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Multilayer Adsorption from Multicomponent Liquid Mixtures on Solid Surfaces

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Multilayer adsorption of multicomponent liquid mixtures on homogeneous and heterogeneous solid surfaces is discussed. Heterogeneity effects of the adsorbent surface have been taken into account in calculation of mole fractions of the components in the first adsorbed layer. The model calculations, illustrating multilayer and heterogeneity effects, have been performed for adsorption of ternary liquid mixtures.

(Keywords: Adsorption on heterogeneous surfaces; Multicomponent liquid mixtures; Multilayer liquid adsorption)

Mehrschicht-Adsorption von flüssigen Mehrkomponentenmischungen auf festen Oberflächen

Es wird die Mehrschichtadsorption auf homogenen und heterogenen Oberflächen diskutiert. Bei der Berechnung der Molbrüche der Komponenten der ersten adsorbierten Schicht wurden Heterogenitäts-Effekte berücksichtigt. Die Modellrechnungen wurden an ternären flüssigen Mischungen vorgenommen.

Introduction

In the majority of papers dealing with the theoretical problems of liquid adsorption on solid surfaces, the monolayer adsorption from binary liquid mixtures is discussed[1–3]. So far the monolayer adsorption from multicomponent liquid mixtures[2] and the multilayer or bilayer adsorption from binary liquid mixtures on homogeneous solid surfaces[4–11] have been discussed. The latter indicates that the mixed liquid multilayers formed on the solid surfaces have been studied in a fragmented fashion with regard to the binary liquid mixtures by assuming the energetic homogeneity of the adsorbent surface. However, a full description of liquid adsorption on solid surfaces comprising

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formation of the multicomponent liquid multilayer has probably not been considered.

In this paper, a simple model for multilayer adsorption from multicomponent liquid mixtures on energetically homogeneous and heterogeneous solid surfaces is proposed. For this model analytical equations for adsorption excess and mole fraction of an arbitrary component in the surface phase are necessary. Model calculations, illustrating the contribution of multilayer effects in the total adsorption, have been performed by using the derived equations. Moreover, the influence of adsorbent heterogeneity and nonideality of the bulk solution on adsorbent excess was studied.

General Considerations

Considering r-layer adsorption from m-component liquid mixtures on solid surfaces, we make the following assumptions:

(a) bulk phase is ideal or nonideal,

(b) surface phase is ideal,

(c) molecular sizes of all components are equal,

(d) the total number of molecules contained in each layer of the surface phase is constant, and

(e) adsorbent surface is energetically homogeneous and heterogeneous.

Let n_t^s and $n^{s(k)}$ denote the total number of molecules in the whole surface phase and the k-th adsorbed layer, respectively. Then,

$$n^{s(1)} = n^{s(2)} = \ldots = n^{s(r)} = n^s \tag{1}$$

and

$$n_t^s = \sum_{k=1}^{r} n^{s(k)} = r\, n^s \tag{2}$$

Let us introduce the symbols: $n_i^{(k)}$ for the number of molecules of the i-th component contained in the k-th adsorbed layer and n_i for the total number of molecules of the i-th component in the surface phase. Then,

$$n_i = \sum_{k=1}^{r} n_i^{(k)} \tag{3}$$

and

$$n_t^s = \sum_{k=1}^{r} \sum_{i=1}^{m} n_i^{(k)} = \sum_{k=1}^{r} n^{s(k)} = \sum_{k=1}^{r} n^s = r\, n^s \tag{4}$$

According to this notation, the mole fraction of the i-th component in the surface phase, y_i is defined as follows:

$$y_i = \frac{n_i}{n_t^s} = \frac{1}{r}\sum_{k=1}^{r}\frac{n_i^{(k)}}{n^s} = \frac{1}{r}\sum_{k=1}^{r}\theta_i^{(k)} \tag{5}$$

where $\theta_i^{(k)}$ is the mole fraction of the i-th component in the k-th adsorbed layer.

