

# ADSORPTION OF ORGANIC SUBSTANCES ON THE FREE WATER SURFACE AND AT THE WATER-MERCURY INTERFACE

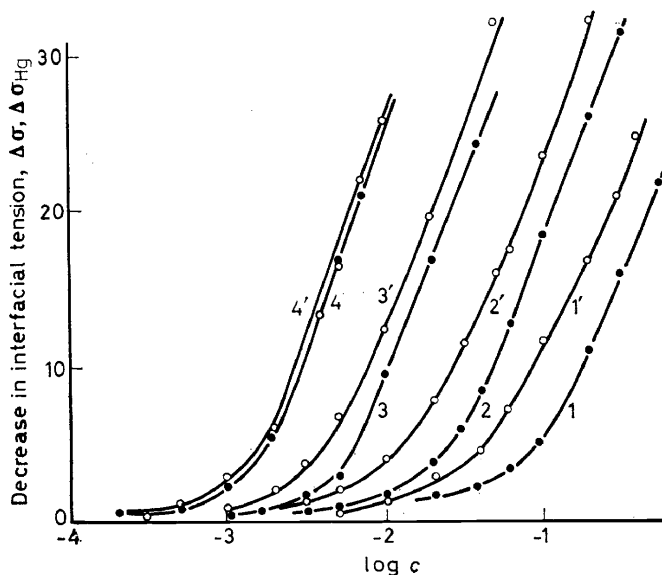
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It is of interest to compare the adsorption phenomena at a free water surface and at the water-mercury interface as this brings out those specific features of these phenomena which depend on the interaction between mercury and adsorbed molecules.

## ADSORPTION OF SATURATED ALIPHATIC COMPOUNDS

Let us consider first the simplest surface-active substances, the saturated aliphatic compounds with one polar group. In recent years the behaviour of these substances at both interfaces has been studied in detail by Kaganovich and Gerovich<sup>1, 2</sup>. In *Figures 1-3* the plots of the decrease in the interfacial tension versus the logarithm of concentration are given for acids



*Figure 1.* Isotherms of the decrease in surface tension for alcohols. Curves 1-4 refer to propyl, butyl, pentyl, hexyl alcohols respectively at the uncharged mercury-solution interface. Curves 1'-4' refer to the same alcohols (respectively) on the free surface of the solution. Supporting electrolyte:  $n \text{ Na}_2\text{SO}_4$  (Kaganovich and Gerovich<sup>2</sup>).

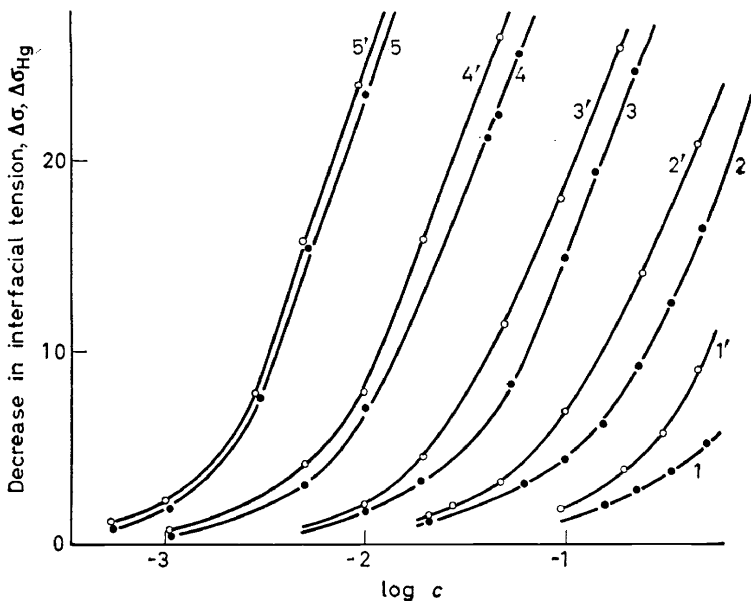


Figure 2. Isotherms of the decrease in surface tension for acids. Curves 1-5 refer to acetic, propionic, butyric, valeric, caproic acids respectively at the uncharged mercury-solution interface. Curves 1'-5' refer to the same acids (respectively) on the free surface of the solution. Supporting electrolyte:  $n \text{ Na}_2\text{SO}_4$  (Kaganovich, Gerovich and Osotova<sup>1</sup>).

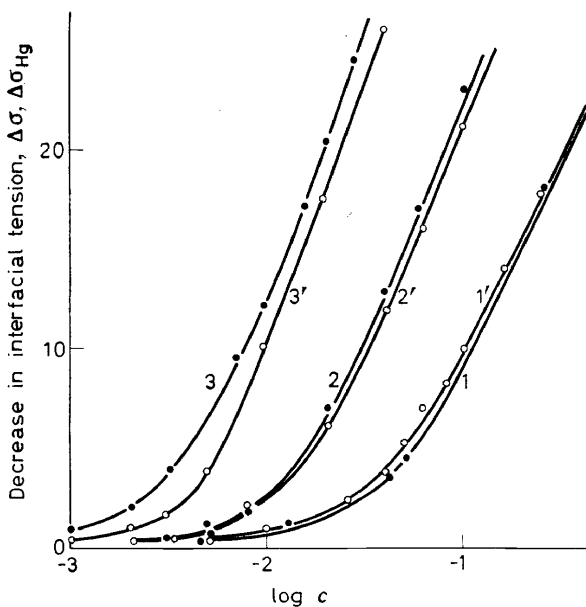


Figure 3. Isotherms of the decrease in the surface tension for amines. Curves 1-3 refer to propylamine, butylamine, pentylamine respectively on the uncharged mercury-solution interface. Curves 1'-3' refer to the same amines (respectively) on the free surface of the solution. Supporting electrolyte:  $n \text{ Na}_2\text{SO}_4$  (Kaganovich and Gerovich<sup>2</sup>).

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(C<sub>2</sub>-C<sub>6</sub>), alcohols (C<sub>3</sub>-C<sub>6</sub>) and amines (C<sub>3</sub>-C<sub>5</sub>) of the fatty series. The data for the mercury-solution interface were obtained from the lowering of the maximum of the electrocapillary curve and thus refer to an uncharged interface. All the solutions contained normal Na<sub>2</sub>SO<sub>4</sub> as supporting electrolyte. It is evident that the adsorption behaviour at the two interfaces do not differ to any great extent. Thus, just as for the adsorption at the interface with air, the Traube rule holds in the case of adsorption on mercury. The mean values of the coefficients for both interfaces are given in *Table 1*. The coefficients have been calculated for the decrease in the surface tension  $\Delta\sigma$ ,  $\Delta\sigma_{\text{Hg}} = 3 (\Delta\sigma \text{ refers to the solution-air, } \Delta\sigma_{\text{Hg}} \text{ to the solution-Hg interface})$ .

