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Academician A. N. FRUMKIN, R. I. KAGANOVICH, and E. S. BIT-POPOVA

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Fig. 2. Electrocapillary curves of solutions: 1 –1.1 N H_2SO_4; 2 –1 N H_2SO_4 + 0.1 M $C_6H_5NH_2 \cdot 1/2H_2SO_4$; 3 –1 N H_2SO_4 + 0.1 M $C_6H_{11}NH_2 \cdot 1/2H_2SO_4$

Figure 2: Fig. 2. Electrocapillary curves of solutions: 1 –1.1 N H_2SO_4; 2 –1 N H_2SO_4 + 0.1 M $C_6H_5NH_2 \cdot 1/2H_2SO_4$; 3 –1 N H_2SO_4 + 0.1 M $C_6H_{11}NH_2 \cdot 1/2H_2SO_4$

Abstract

Full Text

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ADSORPTION OF AROMATIC AND HYDROAROMATIC COMPOUNDS AT THE MERCURY-SOLUTION INTERFACE

A comparison of the adsorption of polar aromatic compounds at the solution-air and mercury-solution interfaces showed that, at the interface with mercury, as compared with the solution-air interface, there is an increase in adsorbability on a positively charged surface and higher negative values of the adsorption potential (^{1}). It was suggested that these effects are connected with the planar arrangement of the molecules in the adsorption layer, owing to which the interaction of the negative atoms of polar groups with the metal is facilitated. A study of the electrocapillary behavior of nonpolar aromatic compounds, carried out later in our laboratory by Gerovich (^{2}), showed that substances such as benzene, naphthalene, and others are also adsorbed preferentially on the positively charged surface of mercury and shift the point of zero charge toward negative potentials.

Fig. 1. Electrocapillary curves of solutions: 1 –1 N Na_2SO_4 + 0.01 N $NaOH$; 2 –the same + 0.1 M $C_6H_5NH_2$; 3 –the same + 0.1 M $C_6H_{11}NH_2$. σ in dyn/cm.

Fig. 2. Electrocapillary curves of solutions: 1 –1.1 N H_2SO_4; 2 –1 N H_2SO_4 + 0.1 M $C_6H_5NH_2 \cdot \frac{1}{2}H_2SO_4$; 3 –1 N H_2SO_4 + 0.1 M $C_6H_{11}NH_2 \cdot \frac{1}{2}H_2SO_4$.

Comparison of the electrocapillary curves of aromatic compounds and the corresponding hydroaromatic compounds (benzene—cyclohexane, naphthalene—decalin) led to the conclusion that the shift of the point of zero charge and adsorption at positive surface charges are due not only to the planar orientation of the molecules of aromatic compounds, but also to the presence of π-electrons, which interact with the surface of mercury, especially when it is positively charged.

The presence of a polar group in the aromatic ring (phenol), in accordance with previously developed views, intensified the effects observed in the adsorption of unsubstituted hydrocarbons.

It was of interest to investigate the adsorption of other polar benzene derivatives.

The electrocapillary curves of aqueous solutions of the substances under study, expressing the dependence of the interfacial tension σ on the electrode potential φ (on the hydrogen scale), were recorded with a Gouy electrometer. The substances used in the work were purified by double distillation or recrystallization. Hexahydrobenzoic acid was synthesized by V. Gerovich according to Zelinsky' s method.

Figure 1 presents the electrocapillary curves of aniline (2) and cyclohexylamine (3) against a background of $1N$ $Na_2SO_4 + 0.01N$ NaOH (1). It is evident from Fig. 1 that aniline is adsorbed on the positively charged mercury surface, whereas in the case of cyclohexylamine an increase in positive charge leads to the disappearance of adsorption. Conversely, on the initially uncharged or negatively charged mercury surface, the adsorbability of cyclohexylamine exceeds that of aniline.

Figure 2 shows the electrocapillary curves of $1.1N$ H_2SO_4 (1) and of H_2SO_4 containing anilinium sulfate (2) and cyclohexylammonium sulfate (3) at $0.1N$ concentration. As is seen from Fig. 2, on the positively charged mercury surface the adsorption of the cyclohexylammonium cation ceases completely; the electrocapillary curve of the salt solution merges with the H_2SO_4 curve. In the case of sulfuric-acid aniline, as has already been shown previously in (3), the cations continue to be appreciably adsorbed even at a positive surface charge, which indicates the predominance of the forces of π-electron interaction of the aromatic ring over the forces of electrostatic repulsion.

We also investigated the electrocapillary behavior of aniline and cyclohexylamine against backgrounds of HCl and HBr (4). It turns out that adsorption of the anilinium ion on the positively charged mercury surface increases in the series $SO_4^{2-} < Cl^- < Br^-$. In the presence of Br^- ions, some adsorption of cyclohexylammonium is also observed. These data suggest that adsorption of the cations increases owing to electrostatic interaction of cations oriented flat in the surface layer with specifically adsorbed anions.