The values y_i and $\theta_i^{(k)}$ fulfil self — evident dependences:

$$\sum_{i=1}^{m} y_i = 1 \tag{6}$$

$$\sum_{i=1}^{m} \theta_i^{(k)} = 1 \tag{7}$$

The adsorption excess of the i-th component may be defined with regarding to the k-th adsorbed layer as well as to the whole surface phase. In the first case we shall use the symbol $n_i^{e(k)}$ for the adsorption excess of the i-th component, whereas, in the other case the symbol n_i^e will be applied. The adsorption excesses n_i^e and $n_i^{e(k)}$ are defined as follows:

$$n_i^e = n_t^s(y_i - x_i) \tag{8}$$

and

$$n_i^{e(k)} = n^s(\theta_i^{(k)} - x_i) \tag{9}$$

where x_i is the mole fraction of the i-th component in the bulk phase, i.e.,

$$\sum_{i=1}^{m} x_i = 1 \tag{10}$$

Replacing in Eq. (8) y_i by Eq. (5), n_t^s by Eq. (2) and taking into consideration Eq. (9), we obtain:

$$n_i^e = \sum_{k=1}^{r} n_i^{e(k)} \tag{11}$$

Moreover, the adsorption excesses n_i^e and $n_i^{e(k)}$ fulfil the following relationships:

$$\sum_{i=1}^{m} n_i^{e(k)} = 0 \tag{12}$$

and

$$\sum_{i=1}^{m} n_i^e = 0 \tag{13}$$

Validity of the relationships expressed by Eqs. (12) and (13) results from Eqs. (6), (7), and (10).

Adsorption on Homogeneous Solid Surfaces

Let us consider some exchange reactions for the process of r-layer adsorption from m-component liquid mixtures. We assume in our considerations that adsorption of the m-th component is the smallest, whereas, adsorption of the 1-st component is the highest. In the other words, adsorption of the succesive components from 1 to m decreases gradually. So, the adsorption process may be considered as a process of the displacing of the weakest component by remaining ones. For the r-th layer, which is the last adsorbed layer, the following exchange reactions may be written:

$$i^{(b)} + m^{(r)} \rightleftarrows i^{(r)} + m^{(b)} \quad \text{for } i = 1, 2, \ldots, m-1 \tag{14}$$

The superscript (b) refers to the bulk phase. The equilibrium constant of this reaction is given by:

$$K_{im}^{(r)} = \frac{\theta_i^{(r)} a_m}{\theta_m^{(r)} a_i} \quad \text{for } i = 1, 2, \ldots, m-1 \tag{15}$$

where

$$a_i = f_i x_i \quad \text{for } i = 1, 2, \ldots, m \tag{16}$$

and f_i is the activity coefficient of the i-th component in the bulk phase. The similar exchange reactions to those expressed by Eq. (14) may be written for each adsorbed layer. Thus, the equilibrium constant, $K_{im}^{(k)}$, describing the transition of a molecule of the i-th component from the $(k+1)$-layer to the k-th adsorbed layer, is defined as follows:

$$K_{im}^{(k)} = \frac{\theta_i^{(k)} \theta_m^{(k+1)}}{\theta_m^{(k)} \theta_i^{(k+1)}} \quad \begin{array}{l}\text{for } i = 1, 2, \ldots, m-1\\ \text{and } k = 1, 2, \ldots, r\end{array} \tag{17}$$

Comparing Eq. (17) for $k = 1$ with Eq. (15), we obtain a formal expression for activity of the i-th component:

$$a_i = \theta_i^{(r+1)} \quad \text{for } i = 1, 2, \ldots, m \tag{18}$$

A simple transformation of Eq. (17) gives:

$$\theta_{im}^{(k)} = K_{im}^{(k)} \theta_{im}^{(k+1)} \tag{19}$$

where

$$\theta_{im}^{(k)} = \theta_i^{(k)} / \theta_m^{(k)} \tag{20}$$

Basing on Eq. (19) we can written:

$$\left[\sum_{i=1}^{m-1} \theta_i^{(k)}\right] / \theta_m^{(k)} = (1-\theta_m^{(k)}) / \theta_m^{(k)} = \sum_{i=1}^{m-1} K_{im}^{(k)} \theta_{im}^{(k+1)} \tag{21}$$

After a simple algebra Eq. (21) gives:

$$\theta_m^{(k)} = 1 \Big/ \left[1 + \sum_{i=1}^{m-1} K_{im}^{(k)} \theta_{im}^{(k+1)} \right] \tag{22}$$

However, substituting Eq. (22) to Eq. (19) we obtain the following expression for the mole fraction of the i-th component in the k-th adsorbed layer:

$$\theta_i^{(k)} = K_{im}^{(k)} \theta_{im}^{(k+1)} \Big/ \left[1 + \sum_{j=1}^{m-1} K_{jm}^{(k)} \theta_{jm}^{(k+1)} \right] \tag{23}$$

