Equilibrium adsorption of an oxygen—nitrogen mixture on zeolite NaX

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Dependences of the Helmholtz energy, entropy, and internal energy in single micropores on the total number of guest molecules and the oxygen to nitrogen ratio were found by analysis of experimental data on adsorption of the binary oxygen—nitrogen mixture on zeolite NaX using the statistical model. A substantially non-ideal character of the adsorption phase, which exhibits negative deviations from Raoult's law, can result from heterogeneity of the adsorption field inside single cavities.

Key words: zeolite, equilibrium adsorption, binary mixtures, thermodynamic functions, molecular statistics.

Multicomponent mixtures are widely used for calculations of industrial adsorption processes. Accuracy of such calculations depends on the degree to which the equilibrium adsorption of gaseous or vapor mixtures can be adequately described. Several models of equilibrium multicomponent adsorption are introduced, such as the model of the ideal adsorption solution (IAST) developed by Myers and Prausnitz,[1] two variants of the model of the vacancy solution,[2—5] and the model of the adsorption solution in which an adsorbent serves as one of the components (stoichiometric adsorption theory).[6,7] These models ignore the mechanism of adsorption in single micropores and assume that parameters such as the composition and pressure are the same for any equilibrium state through the whole volume of the adsorption phase, *i.e.*, the adsorption space is considered as energetically uniform. The same limitation was used[8,9] in the statistical model where the array of zeolite cavities is treated as a large canonical ensemble of quasi-independent open systems. The difference in the composition in different points of the volume of a given adsorption phase was taken into account in the Arnold theory[10] and the theory of heterogeneous adsorption space[11—13] that uses the Polanyi model for analysis of multicomponent systems. However, in these theories, the microscopic size of pores is ignored as well.

A common opinion about an adequate definition of the ideal phase is still lacking. For example, the vacancy models and the stoichiometric theory consider as ideal the adsorption solution, with behavior obeying the Langmuir or, in the case of adsorption of a mixture, the Markham—Benton equation. This implies that almost all adsorption systems are nonideal. By contrast, in the IAST model, the assumption that the adsorption phase is ideal is frequently used. Comparing the results obtained by processing the same data in the framework of different models shows that a particular system can be ideal for one theory and nonideal for another. Heterogeneity of the adsorption field inside a micropore can cause the system to deviate from ideal behavior. In addition, the character of the interaction of molecules of different components (*e.g.*, nonpolar molecules and molecules with a quadruple moment) with the adsorption field can be different. As a result, molecules in the volume of a micropore can be rearranged to change their total internal energy and entropy. Therefore, it is of interest to find a standard definition for ideality of an adsorbed mixture and determine excessive thermodynamic functions using experimental data on adsorption of a binary mixture at different temperatures. At the first step, zeolites characterized by the regular porous structure can be taken as the object of study. We have previously[14] described the binary adsorption of the oxygen—nitrogen mixture on zeolite at the same temperature. In this work, we analyzed the experimental data obtained for the analogous system at three temperatures, which allowed us to determine in addition to the free Helmholtz energy the internal energy and entropy.

Mathematical model

From the large canonical distribution an equation of adsorption equilibrium for adsoprption of the binary gaseous mixture by zeolite can be derived assuming that single cavities are statistically independent. Neglecting the molecular distribution over kinetic energies, this equation can be written in the following form[8,9,14,15]:

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$$a_1 = \frac{\lambda_1}{N_A}\frac{\partial \log \Xi}{\partial \lambda_1}, \quad a_2 = \frac{\lambda_2}{N_A}\frac{\partial \log \Xi}{\partial \lambda_2}. \tag{1}$$

The large statistical sum is:

$$\Xi = \left[\sum_i \sum_j \lambda_1^i \lambda_2^j Q_{i,j}\right]^{a_0 N_A}, \tag{2}$$

where a_1 and a_2/mol kg^{-1} are the sorption values of the 1st and 2nd components; and a_0/mol kg^{-1} is the number of cavities per unit weight of zeolite divided by Avogadro's number N_A. The statistical sum $Q_{i,j}$ is related to the Helmholtz energy ($F_{i,j}$/kJ mol^{-1}) for the cavity containing i molecules of the 1st component and j molecules of the 2nd component:

$$F_{i,j} = -k_B T \log Q_{i,j}. \tag{3}$$

The internal energy of the aggregate of the mixed molecules ($U_{i,j}$/kJ mol^{-1}) and entropy ($S_{i,j}$/J mol^{-1} K^{-1}) can be determined from the Gibbs—Helmholtz equation:

$$U_{i,j} = F_{i,j} - T(\partial F_{i,j}/\partial T), \quad S_{i,j} = U_{i,j} - F_{i,j}. \tag{4}$$

