Nonideality of binary mixtures in the adsorbent micropores

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Analysis of a binary equilibrium in a distinct micropore showed that the nonuniformity of the adsorption field results in a negative deviation of the adsorption solution from ideal behavior. This deviation is due to a decrease in the entropy and internal energy caused by rearrangement of adsorbed molecules. Different interactions between identical and different molecules in distinct micropores also result in a negative deviation from ideal behavior. A criterion was formulated that allows one to elucidate how the deviation from ideality depends on the nonuniformity of the adsorption space and the character of the interaction between molecules in a micropore.

Key words: adsorption equilibrium, binary systems, micropores, nonideality, adsorption solutions.

Most industrial adsorption processes occur in multicomponent systems. Hence, the development of a theoretical view on adsorption requires the improvement of the models of equilibrium adsorption in multicomponent phases. This concerns particularly the Mayers—Prausnitz model of an ideal adsorption solution.[1] All calculations for this model are based on the Gibbs equation and the only postulate on the proportionality between a partial pressure of a component and its molar fraction in the adsorption phase on the curves of constant values of the state function. In these regions, the Gibbs equation is formally similar to the Gibbs—Duhem equation used in the theory of bulk solutions. The approaches in which the Raoult law is postulated to be fulfilled on lines of constant values of the volume of an adsorption mixture,[2] overall pressure;[2] or total sorption[4] are special cases of this model. When these approaches are used for calculation of the adsorption of mixtures, it is sufficient to have the isotherms for pure components. The accuracy of such predictions is usually not high. It is possible to improve the accuracy by going from ideal to nonideal adsorption solutions. However, it is probable in these cases that the activity coefficients will be dependent not only on the composition but also on another parameter, for example, the pressure in the adsorption phase. This will inevitably result in a necessity for the introduction of additional empirical corrections, which will lower the theoretical validity of the model. The use of the methods of statistical thermodynamics seems to be more promising.[5,6]

In this work, the behavior of a binary adsorption solution in micropores is analyzed on the basis of the Gibbs ensemble method without the use of empirical regularities.

Mathematical model

The equation of the adsorption equilibrium can be derived from the Gibbs grand canonical distribution[7] under the suggestion that the zeolite cavities form an ensemble of open statistically independent subsystems. For the adsorption of a binary mixture of gases or vapors these equations have the general form:

$$a_1 = a_0\xi^{-1}\sum_i\sum_j i\,\lambda_1^i\lambda_2^j Q_{i,j}, \qquad a_2 = a_0\xi^{-1}\sum_i\sum_j j\,\lambda_1^i\lambda_2^j Q_{i,j}. \quad (1)$$

Here a_1 and a_2 are the sorption values of the first and second components, respectively; a_0 is the number of cavities in the weight unit of an adsorbent divided by the Avogadro number N_A; ξ is the grand statistical sum referred to one cavity; $Q_{i,j}$ is the statistical sum for i and j molecules of the first and second components, respectively, which are present in the same cavity; and λ_1, λ_2 are the absolute activities:

$$\lambda_1 = \exp(\mu_1/k_B T), \qquad \lambda_2 = \exp(\mu_2/k_B T). \quad (2)$$

In expression (2), μ_1, μ_2/J are the chemical potentials of the components referred to one molecule; T/K is the temperature; k_B is the Bolzmann constant.

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The grand statistical sum is determined by the following expression:

$$\xi = \sum_i \sum_j \lambda_1{}^i \lambda_2{}^j Q_{i,j}. \tag{3}$$

For the subsystem formed in one cavity by i and j molecules of the first and second components, respectively, the statistical sum $Q_{i,j}$ is related to the Helmholz energy $F_{i,j}$ (J) as follows:

$$Q_{i,j} = \exp(-F_{i,j}/k_B T). \tag{4}$$

When the bulk phase behaves as a mixture of ideal gases, then

$$\mu_1 = \mu_1{}^\circ(T) + k_B T \ln p_1, \quad \mu_2 = \mu_2{}^\circ(T) + k_B T \ln p_2. \tag{5}$$

Here $\mu_1{}^0(T)$, $\mu_2{}^0(T)$ are the standard chemical potentials; p_1, p_2/Pa are the partial pressures of the components in the bulk phase.

