Correlation Between Data of Adsorption from Binary and Multicomponent Liquid Mixtures on Solid Surfaces

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Seven years ago Minka and Myers (1973) derived an interesting equation for adsorption from n-component liquid mixtures on homogeneous solid surfaces. A special case of this equation, describing adsorption from ideal liquid mixtures composed from molecules of equal sizes, may be written as follows:

$$x^{s}{}_{\perp i(\underline{n})} = \frac{K_{in}x^{l}_{i(\underline{n})}/x^{l}_{n(\underline{n})}}{1 + \sum_{j=1}^{n-1} K_{jn}x^{l}_{j(\underline{n})}/x^{l}_{n(\underline{n})}} \quad \text{for } i = 1, 2, \ldots, n-1 \tag{1}$$

However, the mole fraction of the n-th component in the surface phase is equal to:

$$x^{s}_{n(\underline{n})} = 1/\left(1 + \sum_{j=1}^{n-1} K_{jn}x^{l}_{j(\underline{n})}/x^{l}_{n(\underline{n})}\right) \tag{2}$$

Equations (1) and (2) may be applied for predicting the mole fractions of all components in the multicomponent ideal surface phase by means of the equilibrium constants K_{in} characterizing the adsorption from binary ideal liquid mixtures "$i + n$" on homogeneous solid surfaces.

Ośćik (1961) also proposed an equation for calculating the mole fractions of components in the multicomponent surface phase by means of data obtained for adsorption of binary liquid mixtures. This equation may be written in the following form:

$$x^{s}_{i(\underline{n})} = \left[(2 - n) + \sum_{\substack{j=1 \\ i \neq j}}^{n} (x^{s}_{i(ij)})^{-1}\right]^{-1} \tag{3}$$

Equation (3) has been obtained by assuming the following relationships (see Ośćik, 1961):

$$\frac{x^{l}_{j(\underline{n})}}{x^{l}_{i(\underline{n})}} = \frac{x^{l}_{j(ij)}}{x^{l}_{i(ij)}} \tag{4}$$

and

$$\frac{x^{s}_{j(\underline{n})}}{x^{s}_{i(\underline{n})}} = \frac{x^{s}_{j(ij)}}{x^{s}_{i(ij)}} \quad \text{for } i \neq j \tag{5}$$

In this note it will be shown that assumption (5) results directly from Equation (1). Moreover, Equation (3) will be generalized to adsorption on heterogeneous solid surfaces. Now, we shall prove the assumption (5). Taking into account Equation (1), we obtain:

$$\frac{x^{s}_{j(\underline{n})}}{x^{s}_{i(\underline{n})}} = K_{ji}\frac{x^{l}_{j(\underline{n})}}{x^{l}_{i(\underline{n})}} \tag{6}$$

where

$$K_{ji} = K_{jn}/K_{in} \tag{7}$$

Equation (6) has been introduced and tested experimentally by Dranoff and Lapidus (1957), and Pieroni and Dranoff (1963) who studied ternary ion exchange systems. However, the relationship (7) has been proved by Minka and Myers (1973).

In the case of adsorption from binary liquid mixture "$i + j$", the ratio of $x^{s}_{j(ij)}$ and $x^{s}_{i(ij)}$ is equal to:

$$\frac{x^{s}_{j(ij)}}{x^{s}_{i(ij)}} = \frac{x^{l}_{j(ij)}}{x^{l}_{i(ij)}}K_{ji} \tag{8}$$

From Equations (6) and (8) follows that if the assumption (4) is satisfied, then the relationship (5) is also valid. Thus, Equations (1) and (2) obtained by Minka and Myers (1973) lead to Ośćik's expression (3).

In comparison to Equation (1), Equation (3) seems to be more convenient for practical calculations. According to this equation, the experimental adsorption data for binary liquid mixtures "$i + j$", $x^{s}_{i(ij)}$, may be directly used for evaluating the mole fraction $x^{s}_{i(\underline{n})}$. However, the calculation of $x^{s}_{i(\underline{n})}$ by means of Equation (1) requires of knowledge of the parameters K_{ij}. These parameters may be determined according to Equation (8) by using the experimental adsorption data $x^{s}_{i(ij)}$ vs. $x^{l}_{i(ij)}$. Thus, the calculation procedure of the mole fraction $x^{s}_{i(\underline{n})}$ utilizing Equation (3) is simpler than that based on Equation (1). Moreover, Equation (3) is more general expression in comparison to Equation (1); this conclusion will be demonstrated later.

