Capacity of Mercury Electrode in Solutions of Capillary-Active Organic Substances

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M. Proskurnin and A. Frumkin measured the capacity of the mercury electrode in a solution of octyl alcohol [1].

For a more detailed study of the influence of adsorption of a capillary-active substance upon the capacity of the double layer, we carried out measurements with ethyl alcohol, normal butyl alcohol and phenol.

All these substances were purified by shaking with mercury and (with the exception of phenol) with potassium carbonate and distilled in an atmosphere of hydrogen. The procedure used in the measurements has been described in previous papers [2].

The electrolyte was a normal solution of Na_2SO_4; the reference electrode, Hg/Hg_2SO_4, $1N$ Na_2SO_4.

The results of the measurements are given in Figs. 1, 2 and 3[3].

In all the figures the potentials are referred to the above-mentioned reference electrode (cathodic polarization). The capacity curve for the pure Na_2SO_4-solution is drawn in a dotted line. In Figs. 2 and 3 electrocapillary curves for Na_2SO_4 and Na_2SO_4 + + organic substance (the upper curves) are given for the sake of comparison [4].

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[1] M. Proskurnin a. A. Frumkin, Trans. Farad. Soc., **31**, 110 (1935).

[2] T. Borissowa a. M. Proskurnin, Acta Physicochimica URSS, **4**, 819 (1936).

[3] The capacity curve for ethyl alcohol is given in the next paper.

[4] The electrocapillary curve for butyl alcohol in Na_2SO_4 is taken from the paper by Gouy, Ann. chim. phys. (8), 291 (1908); the curve for phenol in Na_2SO_4, from the paper by Kabanov a. Ivanishenko, Acta Physicochimica URSS, **6**, 701 (1937).

Like octyl alcohol, all these substances exhibit a decrease in capacity in the middle part of the curve in the neighbourhood of the electrocapillary maximum, corresponding to the region of adsorp-

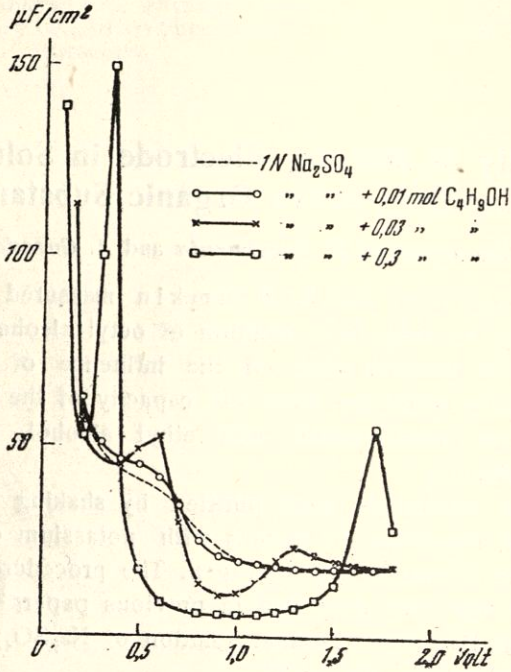

Fig. 1. Butyl alcohol.

tion of the given substance on mercury. This decrease was accounted for[1] by the penetration into the double layer of molecules of

Table 1

Minimum capacity in saturated solutions of alcohols

Alcohols	Capacity, μ F/cm.²
Ethyl alcohol	7,3
Normal butyl alcohol	4,4
Cetyl alcohol[5]	1,0

[5] A. Gorodetzkaja a. A. Frumkin, C. R. Acad. Sci. URSS, 18, 639 (1938).

the organic substance having a lower dielectric constant than the water displaced. The higher the concentration of the organic substance, the greater the decrease in capacity, and the larger the region of adsorption (Fig. 1).

In a saturated solution of an organic substance (when the molecules are oriented perpendicular to the surface of mercury) the

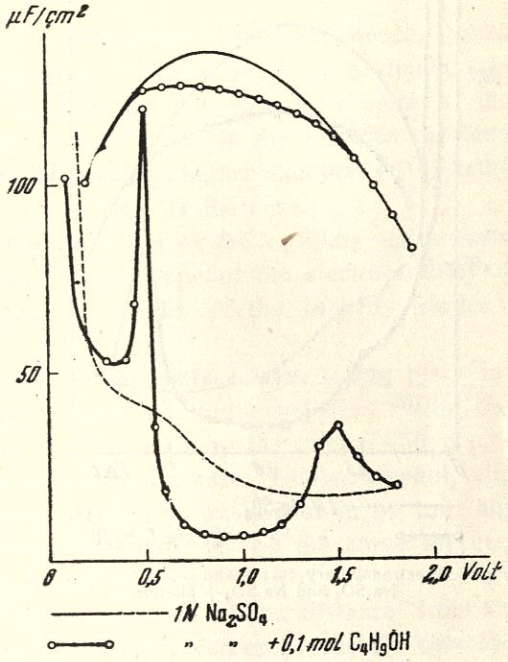

Fig. 2. Electrocapillary curves and capacity curves for Na_2SO_4 and Na_2SO_4 + butyl alcohol.

