THE INFLUENCE OF ASSOCIATION OF ORGANIC ACIDS ON ADSORPTION FROM NONPOLAR SOLVENTS

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Abstract

Full Text

PHYSICAL CHEMISTRY

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THE INFLUENCE OF ASSOCIATION OF ORGANIC ACIDS ON ADSORPTION FROM NONPOLAR SOLVENTS

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A number of authors have shown that, during adsorption from solutions, molecules of organic acids are oriented perpendicular to the surface. Recently, however, new views have appeared on the question of the orientation of molecules of organic acids and of a number of other oxygen-containing organic compounds. Thus, Blackborn and Kipling (1), on the basis of a study of the adsorption on carbon of organic acids from aqueous solutions, point to the possibility of adsorption of both dimers and mono- and dihydrated acid molecules. Kiselev and Shikalova (2) showed that phenol can, during adsorption, assume various positions relative to the surface.

This work is devoted to the study of the influence of association of certain organic acids on the character of their adsorption from cetane and α-methylnaphthalene on natural and artificial adsorbents. As adsorbents we used one of the most active Volga tripolis (No. 120, from the region of the village Kamennyi Yar, Stalingrad oblast) and an industrial sample of silica gel of the KSK grade. The activity of these adsorbents had previously been studied by us in a number of technological processes (3–6). The specific surface area was determined from adsorption of methyl alcohol vapor on a gravimetric adsorption apparatus. For tripoli No. 120, $S = 150$ m^2/g, and for silica gel, $S = 285$ m^2/g.

Fig. 1. Adsorption isotherm of formic acid from solutions in cetane on tripoli No. 120 at 60°.

Cetane and α-methylnaphthalene, after appropriate purification and holding over tripoli and silica gel, had the following constants. **Cetane:** b.p. 152–153°/12 mm, m.p. 16–18°, $d_4^{20} = 0.7734$, $n_D^{20} = 1.4350$; **α-methylnaphthalene:** b.p. 243–245°/760 mm; b.p. 130–132°/30 mm, schematic orientation of dimeric HCOOH molecules on the surface, with dimensions 6.6 Å, 3.2 Å, and $\omega_0 = 20.2$ Å^2

Figure 2: schematic orientation of dimeric HCOOH molecules on the surface, with dimensions 6.6 Å, 3.2 Å, and $\omega_0 = 20.2$ Å^2

$n_D^{20} = 1.6131$. **Anhydrous formic acid** was obtained from an 85% solution by prolonged drying with anhydrous copper sulfate: b.p. 100.5–101.5°, $d_4^{20} = 1.2320$, $n_D^{20} = 1.3712$. **Anhydrous acetic acid** from acetic anhydride and acetic-

acid: b.p. 118-118.5°, m.p. 16°, $d_4^{20} = 1.0478$, $n_D^{20} = 1.3721$. Adsorption experiments were carried out by the method adopted in the Adsorption Laboratory of Moscow University ([2]), at a temperature of 60°, and in some cases at 20°. The acid concentration was determined with an ITR-2 interferometer.

Figures 1 and 2 show adsorption isotherms of formic acid from cetane. The formic acid–cetane system has limited solubility ($C_s(\mathrm{HCOOH}) = 170$ mM/l). In this connection the isotherm has an S-shaped form, characteristic of adsorption from solutions of limited solubility ([7]). Calculation from point B gives the value of the area occupied by a molecule of formic acid on the surface of silica gel, $\omega_{0,\mathrm{exp}} = 10.4$ Å^2. Such a small area cannot be occupied by an HCOOH molecule in any orientation with respect to the surface of the silica gel. This discrepancy is easily explained if it is assumed that the surface is covered by a monolayer of dimeric HCOOH molecules oriented on the surface in the following way:

Fig. 2. Absolute adsorption isotherm of formic acid from solutions in cetane on silica gel No. 120 at 60°.

Fig. 3. Adsorption isotherm of acetic acid from solutions in cetane on KSK silica gel at 20° (1) and on silica gel No. 120 at 20° (2) and at 60° (3).