Thus, Eqs. (1)—(5) demonstrate a relationship between the partial pressures of the components of a mixture and the temperature. All calculations for real systems can be made when the dependence of the Helmholz energy $F_{i,j}$ on the numbers of the molecules i and j of each component and the temperature is known. This information can be obtained from the experimental data on the binaryy adsorption by the least squares method. This allows one to find the thermodynamic functions (the Helmholz energy, internal energy, and entropy) from the macroscopic characteristics for an ensemble of a few molecules in a distinct micropore. This information is highly valuable because it reflects the interaction mechanism for the adsorbed molecules with each other and with zeolite.

When the adsorption phase is known (from any indirect data) to be similar to an ideal solution, then one can attempt to predict the component adsorption from a mixture on the basis of the data for the adsorption of pure components. It is necessary to determine how the ideality of the adsorption solution manifests itself and what the dependence between the Helmholz energy and other thermodynamic functions on the i and j numbers is. In the theory of solutions, the equilibrium vapor—liquid system is treated as an ideal system if the partial prerssure of any component in the gas phase is proportional to its molar fraction in a solution (the Raoult law). The volume fraction can be taken instead of the molar fraction. Then one can suggest that the adsorption solution is ideal if the following relation is fulfilled:

$$F_{i,j} = \frac{iF_{i+j,0} + jF_{0,i+j}}{i+j} - k_B T \ln \frac{(i+j)!}{i!j!}, \tag{6}$$

$$U_{i,j} = \frac{iU_{i+j,0} + jU_{0,i+j}}{i+j}, \tag{7}$$

$$S_{i,j} = \frac{iS_{i+j,0} + jS_{0,i+j}}{i+j} + k_B \ln \frac{(i+j)!}{i!j!}. \tag{8}$$

Here $U_{i,j}$ and $S_{i,j}$ are the internal energy and entropy of the mixture of i and j molecules of the 1st and 2nd components in the cavity. If the second index is equal to zero, the thermodynamic value is referred to the pure first component, and oppositely, the thermodynamic value concerns the pure second component at the zero value of the first index. These values can be determined by processing the experimental data on the adsorption of each component according to Eqs. (1)—(5) with the least-squares method under the assumption that $j = 0$ for the first component and $i = 0$ for the second component. For each component, either several isotherms or the isotherm and calorimetric data on the dependence of the differential heat of adsorption on coverage at the same temperature are required. The second member in the right part of expression (8) is the entropy of mixing. On going to a macrosystem, in a limiting case when i and j become extremely great, one can use the Stirling factorial formula. Then we can write for the specific entropy of mixing:

$$-k_B x_1 \ln x_1 - k_B x_2 \ln x_2,$$

where $x_1 = i/(i+j)$ and $x_2 = j/(i+j)$. The same expression for the entropy of mixing is obtained for an ideal solution, *i.e.*, when the Raoult law is fulfilled. Equation (6) leads to the Marham and Benton equation[8] when the isotherms of pure components are described by the Langmiur equation. Expression (6), as has been shown by us previously,[9] leads also to a postulate[1] that the Raoult law is fulfilled on the curve of a constant pressure in the adsorption phase. Real binary systems can be characterized by the excess thermodynamic functions, which depend on the distribution of the adsorption field in micropores and on the interaction of molecules.

