSSR, otd. khim. nauk **12**, 212 (1962).

[2] *S. G. Ash*, *R. Brown*, and *D. H. Everett*, J. Chem. Soc. Faraday Trans. I **71**, 123 (1975).

[3] *C. E. Brown*, *D. H. Everett*, and *C. J. Morgan*, J. Chem. Soc. Faraday Trans. I **71**, 883 (1975).

[4] *A. I. Rusanov* and *F. M. Kuni*, Dokl. Akad. Nauk SSSR, otd. khim. nauk. **176**, 876 (1967).

[5] *S. Sircar*, *J. Novosad*, and *A. L. Myers*, Ind. Eng. Chem. Fundam. **11**, 249 (1972).

[6] *S. Ono*, Memoris Fac. Eng. Kynshn. Univ. **12**, 1 (1950).

[7] *S. Sircar* and *A. L. Myers*, J. Phys. Chem. **74**, 2828 (1970).

[8] *C. J. Radke* and *J. M. Prausnitz*, AIChE **18**, 761 (1972).

[9] *C. J. Radke* and *J. M. Prausnitz*, J. Chem. Phys. **57**, 714 (1972).

[10] *M. T. Colphart* and *N. Hackerman*, J. Coll. Interface Sci. **43**, 185 (1973).

[11] *M. T. Colphart* and *N. Hackerman*, J. Coll. Interface Sci. **43**, 176 (1973).

[12] *J. Ościk*, *W. Rudziński*, and *A. Dabrowski*, Chem. Phys. Lett. **20**, 444 (1973).

[13] *J. Ościk*, *A. Dabrowski*, *S. Sokolowski*, and *M. Jaroniec*, J. Catalysis Hokkaido Univ. **23**, 91 (1975).

[14] *J. Ościk*, *A. Dabrowski*, *M. Jaroniec*, and *W. Rudziński*, J. Coll. Interface Sci. **56**, 403 (1976).

[15] *J. Ościk*, *A. Dabrowski*, and *W. Rudziński*, Coll. Polymer Sci. **255**, 50 (1977).

[16] *J. Ościk*, *A. Dabrowski*, *W. Rudzinski*, and *M. Jaroniec*, J. Coll. Interface, in press.

[17] *M. Borówko*, *M. Jaroniec*, *J. Ościk*, and *R. Kusak*, J. Coll. Interface Sci. **69**, 311 (1979).

[18] *M. Borówko*, *M. Jaroniec*, and *W. Rudziński*, Z. phys. Chem. **260**, 1027 (1979).

[19] *G. Delmas* and *D. Patterson*, J. Phys. Chem. **64**, 1827 (1960).

[20] *M. Siškova* and *E. Erdös*, Coll. Czech. Chem. Comun. **25**, 1729 (1960).

[21] *M. Siškova* and *E. Erdös*, Coll. Czech. Chem. Comun. **25**, 2599 (1960).

[22] *M. Jaroniec* and *W. Rudziński*, Surface Sci. **52**, 641 (1975).

[23] *T. L. Hill*, J. Chem. Phys. **17**, 762 (1944).

[24] *M. Jaroniec*, J. Chem. Soc. Faraday Trans. II **73**, 933 (1977).
[25] *R. H. Van Dongen* and *J. C. P. Broeckoff*, Surface Sci. **18**, 462 (1969).
[26] *N. N. Griazev* and *A. V. Kiselev*, Z. Fiz. Khim. SSSR **23**, 158 (1954).
[27] *J. Ościk*, Ann. Soc. Chim. Polonorum **31**, 621 (1957).
[28] *J. Ościk*, Ann. Soc. Chim. Polonorum **34**, 745 (1960).
[29] *J. Ościk*, Bull. Acad. Polon. Sci. ser. chim. **9**, 29 (1961).
[30] *J. Ościk*, Bull. Acad. Polon. Sci. ser. chim. **9**, 33 (1961).
[31] *J. Ościk*, Ann Univ. M. Curie-Skłodowska, Sec. AA **17**, 115 (1962).
[32] *C. Minka* and *A. L. Myers*, AIChE **19**, 453 (1973).
[33] *E. Soczewiński*, Anal. Chem. **41**, 179 (1969).