Dynamics of joint adsorption of mutually soluble substances by activated carbons

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A model for the dynamics of isothermal adsorption of a binary mixture of an organic substance, soluble in water, and water vapor in a fixed bed of activated carbon was proposed. It includes the equations of material balance and the Myers—Prausnitz model for equilibrium adsorption. The possibility of formation of the condensed phase during the adsorption of an organic substance on moist activated carbon was shown.

Key words: dynamics of isothermal adsorption, activated carbon, mutually soluble substances.

Most advances in the theory of the dynamics of isothermal and nonisothermal adsorption of one component in a fixed layer of adsorbent have been made within the last years.[1–5] The dynamics of multicomponent adsorption has mainly been studied experimentally,[6–9] and the theoretical studies have been made only for simplified model systems in which individual isotherms are approximated, for example, by the Langmuir equations.[10,11] Real systems are, as a rule, more complicated. Thus, for air separation processes using short cycles of isothermal adsorption on zeolites, a theory has been developed that takes into account the commensurable initial volume concentrations of the components (nitrogen and oxygen) and the change in the overall pressure in the layer.[12,13] The general solution obtained by the method of characteristics proved to be complicated even in a linear approximation for the linear Henry isotherms. The dynamics of adsorption of microadditives from steam-containing gas flows in the layer of activated carbon is no less complicated under real conditions. This is due to some reasons. First, the adsorption isotherm for water vapor on the activated carbon has an unusual S-like shape. Second, according to the theory of equilibrium multicomponent adsorption (see, *e.g.*, ref. 14), the adsorption of mutually soluble components can result in both inhibition of the adsorption of one component by another component (at a high coverage) and an increase in the adsorption of each component at the expense of another (at low coverages). Third, the adsorption capacity of some regions of the layer can be depleted during joint adsorption and the substance will be partially transferred into the condensed phase. Due to this fact, equations for the phase equilibrium should be additionally taken into account in the model.

In this report, analysis of the dynamics of joint isothermal adsorption of an organic substance, indefinitely soluble in water, and water vapor by a fixed layer of activated carbon was proposed, taking into account all the complicating factors mentioned above.

Mathematical model

The starting system of equations should include the equations of material balance with respect to each component as well as the equations for multicomponent adsorption and phase equilibrium. The mechanism of adsorption of a binary mixture has not been adequately studied; therefore the kinetic equations were not included in the original model. The equations of material balance have a common form:

$$\rho_s\frac{\partial a_i}{\partial t}+\frac{v}{RT}\frac{\partial p_i}{\partial x}=D\frac{\partial^2 p_i}{\partial x^2},\ i=1,\ 2. \qquad (1)$$

Here x is the coordinate (m), t is the time (s), a_i is the value of sorption of an organic substance and water vapor (mol kg^{-1}), p_i is the partial pressure of the organic substance and water vapor (Pa), ρ_s is the bulk density (kg m^{-3}), v is the rate of the gas flow per total cross section of the layer (m s^{-1}), T is the temperature (K), D is the coefficient of longitudinal diffusion (m^2 s^{-1}), and R is the gas constant.

The known equations, *e.g.*, the Dubinin—Radushkevich[15] and Dubinin—Serpinskii[16] equations (the latter equation for adsorption of water vapor), can be used for

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1491—1495, August, 1998.

1066-5285/98/4708-1446 $20.00 © 1998 Plenum Publishing Corporation

the individual isotherms. Calculation of the equilibrium adsorption of a mixture of water vapor and an organic substance is possible on the basis of the Myers and Prausnitz model.[14] Previously,[17] conditions for the correct application of this model for adsorption by microporous adsorbents have been determined. However, the Gibbs integral should be calculated repeatedly during integration of the differential equations, and the Dubinin—Radushkevich equation does not allow the integral to be presented in an analytical form. Therefore, we used the same equation based on statistical thermodynamics and applied first by V. A. Bakaev[18] (a cell model) for approximation of the individual isotherms for each component:

$$a = a_0 RT \frac{\partial \ln Q}{\partial \mu}, \quad Q = \sum_{j=0}^{N} \exp\left(\frac{j\mu - N_A F_j}{RT}\right). \tag{2}$$

