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Prediction of the Heterogeneity Parameters for Adsorption of Multicomponent Liquid Mixtures on Solids

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With 1 Figure and 1 Table

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Abstract

The theoretical foundations for predicting the heterogeneity parameters for adsorption from multicomponent non-electrolytic mixtures over the entire range of concentrations are discussed. Several experimental systems were studied by using the proposed theoretical description.

1. Prediction of multicomponent adsorption from data of single-vapour adsorption

Description of adsorption process from multicomponent solutions in terms of the theory of localized adsorption on heterogeneous solids may be considerably simplified by assuming the existence of special relations among adsorption energies of the mixture components [1]. Such studies were performed for the case of identity of the energy distribution functions for solution components or under the assumption of the complete lack of correlation among adsorption energies for different substances [1]. In the papers [2, 3] a new idea was presented; according to this idea the adsorption energies of all mixture components change in the same way on different surface sites. Thus, the following dependence between the adsorption energies of the substances "i" and "j" on a site "*" exists:

$$\int_{E_{i,\min}}^{E_i^*} \chi_i(E_i) dE_i = \int_{E_{j,\min}}^{E_j^*} \chi_j(E_j) dE_j = F^* \quad (1)$$

where E_i is the reduced adsorption energy of the i -th component, $\chi_i(E_i)$ is the distribution function of adsorption energies and F is the integral distribution function.

Equation (1) is equivalent to the existence of the following dependence between adsorption energies of the components "i" and "j":

$$E_j = E_j[F(E_i)] = E_j(E_i); \quad E_i = E_i(E_j). \quad (2)$$

Using the dependences (1) and (2) we may formulate the following form of the well-known integral equation which describes the adsorption from n -component liquid mixture on a heterogeneous solid [1]:

$$x_{i,t}^s = \int_0^1 \frac{K_{0i} x_i^l \exp [E_i(F)]}{\sum_{j=1}^n K_{0j} x_j^l \exp [E_j(F)]} dF, \quad (3)$$

$$\sum_{i=1}^n x_i^l = 1 \quad i = 1, 2, \dots, n.$$

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Above, $x_{i,t}^s$ is the mole fraction of the i -th component in the surface phase, x_i^l is the mole fraction of this component in the bulk phase, and K_i is the equilibrium constant connected with adsorption energy ε :

$$K_i = K_{0i} \exp(E_i) \quad E_i = \varepsilon_i/RT \quad (4)$$

where K_{0i} is the entropy factor and ε_i is the adsorption energy of the i -th component.

Defining the deviation of reduced adsorption energy E_i from the mean energy \bar{E}_i as follows:

$$z_i(F) = E_i(F) - \bar{E}_i \quad \bar{E}_i = \int_0^1 E_i(F) dF. \quad (5)$$

we obtain another form of the integral eq. (3):

$$x_{i,t}^s = \int_0^1 \frac{K_i x_i^l \exp[z_i(F)]}{\sum_{j=1}^n K_j x_j^l \exp[z_j(F)]} dF \quad (6)$$

where the constant K_i is connected with the mean energy \bar{E}_i :

$$K_i = K_{0i} \exp(\bar{E}_i). \quad (7)$$

In comparison to the known form of integral equation [1] containing a complicated multidimensional distribution function $\chi(E_1, E_2, \dots, E_n)$, eq. (6) is the single integral much more convenient for analytical and numerical calculations. Besides, it contains only the values that characterize the corresponding single-component adsorption systems. Thus, eq. (6) may be easily used for prediction of parameters of multicomponent adsorption. In the case of adsorption from multicomponent liquid mixtures over the entire concentration range the data of single-vapour adsorption may be used to predict the multicomponent adsorption equilibrium [2, 4]. It must be also emphasized that the method proposed here, in comparison to the earlier methods, does not limit its usefulness to the case of identity of distribution functions relating to all mixture components [5, 6]. In the special cases eq. (6) enables evaluation of the heterogeneity parameters by using approximate dependences without necessity of applying the full form of the integral equation. For example, for adsorption of two vapours of similar properties and for adsorption of their binary mixture, the distribution functions should be completely correlated, so their dispersions satisfy the following dependence:

