INFLUENCE OF THE NATURE OF A METAL ON THE SEPARATION FACTOR OF HYDROGEN ISOTOPES

V. M. Tsionskii and L. I. Krishtalik

UDC 541.138

This paper is devoted to an investigation of the dependence of the separation factor ($S_{H,T}$) of hydrogen isotopes (protium—tritium) on the nature of the metal. The objects chosen were metals on which the most probable reaction is a slow discharge of hydrogen ions with subsequent rapid electrochemical desorption:

$$H_3O^+ + e^- \rightarrow H_a + H_2O, \qquad (I)$$

$$H_a + H_3O^+ + e^- \rightarrow H_2 + H_2O. \qquad (II)$$

Figure 1 illustrates the results in a plot of $S_{H,T}$ versus η_{H_2} (the potential difference of hydrogen separation) obtained in a solution of 1 N H_2SO_4 at a temperature of 30°C. The same graph shows previous results [1] obtained with a Hg cathode in 1 N H_2SO_4 and hydrochloric solution.* The method of experiment was the same as that used in [1]. In order to insert a lead electrode, the design of the measuring cell was changed accordingly without influencing its general character. The electrodes were prepared and purified as described in [2-6]. With a smooth lead electrode, at 20-25°C, the value of η_{H_2} varies in an interval of 160 mV (according to data from [2-4]). Our results also lie in this interval. The polarization curve obtained with a Tl amalgam (40.6 at% Tl, purity 99.9996%) agreed within the limits of experimental accuracy (± 3 mV) with the data given in [5]. The polarization curves obtained with gallium (purity 99.9997%) in the various experiments differed by at most 10-15 mV, and within these limits they agree with the results of [6].

---

*The latter results were plotted in Fig. 1 such that with given η_{H_2} in 1 N H_2SO_4 and hydrochloric solutions the potential jumps in the dense part of the double layer are equal [1].

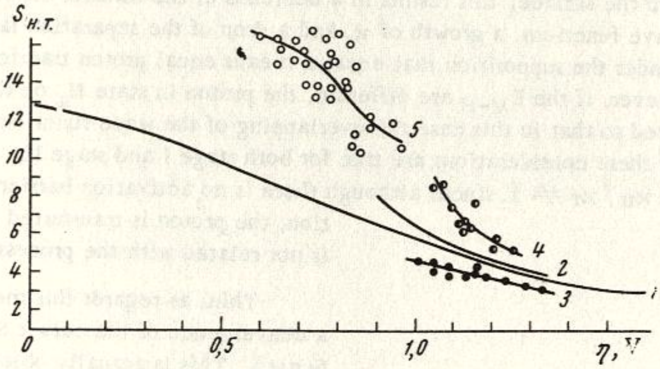

Fig. 1. Dependence of the separation factor on the potential difference of hydrogen separation: 1) Hg, hydrochloric solutions; 2) Hg 1 N H_2SO_4; 3) amalgam with 40.6 at % Tl, 1 N H_2SO_4; 4) Pb, 1 N H_2SO_4; 5) Ga, 1 N H_2SO_4.

Moscow Institute of Electrochemistry, Academy of Sciences of the USSR. Translated from Élektrokhimiya, Vol. 6, No. 2, pp. 265-268, February, 1970. Original article submitted May 28, 1969.

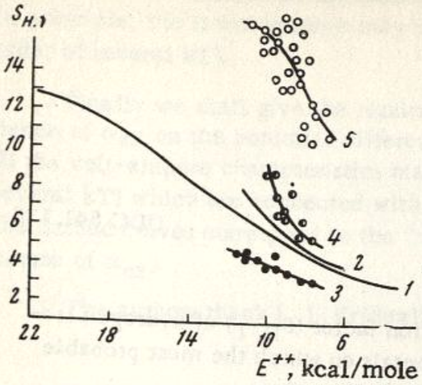

Fig. 2. Dependence of separation factor on the activation energy of hydrogen separation. Same notations as in Fig. 1.

Let us consider our results from the point of view of the theory based on the ideas of Horiuti and Polanyi [7] on an activation by O-H bond stretching. With this model the decrease of S accompanying an increase of the potential difference can be explained by a reduction of the potential barrier and thus by an increase of the tunneling probability of the hydrogen ion which results in a decrease of the difference between the preexponential factors for the isotopes. When different metals are compared with potential differences corresponding to equal activation energies ($E^{\neq}$), i.e., in a first approximation to like potential barriers, in the model considered the S values of all metals must coincide, a fact which cannot be observed (Fig. 2).* With equal activation energies of metals with smaller bond energies (E_{M-H}), owing to the flatter potential curve, the width of the barrier can be a little larger so that the tunneling probability decreases, that is, S will grow and E_{M-H} will decrease. In other words, this model representation lets us expect that, unless the S values of different metals agree perfectly, they should at least drop with given $E^{\neq}$ according to the series: Tl amalgam, Pb, Hg, Ca. This conclusion is not verified by experiment either (Fig. 2).

