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Adsorption Equilibrium of Binary Mixtures in Zeolites and State of Adsorbed Phase

EUGENE A. USTINOV
St. Petersburg State Technological Institute (Technical University), 26 Moskovsky Pr.,
198013 St. Petersburg, Russia
eustinov@mail.wplus.net

LEONID E. KLYUEV
St. Petersburg State University of Technology & Design, 18 B.Morskaya St., 191186 St. Petersburg, Russia

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Abstract. The criterion of ideal behavior of a mixture of a few molecules within a separate zeolite cavity is formulated on the basis of the statistical thermodynamics. The criterion determines the dependence of the Helmholtz free energy, internal energy, and entropy of a molecular aggregate on the ratio of the number of molecules of components 1 and 2. The similarity between this criterion and the criterion of ideal behavior for bulk solutions is shown. Expressions of excess thermodynamic functions of the molecular mixture in a cavity are obtained. The negative magnitude of these excess functions is proposed to be due to rearrangement of molecules under influence of energetic heterogeneity. The calculation procedure of the excess functions has been demonstrated for the system CO_2-C_2H_6-zeolite NaX, the information of both isotherms and isosteric adsorption heats being used simultaneously. The approach offered allows the state of adsorbed mixture in a separate cavity to be analyzed from pure-component and multicomponent experimental data.

Keywords: zeolite, equilibrium theory, multicomponent system, gases phase, adsorbed solution, excess functions

Introduction

There are several groups of theories of multicomponent adsorption equilibrium. In the group of theories of ideal adsorbed solution Raoult's law is postulated along lines of a constant value of any state function. According to the most widely used Ideal Adsorbed Solution Theory (IAST) by Myers and Prausnitz (1965) the Raoult's law should hold at fixed spreading pressure. In this case the Gibbs equation is converted to the Gibbs Duhem equation for phase equilibrium. This postulate is the single and sufficient assumption to obtain the calculation procedure by strict mathematical way. This is the recipe of prediction of mixture behavior based only on information of pure component adsorption isotherms both in the case of non-porous and microporous adsorbents. There are other theories that may be reduced to the IAST. In particular, according to theory of Grant and Manes (1966), Raoult's law holds along the path of constant of adsorbed mixture volume. In contrast, Kidney and Myers (1966) suggested the total amount of mixture adsorbed as the state function for the Raoult's law. Sircar and Myers (1973) considered some other variants. All kinds of such approaches introduce some additional restrictions to the adsorbed solution model, but do not contradict IAST.

Vacancy solution models (Bering et al., 1977; Suwanayuen and Danner, 1980) use the representation that molecules and vacancies (elements of empty space) form a solution, with vacancies are capable to pass through walls of micropores and unaffected by influence of adsorption field. In the case of an ideal solution, the equations obtained lead to the Langmuir isotherm.

Thermodynamics of reversible chemical reactions of joining and exchanging was applied to the adsorption solution model (Tolmachov, 1978), one of the components of the solution being adsorbent.

The theory inhomogeneous adsorption volume (Ustinov, 1987, 1988, 1997) takes into consideration a distribution function of adsorption volume elements. The two states of these elements is assumed to be possible—to be empty or completely saturated, saturation with mixture being occurred at certain pressure and mole fraction in gaseous phase. Given the pure-component isotherms, this approach predicts mixture behavior.

The statistical thermodynamics model, as applied to the adsorption in zeolites, was first constructed by Bakayev (1966). The generalization based upon the analogy of van-der-Waals gas for a binary mixture has been further advanced by Ruthven et al. (1973) and Ruthven (1976).

Both phenomenological and statistical thermodynamics models need additional postulates or relationships to predict mixture behavior using only pure-component data. These simplified approaches were developed for design and optimization of industrial processes. As to fundamental features of the adsorbed phase on the level of individual pores, it seems preferable to use more strict methods based on treatment of precise experimental data rather than any analogies, assumptions or postulates.

In this paper an adsorbed mixture state is considered from a statistical thermodynamics standpoint. The restrictions to be placed over such thermodynamic functions as Helmholtz free energy, internal energy and entropy for a separate cavity are determined by the way to provide ideal mixture behavior in the IAST sense. The idea to compare the results predicted by IAST with “a realistic statistical mechanical model” has been expressed in the original publication by Myers and Prausnitz (1965). This comparison allows the determination of excess thermodynamic functions that carry the information of adsorbate-adsorbate and adsorbate-adsorbent interactions. From this point of view, the behavior of the equilibrium system carbon dioxide-ethane in NaX zeolite (Dunne et al., 1996, 1997) is considered. The reasons for negative values of excess thermodynamics functions are discussed.

Theory

According to the Gibbs ensemble method, each macroscopic system may be represented as a large number of copies of equal volume. Each copy (subsystem) is statistically independent. To satisfy this requirement, the subsystem ordinarily would be a macroscopic, too. In this case surface effects due to the influence of neighboring subsystems becomes negligible. However, being evidently a microsystem, the zeolite cavity may be still considered statistically independent. Bakayev (1966) first applied the grand canonical ensemble distribution to description of equilibrium adsorption of a pure component in a zeolite. Further, Ruthven et al. (1973) and Ruthven (1976) applied this method to binary mixtures. The equations of adsorption equilibrium for binary mixture are

$$a_1 = \frac{\lambda_1}{N_\mathrm{A}} \frac{\partial \log \Xi}{\partial \lambda_1}; \quad a_2 = \frac{\lambda_2}{N_\mathrm{A}} \frac{\partial \log \Xi}{\partial \lambda_2} \tag{1}$$

The grand partition function is (Hill, 1960)

$$\Xi = \xi^\mathrm{M} = \left(\sum_i \sum_j \lambda_1^i \lambda_2^j Q_{i,j} \right)^\mathrm{M}, \quad i v_1 + j v_2 \le V \tag{2}$$

Quantities λ_1 and λ_2 are the functions of the chemical potentials μ_1 and μ_2 of component 1 and component 2 respectively,

$$\lambda_1 = \exp\left(\frac{\mu_1}{k_\mathrm{B} T}\right), \quad \lambda_2 = \exp\left(\frac{\mu_2}{k_\mathrm{B} T}\right) \tag{3}$$

The partition function, $Q_{i,j}$, determines the Helmholtz free energy, $F_{i,j}$, of subsystem (cavity), containing i molecules of component 1 and j molecules of component 2:

$$F_{i,j} = -k_\mathrm{B} T \log Q_{i,j} \tag{4}$$

The grand partition function Ξ is a state function. For that reason, Ξ depends on two variables at constant temperature in binary system, and, as a consequence, Eq. (1) may be rewritten in the following form:

$$N_\mathrm{A}^{-1} k_\mathrm{B} T d \log \Xi = a_0 k_\mathrm{B} T d \log \xi = a_1 d\mu_1 + a_2 d\mu_2 \tag{5}$$

