TEMPERATURE RELATION FOR THE HYDROGEN OVERVOLTAGE IN ETHYLENE GLYCOL SOLUTIONS

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It has been shown in a previous article [1] that the discharge of hydrogen ions from hydrochloric acid ethylene glycol solutions is characterized at low current densities by a barrier-free discharge region. A detailed investigation of this region of the polarization curve in a nonaqueous solvent may give useful information on the effect of the nature of the solvent on the hydrogen overvoltage. Results are given here of an investigation of the temperature relations in the barrier-free and normal regions for hydrogen ion discharge from acid ethylene glycol solutions and their comparison with similar data for aqueous solutions. The polarization curves were recorded in accordance with the method described [1, 2]. The equipment was placed in an air thermostat, which provided a means of maintaining the temperature to an accuracy of ±0.5°C.

Polarization curves are shown in Fig. 1 for the discharge of hydrogen ions from hydrochloric acid solutions of ethylene glycol in a base electrolyte of 0.3 N KI* at various temperatures. For all temperatures the polarization curves at low current densities are characterized by a barrier-free discharge region with slopes of 51, 56, 57, 61, 65, 72 mV for temperatures of 0, 10, 20, 30, 40, 50, and 60°C, respectively. These values are very close to the theoretical values for the slope (calculated values of α are 1.06; 1.00; 1.02; 0.98; 1.03; 0.99; 1.09, respectively). Figure 1 shows curves for one of three series of tests. The disagreement between curves obtained in solutions of the same composition of different series in the barrier-free discharge region did not exceed 4-6 mV.

With the overvoltage $\eta = 400$ mV for all the temperatures the barrier-free discharge is observed. For this value of the overvoltage the data of Fig. 1 were used to plot a curve of log i vs 1/T (Fig. 2) and the slope of this curve was used to determine the actual energy of activation (A). It was equal to 15.2 kcal/mole. The equation $A = A_0 - \alpha\eta F$ was used to calculate the activation energy for the barrier-free discharge of hydrogen at the equilibrium potential A_0. Calculation gives a value $A_0 = 24.4$ kcal/mole.† In aqueous solutions $A_0 = 22.9 \pm 0.5$ kcal/mole [4]. The difference between these values is at the limit of the experimental error. From this it follows that the actual heats of the elementary act of discharge, equal to the actual activation energy of the barrier-free process [4, 5], are almost the same in water and ethylene glycol.

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* At a higher concentration of KI (~1 N) there is a marked reduction of overvoltage also in the barrier-free region. Here, in all probability, there is a transition to discharge of undissociated molecules of HI (or ionic pairs) in a manner similar to effects observed in concentrated aqueous solutions [3]. In an aqueous solution this effect is observed at mean ionic molarities of $\mathrm{HI}_{c\pm} \geqslant 2$ M, and in ethylene glycol at $c_{\pm} \geqslant 0.3$ M. This difference is quite natural since the association of ions in ethylene glycol must be more strongly exhibited due to the lower dielectric constant of ethylene glycol. A similar effect has been noted by the authors previously [2].

† The same value was also obtained in two independent series of tests performed over a narrower temperature range (0-40°C).

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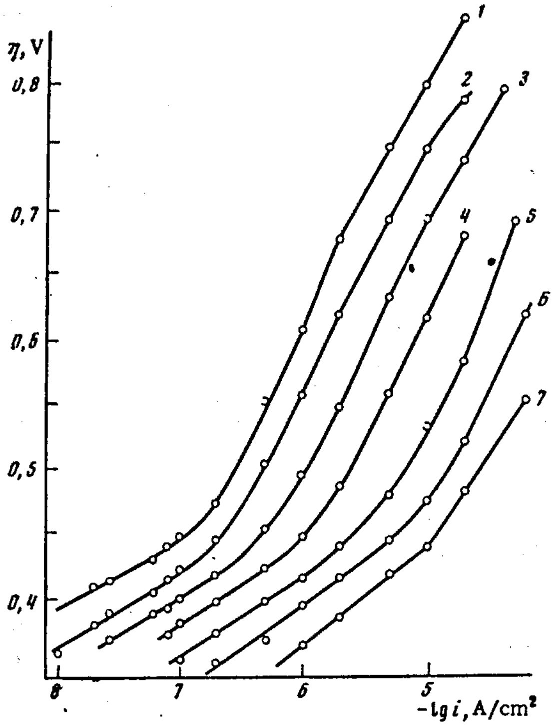