Here μ is the chemical potential of the organic substance or water vapor, Q is the gross canonical sum per one micropore, F_j is the Helmholtz free energy of j molecules of the component in one micropore, a_0 is the number of micropores per unit weight of zeolite divided by the Avogadro number N_A (mol kg^{-1}), and N is the limiting number of molecules of both components in one cage. After expansion of formula (2), one can write:

$$a = a_0 Q^{-1} \sum_{j=0}^{N} j \exp\left(\frac{j\mu - N_A F_j}{RT}\right). \tag{3}$$

The bulk phase is usually close to the ideal phase, therefore

$$\mu = \mu^\circ(T) + RT\ln p, \tag{4}$$

where $\mu^\circ(T)$ is the standard chemical potential. Hence, we obtain a simple formula for the Gibbs integral:

$$\int_0^{p} \frac{a}{p} dp = \frac{a_0}{N} \ln Q. \tag{5}$$

According to Myers and Prausnitz, Raoult's law is fulfilled when going along the line of constant Gibbs integral (*i.e.*, along the line of constant pressure in the adsorption phase II):

$$p_1 = p_1^\circ x_1, \; p_2 = p_2^\circ x_2. \tag{6}$$

Here p_1°, p_2° are the pressures of the 1st or 2nd individual components at the given value of the Gibbs integral, and x_1, x_2 are the molar fractions of these components in the adsorption phase. From this equations it follows that

$$\frac{a_{01}}{N_1} \ln\left(Q_1 \frac{p_1}{x_1}\right) = \frac{a_{02}}{N_2} \ln\left(Q_2 \frac{p_2}{x_2}\right). \tag{7}$$

Solution of this equation gives the composition of the adsorption phase which can be obtained by the method of successive approximations. The absolute values of sorption can be determined after estimating the overall sorption according to the formula

$$a_s(x_1/a_1^\circ + x_2/a_2^\circ) = 1, \; a_1 = x_1 a_s, \; a_2 = x_2 a_s. \tag{8}$$

The a_1°, a_2° values in this formula can be calculated from the individual isotherms for the partial pressures $p_1^\circ = p_1/x_1$ and $p_2^\circ = p_2/x_2$, respectively. Thus, the relation between partial pressures in the mixture and the sorption values of an organic substance and water vapor is determined.

When the condensed phase was formed in the layer of the adsorbent, the composition of the gas phase is determined on the basis of Raoult's law and the molar fractions in the condensed phase (the adsorption phase is not taken into account). The a_i values in the equations of material balance (1) have the meaning of the overall content of each component in the adsorption and condensed phases. By subtracting the adsorption value from a_i, we can find the contents of the components in the condensed phase. The adsorption values can be calculated independently according to the Myers and Prausnitz model for the current values of partial pressures.

On the basis of the model considered, an algorithm for calculation and a program for a personal computer were created to integrate the differential equations of material balance in terms of the cell model for the layer of an adsorbent. During calculation, testing for each cell was continuously carried out to see whether the partial pressure of each component exceeds the pressure above the solution. In the case where the partial pressure is higher than the pressure above the solution, the equations taking into account the existence of a condensed phase were used for the calculation. The Helmholtz free energy for each component was approximated by a polynomial of the fourth degree in the number of molecules in the micropore; the polynomial coefficients were determined by the root-mean square method.