This expression has evident similarity with the Gibbs equation:

$$W d\Pi = a_1 d\mu_1 + a_2 d\mu_2 \tag{6}$$

Here W and Π are the volume of adsorbed solution and spreading pressure, respectively. Both Eqs. (5) and (6) result in the Gibbs Duhem equation when Π and ξ are constant simultaneously. This allows the main postulate in IAST to be reformulated in a more general way. Raoult's law holds along a constant value of the grand partition function, ξ, and the expressions for the dependence of partial pressures in the gaseous phase on molar fractions in adsorption solution being

$$p_1 = p_1^\circ(\xi)x_1, \quad p_2 = p_2^\circ(\xi)x_2 \tag{7}$$

In the case of a non-ideal gaseous phase, the partial pressure of each component should be replaced by its fugacity. Since the grand partition function, ξ, is closely related to the Helmholtz free energy, the question of its dependence on the number of molecules of both components within a cavity has to be resolved to provide the correlation (7). The exact result obtained (Appendix A) may be expressed as follows:

$$F_{m,0} = F_{0,m} + m(\mu_1^* - \mu_2^*) \tag{8}$$

$$F_{i,j} = \frac{i}{i+j}F_{i+j,0} + \frac{j}{i+j}F_{0,i+j} - k_B T \log\frac{(i+j)!}{i!j!} \tag{9}$$

Here μ_1^* and μ_2^* are the chemical potentials of pure components 1 and 2, respectively, at the same value of the grand partition function, ξ (and Π, consequently), as in the case of the binary system. Values μ_1^* and μ_2^* correspond to pressures p_1° and p_2°. According to Eq. (7), it may be written:

$$\mu_1 = \mu_1^* + k_B T \log x_1, \quad \mu_2 = \mu_2^* + k_B T \log x_2 \tag{10}$$

For the macroscopic variables μ_1^* and μ_2^* not to depend upon random numbers of molecules within separate cavities, it leads us immediately to the conclusion that the difference $(\mu_1^* - \mu_2^*)$ in Eq. (8) is to be constant. On the other hand, Eq. (8) requires the amounts of the pure components adsorbed a_1° and a_2° to be rigorously equal at the same value of grand partition function, ξ. Thus, the amounts a_1° and a_2° being equal, the corresponding magnitudes of chemical potentials μ_1^* and μ_2^* (and, as a consequence of $\log p_1^\circ$ and $\log p_2^\circ$) differ from each other by a constant. It should be emphasized that the condition discussed is required by the IAST postulate of the Raoult's law validity rather then by the real mechanism of adsorption equilibrium.

The basic outcome is undoubtedly contained in Eq. (9). The presence of the last term in this equation can be attributed to mixing entropy. Without this term Eq. (9) would be a simple expression of a rule of an average. It is obviously held for an internal energy. Applying the Gibbs Helmholtz equation

$$U_{i,j} = F_{i,j} - T\frac{dF_{i,j}}{dT} \tag{11}$$

the expression for internal energy may be written as follows:

$$U_{i,j} = \frac{i}{i+j}U_{i+j,0} + \frac{j}{i+j}U_{0,i+j} \tag{12}$$

Hence, for $F_{i,j} = U_{i,j} - TS_{i,j}$, the expression for entropy can be also deduced:

$$S_{i,j} = \frac{i}{i+j}S_{i+j,0} + \frac{j}{i+j}S_{0,i+j} + k_B \log\frac{(i+j)!}{i!j!} \tag{13}$$

The system of Eqs. (9), (12), (13) is obtained for an ideal adsorbed phase. In the case of non-ideal behavior it may be written as

$$F_{i,j} = \frac{i}{i+j}F_{i+j,0} + \frac{j}{i+j}F_{0,i+j} - k_B T \log\frac{(i+j)!}{i!j!} + F_{i,j}^{\mathrm{E}} \tag{14}$$

$$U_{i,j} = \frac{i}{i+j}U_{i+j,0} + \frac{j}{i+j}U_{0,i+j} + U_{i,j}^{\mathrm{E}} \tag{15}$$

$$S_{i,j} = \frac{i}{i+j}S_{i+j,0} + \frac{j}{i+j}S_{0,i+j} + k_B \log\frac{(i+j)!}{i!j!} + S_{i,j}^{\mathrm{E}} \tag{16}$$

where $F_{i,j}^{\mathrm{E}}$, $U_{i,j}^{\mathrm{E}}$ and $S_{i,j}^{\mathrm{E}}$ are the excess thermodynamic functions.

It is of interest to apply the Eq. (9) for the particular case when pure component isotherms are described by the Langmuir equation:

$$a_1^\circ = a_m\frac{K_1 p_1^\circ}{1 + K_1 p_1^\circ}, \quad a_2^\circ = a_m\frac{K_2 p_2^\circ}{1 + K_2 p_2^\circ} \tag{17}$$

Let us suppose that $a_m = Na_0$, where N is a saturation limit of molecules in a single cavity. Then (see Appendix B) it can be written for the Helmholtz free energy of the pure components

$$\begin{aligned} F_{m,0} &= -mk_\mathrm{B}T\log K_1 - k_\mathrm{B}T\log\frac{N!}{m!(N-m)!} \\ &\quad + m\mu_1^\circ(T) \\ F_{0,m} &= -mk_\mathrm{B}T\log K_2 - k_\mathrm{B}T\log\frac{N!}{m!(N-m)!} \\ &\quad + m\mu_2^\circ(T) \end{aligned} \tag{18}$$

For the ideal adsorbed phase (the excess functions are equal to zero) it is easily seen that the Helmholtz free energy for a mixture of i and j molecules of the components is given by,

$$\begin{aligned} F_{i,j} &= -ik_\mathrm{B}T\log K_1 - jk_\mathrm{B}T\log K_2 \\ &\quad - k_\mathrm{B}T\log\frac{N!}{i!j!(N-i-j)!} + i\mu_1^\circ(T) \\ &\quad + j\mu_2^\circ(T) \end{aligned} \tag{19}$$

and the isotherms for mixture adsorption are now written as

$$\begin{aligned} a_1 &= a_m\frac{K_1p_1}{1+K_1p_1+K_2p_2}, \\ a_2 &= a_m\frac{K_2p_2}{1+K_1p_1+K_2p_2} \end{aligned} \tag{20}$$

Thus the well-known Langmuir equation for binary system is derived from the new conception of ideal mixture on the level of separate cavity. This result is not surprising. In this case is supposed the adsorption to occur on active centers without interaction of the neighboring molecules. For this reason it does not matter whether the points are apart on the surface or grouped together at N molecules in each cavity. This is obviously the case of an ideal adsorbed phase that confirms the correctness of choice of ideal mixture model as the set of Eqs. (9), (12), (13).

The specific value of mixing entropy is

$$\bar{S}^\mathrm{M}_{i,j} = \frac{1}{i+j}k_\mathrm{B}\log\frac{(i+j)!}{i!j!} \tag{21}$$

In the macroscopic limit, when i and j are very high one may use of Stirling's formula for factorials. Then Eq. (21) may be rewritten as

$$\bar{S}^\mathrm{M} = -x_1k_\mathrm{B}\log x_1 - x_2k_\mathrm{B}\log x_2 \tag{22}$$

Here molar fractions x_1 and x_2 are equal to $i/(i+j)$ and $j/(i+j)$, respectively. This is the common expression of mixing entropy for an ideal mixture that is subject to Raoult's law.

In the case of ideal behavior of the adsorbed phase, adsorption equilibrium may be predicted as follows. Initially it is necessary to find the values of the Helmholtz free energy $F_{m,0}$ and $F_{0,m}$ for pure components 1 and 2, respectively, as a function of the sum of molecules present within a cavity by a treatment of individual isotherms, the system (1)–(4) reduced to a corresponding single component being used. Then one can calculate the amounts of $F_{i,j}$ for each combination of i and j using Eq. (9). Finally, the amounts of both adsorbed components may be calculated for given partial pressures using Eqs. (1)–(4).

