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Fig. 2

Figure 2: Fig. 2

Abstract

Full Text

PHYSICAL CHEMISTRY

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ADSORPTION FROM THREE-COMPONENT SOLUTIONS

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There is a large body of work in the literature on the study of adsorption from binary solutions of various organic substances on a variety of adsorbents. The study of ternary systems is considerably more complicated. The few published investigations give only isolated points, mainly at small, uniform concentrations ($^{1-3}$). In these cases, the concentration of one of the components of the mixture remained practically constant.

Fig. 1. Spatial adsorption isotherm of acetic acid from a ternary mixture: acetic acid—lauric acid—cetane. Open circles—adsorption of acetic acid from cetane; half-shaded circles—adsorption of acetic acid from the ternary mixture.

We have determined adsorption isotherms for ternary systems over a wide concentration range and constructed spatial adsorption isotherms for these systems. In the present work, results are given for adsorption from three-component

system: acetic acid—lauric acid—cetane. As the adsorbent, one of the most active Volga opokas was used (No. 120 from the region of the village Kamennyi Yar, Stalingrad Oblast) (^{3}). Its surface area, determined on a gravimetric apparatus by the adsorption of methanol vapor, proved to be 150 m^2/g. Cetane and acetic acid were purified (see (^{4})). Lauric acid had a melting point of 43-44°. Adsorption experiments were carried out according to the procedure adopted in the adsorption laboratory of Moscow State University (^{5}).

Fig. 3

Figure 3: Fig. 3

Fig. 2. Spatial adsorption isotherm of lauric acid from a ternary mixture. Open circles—adsorption of lauric acid from cetane; half-filled circles—adsorption of lauric acid from the ternary mixture

Much attention was devoted to the analyses of the three-component mixtures. Since only binary mixtures can be analyzed with an interferometer, we developed a special method for analyzing the above-mentioned ternary mixture. In developing the analytical procedure, the different solubilities of the mixture components in water were used. Acetic acid passes completely into the aqueous layer, while the solubility in water of cetane and lauric acid is so negligible that it practically does not affect the readings of such a sensitive instrument as an interferometer. It was also confirmed by a special check that neither cetane nor lauric acid dissolves in an aqueous solution of acetic acid in the concentration range of interest to us. After a number of refinements, the analyses were carried out as follows. To 5 ml of the mixture under investigation, 25 ml of distilled water was added. The resulting mixture was shaken on a mechanical stirrer at room temperature for 30 minutes. The aqueous layer was then separated, centrifuged, and the content of acetic acid in it was determined on an ITR-2 interferometer. The content of lauric acid in cetane after centrifugation was determined on an interferometer.

Figure 1 gives the spatial adsorption isotherm of acetic acid from the ternary mixture acetic acid—lauric acid—cetane. On the plane CAB is shown the adsorption isotherm of acetic acid from cetane (in the absence of lauric acid). An interpretation of the wave-like character of this curve was given by us in an earlier work (4). The presence of lauric acid has a great influence both on the magnitude of adsorption and on the shape of the isotherms (at C_2 = const or C_3 = const). The points located in the space bounded by the coordinates $ABCD$ show the adsorption value $X_2^{(v)}$ of acetic acid from the ternary mixture. In the adsorption of CH_3COOH alone from cetane or in the presence of small amounts

the $C_{11}H_{23}COOH$ part (at $C_3 < 100$ mM/l) the isotherms have an S-shaped character (a system of limited solubility). At larger values of C_3 the system under study becomes infinitely soluble and the isotherm (at C_3 = const) passes through a maximum. As the equilibrium concentrations of lauric acid increase, adsorption decreases—especially sharply at $C_3 \simeq 100$–200 mM/l.

Fig. 3. Spatial adsorption isotherm of acetic and lauric acids from a ternary mixture. Open circles—adsorption of acetic acid from cetane; crossed circles—adsorption of lauric acid from cetane; half-blackened circles—adsorption of acetic and lauric acids from cetane.

In Fig. 2 the values of $X_3^{(v)}$ are given for the same ternary mixture. On the plane CAD the adsorption isotherm of lauric acid from cetane (in the absence of acetic acid) is plotted. Since lauric acid is infinitely soluble in cetane, the isotherm passes through a maximum with a subsequent slow decline. The points located in the space bounded by the coordinates $ABCD$ show the magnitude of the adsorption $X_3^{(v)}$ of lauric acid from the ternary mixture. The adsorption of lauric acid at small values of C_3 and C_2 falls rather rapidly, but then, as C_2 increases at $C_3 = \text{const}$, the adsorption even increases owing to a decrease in the adsorption of acetic acid (see Fig. 1). At $C_2 = \text{const}$, the values of $X_3^{(v)}$ pass through a maximum and retain the same character of the adsorption isotherms as in the absence of acetic acid. However, the position of the maximum on each of the isotherms is lower than in the case of adsorption of lauric acid alone.

In Fig. 3 the adsorption isotherm of both acids from the ternary mixture is shown. Along the axis AC are plotted the summed values $X_2^{(v)}$ and $X_3^{(v)}$. On the planes CAB and CAD are plotted, respectively, the adsorption isotherms of acetic and lauric acids from binary mixtures with cetane. The general character of the adsorption isotherms at $C_2 = \text{const}$ or $C_3 = \text{const}$ remains qualitatively the same as in Fig. 1. This is explained by the fact that the adsorption of acetic acid, in magnitude, considerably exceeds the adsorption of lauric acid.

An analogous change is observed in the character of the isotherms (at $C_3 = \text{const}$): from S-shaped (a system of limited solubility) to isotherms passing through a maximum (a system of unlimited solubility).

Thus, we have studied adsorption from three-component solutions over a wide range of equilibrium concentrations and have shown that mutual limitation in the adsorption of all components of the mixture affects both the magnitude and the character of the adsorption isotherms.

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CITED LITERATURE

1. N. F. Ermolenko, *Izv. AN BSSR*, **3**, 229 (1949).
2. G. Papps, D. F. Othmer, *Ind. and Eng. Chem.*, **5**, 430 (1944).
3. N. N. Gryazev, S. M. Rakhovskaya, Collection of Proceedings of the Conference on Adsorption at Moscow State University, 1957, p. 196.

4. N. N. Gryazev, *DAN*, **118**, No. 1 (1958).

5. A. V. Kiselev, I. V. Shikalova, *ZhFKh*, **30**, 94 (1956).

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