## Equilibrium adsorption of a cyclopentane—benzene vapor mixture on active carbon

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The data on adsorption of cyclopentane, benzene, and their mixture on active carbon were analyzed by the statistical thermodynamic model. A method to describe the state of a binary mixture in single micropores was offered. A substantial negative deviation from Raoult's law predicted by the concept of an ideal adsorption solution is a consequence of a decrease in the excessive Helmholtz energy brought about by progressive filling when values of the excessive energy are positive over a wide range of adsorption. The excessive values found for the entropy and internal energy of a mixture of molecules in a single micropore are negative due to the heterogeneity of the adsorption field. The approach suggested adequately describes the experimental data and can be used for the determination of differential heats of adsorption.

Key words: adsorption, equilibrium, active carbons, vapor mixtures, cyclopentane, benzene.

The theory of multicomponent equilibrium adsorption is important for the development of methods of engineering calculation for various adsorption processes. This is related to the fact that the adsorption processes occur primarily in multicomponent systems. In addition, the model of adsorption equilibrium makes it possible to reveal the patterns of the variation of differential heats of adsorption needed to correctly formulate the energy balance. Finally, adsorption equilibria are present in all kinetic equations.

Among existing theories of multicomponent adsorption as applied to microporous adsorbents, either phenomenological or statistical approaches prevail. The first trend involves different models of the adsorption solution that can conventionally be divided into four groups: ideal solutions, 1-4 vacancy solutions, 5-7 solutions containing an adsorbent as a component, 8,9 and solutions in a heterogeneous adsorption field. 10-12 The theories of ideal adsorption solution suggest that Raoult's law is fulfilled on the line of a constant value for any function of state. The pressure in the adsorption phase 1 (spreading pressure), the volume of the adsorption mixture,2 or the overall sorption value3 can be, in particular, a function of state. The Myers-Prausnitz<sup>1</sup> variant has found the widest use. In the vacancy models, vacancies, i.e, elements that are not susceptible to the effect of the adsorption field and can penetrate through any barriers, are accepted to be a component of the adsorption solution, while use is made of solution thermodynamics. The stoichiometric theory treats the adsorbent as a component of the adsorption solution with a constant volume and is based on the methods of solution thermodynamics.<sup>8,9</sup> The model of the heterogeneous adsorption space represents an adoption of the Polanyi theory of adsorption to multicomponent systems and takes into account the composition distribution over the volume of the adsorbed phase.

The second direction developed for zeolites on the basis of statistical thermodynamics treats the adsorbent as an array of quasi-independent cavities, and that makes it possible to consider them as large canonical ensembles. 13-15

In all concepts outlined above, an attempt is made to predict the behavior of any system rather than to reveal its specific features. Accordingly, they contain a number of postulates (fulfillment of Raoult's law), new physical properties (vacancies), or analogies. For example, Ruthven, 14,15 without sound reasons, compared the mixture adsorbed with the van der Waals gas. In this work, we attempted to analyze the state of the adsorbed mixture in micropores of active carbon by treating experimental data on equilibrium adsorption of cyclopentane and benzene at 298, 313, and 328 K on active carbon AC.\* These data were analyzed by the methods of statistical thermodynamics under the assumption that all micropores are equivalent in size and mean adsorption potential.

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## Mathematical model

The cyclopentane-benzene-active carbon AC system under study exhibits sharply negative deviations from Raoult's law along the lines of the constant pressure in the adsorption phase. Energetic heterogeneity of the adsorption space can be a reason for this behavior. In the limiting case, the energetic heterogeneity becomes evident as condensation is approached and the filling of micropores strictly follows the distribution of adsorption potentials over the micropores. 11 With this mechanism, the system can be close to ideal, whereas the adsorption solution is substantially nonideal from the viewpoint of the IAS model. However, as shown by the preliminary analysis, the system becomes non-ideal when the mechanism of successive filling of micropores takes place. A model of similar micropores with heterogeneous distribution of the adsorption field over the pore volume and a model of micropores with uniform adsorption fields with different adsorption potentials give qualitatively consistent results. Therefore, in this work, we used the model of an adsorbent with similar micropores, which allows the methods of statistical thermodynamics to be applied to adsorption on active carbon.

