EFFECT OF IODIDE ADSORPTION ON HYDROGEN OVERVOLTAGE IN ACIDIC ETHYLENE GLYCOL SOLUTIONS

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It was shown in [1] that the discharge of hydrogen ions on a mercury electrode in dilute hydrochloric acid–ethylene glycol solutions conforms to the theory of moderated discharge. Accordingly, the overvoltage and energy of activation of hydrogen-ion discharge at a given overvoltage are substantially lower than in the corresponding aqueous solutions. This indicates the possibility of experimental detection of a zone of unlimited discharge of hydrogen ions in ethylene glycol. An investigation of the process of unlimited discharge [2] in any new solvent is of great interest because this aids the study of a number of quantities (the adsorption energy of hydrogen, the preexponential factor, etc.) important in the theory of elementary processes.

It is known that the specific adsorption of iodine markedly lowers the hydrogen overvoltage [3-5] and thereby facilitates the experimental detection of the zone of unlimited discharge [2].

In addition, it is of interest to establish a connection between the reduction of the hydrogen overvoltage and the change in the ψ_1-potential in glycol solutions in the usual region of the polarization curve.

Our aim was to investigate the ψ_1-effect and also to detect the zone of unlimited discharge in ethylene glycol–hydrochloric acid solutions.

In addition to the method described in [1], the solutions were purified by electrolysis on a stationary mercury cathode for 60-64 h while simultaneously being purged with hydrogen. During this time the cathode was changed thrice, draining off part of the solution together with the mercury. This resulted in good reproducibility of low overvoltages. In each experiment the acid concentration was determined by titration before and after obtaining the polarization curve. In solutions containing iodide the potential was established relatively slowly in the current density range $-\log i = 6$ to 4.4 A/cm^2, but rapidly at lower current densities. Polarization curves obtained in the forward and reverse direction agreed within the experimental error and did not exceed 2-3 mV.

Figure 1 shows polarization curves of the discharge of hydrogen in hydrochloric acid–ethylene glycol solutions, containing varying amounts of added KI and an inert electrolyte, at a fixed total concentration. Clearly, the overvoltage in the presence of iodide ions is substantially reduced.

The specific adsorption of iodide in identical solutions but not containing hydrochloric acid was determined in [6]. A comparison of the adsorption change with the polarization curves for the corresponding solutions shows that a reduction of the overvoltage in the presence of iodide is found at such potentials as well where, judging from the coincidence of the $C-\varphi$ curves, the desorption of iodide ions is complete. Thus, in solutions corresponding to curves 2 and 3 on Fig. 1, at potentials with minimum overvoltage the capacity curves do not indicate adsorption, while a reduction of overvoltage, though not great, is observed. The potential at which curve 6 coincides with curve 1 of Fig. 1 is 0.15 V more negative than the potential at which the $C-\varphi$ curves of the corresponding solutions coincide.

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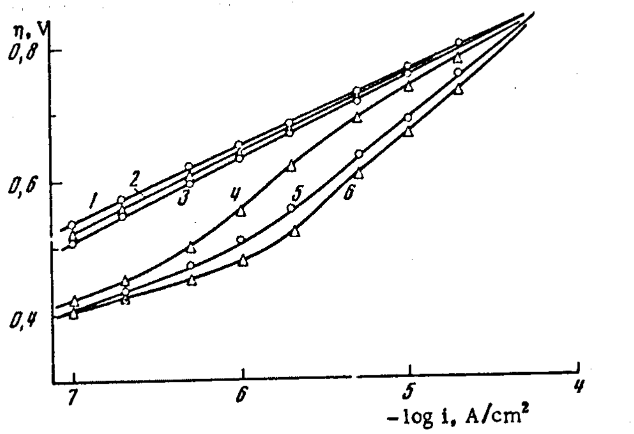

Fig. 1

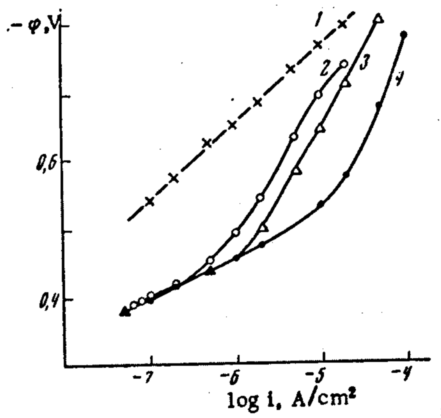

Fig. 2

Fig. 1. Polarization curves for the discharge of hydrogen on a mercury cathode at 20°C in ethylene glycol solutions containing 0.07 N HCl + (0.03 – x) N KCl + xN KI at the following values of x: 1) 0; 2) 0.005; 3) 0.01; 4) 0.1; 5) 0.2; 6) 0.3.

