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

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Comparison of adsorption properties of various organic substances at the solution-mercury and solution-air interfaces, accomplished by Frumkin [1], has shown that in the case of oxygen-containing aliphatic compounds with 3 to 6 carbon atoms (alcohols, acids, acetone), the adsorption potentials have the same sign, and the surface activity is approximately the same for both interfaces.* For halogen-substituted compounds, adsorption at solution-mercury interface is higher than at the solution-air boundary; it increases in the direction from Cl to Br and I derivatives, but the effect is greater at the mercury interface than for the solution surface alone. The aim of this investigation has been a study and comparison of adsorption behavior of perfluorated fatty acids at the solution-mercury and solution-air interfaces.

Trifluoroacetic, perfluoropropionic, and perfluorobutyric acids were distilled in a fractionating column, and the corresponding fractions were collected at constant boiling (accurate to ± 0.25°C) temperatures. The boiling temperatures of these acids, at 760 mm pressure, were 72, 96, and 121°C, respectively.

Electrocapillary curves of the acids (without base electrolyte) were plotted using Gouy's capillary electrometer, at $t = 20 \pm 0.2$°C; a hydrogen electrode immersed in the actual solution was used as a booster electrode. Interface tensions, in 0.1 N solutions, were reproduced to an accuracy of ± 0.3 dyn/cm, in 1 N solutions to ± 0.1 dyn/cm. Surface tension was measured applying the maximum bubble pressure method at 20 ± 0.2°C, and surface tension of CF_3COOH solutions, furthermore, by using a graduated capillary [2]. Discrepancies between the two methods did not exceed ± 0.1 dyn/cm. Differences of the potential at the solution-air interface were measured using Kenrick's vertical jet method, and in other respects the pattern of measurements was similar to that described in [3]. Measurements were made at room temperatures (18 to 22°C). Differences of the potential at circuit terminals: Hg, Hg_2Cl_2, sat. KCl 0.01 N KCl air/invest. solution/Hg, Hg_2Cl_2, sat. KCl, were measured to an accuracy of ± 5 mV.

Figure 1 shows electrocapillary curves for sulfuric, trifluoroacetic, perfluoropropionic, and perfluorobutyric acids of similar concentrations (potentials φ_r at the hydrogen electrode in the investigated solution). At some distance from the maximum, the cathodic curves coincide. The curves diverge most widely just before the maximum. As the anode potential increases this difference decreases, the perfluorated acid curves almost coincide and, as the potential increases still further, become almost parallel, the sulfuric acid curve coinciding with the C_2F_5COOH curve. This indicates weak adsorption of perfluorated acid anions which, at $\varphi_r = +0.2$ to $+0.4$ V in the case of CF_3COOH, is lower than the adsorption of SO_4^{-2}, and equal to that of C_2F_5COOH.

Electrocapillary curves of potassium perfluorobutyrate and butyrate were also plotted (Fig. 2, curves 2 and 3, potentials φ obtained from the pull of the capillary electrometer). The interface tension maximum of the electrocapillary curve of 1 N C_3F_7COOK $|\Delta\sigma_{max}|$ is 56% lower than that in 1.1 N acid. The residual depression indicates anion adsorption on the surface of the uncharged mercury surface. Higher surface activity of the acid solutions is probably due to coupling with ions of hydrogen. Analogous phenomena are observed at the solution-air interface [4, 5]. Some distance from the maximum the anodic curve of 1 N C_3H_7COOK intersects the anodic curve of 1 N Na_2SO_4. The weakly alkaline 1 N potassium butyrate behaves in a similar manner.

An approximate determination of differential capactance C from the electrocapillary curves when $\varphi = -0.2$ to 0.3 v, yields a value of 25 – 24 for 1 N C_3H_7COOK, 22-23 for 1 N C_3H_7COOK, and for 1 N Na_2SO_4 40-36 μF/cm^2.

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*For shorter chain compounds, surface activity is slightly higher for the air boundary.

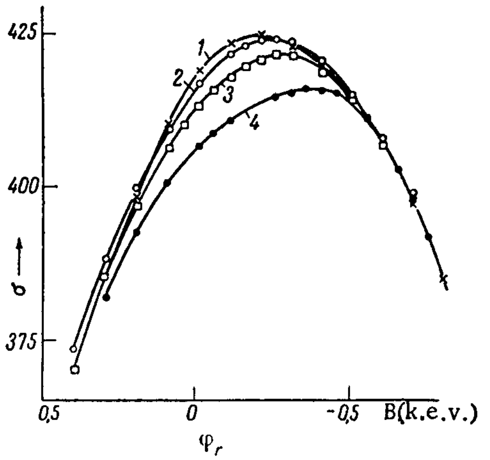

Fig. 1. Electrocapillary curves of perfluorated fatty acids and sulfuric acid. 1) 1.14 N H_2SO_4; 2) 1.07 N CF_3COOH; 3) 1.15 N C_2F_5COOH; 4) 1.09 N C_3F_7COOH. Potentials refer to hydrogen electrode immersed in the investigated solution.