Therefore, processing of experimental data for different temperatures gives all thermodynamic functions attributed to molecular aggregates in particular cavities. The λ_1 and λ_2 values are related to the μ_1 and μ_2 chemical potentials of the components:

$$\lambda_1 = \exp(\mu_1/k_B T), \qquad \lambda_2 = \exp(\mu_2/k_B T). \tag{5}$$

Since the gaseous phase is usually similar to the ideal system, we can write

$$\mu_1 = \mu_1^\circ(T) + k_B T \log p_1, \quad \mu_2 = \mu_2^\circ(T) + k_B T \log p_2. \tag{6}$$

In relations (3), (5), and (6), k_B is the Boltzmann constant; p_1 and p_2/Pa are the partial pressures of the components of the gas phase; T/K is temperature; and $\mu_1^\circ(T)$ and $\mu_2^\circ(T)$ are the standard values of the chemical potentials. Taking into accounts Eqs. (3), (5), and (6), we can write the large statistical sum in the following form:

$$\Xi = \left[\sum_i \sum_j \exp\left(i \log p_1 + j \log p_2 - \Delta F_{i,j}/(k_B T)\right)\right]^{a_0 N_A} \tag{7}$$

For convenience, the sum $i\mu_1^\circ(T) + j\mu_2^\circ(T)$, *i.e.*,

$$\Delta F_{i,j} = F_{i,j} - [i\mu_1^\circ(T) + j\mu_2^\circ(T)], \tag{8}$$

was taken as the standard value of the Helmholtz energy of i molecules of the 1st component and j molecules of the 2nd component in a cavity.

The extended form of equations of adsorption equilibrium for both individual and multicomponent adsorption is well known (see, *e.g.*, Refs. 8 and 9). For individual adsorption of the 1st component, we can write

$$a_1 = a_0 \frac{\sum_{i=1}^{N_1} i \exp[i \log p_1 - \Delta F_{i,0}/(k_B T)]}{\sum_{i=0}^{N_1} \exp[i \log p_1 - \Delta F_{i,0}/(k_B T)]}, \tag{9}$$

where N_1 is the maximum number of molecules of the 1st component in the cavity. The expression for the second component is analogous. Based on the definition of the ideal system given by the IAST model, the criterion of ideality for the Helmholtz energy at the level of a micropore has been formulated earlier.[14] Now consider another way of obtaining the same data from the *a fortiori* simplified model. Let the micropore volume be divided into N cells, each of which contains only one molecule of this or another component ($N_1 = N_2 = N$). The adsorption field is uniform over the micropore volume. Neighboring molecules do not interact with one another. The interactions of molecules of different components with the adsorption field are different. In this case, for the adsorption of an individual component 1, the statistical sum $Q_{i,0}$ is proportional to the number of combinations of N elements with respect to i, and for the Helmholtz energy we obtain

$$\Delta F_{i,0} = -k_B T \log\left[\frac{N!}{i!(N-i)!}\right] - i k_B T \log K_1, \tag{10}$$

where K_1 is a parameter that depends on the temperature and characterizes the interaction of molecules of component 1 with the adsorption field. Inserting Eq. (10) into Eq. (9), gives the Langmuir equation:

$$a = a_0 N \cdot K_1 p_1/(1 + K_1 p_1). \tag{11}$$

This result is expected because single cells are independent subsystems similar to active sites in terms of the Langmuir postulates.