It is clear from *Table 1* that with increasing chain length the surface activity at the interface with mercury increases somewhat faster than at the interface with air. It also increases somewhat more rapidly with increasing concentration of the surface-active substance. This appears to be due to

*Table 1.* Mean values of the coefficients for solution-air and solution-mercury interfaces

Functional group	Coefficient of the Traube rule	
	Solution-air	Solution-Hg
-CH <sub>2</sub> OH	2.8	3.0
-COOH	3.5	3.7
-CH <sub>2</sub> NH <sub>2</sub>	2.8	3.5

stronger attraction between the oriented hydrocarbon chains in the case of adsorption on mercury. A probable reason of this will be given later. Generally speaking, the surface activity at the interface with mercury is somewhat lower than at the interface with air, especially so in the case of alcohols, the reverse relationships being true for amylamine and partly for butylamine. These differences can be explained only by assuming that in spite of the polar group facing the solution and hence being at a distance from the mercury surface, its nature still has some effect upon the change in the work of adsorption when passing from the free surface of the solution to the interface with mercury. The adsorptions, calculated by means of Gibbs equation for both interfaces, are near in their values, as was shown in great detail for ethyl alcohol solutions<sup>3</sup>. The minimal area (estimated using the approximate Gibbs equation) for acids with C<sub>3</sub>-C<sub>6</sub> is 29 Å in the case of the interface with mercury and 29.5 Å for the free surface<sup>1</sup>.

On the whole, in spite of the small differences mentioned, the data obtained on measuring the decrease in the surface tension show the adsorption phenomena to be similar in both cases. But, as will be pointed out later, this similarity is, to some degree, of a casual nature. If a different experimental method is used, namely the determination of the adsorption potential shift, differences become apparent. The adsorption potential shift at the solution-air interface can be determined, for instance, by direct measurements using Kenrick's method<sup>4, 5</sup>, and that at the interface with mercury, from the shift in the point of zero charge. This, in its turn, can be determined from

the position of the maximum on the electrocapillary curve in the presence of the surface-active substance or, in many cases preferably, from the position of the minimum on the differential capacity–potential curve in dilute electrolyte solutions corresponding to the most diffuse structure of the double layer (Figure 4)<sup>6</sup>. The adsorption potential shifts at both interfaces were compared

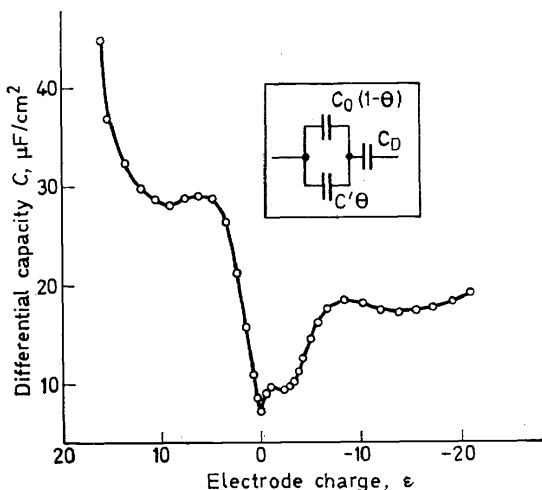


Figure 4. Dependence of the differential capacity upon the electrode charge in  $2 \times 10^{-3}N$  NaF + 0.2 M  $n$ -C<sub>3</sub>H<sub>7</sub>OH solution. Inset: equivalent scheme of the double layer in dilute electrolyte solution in the presence of an organic substance (Frumkin, Damaskin and Survila<sup>6</sup>).

by one of the authors<sup>7</sup> several years ago but at that time the concentration dependence for both interfaces had not yet been investigated and, as a result, some important facts had been left out of account. Figures 5 and 6 show the dependences of the adsorption potential shift  $\Delta\phi_{\epsilon=0}$  upon the adsorbed amount for butylamine<sup>2</sup> and propyl alcohol<sup>6</sup>. It is clear from these figures that whereas the dependence of  $\Delta\phi_{\epsilon=0}$  upon the amount adsorbed  $\Gamma$  to the first approximation is linear at the interface with air, at the interface with mercury the adsorption potential shift is small at small coverages and becomes appreciable only when the coverage is nearly complete. The last result directly follows from the relation for the dependence of the electrode surface charge upon the coverage  $\theta$ :

$$\epsilon = \epsilon_0(1 - \theta) + \epsilon'\theta \quad (1)$$

where  $\epsilon_0$  and  $\epsilon'$  are the surface charges at the coverages  $\theta = 0$  and  $\theta = 1$ , respectively. In deriving Eq. (1), the covered and the uncovered parts of the surface are considered as two capacitors connected in parallel. This assumption is justified if the condition of equipotentiality is fulfilled both on the metal surface and at the interface between the dense part of the double layer and the bulk of the solution<sup>8</sup>. In the case of the metal surface this condition is trivial. In the case of the interface between the dense layer and the bulk of the solution the condition of equipotentiality is fulfilled approxi-

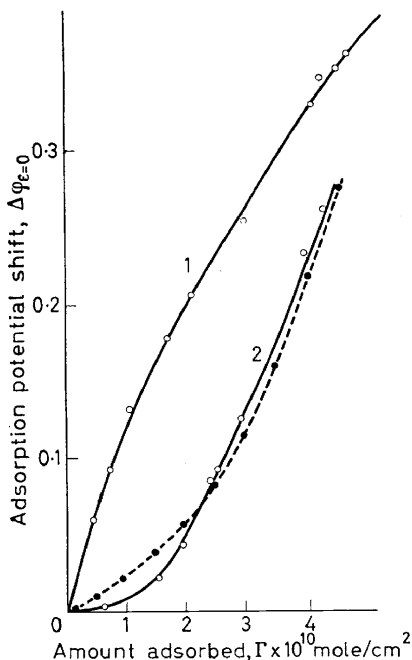


Figure 5. Dependence of the adsorption potentials upon the adsorption of butylamine: 1, solution-air interface; 2, solution-mercury interface; the broken curve has been calculated by means of Eq. (2) with  $\varphi_N = 0.4$  V,  $\Gamma_M = 5 \times 10^{-10}$  mole/cm<sup>2</sup>,  $C_0/C' = 4$  (Kaganovich and Gerovich<sup>2</sup>).

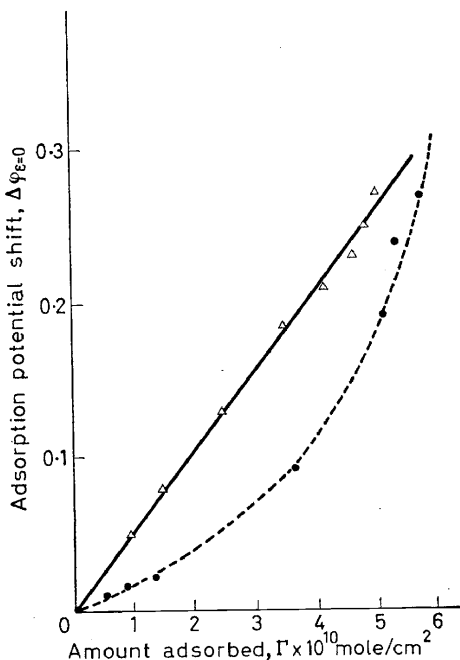


Figure 6. Dependence of the adsorption potentials upon the adsorption of *n*-propyl alcohol:  $\Delta$ , solution-air interface;  $\bullet$ , mercury-solution interface (the values of  $\varphi_{\epsilon=0}$  have been obtained from the position of the minimum on the  $C$  vs.  $\varphi$  curves in dilute NaF solutions). The broken curve is calculated by means of Eq. (2) with  $\varphi_N = 0.31$  V,  $\Gamma_M = 6 \times 10^{-10}$  mole/cm<sup>2</sup>,  $C_0/C' = 3.5$  (Frumkin, Damaskin and Survila<sup>6</sup>).

