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Multicomponent Equilibrium Adsorption on Heterogeneous Adsorbents

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Abstract. A generalized method for prediction of multicomponent adsorption is suggested based on representing that adsorbent volume as energetically inhomogeneous. The method depends on extending the Polanyi potential theory to mixture adsorption. The main feature of the method is that, at constant partial pressure and temperature the composition of an adsorbed phase is not uniform over its volume. Results of applying this theory to non-porous adsorbents have been considered. The prediction ability of the theory is confirmed for the strongly non-ideal system acetone–chloroform–graphitized carbon black. It was shown that the departure from ideal behavior of adsorbed phase is quite close to that for the liquid mixture. Another system considered was oxygen–nitrogen–anatase at 78 K. Although this mixture is ideal, it has been found that there is significant variation in composition over the adsorbed layer due to the difference in the interactions of the quadrupolar N_2 molecule and nonpolar O_2 molecule with the anatase surface.

Keywords: activated carbon, adsorbent surface, equilibrium theory, mixture adsorption, gases phase, adsorbed solution

Introduction

The prediction of mixture adsorption is important to modeling and design of adsorption processes for purification and separation. In previous attempts to develop representations of mixture adsorption several directions have been followed. One of these is based on theoretical constructions that allow both the isotherms of the pure components and their mixtures to be obtained. In particular, the Langmuir model (1918) was extended to mixtures by Markham and Benton (1931). Another example is the vacancy solution model (Bering et al., 1977; Jakubov et al., 1977; Suwanayuen and Danner, 1980). It is supposed that, even in the case of pure component adsorption, the adsorbed phase is a binary mixture, with one of the components being the vacancies. In the case of binary mixture adsorption the adsorbed phase is considered as a ternary solution. Additional assumptions concerning vacancy properties and activity coefficients of vacancy solution give various partition equations for isotherms.

The second direction is independent of the particular form of the pure component isotherms. One of representatives of this group of theories is the widely used Ideal Adsorbed Solution Theory (IAST) (Myers and Prausnitz, 1965). In accordance with this theory it is postulated that Raoult's law should hold along lines of fixed spreading pressure. This postulate allows prediction of mixture adsorption based only on information on the pure component adsorption isotherms.

These two groups of approaches are macroscopic and use phenomenological thermodynamics. In contrast, the third direction is based on a statistical thermodynamic model (Ruthven et al., 1973; Ruthven, 1976). This method is developed for zeolites and uses some simplifications such as analogy with van der Waals gas for molecules in a cavity.

In all cases mentioned it is actually supposed that the adsorbent volume is energetically uniform, so the variation of mixture composition over an adsorbed phase is not essential. In particular, in the IAST the mole fraction of each component is determined as an average value over the whole adsorbed phase, independently of spreading pressure. Most further attempts to take into account energetic heterogeneity have been based on polysite models, with adsorption on an individual site obeying to the Langmuir equation. Partition forms of the isotherm equation depend on choice of a distribution of energy sites. For example, a two-site model was described by Myers (1983) and a polysite model was investigated by Valenzuela et al. (1988). The main disadvantage of approaches like these is that intermolecular interactions are ignored. The theory of inhomogeneous adsorption volume (Ustinov, 1987, 1988, 1997) has been developed by taking into account a distribution function of adsorption volume elements. This approach can be considered as a logical extention of the Polanyi potential theory to mixtures. In this context it should be noticed that the attempt at such a generalization made by Grant and Manes (1966) is not the direct consequence of the potential theory. The method of Grant and Manes applies Raoult's law along lines of constant adsorbed phase volume and involves the implicit assumption that both the pressure and composition are the same over the volume of liquid mixture adsorbed (other conditions being equal). However, this is not thermodynamically consistent.

In this paper a method of analysis and prediction of mixture adsorption is developed on the basis of a strict extension of the Polanyi potential theory. From this perspective the explanation of peculiarities in behavior of ideal and non-ideal systems (O_2–N_2–anatase and acetone–chloroform–graphitized carbon black) are represented. The possibility of applying this method to activated carbon is also discussed.

Theory

In the Polanyi potential theory it is supposed that the whole adsorption volume may be divided into a large number of elements differing one from another by their adsorption potential. In the case of adsorption on nonporous adsorbents, such elements of adsorption volume (EAV) are thin layers between two neighboring equipotential surfaces. It is also implied that the EAV are filled up with the liquid adsorbed phase in strict succession with increasing of pressure, with the only two states being possible for each element—empty or completely saturated. For each adsorbent there is a distribution function of EAV adsorption potential, and with increasing pressure in the gaseous phase, the elements fill sequentially in the direction of increasing of adsorption potential. The last element filled with liquid is on the border of the polymolecular liquid layer and gaseous phase where the pressure is equal to the saturated vapor pressure. This picture is very clear in the case of equilibrium adsorption on non-porous adsorbent surfaces, however it may be easily applied to microporous adsorbents such as activated carbon. In this case a separate micropore may be considered as an element of adsorption volume. Usually, there is a definite distribution function of micropores size and, consequently, of their adsorption potentials. So, the micropores may be divided into separate groups with the same value of adsorption potential, some of them being empty or completely filled. Certainly, the border of empty and filled micropores cannot be imagined as easily as if adsorption occurred on nonporous adsorbent surface in the form of a liquid layer, but formally the mechanism of successive filling of EAV remains the same. It should be noted that after a separate element has been filled, the pressure within it rises sharply up to several hundred atmospheres, with increasing pressure in gaseous phase. This circumstance does not matter for the calculation procedure in the case of pure component adsorption. However, it becomes important for binary and multicomponent equilibrium adsorption because, in the general case, the mixture composition depends on the pressure within the liquid adsorbed phase.