Assume that micropores of active carbon form a large canonical ensemble of open quasi-independent systems. The kinetic energy distribution is neglected. Then the equation of adsorption equilibrium for adsorption of a binary mixture has the following form:

$$a_{1} = a_{0} \sum_{i} \sum_{j} i\omega_{i,j}; \quad a_{2} = a_{0} \sum_{i} \sum_{j} j\omega_{i,j};$$

$$\omega_{i,j} = \xi^{-1} \exp\{(i\mu_{1} + j\mu_{2} - N_{A}F_{i,j})/RT\};$$

$$\xi = \Xi^{1/M} = \sum_{i} \sum_{j} \exp\{(i\mu_{1} + j\mu_{2} - N_{A}F_{i,j})/RT\},$$
(1)

where  $a_1$  and  $a_2/\text{mol kg}^{-1}$  are the uptakes of the 1st and 2nd components of the mixture;  $a_0/\text{mol kg}^{-1}$  is the number of micropores per unit weight of the adsorbent divided by Avogadro's number  $N_A$ ;  $\Xi$  is the large canonical sum;  $\xi$  is the large canonical sum related to one micropore;  $M = a_0N_A$  is the number of micropores per unit weight of active carbon;  $\mu_1$  and  $\mu_2/\text{kJ mol}^{-1}$  are the chemical potentials of components related to one mole;  $F_{i,j}/\text{kJ mol}^{-1}$  is the Helmholtz energy of a mixture of i molecules of the 1st component and j molecules of the 2nd component in a micropore; T/K is temperature; and R = 0.00831 kJ (mol K)<sup>-1</sup>.

Assuming that the gas phase is ideal, we can write for chemical potentials:

$$\mu_1 = \mu_1^{\circ}(T) + RT \ln p_1, \ \mu_2 = \mu_2^{\circ}(T) + RT \ln p_2,$$

where  $\mu_1^{\circ}(T)$  and  $\mu_2^{\circ}(T)$  are the standard values of the chemical potential; and  $p_1$  and  $p_2$ /Pa are the partial pressures of the components. Taking into account the designations introduced, we obtain the following equations of adsorption equilibrium for components of the binary mixture:

$$a_1 = a_0 \frac{\sum\limits_{i} \sum\limits_{j} i p_i^I p_j^J (\mathring{\lambda}_1^\circ)^I (\mathring{\lambda}_2^\circ)^J Q_{i,j}}{\sum\limits_{i} \sum\limits_{j} p_i^I p_j^J (\mathring{\lambda}_1^\circ)^I (\mathring{\lambda}_2^\circ)^J Q_{i,j}} \; ;$$

$$a_{2} = a_{0} \frac{\sum_{i} \sum_{j} j p_{1}^{i} p_{2}^{j} (\lambda_{1}^{*})^{i} (\lambda_{2}^{*})^{j} Q_{i,j}}{\sum_{i} \sum_{j} p_{1}^{i} p_{2}^{j} (\lambda_{1}^{*})^{j} (\lambda_{2}^{*})^{j} Q_{i,j}}.$$
 (2)

In the equations presented,

$$\lambda_1^{\circ} = \exp[\mu_1^{\circ}(T)/RT], \lambda_2^{\circ} = \exp[\mu_2^{\circ}(T)/RT],$$

and  $Q_{i,j}$  is the statistical sum related to the Helmholtz energy by the correlation

$$Q_{i,i} = \exp(-F_{i,i}/k_{\rm B}T),\tag{3}$$

where  $k_{\rm B}$  is the Boltzmann constant. The upper limit of summation in Eqs. (1) and (2) is determined by the condition that the overall volume of molecules in a micropore cannot exceed the volume of this micropore. At sufficiently high values of i and j, the Helmholtz energy increases to such an extent that the probability  $\omega_{i,j}$  for the presence of this number of molecules becomes negligible. Therefore, it is not necessary to specify upper limits. Evidently, individual isotherms are the particular case of Eqs. (1) and (2).