The model system ethanol—water vapor—activated carbon SKT-2 was used for the study of the main regularities of the dynamics of joint adsorption. The adsorption isotherm for ethanol was calculated from the experimental adsorption isotherm for benzene on the same carbon carrier. The coefficient of adsorption similarity was calculated as the ratio of parachors, and the sorption value was determined from the ratio of molar volumes in the liquid phase. Depending on conditions, one can separate several cases of joint adsorption. We considered three cases: *a*) dynamics of adsorption of the mixture of ethanol and water vapor on a dry layer of the adsorbent; *b*) dynamics of adsorption of ethanol from dry air on a moist layer of activated carbon; *c*) dynamics of adsorption of ethanol from a moist flow by a layer of carbon moistened under equilibrium. The results of modeling the dynamics of adsorption for the *a* and *b* cases are presented in this report.

Discussion of the results of modeling the dynamics of joint adsorption of ethanol and water vapor

The model calculation was performed for the conditions of one of the experiments: the initial relative concentrations (p/p_s) of ethanol and water vapor were equal to 0.054 and 0.824, respectively. The number of cells along the length of the layer was chosen to be equal to 40 (the height of one cell is 1 mm). Figure 1 shows the distributions of the ethanol content for two time intervals which differ by a factor of 2. The numbers of the cells positioned along the column in the flow direction and, hence, proportional to the coordinate of the layer are shown on the abscissa axis. The change in the overall content of ethanol along the coordinate of the layer is shown by solid lines, whereas the distribution of the adsorbed ethanol is shown by dotted lines. As can be seen in the figure, an intermediate region exists under conditions where the overall content of ethanol exceeds the content of adsorbed ethanol. The difference corresponds to the amount of ethanol in the condensed phase. The condensed phase may exist in the transport pores of the adsorbent, on the surface of granules, or in the form of a mist. In the intermediate region, the overall content of ethanol somewhat exceeds the equilibrium value which is established after the process has been completed. The amount of adsorbed ethanol in this intermediate region, on the contrary, is lower than the equilibrium value. This is due to the fact that not only ethanol but also water are concentrated in the intermediate region, and ethanol is replaced to a noticeable extent with water in the adsorption phase.

Figure 2 shows the distribution of water along the length of the layer in the same coordinates and under the same conditions. The distribution of the overall water content along the layer is also shown by solid lines, whereas the distribution of adsorbed water is shown by dotted lines. There are two intermediate zones instead of one zone for ethanol. The zone in which the amount of water in the condensed phase exceeds the amount of water in the micropores of activated carbon is located nearer to the inlet section. In front of this zone, another zone is formed in which the condensed phase is generally absent but the amount of adsorbed water is even greater. Ethanol is absent in this zone.

Figure 3 summarizes the curves of the distribution of ethanol and water for the same time instant. It follows from Fig. 3 that the process of joint adsorption develops according to a four-zone model. Zone *A*, next to the inlet section, is in equilibrium with respect to the initial

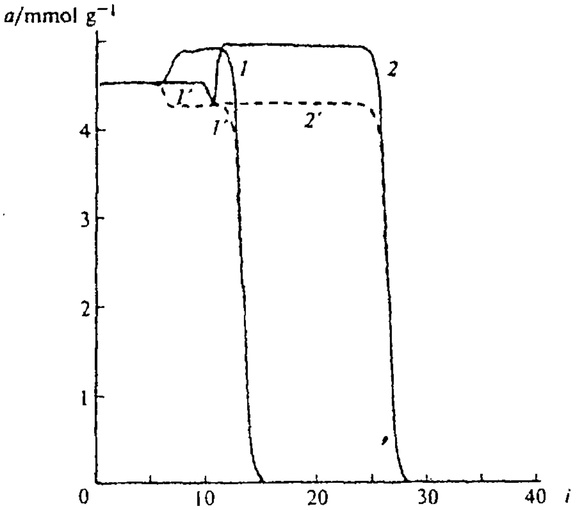

Fig. 1. Distribution of the content of ethanol (*a*) along the length of the layer (*i* is the number of cells): *1*, *2* the overall content, *1'*, *2'* the content in the adsorbed state at the moment t_1 (*1*, *1'*) and $t_2 = 2t_1$ (*2*, *2'*) (see explanation in the text).