mately owing to the high value of the dielectric constant of water<sup>9</sup>. If as a first rough approximation, the capacities of the uncovered and covered parts of the surface  $C_0$  and  $C'$  are considered as constant, an expression for the adsorption potential shift (Eq. 2) can be readily obtained with the help of Eq. (1)

$$\phi_{\epsilon=0} = \phi_N \theta / \left[ \frac{C_0}{C'} (1 - \theta) + \theta \right] \quad (2)$$

where  $\phi_N$  is the value of  $\phi_{\epsilon=0}$  at  $\theta = 1$ , referred to  $\phi_{\epsilon=0}$  at  $\theta = 0$ .

In the case of the free solution surface, one of the equipotential surfaces, the metal surface, is absent and Eq. (2) is inapplicable. Here, to the same approximation, the dipole effects of the adsorbed molecules are additive and in place of Eq. (2), the following relation should be written

$$\phi_{\epsilon=0} = \phi_N \theta \quad (3)$$

Since for aliphatic alcohols, acids and amines with one polar group  $C_0/C'$  is

large (of the order of 4–5), the dependence of  $\phi_{\epsilon=0}$  upon  $\theta$ , i.e. upon adsorption, is essentially different in both cases, as is clear from *Figures 5* and *6*†.

The dashed curves in *Figures 5* and *6* have been calculated by means of Eq. (2). In the first place, the result obtained is of importance in that it confirms the correctness of Eq. (1) in the case of adsorption of aliphatic compounds. Without going into details it should be pointed out that Eq. (1) can be used as a basis for the quantitative theory of adsorption of saturated aliphatic compounds at the mercury–electrolyte interface, depending on the potential and concentration<sup>10, 11</sup>. For the development of this theory, however, it is necessary, in addition to using the conclusions from Gibbs thermodynamics of surface phenomena, to make an assumption regarding the nature of the adsorption isotherm. In the papers quoted above the isotherm suggested by Frumkin<sup>12</sup> was used, which is Langmuir's isotherm corrected for the interaction between the adsorbed molecules.

$$Bc = \frac{\theta}{1 - \theta} \exp(-2a\theta) \quad (4)$$

A positive value of  $a$  indicates the presence of attraction between the molecules of the surface-active substance. Equation (4) determines the dependence of adsorption upon the concentration of the surface-active substance. Of principal importance for the solution of the problem posed is the determination of the dependence of  $B$  upon the potential. The thermodynamic consideration leads to the conclusion that

$$B = B_0 \exp \left[ \frac{-\Delta\sigma_e + C' \phi (\phi_N - \phi/2)}{RT\Gamma_M} \right] \quad (5)$$

where  $\Delta\sigma_e$  is the decrease in the interfacial tension due to the electric field in the absence of the adsorption of the organic substance,  $\phi$  the electrode potential read from the point of zero charge at  $\theta = 0$ ,  $\phi_N$  the value of  $\phi_{\epsilon=0}$  at  $\theta = 1$ ,  $B_0$  the value of  $B$  at  $\phi = 0$  and  $\Gamma_M$  the maximal adsorption. The dependence of adsorption upon the potential and concentration calculated on the basis of this theory can be compared with that found experimentally. However, since the adsorption of the organic substance on the mercury electrode surface is to be calculated from the interfacial tension values by means of Gibbs equation, such verification of the theory is very rough. A much more rigorous verification can be made using the differential capacity measurements. By differentiating Eq. (1), we find

$$C = C_0(1 - \theta) + C'\theta + (\epsilon' - \epsilon_0) \partial\theta/\partial\phi \quad (6)$$

where  $C$ ,  $C_0$  and  $C'$  are differential capacities of the electrode at the coverages  $\theta$ , 0 and 1, respectively. The presence of the term  $(\epsilon' - \epsilon_0) \partial\theta/\partial\phi$  leads to the appearance on the  $C$  vs.  $\phi$  curve of two pronounced maxima (peaks) in the region of  $\phi$  where the coverage changes sharply with the potential

† The decrease in  $\Delta\phi_{\epsilon=0}$  should result in that of the repulsion between the polar groups of the adsorbed particles, which leads to an increase of the effective attraction constant (see above) in passing from the solution–air interface to the interface with mercury.

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(Figure 7). These adsorption-desorption peaks were first detected by Proskurnin and Frumkin<sup>14†</sup>. There is no doubt that a theory that can quantitatively describe a family of curves of such a complex shape as the  $C$  vs.  $\phi$  curves shown in Figure 7, can be considered as being thoroughly verified. The theoretical curves calculated on the basis of the concepts outlined

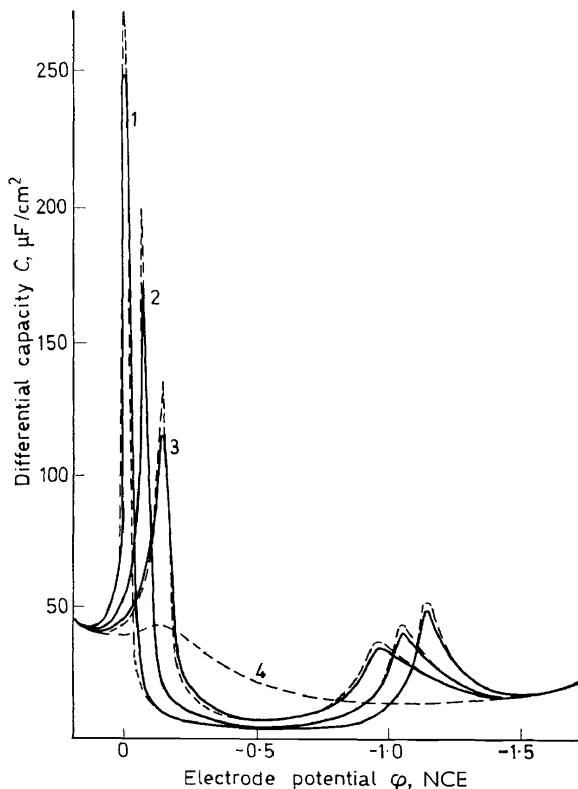


Figure 7. Differential capacity of mercury in  $N$   $\text{Na}_2\text{SO}_4$  solutions with  $n\text{-C}_5\text{H}_{11}\text{OH}$  additions: (1)  $4 \times 10^{-2}$  M; (2)  $2 \times 10^{-2}$  M; (3)  $1 \times 10^{-2}$  M. Solid curves calculated by means of Eq. (7); broken curves, experimental data in corresponding solutions; frequency 450 c/s; (4) ( $C$  in pure  $N$   $\text{Na}_2\text{SO}_4$ . Electrode potential referred to NCE (Lerch and Damaskin<sup>13</sup>).