When the number of molecules in a cavity is constant, the state of this subsystem can be a function of the mutual arrangement of the molecules of both components. Each state is characterized by the intrinsic value of the potential energy. The thermodynamic functions of this subsystem can be determined by the Gibbs canonical distribution:

$$Q_{i,j} = \sum_k g_k \exp(-U^k_{i,j}/k_B T). \tag{9}$$

Here k is the number of a discrete state in which the set of i and j molecules of the first and second components in a cavity can occur; $U_{i,j}{}^k$ is the potential energy of the total subsystem in the k state; g_k is the weight factor. When the interaction of the molecules of both components with the adsorption field is the same or their potentials in any point of the cavity volume differ by the constant value, then a change in the mutual arrangement does not alter the internal energy of the subsystem. In this case, the distribution of the molecules is equally probable and the binary mixture is ideal. When the molecules of both components interact with the adsorption field unequally and the other factors are equal, then their sum energy will be different depending on the arrangement of the molecules in the cavity. The combinations with lower values of the potential energy will be most probable. Some ordering arises in the mutual arrangement of the component molecules, which results in a decrease in the entropy and internal energy as compared to the case of random distribution. Taking into account expression (9), the excess internal energy can be determined as follows:

$$U_{i,j}^{E} = \frac{\sum\limits_{k} g_k U_{i,j}^{k} \exp(-U_{i,j}^{k}/k_{\rm B}T)}{\sum\limits_{k} g_k \exp(-U_{i,j}^{k}/k_{\rm B}T)} - \frac{\sum\limits_{k} g_k U_{i,j}^{k}}{\sum\limits_{k} g_k}. \qquad (10)$$

The second member in the right-hand part of expression (10) is the average energy at infinitely high temperature, when all distributions become equally probable. Let us introduce the $\Delta U_{i,j}{}^{k}$ value that is equal to the difference between the real energy of the subsystem in the k state and the energy under the equally probable distribution:

$$\Delta U_{i,j}^{k} = U_{i,j}^{k} - \sum_{k} g_k U_{i,j}^{k} / \sum_{k} g_k. \qquad (11)$$

Then Eq. (10) can be written as follows:

$$U_{i,j}^{E} = \frac{\sum\limits_{k} g_k \Delta U_{i,j}^{k} \exp(-\Delta U_{i,j}^{k}/k_{\rm B}T)}{\sum\limits_{k} g_k \exp(-\Delta U_{i,j}^{k}/k_{\rm B}T)}. \qquad (12)$$

We consider initially the case when $\Delta U_{i,j}{}^{k}$ is less than $k_{\rm B}T$. Then, if we restrict expansion in the Taylor series to the two first members, we obtain on rearrangement:

$$U_{i,j}^{E} \cong -\sum_{k} g_k (\Delta U_{i,j}^{k})^2/(k_{\rm B}T \sum_{k} g_k) = -\delta_{i,j}{}^2/(k_{\rm B}T). \qquad (13)$$

Here $\delta_{i,j}{}^2$ is a dispersion of the random value $\Delta U_{i,j}{}^{k}$. The same expression is obtained if $\Delta U_{i,j}{}^{k}$ is comparable in its absolute value with $k_{\rm B}T$ and the $\Delta U_{i,j}{}^{k}$ distribution is continuous and described by a lognormal law with the $\delta_{i,j}$ parameter. Hence, the excess internal energy caused by the nonuniformity of the adsorption field inside the distinct cavity is generally negative. This energy is proportional to the disperity of scattering of its value relative to the average value and is inversely proportional to temperature. The excess Helmholz energy $F_{i,j}{}^{E}$ can be found by integration of the Gibbs—Helmholz equation:

$$F_{i,j}^{E} = -T\int T^{-2} U_{i,j}^{E}\,{\rm d}T = -\delta_{i,j}{}^2/(2k_{\rm B}T). \qquad (14)$$

The Helmholz excess energy should be zero at $T \to \infty$. Therefore, the integration constant is equal to zero. As

$F_{i,j}{}^{E} = U_{i,j}{}^{E} - TS_{i,j}{}^{E}$, then

$$TS_{i,j}^{E} = F_{i,j}^{E} = -\delta_{i,j}{}^2/(2k_{\rm B}T). \qquad (15)$$

Thus, the nonuniform adsorption field results in a negative deviation from ideal behavior of the mixture of i and j molecules of the first and second components in a cavity; the excess internal energy is twice the Helmholz excess energy. The $\delta_{i,j}$ parameter depends on i and j and is connected to the distribution function for the adsorption field over the cavity volume as well as to the variation in the interaction between this field and the binary mixture molecules.