In more general cases of non-ideal mixture behavior, the system (14)–(16) can be used to determine the excess thermodynamic function by least squares fitting of experimental data for binary mixture. Toward this end, the following approximations may be suggested:

$$\begin{aligned} U^\mathrm{E}_{i,j} &= \alpha_{i,j} - \frac{\beta_{i,j}}{k_\mathrm{B}T}, \quad TS^\mathrm{E}_{i,j} = -\frac{\beta_{i,j}}{2k_\mathrm{B}T}, \\ F^\mathrm{E}_{i,j} &= \alpha_{i,j} - \frac{\beta_{i,j}}{2k_\mathrm{B}T} \end{aligned} \tag{23}$$

Here $\alpha_{i,j}$ and $\beta_{i,j}$ are functions only of i and j.

Heats of Adsorption

In this paper heats of adsorption measured in experiments are considered as a source of additional information of the mixture state within a separate cavity. It is more safe to evaluate the thermodynamic functions mentioned above as compared to using numerical differentiation of the temperature dependency of partial pressures. If it can be assumed that the gaseous phase is ideal, the Clapeyron equations for isosteric heats of adsorption in a binary system may be written as

$$\begin{aligned} q_1 &= RT^2\left(\frac{\partial\log p_1}{\partial T}\right)_{a_1,a_2}, \\ q_2 &= RT^2\left(\frac{\partial\log p_2}{\partial T}\right)_{a_1,a_2} \end{aligned} \tag{24}$$

The isosteric and differential heats of adsorption are related by

$$q_1 = q_1^{\mathrm{d}} + RT, \quad q_2 = q_2^{\mathrm{d}} + RT \tag{25}$$

Combining Eqs. (24), (25), and (1)–(4) we can write

$$\begin{aligned} q_1^{\mathrm{d}}\varphi_{1,1} + q_2^{\mathrm{d}}\varphi_{1,2} &= N_{\mathrm{A}} \sum_i \sum_j \\ &\quad \times \left(\frac{a_1}{a_0} - i\right) \lambda_1^i \lambda_2^j Q_{i,j} \Delta U_{i,j} \\ q_1^{\mathrm{d}}\varphi_{2,1} + q_2^{\mathrm{d}}\varphi_{2,2} &= N_{\mathrm{A}} \sum_i \sum_j \\ &\quad \times \left(\frac{a_2}{a_0} - j\right) \lambda_1^i \lambda_2^j Q_{i,j} \Delta U_{i,j} \end{aligned} \tag{26}$$

where the following notations are assumed

$$\begin{aligned} \varphi_{1,1} &= \sum_i \sum_j i\left(i - \frac{a_1}{a_0}\right) \lambda_1^i \lambda_2^j Q_{i,j}, \\ \varphi_{1,2} &= \sum_i \sum_j j\left(i - \frac{a_1}{a_0}\right) \lambda_1^i \lambda_2^j Q_{i,j} \\ \varphi_{2,1} &= \sum_i \sum_j i\left(j - \frac{a_2}{a_0}\right) \lambda_1^i \lambda_2^j Q_{i,j}, \\ \varphi_{2,2} &= \sum_i \sum_j j\left(j - \frac{a_2}{a_0}\right) \lambda_1^i \lambda_2^j Q_{i,j} \end{aligned} \tag{27}$$

In Eq. (26) $\Delta U_{i,j}$ is the deviation between the internal energy of an aggregate of i molecules of component 1 and j molecules of component 2 and its internal energy in the bulk gas phase at the same temperature. Binary isotherms include the Helmholtz free energy $F_{i,j}$. The equations for heats of adsorption include both $F_{i,j}$ and $\Delta U_{i,j}$. Consequently, by simultaneous least squares treatment of the experimental adsorption equilibrium data and heats of adsorption it is possible to find the Helmholtz free energy, internal energy, and then entropy of each i, j combination.

The Case of Pure Component Adsorption

The mathematical model described above may be used easily for single component equilibrium. Saving double subscripts for the thermodynamic functions, the equilibrium adsorption equation for the pure component 1 ($p_2 = a_2 = 0$) and for the pure component 2 ($p_1 = a_1 = 0$) can be written as follows

$$\begin{aligned} a_1 &= a_0 \xi_1^{-1} \sum_m m p_1^m \exp\left(-\frac{F_{m,0} - m\mu_1^\circ}{k_{\mathrm{B}}T}\right), \\ \xi_1 &= \sum_m p_1^m \exp\left(-\frac{F_{m,0} - m\mu_1^\circ}{k_{\mathrm{B}}T}\right) \\ a_2 &= a_0 \xi_2^{-1} \sum_m m p_2^m \exp\left(-\frac{F_{0,m} - m\mu_2^\circ}{k_{\mathrm{B}}T}\right), \\ \xi_2 &= \sum_m p_2^m \exp\left(-\frac{F_{0,m} - m\mu_2^\circ}{k_{\mathrm{B}}T}\right) \end{aligned} \tag{28}$$

For heats of adsorption, Eq. (26) gives:

$$\begin{aligned} q_1 &= RT - N_{\mathrm{A}} \\ &\quad \times \frac{\sum_m (m - a_1/a_0) \Delta U_{m,0}\, p_1^m \exp\left(-\frac{F_{m,0} - m\mu_1^\circ}{k_{\mathrm{B}}T}\right)}{\sum_m m(m - a_1/a_0)\, p_1^m \exp\left(-\frac{F_{m,0} - m\mu_1^\circ}{k_{\mathrm{B}}T}\right)} \\ q_2 &= RT - N_{\mathrm{A}} \\ &\quad \times \frac{\sum_m (m - a_2/a_0) \Delta U_{0,m}\, p_2^m \exp\left(-\frac{F_{0,m} - m\mu_2^\circ}{k_{\mathrm{B}}T}\right)}{\sum_m m(m - a_2/a_0)\, p_2^m \exp\left(-\frac{F_{0,m} - m\mu_2^\circ}{k_{\mathrm{B}}T}\right)} \end{aligned} \tag{29}$$

The values $F_{m,0}$ and $U_{m,0}$ are assumed to be the Helmholtz free energy and the internal energy, respectively, of m molecules of pure component 1 in a cavity. Similarly $F_{0,m}$ and $U_{0,m}$ are the Helmholtz free energy and the internal energy, respectively, of m molecules of pure component 2 in a cavity. Equations (28) and (29) allow us to determine the thermodynamic functions for a single cavity from the experimental data of pure-component adsorption equilibrium and heats of adsorption by their simultaneous treatment.

The Analysis of Equilibrium Adsorption of CO_2 and C_2H_6 and their Mixtures in NaX

The equilibrium adsorption of a binary mixture of carbon dioxide and ethane in NaX (Dunne et al., 1996, 1997) is a clear-cut case of a non-ideal system. This is due to the differences between the molecules both in size and type of molecular interactions. It was shown by the authors that the potential field of this zeolite is sharply heterogeneous to quadrupolar CO_2 molecules and almost homogeneous to nonpolar molecules of C_2H_6. For this reason the IAST predictions for both selectivity and heats of adsorption are rather far from experiment. In view of the rearrangement of molecules that occurs in a non-homogeneous field, we shall find it interesting to consider the manifestation of this factor in excess thermodynamic functions for a separate cavity.

