Statistical modeling of equilibrium adsorption of non-ideal mixtures on zeolites

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A new model for equilibrium adsorption of a binary mixture on zeolites that takes into account the energy nonuniformity of the adsorption field in the zeolite cavities was developed on the basis of statistical thermodynamics. The nonuniformity of the adsorption field produces rearrangement of molecules in the cavity volume, decreasing the entropy, internal energy, and Helmholz free energy. A procedure for calculation of the thermodynamic functions from the data on the adsorption of pure components was proposed. The limiting cases of maximum ordering of the molecules in the cavity and their random distribution were considered. The approach proposed was exemplified by the substantially non-ideal system nitrogen—argon—zeolite NaX at 160 K. The proposed model describes the behavior of this mixture much better than that of the ideal adsorbed solution theory.

Key words: adsorption, adsorption equilibrium, zeolites, adsorption of binary mixtures, statistical thermodynamics.

One of promising approaches to the development of calculation procedures for multicomponent adsorption equilibria is based on statistical thermodynamics. Earlier,[1] the adsorption of pure components on zeolites has been considered under assumption that distinct cavities containing different numbers of molecules are statistically independent subsystems, forming a grand canonic ensemble. This approach has been complemented[2,3] with the function of state of an ideal gas similar to the Van der Waals equation. This made possible to express the Helmholz free energy in an explicit form and extend this approach to binary systems.

More predictive models for the adsorption of mixtures should take into account a nonuniformity of the adsorption field distribution within distinct cavities. For this purpose, multicenter models extending the Langmuir model have been considered. The adsorption of mixtures on each type of these centers is described by the Marham and Benton equation.[4] A total amount of an adsorbed component is determined by summing up the corresponding contributions from all centers, taking into account the distribution functions for all centers over the adsorbent—adsorbate interaction energies.[5,6] A drawback of these approaches is ignoring the interaction between the adsorbed molecules. In the case of the adsorption of pure substances, an increase in the isosteric heat of sorption with a coverage cannot be taken into account. In the previously reported[7,8] cellular models for the adsorption of pure components, which are the development of the Bakaev approach,[1] this disadvantage has been cured. However, such an easy generalization of these models to multicomponent adsorption of gases and vapors as it was in the case of the Langmiur equation was impossible.

In this work, we proposed a method that provides means for predicting the multicomponent equilibrium adsorption from the isotherms found for pure components with taking into account the nonuniformity of the adsorption field in the zeolite cavities and interaction between the adsorbed molecules. The zeolite is assumed to be thermodynamically inert, and a variation in its potential due, for example, to the adsorption deformation is not taken into account.

Previously,[9,10] we considered the condition at which the statistical approach corresponds to the Mayers and Prausnitz phenomenological ideal adsorbed solution theory (IAST).[11] This correspondence proved to be possible under the uniform distribution of the adsorption field within each cavity, and a criterion of ideality for the Helmholz energy of an adsorbed mixture was introduced. A comprehensive examination of equilibrium adsorption and the partial heats of adsorption in the CO_2—C_2H_6—zeolite NaX system[12,13] showed that the CO_2 molecules, which possess significant quadroupole

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moments are accumulated in the vicinity of cations, replacing the nonpolar ethane molecules. This rearrangement of molecules reduces all thermodynamic functions as compared to those predicted by the criterion of ideality. As a consequence, the system exhibits substantial negative deviations from Raoult's law, which was used in IAST. At the same time, the energy nonuniformity of an adsorbent manifests itself also in the adsorption of a pure component. For instance, the specific internal energy of ethane decreases (increases in the absolute value) with the number of molecules in the cavity, indicating an increased role of intermolecular interactions. Unlike this, the internal energy of CO_2 increases with an increase in the number of molecules in the cavity. This means that weakening the adsorbent—adsorbate interactions manifests itself to a higher extent than increasing the adsorbate—adsorbate interactions. Unlike ethane, the specific entropy of the CO_2 molecules remains nearly constant with an increase in the number of molecules in the cavity, indicating a substantial ordering of the molecular cluster because of strong ion-quadroupole interaction.

Hence, it is obvious that using the data on the energy nonuniformity of an adsorbent that manifests itself in the isotherm, one can predict the behavior of binary mixtures much more adequately than on the basis of such models as IAST. In this work, the simplest model is considered that takes into account the energy nonuniformity of the adsorbent and allows one to predict the dependences of the selectivity, the composition of the adsorption phase, and the total amount of a mixture absorbed on the partial pressures. The possibilities of the model are exemplified by the essentially nonideal N_2—Ar—zeolite NaX system at comparatively low temperature (160 K).