The excess thermodynamic functions can be associated not only with the nonuniformity of the adsorption field but also with the difference in interaction between identical and different molecules. In this case, changes in the mutual arrangement of two molecules result in a change in their internal energy. As a simple example let us consider a chain of three molecules containing one molecule of the first component. Introduce the following designations: $u_{1,1}$ is the potential energy of interaction between two molecules of the first component, $u_{2,2}$ is the same for interaction between two molecules of the second component, and $u_{1,2}$ refers to molecules of the first and second components. If the molecule of the first component occurs at the beginning or at the end of the chain, the sum potential energy is equal to $u_{1,2} + u_{2,2}$. In the case when this only molecule occurs in the middle of the chain, the sum energy is equal to $2u_{1,2}$. Assume that $u_{2,2} \neq u_{1,1}$ and $2u_{1,2} = u_{1,1} + u_{2,2}$. Then the difference in the chain energies for two variants of the mutual arrangement $u_{1,2} - u_{2,2} = (u_{1,1} - u_{2,2})/2 \neq 0$. However, for an infinite or closed chain the mutual movements of the molecules do not lead to a change in the sum energy if $2u_{1,2} = u_{1,1} + u_{2,2}$. A conclusion can be drawn that the ideal binary mixture in the adsorption state will demonstrate a negative deviation from ideal behavior due to the limited number of molecules in a distinct cavity. The negative value of the excess energy will be inversely proportional to temperature.

A special case is when $2u_{1,2} \neq u_{1,1} + u_{2,2}$. Beginning from some total number of molecules (from three in our case), the excess internal energy will include a value proportional to $2u_{1,2} - u_{1,1} + u_{2,2}$, which is independent of temperature if the $u_{1,2}$, $u_{1,1}$, $u_{2,2}$ values are also independent of temperature. Hence, in the common case, the excess internal energy can be described as follows:

$$U_{i,j}^{E} = \alpha_{i,j} - \beta_{i,j}/(k_{\rm B}T). \qquad (16)$$

In this expression, term $\alpha_{i,j}$ is proportional to the deviation of the interaction potential for different molecules from the arithmetic mean of the interaction potentials for identical molecules; $\beta_{i,j}$ is the value including the dispersion relative to the average energy due to the nonuniformity of the adsorption field $\delta_{i,j}{}^2$. This term is related to a change in the total interaction energy during rearrangement of the molecules. Other excess functions should be as follows:

$$F_{i,j}^{E} = \alpha_{i,j} - \beta_{i,j}/(2k_{\rm B}T), \qquad TS_{i,j}^{E} = -\beta_{i,j}/(2k_{\rm B}T). \qquad (17)$$

When processing the experimental data, the dependences of $\alpha_{i,j}$ and $\beta_{i,j}$ on the i, j values can be approximated by regression equations.

A model system of a linear chain of molecules

The main findings of the model considered can be illustrated by a small idealized system of a chain of the molecules of two components in a nonuniform adsorption field. The program for generation of all possible combinations of the mutual arrangements of the molecules was developed for numerical calculations. For each combination, the interaction energy for the molecules with each other and the external (relative to the chain of molecules) field was calculated. The excess internal energy was calculated according to Eq. (10), and the Helmholz excess energy was determined from the following expression derived by integration of the excess internal energy according to the Gibbs—Helmholz equation:

$$F^E_{i,j} = -\sum_k g_k U^k_{i,j} / (\sum_k g_k - k_B T \ln Q_{i,j} + k_B T \ln \sum_k g_k). \quad (18)$$

