ADSORPTION OF CERTAIN ORGANOHALOGEN AND ORGANOMERCURY COMPOUNDS ON MERCURY

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The present report presents certain conclusions emerging from an analysis of the electrocapillary curves obtained by means of the Gouy electrometer in solutions of β-iodopropionitrile (IPN), β-bromopropionitrile (BPN), β-chloropropionitrile (CPN), β,β'-dicyanoethylmercury (DCEM), β-cyanoethylmercuric iodide (CEMI). [DCEM and CEMI were isolated from the products from electrochemical reduction of IPN and mercury [1]), β-hydroxyethylmercuric chloride (HEMC), and n-propylmercury acetate (PMA).]

The large values for the decrease in interfacial tension and the shift of the electrocapillary maxima toward the negative side in solutions of halogen-substituted compounds had been noticed long ago and had been attributed to specific reaction of the halide with mercury [2]. For ethyl bromide a vertical orientation (with the bromine atom toward the surface) of the molecules adsorbed on mercury had been found with large coverages; the area required for the molecule is 21 Å^2 [3]. A vertical arrangement of the adsorbed molecules on mercury was also found in valeronitrile, and each molecule requires an area of <24 Å^2; however, the electrocapillary maximum was shifted by about 0.27 V to the positive side [4], which indicates orientation of the cyano groups toward the solution.

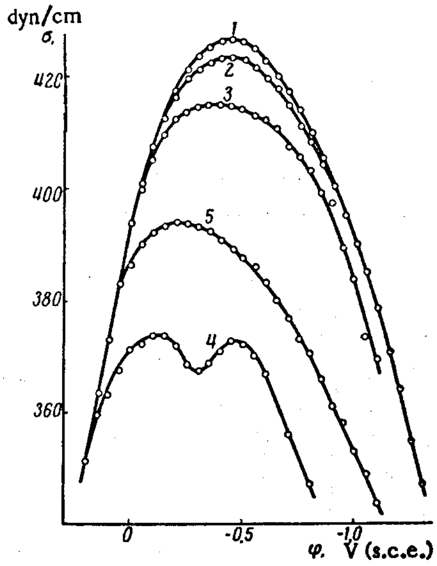

Fig. 1. Electrocapillary curves for mercury in 1 N sodium sulfate solution (1) with additions: 2) 2.5 · 10^{-2} M β-chloropropionitrile; 3) 2.6 · 10^{-2} M β-bromopropionitrile; 4) 2.8 · 10^{-2} M β-iodopropionitrile; 5) 2.7 · 10^{-3} M β,β'-dicyanoethylmercury; the σ values on curves 3 and 4 were obtained 5 min after renewal of the surface.

All the halogenopropionitriles reduce the interfacial tension σ fairly strongly (Fig. 1). The surface activity increases in the order CPN < BPN < IPN. A decrease in σ by the same amount is obtained with greatly differing (by tens of times) concentrations of the halogenopropionitriles, whereas their solubilities differ little (by not more than three times). From this it follows that the surface activity of the halogenopropionitriles is due largely to specific reaction of the halogen with the mercury. The electrocapillary maxima in the presence of halogenopropionitriles are shifted toward less negative potentials (by approximately 0.1 V), and this indicates orientation of the adsorbed dipoles with the positive pole toward the mercury surface. Since the constant dipole moments of the chloro-, bromo-, and iodoalkanes are approximately the same and half the dipole moments of the nitriles, it can be considered that the adsorbed molecules are oriented with the cyano group toward the solution. Since the nitrile group confers hydrophilic characteristics to the alkanes to a much greater degree than halogens, its orientation toward the water seems natural.

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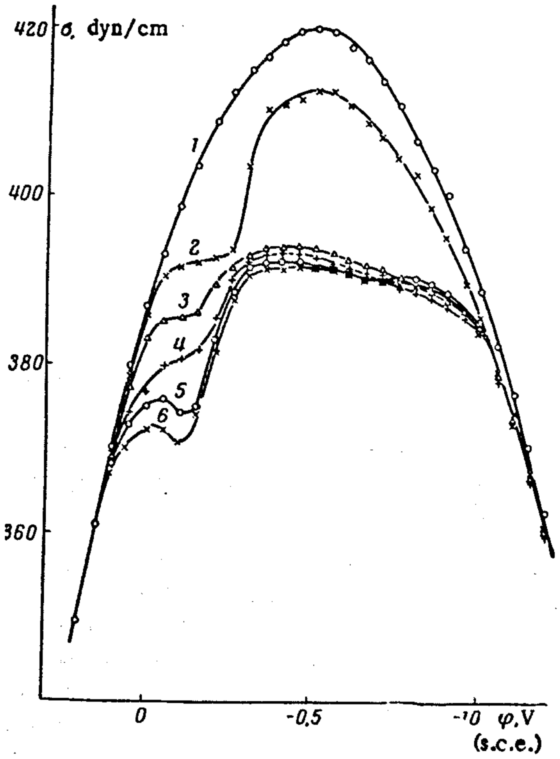


Fig. 2

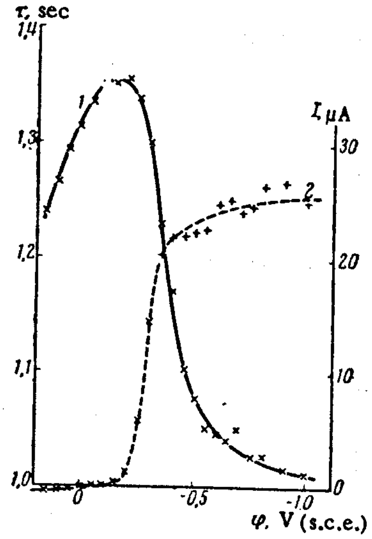
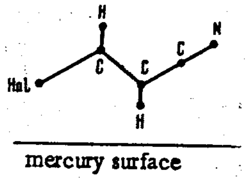


Fig. 3

Fig. 2. Electrocapillary curves for mercury in 1 N sodium acetate solution (1) with additions of propylmercuric acetate: 2) $6.5 \cdot 10^{-3}$; 3) $1 \cdot 10^{-2}$; 4) $2 \cdot 10^{-2}$; 5) $3.25 \cdot 10^{-2}$; 6) $4.37 \cdot 10^{-2}$ M; the σ values were obtained 30 sec after renewal of the surface.

