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1960

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

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DEPENDENCE OF THE SELECTIVE CHARACTER OF ADSORPTION ON THE STRUCTURE OF THE SORBENT

In works ([1–7]) it has been shown that the character of the porosity of a sorbent substantially affects both the dynamics of sorption and the degree of separation of mixtures. It has been established that the greatest separation effect is achieved on finely porous adsorbents, owing to the fact that, as the pore diameter decreases, their adsorption potential sharply increases.

In addition to the structure of the sorbent, the nature of the mixture plays an important role in the sorption method of separating mixtures. We have shown ([8,9]) that, from binary mixtures, the component whose addition causes the system to deviate from ideal behavior is preferentially sorbed. This conclusion opens up a new prospect for the scientific selection of adsorbents and catalysts and for choosing the most optimal conditions for the purification and separation of mixtures. Consequently, the accumulation of quantitative data on adsorption as a function of the structure of the sorbent and the nature of the medium is of definite scientific and practical interest, especially since the majority of existing studies in this field of knowledge cover only the region of dilute solutions. In this connection, we undertook investigations aimed at a more thorough study of the effect of narrowing the pores of the sorbent on the enhancement of selective sorption of mixtures of hydrocarbons differing both in nature and in properties.

In the present work, the adsorption of saturated vapors of binary mixtures—dichloroethane–ethyl alcohol, benzene–ethyl alcohol, chloroform–dioxane, and ethyl alcohol–methyl alcohol—was investigated on two homogeneous-porous silica gels, clay, and activated wood charcoal.

Adsorption was carried out in the vapor phase over the entire range of concentration change. The composition of the adsorbed solution was determined from the change in the composition of the liquid phase. In terms of the character of their porosity, the silica gels taken for study differ greatly from one another. One of them (ASM), according to the classification of A. V. Kiselev ([10]), belongs to the second structural type, and the other (MSK) to the third. Sorbents selected in this way, despite the homogeneity of the chemical nature of their framework, should possess different degrees of selectivity with respect to the components of the binary mixtures mentioned.

The experimental sorption data are presented in Figs. 1 and 2 in the form of equilibrium isotherms expressed in the coordinates: mole fraction of component 2 in the adsorbed phase (N_2^a)—mole fraction of the same component in the equilibrium solution phase (N_2) (Table 1).

As is seen from Fig. 1 (a, b), the equilibrium curves have an S-shaped form, which, as we have already noted earlier, is characteristic of adsorption from binary azeotropic mixtures with positive or negative deviation from Raoult' s law ([8,9]).

Comparison of the data in Fig. 1 shows that positive adsorption of alcohol from the binary mixture dichloroethane–ethyl alcohol is observed when the composition of the equilibrium liquid mixture ranges from 0 to 0.55 mole fraction of alcohol for

mesoporous silica gel and from 0 to 0.29 N_2 for macroporous silica gel. An analogous dependence of sorption is also observed in the benzene—ethyl alcohol system. In this case, mesoporous silica gel exhibits greater selectivity toward the alcohol than does macroporous silica gel. To the right of the points of equality of the compositions of the adsorbate phase and the equilibrium solution, i.e., in the case of equilibrium mixtures containing more alcohol, the sorbent phase is enriched in dichloroethane or benzene. Such an inversion of selectivity may be regarded as a consequence of the thermodynamic properties of a binary mixture of low-molecular components. The selectivity of sorption, other conditions being equal, depends on the presence in the sorbent mass of pores of molecular dimensions (with a diameter of 2-3 molecules), which, owing to the superposition of the fields of opposing walls, possess increased values of the sorption potentials.

Table 1

Selectivity of absorption of methyl alcohol by silica gel from an ethyl alcohol—methyl alcohol mixture

Mole fraction of methyl alcohol in the equilibrium solution	Mole fraction of methyl alcohol in the adsorbent phase: mesoporous silica gel	Mole fraction of methyl alcohol in the adsorbent phase: macroporous silica gel
0.092	0.156	0.103
0.262	0.324	0.293
0.415	0.495	0.459
0.555	0.636	0.611
0.680	0.771	0.719
0.794	0.848	0.825
0.904	0.942	0.935

A. V. Kiselev and co-workers ([11]) showed that reducing the pore diameter of

Figure 1

Figure 1: Figure 1

silica gel from 104 to 38 Å increases the selectivity of sorption of toluene from solutions in heptane and shifts the maximum of its absorption toward more dilute solutions. For mesoporous sorbents, the total sorption potential will be composed of the work performed by the adsorption forces in moving a molecule from the gas phase to a given point on the sorbent surface (the adsorption potential of the sorbent surface),

Fig. 1. Equilibrium curves (N_2^a—N_2) between the adsorbate phase and binary solutions of dichloroethane–ethyl alcohol (a) and benzene–ethyl alcohol (b). 1 –on mesoporous silica gel, 2 –on macroporous silica gel

and of the capillary potential, which is characterized by the magnitude of the energy of the field of capillary forces referred to unit mass of the liquid in the capillary-porous body ([12]).