The excess entropy can be estimated from the known expressions for the internal energy and the Helmholz energy:

$$S^E_{i,j}/k_B = -\sum_k \omega_k \ln(\omega_k/g_k) - \ln\sum_k g_k) . \quad (19)$$

where ω_k is the probability of the realization of the k state:

$$\omega_k = Q^{-1}_{i,j} g_k \exp(-U^k_{i,j}/k_B T). \quad (20)$$

The same energy values are absent from the continuously distributed field in discernible combinations and all $g_k = 1$. Then one can write instead of formula (19):

$$S^E_{i,j} = -k_B \sum_k \omega_k \ln\omega_k - k_B \ln\frac{(i+j)!}{i!j!} . \quad (21)$$

Assume that each unit of a chain of molecules is numbered and filled. A molecule of some component that is a specific unit of a chain is characterized by the constant energy of interaction with the adsorption field., and this energy is different for the molecules of various components. The character of the interaction potential of the molecules with the adsorption field is unimportant to derive the qualitative regularities. Therefore, we accept the following approximation for the difference in the potential energy of the interaction with the adsorption field:

$$\varphi = -A\exp(-nB). \quad (22)$$

Here n is the index number of a molecule in a chain; φ is the change in the potential of interaction with the adsorption field when the molecule of the second component is replaced by the molecule of the first component at the n-site in a chain. The interaction between the molecules is completely determined by two parameters: $u_{1,1} - u_{2,2}$ and $\varepsilon = u_{1,2} - 0.5(u_{1,1} + u_{2,2})$.

To elucidate the effect of the nonuniformity of the adsorption field, let us assume initially that $u_{1,1} - u_{2,2} = 0$ and $\varepsilon = 0$. Let there be A = 10 kJ mol^{-1}, B = 0.25. Figure 1 shows a change in φ along the chain of ten molecules. It is seen that when the molecule of the second component at the beginning of the chain is replaced by a molecule of the first component, the potential energy referred to 1 mole decreases by 7.8 kJ. If such a replacement is carried out at the end of the chain (n = 10), the potential energy decreases only by 0.82 kJ. If different molecules occur on the chain terminals, a change in their positions varies the energy of the whole system by $1.157 \cdot 10^{-20}$ J or 7 kJ based on 1 mole. Therefore, the probability density for the occurence of the first component molecule at the beginning of the chain is higher than that at the end of the chain. That is seen in Fig. 2 where the probabilities of finding the first component molecule at the n-th position of the chain are presented. The total number of molecules is 10 including i molecules of the first component. In the uniform field the mixture of molecules would be ideal. Respectively, the curves presented in the figure would transform into straight lines parallel to abscissa axis (uniform distibution).

Figure 3 shows the integral distribution functions for the energy of the subsystem under consideration for three cases, when 3, 5, and 7 molecues of the first component, respectively, are among 10 molecules. The plot is presented by a set of a great number of points connected with linear segments rather than smoothing curves. Particularly, the number of combinations for i = 5 is equal to 252. Hence, the distribution functions can be assumed to be approximately continuous. It is especially true for real systems, which are characterized by a great number of states. Figure 4 shows the corresponding differential distribution curves. The curves have a peak shape that is symmetrical for an equimolar mixture and somewhat asymmetrical for other cases.

The entropy of the subsystem and its internal energy decrease because of rearrangement of molecules due to the adsorption field. The excess values of these functions can easily be calculated by formulas (12), (19), (20). The Helmholz excess energy can be found from expression (18). Figure 5 presents the calculated dependences of the excess thermodynamic functions on the inverse

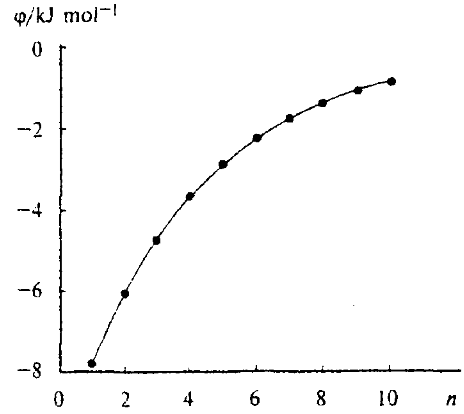

Fig. 1. Dependence of the potential difference for interaction (φ/kJ mol^{-1}) between the molecules of the first and second components and the adsorption field on the length of chain of molecules in the model system.

