Mechanism of an Elementary Act and the Kinetics of the Cathodic Evolution of Hydrogen

6.1. KINETIC ISOTOPE EFFECT AND $\psi_1$-POTENTIAL. LOCALIZATION OF A DISCHARGING ION

It has been mentioned above (see section 4.5) that in the case of hydrogen evolution in acidic solutions, the isotope separation factor depends considerably on the cathode potential. This was explained by the fact that the hydronium ion is attracted towards the electrode by the electric field. Naturally, this effect depends on the strength of the field which acts on the ion. Incidentally, irrespective of the mechanism by which the potential influences the isotope effect, the latter must directly depend not on the total metal solution potential drop, but on the potential difference between the metal and site at which the discharging ion is located. Hence, for different electrolyte solutions with different double-layer structures, the same isotope effect will be observed for identical values of $\phi - \psi_1$, where $\psi_1$ is the local potential at the site of the discharging ion.

This conclusion is in complete agreement with the experimental results. Figure 6.1 shows the $S$ vs $\eta$ dependence for different solutions, viz. for a surface-inactive electrolyte, and for solutions to which specifically adsorbed anions and cations have been added. It can be seen that the results for different solutions differ considerably. If, however, we assume, in accordance with the usual equations of the theory of slow discharge[1], that the change in overpotential at a constant concentration of $\text{H}^+$ ions is exactly equal to the change in the local $\psi_1$-potential (the coefficient $(1 - \alpha)/\alpha$ of the $\psi_1$-potential is equal to unity, since $\alpha = 1/2$ in the Tafel regions for the investigated solutions), the displacement of one curve with respect to the other by the difference in overpotentials enables us to
compare different solutions at the same value of $\phi - \psi_1$. Such a comparison is shown in Figure 6.2 (for solutions with different concentrations of H ions, an appropriate correction has been made to take into account the dependence of overpotential and equilibrium potential on pH) [291]. It can be seen that all the data, when reduced to the same local potential drop, fall on a single curve. It is quite significant that, in spite of the difference in the double layer structure, a consistently good agreement is observed in the presence of both surface-active anions and cations.

It is well known that anions influence the overpotential much more strongly than the potential of the outer Helmholtz plane. On the other hand, Parsons [385] observed that while equating $\Delta \eta$ to the

![Fig. 6.1. Dependence of the isotope separation factor for hydrogen (H and T) at a mercury cathode on overpotential. Solution composition: 0.1M MCl (1); 0.1M HCl + 5 x 10^{-3}M N(C_4H_9)_4Br (2); 2M MCl (3); 1M MCl + 2.9M NaI + 5 x 10^{-3}M N(C_4H_9)_4Br (4).](image)

![Fig. 6.2. Dependence of the isotope separation factor for hydrogen on potential drop $\phi - \psi_1$. Notation: same as in Figure 6.1.](image)