ELECTROLYTIC SEPARATION OF HYDROGEN ISOTOPES IN ALKALINE SOLUTION

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We have found that the separation coefficient S for hydrogen isotopes (protium and tritium) during electrolysis at a mercury cathode in aqueous solutions of 0.02 N $(CH_3)_4NOH$ and 0.02 N $(CH_3)_4NOH$ + 0.18 N $(CH_3)_4NI$ is independent of the electrode potential and solution composition having a value $S = 4.08 \pm 0.13$ in the range of hydrogen-evolution overvoltages (η) from 1.22 to 1.66 at a temperature of 30°C. The values of η agree with those of Korshunov [1].

The independence of S from η contradicts the model of the elementary discharge act proposed by Horiuti and Polyani [2], for which the activation process is the extension of an O—H bond. In this model, the $S(\eta)$ dependence is explained by a change in the probability for proton tunneling with a change in the height of a potential barrier [3]. In this sense there is no fundamental difference between acidic and alkaline solutions. However, in our measurements S is constant, although the activation energy (calculated from polarization measurements in the range 24.5 to 69°C) varied over a wide range (3.6-7.3 kcal/mole). In acidic solutions in this activation-energy range, the value of S changes considerably [3]. From the point of view of the model relating the activation to a reorganization of the solvent [4], a change in the activation energy would have no relation to a decrease in S with increasing η.

The $S(\eta)$ dependence is explained by the approach of an H_3O^+ ion toward the electrode, which increases the probability for a quantum jump of the proton [5]. For H_2O molecules, there is no reason to expect a significant change in their distance from the electrode; hence, one would expect a much weaker dependence of S on η in alkaline solutions than in acidic solutions, as is confirmed experimentally.

LITERATURE CITED

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