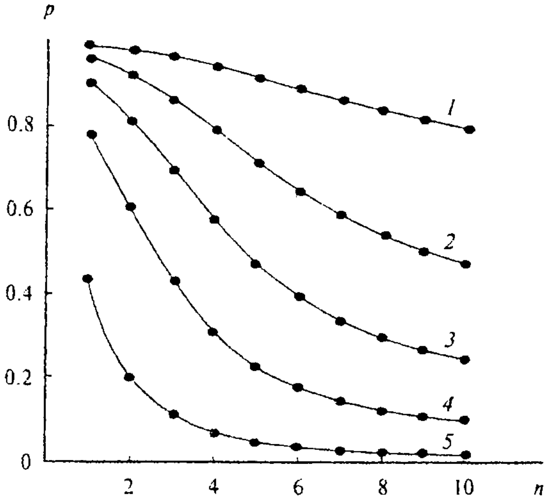

Fig. 2. Distribution of the occurrence probability (p) for the first component molecule along the chain length for an ideal mixture of molecules in the nonuniform field (a change in φ along the chain length is presented in Fig. 1). $T = 293$ K, the total number of molecules $i + j = 10$. The number i of the molecules of the first component: 9 (*1*); 7 (*2*); 5 (*3*); 3 (*4*); 1 (*5*).

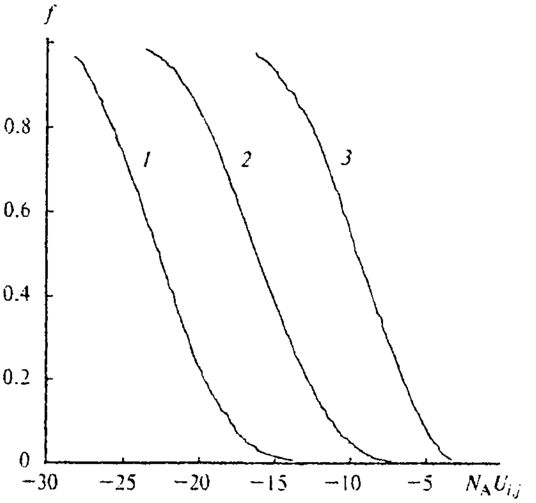

Fig. 3. Integral specific energy distribution functions for the configurations of the molecule chain (f is the number of states with the energy lesser than $N_A U_{i,j}$ divided by the total number of states). The total number of the molecules in the mixture $i + j = 10$. The number of the first component molecules i: 7 (*1*); 5 (*2*); 3 (*3*).

temperature for the model subsystem under consideration at $i = j = 5$. The excess functions are referred to 1 mole. The temperature range for this example is 200 K. As can be seen in the figure, the dependences found for this wide range are close to linear and the Helmholz excess energy $F_{i,j}{}^E$ is close to the product of the temperature and excess entropy $TS_{i,j}{}^E$, as was predicted by Eqs. (14) and (15). The small difference is explained by the fact that the potential energy states distribution differs from the common law, although it is close to it.

