THE EFFECT OF ELECTRIC DOUBLE-LAYER STRUCTURE ON HYDROGEN ISOTOPE SEPARATION AT A MERCURY CATHODE IN ACID SOLUTIONS

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In spite of the relatively large body of experimental material concerning electrolytic hydrogen isotope separation, a more or less systematic study of the effect of electric double-layer structure on the hydrogen isotope separation factor (S) does not exist at the present time.

In the present work, separation in the system protium-tritium (T/H) was studied during electrolysis of acid solutions on a mercury cathode. The analysis for tritium content was similar to that described in [1]. Tritium was introduced into the solutions studied using water with a specific activity of 10^{-3} Ci/ml of H_2O, which was boiled in advance for 2-3 h at 100°C with potassium permanganate and alkali in an ampoule sealed under vacuum and then distilled under vacuum at room temperature. Solutions were prepared with triple-distilled water, all reagents were at least twice distilled or recrystallized. Prior to the experiment the solutions were treated cathodically in compartment 9 (Fig. 1) on platinized platinum and mercury (8) while passing hydrogen and agitating with the magnetic stirrer (10). Mercury from 2 and solution from 9 were then sucked into compartment 5 which was pumped out and purged with hydrogen. The solution volume was sufficiently large so that its enrichment in tritium could be disregarded. The evolving hydrogen was collected beneath stopcock 4 through which samples for analysis were withdrawn.

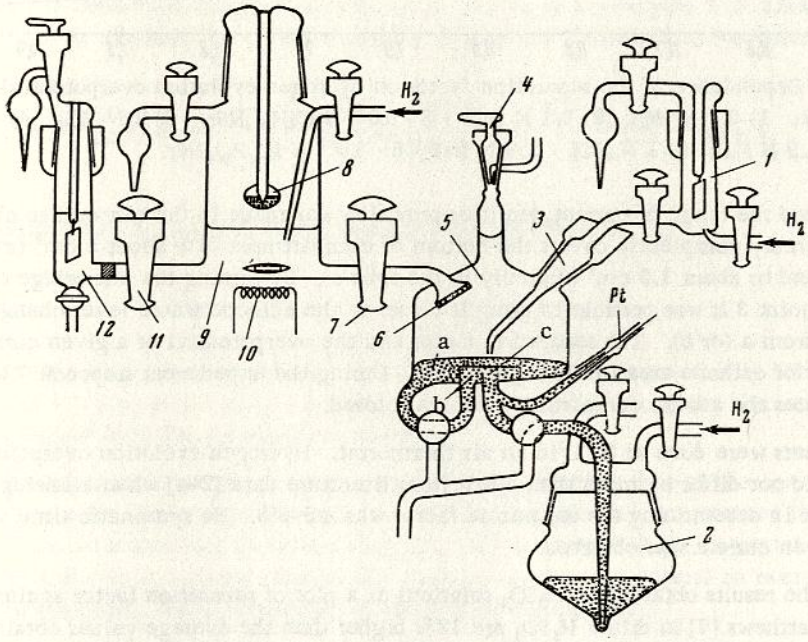

Fig. 1. Measuring cell (explanation in the text).

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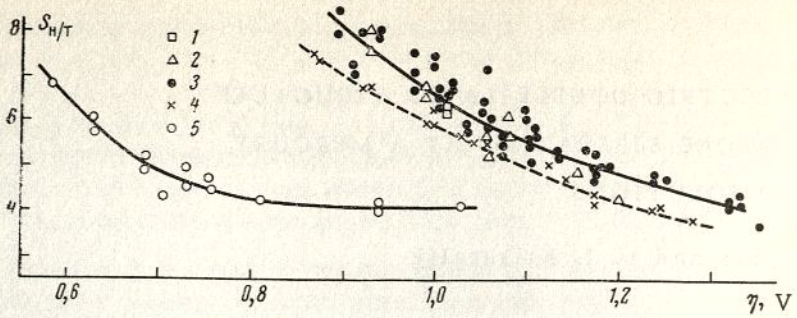

Fig. 2. Dependence of the separation factor on hydrogen evolution overpotential in H_2SO_4 solutions: 1) 0.01; 2) 0.1; 3) 1; 4) 10; 5) 20 N.