Mathematic model

Let us assume that the zeolite cavities with the adsorbate molecules form a grand canonic ensemble. The sorption of any component is proportional to the average number of the molecules of this component in the ensemble within the cavity. Since the distribution of the kinetic energy of the molecules is unimportant in this case, then the grand canonic distribution for the one-component adsorption results in the following expressions for the average number of molecules per a cavity and for the sorption value:

$$
\begin{aligned}
&\langle j\rangle = \xi^{-1}\sum_j j p^j \exp(j - \Delta F_j/k_\mathrm{B}T),\\
&\xi = \sum_j p^j \exp(j - \Delta F_j/k_\mathrm{B}T), \qquad (1)\\
&a = a_0\langle j\rangle.
\end{aligned}
$$

Here p/Pa is the pressure of an adsorbate in the gas phase; F_j/J is the Helmholz free energy for j molecules in the cavity; T/K is the temperature; ξ is the grand statistical sum based on one cavity; a/mol kg^{-1} is the adsorption value; a_0/mol kg^{-1} is the number of cavities per weight unit of a zeolite divided by the Avogadro number N_A. The Helmholz free energy per one molecule in the gas phase at the same temperature is accepted as the standard value. If the gas phase is non-ideal, one use fugacity instead of pressure. All variations in ΔF_j (including the temperature dependence of ΔF_j) can be determined by processing the experimental data on the adsorption of the pure component.

In the case of the binary adsorption, the following expressions are valid:

$$
\begin{aligned}
&a_1 = a_0\xi^{-1}\sum_i\sum_j i p_1^i p_2^j \exp(i + j - \Delta F_{i,j}/k_\mathrm{B}T),\\
&a_2 = a_0\xi^{-1}\sum_i\sum_j j p_1^i p_2^j \exp(i + j - \Delta F_{i,j}/k_\mathrm{B}T), \qquad (2)\\
&\xi = \sum_i\sum_j p_1^i p_2^j \exp(i + j - \Delta F_{i,j}/k_\mathrm{B}T),
\end{aligned}
$$

where p_1, p_2/Pa are the partial pressures for components 1 and 2, respectively; a_1, a_2/mol kg^{-1} are the sorption values for components 1 and 2. The main problem consists in finding the free energy of a mixture of the molecules in the cavity, $\Delta F_{i,j}$, from a set of the values for pure components determined from their adsorption isotherms. In the simplest case, this can be calculated according to the following equation[7,9]:

$$
\Delta F_{i,j} = \frac{i}{i+j}\Delta F_{i+j,0} + \frac{j}{i+j}\Delta F_{0,i+j} - k_\mathrm{B}T\ln\left[\frac{(i+j)!}{i!\,j!}\right], \qquad (3)
$$

Here $\Delta F_{i+j,0}$ and $\Delta F_{0,i+j}$ are changes in the Helmholz energy for the 1st and 2nd pure components, respectively, when the cavity contains $i + j$ molecules. As has been shown earlier,[10,12] this equation corresponds under some additional conditions to the postulate of the ideal adsorbed solution theory that Raoult's law is fulfilled at the curves for a constant pressure in the adsorption phase. The absolute value of the latter term in the right part of the equation is the product of the temperature and entropy of mixing for i molecules of the 1st component and j molecules of the 2nd component. Equation (3) does not take into account the nonuniformity of the adsorption field and, therefore, corresponds to the case when the occurrence of the molecules of the 1st and 2nd components in any part of the cavity volume is equally probable, that is, for random mutual spatial arrangement of the molecules of the 1st and 2nd components.

To take into account the energy nonuniformity of the adsorption space and the difference in the interaction of the molecules of different components with the adsorption field, let us assume the following model. The molecules of one or two components in a distinct cavity form a dense three-dimentional cluster, and each molecule occurs in a definite cell (center of localization). The cartesian coordinates of these cells, or centers, are unvariable. However, only a part of centers is accessible to the molecules. This idealization allows one to take into account interaction between neighboring molecules. In other words, it is assumed that each new molecule entering the cavity occurs most probably next to the previously adsorbed molecules that have formed a spatially ordered structure. Each of the following molecules complements this structure. To simplify the problem, let us assume that only one spatial configuration exists for a given number of molecules in the cavity. This is a limiting case when a probability of any definite mutual arrangement of the molecules is significantly higher than that for all the other modes. As a consequence, the number of centers on which the molecules can localize is always equal to the total number of molecules in the cavity.