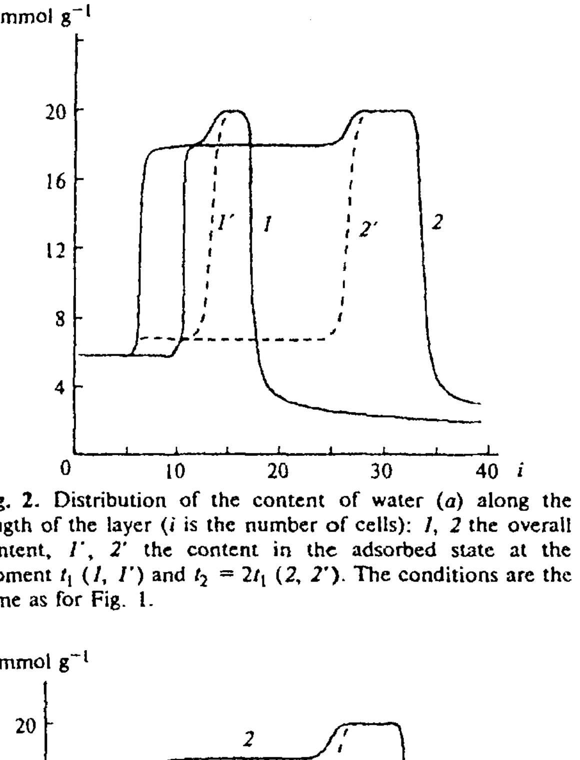

Fig. 2. Distribution of the content of water (*a*) along the length of the layer (*i* is the number of cells): *1*, *2* the overall content, *1'*, *2'* the content in the adsorbed state at the moment t_1 (*1*, *1'*) and $t_2 = 2t_1$ (*2*, *2'*). The conditions are the same as for Fig. 1.

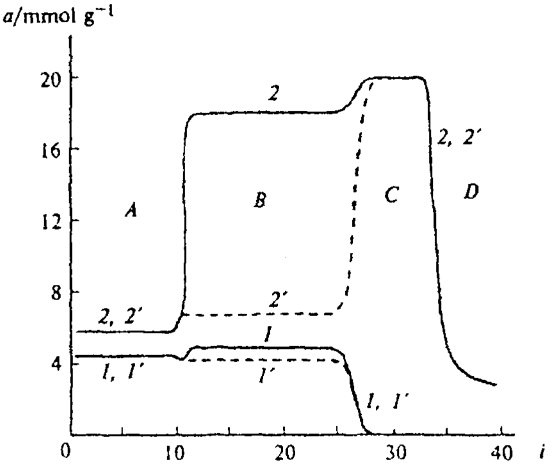

Fig. 3. Distribution of the content of (*a*) ethanol (*1*, *1'*) and water (*2*, *2'*) along the length of the layer (*i* is the number of cells) for the same moment in time: *1*, *2* the overall content, *1'*, *2'* the content in the adsorbed state.

mixture. Zone *B*, the next in the direction of the flow, contains the condensed phase. The overall amount of water in this zone is significantly greater than that in the previous zone. No ethanol and condensed phase are present in zone *C*, but the content of water is very high. Zones *B* and *C* are the result of splitting of the zone of water concentrating. The effect of concentrating is quite simple: the previously adsorbed water is replaced from the adsorption phase by the front of ethanol which moves more slowly. The replaced water is added to water vapor which is continuously introduced in the initial amount, increasing its flow. This determines the enhanced content of water in front of the moving front of ethanol which is better sorbed. However, when the adsorption capacity is exhausted, a portion of the replaced water can be accumulated as a liquid in the region, where the sorption wave of ethanol has already passed, without transfer into the gas phase. The replacing effect of ethanol is not yet manifested in the condensed phase, because adsorption forces do not act here. Thus, the water replaced by the sorption wave of ethanol distributes both in front of this wave (in the adsorbed state) and behind it but in the form of a condensate. Zone *D* is the section of the sorption wave of pure water which is in the steady state in the region of average and high coverages and is broadened in the region of low coverages due to the S-like shape of the isotherm.