On the other hand, combining Eqs. (15) and (19) we have:

$$\theta_{im}^{(k)} = L_{im}^{(k)} a_{im} \tag{24}$$

where

$$L_{im}^{(k)} = \prod_{l=k}^{r} K_{im}^{(l)} \tag{25}$$

and

$$L_{im}^{(r)} = K_{im}^{(r)} \tag{26}$$

Eqs. (23) and (24) lead to the following expression for $\theta_i^{(k)}$:

$$\theta_i^{(k)} = L_{im}^{(k)} a_{im} \Big/ \left[1 + \sum_{j=1}^{m-1} L_{jm}^{(k)} a_{jm} \right] \tag{27}$$

The constant $L_{im}^{(k)}$ characterizes the exchange of a molecule of the i-th component from the bulk phase with a molecule of the m-th component from the k-th adsorbed layer.

According to Eqs. (5) and (27) the mole fraction of the i-th component in the surface phase is expressed as follows:

$$y_i = \frac{1}{r} \sum_{k=1}^{r} \left[L_{im}^{(k)} a_{im} \Big/ \left(1 + \sum_{j=1}^{m-1} L_{jm}^{(k)} a_{jm} \right) \right] \tag{28}$$

Eq. (28) is true for ideal surface phase and nonideal bulk phase. Replacing in them the ratio a_{im} by x_{im} we obtain the expression for adsorption from ideal bulk phase.

A special case of Eq. (28) is the expression for multilayer adsorption from binary liquid mixtures; it is:

$$y_i = \frac{1}{r} \sum_{k=1}^{r} [L_{12}^{(k)} a_{12} / (1 + L_{12}^{(k)} a_{12})] \tag{29}$$

Replacing in Eq. (8) the mole fraction y_i by Eq. (28) we obtain the expression for the adsorption excess of the i-th component. Analogous expression may be obtained by means of Eq. (29) for adsorption of binary liquid mixtures on homogeneous solid surfaces.

Adsorption on Heterogeneous Solid Surfaces

According to the studies of many authors concerning the multilayer adsorption of gases on heterogeneous solid surfaces[12] we assume that the adsorbent heterogeneity has a significant influence on the formation of the first layer. The equilibrium constant $K^{(1)}_{im}$ is a function of difference of the adsorption energies of the i-th and m-th components[3]. Thus, the numerical value of this constant depends on the type of adsorption site. For the s-th type of adsorption sites the mole fraction y_i may be expressed as follows:

$$y_{i,s} = \frac{1}{r}\theta^{(1)}_{i,s} + \frac{1}{r}\sum_{k=2}^{r}\theta^{(k)}_{i} \tag{30}$$

where

$$\theta^{(1)}_{i,s} = L^{(1)}_{im,s}a_{im} \Big/ \left(1 + \sum_{j=1}^{m-1} L^{(1)}_{jm,s}a_{jm}\right) \tag{31}$$

and the superscript s at the symbols $\theta^{(1)}_{i}$ and $L^{(1)}_{im}$ refers to the s-th type of adsorption sites. In Eq. (30) the first term depends on the type of adsorption sites, whereas, the other term, describing the adsorption in second and higher layers is independent on heterogeneity of the adsorbent surface.

Let h_s denotes the fraction of adsorption sites of the s-th type. Then,

$$\sum_{s=1}^{S} h_s = 1 \tag{32}$$

and

$$y_{i,t} = \sum_{s=1}^{S} h_s y_{i,s} = \frac{1}{r}\sum_{s=1}^{S} h_s\theta^{(1)}_{i,s} + \frac{1}{r}\sum_{k=2}^{r}\theta^{(k)}_{i} \tag{33}$$

where $y_{i,t}$ is the mole fraction of the i-th component for a heterogeneous surface, and S the total number of types of adsorption sites. The expression,

$$\theta^{(1)}_{i,t} = \sum_{s=1}^{S} h_s\theta^{(1)}_{i,s} \tag{34}$$

appearing in Eq. (33), describes the monolayer adsorption of the i-th component on a heterogeneous surface. Thus, for $\theta^{(1)}_{i,t}$ the analytical equations derived for monolayer adsorption from multicomponent liquid mixtures on energetically heterogeneous surfaces may be applied[13, 14].