capacity in this portion of the curve must decrease with an increase in the effective length of the organic molecule. The value of capacity measured in saturated solutions of alcohols of the fatty series qualitatively confirms this relation.

As in the case of octyl alcohol, the middle lower portion of the curves, is bounded both on the anode and cathode sides by peaks corresponding to very high capacities (up to 150 μF/cm.²) (Table 1).

A comparison with the corresponding electrocapillary curves (Figs. 2 and 3) shows that the peaks are located at the potentials corresponding to the boundaries of the adsorption region.

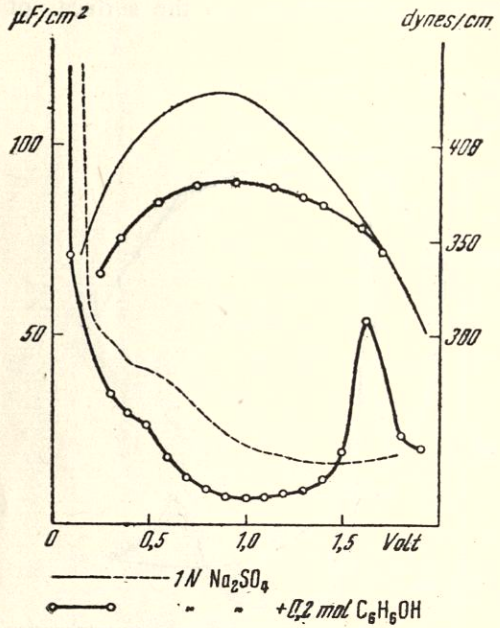

Fig 3. Electrocapillary curves and capacity curves for Na_2SO_4 and Na_2SO_4 + phenol.

In a paper dealing with the influence of the electric field on the adsorption of organic substances at the boundary of two phases[6] A. Frumkin showed that the change in the slope of the electrocapillary curve of a solution of some organic substances observed at the limits of the region of adsorption (see, *e. g.*, the electrocapillary curve of butyl alcohol, Fig. 2) which is especially sharp for a long-chain substance, is accounted for by a very rapid decrease in the surface density of the organic substance, which occurs at certain values of the potential difference at the interface.

[6] Frumkin, Z. Physik, **35**, 792 (1926).

Owing to the nearly complete displacement of the molecules of the organic substance by water molecules taking place in this case, the charge of the double layer considerably changes its value within a very narrow range of polarizations, *i. e.*, the capacity in this portion of the curve must be very high. Mathematically, the peak on the capacity curve is accounted for by the fact that, according to the Lippman equation $\frac{\partial\sigma}{\partial\varphi} = e$, the capacity is the second derivative of the electrocapillary curve and hence, when the slope of the curve is changed, it should reach its maximum value. The height of the peak depends on the rate of change of the slope of the electrocapillary curve; *e. g.*, in the instance of butyl alcohol, the peak at the anodic branch is higher than that at the cathodic end, while with phenol the reverse is the case.

As the concentration of the capillary-active substance decreases, the change in the slope of the electrocapillary curve becomes less sharp and the peaks of the capacity curves become flatter (Fig. 1).

The changes in the surface layer taking place in the region of the peaks have a low but finite velocity. With the frequency of the alternating current used by the authors (50 c. p. s.) these changes could be noted in the case of butyl alcohol, ethyl alcohol and phenol, but this frequency was found to be too high for substances with a longer chain. *E. g.*, on the curve for cetyl alcohol the peaks are not observed at all[5].

With a further increase of the distance from the electrocapillary maximum, the capacity curves practically coincide with that for Na_2SO_4, as the electric field of the double layer now hinders the adsorption of organic molecules.

Conclusions

1. Curves of mercury electrode capacity have been obtained in solutions of capillary-active organic substances, and a physical interpretation of the shape of these curves has been given.

2. It has been established that the minimum capacity in a saturated solution of a capillary-active organic substance decreases

with an increase in the length of the chain of the organic molecule.

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