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Abstract

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ADSORPTION OF PERFLUORINATED FATTY ACIDS AT THE SOLUTION-AIR AND SOLUTION-MERCURY INTERFACES

A comparison of the adsorbability of various organic substances at the solution-mercury and solution-air interfaces, carried out by Frumkin (^{1}), showed that, in the case of oxygen-containing aliphatic compounds with 3-6 carbon atoms in the chain (alcohols, acids, acetone), the adsorption potentials coincide in sign, and the surface activity is approximately the same at both interfaces*. In the case of halogen-substituted compounds, the adsorbability at the solution-mercury interface is greater than at the solution-air interface; it increases on going from Cl^- to Br^- and I^- derivatives, but at the interface with mercury, apparently, to a greater extent than at the free surface of the solution. The aim of the present work was to study and compare the adsorption behavior of perfluorinated fatty acids at the solution-mercury and solution-air interfaces.

Trifluoroacetic, perfluoropropionic, and perfluorobutyric acids were distilled on a rectification column; for the experiments the fraction boiling at a constant temperature (with an accuracy of $\pm 0.25^\circ$) was taken. The boiling points of the acids named were, at a pressure of 760 mm, 72, 96, and 121°, respectively.

Electrocapillary curves of the acids (without supporting electrolyte) were recorded using a Gouy capillary electrometer at $t = 20 \pm 0.2^\circ$; the auxiliary electrode was a hydrogen electrode in the solution under investigation. Values of the interfacial tension in 0.1 *N* solutions were reproduced with an accuracy of ±0.3 dyn/cm, and in 1 *N* solutions with an accuracy of ±0.1 dyn/cm. The surface tension was measured by the maximum bubble-pressure method at $20 \pm 0.2^\circ$, and the surface tension of CF_3COOH solutions, in addition, by the stepped-capillary method (^{2}). Deviations between the results obtained by the two methods did not exceed ±0.1 dyn/cm. Potential differences at the solution-air interface were measured by Kenrick' s vertical-jet method; otherwise the measurement scheme was similar to that described in (^{3}). The measurements were carried out at room temperature (within 18-22°). The values of the potential differences at the ends of the chain:

Hg, Hg_2Cl_2, sat. KCl/0.01 *N* KCl/air/test solution/Hg, Hg_2Cl_2, sat. KCl

were reproduced with an accuracy of ±5 mV.

Fig. 1. Electrocapillary curves of perfluorinated fatty acids and sulfuric acid.

Fig. 1. Electrocapillary curves of perfluorinated fatty acids and sulfuric acid. 1–1.14 N H_2SO_4, 2–1.07 N CF_3COOH, 3–1.15 N C_2F_5COOH, 4–1.09 N C_3F_7COOH. Potentials are referred to the hydrogen electrode in the solution under investigation.

Figure 1 shows the electrocapillary curves of sulfuric, trifluoroacetic, perfluoropropionic, and perfluorobutyric acids, practically identical—

* For compounds with a shorter chain, the surface activity is somewhat greater at the interface with air.

concentration (potentials φ_r relative to the hydrogen electrode in the solution under study). At a sufficient distance from the maximum, the cathodic branches of the curves coincide. The greatest difference between the curves is observed at potentials somewhat more positive than the maximum; with an increase in the anodic potential this difference decreases, the curves for the perfluorinated acids approach one another very closely, and with a further increase in potential they run almost parallel; the curve for sulfuric acid merges with the curve for C_2F_5COOH. This indicates weak adsorbability of the anions of perfluorinated acids, which at $\varphi_r = +0.2 \div +0.4$ V in the case of CF_3COOH proves to be lower than the adsorbability of SO_4^{2-}, and in the case of C_2F_5COOH equal to it.

We also recorded electrocapillary curves for potassium perfluorobutyrate and potassium butyrate (Fig. 2, curves 2 and 3, potentials φ relative to the N.C.E.). The decrease in interfacial tension at the maximum of the electrocapillary curve of $1N$ C_3F_7COOK, $|\Delta\sigma_{\max}|$, decreases by 56% in comparison with the same value for the $1.1N$ acid. The residual decrease indicates adsorption of the anion on the uncharged mercury surface. The higher surface activity in solutions of the acid is probably associated with the formation of ion pairs with the hydrogen ion. An analogous phenomenon is observed at the solution–air interface ([4,5]). At a sufficient distance from the maximum, the anodic branch of $1N$ C_3F_7COOK intersects the anodic branch of $1N$ Na_2SO_4. Weakly alkaline $1N$ potassium butyrate behaves analogously.

Fig. 2

Fig. 2. Electrocapillary curves of solutions of $1N$ Na_2SO_4 (1), $1N$ C_3F_7COOK (2), $1N$ $C_3H_7COOK + 0.01N$ KOH (3)

An approximate determination of the differential capacitance C from the electrocapillary curves gives, at $\varphi = -0.2 \div 0.3$ V, a value of 25-24 in the case of $1N$ C_3F_7COOK, 22-23 in the case of $1N$ C_3H_7COOK, whereas for $1N$ Na_2SO_4, C is 40-36 $\mu F/cm^2$. The decrease in double-layer capacitance in the case of perfluorobutyrate and butyrate can probably be explained by the fact that the fluorocarbon and hydrocarbon chains of the anions approach the electrode surface closely and reduce the dielectric permittivity in the double layer.