In the case of the binary mixture, analogous considerations lead to the following expression for a change in the Helmholtz energy:

$$\frac{\Delta F_{i,j}}{k_B T} = -\log\left[\frac{N!}{i!\,j!(N-i-j)!}\right] - i \log K_1 - j \log K_2. \tag{12}$$

Then for the large statistical sum we obtain instead of Eq. (7):

$$\Xi = [(1 + K_1 p_1 + K_2 p_2)^N]^{a_0 N_A}. \tag{13}$$

Taking into account system (1) for adsorption of component 1, we have

$$a_1 = a_0 N \cdot K_1 p_1/(1 + K_1 p_1 + K_2 p_2). \tag{14}$$

As should be expected, we arrived at the Markham—Benton equation for the binary mixture because individual isotherms are described by the Langmuir equation. Comparison of Eqs. (10) and (12) shows that the expression for the Helmholtz energy of the mixture $F_{i,j}$ can be presented in a more general form:

$$\Delta F_{i,j} = \frac{i}{i+j}\Delta F_{i+j,0} + \frac{j}{i+j}\Delta F_{0,i+j} - k_BT\log\left[\frac{(i+j)!}{i!j!}\right], \quad (15)$$

where $\Delta F_{i+j,0}$ is the change in the Helmholtz energy for pure component 1 in the cavity under the condition that the number of molecules is equal to the sum of i and j. Similarly, $\Delta F_{0,i+j}$ is the change in the Helmholtz energy for pure component 2 in the cavity if it contains $i + j$ molecules. The expression obtained defines the condition of the ideal adsorption phase in a more general form than the initial model does. In fact, the same expression can also be obtained from another ideal system, the Myers—Prausnitz model. In the asymptotic limit for the macrosystem, Eq. (15) results, taking into account the Stirling formula, in the equation for the Helmholtz energy of the ideal solution (*i.e.*, for which Raoult's law is fulfilled). For the nonideal adsorption phase, in the following classical theory of solutions, an additional term, the excessive Helmholtz energy $\overline{F}^E_{i,j}$, can be introduced into Eq. (15):

$$\Delta\overline{F}_{i,j} = \frac{i\Delta\overline{F}_{i+j,0} + j\Delta\overline{F}_{0,i+j}}{i+j} - \frac{RT}{i+j}\log\left[\frac{(i+j)!}{i!j!}\right] + \overline{F}^E_{i,j}. \quad (16)$$

This expression was obtained for molar values of the Helmholtz energy. The temperature dependence of $\overline{F}^E_{i,j}$ makes it possible to determine excessive values of the internal energy and entropy making use of expressions similar to Eqs. (4). Then the change in the entropy (ΔS/J mol K^{-1}) and internal energy (ΔU/kJ mol^{-1}) can be written in the following form:

$$\Delta S_{i,j} = \frac{i}{i+j}\Delta S_{i+j,0} + \frac{j}{i+j}\Delta S_{0,i+j} - k_B\log\left[\frac{(i+j)!}{i!j!}\right] + S^E_{i,j},$$

$$\Delta U_{i,j} = \frac{i}{i+j}\Delta U_{i+j,0} + \frac{j}{i+j}\Delta U_{0,i+j} + U^E_{i,j}. \quad (17)$$

In the first approximation, the $\overline{S}^E_{i,j}$ and $\overline{U}^E_{i,j}$ values can be considered as functions of i and j only. Then, using any appropriate form of approximation (for example, the regression equation), the $\overline{S}^E_{i,j}$ and $\overline{U}^E_{i,j}$ values can be found by processing of the experimental data by the least-squares method.

Results and Discussion

We used the model considered for processing of the experimental data on equilibrium adsorption of oxygen, nitrogen, and their mixtures on zeolite NaX[16] obtained in a volumetric unit with circulation of an adsorbate without sampling. In different series of experiments, the total number of one of the components (oxygen or nitrogen) was retained, whereas another component was added in small portions until equilibrium was achieved. The measurements were carried out at three temperatures (253.2, 272.7, and 303.8 K). Adsorption of pure components and their mixtures was measured for each temperature. Prior to the experiments, a zeolite sample in the form of a pellet obtained by compacting the powder without a binder (the micropore volume 0.329 cm^3 g^{-1}) was activated at 400 °C for 30 h.

