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Abstract

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Adsorption of Vapor Mixtures and the Structure of Adsorbents

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The study of the adsorption of binary vapor mixtures on solid adsorbents generally makes it possible to reveal the existence of clearly noticeable regions associated with the mechanism of sorption (adsorption proper, capillary condensation), and provides an opportunity to establish certain features of the adsorption process that depend on the structure of the adsorbent. These features appear most distinctly when experimental data on the adsorption of vapor mixtures are represented in the form of curves giving the dependence of the adsorption of one of the components, a_2 (the more strongly adsorbed component in the region of low fillings), on the adsorption of the other component, a_1 (the less strongly adsorbed component), as the pressure of a vapor mixture of constant composition is increased. Consideration of such curves for various systems has led us to the conclusion that all the systems studied may be divided into two main types. The first of them corresponds to adsorption on adsorbents characterized by very fine pores, comparable in order of magnitude with the dimensions of the adsorbing molecules (activated carbons, zeolites), while the second corresponds to adsorption on more broadly porous, or altogether nonporous, adsorbents (silica gels, oxides, nonporous crystals, graphitized carbon blacks). Below we shall consider characteristic examples of systems of both types.

Type 1. In Fig. 1a are shown curves for the dependence of the adsorption of diethyl ether (a_2) on the adsorption of ethyl chloride (a_1) at constant values of the mole fraction N_{g_2} of diethyl ether in the gas phase, obtained on the basis of an experimental study by the volume-weight method in our laboratory of the system C_2H_5Cl—$C_4H_{10}O$–activated carbon at 50° ([1]). The curves N_{g_2} = const were constructed for values of N_{g_2} equal to 0.3; 0.5; 0.6; 0.8; and 0.9. Along the coordinate axes are plotted the quantities a_2 and a_1, in mmol/g, the points A and B corresponding to the limiting values of sorption on the adsorption isotherms of the pure components, while the field OAB bounds the region of variation of the variables a_2 and a_1. The curves N_{g_2} = const in this system at first rise steeply, then pass through a maximum (clearly noticeable at N_{g_2} 0.3 and 0.5), and with further increase of the total pressure p_{12} deviate toward the abscissa axis.

Figure 1: Two types of curves $N_{g_2} = \text{const}$.

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In other words, upon isothermal compression over the adsorbent of a very large amount of vapor of constant composition, the adsorption of each component first increases with increasing p_{12}, and then the adsorption of C_2H_5Cl continues to increase, while the adsorption of $C_4H_{10}O$ begins to decrease; i.e., in the region of high fillings of the adsorption volume there occurs partial displacement of the ether by ethyl chloride. This effect probably also exists at $N_{g_2} > 0.6$; however, this region was not studied experimentally, since the apparatus was not designed for pressures higher than atmospheric. For a qualitative and by no means complete explanation of such a course of the curves $N_{g_2} = \text{const}$, let us first note that, with increasing degree of filling along each of the curves $N_{g_2} = \text{const}$, the coefficient of adsorption selectivity $\alpha_2 = (N_{g_1}/N_{g_2}) \cdot (a_2/a_1) = k \cdot a_2/a_1$ decreases, while in the region of high fillings a further increase in pressure p_{12} causes only a very slow increase in the total adsorption a_{12} of both components, owing to the limited adsorption volume. The decrease

a_2 with increasing a_{12} is characteristic of all the studied cases of adsorption of vapor mixtures on real adsorbents with a heterogeneous surface. If, in the region of large fillings, the adsorption volume $a_1v_1 + a_2v_2 \approx \text{const}$ (where v_1 and v_2 are the molar volumes of the components) and, at the same time, the ratio $a_2/a_1 = ka_2$ is a decreasing function of p_{12}, then, first, $a_1\left(1 + k\frac{v_2}{v_1}a_2\right) \approx \text{const}$, and, second, when a_2 decreases with increasing p_{12} along the curve $N_{g_2} = \text{const}$, the adsorption a_1 must increase and the adsorption a_2 must decrease. Thus, the partial displacement from the adsorption volume of one component by the other along the curves $N_{g_2} = \text{const}$ at large fillings, and consequently the appearance of maxima on these curves, may formally be regarded as a consequence of the limited adsorption volume of the micropores. This volume