We have previously established  $^{16}$  the relation between the Helmholtz energy  $F_{i,j}$  of a mixture of molecules and the values of the Helmholtz energy of pure components for ideal behavior of the adsorption phase. For non-ideal behavior of the adsorption phase, the Helmholtz energy for a mixture of molecules is given by

$$F_{i,j} = \frac{i}{i+j} F_{i+j,0} + \frac{j}{i+j} F_{0,i+j} - k_B T \ln \frac{(i+j)!}{i!j!} + F_{i,j}^E,$$
(4)

where  $F_{i,j}^E$  is the excessive Helmholtz energy. When both components form an ideal mixture, the absolute value of the penultimate term on the right side is the product of temperature and entropy of mixing i molecules of the 1st component and j molecules of the 2nd component. For very high i and j values, using the Stirling formula, we can find the expression describing the entropy of mixing for the ideal mixture that obeys Raoult's law. If the excessive Helmholtz energy is equal to zero, Eq. (4) is transformed into the Myers—Prausnitz postulate for the ideal adsorption solution, according to which Raoult's law is fulfilled along the lines of constant pressure of the adsorption phase.\* The excessive energy.  $F_{i,j}^E$  should not necessarily be equal to zero, because intermolecular interactions inside homo-

<sup>\*</sup> Strictly speaking, the Myers—Prausnitz postulate and Eq. (4) are equivalent at  $F_{i,j}^E = 0$  when two additional conditions are fulfilled: similarity of isotherms of pure components with the affinity factor equal to unity and the same maximum number of molecules in the cavity. <sup>16</sup>

geneous and heterogeneous mixtures of molecules can differ, and the adsorption field can show heterogeneity even within a single micropore. By treating the experimental data on adsorption of a mixture by the least-squares method it is possible to determine the dependences of the Helmholtz excessive energy on the total number of molecules and the ratio of molecules of the 1st to 2nd components in a single micropore. If the experimental data are obtained for the same system at different temperatures, the internal energy  $U_{i,j}$  and the excessive internal energy  $U_{i,j}^E$  can be found by making use of the Gibbs—Helmholtz equation:

$$U_{i,j} = F_{i,j} - T \frac{dF_{i,j}}{dT}, \quad U_{i,j}^E = F_{i,j}^E - T \frac{dF_{i,j}^E}{dT}.$$
 (5)

When the Helmholtz energy and the internal energy are known, the entropy for each composition of molecules in a micropore can easily be found. In order not to specify the values of standard chemical potentials in explicit form, we can proceed from the Helmholtz energy to arrive at the difference

$$\Delta F_{i,j} = F_{i,j} - i\mu_1^{\circ}(T)/N_A - j\mu_2^{\circ}(T)/N_A. \tag{6}$$

Here the value of the Helmholtz energy of i + j molecules in the gas phase at the same temperature and a pressure of 1 Pa is accepted as the standard. Then substituting, Eq. (4) yields:

$$\Delta F_{i,j} = \frac{i}{i+j} \Delta F_{i+j,0} + \frac{j}{i+j} \Delta F_{0,i+j} - k_{\rm B} T \ln \frac{(i+j)!}{i!j!} + F_{i,j}^{E} (7)$$

Accepting the enthalpy of i molecules of the 1st component and j molecules of the 2nd component in the gas phase at the same temperature as the standard value, we can calculate changes in the internal energy

$$\Delta U_{i,j} = \Delta F_{i,j} - T \frac{\mathrm{d}\Delta F_{i,j}}{\mathrm{d}T}.$$
 (8)

In this case, we obtain for the change in entropy:

$$T\Delta S_{i,i} = \Delta U_{i,i} - \Delta F_{i,i}. \tag{9}$$

The algorithm for processing experimental data can be described as follows.