The change in the relative pressures of ethanol and water vapor at the outlet of the flow from the layer (the outlet curves) is shown in Fig. 4. The values of the specific volume of the gas passed through the layer of the adsorbent (m^3 kg^{-1}) are shown on the abscissa axis. The outlet curve for ethanol has two sections which are slightly distinguished in the scale used. The first section corresponds to zone *B*, and the ethanol concentration here is somewhat higher than the initial concentration. This is due to the small replacement effect of the adsorbed water for ethanol. The outlet curve for water vapor is substantially more complicated. Initially, a spreading section of the sorption wave of pure water comes out from the layer after a breakthrough. Then the concentration of water vapor increases drastically, and this corresponds to the steady state of this sorption wave. The increase in the concentration up to the concentration of saturated water vapor is in fact governed by the nearly complete filling of the adsorption space in zone *C* which contains no ethanol. Then the section follows where the concentration of water vapor decreases but remains higher than the initial concentration. This section corresponds to zone *B* in which ethanol is already present and the condensed phase appeared. The condensed phase is a binary solution, and the concentration of water vapor above it is determined according to Raoult's law on the basis of the molar fraction of water. Finally, after exit from zone *B*, the concentration of water vapor becomes equal to the initial concentration.

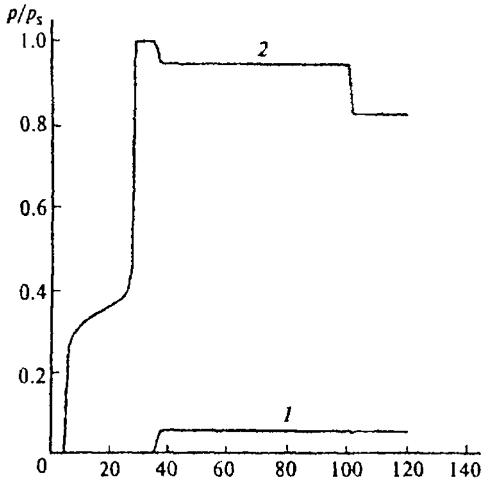

Fig. 4. The outlet curves for ethanol (*1*) and water vapor (*2*) during adsorption of the mixture on the dry layer. V/m^3 s^{-1} is the space velocity of the carrier gas, t/s is time, G/kg is the weight of the adsorbent in the column.

As the analysis showed, the dynamics of adsorption of pure ethanol on the preliminarily moistened carbon has some distinguishing features. However, in this case, a zone also arises in which ethanol and water are partially present in the condensed phase. As the rise of the condensed phase is a temporary phenomenon (it is absent at the beginning and at the end of the process), its appearance and disappearance should be accompanied by an increase and subsequent decrease in the weight of the column during adsorption. This phenomenon is observed experimentally during measurement of Δm of the dynamic tube on the analytical balance after equal time intervals. The appearance of the zone of condensation was readily seen as a mist inside the glass dynamic tube. This zone gradually extended and simultaneously moved along the direction of the air flow.

Modeling of this experiment was performed for an initial relative pressure of water vapor (during moistening) of 0.95 and an initial relative pressure of pure ethanol (during the subsequent replacement of water) of 0.474. Figure 5 shows the calculated distribution of the content of ethanol and water at the same time instant. One can distinguish three zones in the layer. In the first zone (*A*), pure ethanol is present, because water has been completely replaced. The value of the ethanol sorption in this zone is in equilibrium relative to its initial concentration. In zone *C* farthest removed from the inlet section, ethanol is absent; here preadsorbed water occurs. The boundary between zones *B* and *C* corresponds to the forward section of the sorption wave of ethanol. All the water replaced by it from micropores remains behind the front of ethanol, *i.e.*, in zone *B*. Water transfers from the adsorption phase to the condensed phase in which ethanol is also accumulated. This can be explained by two reasons. First, replacement of water requires energy consumption, hence the adsorption front is retarded. Second, the ethanol vapor which is fed to the inlet of the column cannot be adsorbed in zones *A* and *B*, but it can be absorbed in indefinite amounts by the condensate formed. The amounts of