Individual isotherms were processed by Eq. (9), in which the temperature dependence of the Helmholtz energy is presented in the form:

$$\Delta F_{i,0} = \Delta U_{i,0} - T\Delta S_{i,0}, \quad \Delta F_{0,j} = \Delta U_{0,j} - T\Delta S_{0,j}. \quad (18)$$

Here the change in the internal energy $\Delta U_{i,0}$ and entropy $\Delta S_{i,0}$ of i oxygen molecules and $\Delta U_{0,j}$ and $\Delta S_{0,j}$ of j nitrogen molecules in the cavity are assumed as temperature-independent. The $\Delta U_{i,0}$ and $\Delta U_{0,j}$ values were approximated by polynomials of the 4th power with respect to i or j, respectively. Similarly, $\Delta S_{i,0}$ and $\Delta S_{0,j}$ were approximated by polynomials of the 5th power. The maximum number of oxygen molecules in the cavity was accepted as equal to 17, and that of nitrogen was accepted to be 16. The value of 0.644 mol kg^{-1} was used for a_0. The sum of squares of deviations of calculated and experimental values of the logarithm of the pressure was minimized. The experimental data on the adsorption of oxygen and nitrogen obtained at three different temperatures and the isotherms calculated from Eq. (9) are presented in Fig. 1, *a* and *b*, respectively. In both cases, the mean-square deviation of the calculated and experimental pressure values is lower than 1.3%. Using the coefficients found for the polynomials, we calculated the changes in entropy ($\Delta S_{i+j,0}$ and $\Delta S_{0,i+j}$) and internal energy ($\Delta U_{i+j,0}$ and $\Delta U_{0,i+j}$) of the individual components that are collected in Eq. (17) to determine the change in entropy $\Delta S_{i,j}$ and internal energy $\Delta U_{i,j}$ during adsorption of the mixture. The following regression equations were used for the excess values of the entropy and inner energy:

$$S^E_{i,j} = ij\sum_{k=0}^{n}\sum_{l=0}^{k} b_{k,l}i^l j^{k-l}, \quad U^E_{i,j} = ij\sum_{k=0}^{n}\sum_{l=0}^{k} c_{k,l}i^l j^{k-l}. \quad (19)$$

The coefficients of the regression equations were calculated by processing of the whole body of experimental data on adsorption of the oxygen—nitrogen mixture at three temperatures by the least-squares method. For $n = 3$, the overall number of coefficients is equal to 12. The sums of the squares of deviations of the logarithms of the total pressure and selectivity, *i.e.*, $(a_2p_1)/(a_1p_2)$, were minimized. The overall number of experimental points used for simultaneous processing at three temperatures was 297. The mean-square deviation of the calculated and experimental values of selectivity is equal to 4.8%, and the deviation of the calculated values of the overall pressure from the experimental value is 1.5%.

The calculated and experimental selectivities at 253.2 K for some experiments is compared in Fig. 2. The results of processing data from the series in which the total