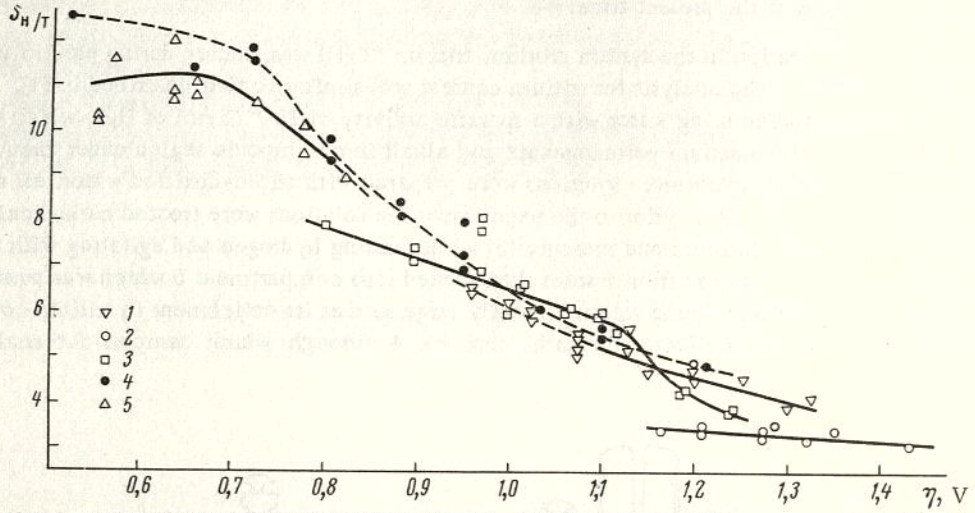

Fig. 3. Dependence of the separation factor on hydrogen evolution overpotential in the solutions: 1) 0.1 N HCl; 2) 0.1 N HCl + $5 \cdot 10^{-3}$ N$(C_4H_9)_4NBr$; 3) 2 N HCl; 4) 1 N HCl + 2.9 N NaI; 5) 1 N HCl + 2.9 N NaI + $5 \cdot 10^{-3}$ N $(C_4H_9)_4NBr$.

In order to expand the range of current densities provision was made in the test cell to change the cathode area from 20 cm^2 (mercury completely covers the bottom of compartment 5) to about 5 cm^2 (mercury drained from the angular space a) and to about 1.5 cm^2 (mercury in the tube c). By turning the salt bridge of the reference electrode 1 in the ground joint 3 it was possible to bring it closer to the cathode whose level changed somewhat when mercury was drained from a (or b). The separation factor and the overpotential at a given current density and solution were independent of cathode area in all experiments. During the experiment stopcock 7 was open, and stopcock 11, which separates the anodic compartment 12, was closed.

The measurements were done at 30°C in an air thermostat. Hydrogen evolution overpotentials in dilute acid solutions, as a rule, did not differ by more than 5 mV from literature data [2-4] when allowing for a temperature correction.* The error in determining the separation factor was ±5-6%. No systematic time variation of the separation factor at a given current was observed.

Figure 2 gives the results obtained in H_2SO_4 solutions as a plot of separation factor against overpotential. The data of Bockris and Matthews [7] in dilute H_2SO_4 are 12% higher than the average values obtained by us, and this is within the limits of experimental scatter of the data (± 6% for us and ± 8% in [7]). Neither the separation factor nor the character of its variation in these solutions depended on acid concentration over the range from 0.01 to 1 N. In these solutions the shift of the equilibrium potential (φ_0) and the variation of the ψ_1 potential compensate each other [8], so that with the coincidence of the corresponding curves one has no indication as to the parameter on which S directly depends, viz., on η or on the potential drop in the compact part of the double layer ($\Delta\varphi$). A clearer indication can be obtained from experiments where a substantial change in the ψ_1 potential takes place,

* Overpotentials in other solutions were also close to experimental data in [2, 5, 6] although quantitative comparison is not entirely rigorous because of incomplete match of the experimental conditions.