Following the Polanyi model, let us consider the equilibrium adsorption of a vapor mixture of n components on a flat surface. Under the influence of a potential field, the layer of liquid mixture of volume W^S appears near the solid surface. Along the normal to the surface such characteristics as hydrostatic pressure, Gibbs free energy, adsorption potential and composition vary with distance from the surface. Let us consider a thin layer between two neighboring equipotential surfaces within the condensed film. The volume of liquid between the adsorbent surface and the thin layer is $W(W \leq W^S)$. The thin layer thus distinguished may be characterized by a three-dimensional hydrostatic pressure Π, values of chemical potential μ_i, potential energy u_i of i-th component interaction with the adsorption field and pressure p_i° for each pure component i corresponding with the volume adsorbed $W(i = 1..n)$. The main idea that readily leads to the final equations is the equivalence of chemical potential for each component in any point of equilibrium system. The chemical potential of component i in gaseous phase (considered as ideal for simplification) on infinite removal from the solid surface of adsorbent is

$$\mu_i = \mu_i^{\circ}(T) + RT \ln p_i \tag{1}$$

In the layer under consideration the chemical potential of component i may be written as

$$\mu_i = \mu_i^{\circ}(T) + RT \ln p_i^{\mathrm{s}} + RT \ln(x_i \gamma_i) + u_i + \int_{\Pi^{\mathrm{s}}}^{\Pi} v_i^* \, d\Pi \tag{2}$$

The sum of first and second terms in the right side of this equation is the chemical potential of pure component i in the state of saturated liquid at its normal boiling point (p_i^{s} is the vapor pressure of saturated liquid for the pure component i at the same temperature). The third term in the right side of the equation is associated with the entropy of mixing and describes the change in chemical potential of i-th component in the presence of other components. If a liquid mixture takes place under the influence of an adsorption filed, the chemical potential of i-th component changes in value of its interaction potential energy with the adsorbent u_i. Partial molar volume v_i^* is commonly imagined to be incompressible. The latter as well as independence of partial molar volume v_i^* on Π may be assumed in order to simplify further transformations. As previously mentioned, the pressure in the liquid layer rises sharply towards the solid surface due to the potential gradient. So, the value of pressure averaged over the liquid layer is significantly greater than the value Π^S on the layer surface that allows the Π^S to be replaced by zero in the lower integration limit. Consequently, the integral is approximately equal to $v_i^* \Pi$. The sum of the five terms in the right side of Eq. (2) is the chemical potential of i-th component of the liquid mixture which is affected by the adsorption field and the hydrostatic pressure induced by the potential energy gradient.

The equivalence of chemical potentials in gaseous and liquid phases means that the right sides of the Eqs. (1) and (2) must be equal one another. Consequently:

$$RT \ln\left(\frac{p_i^{\mathrm{s}}}{p_i}\right) + RT \ln(x_i \gamma_i) + u_i + v_i^* \Pi = 0 \tag{3}$$

The potential energy u_i may be expressed from the pure-component isotherm. Being applied to the single component i ($x_i = 1, \gamma_i = 1$) for the surface of liquid layer ($\Pi = \Pi^S \approx 0$) Eq. (3) can be reduced to:

$$RT \ln\left(\frac{p_i^{\mathrm{s}}}{p_i^{\circ}}\right) + u_i = 0 \tag{4}$$

As it is easily seen this equation closely corresponds with mathematical formulation of the original potential theory. Combining Eqs. (3) and (4), we obtain

$$RT \ln\left(\frac{p_i^{\circ} x_i \gamma_i}{p_i}\right) + v_i^* \Pi = 0, \quad i = 1..n \tag{5}$$

The values of mole fraction x_i are related through the obvious condition:

$$\sum_{i=1}^{n} x_i = 1 \tag{6}$$

The system of $n+1$ Eqs. (5) and (6) contains $n+1$ variables (Π and n values of x_i) and can be solved if the dependence of activity coefficients γ_i on mixture composition is known. The Eq. (5) may be also written for the boundary of the layer where $\Pi = 0$, $x_i = x_i^S, \gamma_i = \gamma_i^S$. It leads to the following system of equations:

$$\sum_{i=1}^{n} x_i^S = 1, \qquad x_i^S \gamma_i^S = p_i / p_i^{\circ}(W^S), \quad i = 1..n \tag{7}$$

The dependence of pure component pressure p_i° on the adsorbed phase volume W is easily determined from individual isotherms, because for pure component i, W is equal to the product $v_i^* a_i^{\circ}$. Consequently, if the dependence of activity coefficients on composition is known, the root of Eq. (7) is the volume of adsorbed phase W^S. The amount of component i in the adsorbed layer may be then determined as follows:

$$a_i = \int_0^{W^S} \left(\frac{x_i}{\sum_{k=1}^{n} x_k v_k^*}\right) dW, \quad i = 1..n \tag{8}$$

Consequently, given partial pressures, the algorithm for the calculation of the amounts adsorbed may be roughly divided into four steps. (a) Individual isotherms should be determined in coordinates $W - p_i^{\circ}$, where $W = v_i^* a_i^{\circ}$. (b) The mixture adsorbed volume W^S should be found by solving of Eq. (7). (c) Within the region $0 \le W \le W^S$ the number of values of W must be chosen, say, with a constant step ΔW. For each value W the values of P_i° must be determined from the corresponding pure component isotherms. Further, the solution of systems (5) and (6) gives the composition $(x_1, x_2, \ldots, x_n)$ of the adsorbed mixture that corresponds to the volume W between adsorbent's surface and current equipotential surface within the condensed layer. (d) The amount of each component adsorbed may be finally calculated by integrating over the entire layer volume in accordance with formula (8).