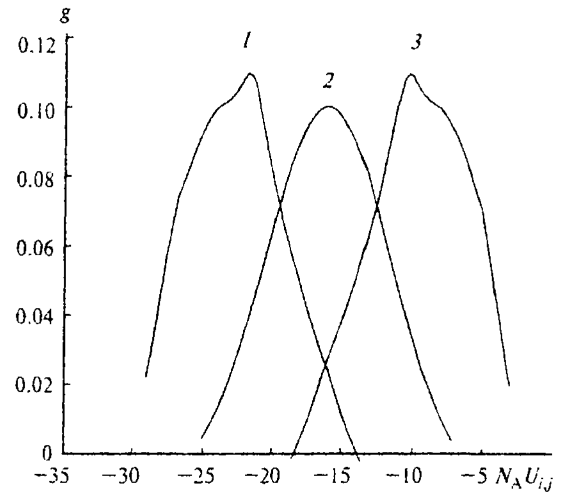

Fig. 4. Differential distribution functions $g = df/d(N_A U_{i,j})$ for the conditions presented in Fig. 3.

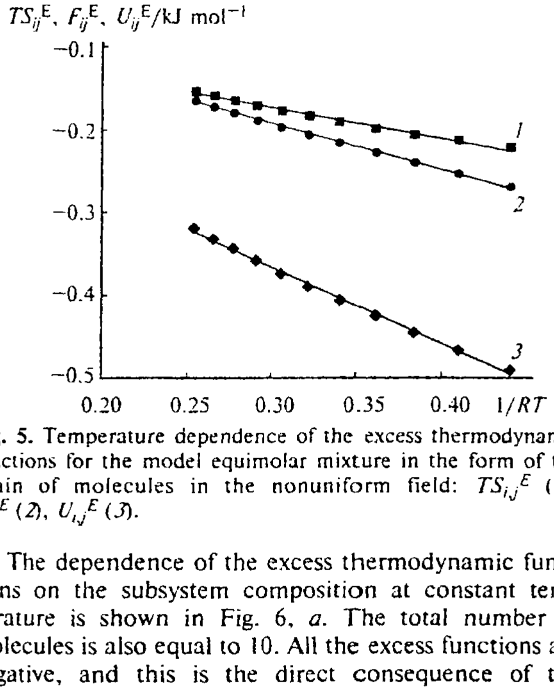

Fig. 5. Temperature dependence of the excess thermodynamic functions for the model equimolar mixture in the form of the chain of molecules in the nonuniform field: $TS_{i,j}{}^E$ (*1*), $F_{i,j}{}^E$ (*2*), $U_{i,j}{}^E$ (*3*).

The dependence of the excess thermodynamic functions on the subsystem composition at constant temperature is shown in Fig. 6, *a*. The total number of molecules is also equal to 10. All the excess functions are negative, and this is the direct consequence of the energy nonuniformity of the system under consideration.

We also performed model calculations for more complicated cases. When $\varepsilon = 0$ but $u_{1,1} - u_{2,2} \neq 0$, then all the excess thermodynamic functions decrease somewhat. However, this correction is not great if the absolute value of the difference $u_{1,1} - u_{2,2}$ does not exceed 1—2 kJ/mol. The dependence of the excess values on the ε parameter is more pronounced. The corresponding curves for $u_{1,1} - u_{2,2} = 0$ and $\varepsilon = 0.4$ are presented in Fig. 6, *b*. The distribution of the adsorption field is the same as in the previous case. The excess internal energy and Helmholz energy increase but remain negative despite the excess entropy decrease. Calculations show that this thermodynamic function remains unchanged and