Recently, Jaroniec (1978) generalized Equations (1) and (2) to adsorption on heterogeneous solid surfaces of quasi-gaussian energy distribution. Equations, derived by Jaroniec (1978), may be written as follows:

$$x^{s}_{i(\underline{n})} = \frac{(\overline{K}_{in}x^{l}_{i(\underline{n})}/x^{l}_{n(\underline{n})})^{m}}{1 + \sum_{j=1}^{n-1} (\overline{K}_{jn}x^{l}_{j(\underline{n})}/x^{l}_{n(\underline{n})})^{m}} \tag{9}$$

and

$$x^{s}_{n(\underline{n})} = 1/\left[1 + \sum_{j=1}^{n-1} (\overline{K}_{jn}x^{l}_{j(\underline{n})}/x^{l}_{n(\underline{n})})^{m}\right] \tag{10}$$

The parameter m, determining the shape of the energy distribution function, is an average parameter characteristic for the whole adsorption system with n-component liquid mixture. For adsorption from binary mixture "$i + j$" we have:

$$x^{s}_{j(ij)} = \frac{(\overline{K}_{ji}x^{l}_{j(ij)}/x^{l}_{i(ij)})^{m_{ij}}}{1 + (\overline{K}_{ji}x^{l}_{j(ij)}/x^{l}_{i(ij)})^{m_{ij}}} \tag{11}$$

and

$$x^{s}_{i(ij)} = 1/[1 + (\overline{K}_{ji}x^{l}_{j(ij)}/x^{l}_{i(ij)})^{m_{ij}}] \tag{12}$$

Similarly as in the case of the parameter m, the parameter m_{ij} characterizes the adsorption of binary liquid mixture "$i + j$" on a given adsorbent surface. Thus, the numerical values of the parameters m and m_{ij} may be different. Equations (9), (11) and (12) generate the following relationships:

$$\left(\frac{x^{s}_{j(\underline{n})}}{x^{s}_{i(\underline{n})}}\right)^{\frac{1}{m}} = \overline{K}_{ji}\frac{x^{l}_{j(\underline{n})}}{x^{l}_{i(\underline{n})}} \tag{13}$$

and

$$\left(\frac{x^{s}_{j(ij)}}{x^{s}_{i(ij)}}\right)^{\frac{1}{m_{ij}}} = \overline{K}_{ji}\frac{x^{l}_{j(ij)}}{x^{l}_{i(ij)}} \tag{14}$$

where

$$\overline{K}_{ji} = \overline{K}_{jn}/\overline{K}_{in} \tag{15}$$

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It follows from the theory of adsorption to heterogeneous solid surfaces (Jaroniec, Patrykiejew, Borówko, 1980) that the constant $\overline{K}_{ij}$ determines the position of quasigaussian distribution function on the energy axis. However, the parameter m_{ij} determines the width of this distribution for adsorption system with liquid mixture "$i + j$", whereas, the parameter m determines the width of this function for adsorption system with $\underline{n}$-component liquid mixture. Thus, the equilibrium constants $\overline{K}_{ij}$ are practically independent upon the heterogeneity parameters m and m_{ij}. It means that the constants $\overline{K}_{ij}$ appearing in Equations (13) and (14) are identical.

Taking into account the assumptions (4) and combining Equations (13) and (14), we get:

$$\frac{x^s_{j(\underline{n})}}{x^s_{i(\underline{n})}} = \left(\frac{x^s_{j(ij)}}{x^s_{i(ij)}}\right)^{m/m_{ij}} \quad \text{for } i \neq j \tag{16}$$

Equation (16) defines the relationship between the mole fractions of the i-th and j-th components in n-component and binary surface phases formed on heterogeneous solid surfaces of quasigaussian energy distribution.