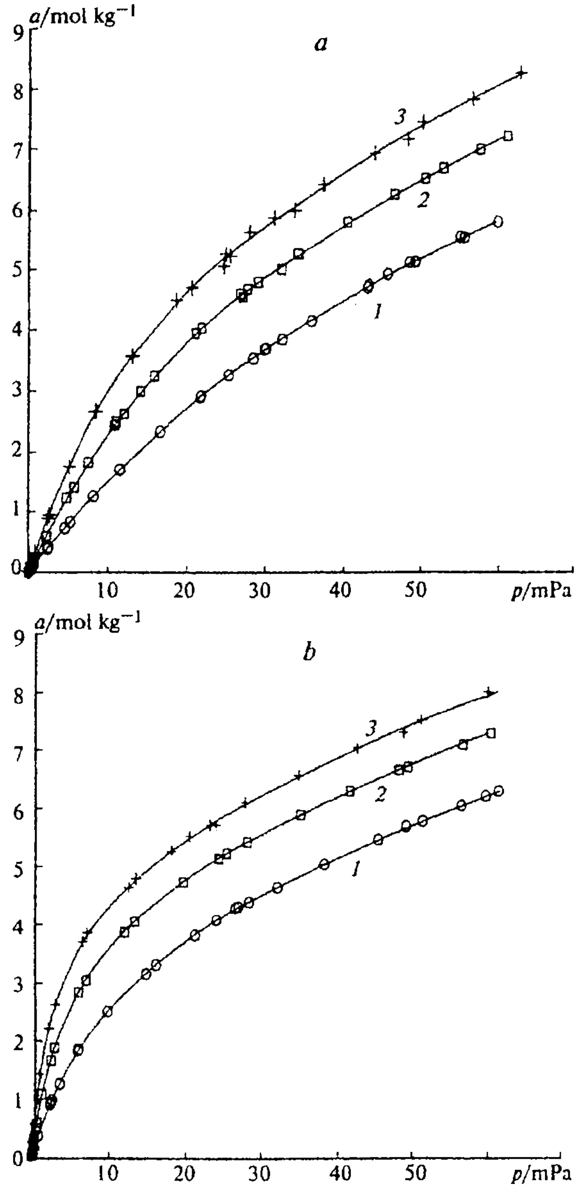

Fig. 1. Individual adsorption isotherms of oxygen (*a*) and nitrogen (*b*) on zeolite NaX. Sorption (*a*) as a function of pressure (*p*) at T/K = 303.8 (*1*); 272.7 (*2*), and 252.2 (*3*). Points indicate the experimental data; solid lines are the results of calculations by Eq. (9).

amount of nitrogen is retained constant in the system are shown in Fig. 2, *a*. One portion of nitrogen is in the gas phase, whereas another is in the adsorbed phase. When oxygen is added to the system, the adsorbed nitrogen is partially displaced, and its partial pressure in the gaseous phase increases. However, the molar fraction of nitrogen decreases in both the adsorption and gaseous phases. The calculated dependences for selected values of coefficients in Eqs. (19) are shown by solid lines. For comparison, curves calculated according to Myers and Prausnitz are presented as dotted lines. Similar dependences for experiments in which the amount of oxygen in the system was maintained constant are presented in Fig. 2, *b*. In all cases, the selectivity decreases as the total pressure and the fraction of oxygen in the