It follows from the papers[13, 14] that for $\theta^{(1)}_{i,t}$ the following equation may be used:

$$\theta^{(1)}_{i,t} = \frac{(\bar{L}^{(1)}_{im} a_{im})^{\nu}}{1 + \sum_{j=1}^{m-1} (\bar{L}^{(1)}_{jm} a_{jm})^{\nu}} \tag{35}$$

and

$$\theta^{(1)}_{i,t} = \frac{\bar{L}^{(1)}_{i1} a_{im}}{z} \, \frac{(\bar{L}^{(1)}_{1m} z)^{\nu}}{1 + (\bar{L}^{(1)}_{1m} z)^{\nu}} \tag{36}$$

where

$$z = a_{1m} + \sum_{j=2}^{m-1} L^{(1)}_{j1} a_{jm} \tag{37}$$

The constant $\bar{L}^{(1)}_{jm}$ is an average value of $L^{(1)}_{im,s}$ for $s = 1, 2, \ldots, S$, whereas, the parameter ν is a measure of energetic heterogeneity of the adsorbent surface.

Experimental studies for adsorption of binary liquid mixtures show that parameter ν assume very often the values from zero to unity. For $\nu = 1$ Eqs. (36) and (37) reduce to the expression derived for a homogeneous surface.

Substituting Eqs. (36) and (37) to Eq. (33), and expressing in a full form the quality of the i-th component adsorbed in the second and higher layers, we obtain:

$$y_{i,t} = \frac{1}{r} \frac{(\bar{L}^{(1)}_{im} a_{im})^{\nu}}{1 + \sum_{j=1}^{m-1} (\bar{L}^{(1)}_{jm} a_{jm})^{\nu}} + \frac{1}{r} \sum_{k=2}^{r} \frac{L^{(k)}_{im} a_{im}}{1 + \sum_{j=1}^{m-1} L^{(k)}_{jm} a_{jm}} \tag{38}$$

and

$$\begin{aligned} y_{i,t} &= \frac{1}{r} \frac{\bar{L}^{(1)}_{i1} a_{im}}{z} \frac{(\bar{L}^{(1)}_{1m} z)^{\nu}}{[1 + (\bar{L}^{(1)}_{1m} z)^{\nu}]} + \\ &+ \frac{1}{r} \sum_{k=2}^{r} \frac{L^{(k)}_{im} a_{im}}{1 + \sum_{j=1}^{m-1} L^{(k)}_{jm} a_{jm}} \quad \text{for } i = 1, 2, \ldots, m-1 \end{aligned} \tag{39}$$

The total mole fraction of the i-th component in the 1-st adsorbed layer may be evaluated as follows:

$$\theta^{(1)}_{i,t} = r\, y_{i,t} - \sum_{k=2}^{r} \theta^{(k)}_{i} \tag{40}$$

It follows from Eq. (35) that for two different components "i" and "j" the following relationship is satisfied:

$$\ln\frac{\theta_{i,t}^{(1)}}{\theta_{j,t}^{(1)}} = \nu \ln \bar{L}_{ij}^{(1)} + \nu \ln a_{ij} \tag{41}$$

where

$$\bar{L}_{ij}^{(1)} = \bar{L}_{im}^{(1)} / \bar{L}_{jm}^{(1)} \tag{42}$$

However, Eq. (36) leads to the following relationship:

$$\ln\frac{\theta_{i,t}^{(1)}}{\theta_{j,t}^{(1)}} = \ln \bar{L}_{ij}^{(1)} + \ln a_{ij} \tag{43}$$

Eq. (43) has been obtained from Eq. (36), which was obtained for heterogeneous surfaces of quasi*gaussian* distribution[15].

The identical dependence as Eq. (43) may be obtained from Eq. (31) for homogeneous surfaces.

Taking into account the above arguments and comparing Eqs. (41) and (43) we can conclude that Eq. (41) is more universal in comparison to Eq. (43).

