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Abstract

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CATALYTIC EVOLUTION OF HYDROGEN ON MERCURY AT HIGH COVERAGES OF THE ELECTRODE SURFACE BY CATALYST

In work (^{1}) the process of the catalytic evolution of hydrogen on mercury from hydrochloric-acid solutions of diphenylamine was studied under conditions in which the degree of coverage of the electrode surface by diphenylamine is related to the bulk concentration of the catalyst according to Henry' s law, and it was shown that the stage limiting the rate of the process is the discharge of diphenylammonium ions. In this sense the result obtained agrees with the conclusion of Frumkin and Andreeva (^{3}). As was indicated by Frumkin (^{2}), the regularities of the reduction process in the case of high coverages of the surface by an electroactive substance may be different from those in the case of low coverages. Therefore it seemed of interest to investigate the behavior of hydrochloric-acid solutions of diphenylamine in the region of high coverages of the mercury surface by the catalyst.

In (^{3}) it was suggested that the decrease in the overvoltage of hydrogen evolution from hydrochloric-acid solutions of diphenylamine is associated with a shift of the ψ_1-potential in the positive direction as a result of adsorption, facilitating the discharge of specifically adsorbed diphenylammonium cations. However, in reality, near the potential of zero charge of mercury, and when the concentration of HCl is not too high, molecules of diphenylamine are adsorbed mainly on the electrode (^{1}). The consequence of this should be a shift of the point of zero charge of mercury in the negative direction, as usually occurs in the case of adsorption on mercury of molecules containing a considerable number of π-electrons (^{4}). Measurement of electrocapillary curves shows that this shift reaches 60 mV in a solution containing $2 \cdot 10^{-4}$ M diphenylamine and 0.2 M HCl + 0.8 M KCl (Fig. 1a, curve 4).

The influence of adsorption of diphenylammonium becomes noticeable at more negative potentials. Figure 1a presents electrocapillary curves (curves 2 and 5) obtained under conditions in which the concentration of unprotonated catalyst molecules was almost the same, but the concentration of diphenylammonium ions under the conditions of curve 5 was 8 times greater than under the conditions of curve 2 (the concentration of diphenylammonium cations was calculated from the value of the dissociation constant of diphenylamine hydrate, $K = 6.9 \cdot 10^{-14}$ (^{5})). As can be seen, curves 2 and 5 practically coincide in

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

the potential region from −0.1 to −0.7 V (N.C.E.); however, at more negative potentials they diverge, with curve 5, obtained in a solution with the higher content of diphenylammonium ions, lying below curve 2.

The better adsorbability of diphenylammonium ions at negative potentials is also indicated by the results of measuring the differential capacitance of the double layer in solutions of diphenylamine in more concentrated HCl, from which it follows that the potential of maximum adsorption of diphenylammonium ions is 200 mV more negative than the potential of maximum adsorption of diphenylamine.

In 6.5 M HCl, adsorption of diphenylammonium ions leads to a shift of the point of zero charge of mercury in the positive direction, which may reach 80 mV (Fig. 1b, curve 4).

Consideration of the electrocapillary curves leads to the conclusion that, at a degree of coverage of the mercury surface θ close to unity, both diphenylamine molecules and diphenylammonium cations are oriented perpendicular to the mercury surface: at $\theta = 0.9$, the surface area per adsorbed particle is 30-40 Å^2 in 0.2 M HCl and in 1 M HCl, which is considerably less than the area occupied by a diphenylamine molecule in a flat arrangement (about 100 Å^2).

Fig. 1. *a*—electrocapillary curves of solutions of 0.2 M HCl + 0.8 M KCl + $xM(C_6H_5)_2NH$.
1—$x = 0$; 2—$x = 0.4 \cdot 10^{-4}$; 3—$x = 1 \cdot 10^{-4}$; 4—$x = 2 \cdot 10^{-4}$;
5—solution composition 1 M HCl + $2 \cdot 10^{-4}$ M $(C_6H_5)_2NH$.
b—electrocapillary curves of solutions of 6.5 M HCl + $xM(C_6H_5)_2NH$.
1—$x = 0$; 2—$x = 1.5 \cdot 10^{-4}$; 3—$x = 3.35 \cdot 10^{-4}$; 4—$x = 5.4 \cdot 10^{-4}$.

The shift of the point of zero charge of mercury that we observed toward more negative potentials in diphenylamine solutions in 0.2 M HCl indicates that, in the decrease of the overvoltage of hydrogen evolution in the presence of diphenylamine, the decisive role is played not by a change in the potential drop in the compact part of the double layer, but by a change in the nature of the discharge stage. Namely, the discharge of diphenylammonium ions leads to the formation of adsorbed $(C_6H_5)_2NH_2$ radicals, whose adsorption energy on the mercury surface is evidently greater than the adsorption energy of H atoms formed during the discharge of hydrogen ions (^{6}).

Fig. 2. Polarization curves of solutions of 1 M HCl + $xM(C_6H_5)_2NH$.
1—$x = 0$; 2—$x = 4.85 \cdot 10^{-5}$; 3—$x = 9.6 \cdot 10^{-5}$; 4—$x = 1.33 \cdot 10^{-4}$; 5—$x = 2.66 \cdot 10^{-4}$;

Fig. 3. Dependence of the discharge current of diphenylammonium ions on the surface concentration of an equilibrium mixture of diphenylamine and diphenylammonium. Potential −0.85 V (N.C.E.)

Figure 3: Fig. 3. Dependence of the discharge current of diphenylammonium ions on the surface concentration of an equilibrium mixture of diphenylamine and diphenylammonium. Potential −0.85 V (N.C.E.)