Equilibrium Adsorption of Pure Gases

A commercial sample of NaX ($Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]\cdot xH_2O$), described by Dunne and coworkers is characterized by the value of a_0 equal to 0.596 mole per kilogram. The deviations of entropy and internal energy at constant number of molecules within a cavity are supposed to be independent of temperature in the region of interest. The dependencies of entropy and internal energy on number of molecules the component 1 are given by polynomial approximations:

$$\Delta S_{m,0} = \sum_{k=1}^{n} b_k m^k, \quad \Delta U_{m,0} = \sum_{k=1}^{l} c_k m^k \tag{30}$$

Similarly for the component 2

$$\Delta S_{0,m} = \sum_{k=1}^{n} d_k m^k, \quad \Delta U_{0,m} = \sum_{k=1}^{l} e_k m^k \tag{31}$$

The standard quantity of entropy was adopted to be equal to the entropy of the bulk phase at standard pressure (1 Pa) and the same temperature. Consequently,

$$\begin{aligned} F_{m,0} - m\mu_1^\circ(T) &= \Delta F_{m,0} - mk_BT = \Delta U_{m,0} \\ &\quad - T\Delta S_{m,0} - mk_BT \\ F_{0,m} - m\mu_2^\circ(T) &= \Delta F_{0,m} - mk_BT = \Delta U_{0,m} \\ &\quad - T\Delta S_{0,m} - mk_BT \end{aligned} \tag{32}$$

The coefficients b_k, c_k, d_k and e_k, (for $n = 5$, $l = 4$) have been determined by least squares method with using both of equations (28) and (29) simultaneously, the functional to be minimized being as follows

$$\sum_r \left[\left(\log p_r^{\text{cal}} - \log p_r^{\text{exp}}\right)^2 + \left(\frac{q_r^{\text{cal}}}{q_r^{\text{exp}}} - 1\right)^2 \right] \tag{33}$$

Here r is the number of an experimental point. The superscripts 'cal' or 'exp' point to calculated or experimental values of variables, respectively. It is also assumed that the notations p and q (without subscripts 1 or 2) are the pressure and the isosteric heat of adsorption, respectively, either of pure component 1 or pure component 2.

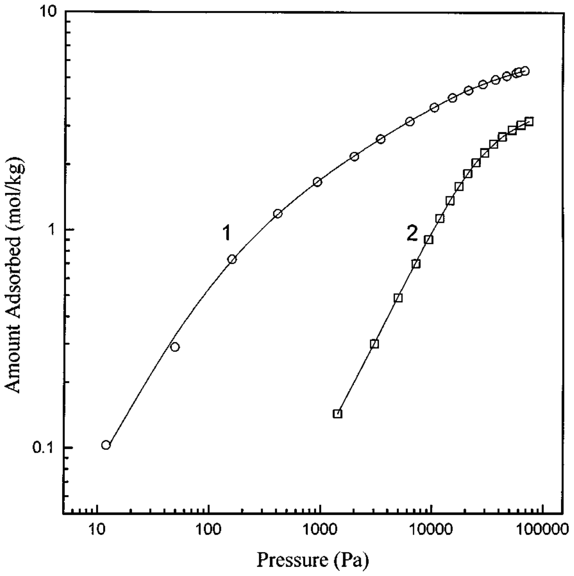

Figure 1. Pure component isotherms of CO_2 at 31.4°C (1) and C_2H_6 at 32.4°C (2) in NaX. Solid lines are calculated by Eq. (28).

It was observed that the upper limit of summation in Eqs. (26) and (27) can be infinity. Nevertheless, the probability of finding more than 7 molecules of ethane and 10 molecules of carbon dioxide within a cavity becomes negligible. Thus, it may be concluded from the analysis of experimental data that saturation limits are 7 and 10 molecules per cavity for CO_2 and C_2H_6, respectively. Figures 1 and 2 show the experimental data for the pure component isotherms and isosteric heats of adsorption as a function of amount adsorbed. The solid lines are the result of calculation with coefficients found by least squares. The dependence of specific internal energy related to k_BT for number of molecules within a cavity is plotted in Fig. 3. It is easily seen that average internal energy per molecule of CO_2 grows with increasing of number of molecules in cavity. This may be explained as follows. Adding each new molecule of CO_2 increases the CO_2-CO_2 interaction. On the other hand, the average ion–quadrupole interaction decreases, and the latter predominates. To the contrary, the specific internal energy of nonpolar ethane decreases with loading because of the relatively weak gas–solid interaction and the insignificant potential field dispersion. Thus, the potential field in a cavity

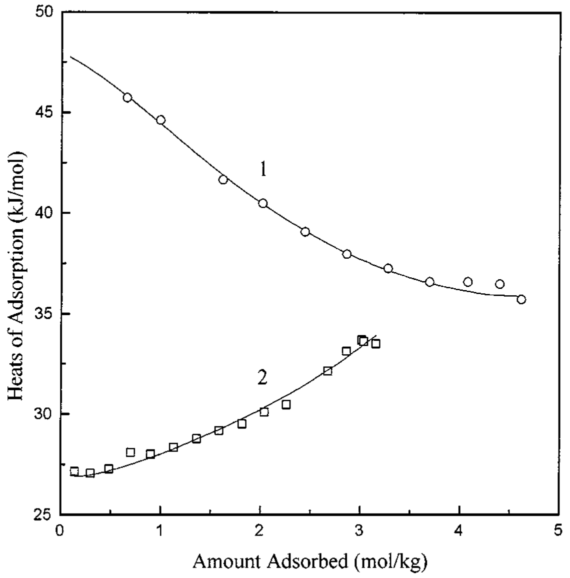

Figure 2. Isosteric heats of adsorption for CO_2 at 31.4°C (1) and C_2H_6 at 32.4°C (2) in NaX. Solid lines are calculated by Eq. (29).

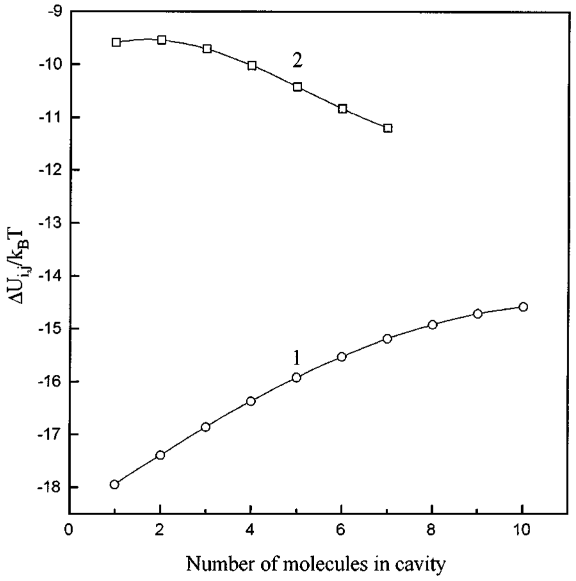

Figure 3. Dependencies of specific internal energies of pure CO_2 at 31.4°C (1) and pure C_2H_6 at 32.4°C (2) in NaX on number of molecules in a zeolite cavity.

is nearly homogeneous in relation to ethane and essentially heterogeneous to carbon dioxide.