The first of these (calculated per unit surface area) depends on the chemical nature of the surface of the solid, whereas the magnitude of the capillary potential is determined mainly by the physical structure of the solid. This means that sorbents with strongly developed fine porosity will possess not only high values of sorption potentials, but also high selectivity of sorption. The capillary potential of such sorbents will, as it were, reproduce a certain free

a surface having a definite magnitude of sorption potential and apparently capable of exhibiting properties analogous to those of the forces of the adsorption field of the sorbent surface. Therefore it is difficult to expect a proportional dependence between the magnitudes of selective sorption and the specific surface areas of sorbents belonging to different structural types.

The data of I. E. Neimark[^6] on the chromatographic separation of hydrocarbons confirm what has been said. The degree of selectivity of sorbents depends not only on the magnitude of their sorption potential, but also on a whole series of other causes, on which we shall briefly dwell.

First, sorbents, depending on the character and chemical nature of the surface and on their affinity for the components of the mixture, may increase or decrease the selectivity of absorption. Here two cases should be distinguished: (a) with a positive deviation of a binary mixture from Raoult' s law and the presence of an affinity of the sorbent for the component of the mixture whose addition causes the mixture to deviate from additivity, the degree of selectivity increases; (b) with a negative deviation of the properties of the mixture from additivity, the degree of selectivity will decrease.

In the opposite case, when the sorbent exhibits a greater affinity for the component whose removal increases the irreversibility of the system, in systems with

Fig. 2. Equilibrium curves (N_2^a—N_2) between the adsorbent phase and a binary chloroform–dioxane solution: 1 –on finely porous silica gel, 2 –on clay, 3 –on activated carbon

Figure 2: Fig. 2. Equilibrium curves (N_2^a—N_2) between the adsorbent phase and a binary chloroform–dioxane solution: 1 –on finely porous silica gel, 2 –on clay, 3 –on activated carbon

a positive deviation from additivity the degree of selectivity decreases, whereas in systems with a negative deviation it increases.

Fig. 2. Equilibrium curves (N_2^a—N_2) between the adsorbent phase and a binary chloroform–dioxane solution: **1** –on finely porous silica gel, **2** –on clay, **3** –on activated carbon

To illustrate what has been said, let us consider the selectivity of sorption from a binary chloroform–dioxane mixture on finely porous silica gel ASM, clay from the Vitebsk region, and wood activated carbon BAU (Fig. 2).

From the data of Fig. 2 it is seen that finely porous silica gel, owing to its affinity for dioxane–the component that causes the mixture to deviate from ideality–has a lower sorption selectivity than clay and carbon.

Let us consider the causes responsible for such a character of adsorption. The chloroform–dioxane mixture, like chloroform–acetone mixtures[^13] and chloroform–ethyl ether mixtures[^14], as thermodynamic studies have shown[^15], belongs to systems with a negative deviation from Raoult' s law. The formation of such mixtures predominantly occurs in those cases when the components of the solution possess an increased mutual attraction, which leads to the formation of solvates or chemical compounds between the mixing molecules. In other words, the mixing of two liquids with a large difference in internal pressures must usually be accompanied by a deviation of the properties of the mixture from Raoult' s law. From the thermodynamic point of view, such mixtures are characterized by increased irreversibility or, what is the same, by a large excess of free energy.

during the formation of one gram-mole of the real solution F^r, than during the formation of one gram-mole of the ideal solution F^i (16). In the present case the difference between these quantities F° is negative.

$$F^\circ = F^r - F^i.$$

Silica gel, as already mentioned, having an increased affinity for dioxane, in sorbing it performs work on the system directed toward increasing the free energy of the mixture. This means that, in the sorption by silica gel of a certain volume of a chloroform–dioxane mixture, less work is gained than in the sorption of the same volume of this mixture by clay or charcoal. An analogous

dependence is also observed in sorption from mixtures of dichloroethane–ethyl alcohol and benzene–ethyl alcohol, where fine-pored silica gel, for the same reasons, to the right of the points of equality of the compositions of the solution in the adsorbent phase and in the equilibrium bulk phase, exhibits a lower selectivity of sorption than coarse-pored silica gel (Fig. 1).

Conversely, in the case of systems with positive deviation from Raoult' s law, sorption of the component that causes the system to deviate from additivity is accompanied by a decrease in free energy and an increase in the thermodynamic stability of the mixture. The degree of selectivity in this case, other conditions being equal, increases in the direction of increasing affinity of the adsorbent for the component sorbed positively (Table 1 and Fig. 1).

In conclusion, we wish to emphasize that fine-pored sorbents, in combination with the chemical nature of their surface and the thermodynamic properties of the binary solution, are responsible for the selectivity of sorption of the components of a binary mixture.

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Received
18 VII 1960

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