It is important to note that the values of vapor pressure of saturated liquids for pure components p_i^s are not present in the final system of Eqs. (5)–(8). This leads to the conclusion that the result obtained is probably more general than the Polanyi physical image used for mathematical formulation of the model of inhomogeneous adsorption volume. In particular the identification of the adsorbed phase as a normal liquid mixture seems to be unnecessary in the general case.

The Case of Ideal Adsorbed Solution

In this case the activity coefficients are to be equal to unity, and the Eq. (5) may be rewritten as follows

$$x_i = \left(\frac{p_i}{p_i^\circ}\right) \exp\left(-\frac{v_i^* \Pi}{RT}\right) \tag{9}$$

Summing over all components, taking account of the condition (6), leads to the equation containing Π as the only unknown variable:

$$\sum_{i=1}^{n} \left(\frac{p_i}{p_i^\circ}\right) \exp\left(-\frac{v_i^* \Pi}{RT}\right) = 1 \tag{10}$$

The value of pressure Π having been found as a root of this equation at given value of W, the mixture composition may be easily determined from Eqs. (9). The calculation of the amounts adsorbed can be reached also by using Eq. (8).

The Case of Homogeneous Composition

Consider the situation that the following equality is held for any i and j:

$$\frac{RT}{v_i^*}\left(\frac{\partial \ln p_i^\circ}{\partial W}\right)_T = \frac{RT}{v_j^*}\left(\frac{\partial \ln p_j^\circ}{\partial W}\right)_T = \varphi \tag{11}$$

Combining Eqs. (5) and (11) gives the following expression:

$$\frac{RT}{v_i^*}\frac{\partial \ln(x_i\gamma_i)}{\partial W} = \frac{RT}{v_j^*}\frac{\partial \ln(x_j\gamma_j)}{\partial W} = \frac{\partial \Pi}{\partial W} - \varphi \tag{12}$$

In the general case this relationship is possible only if each term is equal to zero. This means that the mole fraction of each component is not a function of distance from the surface of the adsorbent.

The system (11) leads to the following expression for any pure component i:

$$W = a_i^\circ v_i^* = f(\varepsilon), \quad \varepsilon = RT\beta^{-1} \ln(p_i^\circ/B_i), \quad \beta = \frac{v_i^*}{v_{\mathrm{st}}^*} \tag{13}$$

Here β is the coefficient of adsorption similarity; v_{st}^*—is molar volume of any standard liquid. The integration constant B_i, in the general case, is a function of temperature. In particular it may be equal to the saturated vapor pressure p_i^s. Consequently, Eq. (13) is equivalent to the requirement that the individual isotherms may be reflected by the single characteristic curve in coordinates W versus ε. In order to provide the same composition over the adsorbed phase the coefficient β must be proportional to molar volume for each component.

As the composition of the adsorbed phase is uniform over its volume, the set of mole fraction x_i can be determined by solving Eq. (7) for the boundary between the liquid layer and vapor phase. Consequently:

$$\left(\frac{RT}{v_i^*}\right) \ln\left(\frac{p_i^s x_i \gamma_i}{p_i}\right) = \left(\frac{RT}{v_j^*}\right) \ln\left(\frac{p_j^s x_j \gamma_j}{p_j}\right) = f(W^S) \tag{14}$$

If the adsorbed solution is ideal this equation will completely coincide with the Grant and Manes model. It is evident that the IAST is also valid under the restrictions introduced.

On the whole, in the framework of potential theory, the Grant and Manes model and the IAST are correct only if the pure component isotherms are similar, with affinity coefficients β being proportional to the mole volume of the respective liquids. This is the only condition that provides composition uniformity within the liquid layer.

Binary Mixture Adsorption

In this case Eq. (5) may be simplified by excluding the effect of pressure Π:

$$(v_1^*)^{-1} \ln\left(\frac{p_1^\circ x_1 \gamma_1}{p_1}\right) = (v_2^*)^{-2} \ln\left(\frac{p_2^\circ x_2 \gamma_2}{p_2}\right), \quad 0 \le W \le W^S \tag{15}$$

The volume of the adsorbed mixture is given by the root of following equation:

$$x_1^S\gamma_1^S = \frac{p_1}{p_1^\circ}(W^S), \qquad x_2^S\gamma_2^S = \frac{p_2}{p_2^\circ}(W^S) \qquad (16)$$

Amounts adsorbed may then be calculated by integrating the mixture composition over the whole volume adsorbed:

$$a_i = \int_0^{W^S} \frac{x_i}{x_1 v_1^* + x_2 v_2^*}\, dW, \quad i = 1..2 \qquad (17)$$

Discussion

To analyze the main features of the model two binary systems have been chosen. They are related to non-porous adsorbents.

Acetone–Chloroform–Graphitized Carbon Black

This system was described by Bering et al. (1969). The authors obtained isotherms for pure components and their mixtures at 30 and 50°C by combination of volumetric and gravimetric technique. In the case of mixtures there were separate series of measurements for constant amounts of acetone or chloroform in the measuring cell. This cell contained dead volume of 126 cm^3 and sample of about 10 g. The carbon black was prepared by heat treatment at 2800°C for 26 hours. Before each series of experiments the sample had been treated at 420–450°C at vacuum of $1 \cdot 10^{-5}$ torr for 7–8 hours. The monolayer volume determined by the BET equation at 30°C corresponded to 0.0595 mmol/g for acetone and 0.0582 mmol/g for chloroform. Figure 1 shows the individual isotherms for acetone and chloroform in the form of characteristic curves in coordinates $W - RT\ln(p_i^s/p_i^\circ)$, where $W = a_i^\circ v_i^*$ ($i = 1$ for acetone and $i = 2$ for chloroform). Dashed and dotted lines sign monolayer volume for acetone and chloroform, respectively. For the temperature 30°C we have accepted that p_i^s and v_i^* are equal to the vapor pressure and molar volume of the saturated liquid, respectively. However for the temperature 50°C the values of p_i^s and v_i^* have been found by least squares fitting to ensure the best coincidence the isotherms of each component. In particular, the calculated value of p_1^s is appears to be equal to 81017 Pa, while the real value of p_1^s is equal to 81342 Pa. Similarly, for chloroform it has been obtained by least squares that $p_2^s = 66996$ Pa, while the real value for 50°C is 68180 Pa. Such excellent agreement is unlikely to be fortuitous and probably points to close similarity of adsorbed and liquid phases.