Figure 4 illustrates the change of specific entropy with increasing number of molecules. These curves are also informative. The essential fall of the specific entropy of ethane with coverage indicates the decrease of indeterminacy in mutual disposition. Consequently, the dispersion of potential energy becomes rather small, especially at saturation limit. As opposed to this, the specific entropy of carbon dioxide is nearly constant up to approximately 8 molecules per cavity. This appears to be associated with strong interactions of Na^+ ion–quadrupole moment of CO_2 that results in a partial loss in molecular mobility with the emergence of an ordered structure. This is exhibited in the decrease of entropy. The low values of entropy (and, hence, its insignificant change) are due to the relatively small dispersion in internal energy at any constant number of molecules (in the canonical ensemble). It, however, does not mean that the average energy is not function of a number of molecules within a cavity.

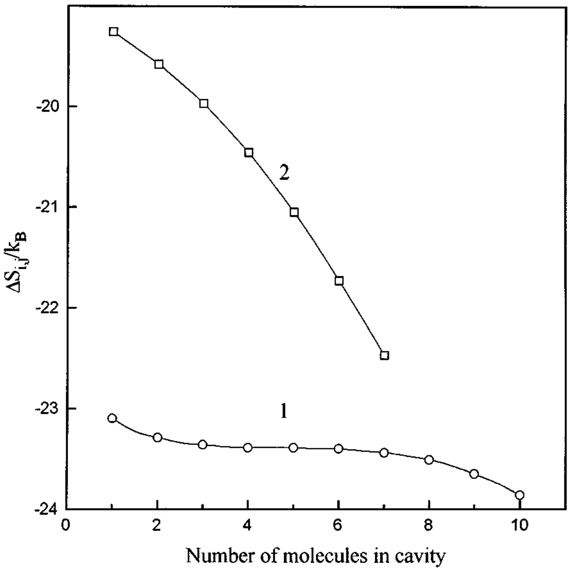

Figure 4. Dependencies of specific entropy of pure CO_2 at 31.4°C (1) and pure C_2H_6 at 32.4°C (2) in NaX on number of molecules in a zeolite cavity.

Adsorption of Binary Mixtures

The equilibrium adsorption of binary mixtures of CO_2 and C_2H_6 has been studied in the paper mentioned above, with the amount of ethane kept approximately constant. In the first series the preloading of ethane was 1.43 mol/kg at 29.4°C. In the other series the amount of ethane was kept at a higher level (2.57 mol/kg) at 28.94°C. Both partial pressures at different amounts of CO_2 adsorbed and individual heats of adsorption q_1 and q_2 were measured.

The calculation of mixture equilibrium was realized by Eqs. (1)–(4) and Eq. (26) for the heats of adsorption. The thermodynamic functions for each combination of i and j molecules in a cavity were calculated by Eqs. (14)–(16), with the values of the single component functions being determined previously from pure-component data. Equation (23) was used to calculate the excess functions. For the variables $\alpha_{i,j}$ and $\beta_{i,j}$, the following regression equations were used:

$$\alpha_{i,j} = \sum_{k=1}^{s} \sum_{l=1}^{s-k+1} A_{k,l} i^k j^l, \quad \beta_{i,j} = \sum_{k=1}^{g} \sum_{l=1}^{g-k+1} B_{k,l} i^k j^l \tag{34}$$

For the above equation numbers s and g were equal to 3 and 2, respectively. Hence, the total number of regression coefficients was equal to 9. The main goal in this paper was focused on the determination of the regression coefficients by least squares to have an opportunity to analyze real properties of adsorbed mixtures. We have used the functional to be minimized consisting of sums of squared deviations of four variables, namely logarithms of partial pressures and individual heats of adsorption.

The regression coefficients found by least squares were further used for calculation of partial pressures, selectivity, heats of adsorption, and excess thermodynamic functions. For example, selectivity curves obtained by such a way are plotted in Figs. 5 and 6 at low and high preloading of ethane, respectively. Comparison with experimental points shows that the number of coefficients and their numeric values were chosen correctly. Undoubtedly, this procedure is not a prediction. Nevertheless, for the ideal mixture limit the calculations may be performed with pure-component adsorption data. Curves 2 in Figs. 5 and 6 apply when the excess functions are equal to zero. Curves 3 apply to an ideal mixture but in accordance with IAST. The slight deviations of these curves are caused by the circumstance that condition (8) is defaulted. Speaking strictly, in that case the IAST postulate of Raoult's law is inconsistent with the statistical thermodynamic theory. Complete agreement of these approaches is reached only in the case in which the pure-component isotherms are coincident, with an affinity coefficient equal to 1.

Molecules of CO_2 are evidently to displace molecules of C_2H_6 near to Na^+ ions because of the strong ion–quadrupole interaction. It results in a decrease of potential energy as compared with the value predicted for an ideal mixture. That is why the heats of adsorption are higher to certain extent than could be expected for ideal mixture behavior. Figure 7 shows the

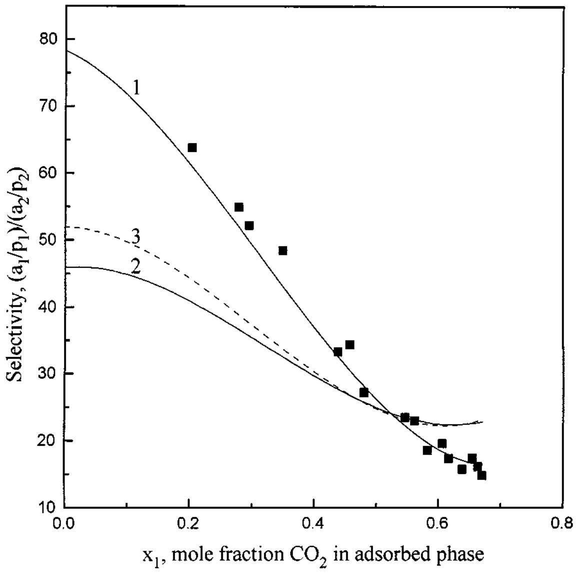

Figure 5. Selectivity for adsorption of mixtures of CO_2 and C_2H_6 at 29.4°C, constant amount of C_2H_6 adsorbed ≈1.431 ± 0.055 mol/kg. (■) experimental data; (1) statistical thermodynamic theory; (2) statistical thermodynamic theory for the ideal mixture; (3) (dashed lines) IAST predictions.

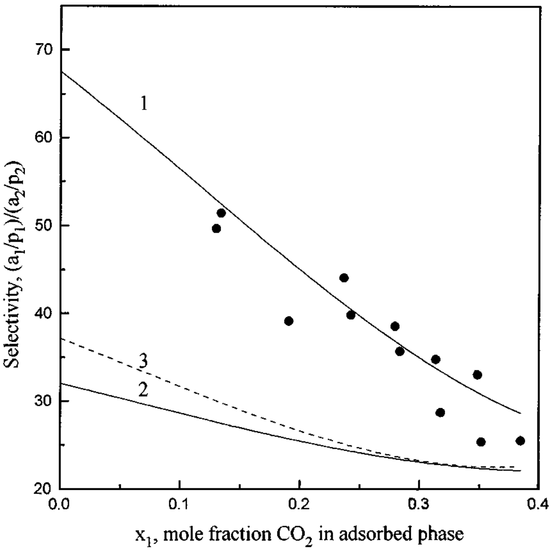

Figure 6. Selectivity for adsorption of mixtures of CO_2 and C_2H_6 at 28.94°C, constant amount of C_2H_6 adsorbed ≈2.57 ± 0.04 mol/kg. (●) experimental data; (1) statistical thermodynamic theory; (2) statistical thermodynamic theory for the ideal mixture; (3) (dashed lines) IAST predictions.