$$\sigma_{12} = |\sigma_1 - \sigma_2| \quad (8)$$

For the quasigaussian distribution the dispersion σ_i may be evaluated as follows [2]:

$$\sigma_i = \frac{\pi}{\sqrt{3}} \sqrt{\frac{1}{m_i^2} - 1}. \quad (9)$$

In the model Fig. 1 the idea for predicting the heterogeneity parameters for adsorption of binary liquid mixtures by using the energy distribution functions related to single-

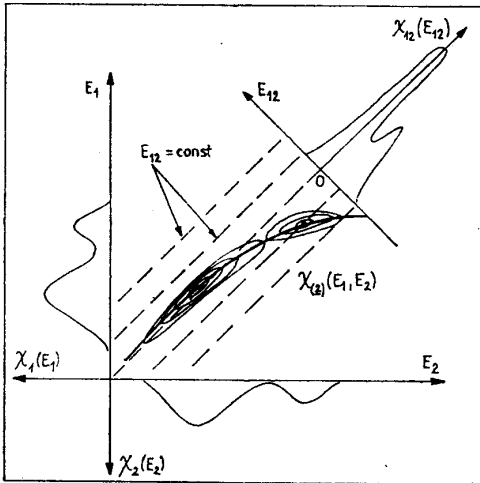


Fig. 1. Correlations among the energy distribution functions for adsorption of pure components $\chi_i(E_i)$, for adsorption of their binary gas mixture $\chi_{(2)}(E_1, E_2)$, and for adsorption for their binary liquid mixture $\chi_{12}(E_{12})$

vapour adsorption systems is presented in a schematic way. The distribution $\chi_{12}(E_{12})$ was calculated by integrating along the dashed lines, which denote the constant value $E_{12} = E_1 - E_2$:

$$\chi_{12}(E_{12}) = \int_{\Delta E_1} \chi_{(2)}(E_1, E_1 - E_{12}) dE_1 = \int_{\Delta E_2} \chi_{(2)}(E_{12} + E_2, E_2) dE_2. \quad (10)$$

Above, $\chi_{12}(E_{12})$ is the distribution of differences of adsorption energies E_1 and E_2 , $\chi_{(2)}$ is the two-dimensional distribution, and ΔE_1 , ΔE_2 are the integration areas.

The prediction method proposed here was checked for adsorption of binary liquid mixtures by using the experimental data of pure vapour adsorption [2]. The results obtained proved its usefulness and reliability for predicting the heterogeneity parameters which characterize multicomponent adsorption.

2. Prediction of heterogeneity parameters for multicomponent liquid adsorption by using the data of adsorption from binary liquid mixtures

An alternative method for predicting the heterogeneity parameters is to relate the adsorption data for multicomponent mixtures to adsorption data for the corresponding binary solutions. Thus, eq. (6) may be written as a function of the energy differences for the i -th component and the n -th reference substance:

$$x_{i,t}^s = \int_0^1 \frac{K_{in} x_{in}^l \exp [z_{in}(F)]}{1 + \sum_{j=1}^{n-1} K_{jn} x_{jn}^l \exp [z_{jn}(F)]} dF \quad (11)$$

where

$$K_{in}x_{in}^i = K_i x_{ij}^i / (K_n x_n^i) \quad (12)$$

and

$$z_{in}(F) = z_i(F) - z_n(F). \quad (13)$$

The parameters K_{in} and the functions $z_{in}(F)$ characterize binary adsorption and this fact enables the prediction of heterogeneity parameters for multicomponent adsorption. For special cases it is also possible to use the approximate dependences similar to (8) instead of applying the full form of eq. (11):

$$\sigma_{12} = \sigma_{13} + \sigma_{23} \quad \text{or} \quad \sigma_{12} = |\sigma_{13} - \sigma_{23}|. \quad (14)$$

However, for the symmetrical distributions the functions $z_{in}(F)$ and $-z_{in}(F)$ for binary mixtures are not distinguishable with respect to adsorption isotherm (they do not give information which component has greater energy dispersion). It may cause the essential errors in the multicomponent adsorption prediction. So, the problem of choice of the reference component is of great importance in the analysis of such adsorption systems.