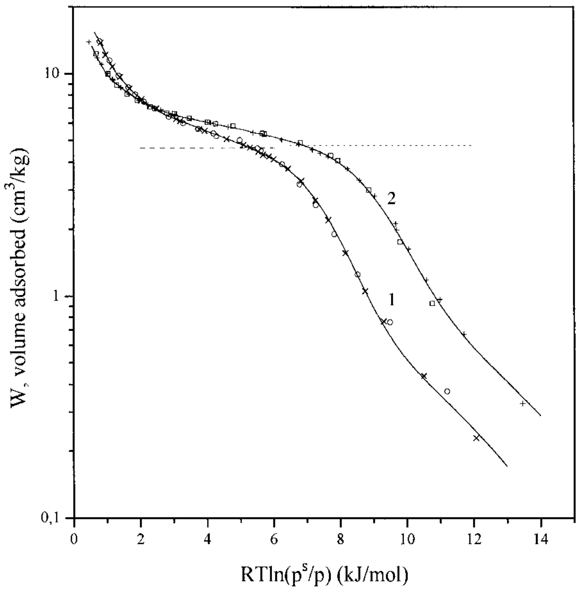

Figure 1. Isotherms of acetone (1, ○, ×) and chloroform (2, □, +) on graphitized carbon black. Temperature, °C: (○, □)—30, (×, +)—50.

However, the temperature expansion coefficients of the adsorbed phase ($3.13 \cdot 10^{-3}$ K^{-1} for acetone and $1.7 \cdot 10^{-3}$ K^{-1} for chloroform) proved to be much greater than those for corresponding liquids ($1.55 \cdot 10^{-3}$ K^{-1} and $1.3 \cdot 10^{-3}$ K^{-1} for acetone and chloroform, respectively). Most likely, this difference suggests a more friable structure for the adsorbed phase as compared with the liquid phase due to the influence of the adsorbent surface that has another structure. However all points for each component are situated on the corresponding characteristic curves, and, hence, the main Polanyi postulate is satisfied. It is extremely interesting to note that the temperature invariance is valid not only in the region of a polymolecular adsorption but also within the first monolayer loading (below dashed and dotted lines). This allows us to conclude that the surface of carbon black is highly energetically inhomogeneous, so the loading of the first monolayer occurs strictly consecutively in the direction of increasing of potential of surface parts.

Experimental data for mixed vapor adsorption at 50°C are represented in Figs. 2 and 3. Figure 2 shows the dependencies of chloroform partial pressure on acetone partial pressure along lines of fixed total amount of chloroform in the measuring cell (horizontal curves) and acetone (vertical curves). Analogous

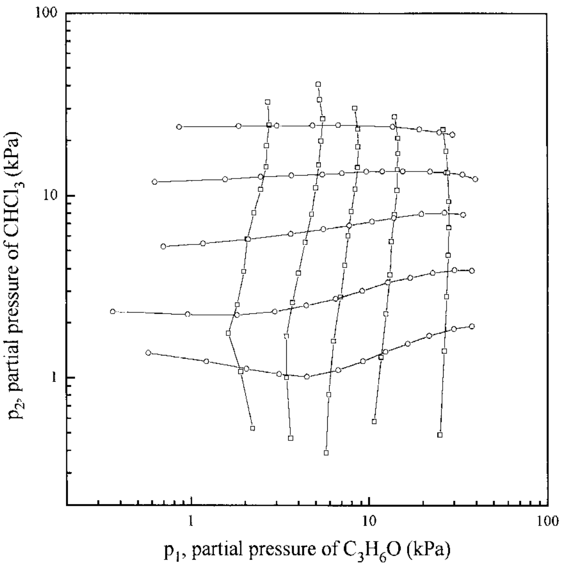

Figure 2. Interdependence of partial pressures along lines of constant amount of acetone (vertical curves) and chloroform (horizontal curves) in measuring cell at 50°C.

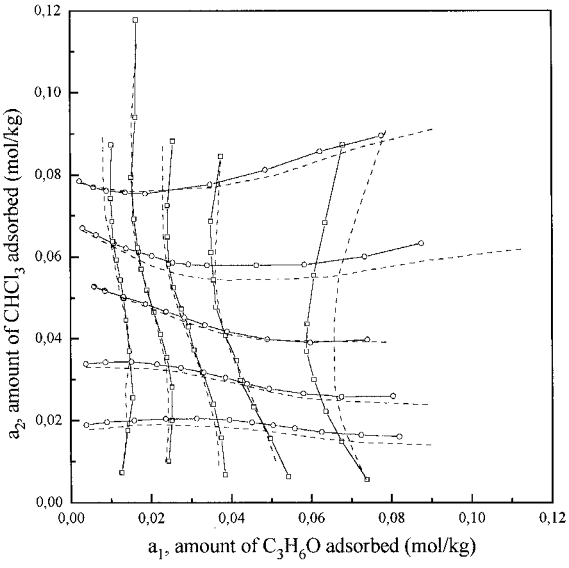

Figure 3. Interdependence of amounts adsorbed along lines of constant amount of acetone (vertical curves) and chloroform (horizontal curves) in measuring cell at 50°C. Dashed lines are calculated by suggested model.

dependencies for the adsorbed phase are represented in Fig. 3. One may see that there are three situations. (1) In the range of low total amount of mixture adsorbed, addition of one component leads to an increase of the other component. (2) If the adsorption of one component greatly exceeds the other, the adsorption becomes competitive. For example, the addition of acetone depresses the adsorption of chloroform and *vice versa*. (3) In the case of high and commensurable component loading the adsorption of each component is increased by the presence of the other component.