Hence, the term "center" acquires a wider meaning. Some centers can be connected with the zeolite, particularly with its cations. Other centers can be referred as the points of stable equilibrium next to the previously adsorbed molecules. The centers appear successively on filling the cavity. In a general case, we can apply the term "localization" to the stable positions of the molecules adsorbed rather than to the points concerning the adsorbent only. For the sake of simplicity, the coordinates of any center are taken as constant, *i.e.*, the addition of each new molecule (regardless of what a component) does not change the position of all previously adsorbed molecules. A scheme of filling the cavities proposed suggests definite enumeration of the centers (localizations). One can enumerate these centers, for example, as follows. A single molecule in the cavity (regardless of what a component) is positioned in the center number 1. Two molecules in the cavity occupy centers with the numbers 1 and 2, *etc.* It is obvious that the sequence of filling the centers is connected with the energies of interaction between the molecules and an adsorbent. However, it does not mean that the energy of such an interaction for each following molecule is less in the absolute value. For example, the first molecule interacts with one of cations, and the second molecule interacts with another cation and simultaneously with the first molecule. It is probable that a change in the energy due to the adsorption of the second molecule occupying the center number 2 is greater in the absolute value than the energy change upon the adsorption of the first molecule, but alternative order of filling is impossible in the framework of the model. Thus, if k molecules are in the cavity, then the following $(k + 1)$-molecule will occupy the center with the number $(k + 1)$. One can present this scheme of filling in such a way that a part of the centers of localization in which the molecules can occur at the maximum filling of a cavity are inaccessible at less number of the molecules, *i.e.*, only k primary centers are accessible for k molecules. The molecules can change their positions with each other, and it is important for the adsorption of a mixture of substances. Let us accept also that the behavior of the molecule depends only on the number of a component and the ordinal number of the center that should be occupied. In other words, the behavior of the molecule of any component on the k center is independent of not only the overall number of the molecules in the cavity (the overall number of the molecules is obviously higher than k) but also of the molecular composition and the mode of arrangement of the molecules in accessible centers. Some of these centers can be associated with cations or atoms of the zeolite crystal lattice, whereas other centers can be the points of stable equilibrium of the molecule next to the neighbouring molecules. Despite a simplified character, the model takes into account the interaction of molecules both with the adsorbent and with each other.

The main relationships for thermodynamic functions of adsorbed substances in the zeolite cavity can be derived by different ways. Therefore, the further assumtions are not solely possible to obtain the same result. Below we present one of logical schemes for the derivation of the required equations.

We can assume for generality that a molecule occuring at any center has not a single value of the potential energy but a wide set of these values, which is due, for example, to the difference in the mutual orientation of nonspheric molecules. Let us further accept that the distribution function of the potential energy states of the molecule positioned at the k center obeys a lognormal law.

$$f_l = \frac{1}{\sqrt{2\pi}\delta_l(k)}\exp\left[-\left(\frac{u-u_l(k)}{\sqrt{2}\delta_l(k)}\right)^2\right], \tag{4}$$

here $u_l(k)$, $\delta_l(k)$ are the parameters of the normal distribution for the molecule of the l component (l = 1, 2) that is located at the k center. The probability of any state is proportional to the Bolzmann factor, $\exp(-u/k_BT)$. Then the average potential energy of the molecule at the k center will be as follows

$$\frac{\int_{-\infty}^{\infty} uf_l\exp(-u/k_BT)}{\int_{-\infty}^{\infty} f_l\exp(-u/k_BT)} = u_l(k) - \frac{\delta_l^2(k)}{k_BT}.$$

Now, we can determine a change in the internal energy for any combination of i molecules of the 1st component and j molecules of the 2nd component:

$$\Delta U_I(i,j) = u_I(i,j) - \delta_I{}^2(i,j)/k_BT, \tag{5}$$

where

$$u_I(i,j) = \sum_{k\in I} u_1(k) + \sum_{k\notin I} u_2(k),$$
$$\delta_I{}^2(i,j) = \sum_{k\in I}\delta_1^2(k) + \sum_{k\notin I}\delta_2^2(k). \tag{6}$$

In these relations, I means a set of centers occupied by the molecules of the 1st component ($|I| = i$) and $I \subset M$, where $M = 1 : (i + j)$. The $u_I(i,j)$ and $\delta_I{}^2(i,j)$ values are the parameters of the distribution function of the potential energy states for the whole cluster (for the case of arrangement of the molecules over the centers):

$$f_I(i,j) = \frac{1}{\sqrt{2\pi}\delta_I(i,j)}\exp\left[-\left(\frac{u-u_I(i,j)}{\sqrt{2}\delta_I(i,j)}\right)^2\right]. \tag{7}$$

It is interesting that the distribution function of states for the whole cluster also obeys a lognormal law. The average value of the change in the internal energy with taking into account all possible combinations of the mutual arrangement of the molecules over the occupied centers can be expressed as follows:

$$\Delta U_{i,j} = \frac{\sum\limits_{I\subset M,|I|=i}\int_{-\infty}^{\infty} uf_I(i,j)\exp(-u/k_BT)du}{\sum\limits_{I\subset M,|I|=i}\int_{-\infty}^{\infty} f_I(i,j)\exp(-u/k_BT)du}. \tag{8}$$

After integration we obtain the following expression:

$$\Delta U_{i,j} = \\ = \frac{\sum\limits_{I\subset M,|I|=i}\Delta U_I(i,j)\exp[-(u_I(i,j)-\delta_I^2(i,j)/2k_\mathrm{B}T)/k_\mathrm{B}T]}{\sum\limits_{I\subset M,|I|=i}\exp[-(u_I(i,j)-\delta_I^2(i,j)/2k_\mathrm{B}T)/k_\mathrm{B}T]}. \tag{9}$$