- 1. The dependences of the Helmholtz-energy  $\Delta F_{l,0}$  of the 1st component and  $\Delta F_{0,j}$  of the 2nd component on the number of molecules in a micropore and temperature are determined from individual isotherms. Approximation is possible by polynomials with respect to powers i or j of the number of molecules. The temperature dependences of the polynomial coefficients in the first approximation can be specified in a linear form, which implies the temperature-independent character of the internal energy and entropy.
- 2. The values of changes in the Helmholtz energy for any combinations of the numbers of molecules of adsorbed components in a micropore are determined

from Eq. (7). The excessive Helmholtz energy is approximated, for example, by the regression equation, whose coefficients are determined by the processing of experimental data on adsorption of a binary mixture by the least-squares method.

3. The changes in the internal energy and entropy of the variety of i molecules of the 1st component and j molecules of the 2nd component in a single micropore are determined using Eqs. (8) and (9).

## Results and Discussion

At the first step, the experimental data on the individual adsorption of cyclopentane and benzene at 298.15, 313.15, and 328.15 K were processed. The dependences of the entropy and internal energy on the number of molecules were approximated by polynomials of the 7th and 8th powers, respectively, and the zero term was absent. Further increase in the power of the polynomials did not result in an increase in the accuracy of approximation. To determine the polynomial coefficients (13 coefficients for each isotherm), we minimized the sum of squares of deviations of the calculated values of logarithms of partial pressures of the components in the gas phase from the experimental values. The  $a_0$  value was also calculated by the least-squares method and accepted as 0.433 mol kg<sup>-1</sup> in further calculations. The maximum volume of the adsorption space is equal to the product of  $a_0$  and the volume of one micropore. Unlike zeolites, for which the volume of one cavity can be determined from crystallographic data, the exact volume of one micropore of active carbons is unknown, and the  $a_0$  value can only be estimated. The whole body of experimental data at different temperatures simultaneously for two substances was used in the computer program developed for processing the adsorption isotherms of pure components. The  $a_0$  value was considered as the temperature-independent constant common for cyclopentane and benzene. This substantially decreases the influence of experimental errors on the parameters under determination. Changes in the Helmholtz energy ( $\Delta F_{i,0}$  and  $\Delta F_{0,j}$ , respectively) were calculated from Eq. (9), which is also valid when one of the subscripts is equal to zero. For this purpose, we found changes in the entropy ( $\Delta S_{i,0}$  for the 1st component and  $\Delta S_{0,j}$  for the 2nd -component) and in the internal energy ( $\Delta U_{i,0}$  and  $\Delta U_{0,j}$ ), which were assumed as temperature-independent.

The experimental and calculated isotherms for cyclopentane and benzene at 298.15 K are shown in Fig. 1. The coincidence of the calculated and experimental data for other temperatures is also good. For processing the experimental data, we took into account the final range of the isotherms, where, according to the point of inflection of the curves, capillary condensation in mesopores of the adsorbent is observed. We attempted thus to establish the dependence of the differential heats of adsorption over a wider range of pore

filling. The equations for calculating the differential heats of adsorption derived from the system of equations (2) and the Clapeyron—Clausius equation become

$$q_2 = -\frac{\sum_{j} (j - \langle j \rangle) \Delta U_{0,j} \omega_{0,j}}{\sum_{j} (j - \langle j \rangle) \omega_{0,j}}.$$
 (10)

Here  $\langle i \rangle$  and  $\langle j \rangle$  are the average over the ensemble numbers of molecules in the micropore for the first and second components, respectively, and  $a_1 = \langle i \rangle a_0$  and  $a_2 = \langle j \rangle a_0$ . The probability  $(\omega_{i,0})$  for the presence of i molecules of the 1st component in the micropore depends on the pressure of this component  $(p_1)$  and the change in the Helmholtz energy ( $\Delta F_{i,0}$ ) of i molecules. Similarly, the probability  $(\omega_{0,j})$  for the presence of j molecules of the 2nd component in the micropore depends on the pressure of this component  $(p_2)$  and the change in the Helmholtz energy  $(\Delta F_{0,j})$  of j molecules. Therefore, for the calculation of the differential heats of sorption  $q_1$  and  $q_2$ , the pattern of variations of the Helmholtz energy and internal energy should be established. The heat values obtained depend on the particular pressure in the given gas phase and, hence, on the sorption value.