The experimental data were processed according to Eqs. (15)–(17). Specific volumes v_1^* and v_2^* were set equal to the values for liquid acetone and chloroform at 50°C (79.19 and 83.95 cm^3/mole, respectively). Activity coefficients were correlated by the Margules equation:

$$\gamma_1 = \exp(\alpha x_2^2), \qquad \gamma_2 = \exp(\alpha x_1^2) \qquad (18)$$

It was found by least squares that the coefficient α is equal to -0.72, indicating negative deviations from Raoult's law. For the liquid solution α is equal to -0.81. This value was found by treating the dependence of $\gamma_2 x_2$ on $\gamma_1 x_1$. The nearness of these values of α indicates the similarity of liquid and adsorbed phases.

Some of the results that follow from the suggested model are presented in Fig. 3 where the dashed lines are calculated from Eqs. (15)–(17). It should be noted that very small divergences in predicted and calculated points are caused mainly by slight thermodynamic inconsistency of the experimental data (which is quite natural because of the difficulty of achieving proper equilibrium), while the suggested model includes the Gibbs equation as the one of its elements.

One more piece of information may be extracted by using of Eq. (16): Given partial pressures p_1 and p_2 and the mixture adsorbed volume $W^S (W^S = v_1^* a_1 + v_2^* a_2)$, one can calculate values of p_1° and p_2° from the pure component isotherms and, consequently, the magnitudes of the products of activity coefficients and mole fractions $\gamma_1 x_1$ and $\gamma_2 x_2$ on the surface of the condensed film. The quantitative dependence of $\gamma_2 x_2$ on $\gamma_1 x_1$ shows deviations from Raoult's law. In the case of an ideal adsorbed solution this dependence becomes linear. Concave curve would point to negative deviations from Raoult's law. The real dependence is represented in Fig. 4. It is remarkable that all points lie very closed to the single concave curve that is plotted for the binary liquid mixture data. This coincidence may be considered as a conclusive evidence of the similarity in behavior of liquid and adsorbed phases.

The change of composition over the thickness of the condensed film is represented in Fig. 5. There are two curves calculated for two different values of mole fraction in gaseous phase (0.2 and 0.4) at total pressure 50 kPa. It is seen that the concentration of chloroform

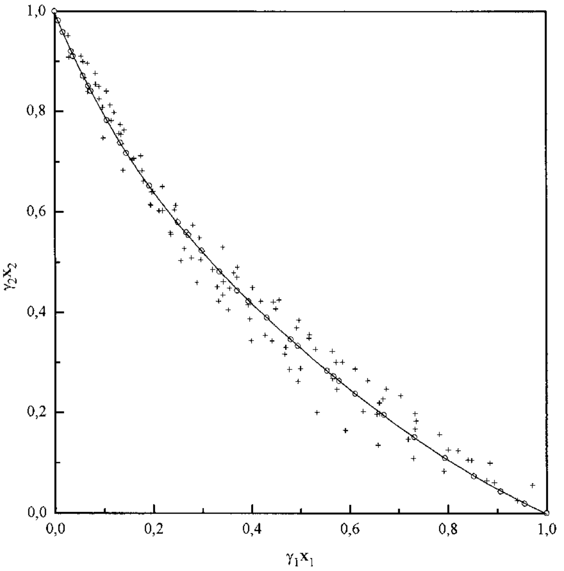

Figure 4. Activity interdependence for mixture layer surface at 50°C. (+)—experiment, (solid line, ○)—data for the liquid mixture of acetone and chloroform for the same temperature.

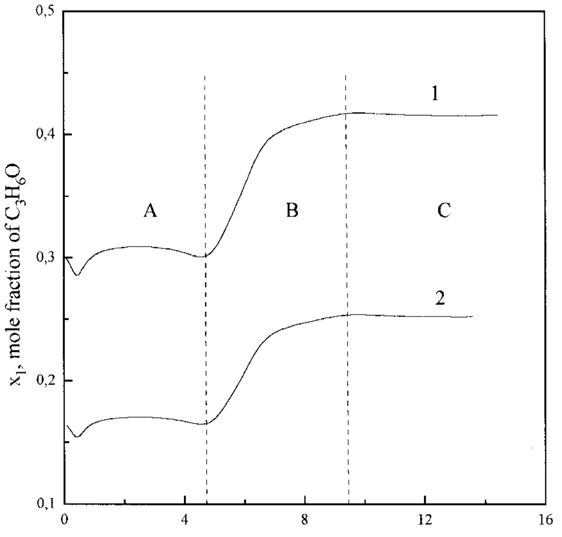

Figure 5. Variation of composition over adsorbed layer thickness. Total pressure in gaseous phase is equal to 50 kPa. Mole fraction of acetone in gaseous phase: (1)—02, (2)—0.4. Bands *A*, *B* and *C* sign the first, second and third monolayer, respectively (50°C).

in the first monolayer is higher than in the third one. This may be considered as one of the main results that shows the necessity of taking into account variation of composition over the adsorbed phase.