The right part of this expression can be written as the derivative of the logarithm of denominator with respect to inverse temperature:

$$\Delta U_{i,j} = k_\mathrm{B}T\ln Q_{i,j} - T\frac{dk_\mathrm{B}T\ln Q_{i,j}}{dT}, \tag{10}$$

where

$$Q_{i,j} = \sum_{I\subset M,|I|=i}\exp\left[-\frac{1}{k_\mathrm{B}T}\left(u_I(i,j)-\frac{\delta_I^2(i,j)}{2k_\mathrm{B}T}\right)\right]. \tag{11}$$

Comparing Eq. (10) with the Gibbs—Helmholz equation, one can conclude that a physical meaning of $k_\mathrm{B}T\ln Q_{i,j}$ is the change in the Helmholz free energy of a mixture of $(i + j)$ molecules and $Q_{i,j}$ is the statistical sum. Then, for the Helmholz free energy we obtain finally:

$$\Delta F_{i,j} = -k_\mathrm{B}T\ln\left[\sum_{I\subset M,|I|=i}\exp(-\Delta F_I(i,j)/k_\mathrm{B}T)\right], \tag{12}$$

where

$$\Delta F_I(i,j) = u_I(i,j) - \frac{\delta_I^2(i,j)}{2k_\mathrm{B}T}. \tag{13}$$

In the case of adsorption of the 1st pure component $(j = 0)$

$$\Delta F_{i,0} = \Delta F_I(i,0) = \sum_{k=1}^{i}u_1(k) - \frac{1}{2}\sum_{k=1}^{i}\frac{\delta_1^2(k)}{k_\mathrm{B}T}. \tag{14}$$

Similarly, for adsorption of the 2nd pure component $(i = 0)$

$$\Delta F_{0,j} = \Delta F_I(0,j) = \sum_{k=1}^{j}u_2(k) - \frac{1}{2}\sum_{k=1}^{j}\frac{\delta_2^2(k)}{k_\mathrm{B}T}. \tag{15}$$

From this one can readily derive the equation for the Helmholz free energy $\Delta F_I(i,j)$ for the particular case of the arrangement of the molecules of different components over accessible centers of the cluster from the Helmholz energies for pure components:

$$\Delta F_I(i,j) = \sum_{k\in I}(\Delta F_{k,0} - \Delta F_{k-1,0}) + \sum_{k\notin I}(\Delta F_{0,k} - \Delta F_{0,k-1}). \tag{16}$$

Hence, after the free energies of pure components for different number of molecules in the cavity were found, the free energy of a mixture of the molecules can be estimated from Eqs. (12) and (16). When the experimental isotherms for pure components were measured at various temperatures, one can determine the internal energy of adsorbed molecules in the cavity using the Gibbs—Helmholz equation:

$$\begin{aligned}\Delta U_{i,0} &= \Delta F_{i,0} - T\frac{d\Delta F_{i,0}}{dT} + ik_\mathrm{B}T,\\ \Delta U_{0,j} &= \Delta F_{0,j} - T\frac{d\Delta F_{0,j}}{dT} + jk_\mathrm{B}T.\end{aligned} \tag{17}$$

Here the internal energy of the same number of molecules in the gas phase at the same temperature is accepted as the standard value. The formulas for calculation of the internal energy of a mixture of molecules are the following:

$$\Delta U_I(i,j) = \sum_{k\in I}(\Delta U_{k,0} - \Delta U_{k-1,0}) + \sum_{k\notin I}(\Delta U_{0,k} - \Delta U_{0,k-1}), \tag{18}$$

$$\Delta U_{i,j} = \frac{\sum\limits_{I\subset M,|I|=i}\Delta U_I(i,j)\exp[-\Delta F_I(i,j)/k_BT]}{\sum\limits_{I\subset M,|I|=i}\exp[-\Delta F_I(i,j)/k_BT]}. \tag{19}$$

The change in entropy is described as follows:

$$T\Delta S_{i,j} = \Delta U_{i,j} - \Delta F_{i,j}. \tag{20}$$

From the relations (12) for $\Delta F_{i,j}$ and (19) for the internal energy of a mixture of molecules in the cavity, we can estimate the upper and lower limits of these values. The following relationships are valid for upper estimate:

$$\begin{aligned}\Delta F_{i,j}{}^{(\max)} &= \left(C_{i+j}^{i}\right)^{-1}\sum_{I\subset M,|I|=i}\Delta F_I(i,j) - k_\mathrm{B}T\ln C_{i+j}^{i},\\ \Delta U_{i,j}{}^{(\max)} &= \left(C_{i+j}^{i}\right)^{-1}\sum_{I\subset M,|I|=i}\Delta U_I(i,j),\end{aligned} \tag{21}$$

which correspond to the equally probable occurrence of the molecule of the 1st or 2nd component at any accessible center and can be considered as a criterion for ideal behavior of a molecular mixture. In other words, this corresponds to the energetically uniform adsorption space. The first relationship is exactly equivalent to Eq. (3) for $\Delta F_{i,j}$, which, in its turn, agrees with the IAST postulate that Raoult's law is fulfilled for the curves of a constant pressure in the adsorption phase. The second relationship can be reduced to the following form:

$$\Delta U_{i,j}{}^{(\max)} = (i\Delta U_{i+j,0} + j\Delta U_{0,i+j})/(i + j). \qquad (22)$$

To estimate the minimum $\Delta F_{i,j}$, we obtain from Eq. (12)

$$\Delta F_{i,j}{}^{(\min)} = \min\{\Delta F_I(i,j)\} - k_B T\ln[(i + j)!/(i!j!)]. \qquad (23)$$

This expression corresponds to the maximum ordering of the spatial arrangement of molecules in the nonuniform adsorption field. All the manifold of modes of actual behavior of binary systems occurs between these two extreme cases.