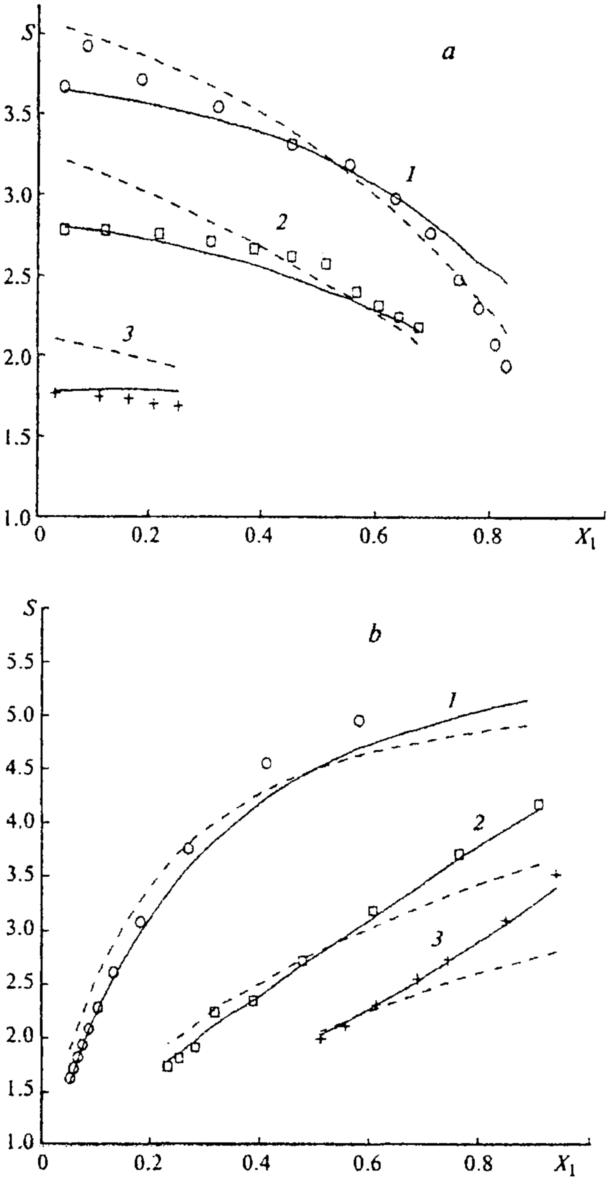

Fig. 2. Selectivity $S = (a_2/p_2)/(a_1/p_1)$ as a function of the molar fraction of oxygen in the adsorption phase (α) at 252.2 K. *a*, on lines of constant total amount of nitrogen in the measuring cell: *1*, 2.66; *2*, 5.04; and *3*, 14.48 mol kg^{-1} (solid lines are data calculated by the molecular statistical model proposed for the found coefficients of regression equations (19); dotted lines are data calculated by the Myers—Prausnitz IAST model); *b*, on lines of constant total amount of oxygen in the measuring cell: *1*, 1.42; *2*, 6.27; and *3*, 12.95 mol kg^{-1} (solid lines are calculations by the proposed model; dotted lines are calculations by the IAST model).

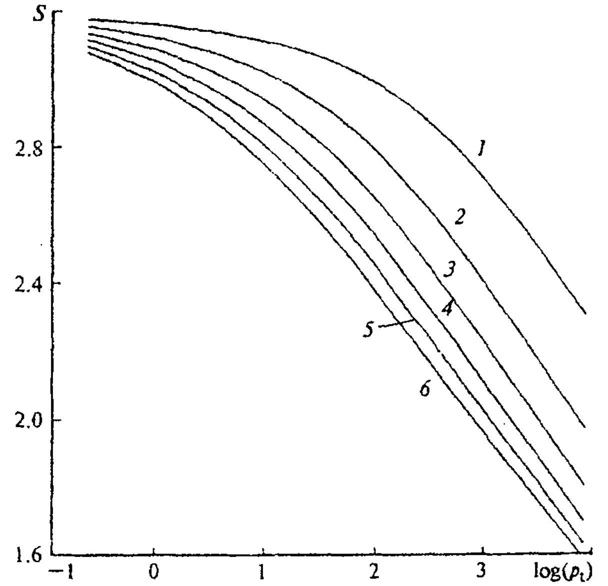

Fig. 3. Effect of the total pressure (p_t/MPa) on the selectivity at 293.2 K on lines of constant composition in the gas phase; oxygen fraction y_1 = 1.0 (*1*); 0.8 (*2*); 0.6 (*3*); 0.4 (*4*); 0.2 (*5*); and 0.0 (*6*).

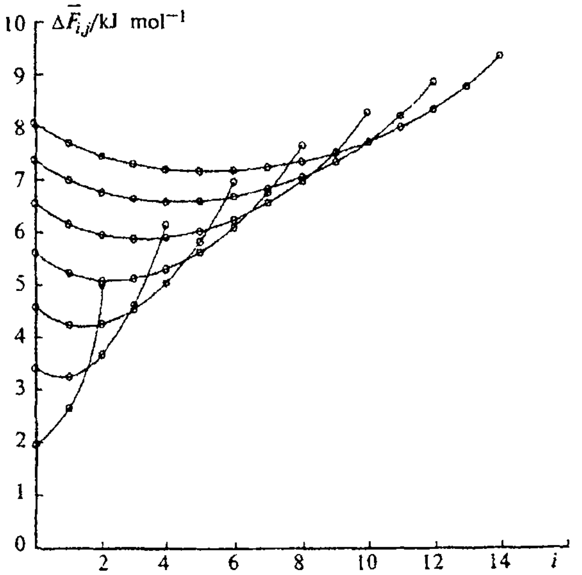

Fig. 4. Specific Helmholtz energy ($\Delta\bar{F}_{i,j}$) as a function of the number of oxygen molecules (*i*) in a cavity of zeolite NaX at 272.7 K on lines along which the total number of molecules is constant.

equilibrium phases increase. This is illustrated in Fig. 3 by calculated dependences of the selectivity on the total pressure for mixtures with constant composition of the gaseous phase.

