THE CATALYTIC EVOLUTION OF HYDROGEN AT A MERCURY ELECTRODE AT HIGH COVERAGE OF THE SURFACE WITH CATALYST

Academician A. N. Frumkin, D. I. Dzhaparidze,
and G. A. Tedoradze

The Institute of Electrochemistry of the Academy of Sciences of the USSR

Translated from Doklady Akademii Nauk SSSR, Vol. 152, No. 1,
pp. 164-167, September, 1963
Original article submitted June 8, 1963

In a previous paper [1] we investigated the catalytic evolution of hydrogen at a mercury surface from solutions of diphenylamine in hydrochloric acid, under conditions such that the extent of coverage of the electrode surface with diphenylamine was related to the volume concentration of the catalyst in accordance with Henry's law, and it was shown that the rate-limiting stage of the process was the discharge of diphenylammonium ions. In this respect the conclusions were similar to those of Frumkin and Andreeva [3]. Frumkin showed [2] that the mechanism of the reduction process in the case of high coverage of the surface with an electrically active material might be different from that in the case of low coverage. It was therefore of interest to investigate the behavior of solutions of diphenylamine in hydrochloric acid in the region of high coverage of the mercury surface with catalyst.

It was suggested [3] that the reduction in overvoltage for hydrogen evolution from solutions of diphenylamine in hydrochloric acid was associated with a shift of the ψ_1-potential in the positive direction, as the result of adsorption which facilitated the discharge of specifically adsorbed diphenylammonium cations. However, close to the zero discharge potential of mercury at an electrode, with not too high an HCl concentration, it is mainly diphenylamine molecules which are adsorbed [1]. Thus, there should be a shift in the zero discharge point of mercury in a negative direction, as is normally the case for adsorption on mercury of molecules containing several π-electrons [4]. Measurements of electrocapillary curves showed that this shift amounted to 60 mV in a solution $2 \cdot 10^{-4}$M in diphenylamine, 0.2 M in HCl, and 0.8 M in KCl (Fig. 1a, curve 4).

The effect of diphenylammonium adsorption became appreciable at more negative potentials. Fig. 1a shows electrocapillary curves (curves 2 and 5) obtained under conditions such that the concentrations of nonprotonated catalyst molecules were almost the same, but the concentration of diphenylammonium ions under the conditions for curve 5 was eight times that under the conditions for curve 2 (the concentrations of diphenylammonium cations were calculated from a value of $K = 6.9 \cdot 10^{-14}$ [5] for the dissociation constant of diphenylamine hydrate). It is clear that

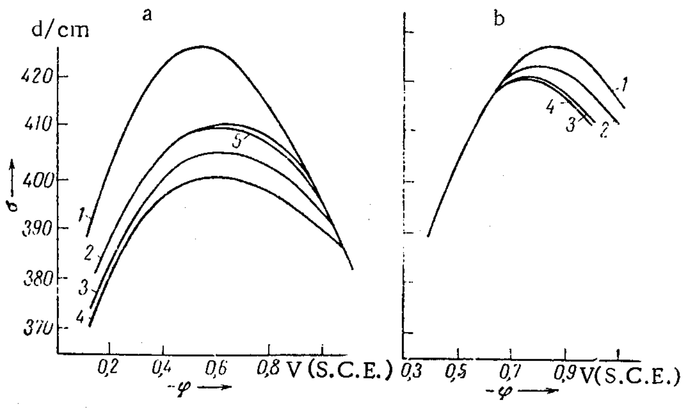

Fig. 1. a) Electrocapillary curves of solutions 0.2 M in HCl, 0.8 M in KCl, and xM molar in$(C_6H_5)_2NH$: 1) x = 0; 2) x = $0.4 \cdot 10^{-4}$; 3) x = 10^{-4}; 4) x = $2 \cdot 10^{-4}$; 4) x = $2 \cdot 10^{-4}$; 5) solution composition M HCl + $2 \cdot 10^{-4}$M $(C_6H_5)_2NH$. b) Electrocapillary curves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