Fig. 1. Two types of curves $N_{g_2} = \text{const}$.
a–C_2H_5Cl–$C_4H_{10}O$–activated carbon;
b–C_2H_5Cl–H_2O–activated carbon;
v–CH_3COCH_3–$CHCl_3$–silica gel;
g–N_2–O_2–anatase.

is practically filled already at comparatively low pressures, and with an increase in p_{12} only the composition of the adsorption solution can change.

Curves $N_{g_2} = \text{const}$ with maxima, similar to those shown in Fig. 1a, were obtained by us in all the studied cases of adsorption of binary vapor mixtures on activated carbons and on synthetic zeolites. Among the multicomponent adsorption systems of this type studied by us are the following: C_2H_5Cl–$C_4H_{10}O$–activated carbon (1) at 50 and 71°, $C_4H_{10}O$–$CHCl_3$–zeolite NaX at 60 and 72°, $C_4H_{10}O$–$CHCl_3$–activated carbon at 60°, and C_2H_5Cl–H_2O–activated carbon (2) at 75°. In Fig. 1b, as an illustration, the curves $N_{g_2} = \text{const}$ are given for

the case of adsorption of mixtures of ethyl chloride vapor (a_2) and water (a_1) on activated carbon at N_{g_2} from 0.1 to 0.4. In this system, the displacement of ethyl chloride by water at large fillings is especially clearly noticeable.

Type 2. In Fig. 1*v* is shown a family of curves $N_{g_2} = \text{const}$, constructed on the basis of experimental data obtained by us in the study of adsorption of mixtures of acetone vapor (a_2) and chloroform (a_1) on silica gel.

with a specific surface area, according to nitrogen, of $S_{\text{BET}} = 580$ m^2/g and a total pore volume $v_s = 0.47$ cm^3/g. The coordinates of the points of the slightly convex curve AB give the values of the limiting sorption of the components from saturated vapor, and the field OAB determines the entire range of variation of the variables a_2 and a_1. The curves shown in the figure, $N_{g_2} = \text{const}$, are given for values of N_{g_2} from 0.1 to 0.9 at intervals of 0.2. Each of these curves expresses the process of simultaneous sorption of both components during isothermal compression above the adsorbent, under equilibrium conditions, of a very large quantity of vapor of unchanged composition N_{g_2}, from a very low initial pressure to a relative pressure $h_{12} = 1$, i.e., to the pressure of saturated vapor above an equilibrium bulk solution of composition N_{l_2}. The dependence of N_{g_2} on N_{l_2} for binary solutions of acetone in chloroform, which we do not give here, was taken from work ([3]). All the curves $N_{g_2} = \text{const}$ in Fig. 1b at first rise steeply upward (similarly to the corresponding curves in Figs. 1a and 1b), and then decrease their slope and proceed further as rectilinear segments (where, in contrast to curves of the first type, the slope of these segments remains positive) up to intersection with the bounding line AB. If the increments of adsorption of the two components are denoted by Δa_2 and Δa_1, then along the linear portions CD the ratio of these increments, $\Delta a_2/\Delta a_1$, remains constant and equal to the ratio N_{l_2}/N_{l_1}, i.e., to the ratio of the mole fractions of the two components in the bulk solution that is formed upon condensation of vapor of composition N_{g_2} (in the absence of adsorbent) at the saturation pressure. It follows from this that, first, along each linear segment CD a solution of constant composition is sorbed, and second, that the composition of this sorption solution is equal to the composition of the bulk solution N_{l_2} that is in equilibrium with saturated vapor of composition N_{g_2}.