The dependences of the molar Helmholtz energy on the number of oxygen molecules in a zeolite cavity with the total number of molecules unchanged are presented in Fig. 4. The composition changes from pure nitrogen to pure oxygen along each curve, and the overall number of molecules is equal to the abscissa of the right utmost point on this curve. It is seen that all curves have a minimum. Evidently, the entropy of the mixture increases when oxygen and nitrogen molecules are mixed. The molar internal energy as a function of the number of oxygen molecules with the total number of molecules in the zeolite cavity unchanged is shown in Fig. 5. This number is also equal to the abscissa of the final point at

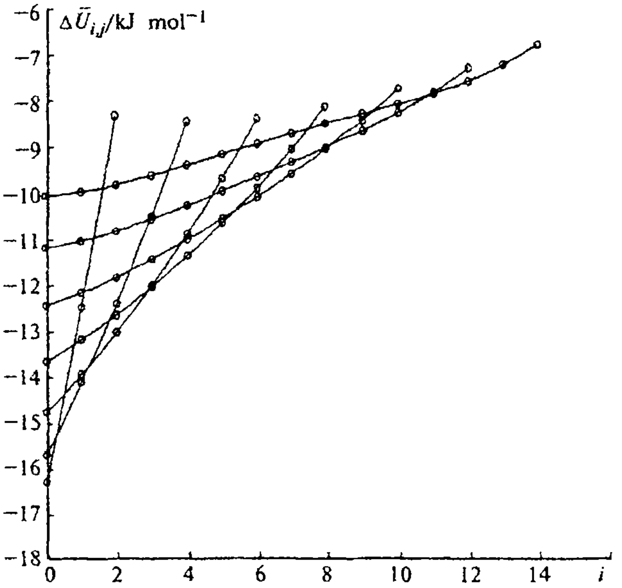

Fig. 5. Changes in the specific internal energy of the mixture of molecules ($\Delta\bar{U}_{i,j}$) in a zeolite cavity with the number of oxygen molecules (*i*) at 272.2 K on lines along which the total number of molecules is constant.

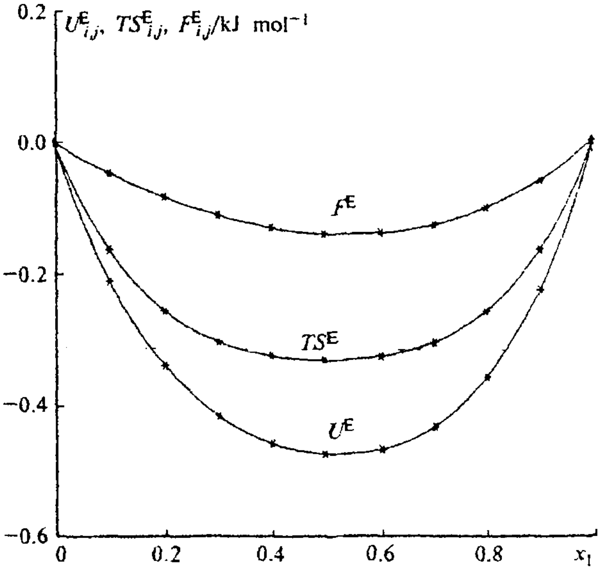

Fig. 6. Excessive values of the Helmholtz energy (F^E), entropy (S^E), and internal energy (U^E) for the mixture of molecules in a zeolite NaX cavity with 272.2 K with different fractions of oxygen molecules when the total number of molecules in the cavity is equal to 10.

the right of each curve. The internal energy is intimately related to the partial heats of sorption in the binary system, information on which is useful, for example, for analysis of adsorption separation of the air components. The conventional way of determining the heats of sorption is based on the Clapeyron—Clausius equation.