The dependences of the differential heats of sorption calculated for 298.15 K are presented in Fig. 2. As can be seen, the differential heats of sorption for cyclopentane and benzene vary in the same way. The initial decrease in q with progressive filling is most likely the consequence of the energetic heterogeneity in the volume of single micropores and, probably, due to adsorption of the first portions of the sorbed component on very

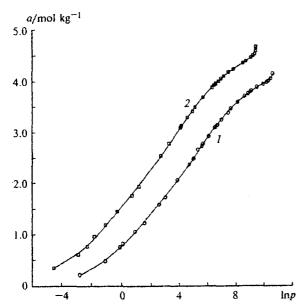


Fig. 1. Adsorption isotherms of cyclopentane (1) and benzene (2) on the active carbon AC at T = 298.15 K (a is the sorption,  $\rho/\text{Pa}$  is the pressure, and solid lines are the calculation by the statistical model).

strong sites. As adsorption increases, new molecules are localized in the remaining volume of the micropore, where the adsorption potential is weaker. The further increase in the differential heats of sorption is most likely due to the interaction between the adsorbed molecules. It is distinctly seen on the curves that a sharp decrease in the differential heat of sorption corresponds to adsorption of nine molecules per micropore for cyclopentane and ten molecules per micropore for benzene. Probably, these numbers are limiting for adsorption in micropores, and further adsorption occurs already in mesopores to produce substantially lower heats. When the uptake increases to infinite values, the heats of adsorption approach the heats of evaporation, because adsorption in micropores is followed by condensation in larger mesopores and then in macropores. The similarity in values found for the heat of sorption of each component in the region of higher fillings and for heats of evaporation indicate that the mathematical treatment of the experimental data for individual isotherms was correctly performed. Only the differential heat of sorption for cyclopentane obtained for higher fillings is somewhat lower than the heat of evaporation. This is related to errors of experimental measuring of the pressure in a narrow range of temperatures.

Further treatment of the data on binary equilibrium adsorption was performed for the region where adsorption occurs in the micropore volume only. For this purpose, the points for which the total volume of the adsorbed mixture exceeded the micropore volume were excluded from the calculation. The experiment was specific in that the volume of the gas phase of the measur-

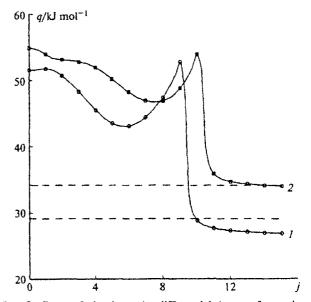


Fig. 2. Plots of the isosteric differential heats of sorption  $(kJ \text{ mol}^{-1})$  against the average number of molecules (j) per micropore for cyclopentane (I) and benzene (2) (T = 298.15 K; dotted lines designate the heats of evaporation at 298.15 K calculated by the equation).

ing cell was very small. This made it possible to maintain a constant adsorption value for one component during stepwise introduction of the second component. This scheme allowed us to determine exactly the sorption values and the overall pressure measured by a detector. This information is available for the determination of the partial pressures of the components by the Gibbs equation. In fact, it follows from the Gibbs equation that

$$\frac{\partial a_1}{\partial \mu_2} = \frac{\partial a_2}{\partial \mu_1}.$$
 (11)

Thus, of four variables for the binary equilibrium system at the same temperature (for example,  $a_1$ ,  $a_2$ ,  $p_1$ , and  $p_2$ ) only three variables are independent. In this case, these are the adsorption values of the 1st and 2nd components and the total pressure in the gas phase. The composition of the gas phase and, hence, partial pressures can be calculated by Eq. (11). For control in a few experiments, the gas mixture was analyzed by chromatography.