Fig. 3. Dependence of drop time (1) and current strength (2) on potential in $4 \cdot 10^{-3}$ M solution of propylmercuric acetate with 1 N sodium acetate as supporting electrolyte.

In the case of bromopropionitrile and chloropropionitrile the adsorption isotherms are S-shaped and can be described approximately by the Frumkin equation; at −0.4 V the $\Gamma_{\max}$ values are practically the same and equal to $6 \cdot 10^{-10}$ mole/cm². This value corresponds to the area of about 30 Å² required for one molecule of chloropropionitrile and bromopropionitrile. The areas calculated from models of these molecules are practically the same for both compounds and amount to about 30 Å² for the flat and 20 Å for the vertical orientation. These data together with data on the shift of the electrocapillary maximum make it possible to propose the following orientation of the adsorbed molecules:



It should be noted that in the case of iodopropionitrile the form of the electrocapillary curve depends on the interval between the formation of the fresh mercury–solution interface and measurement of the interfacial tension. The appearance of a minimum and two maxima, as on curve 4 in Fig. 1, with the presence of one component indicates the existence of a redox system [5]. This and certain other features of the electrocapillary curve of iodopropionitrile and also of bromopropionitrile will be discussed in the next report. It is probably impossible to obtain the correct form of the isotherm for iodopropionitrile from the electrocapillary curve. The value for the maximum adsorption of iodopropionitrile ($\Gamma_{\max} \approx 8\text{-}10 \cdot 10^{-10}$ mole/cm²) also cannot be accepted unconditionally.

Dicyanoethylmercury was found to be the most surface active of all the compounds which we investigated, and shifted the electrocapillary maximum most strongly to the positive side (by approximately 0.25 V). The adsorption isotherm was also S-shaped, and the $\Gamma_{\max}$ value at −0.4 V was $\sim 8 \cdot 10^{-10}$ mole/cm², which corresponds to an area of about 20 Å^2 occupied by the molecule. For monolayer adsorption the obtained area corresponds to vertical orientation of the linear molecule; here the positions of the two cyano groups are nonequivalent (one toward the surface and the other toward the solution), the mercury atom is removed from the surface, and the constant dipole moment is equal to zero. For the molecules of the symmetrical organomercury compounds in the absence of complex formation a linear structure (C−Hg−C angle 180°) is adopted, and (on the condition of free rotation) there is no dipole moment. However, the large shift of the electrocapillary maximum is most simply explained by a flat position of the adsorbed molecule with the mercury atom in contact with the surface and the cyano groups facing the solution. This, however, requires an area of 40-60 Å^2. This question requires further investigation.

Cyanoethylmercuric iodide is extremely poorly soluble in water (about 10^{-4} M) and gives too small a decrease in σ to make it possible to obtain any data on its behavior.

Hydroxyethylmercuric chloride and propylmercuric acetate dissolve significantly better but, like cyanoethylmercuric iodide, are reduced early. Here ethylene (which hardly reduces the σ value) is formed from hydroxyethylmercuric chloride, and dipropylmercury (DPN) is formed from propylmercuric acetate. Therefore, on the electrocapillary curves of both compounds there are regions corresponding to adsorption of the initial and final compounds and also a transitional region (Fig. 2). In the latter σ depends largely on the time which has elapsed from the moment of renewal of the surface. For propylmercuric acetate from the σ, log c relation (where c is the concentration of propylmercuric acetate in the volume of the solution) for 0.0 V it is possible to determine the approximate value of $\Gamma_{\max}$, equal to $4 \cdot 10^{-10}$ mole/cm^2 (about 45 Å^2 per molecule). For all its concentrations except one the right branches of the electrocapillary curves for propylmercuric acetate practically coincide and are essentially the electrocapillary curve of a saturated solution of dipropylmercury. An approximate evaluation (from the two points for concentrations of $6.5 \cdot 10^{-3}$ and $1 \cdot 10^{-2}$ M, assuming the latter to be the concentration of the saturated solution of dipropylmercury) gives $\Gamma_{\max} \geq 9 \cdot 10^{-10}$ mole /cm^2 for −0.5 V (≤20 Å^2 per molecule), which is close to the value for dicyanoethylmercury and can also be attributed to vertical orientation of dipropylmercury.

It is interesting that in solutions of propylmercuric acetate the drop time does not increase but decreases abruptly at potentials corresponding to the beginning of its electrochemical reduction (Fig. 3). This may be due to the initial formation of propylmercury radicals, which greatly reduce σ. In fact, at the potentials of electrochemical reduction of propylmercuric acetate very low σ values, which increase to certain steady values in a fraction of a second, were observed during measurements on the Gouy electrometer at the very first moments after formation of the new surface. The increase in σ may be due to secondary reactions of the propylmercury radicals, e.g., dimerization.

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