The dependences of the excessive thermodynamic functions on the composition in a zeolite cavity are presented in Fig. 6. The calculation was performed for the particular case in which the total number of molecules in the cavity was equal to 10. However, for any number of molecules in the cavity, the curves presented have the same shape. As can be seen in Fig. 6, all excessive thermodynamic functions are negative. This can clearly be explained by the influence of the heterogeneity of the adsorption field in the volume of a cavity. In this case, the molecules are rearranged to minimize the internal energy. On the other hand, the heterogeneous adsorption field results in some ordering of the molecular arrangement, which leads to a decrease in entropy. The internal energy and entropy have opposite signs in the expression of the Helmholtz energy; therefore, excessive Helmholtz energy can be both negative and positive. However, analysis of various known systems shows that all excessive thermodynamic functions with a high probability are negative. Considerable negative values of the excessive Helmholtz energy, entropy, and internal energy are also characteristic for systems that are ideal or almost ideal in the IAST model of Myers and Prausnitz. For example, treating the system under consideration in terms of the IAST model results in comparatively low mean-square deviations: 8.5% for selectivity and 4.2% for total pressure, taking into account that the procedure of experimental data processing gives 4.8 and 1.5%, respectively. A similar calculation by the model proposed for the ideal system in which the excessive thermodynamic values are equal to zero results in a rougher result (11.9 and 6.5%, respectively). Thus, the Myers—Prausnitz model of the ideal adsorption solution satisfactorily describes the nonideal system. This contradiction is due to the fact that fulfillment of Raoult's law (postulated in IAST) along a line of constant Gibbs integral values as applied to zeolites takes place under the condition that selectivity is independent of both the composition and the total pressure. This is possible only in the case where the maximum values of the numbers of molecules in the cavity are the same for both components, and the isotherms of pure components are similar. In all other cases, the model of the ideal adsorption solution retains its significance for engineering calculations, but contradicts the molecular statistical approach based on the method of Gibbs ensembles.

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The procedure developed for treatment of experimental data on equilibrium binary adsorption on zeolites based on the method of Gibbs ensembles can efficiently be used for the determination of the Helmholtz energy, entropy, and internal energy of a mixture of molecules in a zeolite cavity. The formulated criterion of system ideality makes it possible to estimate the reasons for deviation in behavior of the adsorption phase from the ideal system. It was shown for the oxygen—nitrogen—zeolite NaX system that all excessive thermodynamic functions, Helmholtz energy, entropy, and internal energy, are negative. This effect is most likely due to the heterogeneity of the adsorption field in the volume of cavities. The further development of this approach can include elaboration of specific models that consider this heterogeneity.

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References

1. A. L. Myers and J. M. Prausnitz, *AIChE J.*, 1965, **11**, 121.
2. B. P. Bering, V. V. Serpinskii, and T. S. Yakubov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 727 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1977, **26** (Engl. Transl.)].
3. T. S. Yakubov, B. P. Bering, and V. V. Serpinskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 991 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1977, **26** (Engl. Transl.)].
4. S. Suwanayuen and R. P. Danner, *AIChE J.*, 1980, **26**, 68.
5. S. Suwanayuen and R. P. Danner, *AIChE J.*, 1980, **26**, 73.
6. A. M. Tolmachev, *Zh. Fiz. Khim.*, 1978, **52**, 1050 [*Sov. J. Phys. Chem.*, 1978, **52** (Engl. Transl.)].
7. A. M. Tolmachev, *Adsorbtsiya v mikroporakh* [*Adsorption in Micropores*], Moscow, Nauka, 1983, p. 26 (in Russian).
8. D. M. Ruthven, K. F. Loughlin, and K. A. Holbarow, *Chem. Eng. Sci.*, 1973, **28**, 701.
9. D. M. Ruthven, *AIChE J.*, 1976, **22**, 753.
10. J. R. Arnold, *J. Am. Chem. Soc.*, 1949, **71**, 104.
11. E. A. Ustinov, *Zh. Fiz. Khim.*, 1987, **61**, 2103 [*Russ. J. Phys. Chem.*, 1987, **61** (Engl. Transl.)].
12. E. A. Ustinov, *Zh. Fiz. Khim.*, 1988, **62**, 1441 [*Russ. J. Phys. Chem.*, 1988, **62** (Engl. Transl.)].
13. E. A. Ustinov, *Zh. Fiz. Khim.*, 1997, **71**, 1296 [*Russ. J. Phys. Chem.*, 1997, **71** (Engl. Transl.)].
14. E. A. Ustinov, N. S. Polyakov, and F. Stöckli, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1070 [*Russ. Chem. Bull.*, 1998, **47**, 1055 (Engl. Transl.)].
15. V. A. Bakaev, *Dokl. Akad. Nauk SSSR*, 1966, **167**, 369 [*Dokl. Chem.*, 1966, **167** (Engl. Transl.)].
16. M. B. Gorbunov, A. M. Arkharov, N. A. Gorbunova, I. A. Kalinnikova, and V. V. Serpinskii, Dep. VINITI, 1984, No. 1600-84 Dep. (in Russian).

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