above are given in Figure 7 by dashed lines. The agreement between theory and experiment can be seen to be excellent. But in order to obtain such agreement, it was necessary to make an additional assumption, viz., as shown by Damaskin<sup>16</sup>, the quantity  $a$  in Eq. (4) is not a constant, but to a degree depends linearly upon  $\phi$ :

$$a = a_0 + \beta\phi \quad (7)$$

Such dependence can arise as the result of introducing a correction taking

† Unfortunately, in polarographic literature these maxima are often referred to as "ten-symmetric peaks", which is unreasonable, since at the potential corresponding to the peak on the  $C$  vs.  $\phi$  curve, the curve of the dependence of the interfacial tension  $\sigma_{\text{Hg}}$  upon  $\phi$  shows neither a maximum nor a break, but only a certain change in direction<sup>15</sup>.

account of the fact that the condition of equipotentiality of the solution layer adjoining the dense part of the double layer is not quite rigorously fulfilled<sup>17</sup>.

The mathematical relation used in calculating the theoretical curves is of the form:

$$C = C_0(1 - \theta) + C' \theta + \frac{[\epsilon_0 + C'(\phi_N - \phi) + RT \Gamma_M \beta(1 - 2\theta)]^2 h}{RT \Gamma_M} \quad (8)$$

$$\text{where } h = \frac{\theta(1 - \theta)}{1 - 2a\theta(1 - \theta)} \quad (9)$$

Eq. (8), but without the term with  $\beta$ , was first obtained by Hansen, Minturn and Hickson<sup>18</sup>. Thus, the comparison of the behaviour of aliphatic compounds at the solution-air and the solution-mercury interfaces helps to consolidate the general theory of adsorption of aliphatic compounds at the latter.

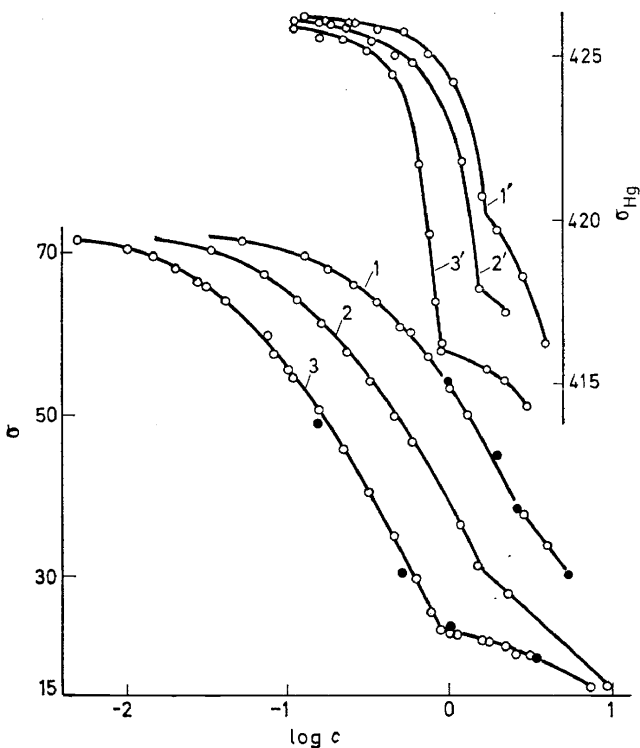
However, by confining ourselves to the comparison of this behaviour only in the case of the simplest saturated compounds with one polar group, we would be in danger of leaving out of account many important features of these phenomena. The compounds considered by us so far are oriented at both interfaces with the polar group turned towards water and the hydrocarbon chain towards mercury or air, respectively. Judging by the minimal value of the area  $S_\infty = 29 \text{ \AA}^2$ , this orientation is not perfect, but it should be the better defined, the larger the coverage. As has been already mentioned, in the case of alcohols and acids with  $C_4-C_6$  at large coverages the adsorptivity changes little when passing from the interface with air to that with mercury (*Figures 1 and 2*). In interpreting this result, it is necessary to bear in mind that the adsorption from solutions involves the displacement of solvent molecules from the interface. The importance of this fact for the understanding of the adsorption at the mercury-electrolyte interface was emphasized by Bockris, Devanathan and Müller<sup>19</sup>. Thus, if the adsorptivity of the compounds in question practically does not change when passing from the interface with air to that with mercury, this means that the gain in free energy on contact of mercury with the hydrocarbon tails of organic molecules, probably in the first place with methyl groups, is approximately compensated by the consumption of the free energy necessary for the removal of water molecules displaced by the methyl groups from the interface. In other words, in both cases, the adsorption is mainly due to the expulsion of the hydrocarbon chain from the bulk of the solution. Such compensation, however, cannot be general. This is evident, for instance, from the consideration of the aliphatic compounds with a flat orientation at the interface. The flat orientation is to be expected in the case of hydrocarbons without polar groups, at any rate at small surface coverages. The surface activity of saturated hydrocarbons at both interfaces has been recently investigated at our laboratory<sup>20</sup>. Although, on account of low solubility and volatility of hydrocarbons, the data obtained are not very accurate, they clearly indicate that there is a large decrease in adsorptivity when passing to the interface with mercury. Thus, when 0.1 N CsCl is saturated with hexane, the decrease in  $\sigma$  at the interface with air is 5.0 dyne/cm and at the interface with the uncharged mercury surface, only  $0.7 \pm 0.2$  dyne/cm, i.e. seven times as little.

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The displacement of the water molecules from the mercury surface by the methylene groups of the hydrocarbon chain, which is inevitable in the case of flat orientation of the adsorbed molecule, leads to a decrease in the free energy gain when the hydrocarbon molecule is transferred from the bulk of the solution to the surface. This phenomenon is also observed in the case of the adsorption of perfluorinated compounds described in the next section.

### ADSORPTION OF HALOGENATED AND SULPHUR COMPOUNDS

Like the saturated aliphatic compounds, the perfluorinated compounds are known to display a high surface activity at the solution-air interface<sup>21</sup>,



*Figure 8.* Dependence of  $\Delta\sigma$  and  $\Delta\sigma_{\text{Hg}}$  upon the concentration  $c$  (mole/litre) of perfluorinated fatty acids. Interface with air (curves 1, 2, 3); with mercury (curves 1', 2', 3'). Curves: 1,1'  $\text{CF}_3\text{COOH}$ ; 2,2'  $\text{C}_2\text{F}_5\text{COOH}$ ; 3,3'  $\text{C}_3\text{F}_7\text{COOH}$  (Frumkin, Kusnezov and Kaganovich<sup>22</sup>). Black dots according to H. Klevens and J. Davies<sup>20</sup>. Inflexions on the curves are due to the formation of micelles.

but are only slightly active at the interface with mercury (*Figure 8*)<sup>22</sup>. At  $\Delta\sigma = \Delta\sigma_{\text{Hg}} = 1.4$  dyne/cm, the surface activity of trifluoroacetic acid is 15 and that of perfluorobutyric acid 56 times as large at the interface with air as at that with mercury. Thus, the gain in free energy in the case of wetting of mercury with the  $-\text{CF}_3$  and  $-\text{CF}_2-$  groups is much smaller than upon wetting with water.