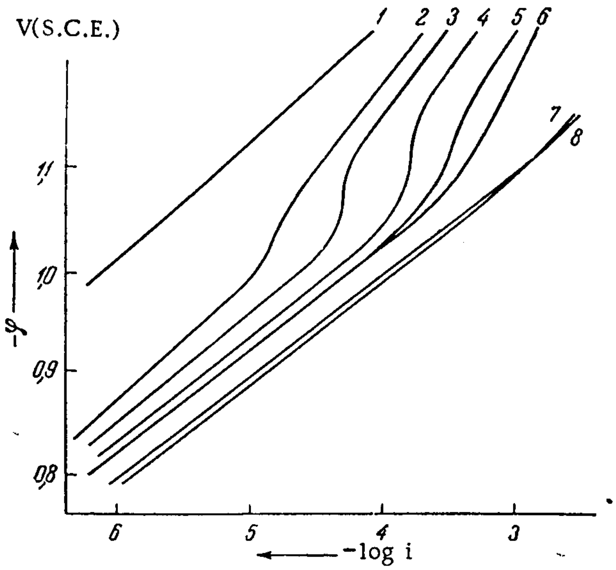

Fig. 2. Polarization curves of solutions M in HCl and xM in$(C_6H_5)_2NH$: 1) x = 0; 2) x = $4.85 \cdot 10^{-5}$; 3) x = $9.6 \cdot 10^{-5}$; 4) x = $1.33 \cdot 10^{-4}$; 5) x = $2.66 \cdot 10^{-4}$; 6) x = $3.6 \cdot 10^{-4}$; 7) x = $1.48 \cdot 10^{-3}$; 8) x = $1.9 \cdot 10^{-3}$.

curves 2 and 5 practically coincide in the potential region -0.1 to -0.7 V (S.C.E.) but diverge at more negative potentials, where curve 5, obtained with a solution containing a higher concentration of diphenylammonium ions, lies below curve 2.

The higher adsorption of diphenylammonium ions at negative potentials was also shown by the results of measurements of the differential capacity of the double layer in diphenylamine solutions with higher HCl concentrations; it followed from these that the potential for maximum adsorption of diphenylammonium ions was 200 mV more negative than the potential for maximum adsorption of diphenylamine.

In 6.5 M HCl adsorption of diphenylammonium ions led to a shift of the zero discharge point of mercury in the positive direction, which could amount ot 80 mV (Fig. 1b, curve 4).

Consideration of these electrocapillary curves led to the conclusion that, when the degree of coverage θ of the mercury surface was near unity, both the diphenylamine molecules and the diphenylammonium cations were oriented perpendicular to the mercury surface: at θ = 0.9, the surface occupied by an adsorbed particle was 30-40 A^2 in 0.2 M HCl and in M HCl, considerably less than the area occupied by a diphenylamine molecule located parallel to the surface (about 100 A^2).

The observed shift in the zero discharge point of mercury to a more negative potential, in solutions of diphenylamine in 0.2 M HCl, showed that the main factor in the lowering of overvoltage for hydrogen evolution in the presence of diphenylamine was not a change in the potential drop across the dense part of the double layer, but was a change in the nature of the discharge stages. In fact, the discharge of diphenylammonium ions led to the formation of adsorbed $(C_6H_5)_2NH_2$ radicals, whose adsorption energy on the mercury surface would clearly be greater than that of H atoms, formed by the discharge of hydrogen ions [6].

Figure 2 shows polarization curves for the catalytic evolution of hydrogen from M HCl with various volumetric concentrations of diphenylamine. It follows from this figure that, at a given current density i, the overvoltage began to decrease with increasing volumetric concentration of catalyst. However, starting at a diphenylamine concentration of $1.48 \cdot 10^{-3}$M, a further increase in volumetric concentration of catalyst (at $i < 1.2 \cdot 10^{-3}$ A/cm^2) led to an increase in overvoltage. At catalyst concentrations of $1.9 \cdot 10^{-3}$M and above, the overvoltage for hydrogen evolution was practically independent of the volumetric concentration of diphenylamine, owing to the small change in θ. At $i > 1.3 \cdot 10^{-3}$ A/cm^2, an increase in diphenylamine concentration up to saturation produced a continuous decrease in overvoltage.

It should also be noted that, for a given diphenylamine concentration and in the low current density region, the difference in overvoltage for hydrogen evolution between HCl solutions containing and not containing diphenylamine increased with increasing negative potential; this was particularly noticeable at high catalyst concentrations. The effect was undoubtedly associated with the increase in surface concentration of diphenylammonium ions at negative potentials. With a further increase in negative potential, the polarization curves obtained with different diphenylamine concentrations drew together, as the result of approach to the desorption potential of the organic compound; this has been demonstrated in previously published papers [3, 1].

We constructed a curve for the relation between the catalytic current density for hydrogen evolution from 1M HCl at constant potential and the degree of coverage of the mercury surface by catalyst (calculated from the decrease in differential capacity) at constant potential (Fig. 3). It is clear from this curve that the current began by increasing almost linearly with increasing θ, then, after a small arrest, increased rapidly until θ was 0.89, and subsequently fell with increasing θ.