6–$x = 3.6 \cdot 10^{-4}$; 7–$x = 1.48 \cdot 10^{-3}$; 8–$x = 1.9 \cdot 10^{-3}$.

Figure 2 shows the polarization curves of the catalytic evolution of hydrogen from 1 M HCl at various bulk concentrations of diphenylamine. It follows from Fig. 2 that, as the bulk concentration of the catalyst increases, at a given current density i the overvoltage initially decreases. However, beginning with a diphenylamine concentration of $1.48 \cdot 10^{-3}$ M, an increase in the bulk concentration of the catalyst (at $i < 1.2 \cdot 10^{-3}$ A/cm^2) leads to an increase in the overvoltage. At a catalyst concentration of $1.9 \cdot 10^{-3}$ M and higher, the overvoltage of hydrogen evolution is almost independent of the bulk concentration of diphenylamine because of the small change in θ. At $i > 1.3 \cdot 10^{-3}$ A/cm^2, increasing the concentration of diphenylamine up to saturation causes a monotonic decrease in the overvoltage.

Fig. 3. Dependence of the discharge current of diphenylammonium ions on the surface concentration of an equilibrium mixture of diphenylamine and diphenylammonium. Potential −0.85 V (N.C.E.)

It should also be noted that, at a given concentration of diphenylamine in the region of low current densities, as the negative potential increases the difference in the overvoltage of hydrogen evolution from HCl solutions containing diphenylamine and not containing it increases; this is especially clearly seen in the case of high catalyst concentrations. This effect is undoubtedly associated with an increase in the surface concentration of diphenylammonium ions at negative potentials. With a further increase in the negative potential, the polarization curves obtained at different concentrations of diphenylamine come closer together as a result of approaching the desorption potentials of the organic substance, as was discussed in previously published works ([3],[1]).

We constructed a graph of the dependence of the density of the catalytic current of hydrogen evolution from 1 M HCl at constant potential on the degree of filling of the mercury surface by the catalyst (calculated from the decrease in differential capacitance) at the same potential (Fig. 3). From Fig. 3 it is seen that, as θ increases, the current first increases almost linearly, then, after a small delay, again rises sharply and, on reaching a filling of 0.89, falls with further growth of θ.

The most probable reason for the decrease in the reduction rate of diphenylammonium ions as θ approaches unity is the difficulty of forming the activated complex at high surface concentrations of the catalyst, which is inevitable if, in

Fig. 4. Polarograms of solutions of 6.5 M HCl + xM(C6H5)2NH. 1 –x = 0; 2 –x = 1.8 • 10–4; 3 –x = 3.6 • 10–3. Capillary with paddle; drop time 0.26 s; mercury flow rate 1.43 mg/s

Figure 4: Fig. 4. Polarograms of solutions of 6.5 M HCl + xM(C6H5)2NH. 1 –x = 0; 2 –x = 1.8 • 10–4; 3 –x = 3.6 • 10–3. Capillary with paddle; drop time 0.26 s; mercury flow rate 1.43 mg/s

the transition state, the reacting particle occupies a larger area on the electrode surface than in the initial adsorbed state. The absence of a linear dependence of i on θ in the range $\theta = 0.53$–0.9 is apparently connected with a violation of proportionality between the surface concentration of diphenylammonium ions (on which the density of the catalytic current depends) and the experimentally determined value of θ, which expresses the sum of the fillings of the electrode by molecules of diphenylamine and diphenylammonium. The observed course of the curve, as will be shown in another communication, apparently can be interpreted by taking into account the interaction between adsorbed molecules and the competition between diphenylamine molecules (better-adsorbing cations) and diphenylammonium ions (bulk-

the surface concentration of which considerably exceeds the concentration of molecules).

The catalytic evolution of hydrogen from concentrated HCl solutions containing diphenylamine was studied by the polarographic method. As follows from Fig. 4, in this case, with increasing bulk concentration of diphenylamine, the overvoltage of hydrogen evolution first decreases and then increases. However, in 6.5 M HCl, in contrast to what is observed in the case of 1 M HCl, beginning with a certain bulk concentration of the catalyst, the hydrogen overvoltage in the presence of diphenylamine exceeds the overvoltage in HCl in its absence.

Fig. 4. Polarograms of solutions of 6.5 M HCl $+ xM(\mathrm{C_6H_5})_2$NH. 1 $-x = 0$; 2 $-x = 1.8 \cdot 10^{-4}$; 3 $-x = 3.6 \cdot 10^{-3}$. Capillary with paddle; drop period 0.26 s; mercury outflow rate 1.43 mg/s.

It is impossible to explain the increase in overvoltage with increasing catalyst concentration in these experiments by the reasons that were analyzed as applied to the polarization curves obtained with 1 M HCl, since, owing to the short lifetime of the drop (less than 0.5 s), the coverage of the surface by the catalyst was considerably less than unity. In this case it should be taken into account that, with increasing concentration of hydrochloric acid, the discharge current of hydrogen ions increases and becomes comparable with the discharge current of diphenylammonium ions. With increasing bulk concentration of diphenylammonium ions, owing to the shift of the ψ_1-potential in the positive direction (see Fig. 1b), the rate of discharge of hydrogen ions decreases. If the discharge current of hydrogen ions decreases more rapidly than the discharge current of diphenylammonium ions increases, then the total current will decrease and the overvoltage of hydrogen evolution will increase.

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Note: Figure translations are in progress. See original paper for figures.