In Fig. 3, the dependences of $\sigma_{\max}$ on the logarithm of concentration (curves

$1'$—$3'$) are compared with the surface-tension isotherms at the solution-air interface (curves 1—3). The surface activity of perfluorinated fatty acids at the solution-air interface at 25° has already been studied by a number of authors ([4–7]). Our isotherms, obtained at 20°, differ little from the literature data; in Fig. 3 they are compared with results obtained by the ring-detachment method ([4]). Breaks in the surface-tension isotherms were explained by association of perfluorinated fatty acids in aqueous solution ([4–9]), although the concentrations at which these breaks are observed exceed the bulk critical micelle concentrations found by other methods ([8,9]).

At the solution-air interface, down to σ of about 40 dyn/cm, i.e., up to the break in the CF_3COOH isotherm, Traube' s rule is obeyed. The values of the Traube coefficient k reported in the literature ([10,11]) range from 2.8 for the first three members of the homologous series to 3.1-3.4, on average 3.2, for the higher homologs. The increase in k with chain length is probably associated with inter-

interaction of sufficiently long fluorocarbon chains. According to our data, for the first three members of the homologous series of perfluorinated acids $k = 2.9$, which corresponds to an adsorption work of the CF_2 group equal to 610 cal/mole.

The isotherms obtained by us, $\sigma_{\max}$—$\lg C$, also have an anomalous form, with breaks observed at approximately the same concentration as at the solution—air interface (see Fig. 3, curves $1'$—$3'$). The acid concentration corresponding to the value $\Delta\sigma_{\max} = 1.4$ dyn/cm, when the chain length is increased by one CF_2 group, decreases by approximately a factor of 1.5. With further increase in $\Delta\sigma_{\max}$, the distance between the isotherms of CF_3COOH and C_3F_7COOH along the concentration axis remains constant (up to the break in the $\sigma_{\max}$—$\lg C$ isotherm of CF_3COOH) and, for example, at $\Delta\sigma_{\max} = 6.0$ corresponds to an increase in activity upon chain elongation by two CF_2 groups by a factor of $1.5^2 = 2.25$; however, the increase in activity in going from CF_3COOH to C_2F_5COOH is smaller than in going from C_2F_5COOH to C_3F_7COOH. The reason for this has not yet been established.

Figure 3

Fig. 3. Isotherms of surface tension and interfacial tension at the maxima of electrocapillary curves. 1—CF_3COOH, 2—C_2F_5COOH, 3—C_3F_7COOH. Primes on the numerals refer to the solution—mercury interface. Open points are our data; black points are data from (7), obtained at 25°.

The dependences of the shift of the points of zero charge (p.z.c.) of mercury $\varepsilon_{\mathrm{Hg}}$ and of the adsorption potentials at the solution—air interface ε on concentration (Fig. 4) show that, for example, at $\varepsilon = \varepsilon_{\mathrm{Hg}} = -100^*$ mV, the acid concentration, with an increase in the length of the fluorocarbon chain by two CF_2 groups, decreases by $2.35^2 = 5.5$ in the case of the solution—mercury interface and by $4.1^2 = 16.8$ in the case of the solution—air interface. Thus the Traube coefficient, determined from the magnitude of the electric effects, in both cases proves to be larger than the same coefficient found from measurements of surface tension: namely, by a factor of 1.4 in the case of the interface with air and approximately by a factor of 1.6 in the case of the interface with mercury. Apparently, the increase in the adsorption potential with increasing length of the fluorocarbon chain is associated not only with an increase in adsorbability, but also with a change in the orientation of the C—F bonds, leading to an increase in the dipole moment per adsorbed molecule.

At $\Delta\sigma = \Delta\sigma_{\text{max}} = 1.4$ dyn/cm, the surface activities of trifluoroacetic, perfluoropropionic, and perfluorobutyric acids at the solution—air interface are approximately 15, 29, and 56 times greater than at the solution—mercury. These values show that the differences in the works of adsorption at the boundaries under consideration, for sufficiently small $\Delta\sigma$, can with good approximation be expressed by the relation $\Delta\lambda^{\emptyset}_{\text{uks}} + nRT\ln(2.9/1.5)$, where $\Delta\lambda^{\emptyset}_{\text{uks}}$ is the difference in the works of adsorption of CF_3COOH at the two boundaries, equal to 1560 cal/mol, and n is the number of CF_2 groups in the perfluoro acid molecule. The question of the works of adsorption of CF_3- and CF_2-groups at the solution—air and solution—mercury boundaries will be considered in more detail in another communication.

Fig. 4

Fig. 4. Dependences of the adsorption potentials at the solution—air boundary and of the shift of the z.c.p. of mercury on the concentration of solutions of perfluorinated fatty acids. 1—CF_3COOH, 2—C_2F_5COOH, 3—C_3F_7COOH. Primes on the numbers refer to the solution—mercury boundary.

It follows from the foregoing that the surface activity of fluoro-substituted compounds at the boundary with mercury is considerably reduced in comparison with the activity at the free surface of the solution. Such a result seems incomprehensible unless one takes into account that the adsorption process is accompanied by the departure of water molecules from the surface layer into the bulk of the solution. The significance of the latter circumstance has recently been especially emphasized by Bockris and co-workers ([12]). The behavior of fluoro-substituted compounds indicates that, when calculated per equal area occupied in the surface layer, the gain in free energy upon transfer of CF_3- and CF_2-groups from the bulk of the solution to the mercury surface is smaller than in the case of the analogous transfer of water molecules, in contrast to what occurs in the case of other halogen-substituted compounds, especially bromo- and iodo-substituted ones.

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* The minus sign indicates that the negatively charged ends of the dipoles of the adsorbed molecules are oriented outward from the solution, as is also the case for other halogen-substituted compounds.

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