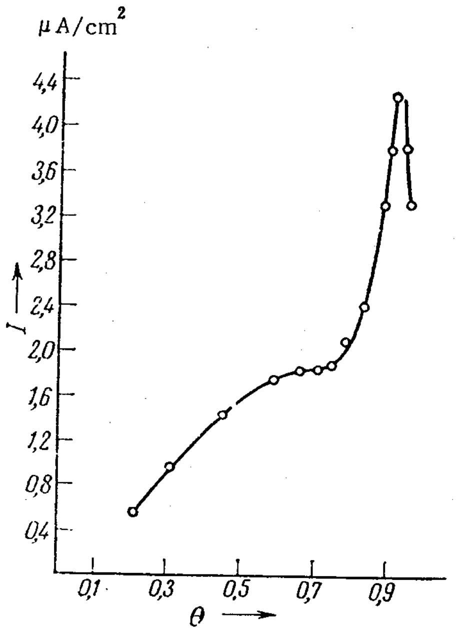

Fig. 3. Relation between the discharge current of diphenylammonium ions and the surface concentration of the equilibrium mixture of diphenylammonium. The potential was -0.85 V (S.C.E.).

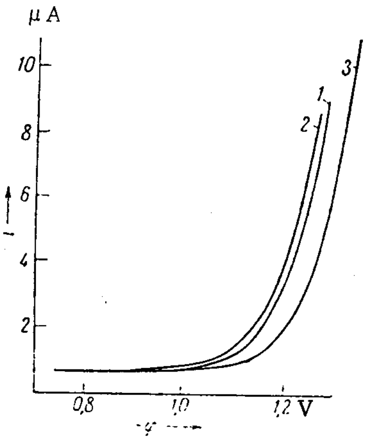

Fig. 4. Polarograms for solutions of 6.5 M HCl + xM $(C_6H_5)_2NH$: 1) x = 0; 2) x = 1.8 · · 10^{-4}; 3) x = 3.6 · 10^{-3}. Capillary with shoulder; drop time 0.26 sec; mercury flow rate 1.43 mg/sec.

The most probable reason for the decrease in rate of diphenylammonium ion reduction when θ was approximately unity was the difficulty in formation of an active complex at high surface concentrations of catalyst. This would be unavoidable if the reacting particle in the transition state occupied a greater area on the surface than when in the initial adsorbed state. The absence of a linear relation between i and θ in the θ range 0.53 to 0.9 was evidently associated with a lack in proportionality between the surface concentration of diphenylammonium ions (on which the catalytic current density depended) and the experimentally determined value of θ which expressed the total coverage of the electrode by diphenylamine molecules and diphenylammonium ions. The observed course of the curves, as will be shown in another paper, could evidently be interpreted by calculating the interaction between the adsorbed molecules and the competition between diphenylamine molecules (adsorbed preferentially to cations) and diphenylammonium ions (whose volumetric concentration in the solution considerably exceeded the concentration of molecules).

Catalytic hydrogen evolution from concentrated HCl solutions, containing diphenylamine, was also investigated by the polarographic method. Figure 4 shows that the overvoltage for hydrogen evolution at first decreased with increasing volumetric concentration of diphenylamine, and then decreased. However, in 6.5 M HCl, as opposed to what was observed with 1M HCl, beginning at a definite volumetric concentration of catalyst, the hydrogen overvoltage in the presence of diphenylamine exceeded the overvoltage in HCl in the absence of diphenylamine.

It was not possible to explain the increase in overvoltage with increasing catalyst concentration in these experiments in terms of the same factors as were considered applicable to the polarization curves obtained in 1M HCl, because, owing to the short life of the drop (less than 0.5 sec), the coverage of the surface would have been considerably less than unity. It was considered that, in this case, the discharge current of the hydrogen ions increased with increasing hydrochloric acid concentration and became comparable with the discharge current of diphenylammonium ions. With increasing volumetric concentration of diphenylammonium ions the shift in $\psi_1$potential in the positive direction (see Fig. 1b) would depress the rate of hydrogen ion discharge. If the hydrogen ion discharge current dropped more rapidly than the diphenylammonium ion discharge current increased, then the total current would decrease and the overvoltage for hydrogen evolution would increase.

LITERATURE CITED

1. G. A. Tedoradze and D. I. Dzhaparidze, Izv. AN SSSR, OKhN, 402 (1963).
2. A. B. Érshler, G. A. Tedoradze, and S. G. Mairanovskii, DAN, 145, 1324 (1962).
3. A. N. Frumkin and E. P. Andreeva, DAN, 90, 417 (1953).
4. M. A. Gerovich, DAN, 105, 1278 (1955).
5. C. Glasstone, Introduction to Electrochemistry [Russian translation] (IL, 1951), p. 429.
6. S. G. Mairanovskii, DAN, 114, 1272 (1958); 120, 1294 (1958); 132, 1352 (1960); 133, 162 (1960).