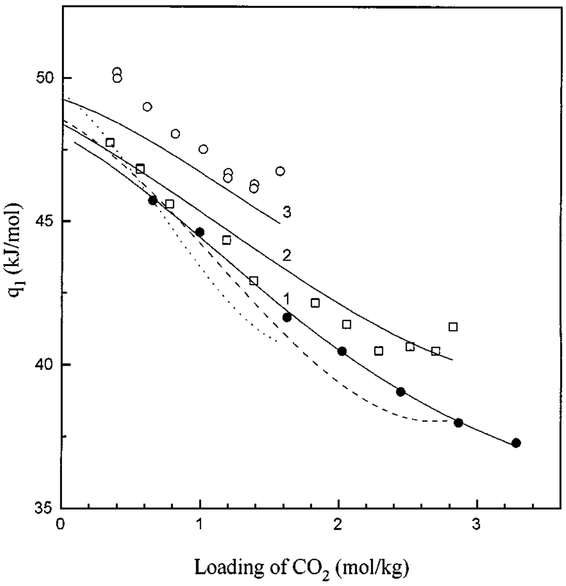

Figure 7. Individual isosteric heats of adsorption for CO_2 from mixtures of CO_2 and C_2H_6 in NaX. (Points) experimental data; (solid lines) results of approximation by the model suggested; (dashed line) IAS prediction for low preloading of C_2H_6; (dotted line) IAS prediction for high preloading of C_2H_6. (●, 1) pure CO_2 at 31.4°C. Amount of C_2H_6 preloaded: (□, 2, dashed line) 1.431±0.055 mol/kg at 29.4°C, (○, 3, dotted line) 2.57 ± 0.04 mol/kg at 28.94°C.

dependence of the partial heats of adsorption of CO_2 on amount of CO_2 adsorbed at 3 values of constant amount of C_2H_6: 0, 1.431, and 2.57 mol/kg. The solid lines are the result of calculation by the suggested statistical thermodynamic model for the regression coefficients found by least squares. Curve 1 is the dependence of isosteric heat of pure CO_2 on the amount adsorbed. It is seen from a comparison of the three curves that adding of ethane (at other conditions being equal) leads to the increase of the isosteric heat of CO_2 adsorption. This tendency is evident, since the adsorbing molecules of CO_2 interact with both adsorbent and the C_2H_6 preloaded earlier. The dashed and dotted lines are calculated by the IAST for the values of the amount adsorbed of ethane 1.431 and 2.57 mol/kg, respectively. These curves show that the IAST prediction conflicts with the real mechanism of adsorption since the increase of ethane preloading accompanies with the decrease of the partial heats for CO_2 (except the region of low values of CO_2 loading).

Figure 8 represents the dependence of the partial isosteric heats of ethane on CO_2 loading at the two levels of ethane amount adsorbed: 1.431 mol/kg (1) and 2.57 mol/kg (2). The increase of CO_2 loading at constant value of C_2H_6 preloaded, as it is expected, leads to the increase of partial heats of CO_2 adsorption. However, the calculation by the IAST (dashed and dotted lines) shows also the contrary tendency.

The difference in interaction of molecules of carbon dioxide and ethane with Na^+ ions causes the rearrangement of molecules within a cavity. Ideal mixture behavior implies equiprobable random distribution of molecules of each component within the volume of a micropore. It ensures the maximum entropy of system. The effect of molecular rearrangement under influence of an inhomogeneous adsorption field leads to emergence of order in the mutual disposition of molecules and, as a consequence, to a decrease in entropy. Thus, excess values of internal energy and entropy are to be negative. Figure 9 shows the dependence of specific excess molar thermodynamic functions upon composition for a constant total number of molecules in a cavity ($i + j = 7$). The excess Helmholtz free energy is also negative. It means that decreasing internal energy, as affected by non-uniform potential field distribution, is more significant than the corresponding change of entropy. Figures 10 and 11, respectively, illustrate the internal energy end entropy dependence on number of molecules of CO_2, with total number of molecules in cavity being constant along each curve. The last point

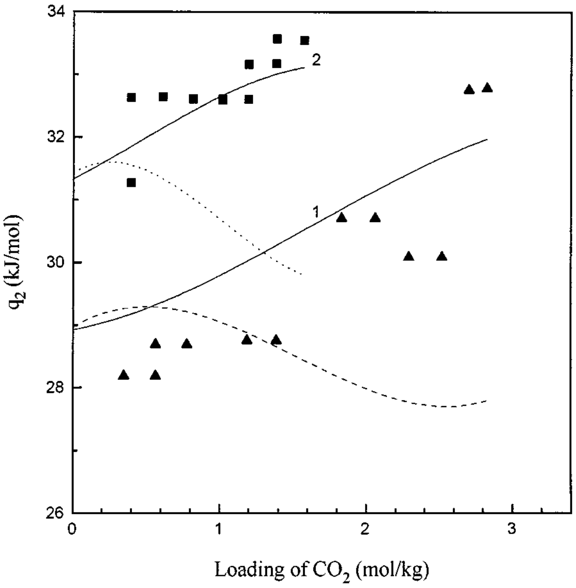

Figure 8. Individual isosteric heats of adsorption for C_2H_6 from mixtures of CO_2 and C_2H_6 in NaX. (Points) experimental data; (solid lines) results of approximation by the model suggested; (dashed line) IAS prediction for low preloading of C_2H_6; (dotted line) IAS prediction for high preloading of C_2H_6. Amount of C_2H_6 preloaded: (▲, 1, dashed line) 1.431 ± 0.055 mol/kg at 29.4°C, (■, 2, dotted line) 2.57 ± 0.04 mol/kg at 28.94°C.

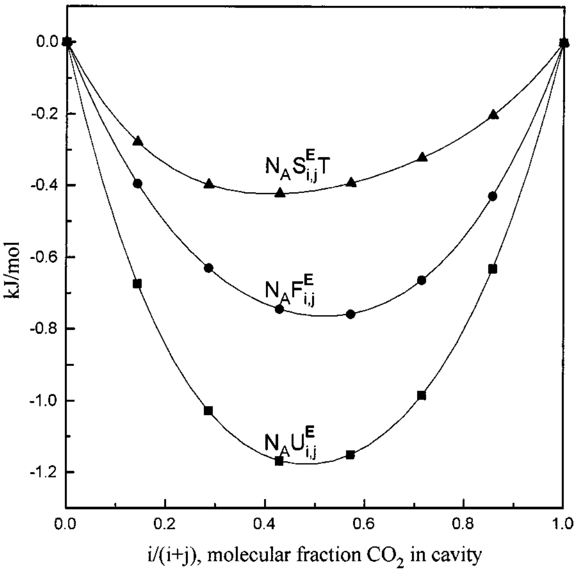

Figure 9. Excess Helmholtz free energy (●), excess internal energy (■) and excess entropy (▲) of molecular mixture in a single cavity as a function of number of carbon dioxide molecules. Total number of molecules is equal to 7 (29°C).