Results and Discussion

The adsorption of an N_2—Ar mixture on zeolite NaX was analysed using the above theory.[14—16] The experimental setup and the procedure of measurements have been described in detail.[15] The adsorption of mixtures was studied volumetrically at the temperature of 160 K. Seven sets of experimental runs were carried out, in which the amount of one component in the measuring cell remained constant but the component was redistributed between the adsorbent and free volume as the known amount of the second component was added. By measuring the composition and total pressure in the gas phase of the cell, one can determine the adsorption of each component. The calculated a_0 value for zeolite NaX with the ratio SiO_2/Al_2O_3 = 2.3 was 0.59 mol kg^{-1}.

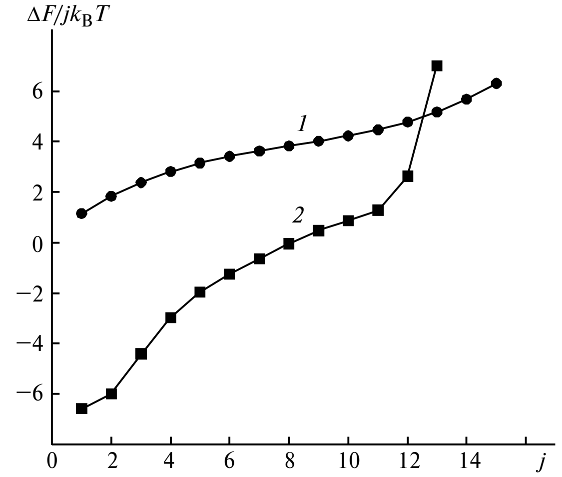

Fig. 2. The Helmholz free energy (ΔF) per one molecule of N_2 (*1*) and Ar atom (*2*) as a function of the number of particles in the zeolite cavity upon adsorption of pure components at 160 K; calculation was carried out by Eq. (1).

The adsorption isotherms for N_2 and Ar on the zeolite at 160 K (Fig. 1, solid lines) were determined according to Eq. (1) after the coefficients of polynoms describing the variation in $\Delta F_{i,j}$ with the number of molecules in a cavity were found by the least-square method. These dependences referred to one molecule are presented in Fig. 2. The $\Delta F_{i,j}$ value in the gas phase at 160 K and a pressure of 1 kPa is accepted as the standard. The curves presented contain the main information needed for the calculation of the binary adsorption equilibrium.

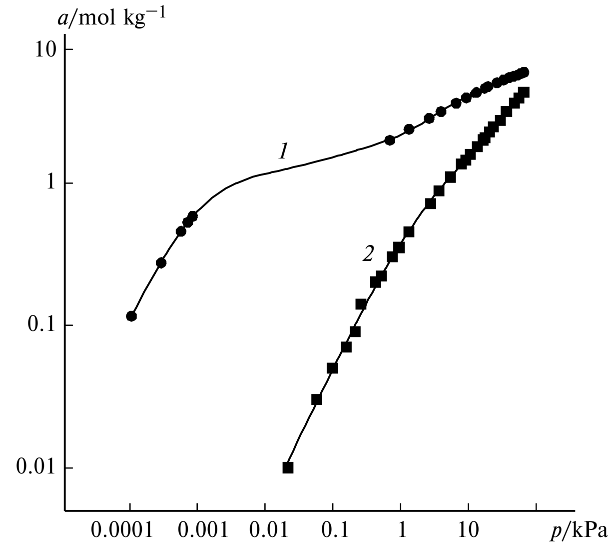

Fig. 1. Adsorption isotherms for N_2 (*1*) and Ar (*2*) on zeolite NaX at T = 160 K.

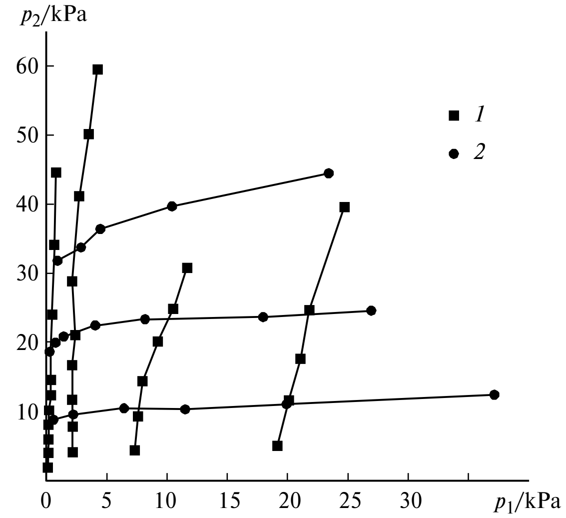

Fig. 3. Partial pressure of argon (p_2/kPa) as a function of partial pressure of nitrogen (p_1/kPa) in the series with the constant content of N_2 in the measuring cell (*1*) and in the series with the constant content of argon (*2*) at 160 K.