Nitrogen–Oxygen–Anatase

Equilibrium adsorption of N_2–O_2 mixtures on anatase at 78.2 K was investigated by Arnold (1949). Measurements in different series were carried out at fixed molar fractions in gaseous phase. In each case the dependence of N_2 and O_2 adsorption on total pressure was obtained. The specific surface area of the sample was 13.81 m^2/g. Being almost ideal, this system is of great interest because of essential difference in interaction of oxygen and quadrupolar nitrogen with anatase surface. The feature of experiment was that mixture adsorption was measured in separate series of experiments at different total pressure with constant composition in gaseous phase. Individual isotherms of oxygen and nitrogen are presented in Fig. 6 in logarithmic coordinates. It was supposed that the molar volumes of O_2 and N_2 at 78.2 K are equal to 26.54 and 34.84 cm^3/mol, respectively. In the case of mixture adsorption the volume W^S at given values of partial pressures was determined as a root of Eq. (16), where activity coefficients are equal to unity. On the other hand, it is known that the experimental value of the adsorbed phase volume as sum of $v_1^* a_1$ and $v_2^* a_2$. The correlation between experimental and predicted values of adsorbed volume is shown in Fig. 7. One may conclude that the proposal theory works quite well, especially when it is considered that the experimental information from the original paper

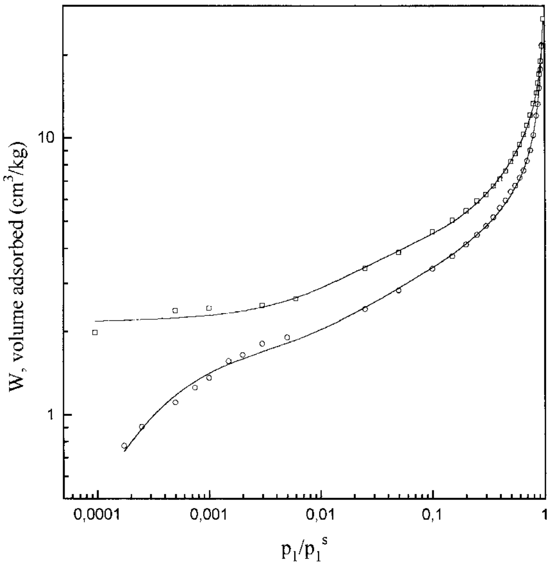

Figure 6. Isotherms of oxygen (○) and nitrogen (□) on anatase at 78.2°K.

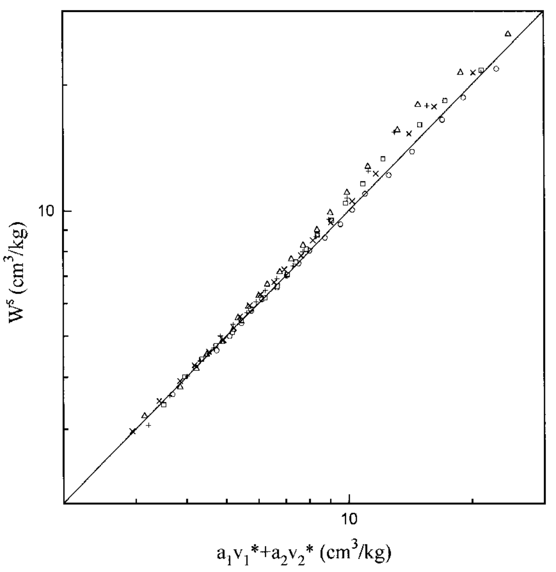

Figure 7. Correlation between calculated and experimental values of O_2–N_2 mixture volume adsorbed on anatase at 78.2°K. Mole fraction of O_2 in gaseous phase: (○)—0.149, (□)—0.298, (△)—0.502, (+)—0.702, (×)—0.853.

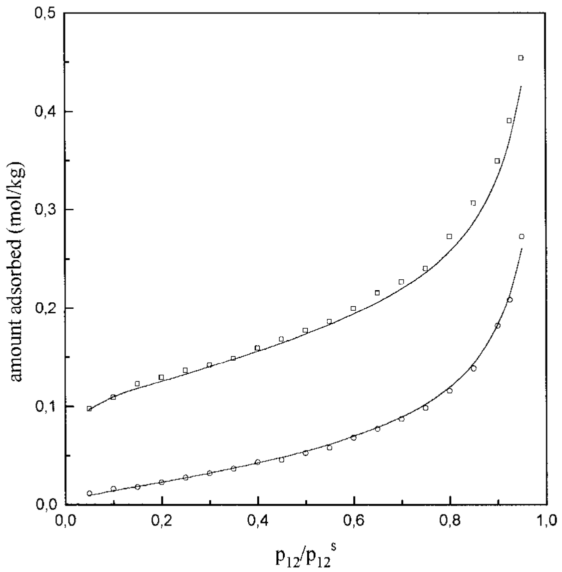

Figure 8. Dependence of oxygen (○) and nitrogen (□) amounts adsorbed on total pressure p_{12} in gaseous phase at O_2 mole fraction is equal to 0.149. (78.2°K). p^s_{12} is the saturation pressure for liquid–vapor equilibrium at the same temperature and gaseous phase composition.