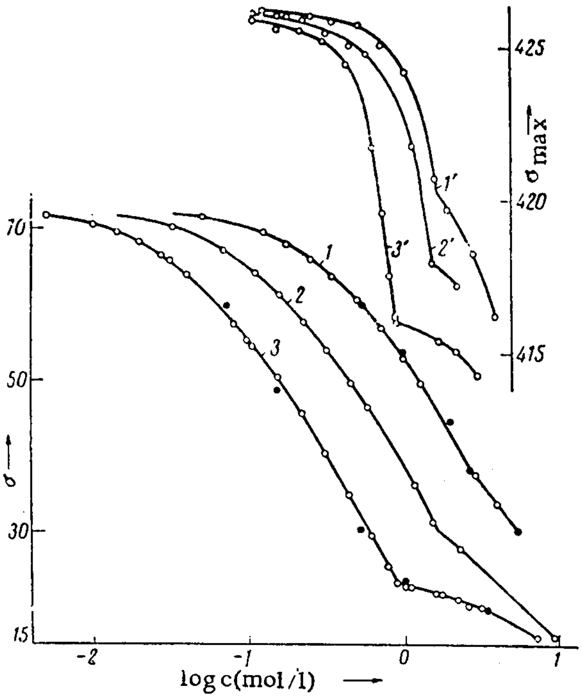

Fig. 3. Isotherms of surface and interface tensions at maxima values of electrocapillary curves. 1) CF_3COOH; 2) C_2F_5COOH; 3) C_3F_7COOH. Dashed figures refer to solution-air interface. Small circles refer to data derived in our experiments, black dots refer to data obtained at 25°C in [7].

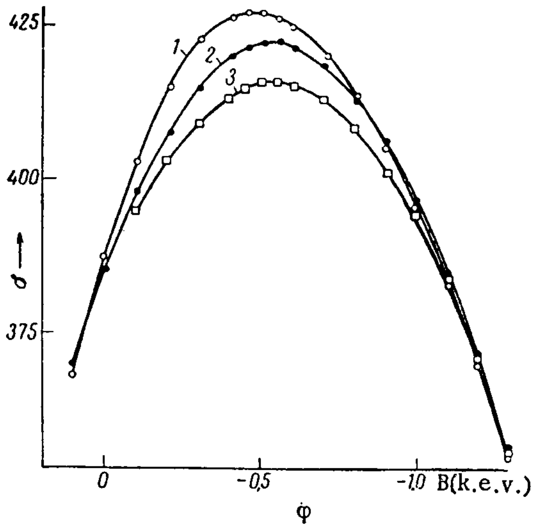

Fig. 2. Electrocapillary curves of solutions 1 N Na_2SO_4 (1), 1 N C_3H_7COOK(2), 1 N C_3H_7COOK + 0.01 N KOH (3).

Lowering of the double layer capacitance, in the case of perfluorobutyrate and butyrate, can probably be explained by a tendency of the fluorocarbon and hydrocarbon anion chains to distribute themselves near the electrode surface, lowering the dielectric penetrability of the double layer.

In Fig. 3, the dependence of σ_{max} on the logarithm of concentration (curves 1'-3') is compared with surface tension isotherms at the solution-air (curves 1-3) interface. Surface activity of perfluorated fatty acids, at the solution-air interface at 25°C, has already been investigated by many authors [4-7]. Isotherms obtained in our experiments at 20°C do not significantly differ from those quoted in the literature, compared in Fig. 3 with the results obtained by the ring method [4]. The breaks in the surface tension isotherms are explained by association of perfluorated fatty acids in water solution [4-9], although the concentrations at which these breaks occur exceed the critical concentrations of micelle formation, as determined by other methods [8, 9].

At the solution-air interface, to σ approximately 40 dyn/cm, i.e., up to the break in the CF_3COOH isotherm, the Traube rule applies. The magnitudes of Traube coefficients $\underline{k}$, which are quoted in the literature [10, 11], vary from 2.8 for the first three members of a homologous series, to 3.1-3.4 for the middle, and 3.2 for higher homologs. Increase of $\underline{k}$ with increase in chain length is probably due to interaction of sufficiently long fluorocarbon chains. According to our data for the first three members of a homolog series of perfluorated acids, k = 2.9 which corresponds with the work of adsorption of the CF_2-group, equal to 610 cal/mol.