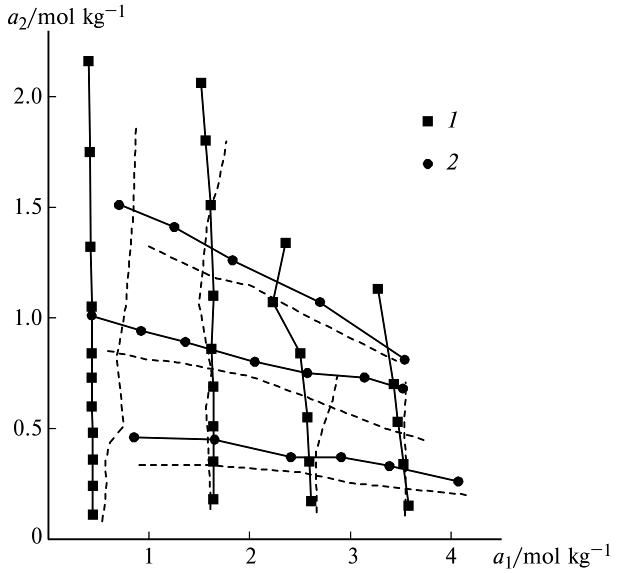

Fig. 4. Argon sorption (a_2/mol kg^{-1}) as a function of nitrogen sorption (a_1/mol kg^{-1}) in the set of runs with the constant content of N_2 in the measuring cell (*1*) and in the set with the constant content of argon (*2*) at 160 K; dotted lines — calculation according to the proposed model.

The experimental dependence between the partial pressures of Ar and N_2 is shown in Fig. 3. The vertical lines correspond to the experimental runs in which the overall amount of N_2 in the measuring cell was maintained constant. Nitrogen was partially removed from the adsorption phase after admission of each new portion of argon. Therefore, the nitrogen partial pressure slightly increased. The horizontal lines concern the runs in which the N_2 content was successively increased whereas the total amount of Ar in the measuring cell remained constant. Similar curves for the Ar sorption *vs.* N_2 sorption values are shown for different experimental sets in Fig. 4. Dotted curves were calculated according to the model proposed. Comparatively low deviations from the experimental curves are due not only to an approximate character of the model but also to the thermodynamic inaccuracy of the experimental data because of slow equilibration.

To analyze the experimental data on the adsorption of mixtures and evaluate the predictivity of a model, one often use a selectivity determined as follows:

$$S_{1,2} = (X_1/Y_1)/(X_2/Y_2).$$

Here x and y are the molar fractions of the components in the adsorption and gas phases; indices 1 and 2 are referred to N_2 and Ar, respectively.

The plot for the selectivity *vs.* the molar fraction of N_2 in the adsorption phase for one set of runs is shown in Fig. 5. In this set, the total amount of N_2 in the measuring cell was maintained constant. As Ar was added to this cell, the molar fraction of nitrogen in the adsorption phase decreased. The selectivity S_{12} is plotted on the ordinate axis in the logarithmic scale. The experimental values are shown by points. Curve *1* was calculated according to our model, and curve *2* corresponds to the hypothetical case of random arrangement of the molecules of both components in the zeolite cavities. This case would be possible only under the conditions that the molecules of different substances are close in a character of interaction with the adsorption field (for example, both molecules are nonpolar) or the adsorption field is uniformly distributed over the cavity volume.

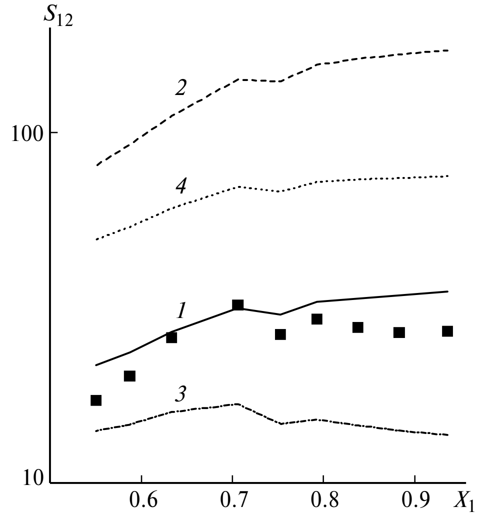

Fig. 5. A change in the selectivity $S_{1,2} = (X_1/Y_1)/(X_2/Y_2)$ with the composition of the adsorbed phase in the set of runs with the constant content of N_2 in the measuring cell (index 1 concerns nitrogen): *1*, prediction of the model proposed; *2*, calculation for random distribution of molecules in the zeolite cavities; *3*, calculation for absolutely ordered molecular structure; *4*, prediction of the IAST model; points denote experiment.