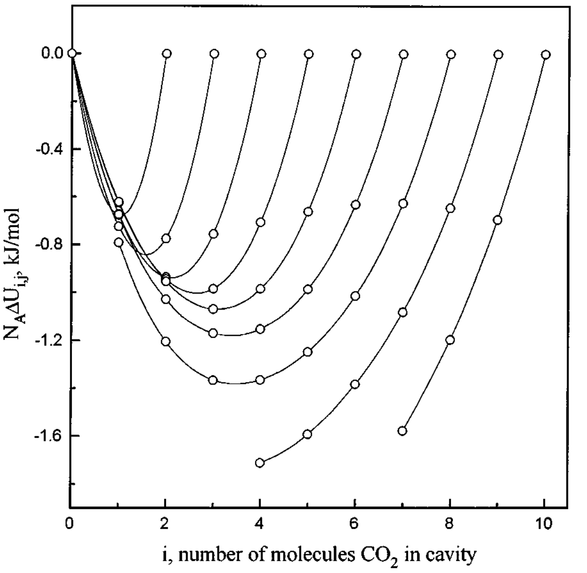

Figure 10. Dependencies of excess internal energy of molecular mixture in a single cavity on number of carbon dioxide molecules along the lines of constant total number of molecules (29°C).

of each curve corresponds to pure carbon dioxide. So, the abscissa value of the last point is numerically equal to the total number of molecules for the curve. On the other hand, the volume of a CO_2 molecule is lower than

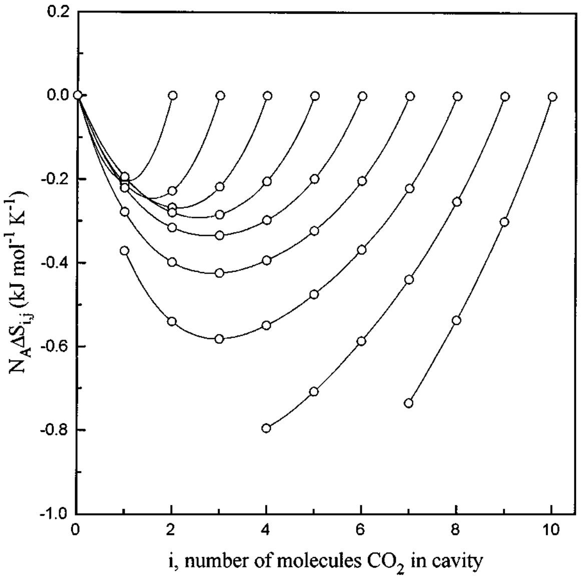

Figure 11. Dependencies of excess entropy of molecular mixture in a single cavity on number of carbon dioxide molecules along the lines of constant total number of molecules (29°C).

that of ethane. Consequently, the volume of the molecular aggregate increases with substitution of CO_2 by C_2H_6 up to its maximum value bounded by the volume of cavity. For this reason curves corresponding to higher total numbers of molecules are broken on their left ends.

The last three figures (Figs. 9, 10 and 11) illustrate the main result of this research. The excess functions carry important information of the potential field distribution within a separate cavity. The procedure suggested is free from any postulates and empirical agreements. Being based on reliable statistical thermodynamic method, the approach may be considered as a tool for analysis of various binary systems on the microscopic level. Equilibrium adsorption of CO_2-C_2H_6 mixtures is one of the interesting examples of sharply non-ideal mixture behavior. Accumulation of data for a large number of binary systems will probably allow description of the molecular mixture state affected by inhomogeneous potential fields.

Conclusions

Analysis of the IAST as applied to the adsorption in zeolites allowed us to formulate the criterion of ideal behavior of adsorbed solution on a microscopic level. Expressions for Helmholtz free energy, internal energy and entropy of molecular mixtures in a separate cavity for the case of ideal mixture behavior are obtained. The novel procedure is developed to determine excess thermodynamic functions by treatment of experimental data of equilibrium mixture adsorption and heats of adsorption simultaneously. The system of carbon dioxide–ethane–NaX zeolite has been considered from this viewpoint. The dependence of excess functions upon the total number of molecules within a separate cavity and molecular fractions was found, the excess functions appear to be negative. It was shown that the heterogeneity of the adsorption field in a cavity results in molecular rearrangement followed by decrease of internal energy, with the ordering of molecular structure being accompanied by decreased entropy. The rearrangement may be attributed to substituting quadrupolar CO_2 molecules for nonpolar ethane close to Na^+ ions. The results correspond to analysis of pure-component equilibria. In particular, the entropy of carbon dioxide is essentially less than that of ethane, which points to a more ordered structure of CO_2 owing to ion–quadropole interactions as compared with ethane. It allows us to assume that further investigations based on detailed analysis of molecular mixtures in the terms of the canonical ensemble will probably allow development of a calculation procedure for prediction of a mixture behavior from pure-component data.

Appendix A

The grand partition function may be rewritten as follows:

$$\xi = \sum_m \sum_{j=0}^{m} \exp\left[\frac{(m-j)\mu_1 + \mu_2 - F_{m-j,j}}{k_B T}\right] \quad \text{(A1)}$$

Here m is total number of molecules within a cavity; $m - j = i$—number of component 1 molecules. According to the IAST for an ideal mixture

$$\mu_1 = \mu_1^* + k_B T \log x_1, \quad \mu_2 = \mu_2^* + k_B T \log x_2 \quad \text{(A2)}$$

where μ_1^* and μ_2^* are chemical potentials for pure-component adsorption which provide the same value of ξ. Substituting (2) into (1), we obtain

$$\xi = \sum_m \sum_{j=0}^{m} x_1^{m-j} x_2^{j} \exp\left[\frac{(m-j)\mu_1^* + \mu_2^* - F_{m-j,j}}{k_B T}\right] \quad \text{(A3)}$$

For pure-component 1, ξ is written as

$$\xi = \sum_m \exp\left(\frac{m\mu_1^* - F_{m,0}}{k_B T}\right) \quad \text{(A4)}$$

Since the value of ξ in (4) is the same as in (3), we can equate expressions to the right of the sums on m and write the system of the algebraic equations:

$$\sum_{j=0}^{m} x_1^{m-j} x_2^{j} \exp\left[\frac{(m-j)\mu_1^* + j\mu_2^* - F_{m-j,j}}{k_B T}\right] = \exp\left(\frac{m\mu_1^* - F_{m,0}}{k_B T}\right), \quad m = 1, 2, \ldots \quad \text{(A5)}$$

For $m = 1$ we obtain

$$x_1 \exp\left(\frac{\mu_1^* - F_{1,0}}{k_B T}\right) + x_2 \exp\left(\frac{\mu_2^* - F_{0,1}}{k_B T}\right) = \exp\left(\frac{\mu_1^* - F_{1,0}}{k_B T}\right)$$

Since $x_2 = 1 - x_1$, simplification this expression yields

$$F_{1,0} = F_{0,1} + \mu_1^* - \mu_2^*$$

Using this equation, solution of the Eq. (A5) at $m = 2$ gives

$$F_{2,0} = F_{0,2} + 2(\mu_1^* - \mu_2^*)$$
$$F_{1,1} = \frac{(F_{2,0} + F_{0,2})}{2} - k_B T \log 2$$

Recurrently solving the system (5) at ever growing values of m, we obtain the following system

$$F_{m,0} = F_{0,m} + m(\mu_1^* - \mu_2^*) \quad \text{(A6)}$$

$$F_{i,j} = \frac{i}{m} F_{m,0} + \frac{j}{m} F_{0,m} - k_B T \log \frac{m!}{i!j!}, \quad m = i + j \quad \text{(A7)}$$

It is evident from Eq. (6) that the residual $(\mu_1^* - \mu_2^*)$ must be constant at constant temperature. So,

$$\mu_1^* - \mu_2^* = \mu_1^\circ - \mu_2^\circ - k_B T \log\left(\frac{x_1/p_1}{x_2/p_2}\right) = \text{const}$$

Consequently, the selectivity denoted as $S_{12} = (x_1/p_1)/(x_2/p_2)$ is to be constant. This is an obligatory condition for Raoult's law to be valid.