The values given for the lengths of interatomic bonds and atomic radii were taken by us from the literature ([1,8,9]). With this orientation, $\omega_0 = 20.2$ Å^2 agrees well with the value obtained for the dimer, $\omega_{0,\mathrm{exp}} = 2 \cdot 10.4 = 20.8$ Å^2. For other positions of the formic acid dimer on the surface, there are larger discrepancies in the values of ω_0 and $\omega_{0,\mathrm{exp}}$.

Figure 3 presents adsorption isotherms of acetic acid from cetane on support No. 120 and on KSK silica gel. The acetic acid–cetane system has limited solubility ($C_{s(\mathrm{CH_3COOH})} = 1080$ mM/l). The isotherms have an undulating form. On all three isotherms there are two bends, especially clearly expressed for support No. 120. The first of them corresponds to coverage of the adsorbent surface by monomeric acetic acid molecules oriented, apparently, parallel to the surface ($\omega_0 = 25.5$ Å^2; $\omega_{0\,\mathrm{exp}} = 33.3$ Å^2). With orientation perpendicular to the surface, an acetic acid molecule would have to occupy an area of 20.5 Å^2.

Fig. 4. Adsorption isotherm of acetic acid from solutions in cetane (1) and α-methylnaphthalene (2) on support No. 120 at 60°

Figure 3: Fig. 4. Adsorption isotherm of acetic acid from solutions in cetane (1) and α-methylnaphthalene (2) on support No. 120 at 60°

Scheme of acetic acid adsorption: $C_2 < 200$ mM/l, adsorption of monomers; $C_2 \approx$ 200–400 mM/l, adsorption with partial association; $C_2 > 400$ mM/l, adsorption of dimers

Figure 4: Scheme of acetic acid adsorption: $C_2 < 200$ mM/l, adsorption of monomers; $C_2 \approx$ 200–400 mM/l, adsorption with partial association; $C_2 >$ 400 mM/l, adsorption of dimers

The second horizontal segment on the isotherm corresponds to coverage of the surface by dimeric molecules. The octahedron plane of the dimer, as also of the formic acid dimer, is oriented perpendicular or inclined to the adsorbent surface, which is apparently associated with the influence of the arrangement of neighboring rings. In this case the obtained experimental values of $\omega_{0\,\mathrm{exp}}$ agree well with the calculated ones ($\omega_{0\,\mathrm{exp}} = 31.2$ Å^2 and $\omega_0 = 31.5$ Å^2, respectively). The absence of two horizontal segments on the formic acid adsorption isotherm is explained by the greater tendency of the latter to form associated molecules as compared with acetic acid.

Fig. 4. Adsorption isotherm of acetic acid from solutions in cetane **(1)** and α-methylnaphthalene **(2)** on support No. 120 at 60°.

Figure 4 shows the adsorption isotherm of acetic acid from cetane and α-methylnaphthalene at 60°. The acetic acid—α-methylnaphthalene system is infinitely soluble. The value of $x_2^{(v)}$ first increases and then begins to decrease linearly. In Fig. 4 only the initial part of the isotherm is shown, up to $C_2 \approx 1000$ mM/l. At small equilibrium concentrations $C_{2(\mathrm{CH_3COOH})}$, both curves have two bends.

On the basis of the data presented above, we propose the following scheme explaining the adsorption of acetic acid from high-molecular paraffinic and aromatic hydrocarbons on the surface of siliceous natural and artificial sorbents:

$C_2 < 200$ mM/l	$C_2 \approx$ 200–400 mM/l	$C_2 > 400$ mM/l
adsorption of monomers	adsorption with partial association	adsorption of dimers

For the monomer region: 6.35 Å, $\omega_0 = 25.5$ Å^2.

For the dimer region: 7.9 Å, $\omega_0 = 31.5$ Å^2.

Thus, in connection with the association of organic acids during adsorption from nonpolar solvents established in this work and its influence on the character of the adsorption isotherms, one may expect that a similar

association during adsorption also occurs for a number of other compounds capable, through the formation of hydrogen bonds, of giving dimeric and more complex associates.

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