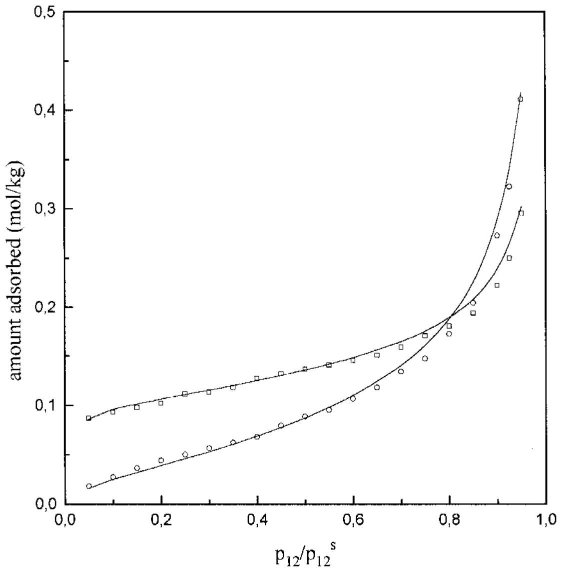

Figure 9. Equilibrium adsorption of O_2–N_2 mixture on anatase for 0.298 mole fraction of O_2 in gaseous phase.

were presented in graphical form and, consequently, could not be extracted with high precision. However, there are some difficulties in the prediction of amounts adsorbed, which are caused by the lack of accurate pure component isotherms at low pressures. Such errors are evidently associated with the need to integrate mole fractions over the adsorbed volume starting from zero coverage, although the exact composition at low coverage is unknown. A similar difficulty is typical of the IAST. To overcome this problem the appropriate ratio of Henry constants was selected to provide the best fitting of experimental points. Figure 8 displays variation of amounts of O_2 and N_2 in adsorbed phase with total pressure at constant composition of the gas phase ($y_1 = 0.149$). Analogous curves are presented in Fig. 9 at 0.298 mole fraction of O_2 and Fig. 10 at a relatively higher value of molar fraction of oxygen ($y_1 = 0.702$). In this case the nitrogen adsorption is significantly depressed, and one more feature has appeared. It is interesting that amount of N_2 adsorbed remains nearly constant with increase of total pressure over a wide range, while the O_2 loading increases monotonically. It seems likely that in the first monolayer the adsorption of N_2 predominates as a result of the N_2 quadrupole moment interactions with surface charges. Nevertheless, being smaller, molecules of oxygen become more competitive at high pressure. In the adsorbed phase the hydrostatic pressure may attain several hundreds or even exceed one thousand atmospheres. For this reason the amount of nitrogen, which is concentrated mainly in the first monolayer, decreases with total pressure in gaseous phase (at constant composition), while in the other monolayers the amount of N_2 increases.

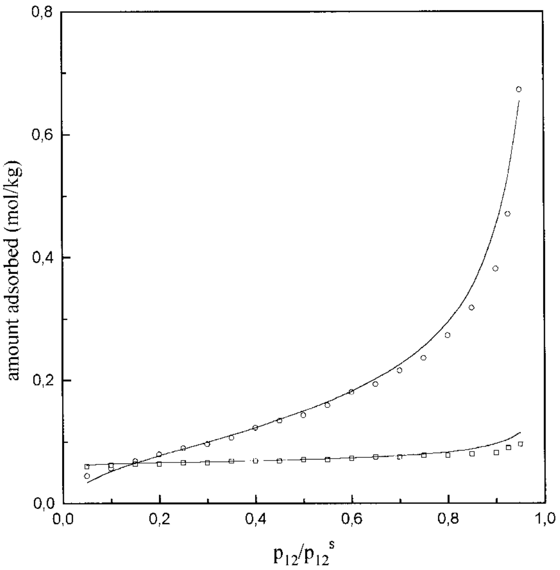

Figure 10. Equilibrium adsorption of O_2–N_2 mixture on anatase for 0.702 mole fraction of O_2 in gaseous phase.

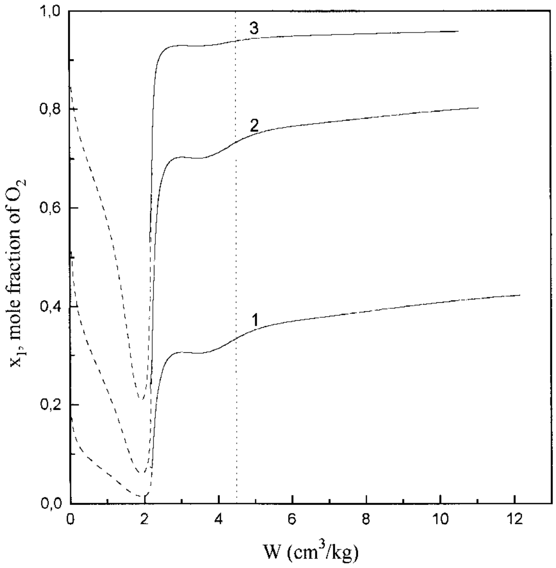

Figure 11. Variation of O_2–N_2 mixture composition over the adsorbed layer thickness at relative total pressure $p_{12}/p_{12}^s = 0.8$. Mole fraction of O_2: (1)—0.149, (2)—0.502, (3)—0.853.

These tendencies may compensate one another, leading to the behavior shown in Fig. 10. Such behavior of the ideal binary mixture is especially difficult to describe by approaches, which do not account for the fact that composition of an adsorbed solution varies over its volume. At the same time the approach suggested here results in excellent agreement between predicted curves (solid lines) and experimental points (as well as at the others values of molar fraction of oxygen in gaseous phase). Figure 11 shows distributions of the molar fraction of oxygen over the liquid mixture volume condensed near to the anatase surface, which are calculated at different compositions in gaseous phase and the same value of relative pressure ($p_{12}/p_{12}^s = 0.8$). Solid lines are for the region where we have experimental data for the pure component adsorption both for oxygen and nitrogen. Dashed lines are extrapolations, which are, evidently, not very reliable. A dotted line indicates the monolayer volume in the case of pure N_2 adsorption. To the right of this line the abscissa may be considered as approximately proportional to surface distance. To the left of the dotted line W is equal to a part of the first monolayer volume filled by an adsorbed mixture that corresponds to definite composition and total pressure in the gas phase. The abscissa of the end of each curve is the total volume of liquid film. One can see from Fig. 11 that when approximately half of the first monolayer volume is filled, the concentration of nitrogen in the adsorbed phase drops sharply. This may be because, at this point surface charges are fully saturated so no further solid—quadrupole type interactions are possible for the additional adsorbed N_2 molecules. Consequently, the simultaneous analysis of pure—component and multicomponent adsorption may provide some information concerning surface structure.