Appendix B

Let N be the number of molecules necessary to entirely fill a cavity both of component 1 and component 2. Let us assume further, that the Helmholtz free energies are described by following equations:

$$\begin{aligned} F_{m,0} &= -mk_{\mathrm{B}}T \log K_1 - k_{\mathrm{B}}T \log \frac{N!}{m!(N-m)!} \\ &\quad + m\mu_1^{\circ}(T) \\ F_{0,m} &= -mk_{\mathrm{B}}T \log K_2 - k_{\mathrm{B}}T \log \frac{N!}{m!(N-m)!} \\ &\quad + m\mu_2^{\circ}(T) \end{aligned} \tag{B1}$$

In that case for the component 1 we obtain

$$\begin{aligned} \lambda_1^m Q_{m,0} &= \exp\left(\frac{m\mu_1^* - F_{m,0}}{k_B T}\right) \\ &= \frac{N!}{m!(N-m)!}\left(K_1 p_1^{\circ}\right)^m \end{aligned} \tag{B2}$$

For the grand partition function it gives

$$\begin{aligned} \xi_1 &= \sum_{m=0}^{N} \lambda_1^m Q_{m,0} = \sum_{m=0}^{N} \frac{N!}{m!(N-m)!}\left(K_1 p_1^{\circ}\right)^m \\ &= \left(1 + K_1 p_1^{\circ}\right)^N \end{aligned} \tag{B3}$$

Then the isotherm can be written as follows

$$a_1^{\circ} = a_0 \frac{d \log \xi_1}{d \log p_1^{\circ}} = a_m \frac{K_1 p_1^{\circ}}{1 + K_1 p_1^{\circ}}, \quad a_m = a_0 N \tag{B4}$$

Completely similarly, for the component 2 we can write

$$\begin{aligned} \xi_2 &= \sum_{m=0}^{N} \lambda_2^m Q_{0,m} = \sum_{m=0}^{N} \frac{N!}{m!(N-m)!}\left(K_2 p_2^{\circ}\right)^m \\ &= \left(1 + K_2 p_2^{\circ}\right)^N \end{aligned} \tag{B5}$$

$$a_2^{\circ} = a_0 \frac{d \log \xi_2}{d \log p_2^{\circ}} = a_m \frac{K_2 p_2^{\circ}}{1 + K_2 p_2^{\circ}}, \quad a_m = a_0 N \tag{B6}$$

Thus, for the Helmholtz free energy given by Eq. (B1) pure-component isotherms are described by the Langmuir equation.

In the case of binary mixture adsorption, according to IAST, Raoult's law should hold along the constant ξ (that is equivalent to the constant spreading pressure). Hence, $\xi_1 = \xi_2$ that can be expressed by following form

$$\left(1 + K_1 p_1^{\circ}\right)^N = \left(1 + K_2 p_2^{\circ}\right)^N$$

It means that $K_1 p_1^{\circ} = K_2 p_2^{\circ}$ and

$$\mu_1^* - \mu_2^* = \mu_1^{\circ} - \mu_2^{\circ} + k_{\mathrm{B}}T \log\left(\frac{K_2}{K_1}\right) = \text{const}$$

Consequently, the requirement of constancy of the selectivity is valid, providing that Raoult's law is also valid in that case.

Combining (1) and (9) in the main text yields the Helmholtz free energy of molecular mixture

$$\begin{aligned} F_{i,j} &= -ik_{\mathrm{B}}T \log K_1 - jk_{\mathrm{B}}T \log K_2 \\ &\quad - k_{\mathrm{B}}T \log \frac{N!}{i!j!(N-i-j)!} + i\mu_1^{\circ}(T) \\ &\quad + j\mu_2^{\circ}(T) \end{aligned} \tag{B7}$$

It leads to the following expressions

$$\begin{aligned} \lambda_1^i \lambda_2^j Q_{i,j} &= \exp\left(\frac{i\mu_1 + j\mu_2 - F_{i,j}}{k_{\mathrm{B}}T}\right) \\ &= \frac{N!}{i!j!(N-i-j)!}(K_1 p_1)^i (K_2 p_2)^j \end{aligned} \tag{B8}$$

$$\begin{aligned} \xi &= \sum_{i=0}^{N} \sum_{j=0}^{N-i} \lambda_1^i \lambda_2^j Q_{i,j} \\ &= \sum_{m=0}^{N} \frac{N!}{m!(N-m)!}(K_1 p_1 + K_2 p_2)^m \\ &= (1 + K_1 p_1 + K_2 p_2)^N \end{aligned} \tag{B9}$$

Finally, we obtain

$$\begin{aligned} a_1 &= a_m \frac{K_1 p_1}{1 + K_1 p_1 + K_2 p_2}, \\ a_2 &= a_m \frac{K_2 p_2}{1 + K_1 p_1 + K_2 p_2} \end{aligned} \tag{B10}$$

Nomenclature

a	Amount adsorbed, mol/kg
a_0	Number of cavities, expressed in moles, per mass unit of adsorbent, mol/kg
F	Helmholtz free energy of an aggregate of the number of molecules specified, J
F^{E}	Excess Helmholtz free energy, J

i and j	Number of molecules of components
k_B	Boltzmann constant, $=1.38 \times 10^{-23}$ J/K
m	Total number of molecules of both components
M	Number of cavities per mass unit of pure adsorbent, kg^{-1}
N_A	Avogadro number, $=6.02 \times 10^{23}$
p	[Partial] pressure of adsorptive, Pa
p°	Equilibrium pressure for pure component at the same value of grand partition function that for mixture, Pa
q	[Partial] isosteric heats of adsorption, kJ/mol
q^d	[Partial] differential heats of adsorption, kJ/mol
Q	Partition function
S	Entropy of molecules in a cavity, J/K
S^E	Excess entropy of molecules in a cavity, J/K
S^M	Mixing entropy of molecules in a cavity, J/K
T	Absolute temperature, K
U	Internal energy of molecules in a cavity, J
U^E	Excess internal energy of molecules in a cavity, J
v	Volume of a single molecule, m^3
V	Volume of a separate cavity, m^3
W	Volume of adsorbed solution, m^3/kg
x	Molar fraction

Greek Letters

λ	Function defined by Eq. (3)
μ	Chemical potential of a component, J/molecule
μ^*	Chemical potential of a pure component as defined by Eq. (10), J/molecule
μ°	Standard chemical potential of a component corresponding to some standard pressure, J/molecule
Ξ	Grand partition function
ξ	Grand partition function related to a single cavity
Π	Spreading pressure of adsorbate, Pa

Subscripts

1	Component 1
2	Component 2

if double subscripts are specified, the first is the number of molecules of component 1 and the second is the number of molecules of component 2

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