The excessive values of entropy and internal energy were determined as regression equations

$$S_{i,j}^{E} = \sum_{k=1}^{n} \sum_{l=1}^{n-k+1} A_{k,l} i^{k} j^{l}, \quad U_{i,j}^{E} = \sum_{k=1}^{n} \sum_{l=1}^{n-k+1} B_{k,l} i^{k} j^{l}.$$
 (12)

Coefficients  $A_{k,l}$  and  $B_{k,l}$  were derived by the least-squares method from the experimental data on adsorption of a cyclopentane—benzene mixture and taking into account all available information for all three temperatures. The functional that was minimized con-

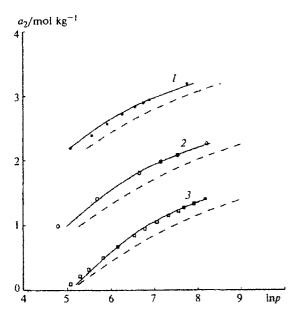


Fig. 3. Adsorption of benzene  $(a_2)$  as a function of total pressure (p/Pa) along the lines of constant content of cyclopentane at  $a_1/\text{mol kg}^{-1} = 0.883$  (1), 1.759 (2), and 2.51 (3) (T = 298.15 K; solid lines are the calculation by model (2)—(10); dotted lines are the calculation by IAS).

tained squares of deviations of the logarithm of the total pressure and selectivity determined by chromatographic analysis. The coefficients of the regression equations (12) were obtained by minimization. The nnumbers (the upper limit of summation) were chosen as equal to three for excessive entropy and two for excessive internal energy and that corresponds to six  $A_{k,l}$  coefficients and three  $B_{k,l}$  coefficients. In choosing the number of coefficients, we attempted to reveal the maximum information with the minimum dependence of the sought constants on one another. The body of experimental data included 168 points at different temperatures. The experimental dependences of the sorption of benzene on the total pressure along lines of constant values of cyclopentane sorption are presented in Fig. 3. Agreement between the calculated and experimental data is very good. For comparison, the results of calculation by the IAS model are also presented in Fig. 3. It can easily be seen that the total pressure in the gas phase is substantially lower than that predicted by the IAS model for the same value of sorption. This indicates a significant negative deviation in the properties of the adsorption solution from the properties common to the ideal. The dependences of cyclopentane sorption on the overall pressure for the experiments in which the benzene sorption was maintained unchanged look similarly (see Fig. 4). The negative deviation from Raoult's law observed for the mixture of cyclopentane and benzene in the adsorption solution is a very important specific feature of the system under study considering that a standard liquid

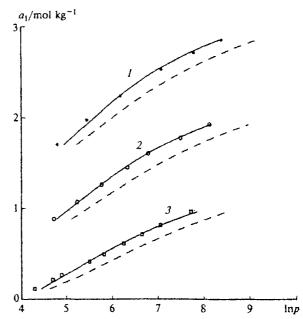


Fig. 4. Adsorption of cyclopentane  $(a_1)$  as a function of total pressure (p/Pa) along the lines of constant content of benzene at  $a_2/\text{mol kg}^{-1} = 1.039$  (1), 2.051 (2), and 3.078 (3) (T = 298.15 K; solid lines are the calculation by model (2)—(10); dotted lines are the calculation by IAS).

solution exhibits a substantial positive deviation from the ideal solution.

The dependences of the excessive specific thermodynamic functions on the molar fraction of cyclopentane at a constant filling of five molecules per micropore are presented in Fig. 5. Evidently, the negative value of the excessive internal energy is related to the heterogeneity of the adsorption field inside a single micropore and to the difference in interactions with this field showed by cyclopentane and benzene molecules. It can be expected that benzene molecules occupy the areas of a micropore where the potential fields governing the interaction with the guest molecules are lower than those preferred by cyclopentane. Therefore, the value of the average internal energy of the mixture of molecules in the micropore becomes lower than in the case of uniform distribution. On the other hand, the appearance of a certain order in the mutual arrangement of molecules with respect to the chaotic distribution results inevitably in a decrease in entropy. This is evident in Fig. 5, which demonstrates the dependence of the product of the temperature and the excessive specific (molar) entropy on the ratio of the number of molecules of the components of the mixture at a constant filling of five molecules per micropore. In the whole region, the excessive entropy is negative.