A sharp decrease in adsorptivity when passing from the free surface of the solution to the interface with mercury was observed for the first time in the case of perfluorinated compounds. On the contrary, the cases when an increase in adsorptivity was observed accompanying this transition are very numerous, have been known for a long time and were considered in a review by one of the authors published in *Colloid Symposium Annual*<sup>7</sup>. Apparently, there are hardly any important new experimental data available on this kind of behaviour in the case of aliphatic compounds and therefore we shall not discuss this problem in detail. It should only be mentioned that an increase in the adsorptivity of saturated aliphatic compounds is observed in the case of compounds with a large number of oxygen-containing polar groups, bromo- and iodo-substituted compounds, as well as thiocompounds. Thus, at molar concentration  $\Delta\sigma$  for glycerol is 0.4 and  $\Delta\sigma_{\text{Hg}}$  9.3, for saccharose 2.0 and 23.8, respectively. The most likely hypothesis is that the adsorbed molecules of these compounds lie flat at the interface, so that their polar groups come into direct contact with the metal. Another circumstance points in favour of the flat orientation, viz., that unlike the compounds with one polar group, the positive values of  $\Delta\sigma_{\epsilon=0}$  due to the C—O bond being oriented with carbon turned towards mercury, fall almost to zero and in some cases (e.g. malonic acid) even change their sign. This change is probably due to hydrogen in the O—H bond being turned towards the solution<sup>†</sup>. The increase in the surface activity in the case of bromo and iodo substituted compounds involves larger adsorption potential shifts. Thus for  $\beta$ -iodopropionic acid in 0.3 M solution  $\Delta\phi_{\epsilon=0}$  at the interface with mercury is  $-0.32$  V, whereas at the interface with air the potential shift at the same concentration is only  $-0.13$  V, with a limiting value  $-0.15$  V<sup>24</sup>. This points to the existence of interaction between Br or I atoms and mercury involving the formation of covalent bonds, which, however, in a definite potential range does not lead to the rupture of the C—Hg bond. Similar phenomena are observed in the case of adsorption at the interface with mercury of compounds containing bivalent sulphur<sup>7, 25</sup>.

The behaviour of thiourea, which at the interface with air causes a slight increase of surface tension and at the interface with mercury at molar concentration<sup>7</sup> lowers it by 39.7 units, has attracted lately the interest of many investigators<sup>11, 26, 27</sup>. In case of chlorosubstituted compounds, the increase in adsorptivity when passing to the interface with mercury is quite small, whereas in the case of fluoro derivatives, as discussed above, the water displacement from the mercury surface becomes energetically disadvantageous. Thus, in order to characterize the changes in the adsorptivity when passing from the solution-air interface to that with mercury in the case of saturated aliphatic compounds it is necessary to know in the first place the ratio of the gain in free energy due to the contact with mercury in the case of an uncovered surface of water to that in the case of the surface covered with adsorbed molecules. Since when comparing the standard free energies at both interfaces it is necessary to take into consideration the number of water molecules displaced by the organic molecule from the inter-

<sup>†</sup> Recently small negative values of the adsorption shift of the potential in the case of compounds with two polar groups (maleic and fumaric acids) have been observed also at the air-solution interface<sup>23</sup>.

face during the process of adsorption, the adsorptivity ratio could be expected to differ somewhat depending on the coverage and hence on the concentration of the solution. Indeed, the orientation of adsorbed molecules in the surface layer and, hence, the number of water molecules displaced by one adsorbed molecule should change with the coverage. However, in the case of aliphatic compounds considered by us, the changes in orientation have little effect upon the adsorption behaviour and to the first approximation can, apparently, be neglected. This is not the case with aromatic compounds.

### ADSORPTION OF AROMATIC COMPOUNDS

The main difference in the adsorption behaviour of aromatic compounds at the interface with mercury compared to that at the interface with air is determined by the interaction of the  $\pi$ -electrons with the metal surface, which is especially apparent when the latter is positively charged<sup>†</sup>. The role of the  $\pi$ -electronic interaction was first recognized by Gerovich<sup>28</sup> at

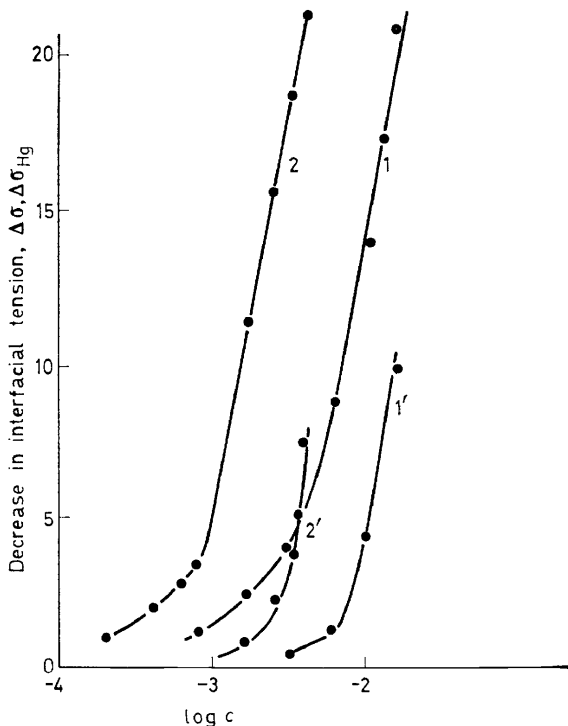


Figure 9. Dependence of  $\Delta\sigma$  and  $\Delta\sigma_{\text{Hg}}$  upon the concentration of benzene and toluene. Interface with mercury (curves 1, 2); with air (curves 1', 2'). Curves: 1,1' benzene; 2,2' toluene. Supporting electrolyte: 0.1 N  $\text{Na}_2\text{SO}_4$  (Kaganovich, Gerovich and Gusakova<sup>20</sup>).

<sup>†</sup> The  $\pi$ -electronic interaction is observed also in the case of the adsorption of unsaturated aliphatic compounds, especially when there are several double bonds in the molecule<sup>28</sup>. But the relevant experimental data are scarce as yet and we shall not discuss them here.