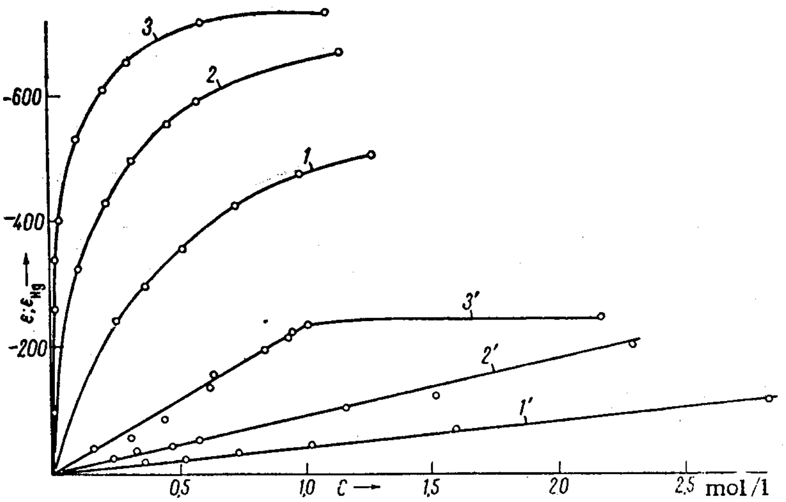

Fig. 4. Dependence of adsorption potentials at solution-air interface and displacement of the zero charge points of H_g on the concentration of perfluorated fatty acid solutions. 1) CF_3COOH; 2) C_2F_5COOH; 3) C_3F_7COOH. Numbers with primes refer to solution-mercury interface.

The $\sigma_{max}-\log c$ isotherms obtained in our experiments also exhibit certain anomalies; the breaks occur at approximately the same concentration as in the case of the solution-air interface (Fig. 3, curves 1'-3'). Acid concentration, corresponding to $\Delta\sigma_{max}$ = 1.4 dyn/cm, decreases approximately 1.5 times if the chain length is increased by one CF_2- group. With a further increase of $\Delta\sigma_{max}$ the distance between the CF_3COOH and C_3F_7COOH isotherms remains constant along the concentration axis (up to the break on the isotherm $\sigma_{max}-\log c$ CF_3COOH) and, for instance at $\Delta\sigma_{max}$ = 6.0, tallies with the increase in activity due to chain elongation by two CF_2- groups, by $1.5^2 = 2.25$ times; increased activity, however, at the transition from CF_3COOH to C_2F_5COOH is lower than at the transition from C_2H_5COOH to C_3F_7COOH. The reason for this is not yet known.

The relationship of the displacement of zero charge points of mercury ε_{Hg} and of the adsorption potentials at the solution-air interface ε to concentration (Fig. 4) shows that, for instance, when $\varepsilon = \varepsilon_{Hg} = -100$* mV, the concentration of acid, with increase of the fluorocarbon chain length by two CF_2-groups, decreases $2.35^2 = 5.5$ times for the solution-mercury interface, and $4.1^2 = 16.8$ times for the solution-air interface. In this manner, the Traube coefficient determined from the magnitudes of the electrical effects is higher in both the cases than that derived from the measurements of the surface tension, i.e., 1.4 times higher for the air boundary and approximately 1.6 times higher for the mercury boundary. It appears that the rise of adsorption potential with increase of the fluorocarbon chain length is connected not only with increased adsorption capacity, but also with a change in the orientation of the C-F-bonds, leading to increased dipole moment of the adsorbed molecule.

When $\Delta\sigma = \Delta\sigma_{max}$ = 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 higher than at the solution-mercury interface. This implies that the different work of adsorption for the investigated interfaces, at sufficiently small $\Delta\sigma$ values, can be expressed fairly precisely in the following equation $\Delta\lambda^{\phi}_{acet} + nRT\ln 2.9/1.5$, where $\Delta\lambda^{\phi}_{acet}$ is the difference in the work of adsorption of CF_3COOH at both interfaces, equal to 1560 cal/mol, and $\underline{n}$ is the number of CF_2-groups in one molecule of the perfluorated acid. The question of the work of adsorption of CF_3- and CF_2-groups at solution-air and solution-mercury interfaces will be considered in detail in a further report.

From our investigation it is evident that fluorination considerably reduces surface activity at the mercury interface, as compared with the activity of a free solution surface. This is difficult to accept without considering that the adsorption process is accompanied by transference of molecules of water from the surface layer to the solution. The significance of this phenomenon was recently emphasized by Bockris et al., [12]. The behavior of fluorosubstituted compounds indicates that, in calculations involving identical surface layers, the free energy gained by the

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* Negatively charged dipole terminals of adsorbed molecules are oriented from outside of the solution, as is generally the case with halogen substituted compounds.

transition of CF_3- and CF_2-groups from the solution to the mercury surface is smaller than for an analogous transition of molecules of water, in contrast to other halogen substituted, particularly bromo and iodo, compounds.

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