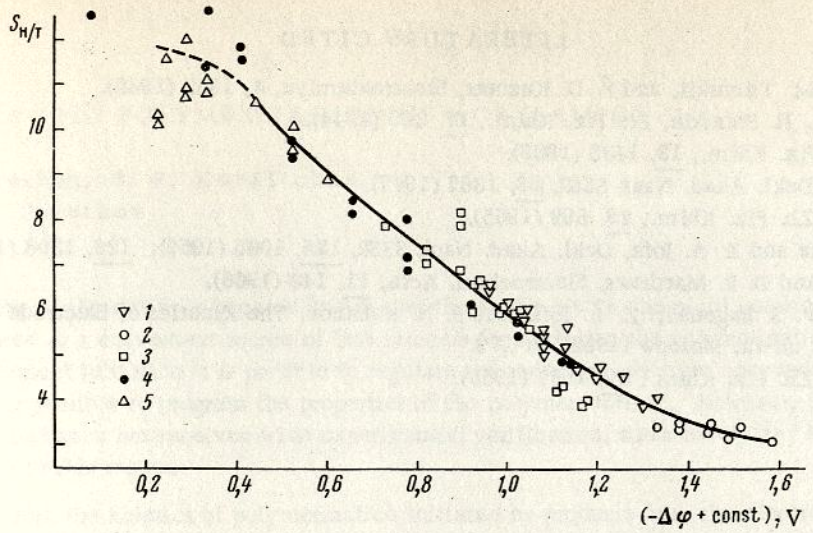

Fig. 4. Dependence of the separation factor on the potential drop in the compact part of the double layer: 1) 0.1 N HCl; 2) 0.1 N HCl + $5 \cdot 10^{-3}$ N $(C_4H_9)_4NBr$; 3) 2 N HCl; 4) 1 N HCl + 2.9 N NaI; 5) 1 N HCl + 2.9 N NaI + $5 \cdot 10^{-3}$ N $(C_4H_9)_4NBr$.

particularly at constant hydrogen ion concentration (Fig. 3). It is seen from these data that S is not an unequivocal function of η. We now examine the dependence of S on $\Delta\varphi = \varphi - \psi_1$, where ψ_1 must be understood as the potential in the point where the discharging ion is found, and not some averaged potential in the plane of closest approach of the ions to the cathode. Therefore, the ψ_1 potential must be determined from kinetic data.

It is not necessary to determine the absolute value of $\Delta\varphi$ in order to compare S in different solutions. We select one of the solutions as standard. At constant current density the difference in overpotentials in two solutions is [8]:

$$(\eta - \eta_{st})_i = -\frac{1-\alpha}{\alpha}\frac{RT}{F}\ln\frac{[H^+]}{[H^+]_{st}} + \frac{1-\alpha}{\alpha}(\psi_1 - \psi_{1\,st}). \quad (1)$$

Accounting for the definition of $\Delta\varphi$ and the Nernst equation, one gets from Eq. (1):

$$(\Delta\varphi - \Delta\varphi_{st})_\eta = -\frac{\alpha}{1-\alpha}(\eta - \eta_{st})_i. \quad (2)$$

In these equations α is assumed to be independent of solution composition. In practically all our experiments α = 0.5. Thus in going from S = S(η) to S = S($\Delta\varphi$ + const), S(η) must be shifted along the abscissa by a quantity $(\eta - \eta_{st})_i$ which is determined from the polarization curves.

Figure 4 gives the dependence of the separation factor on the potential drop in the constant part of the double layer.* The good agreement – within experimental error limits – between results obtained in solutions of different composition shows that the separation factor almost always is only a function of the potential drop in the compact part of the double layer and that at a given value of this quantity, it does not depend on overpotential, the equilibrium potential of the electrode, the ψ_1 potential, or electrolyte composition.

The average values of S in dilute H_2SO_4 and HCl differ by 4-8%; taking into account the error in the measurements one cannot say how real this difference is and what its possible reasons are. In concentrated H_2SO_4 solutions S is noticeably lower than in dilute solutions (Fig. 2), particularly when plotted as S against $\Delta\varphi$. This difference can be explained by the fact that HSO_4^-, not H_3O^+ is the most probable proton source in concentrated acid [9].†

* Figure 4 is constructed so that for the standard solution, 0.1 N HCl, it has been conditionally assumed that $\Delta\varphi$ + const = η_{st}.

† In other solutions, the basic reaction is hydrogen ion discharge, even at rather high total electrolyte concentration [9].

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