The internal energy and the entropy have opposite signs in the expression obtained for the Helmholtz energy. Therefore, with negative excessive internal energy and entropy, the excessive Helmholtz energy can be both negative and positive. Positive excessive Helmholtz energy indicates that molecules in a homogeneous mixture, such as benzene—benzene or cyclo-

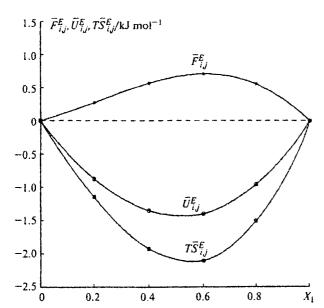


Fig. 5. Dependences of the excessive thermodynamic functions (recalculated per mole) for adsorption of a mixture consisting of cyclopentane and benzene on the molar fraction of cyclopentane (T = 298.15 K; five molecules of the mixture per micropore).

pentane-cyclopentane, interact more strongly than molecules in heterogeneous mixtures, such as benzenecyclopentane. If the adsorption field was uniformly distributed over the volume of a micropore, the positive excessive Helmholtz energy would be still higher. This result agrees with the behavior of a solution of cyclopentane and benzene, which is characterized by positive deviation from Raoult's law. The calculated excessive Helmholtz energy is positive, although the adsorption solution showed considerable negative deviation from ideal behavior. The reason for this apparent contradiction is seen in Fig. 6, which demonstrates the dependences of the excessive specific Helmholtz energy on the number of cyclopentane molecules along lines plotted for constant values of the total number of guest molecules ranging from 4 to 9. The last point on each curve corresponds to pure cyclopentane, and its abscissa is equal to the total number of molecules that was maintained constant. As can be seen in Fig. 6, when the total number of guest molecules in the micropore increases, the positive excessive Helmholtz energy decreases and goes to the negative region as the uptake approaches maximum filling of the micropore by the mixture of molecules. In this case, the effect of spatial ordering of molecules resulting in a decrease in entropy is probably much more pronounced than a decrease in the internal energy due to the rearrangement of molecules in the heterogeneous adsorption field. It follows from the system of equations (1) that the lower the Helmholtz energy for any combination of molecules of the 1st and 2nd components, the higher the probability  $\omega_{i,i}$  for this combination. Therefore, a decrease in the

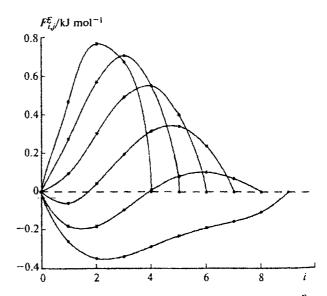


Fig. 6. Dependences of the excessive Helmholtz energy  $(F_{i,j}^E)$  for a mixture composed of cyclopentane and benzene molecules in a micropore of the active carbon AC on the number of cyclopentane molecules along lines plotted for constant values of the total number of cyclopentane and benzene molecules in a micropore (T = 298.15 K).

excessive Helmholtz energy with an increase in the total number of molecules in the micropore results in an incremental increase in the statistical sums  $(Q_{i,j})$  and, hence, in an increase in the contribution of the terms of the sums in Eqs. (2) which correspond to a higher i+j value. This results in an increase in the total concentration of the mixture adsorbed at the same values of partial pressures and leads to negative deviation from Raoult's law.

Thus, negative deviation of the adsorption solution from ideal behavior can result both from negative excessive Helmholtz energy and decrease in the excessive energy with increase in the number of guest molecules in the micropore. The analysis of experimental data on equilibrium adsorption of the binary cyclopentane-benzene mixture on active carbon showed that at low fillings the excessive Helmholtz energy is positive, whereas it attains negative values in region of micropore filling near the limiting value. Negative values of the excessive internal energy and entropy can be considered as a criterion of energy heterogeneity of the volume of a single micropore. We showed that the model of regular microporous structure can be used for the description of individual and binary adsorption of vapor by active carbons using the method of statistical thermodynamics. Accumulation of information on the thermodynamic functions of the adsorption phases held in micropores of active carbons makes it possible to describe in more detail the interaction of adsorbed molecules with the adsorbent and to establish the general features governing equilibrium adsorption of multicomponent mixtures useful in engineering calculations.

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