our laboratory. This problem was investigated further by Blomgren and Bockris<sup>29</sup>, Conway<sup>30</sup>, and Frumkin and Kaganovich<sup>31</sup>. As a simple example let us take benzene. The value of  $\Delta\sigma$  for 0.1 N Na<sub>2</sub>SO<sub>4</sub> saturated with benzene at 25° is 10 dyne/cm, whereas  $\Delta\sigma_{\text{Hg}}$  is 22 dyne/cm<sup>20</sup>. As follows from *Figure 9*, the difference in adsorptivity increases with the dilution, i.e. the effect of the  $\pi$ -electronic interaction is more apparent in more dilute solutions. This can be explained by the fact that in dilute solutions the benzene molecules lie flat on the interface with mercury, whereas with increasing concentration they assume an oblique position. This is in agreement with the value of the limiting area per benzene molecule (35 Å<sup>2</sup>) and the shape of the differential capacity-potential curves<sup>32</sup>. Such an increase in adsorptivity is observed also in the case of a number of benzene derivatives<sup>7</sup>. Thus, at 0.1 M concentration the relevant  $\Delta\sigma$  figures for phenol, pyrocatechol, hydroquinone and resorcinol are 11.6, 3.0, 1.1 and 2.1, respectively, whereas the values of  $\Delta\sigma_{\text{Hg}}$  are 36.6, 29.7, 28.0 and 29.7. This effect is especially pronounced in the case of aniline, for which  $\Delta\sigma$  in 0.01 M solution is 0.3 and  $\Delta\sigma_{\text{Hg}}$  17.40; in 0.1 M solution the corresponding values are 10.0 and 47.0, respectively. The increase in adsorptivity cannot, however, be completely attributed to the  $\pi$ -electronic interaction, the interaction of mercury with the polar group, which is facilitated by a more flat orientation of the molecule, being also of essential importance. This is evident, in particular, from the fact that in some cases the introduction of the polar group into the benzen molecule, while decreasing, as would be expected,  $\Delta\sigma$ , does not lower but even somewhat raises  $\Delta\sigma_{\text{Hg}}$ . Thus for 0.01 M benzene  $\Delta\sigma$  and  $\Delta\sigma_{\text{Hg}}$  are equal to 4.2 and 13.9 dyne/cm, respectively, whereas for aniline, as previously indicated, they are equal to 0.3 and 17.4†.

A more flat orientation of adsorbed molecules of aromatic compounds at the interface with mercury has some other consequences. Thus, marked differences in the adsorption behaviour of *p*- and *o*-dioxibenzenes<sup>33</sup> at the interface with air, at which the orientation of the hydroquinone molecules is more nearly flat than that of pyrocatechol, are to a considerable extent eliminated when passing to the interface with mercury.

### Adsorption of phenols

The adsorption of phenols leads to a large shift in the point of zero charge in the direction of more negative potentials. Thus, in 0.1 M hydroquinone solution  $\Delta\phi_{\epsilon=0} = -0.20$ . This shift seems to be partly dependent on the orientation of the O—H bond with hydrogen turned towards the solution, the C—O bond lying parallel to the interface, and partly on the  $\pi$ -electrons of the ring being drawn off in the direction of mercury. At present it does not seem possible to determine the relative importance of these two factors. The importance of the orientation of the polar group is also evidenced by the experimentally observed dependence of  $\Delta\phi_{\epsilon=0}$  upon the adsorbed amount

† The possibility for the polar group to interact with mercury due to a more flat orientation of the adsorbed molecule leads to an increase in adsorptivity when passing to the interface with mercury also in the case of saturated alicyclic compounds<sup>31</sup>, although to a lesser extent than for aromatic ones. Thus, for 0.1 M cyclohexylamine solution  $\Delta\sigma = 23.6$ ,  $\Delta\sigma_{\text{Hg}} = 43.7$ . However, whereas aromatic compounds remain in the adsorbed state even if the mercury surface is positively charged, saturated alicyclic compounds, just as the compounds of the fatty series, are completely desorbed under these conditions.

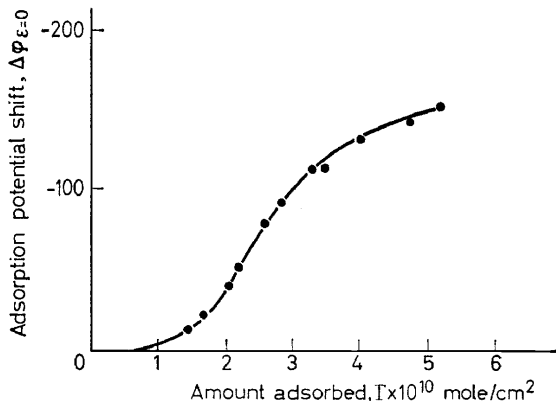


Figure 10. Dependence of  $\Delta\phi_{\epsilon=0}$  upon the adsorption of phenol at the mercury-solution interface. Supporting electrolyte  $N Na_2SO_4$  (Kaganovich, Gerovich and Gusakova<sup>20</sup>).

in the case of phenol (Figure 10). Whereas at small coverages, the absolute value of  $\Delta\phi_{\epsilon=0}$ , just as in the case of aliphatic alcohols, rises faster than  $\Gamma$ , at large coverages, where the flat orientation of the phenol molecule is disturbed, the increase in  $|\Delta\phi_{\epsilon=0}|$  slows down. In other words, the negative shift in the potential of zero charge per one adsorbed molecule decreases. Blomgren, Bockris and Jesh<sup>29</sup> also arrive at the conclusion about the flat orientation of the aromatic radicals (phenyl and naphthyl radicals).

### Adsorption of aniline

The examination of the electrocapillary curves of some aromatic compounds, aniline, in particular, has already shown that the orientation of adsorbed molecules can vary with the potential<sup>7</sup>. These phenomena have an especially marked effect upon the  $C$  vs.  $\phi$  curves. In Figure 11 is given the  $C$  vs  $\phi$  curve of 0.1 M aniline solution with KCl as supporting electrolyte<sup>34</sup>. The curve shows two peaks and at the first glance is similar to the curves of saturated aliphatic compounds. A more detailed examination leads, however, to different conclusions. The cathodic peak actually proves to be the adsorption-desorption peak, limiting the adsorption region of aniline. However, when passing to more positive potentials than that of the anodic peak, aniline is not desorbed, as is evident from the comparison of the electrocapillary curves of the aniline solution and the supporting electrolyte (Figure 12). Adsorbed aniline molecules only change their orientation at the interface from a somewhat oblique to a completely flat one. As is clear from Figure 11, in the case of such flat orientation, aniline has no effect upon the differential capacity. In other words, the drawing off of the  $\pi$ -electrons towards the metal surface results in positive charges appearing at the aniline-solution interface replacing the metal surface charges in the electric double layer. In a certain potential range the change in the orientation of adsorbed aniline molecules can occur at a constant potential as well, depending on the aniline concentration. This results in the adsorption isotherms having an abnormal shape (Figure 13). In this potential range, the rising concentration

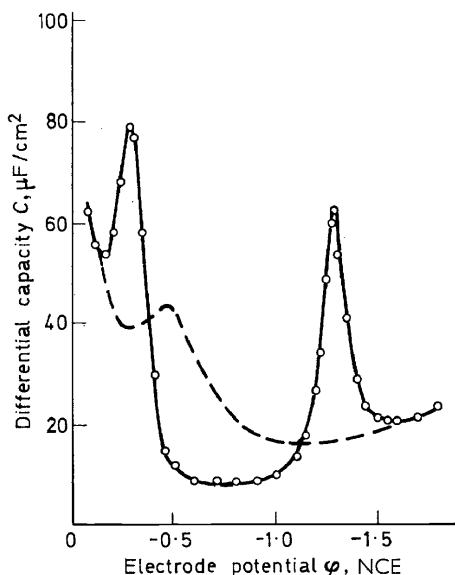


Figure 11. Dependence of the differential capacity  $C$  upon the potential for mercury in  $0.1 \text{ M C}_6\text{H}_5\text{NH}_2 + \text{N KCl}$ . The broken curve is for mercury in  $\text{N KCl}$ . Potentials referred to NCE (Damaskin *et al.*<sup>34</sup>).