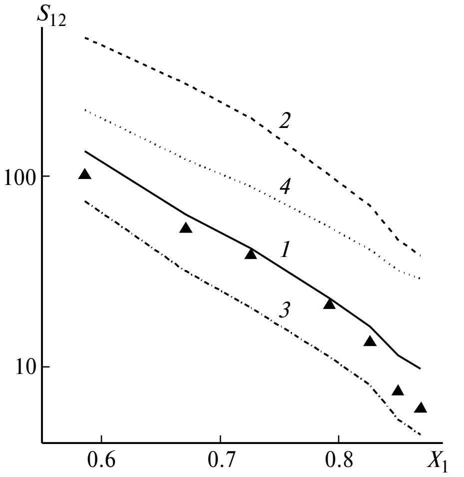

Fig. 6. Dependence of the selectivity $S_{1,2} = (X_1/Y_1)/(X_2/Y_2)$ on the molar fraction of N_2 in the adsorption phase in the set of runs with the constant amount of Ar in the measuring cell; curves *1—4* correspond the same conditions as in Fig. 5; points denote experimental data.

Under this condition, entropy as a measure of disordering of the structure reaches a maximum value. The potential energy of the cluster and $\Delta F_{i,j}$ also reaches maximum. The Helmholz free energy was calculated by Eq. (3) that is equivalent to Eq. (21). The sorption values needed for the calculation of selectivity were further determined according to Eq. (2). Curve *3* corresponding to the limiting case of the maximum ordered structure was calculated by Eq. (23). Curves *2* and *3* are the bounds for the region where the experimental points and curves calculated according to any thermodynamically correct theory should occur. In particular, curve *4* was calculated according to the IAST and is positioned inside the allowable interval. Similar plots are shown in Fig. 6 for the sets in which the total amount of Ar in the measuring cell was maintained constant and the amount of N_2 increased on going from one equilibrium point to another.

Due to existence of the boundaries of the region of allowable selectivities, the evaluation of predictivity of any model becomes more objective. It follows from Figs. 5 and 6 that the theory proposed adequately describes the experimental data whereas the IAST model overestimates the $S_{1,2}$ values. This fact becomes more obvious when taking into account that selectivity is plotted on the ordinate axis in a logarithmic scale. It also follows from the figures that the actual behavior of molecular mixtures within the cavities is markedly closer to that typical of the ordered structure rather than the random system. The feature of the system under study is clearly presented in Fig. 7, which shows probabilities of the occurrence of the N_2 molecule in specific stable positions (centers of localization). Each curve corresponds to the certain N_2 : Ar ratio in the zeolite cavity. The overall number of molecules in the cavity was accepted to be 8 for all curves. In particular, curve *1* corresponds to the case when one N_2 molecule and 7 Ar atoms are in the cavity. It follows from this curve that a single N_2 molecule will prove almost necessarily in the center of localization with the 1st or 2nd ordinal number, which can be associated with a position near cations. This conclusion can be drawn because the N_2 molecule possessing a quadroupole moment replaces the Ar atoms in the vicinity of cations with the most probability. Curve *2* was calculated for the case when 3 N_2 molecules and 5 Ar atoms are in the cavity. The probability of the Ar atom occurrence in positions 1 or 2 is less than 2%. The same tendency is maintained for all the curves: as the number of the center of localization increases, which corresponds to the moving from cations, the probability of finding the Ar atoms increases.

When the spatially ordered structure arises, $\Delta F_{i,j}$ decreases as compared to its value for the random molecule distribution. Fig. 8 shows the excess Helmholz energy per one molecule *vs.* the composition of a molecular mixture in the zeolite cavity. The excess Helmholz energy was determined with respect to the value estimated from Eq. (3). Eq. (3) is valid for the situation when the adsorption field in the cavity is uniformly distributed over its volume (in this case, the excess energy would be 0). On the abscissa axis the $X_1 = i/(i + j)$ value is plotted, where i and j are the numbers of the N_2 and Ar molecules in the cavity, respectively, and the overall number of the molecules in the cavity is $i + j = 10$. Curve *1* is the interpolated curve passing through the points calculated according to our model. The excess Helmholz energies for different ratios of i and $i + j$ are maked by points. Curve *2* is the result of the correlation