Model Calculations

The model calculations have been performed for ideal ternary liquid mixtures. Figs. 1-3 show the influence of different adsorption parameters, appearing in Eqs. (38) and (39), on the adsorption excess of the 3-rd component. Fig. 1 illustrates the effects connected with formation of the multilayer. The adsorption excess of the 3-rd component in the k-th layer, presented in Figs. 1 and 2 (dashed lines), was calculated according to the following equation:

$$n_3^{e(k)} = n^s \left[\frac{1}{1 + x_{13}\,(L_{13}^{(k)} + L_{23}^{(k)} x_{21})} - x_3\right] \quad \text{for } k = 2, 3, 4 \tag{44}$$

Moreover, we assumed that the constants $L_{j3}^{(k)}$, defining in Eqs. (25) and (26) satisfy the condition:

$$L_{j3}^{(k+1)} / L_{j3}^{(k)} = a = const \quad \text{for } k = 2, 3 \tag{45}$$

In Fig. 1 the total adsorption excess of the 3-rd component in the multilayer, i.e.,

$$n_3^{e(2+3+4)} = n_3^{e(2)} + n_3^{e(3)} + n_3^{e(4)} \tag{46}$$

is also presented (solid lines).

Fig. 1 shows the calculations for $n^s = 1.0$, $x_{21} = 1.0$, $K_{13}^{(2)} = 1.25$, $K_{23}^{(2)} = 1.00$, $a = 1.0$ (Fig. 1a) and 0.9 (Fig. 1b).

For $a = 1$, the constants $L_{13}^{(k)}$ and $L_{23}^{(k)}$ are equal or greater than unity; it means that the 3-rd component adsorbs most weakly. The

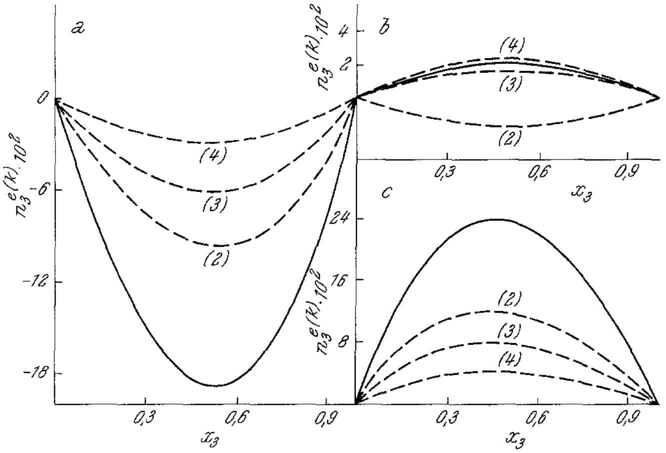

Fig. 1. Theoretical excess adsorption isotherms calculated according to eqs. (44) (dashed lines) and (46) (solid lines). Adsorption parameters are equal to: $n^s = 1.0$, $r = 4$, $x_{21} = 1.0$ and *a* $K_{13}^{(2)} = 1.25$, $K_{23}^{(2)} = 1.0, a = 1.0$; *b* $K_{13}^{(2)} = 1.25$, $K_{23}^{(2)} = 1.0$, $a = 0.9$; *c* $K_{13}^{(2)} = 0.9, K_{23}^{(2)} = 0.8$, $a = 1.0$

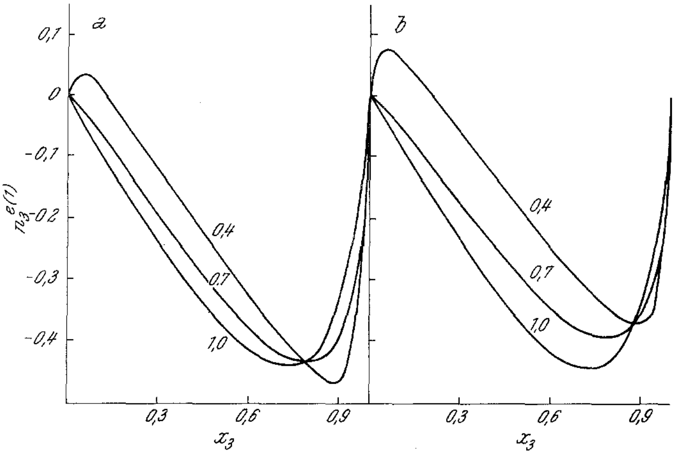

Fig. 2. Theoretical excess adsorption isotherms calculated according to eqs. (35) (part a) and (36) (part b) for $K_{13}^{(1)} = 5.0$, $K_{23}^{(1)} = 4.0$ and different values of ν. The other parameters as in Fig. 1*a*

adsorption excess of this component in a given layer is smaller than zero and increases gradually beginning from the second layer. For $a < 1.0$ this sequence is also satisfied. Additionally, we observe the change of sign of the excess adsorption isotherms $n_3^{e(k)}$ (see Fig. 1*b*): $n_3^{e(2)}$ is smaller than zero, however, $n_3^{e(3)}$ and $n_3^{e(4)}$ are greater than zero in the whole concentration region of x_3.