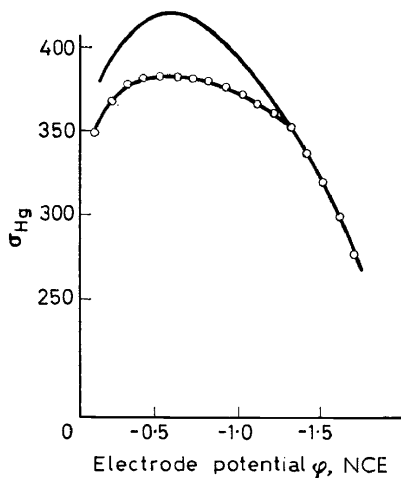


Figure 12. Electrocapillary curves of the solutions:  $\text{N KCl}$  (top curve) and  $\text{N KCl} + 0.1 \text{ M C}_6\text{H}_5\text{NH}_2$  (bottom curve).  $\phi$  referred to NCE (Damaskin, *et al.*<sup>34</sup>).

at first leads to a limiting surface coverage with aniline molecules, corresponding to their flat orientation, which is followed by a further increase in adsorption due to the orientation of the aniline molecules approaching the vertical position. Thus, the anodic peak on the  $C$  vs.  $\phi$  curve in Figure 11 is a reorientation peak. These differ from the adsorption-desorption peaks also in their frequency dependence. The decrease of the height of these

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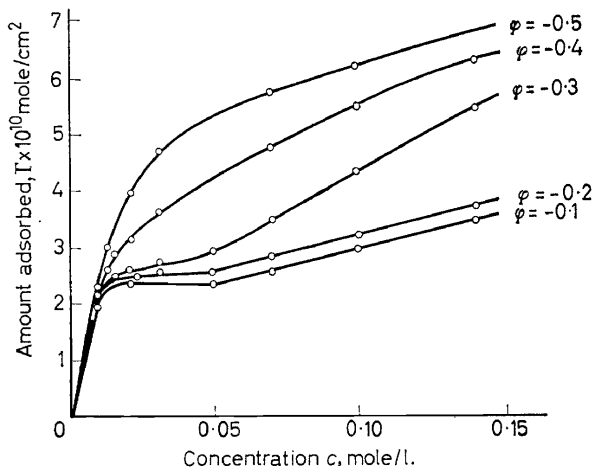


Figure 13. Dependence of adsorption upon the concentration of aniline in the presence of KCl at different  $\varphi$  (NCE).

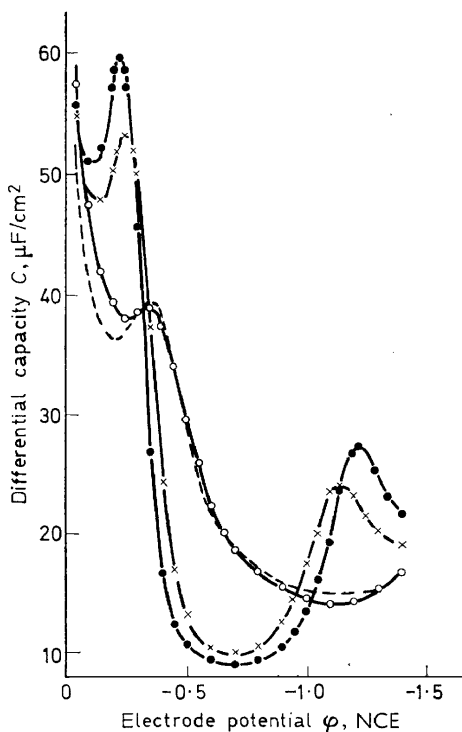
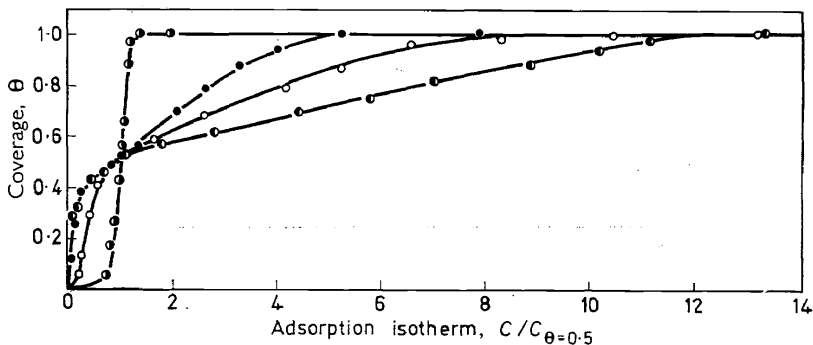


Figure 14. Dependence of the differential capacity  $C$  upon the potential for mercury in  $C_6H_5NH_2 + HCl$  solutions. (—) 0.1 N HCl; (○—○), 0.1 N HCl + 0.1 M  $C_6H_5NH_2$ ; (×—×) 0.06 N HCl + 0.1 M  $C_6H_5NH_2$ ; (●—●) 0.04 N HCl + 0.1 M  $C_6H_5NH_2$  (Dyatkina and Damaskin<sup>35</sup>).

peaks with rising a.c. frequency occurs much more slowly than the decrease of the height of adsorption-desorption peaks<sup>44</sup>. In the case of the protonated  $C_6H_5NH_3^+$  molecule, the flat orientation is observed over a wider potential range. As follows from *Figure 14*, the  $C$  vs.  $\phi$  curve in  $0.1 \text{ M } C_6H_5NH_2 + 0.1 \text{ N HCl}$  almost coincides with that in  $0.1 \text{ N HCl}$ <sup>35</sup>. Although the adsorptivity of the  $C_6H_5NH_3^+$  ions is much smaller than that of the  $C_6H_5NH_2$  mole-



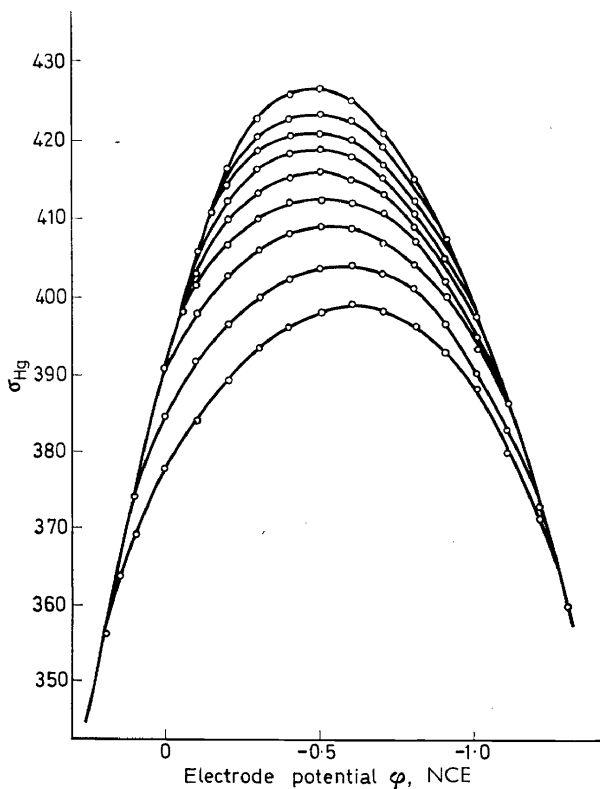
*Figure 15.* Adsorption isotherms of 2,4-lutidine. Abscissa: the ratio of  $C$  to the value of  $C$  at which  $\theta = 0.5$ . Potentials referred to Ag, AgCl, saturated KCl electrode. (●) 0.3 V; (○) 0.5 V, (◐) 0.8 V, (◑) 1.1 V (Nürnberg and Wolff<sup>38</sup>).