The angular coefficient of each of the linear segments CD, equal to N_{l_2}/N_{l_1}, is uniquely determined from the phase diagram of the bulk solutions of the components, and the composition of the solution sorbed along CD is completely independent of the properties of the adsorbent. On this basis it may be concluded that, upon compression of vapor of constant composition, initially both components are adsorbed on the free surface of the solid, and here, during adsorption in the first layer, the specificity of the action of the adsorption field is fully manifested. In accordance with the greater adsorbability of acetone, the adsorption solution proves to be richer in acetone than the bulk solution at the same vapor composition. However, after the filling of approximately one statistical adsorption layer (marked in Figs. 1c and 1d by a dashed line), the subsequent sorption process loses its specificity. In this region (after point

C), an increase in vapor pressure causes the appearance of a condensed phase whose composition is practically no different from the composition of the liquid obtained upon ordinary condensation of this vapor. Sorption in the region CD may proceed either by the mechanism of polymolecular adsorption or by the mechanism of capillary condensation. In connection with the presence of a region of sorption hysteresis on the individual adsorption isotherms, it seems very likely that in the region CD we are dealing mainly with a process of capillary condensation. Capillary condensation in this case begins long before the point of onset of sorption hysteresis, as is seen in Fig. 1c, where the line GH is drawn through the points of onset of hysteresis measured for the isotherms of the pure components and calculated by the Kelvin equation for $N_{g_2} = \text{const}$. Each of the curves $N_{g_2} = \text{const}$ retains linearity in a certain region lying to the left of the curve GH.

We obtained an analogous family of curves $N_{g_2} = \text{const}$ for the case of adsorption of mixtures of the same substances on another, more coarse-pored silica gel. In accordance with the larger pore volume and the more developed hysteresis loop, we obtained a more extended linear region CD on the curves $N_{g_2} = \text{const}$. Along with this, when processing the experimental data of Brigleb and Schölze ([4]), we found that, in the adsorption of mixtures of acetone and chloroform on glass beads, for the region of polymolecular

adsorption and capillary condensation the slopes of the linear portions of the curves $N_{g_2} = \text{const}$ are also equal to N_{l_2}/N_{l_1}.

In Fig. 12 we give the curves $N_{g_2} = \text{const}$, constructed by us from Arnold' s data [6] for the adsorption of mixtures of nitrogen (a_2) and oxygen (a_1) vapors on anatase at 78° K. In constructing these curves (carried out for the mole fraction of nitrogen N_{g_2} equal to 0.15; 0.30; 0.50; 0.70; 0.85), the linear portions of the curves $N_{g_2} = \text{const}$ in the region of polymolecular adsorption were drawn with slopes determined in advance from the phase diagram of the N_2—O_2 system.

On the basis of what has been said, one may think that both in polymolecular adsorption and in capillary condensation sorption in the second and subsequent layers is nonspecific and leads to the formation of a condensed phase whose composition, to a first approximation, is determined only by the nature of the substances being adsorbed and does not depend on the properties of the adsorbent. Thus we arrive at confirmation of the well-known principle concerning the small sphere of action of adsorption forces, by which Langmuir was always guided in his investigations of surface phenomena.

With reference to adsorption from solutions, a number of works have advanced the assumption that the change in the concentration of a solution at the interface with a solid is localized predominantly in the first adsorption layer. From our point of view, the curves in Fig. 1b, c may be regarded as direct experimental confirmation of this hypothesis.

The existence of two types of adsorption behavior of binary vapor mixtures

makes it especially obvious that practically the entire volume of micropores of activated carbons or zeolites is filled as a result of a purely adsorption mechanism, and capillary condensation plays no role at all in this process.

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REFERENCES

[1] B. P. Bering, V. V. Serpinsky, S. I. Surinova, *Izv. AN SSSR, ser. khim.*, 1964, No. 3. [2] B. P. Bering, V. V. Serpinsky, *Izv. AN SSSR, OKhN*, 1959, No. 7, 1186. [3] J. Zawidzki, *Zs. phys. Chem.*, **35**, 129 (1900). [4] G. Brigleb, H. Scholze, *Monatsh. Chem.*, **85**, 731 (1954). [5] I. R. Arnold, *J. Ami. Chem. Soc.*, **71**, 104 (1949).

Note: Figure translations are in progress. See original paper for figures.