Table 1

Base solution	Substance studied	Concentration, mol/l	$\Delta\sigma_1$	$\Delta\sigma_2$
$1N$ Na_2SO_4	Aniline	0.1	47.0	10.0
$1N$ Na_2SO_4	»	0.0045	10.0	–
$1.1N$ H_2SO_4	»	0.1	6.0	0.4
$1.1N$ HBr	»	0.1	11.3	0.7
$1N$ Na_2SO_4	Cyclohexylamine	0.1	43.7	23.6
$1N$ Na_2SO_4	»	0.01	23.6	–
$1.1N$ Na_2SO_4	»	0.1	7.5	1.0
$1.1N$ HBr	»	0.1	13.0	1.3
$0.1N$ H_2SO_4	Benzoic acid	0.01	19.2	2.5
$0.1N$ H_2SO_4	» »	0.0005	2.5	–
$0.01N$ KOH	» »	0.05	20.5	0.4
$0.1N$ H_2SO_4	Hexahydrobenzoic acid	0.01	20.5	6.0
$0.1N$ H_2SO_4	Same	0.0027	6.0	–
$0.01N$ KOH	» »	0.05	2.5	–

For comparison of the surface activity of the substances under study at the water-air and water-mercury interfaces, some measurements of surface tension were carried out by the maximum bubble-pressure method; the results are given in Table 1. $\Delta\sigma_1$ denotes the decrease in interfacial tension in going from the maximum of the electrocapillary curve of the base solution to the maximum in the presence of the adsorbing–

of the substance, $\Delta\sigma_2$ is the corresponding lowering of the surface tension of the base solution.

It follows from Table 1 that the surface activity of the compounds investigated increases substantially on going from the free surface of the solution to the boundary with mercury. Assuming that equal values of the decrease in interfacial tension at the two interfaces correspond to equal adsorption values, i.e., that the equations of state of the adsorbed layers at the two interfaces are identical, from the data of Table 1, using the equation

$$|\Delta g_0| = RT \ln \frac{C_1}{C_2}$$

one can calculate $|\Delta g_0|$–the increase in the absolute value of the standard free energy of adsorption on going from the solution–air interface to the boundary with mercury (C_1 and C_2 are the concentrations of the dissolved substance that cause the same decrease in σ, respectively, at the boundary with air and with mercury). In the case of aniline (at $\Delta\sigma_1 = \Delta\sigma_2 = 10.0$), $|\Delta g_0| = 1.80$ kcal; in the case of cyclohexylamine (at $\Delta\sigma_1 = \Delta\sigma_2 = 23.6$), $|\Delta g_0| = 1.34$ kcal.

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

Fig. 3. Electrocapillary curves of solutions: 1 $-0.1\,N$ H_2SO_4; 2 –the same $+\,0.01\,M$ C_6H_5COOH; 3 –the same $+\,0.01\,M$ $C_6H_{11}COOH$

Fig. 4. Electrocapillary curves of solutions: 1 $-0.01\,N$ KOH; 2 $-0.05\,N$ KOH $+\,0.05\,N$ C_6H_5COOK; 3 $-0.05\,N$ KOH $+\,0.05\,N$ $C_6H_{11}COOK$

It is noteworthy that, in the case of cyclohexylamine, there is a noticeable increase in the gain in adsorption energy on going to the boundary with mercury, which is not observed, for example, in the case of long-chain aliphatic alcohols (1). Possibly this effect is associated with the flat orientation of the adsorbed cyclohexylamine molecule. The indicated gain in energy increases by $\Delta|\Delta g_0| =$ 0.46 kcal on going from cyclohexylamine to aniline; this shows that interaction with the π-electrons of the ring, although to a much lesser degree than on a positively charged surface, is also manifested in the case of an uncharged mercury surface. At the free surface of the solution, the surface activity of cyclohexylamine, owing to its larger molecular volume, is noticeably greater than the activity of aniline; as a result of π-electron interaction this difference disappears on going to the boundary with mercury. The surface activity of anilinium and cyclohexylammonium ions is much lower than the activity of the corresponding neutral molecules; however, between the adsorbabilities of the two cations the same relationships are preserved as in the case of the molecules. Whereas the cyclohexylammonium cation is adsorbed approximately 2–2.5 times more strongly than the anilinium ion at the boundary with air, this difference is smoothed out on going to the boundary with mercury. The value $\Delta|\Delta g_0|$ in this case is also $\simeq 0.4$ kcal. As is seen from Fig. 2, despite the repulsion of the cation as a whole, the π-electron interaction increases sharply when a positive charge is present on the mercury surface.

The role of the interaction of π-electrons with the mercury surface in the adsorption of anilinium and other analogous cations in $0.1\,N$ HCl solutions

This was also indicated by Blomgren and Bockris (⁀5), who quantitatively studied this adsorption at various potentials. However, these authors did not take into account that, as is evident from the example of cyclohexylammonium, appreciable adsorption effects are also observed in the absence of this interaction. In the case of a free water surface, the latter are evidently determined by the displacement of the organic cation from the bulk of the solution.

Figure 3 gives electrocapillary curves for 0.01 M solutions of benzoic (2) and hexahydrobenzoic (3) acids against a background of 0.1 N H_2SO_4 (1). As can be seen, the curve for hexahydrobenzoic acid, on transition to positive surface charges, almost completely merges with the background curve, which indicates cessation of adsorption under these conditions, whereas the adsorption of benzoic acid retains an appreciable magnitude under the same conditions.

The results of an investigation of the electrocapillary behavior of the potassium salts of benzoic (Fig. 4, 2) and hexahydrobenzoic (Fig. 4, 3) acids show the extent to which the surface activity of the anion increases as a result of the π-electron effect.

Comparison of the surface activity of benzoic and hexahydrobenzoic acids at the solution—air and mercury—solution interfaces leads to conclusions analogous to those obtained in the case of aniline and cyclohexylamine. The value of $|\Delta g_0|$ for benzoic acid is 1.74 kcal (at $\Delta\sigma_1 = \Delta\sigma_2 = 2.5$) and only 0.76 for hexahydrobenzoic acid ($\Delta\sigma_1 = \Delta\sigma_2 = 6.0$). Thus, the additional energy gain due to interaction with the π-electrons of the ring reaches in this case almost 1 kcal. It is noteworthy that the surface activity of benzoic acid at the boundary with mercury decreases only by a factor of 5 on going from the neutral molecule to the anion, whereas for hexahydrobenzoic acid the corresponding coefficient is approximately 40.

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