Fig. 2. Polarization curves for the discharge of hydrogen on a mercury cathode at 20°C in ethylene glycol solutions of the following compositions: 1) 0.07 N HCl + 0.3 N KI; 3) 0.5 N HCl + 0.3 N KI; 4) 1.0 N HCl + 0.05 N TBA I + 0.1 N TMA = Cl.*

In aqueous solutions the overvoltage is reduced only at such potentials where appreciable adsorption of iodide occurs, as indicated by the capacity data [3, 7]. In ethylene glycol solutions the overvoltage appears to be more sensitive to the adsorption of iodide than the electrode capacity is. It is difficult to explain this using the model of plane homogeneous condensers, corresponding to the inner and outer plate of a tight double layer. Indeed, we observed a reduction of the overvoltage amounting to 50 mV at more negative potentials than in the region of coincidence of the C – φ curves. If this effect is ascribed completely to the potential change within the Helmholtz surface, ψ^i, and if the capacity of the condenser formed by the inner and outer plates (K_V) amounts to ~30 μF/cm² [6], then such potential shift corresponds to a charge of ~1.5 μC/cm², i.e., well beyond the limits of experimental error in determining the charge from capacity data. Therefore, it seems more probable that such large sensitivity of the rate of discharge to a very small amount of adsorbed anions should be attributed to the effect of the discreteness of their charge. With this small number of adsorbed anions there is virtually no averaging out of the value of ψ^i over the whole surface. Thus, local potential shifts are produced, sufficient for noticeable acceleration of discharge. The differences in the behavior of aqueous and ethylene glycol solutions can be due to differences in developing the effect of discreteness because of the different solvent structure and correspondingly different shielding of charge.

With a larger amount of adsorbed iodide the ψ_1-effect is naturally intensified. The maximal reduction of overvoltage (~200 mV) observed by us is significantly greater than the negative shift of the potential of the exterior Helmholtz surface, $\Delta\psi^0 \simeq 20$ mV, estimated from the results of [6], and is of the order of magnitude, though somewhat larger than, the ψ^i-shift (~120 mV). A qualitatively analogous situation is also observed in aqueous solutions [3].

At lower overvoltages the slope of the polarization curves decreases to about 55 mV and the curves at various iodide concentrations virtually coincide. Such a behavior is typical for unlimited discharge of hydrogen ions [2].

In order to investigate the zone of unlimited discharge in greater detail, it was desirable to widen the limits of current density at which unlimited discharge is observed.

In [7] it was shown that in the presence of tetrabutylammonium hydroxide the adsorption of iodide ions is enhanced, thereby a reduction in the hydrogen overvoltage is possible. In glycol solutions tetraalkylammonium cations desorb at very negative potentials [8]. It can be assumed that their presence in

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*As in Russian original – Publisher.

the solution will shift the potential of desorption of iodide ions in the negative direction, thus expanding the zone of unlimited discharge.

As seen from Fig. 2, tetraalkylammonium cations indeed expand the zone of current density at which unlimited discharge is observed.

Curves 2-4 on Fig. 2 coincide at low current densities. In the region $-\log i = 6$ to 7.2 A/cm^2 the curve has a slope of about 55 mV. Apart from this, the change in the composition of the solution (the concentration of acid and of iodide in the presence of surface-active cations) does not affect the overvoltage, i.e., no ψ_1-effects are observed. This section of the curve unequivocally points to the existence of unlimited discharge of hydrogen atoms in acidic ethylene glycol solutions.

It should be noted that in aqueous solutions unlimited discharge could be observed only at considerably higher concentrations of iodide. This is explained by two factors: firstly, the overvoltage of hydrogen in ethylene glycol is considerably lower than in water [1] and, secondly, in glycol solutions the rate of discharge appears to be more sensitive to the presence of iodide, as noted above. Hence, the process passes into the unlimited discharge zone at significantly lower KI concentrations in ethylene glycol.

It is important that the polarization curves of the unlimited zone virtually coincide in glycol and in aqueous solutions. Thus, in ethylene glycol at 20°C and $\log i = -7$, $\eta = 400 \pm 4$ mV and for water $\eta = 413 \pm 5$ mV [9, 10]. This is not unexpected if we consider that the energy of adsorption of atomic hydrogen (more exactly, the sum of this energy and the adsorption energy of the solvent) cannot differ appreciably in various solvents. At unlimited discharge the real activation energy at the equilibrium potential is equal to the corresponding heat of adsorption. Hence, the coincidence of the polarization curves in water and in glycol offers strong evidence that the observed difference between the hydrogen overvoltages in these two solvents in the regular discharge zone is caused by the difference of the energies required for solvent reorganization.

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