For $m = m_{ij} \neq 1$ Equation (16) reduces to Equation (5); it means that Equation (3) is valid and more general than Equation (1). However, for $m \neq m_{ij}$ we obtain:

$$x^s_{i(\underline{n})} = \left\{1 + \sum_{\substack{j=1\\ i\neq j}}^{n} \left[(x^s_{i(ij)})^{-1} - 1\right]^{m/m_{ij}}\right\}^{-1} \tag{17}$$

The parameters m_{ij} and $\overline{K}_{ij}$ may be determined according to Equation (14) by using the adsorption data for binary liquid mixture "$i + j$". If the parameters m_{ij} for different liquid mixtures "$i + j$" are practically identical, i.e., $m_{ij} = m$ for $i, j = 1, 2, \ldots, n$ and $i \neq j$, then Equation (9) may be used to calculate $x^s_{i(\underline{n})}$. However, Equation (17) should be applied to evaluate $x^s_{i(\underline{n})}$ when the heterogeneity parameters m_{ij}, obtained from adsorption data for binary liquid mixtures "$i + j$" ($i = 1, 2, \ldots, n$ and $i \neq j$) are different. Evaluation of $x^s_{i(\underline{n})}$ by means of Equation (17) requires of knowledge of the parameters m_{ij}, m and the adsorption data $x^s_{i(ij)}$ only. Since the values of $x^l_{i(ij)}$ corresponding to the values of $x^s_{i(ij)}$ are known for suitable liquid mixtures "$i + j$", the mole fractions $x^l_{i(\underline{n})}$ for different components "i" may be determined by means of Equation (4). Practical use of Equation (17) for predicting the adsorption from n-component liquid mixtures is slightly restricted by the parameter m. As it was mentioned above the parameter m characterizes the whole multicomponent adsorption system and it is an average of the parameters m_{ij} describing the adsorption of liquid mixtures "$i + j$". In the first approximation the arithmetic average of the parameters m_{ij} may be assumed for m. Such procedure has a certain substantiation in experimental studies. Namely, the studies of Dabrowski and Jaroniec (1980, 1980), concerning the adsorption of binary liquid mixtures, show that Equation (11) is very useful to interpret the experimental data. It follows from these investigations that for many adsorption systems the parameters m_{ij} lie between the values 0.6 and 1.0.

A more exact studies concerning the relationship between the parameters m and m_{ij} require the experimental data for adsorption from multicomponent and binary liquid mixtures. Unfortunately, the lack of such experimental data for adsorption of multicomponent and binary liquid mixtures satisfying Equations (9) and (11) makes the testing of Equation (17) impossible.

The above discussion shows that Equation (17) seems to be more useful for practical applications than Equation (9); the reasons of this are analogous as in the case of Equations (3) and (1). Moreover, Equation (17) has a most general form. The other equations discussed in this paper are the special cases of Equation (17).

In conclusion we can drawn that Equation (3) is valid for adsorption of liquid mixtures on homogeneous solid surfaces. This equation is also valid for adsorption systems with heterogeneous surface satisfying the condition $m = m_{ij}$. However, for adsorption systems with heterogeneous surface showing $m \neq m_{ij}$ Equation (17) has been desired.

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NOTATION

K_{ji} = equilibrium constant describing the exchange of molecules of the j-th and i-th components in the bulk and surface phases on a homogeneous adsorbent
$\overline{K}_{ji}$ = averaged equilibrium constant K_{ji} for heterogeneous surfaces of quasigaussian energy distribution, determining the position of the distribution function on the energy axis
m = heterogeneity parameter characteristic for adsorption from a given n-component liquid mixture on solid surface, determining the shape of quasigaussian energy distribution
m_{ij} = heterogeneity parameter analogous to m, characteristic for adsorption of binary liquid mixture "$i + j$" on solid surface
n = number of components in liquid mixture
$x_{i(ij)}$ = mole fraction of the i-th component in two-component phase "$i + j$"
$x_{i(\underline{n})}$ = mole fraction of the i-th component in n-component phase

Vectors

$\underline{n}$ = $(1, 2, \ldots, n)$, n-dimensional vector written at symbols referring to n-component liquid mixtures

Superscripts

l = reference to the bulk phase
s = reference to the surface phase

Subscripts

i = component No. i
j = component No. j

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