In order to confirm the validity of model proposed several experimental data of adsorption from binary liquid mixtures "1 + 2", "1 + 3" and "2 + 3" were ana-

Table 1. Parameter values for the linear form of Langmuir-Freundlich equation characterizing adsorption of binary liquid mixtures on silica gel (A-E) [5, 6] and on charcoal (F-H) [7]

Code	System	$\ln K_{ij}$	m_{ij}	σ_{ij}	$\frac{\sigma_{12} - \sigma_{13} - \sigma_{23} }{\sigma_{12} + \sigma_{13} + \sigma_{23}}$
A	n-heptane(1) + methylethyl ketone(3)	-7.9	0.45	3.60	0.09
B	benzene(2) + methylethyl ketone(3)	-5.5	0.52	2.95	
C	n-heptane(1) + benzene(2)	-2.04	1.00	0.0	
D	n-heptane(1) + diethyl ketone(3)	-6.26	0.39	4.28	0.15
E	benzene(2) + diethyl ketone(3)	-5.26	0.50	3.14	
F	chlorobutane(1) + carbon tetrachloride(3)	-0.70	0.70	1.85	0.02
G	trichlorethane(2) + carbon tetrachloride(3)	0.20	0.81	1.31	
H	chlorobutane(1) + trichloroethane(2)	-1.12	0.95	0.60	

lysed. These experimental data were published elsewhere [5-7]. In Table 1 the values of heterogeneity parameters m_{ij} and equilibrium constants $\ln K_{ij}$ are compared for the systems investigated. The parameters were determined from the linear form of the Langmuir-Freundlich equation:

$$\ln x_{ij,i}^i = m_{ij} \ln K_{ij} + m_{ij} \ln x_{ij}^i \quad (15)$$

where

$$x_{ij,i}^s = x_{i,i}^s/x_{j,i}^s, \quad x_i + x_j = 1.$$

Note that parameter $m_{i,j}$ is connected with the dispersion $\sigma_{i,j}$ by the relationship analogous to eq. (9).

We analysed the systems *A-E* by using the optimization method [6] and the systems *F-H* by using a graphical procedure for the value of maximal adsorption given in the paper [7].

Let us consider the dependence (14) correlating the energy dispersions for all systems from Table 1. We may state that eq. (14) is fulfilled well for all systems investigated and the best correlation is observed for the mixtures *F, G, H*. However, regarding the values of relative error defined in Table 1, we can find quite good agreement between the experiment and theoretical predictions for all systems investigated. It shows the usefulness of the above description for predicting the multicomponent adsorption equilibria as well as confirms physical reality of the starting assumption (2).

References

- [1] JARONIEC, M.: in *Advances in Colloid and Interface Science*. vol. 18, p. 149. Amsterdam: Elsevier 1983.
- [2] MARCZEWSKI, A. W., A. DERYŁO-MARCZEWSKA and M. JARONIEC: *Chem. Scripta* **28** (1988) 173.
- [3] MARCZEWSKI, A. W., A. DERYŁO-MARCZEWSKA and M. JARONIEC: *Monatsh. Chemie* **120** (1989) 225.
- [4] MYERS, A. L., and J. M. PRAUSNITZ: *AIChE J.* **11** (1965) 121.
- [5] JARONIEC, M., J. OŚCIK and A. DERYŁO: *Acta Chim. Acad. Sci. Hung.* **106** (1981) 257.
- [6] DERYŁO-MARCZEWSKA, A., M. JARONIEC, J. OŚCIK, A. W. MARCZEWSKI and R. KUSAK: *Chem. Engng. Sci.* **42** (1987) 2143.
- [7] BLACKBURN, A.: *J. Chem. Soc.* 1957, 2373.