Fig. 1. Polarization curves in ethylene glycol solution of 0.3 N KI+0.05 N HCl at temperatures of: 1) 0; 2) 10; 3) 20; 4) 30; 5) 40; 6) 50; 7) 60°C.

The apparent (i.e., at constant volumetric concentration) actual heat of the elementary act at the equilibrium potential is determined by the heat of adsorption of an atom of H on the metal and by the heat of adsorption of the base remaining after removal of the proton (in this case the molecule H_2O or $C_2H_4(OH)_2$). The heat of adsorption of H atoms on a mercury surface in a solution differs from the heat of adsorption from the gas phase by a small amount. This is related in the first case to the need for H adsorption to remove a solvent molecule from the metal surface, and secondly with the non-valent basically repulsive interaction between the adsorbed atom and the closest molecule of solvent. The difference between the first effect in water and glycol is not large, being the difference between two small values of the order of the heat of physical adsorption of the solvent molecules. Furthermore, this effect is opposite in sign to the other effect referred to above, the direct effect of the heats of adsorption of water and glycol molecules, so that these two small effects must compensate each other to a large extent. There must also be little difference in the reaction between an adsorbed atom and the closest solvent molecule. In both cases the main contribution to this effect must in all probability come from the reaction with the oxygen atom to which the proton was bound before the act of discharge. The valency states of the oxygen in H_2O and $C_2H_4(OH)_2$ are very similar and one would therefore expect very similar reaction energies. Accordingly, from the theoretical point of view one should expect similar values for the actual apparent heats of discharge in these two solvents. The experiments completely supported this assumption.

Polarization curves are given in Fig. 3 for a solution of 0.05 N HCl+1 N $NaClO_4$; the corresponding Arrhenius relations are given in Fig. 4. The activation energy for the normal discharge at the equilibrium potential, found from this data, is 23.9 ± 0.3 kcal.* In an aqueous solution for the corresponding value is 21.9 kcal [6, 7]. The actual apparent activation energy of the normal discharge depends on the same factors as the activation energy of the barrier-free discharge and also upon the reorganization energy of the solvent and the adsorption energy of the donor proton. In both aqueous and glycol solutions the hydrogen ion does not possess marked adsorbability [2]; consequently one may anticipate only small differences in its adsorption energies. The closeness of the activation energies in both solvents shows the closeness of the reorganization energy of the polar solvent in both cases.

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* In another series of experiments it was found that $A_0 = 21.3 \pm 0.8$ kcal. However, these data are less reliable since in these experiments there was an unexplained reduced slope of the polarization curves ($\alpha = 0.55 \pm 0.02$).