Conclusion

The Polanyi theory was extended to multicomponent adsorption equilibrium. The theory may be used both to predict mixture behavior and for analysis of adsorption solution and adsorbent surface structures. Information of mixture adsorption may afford the opportunity to reconstruct pure component isotherms in the region of very small pressures, where experimental measurements become problematic. The system of equations obtained does not contain such characteristics of liquid phase equilibrium as saturated vapor pressures and does not require the pure component isotherms to be similar. We may conclude that the model is more general and may be applied to adsorption on microporous adsorbents such as activated carbons. The approach depends on the assumption that molecules in the adsorbed phase are incompressible. Thus, the main restriction of this approach is that the adsorbed components must be vapors or liquids. In this case adsorption occurs as a consecutive filling of micropores distributed over the adsorption potentials. Formal application this model to gaseous mixture adsorption, as a rule, leads to appropriate results, which are generally no worse than those obtained by the IAST.

Nomenclature

a_i	amount adsorbed of a component i from mixture (mol/kg)
a_i°	amount adsorbed of a single component i (mol/kg)
p_i	partial pressure of i-th component (Pa)
p_i°	equilibrium pressure for pure component i at the same value of adsorbed volume W that for mixture (Pa)
P_i^s	saturated vapor pressure (Pa)
T	absolute temperature (K)
u_i	interaction potential of i-th component with adsorbent (kJ/mol)
v_i^*	partial molar volume of component i in adsorption solution (cm^3/mol)
W	volume of adsorbed solution (cm^3/kg)
x_i	molar fraction of a component i in adsorbed phase

Greek letters

μ_i	chemical potential of a component i (kJ/mol)
μ_i°	standard chemical potential of a component i (kJ/mol)
Π	pressure inside of adsorption solution (Pa)
γ_i	activity coefficient of component i

Superscripts

S	denote that a variable related to the surface of condensed film of liquid mixture

References

Arnold, J.R., "Adsorption of Gas Mixtures Nitrogen–Oxygen on Anatase," *J. Am. Chem. Soc.*, **71**, 104–110 (1949).

Bering, B.P., N.M. Pavlyuchenko, and V.V. Serpinski, "Adsorption of Mixture of Acetone and Chloroform on Graphitized Carbon," *Izv. Akad. Nauk Belarus SSR. Ser. Khim.*, 39–44 (1969). (In Russian).

Bering, B.P., V.V. Serpinski, and T.S. Jakubov, "Osmotic Theory of Gas Mixtures Adsorption. 1. Integral of Gibbs Equation and Adsorption Isotherm," *Izv. Akad. Nauk SSSR. Ser. Khim.*, 121–127 (1977). (In Russian).

Grant, R.J. and M. Manes, "Adsorption of Binary Hydrocarbon Gas Mixtures on Activated Carbon," *Ind. Eng. Chem. Fundam.*, **5**, 490–498 (1966).

Jakubov, T.S., B.P. Bering, and V.V. Serpinski, "Osmotic Theory of Gas Mixtures Adsorption. 2. General Equation of Gas Mixtures Adsorption Isotherm," *Izv. Akad. Nauk SSSR. Ser. Khim.*, 991–996 (1977). (In Russian).

Langmuir, I., "The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum," *J. Am. Chem. Soc.*, **40**, 1361–1403 (1918).

Markham, E.C. and E.F. Benton, "The Adsorption of Gas Mixtures by Silica," *J. Am. Chem. Soc.*, **53**, 497–507 (1931).

Myers, A. L., "Activity Coefficients of Mixtures Adsorbed on Heterogeneous Surfaces," *AIChE J.* **29**, 691–693 (1983).

Myers, A.L. and J.M. Prausnitz, "Thermodynamics of Mixed-Gas Adsorption," *AIChE J.*, **11**, 121–127 (1965).

Ruthven, D.M., "Sorption of Oxygene, Nitrogen, Carbon Monoxide, Methane, and Binary Mixtures of These Gases in 5 A Molecular Sieve," *AIChE J.*, **22**, 753–759 (1976).

Ruthven, D.M., K.F. Loughlin, and K.A. Holbarow, "Multicomponent Sorption Equilibrium in Molecular Sieve Zeolites," *Chem. Eng. Sci.*, **28**, 701–709 (1973).

Suwanayuen, S. and R.P. Danner, "Vacancy Solution Theory of Adsorption From Gas Mixtures," *AIChE Journal*, **26**, 76–83 (1980).

Tolmachov, A.M., "Thermodynamics of Adsorption. Chemical Potentials of Sorption Solution Components and Some Features of Adsorption Phase of Bounded Volume," *Zh. Fiz. Khimii*, **52**, 1050–1052 (1978). (In Russian).

Ustinov, E.A., "Equilibrium Mixtures Adsorption in Carbon Adsorbents," *Zh. Fiz. Khimii*, **61**, 2103–2107 (1987). (In Russian).

Ustinov, E.A., "Thermodynamics and Calculation of Multicomponent Adsorption," *Zh. Fiz. Khimii*, **62**, 1441–1454 (1988). (In Russian).

Ustinov, E.A., "Equilibrium Adsorption in System of Oxygen–Nitrogen–Anatase," *Zh. Fiz. Khimii*, **71**, 1296–1299 (1997). (In Russian).

Valenzuela, D.P., A.L. Myers, O. Talu, and I. Zwiebel, "Adsorption of Gas Mixtures: Effect of Energetic Heterogeneity," *AIChE J.*, **34**, 397–402 (1988).