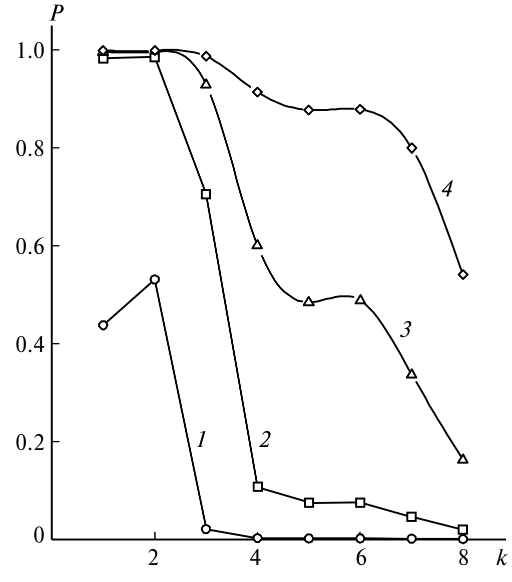

Fig. 7. The probability of occurrence of N_2 molecule in various stable positions (centers of localization) inside the zeolite cavity. k is the ordinal number of the center of localization. The overall number of molecules in the cavity $i + j = 8$. Among them the number of nitrogen molecules i: 1 (*1*), 3 (*2*), 5 (*3*), 7 (*4*).

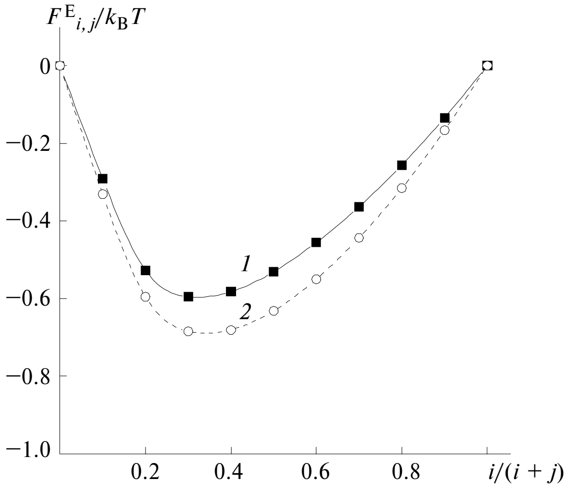

Fig. 8. Dependence of the Helmholz excess energy (per one molecule) on the fraction of N_2 in a molecular mixture inside the cavity $X_1 = i/(i + j)$; the overall number of molecules in the cavity $i + j = 10$; *1*, interpolation over points calculated according to the model proposed; *2*, correlation of the experimental data.

of experimental data by an algorithm, which is not connected with any theory, and this correlation uses only the regression equation for the Helmholz free energy as a function of the number of molecules of the 1st and 2nd components. In this case, the number of fitting parameters (coefficients of the regression equation) is three. When the number of these parameters is increased to six, an accuracy of describing the experimental data does not change and remaining deviations are connected with only small inaccuracies of the experimental relationships, which are due to difficulties of equilibration because of the prolonged replacement of molecules by other molecules.

In this connection, it is interesting that in the series in which the total amount of Ar in the system was maintained constant, the first points corresponding to low values of the N_2 sorption dropped out (by one in each set). This phenomenon can be explained by the fact that the ion-quadroupole interactions are short-range. Therefore, the N_2 molecule added into the cavity to several Ar atoms (a fraction of them blocks cations) cannot replace immediately the Ar atom next to cation. Only when N_2 occurs near this cation due to the heat motion of molecules, strong interaction between N_2 molecule and a cation arises. This situation will be stable, but the probability of such an event is rather small, resulting in too prolonged equilibration. These clearly non-equilibrium points were not taken into account in processing the experimental data. It follows from a comparison of the curves presented in Fig. 8 that calculation in the framework of the theory under question gives reasonable result.

The binary adsorption model proposed is a logic development of the multicenter models and IAST adapted for the statistical method of the analysis of equilibrium adsorption on zeolites. The assumption on random mutual distribution of molecules of different components in distinct zeolite cavities is present inexplicitely in the context of IAST. The effect of rearrangement of the molecules caused by the nonuniform distribution of the adsorption field over the cavity volume that results in a decrease in the Helmholz free energy is taken into account in the method proposed. Analysis of the probability of the molecule distribution over the centers of localization showed that the N_2 molecules possessing, unlike the Ar atoms, a quadroupole moment occur predominantly in the centers of localization with low ordinal numbers, which can be identified with the positions near cations. The model allowed us to find analytical expressions for the evaluation of minimum and maximum $\Delta F_{i,j}$. In its turn, it makes possible to find in every case the boundaries of the region of the allowable values of any macroscopic parameters, *e. g.*, the composition of the adsorption phase, the total amount of the adsorbed mixture, selectivity, *etc.* When the isotherms of pure compounds for various temperatures or the heats of adsorption in addition to the single isotherm are known, the model allows one to estimate the partial heats of adsorption and perform a complete analysis of the adsorption phase including determination of such thermodynamic functions as the entropy, internal energy, and Helmholz free energy. Comparison of the model proposed with the experimental data on equilibrium adsorption of various binary mixtures on zeolites, including the adsorption of the essentially nonideal, from the IAST point of view, mixture of N_2 and Ar on zeolite NaX, showed the best predictivity of the model as compared to known approaches. The proposed computational algorithm can be readily extended to ternary mixtures.

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