cules, the disappearance of the effect of the capacity decrease cannot be attributed to the small coverage as  $\Delta\sigma_{Hg}$  in acid solution of the concentration indicated is as much as 7 dyne/cm. The flatly oriented  $C_6H_5NH_3^+$  molecules have almost as little effect upon the electric double layer as a thin layer of a metallic conductor. In the solutions containing an excess of  $C_6H_5NH_2$  compared to HCl, the specific features of the  $C$  vs.  $\phi$  curve of aniline become apparent. The electrocapillary measurements carried out by Gerovich and Polianovskaya<sup>28</sup>, Blomgren and Bockris<sup>29</sup>, and Conway and Barradas<sup>30</sup> also lead to the conclusion that the dependence of the surface charge upon the coverage of the surface with the aniline ions is small.

The orientation of the molecules of aromatic compounds at the interface has a determining influence upon the interaction between them and, hence, upon the shape of the adsorption isotherm. The flatly oriented molecules repel one another, but as their position becomes oblique, a van der Waals attraction between adsorbed molecules may come into play alongside with the repulsion of the parallel orientated dipoles, the van der Waals attraction prevailing at sufficiently negative potentials as the orientation of the molecules approaches the vertical position. The quantitative picture of these phenomena is determined by the ratio of the dipole effect and the van der Waals attraction and differs for different aromatic compounds. The change in the shape of the adsorption isotherm is particularly pronounced in the case of pyridine and its derivatives<sup>36, 37, 38</sup>. In *Figure 15* are given the adsorption isotherms for 2,4-lutidine measured at different potentials according to Nürnberg and Wolff<sup>38</sup>, which clearly show the transition from the repulsive to the attractive interaction. Unfortunately, there are not enough data available as yet on the adsorption behaviour of this group of compounds at the interface with air.

**Adsorption of perfluorinated aromatic compounds**

Recently at our laboratory has been investigated the adsorption behaviour of some perfluorinated aromatic compounds: perfluoroaniline, perfluorophenol and perfluorobenzoic acid<sup>39, 40</sup>. The drawing off of the  $\pi$ -electrons by fluorine atoms leads to a sharp decrease in the  $\pi$ -electronic interaction of the adsorbed molecules with mercury, resulting, in particular, in the complete disappearance of adsorption on the positively charged surface, which is so characteristic of aromatic compounds (*Figure 16*). However, the flat orientation of adsorbed molecules, due to which the dipole bond C—F



*Figure 16.* Electrocapillary curves of 0.1 N  $\text{Na}_2\text{SO}_4 + \text{C}_6\text{F}_5\text{OH}$  solutions. The concentrations of  $\text{C}_6\text{F}_5\text{OH}$  from top to bottom:  $0$ ,  $1.13 \times 10^{-3}$ ,  $2.26 \times 10^{-3}$ ,  $4.53 \times 10^{-3}$ ,  $9.06 \times 10^{-3}$ ,  $1.181 \times 10^{-2}$ ,  $3.62 \times 10^{-2}$ ,  $7.25 \times 10^{-2}$  and 0.145 M (Damaskin *et al.*<sup>40</sup>).

comes into contact with mercury, leads to some differences in the adsorption behaviour of perfluorinated aromatic compounds compared to perfluorinated compounds of the fatty series. Thus, although the increase in adsorptivity when passing from aniline to perfluoroaniline is much less than at the interface with air, this transition involves an increase in adsorptivity and not a decrease, as was the case, for instance, upon the transition from *n* butyric to perfluorobutyric acid<sup>22</sup>.

Since in the case of adsorption of perfluorinated aniline and phenol at the

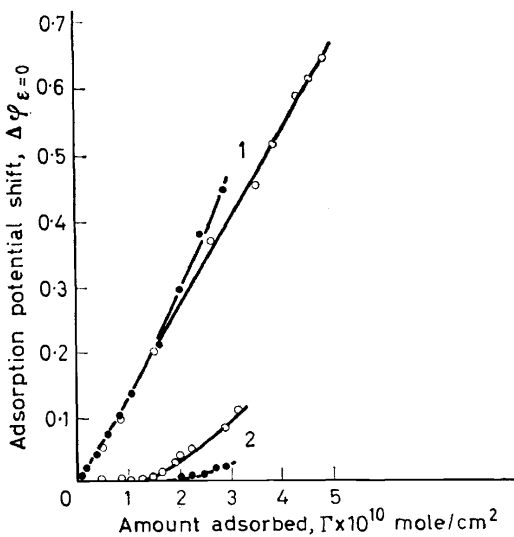


Figure 17. Dependence of the adsorption potential upon the adsorption of pentafluorophenol (○—○) and pentafluoroaniline (●—●). Curves: 1, air-solution interface; 2, mercury-solution interface (B. Damaskin *et al.*<sup>40</sup>).

interface with air, their molecules are oriented “edgewise”, some of the fluorine atoms prove to be turned outwards. This results in the appearance of high negative potential differences between air and the solutions of these compounds. These effects almost disappear at the interface with mercury due to the flat orientation of these compounds and under the influence of the factors discussed above (Figure 17). In this case the ratio of the adsorption potentials at both interfaces is essentially different from that observed in the case of phenols.

To conclude the comparison of the adsorption behaviours at both interfaces it would be expedient to consider another interesting difference. Since the classical investigations of Langmuir, the adsorption at the interface between the solutions of low-molecular organic compounds and air has been known to terminate in the formation of a monolayer. At the interface with mercury polymolecular layers are formed, as was shown for the first time by Frumkin, Gorodetskaya and Tchugunov<sup>41</sup> for the cases of caproic acid and phenol at concentrations approaching saturation. This result was many times corroborated in subsequent studies by the measurements of electrocapillary curves and differential capacity<sup>40-43</sup>. The detailed structure of these polymolecular layers has not yet been determined. Their formation can be favoured both by the more flat orientation of the adsorbed molecules at the interface with mercury and by the van der Waals interaction of the adsorbed molecules with it. The fact that the appearance of the polylayers in caproic acid solutions does not affect  $\Delta\phi_{\epsilon=0}$  shows that in this case the formation of a dual layer cannot be considered as an intermediate step in the transition from a monolayer to polylayers. Apparently, an even number of additional layers with orientations compensating the dipole effects, perhaps in the shape of islets, is at once formed on the monolayer.

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