The above considerations are, strictly speaking, only applicable to S in stage I, while the quantity measured is also influenced by stage II [9]. For metals with high potential differences stage II in all probability is a nonactivation state and the particles discharged will be water molecules [10]. According to the Horiuti-Polanyi model S = 1 for a nonactivation state or, in the absence of an activation barrier, neither the difference of zero energies nor tunneling will play a role. In this case, however, the total value of S would not exceed 2 which is in contradiction with the experiment.†

In agreement with the model of the elementary event of hydrogen ion discharge developed by Dogonadze, Kuznetsov, and Levich [12], solvent reorganization is a process causing activation; however, the transfer of a proton from the ion to the metal takes place without changing the energy of the system. The transition probability ($\varkappa$) is the higher, the higher the degree of overlapping of the proton wave functions referring to the states of the adsorbed hydrogen and the hydroxonium ion. The value of $\varkappa$ depends on the mass of the hydrogen ion ($\varkappa_H > \varkappa_D > \varkappa_T$) and on the transfer distance of the proton. The potential dependence of S can be explained by the fact that, as the potential grows, i.e., as the negative surface charge of the electrode is raised, the force is intensified by which the hydroxonium ion is attracted to the surface; this results in a decrease of the transfer distance of the proton, an increase of the overlapping of the wave functions, a growth of $\varkappa$, and a drop of the separation factor. For two metals with equal surface charges (q), under the supposition that equal q means equal proton transfer distances, the separation factors must be equal. However, if the E_{M-H} are different, the proton in state H_a on the metal with the higher bond energy will be more localized so that in this case the overlapping of the wave functions will be smaller and thus S higher. It is important that these considerations are true for both stage I and stage II. Here, even for nonactivation electrochemical desorption $\varkappa_H / \varkappa_T \neq 1$, since, although there is no activation barrier for the solvent's reorganization, the proton is transferred with a probability $\varkappa < 1$ ($\varkappa$ is not related with the process of solvent reorganization).

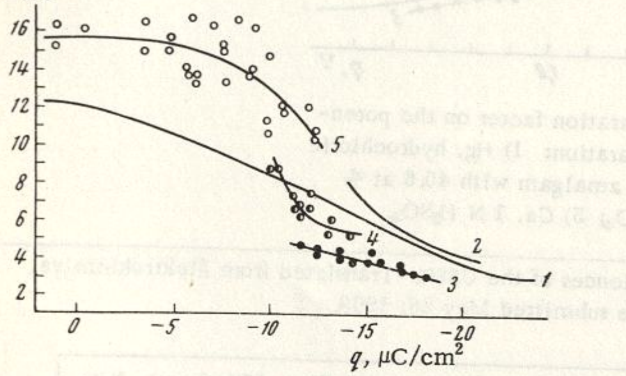

Fig. 3. Dependence of separation factor on the surface charge of the electrode. Same notations as in Fig. 1.

Thus, as regards this mechanism, we have to expect a convergence of the curves S(q) compared with the curves $S(\eta_{H_2})$. This is actually observed experimentally (Fig. 3).‡ A perfect coincidence however, need not take place as S must grow with increasing E_{M-H} because of the decreasing

---

* For different metals the quantity $E^{\neq}$ is calculated from data compiled in [8].

† With nonactivation desorption involving H_3O^+ ions the total value of $S \leq 2K$, K being the separation factor of the reaction $HTO + H_3O^+ \rightleftharpoons H_2TO^+ + H_2O$, $K = 1{,}7$ [11], i.e., $S \leq 3.4$, which also is essentially lower than the experimental value.

‡ To pass over from the coordinates S, η_{H_2} to the coordinates S, q we can use the data on the surface charge for Ga from paper [13], Hg from [14], Tl amalgam from [15], and Pb from [16].

proton transfer probability. From Fig. 3 we see that with given q the quantity S will actually decrease according to the series Ga, Hg, Pb, Tl amalgam, i.e., in the same order according to which E_{M-H} decreases.

LITERATURE CITED

1. V. M. Tsionskii and L. I. Krishtalik, Élektrokhimiya, 5, 1184 (1969).
2. B. Kabanov, S. Filippov, L. Vanyukova, Z. Iofa, and A. Prokof'eva, Uh. Fiz. Khim., 13, 341 (1939).
3. Ya. Kolotyrkin and N. Buné, Zh. Fiz. Khim., 21, 581 (1947).
4. U. V. Pal'm and V. É. Past, Dokl. Akad. Nauk SSSR, 146, 1374 (1962).
5. J. N. Butler, E. A. Barron-Apps, and M. L. Meehan, Trans. Faraday Soc., 61, 2509 (1965).
6. K. Sabo and I. A. Bagotskaya, Dokl. Akad. Nauk SSSR, 150, 128 (1963); E. Preis, K. Sabo, S. Raicheva, and I. A. Bagotskaya, Élektrokhimiya, 2, 1209 (1966).
7. J. Horiuti and M. Polanyi, Acta Phisicochim. URSS, 2, 505 (1935).
8. V. Tsionskii, Élektrokhimiya, 5, 1500 (1969).
9. J. O'M. Bockris and S. Srinivasan, J. Electrochem. Soc., 111, 844, 853, 858 (1964).
10. I. L. Krishtalik, Élektrokhimiya, 4, 877 (1968).
11. W. J. Albery, Progress in Reaction Kinetics, Ed. G. Porter, 4, 353 (1967).
12. R. R. Dogonadze, A. M. Kuznetsov, and V. G. Levich, Élektrokhimiya, 3, 739 (1967).
13. A. N. Frumkin, I. A. Bagotskaya, and N. B. Grigor'ev, Dokl. Akad. Nauk SSSR, 157, 957 (1964).
14. D. C. Grahame, Chem. Revs., 41, 441 (1947).
15. A. N. Frumkin and A. V. Gorodetskaya, Z. Phys. Chem., A136, 451 (1928).
16. K. V. Rybalka and D. I. Leikis, Élektrokhimiya, 3, 383 (1967).