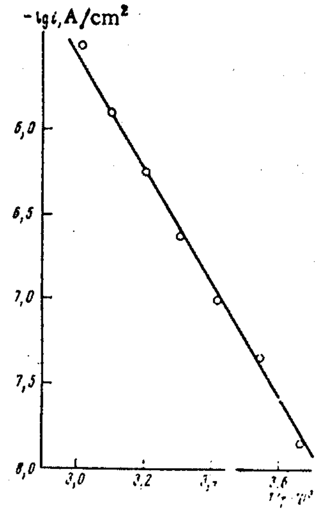

Fig. 2

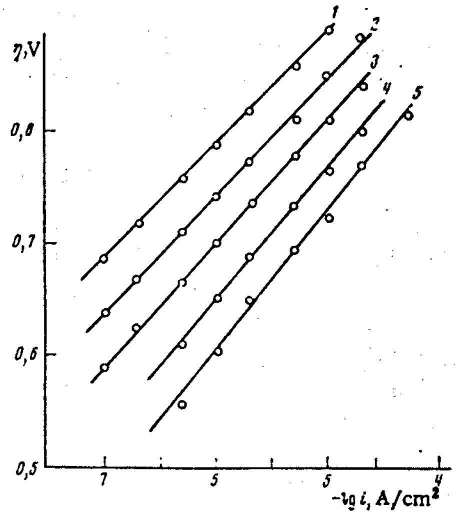

Fig. 3

Fig. 2. Temperature relation for the rate of hydrogen evolution in a solution of 0.3 N $KI + 0.05$ N HCl at $\eta = 400$ mV.

Fig. 3. Polarization curves in an ethylene glycol solution of 1 N $NaClO_4 + 0.05$ N HCl at temperatures of: 1) 0; 2) 10; 3) 20; 4) 30; 5) 40°C.

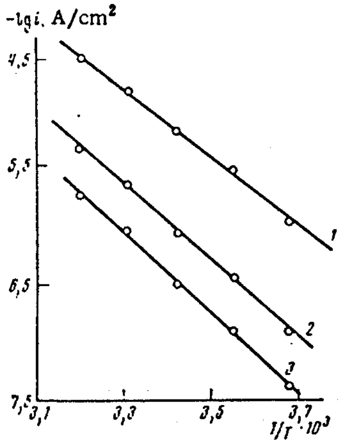

Fig. 4. Temperature relations for the rate of evolution of hydrogen in a solution of 1 N $NaClO_4$ + 0.05 N HCl at overvoltages of: 1) 800; 2) 700; 3) 650 mV.

The small difference, at the limit of experimental error, in the activation energy of the normal discharge in water and ethylene glycol ($\leqslant 2.0$ kcal) is partially explained by the small changes in the actual heat of the elementary act of the process, as evident from data relating to the barrier-free discharge ($\Delta A_0 = 1.5$ kcal). The corresponding contribution to the difference in the activation energy for the normal discharge is $\alpha \times 1.5 \simeq 0.7$ kcal. It is possible that the remaining difference (of the order of 1 kcal) is related to the great difficulty of introducing the hydrogen ion into the structured monolayer of ethylene glycol molecules at the electrode surface.

From the data in Figs. 2 and 4 the actual pre-exponential terms (K^p, A/cm²) were found to be as follows: for the barrier-free discharge $\log K_b^p = 4.3$, for normal discharge $\log K^p = 6.0$. In order to compare these values with one another and with the values for aqueous solutions it is necessary to know the entropy changes during the electrode process, i.e., those unavailable for a strict thermodynamic definition of the entropy of the H^+ ions.

A method has been suggested earlier for determining the entropy of an electrode process from the activation energies of the normal and barrier-free discharge and the overvoltage, corresponding to the point of intersection of the appropriate Tafel' lines [8]. The present authors have used this method to find the standard entropy of the hydrogen ion in ethylene glycol as equal to -7.8 ± 2 eu. This value is ~ 11 eu more negative than the standard entropy of H^+ in water found by the same method [9] (if the standard concentration is expressed not by the molarity, but by the mole fraction the difference is ~ 13 eu). Although this data is not very accurate it may be concluded that the more negative entropy of the H^+ in ethylene glycol indicates a lesser disordered structure of the solvent during proton solvation in the ethylene glycol in comparison with water.

It has been shown in [9] that the method described above for determining the entropy contains assumptions regarding the equality of tunnelling factors for the normal and barrier-free discharges. Consequently, there is no sense in using the values found above to compare the pre-exponential terms. In the literature there are no evaluations of the absolute entropies of ions in ethylene glycol obtained by other methods.

The actual pre-exponential terms for barrier-free and particularly for normal discharges in ethylene glycol are greater than in water (log $K_b^p = 3.0$ [4] and log $K^p = 3.9$ when $c_{H^+} = 0.1$ [6]). This compensates the small difference in the activation energy since the overvoltages in the barrier-free region practically coincide, while in the normal region the overvoltages are lower in the ethylene glycol.

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