Fig. 1*c* shows the model calculations for $a = 1.0$ by assuming the parameters $K_{13}^{(2)}$ and $K_{23}^{(2)}$ smaller than unity. Then, the 3-rd component adsorbs strongly than the 1-st and the 2-nd components and the adsorption excesses $n_3^{e(k)}$ for $k = 2$, 3 and 4 are greater than zero in the whole concentration region of x_3. Thus, the sequence of the functions $n_3^{e(k)}(x_3)$ showed in Fig. 1*c* is contrary in comparison to that presented in Fig. 1*a*.

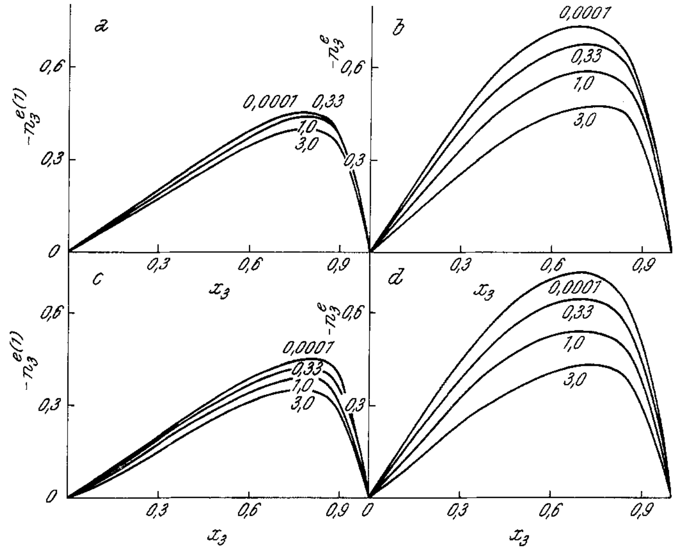

Fig. 3. Theoretical excess adsorption isotherms calculated according to eqs. (35) (part a), (38) (part b), (36) (part c) and (39) (part d) for different values of x_{21}. The parameters are equal to: $n^s = 1.0$, $r = 4$, $a = 1.0$, $K_{13}^{(1)} = 5.0$, $K_{23}^{(1)} = 4.0$, $K_{13}^{(2)} = 1.25$, $K_{23}^{(2)} = 1.0$ and $\nu = 0.7$

Fig. 2 shows the influence of the heterogeneity parameter ν on the adsorption excess of the 3-rd component in the first layer. The numerical calculations have been made according to Eqs. (35) (Fig. 2*a*) and (36) (Fig. 2*b*) for $K_{13}^{(1)} = 5.0$, $K_{23}^{(1)} = 4.0$ and three values of ν: 1.0, 0.7 and 0.4 (other adsorption isotherms parameters as in Fig. 1*a*). Changing the heterogeneity parameter ν from unity (homogeneous surface) to zero we observe a transition of the excess adsorption from the U-type to the S-type. Both equations, (35) and (36), give similar excess adsorption isotherms for different values of ν.

Fig. 3 shows the dependence of $n_3^{e(1)}$ (parts a, c) and n_3^e (parts b, d) upon the value of x_{21}. The model calculations have been made for the adsorption parameters: $\nu = 0.7$, $K_{13}^{(1)} = 5.0$, $K_{23}^{(1)} = 4.0$, $K_{13}^{(2)} = 1.25$,

$K_{23}^{(2)} = 1.0$, $r = 4$, $a = 1.0$ and $n^s = 1.0$. The isotherms showed in Figs. 3*a* and 3*b* were calculated according to Eq. (38), whereas, Figs. 3*c* and 3*d* present the calculations performed by applying Eq. (39). The adsorption isotherm (39) is more sensitive on a change of the value of x_{21} than that expressed by Eq. (38).

The model calculations presented in Figs. 1-3 show that Eqs. (38) and (39) predict different types of the excess adsorption isotherms. This makes Eqs. (38) and (39) attractive equations for the study of multilayer adsorption from multicomponent liquid mixtures on solid surfaces.

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