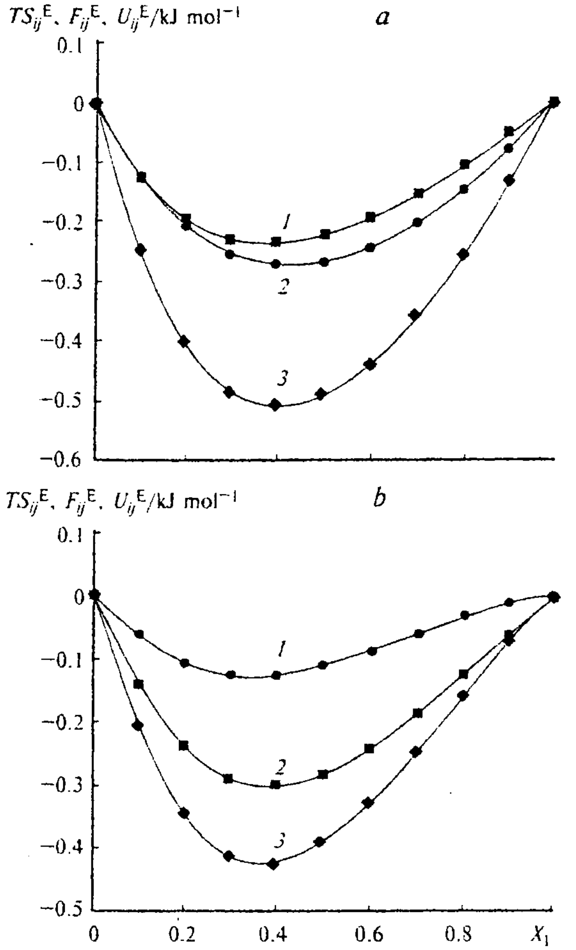

Fig. 6. Changes in the excess thermodynamic functions for an ideal mixture (the potentials of pair interactions between identical and different molecules are the same): $TS_{i,j}^E$ (*1*), $F_{i,j}^E$ (*2*), $U_{i,j}^E$ (*3*). *a*) In the nonuniform field for the model system on the curve of the constant total number of molecules ($i + j = 10$), $T = 293$ K; *b*) for the nonideal model mixture ($\varepsilon = 0.4$).

close to zero in the uniform field when the parameter ε changes. Hence, a decrease in entropy as a result of the energetic nonuniformity is enhanced by the nonideality of the mixture.

Results and Discussion

It was found that the nonuniformity of the adsorption field inside distinct micropores can lead to negative values of the excess internal energy, entropy, and the Helmholz energy upon the adsorption of binary mixtures. This effect arises when the difference in the interaction potentials for the molecules of one and another component with the adsorption field changes over the volume of a distinct micropore. This is possible, for example, when the molecules of only one component of the mixture have a quadrupole moment. The potential of the interaction of a quadrupole molecule with a cation in a cavity of zeolite decreases sharply with distance, and the adsorption field in the zeolite cavity seems to be essentially nonuniform toward this molecule. The adsorption field will be more uniform or nearly uniform toward the molecule of another component that has no quadrupole moment. Then the molecules of the first component will occur near cations with higher probability. For this reason, the rearrangement of the molecules occurs in such a way that the internal energy of the subsystem formed by the set of molecules in distinct micropores decreases as compared to the random distribution. The appearance of ordering in the mutual arrangement of the molecules of various components can affect the value of the negative excess entropy. When the molecules of two components form an ideal mixture in the uniformly distributed adsorption field (the excess thermodynamic functions are equal to zero), the excess internal energy in the energetically nonuniform space inside a distinct micropore proves to be ~2 times lower than the product of temperature and excess entropy. Hence, the Helmholz excess energy is also negative, and the numeral value of $TS_{i,j}^E$ is very close to $F_{i,j}^E$ for any molecule ratio. The proximity of these values determined from the adsorption measurements can indicate the very small excess potential of the pair interaction and apparently the ideal behavior of the bulk solution. All the excess thermodynamic functions change nearly linearly as the reciprocal temperature. A free member in such dependence is equal to 0 when the excess energy of pair interaction ε is equal to 0. When $\varepsilon > 0$, the Helmholz excess energy $F_{i,j}^E$ is greater than $TS_{i,j}^E$, and conversely, $\varepsilon < 0$ when $F_{i,j}^E < TS_{i,j}^E$.

The regularities found seem to have a general character. On their basis, a suggestion was made that the number of states of the subsystem formed by the population of molecules in a distinct micropore can be great and the corresponding probability density distribution function for potential energy is nearly continuous and bell-shaped.

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