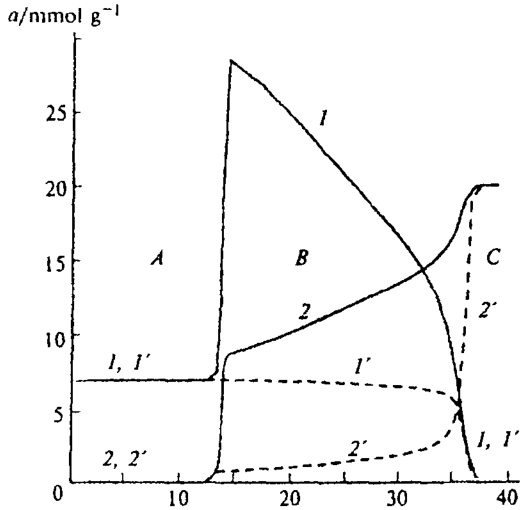

Fig. 5. Distribution of the content of (*a*) ethanol (*1, 1'*) and water (*2, 2'*) along the length of the layer (*i* is the number of cells) during the adsorption of the ethanol vapor from dry air on the moist layer of activated carbon: *1, 2* the overall content, *1', 2'* the content in the adsorbed state.

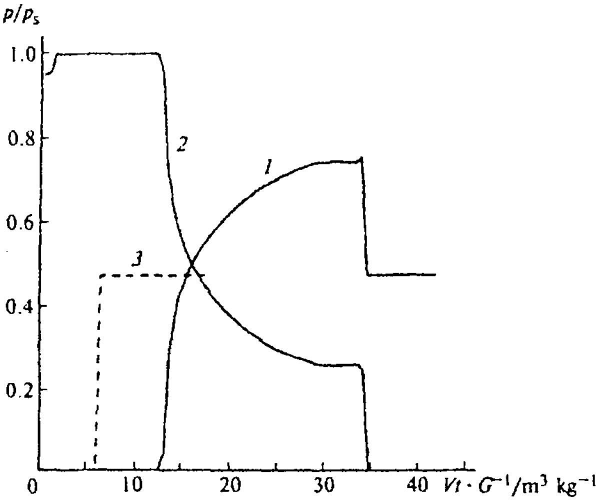

Fig. 6. The outlet curves for ethanol (*1*) and water vapor (*2*) during adsorption of the ethanol vapor in dry air by the moist layer of activated carbon; *3* the calculation for the dry layer.

ethanol and water in the condensate are equal to the differences in the ordinates of the solid and dotted lines. Unlike the previous case, the composition of the condensate is not constant in the intermediate zone and in time the condensate is enriched with ethanol.

Figure 6 presents the calculated outlet curves for ethanol and water vapor. After breakthrough of ethanol, its concentration, as seen in Fig. 6, increases smoothly and reaches a value that significantly exceeds the initial concentration of ethanol and then it drastically drops to the initial value. The outlet curve for ethanol taken in the same initial concentration but adsorbed on the dry layer of carbon is presented as a dotted line for comparison. In this case, the breakthrough occurs substantially earlier. Thus, when substances infinitely soluble in water are adsorbed, the capacity of the moist layer can be substantially higher than that of the dry layer.

The regularities considered do not include all the peculiarities of the dynamics of the adsorption of organic substances dissolved in water from moist media. The more complete description of the dynamics of joint adsorption seems to require development of a kinetic model of adsorption of the binary mixture organic substance—water vapor by activated carbons and comparison with the experimental results.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 98-03-32397a).

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Received June 4, 1997;
in revised form November 3, 1997