Calculation of the experiment parameters by the steep ascent method and the results of gradient movement are given in Table 2. As starting point of gradient movement the conditions of experiment No. 5 (Table 1) were taken.

With gradient movement the material and current yields of IVA increased. Continuation of further gradient movement was not expedient since the fall of current density increased the duration of the electrolysis and the increase of temperature promoted degradation of the IVA which was formed.

Taking this into consideration, for the electrosynthesis of IVA in an alkali medium at an impregnated graphite electrode the following conditions can be recommended: IAA concentration, 0.25 M; nickel sulfate, 7 g/liter; current density, 30 mA/cm^2; temperature 64°C. Current yield was 99.5%. IVA synthesized in this way was a purer product compared with that obtained by chemical oxidation of IAA with potassium permanganate and subsequent distillation (Fig. 2).

LITERATURE CITED

1. B. S. Remorov, V. P. Ponkratov, I. A. Avrutskaya, and M. Ya. Fioshin, Élektrokhimiya, 16, No. 6, 877-880 (1980).
2. B. S. Remorov, I. A. Avrutskaya, and M. Ya. Fioshin, Élektrokhimiya, 16, No. 5, 723-726 (1980).
3. USSR Author's Certificate No. 297278; Byull. Izobret., No. 29 (1971).
4. B. S. Remorov, I. A. Avrutskaya, and M. Ya. Fioshin, Élektrokhimiya, 17, 643 (1981).

INFLUENCE OF IODIDE ON THE EVOLUTION OF HYDROGEN FROM ACID SOLUTIONS AT A GALLIUM CATHODE

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Two limiting cases of the influence of the specific absorption of iodide on the kinetics of the evolution of hydrogen from acid solutions are known. In the case of mercury, the addition of iodide to the solution decreases the overvoltage through a displacement in the negative direction of the ψ_1-potential in the plane where the discharging hydroxonium ion is located [1, 2]. Such a change in the ψ_1 potential leads to an increase (at the same overvoltage) in the kinetic isotope effect [3]. In contrast to mercury, on iron the adsorption of iodide considerably increases the overvoltage [4, 5], but it does not change the kinetic isotope effect [6]. For a number of metals (gallium [7], lead [8], and cadmium [9]), the overvoltage of the evolution of hydrogen increases only slightly when iodide is added to the solution. To explain the influence of iodide on the kinetics of the evolution of hydrogen on all metals except mercury two possibilities are usually employed: either the assumption that the adsorption of iodide leads to a change in the energy of adsorption of atomic hydrogen (E_{M-H}) or the idea of a complex structure of the double layer.

The kinetic isotope effect (KIE) is sensitive to a change in the ψ_1 potential and simultaneously depends on E_{M-H}. The sensitivity of the KIE to the ψ_1 potential is due to the fact that the difference in the probability of a quantum-mechanical jump of a particle depends on the distance of the jump and, in the case of acid solutions, on how close to the electrode the discharging H_3O^+ ion is located. The latter is determined by the force acting on the ion on the part of the electrode, i.e., by the jump in potential between the electrode and the position where the discharging ion is located. This explains, in particular, the decrease in the KIE with a rise in the negative potential [3]. At a constant potential, however, the KIE must change if the ψ_1-potential has changed, since on it depends the potential in the dense part of the double layer. All this is true if the adsorption processes changing the ψ_1-potential do not involve changes in E_{M-H} (as takes place on mercury), since a decrease in E_{M-H} leads to a decrease in the KIE. We have previously [10] revealed the dependence of the

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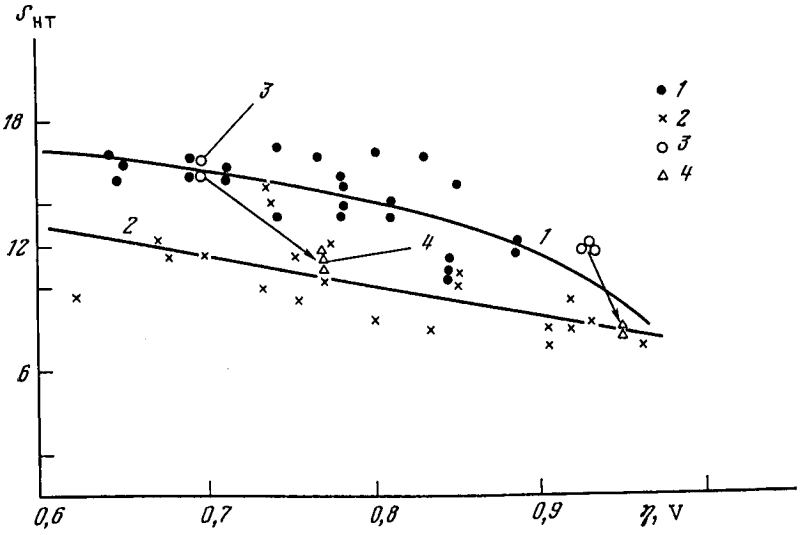

Fig. 1. Dependence of the distribution coefficient on the overvoltage on gallium in 0.5 M H_2SO_4 (1, 3) and in 0.5 M H M_2SO_4 + 1 M KI (2, 4).

KIE on E_{M-H} by comparing the isotope effects obtained on various metals at the same charge of the electrode (q), i.e., thereby excluding a dependence of the KIE on the force acting on the discharging H_3O^+ ion. All that has been said above permits the use of the isotope effect for elucidating the mechanism of the influence of iodide on the kinetics of the evolution of hydrogen.

In the present investigation we have measured the protium-tritium distribution coefficient in the evolution of hydrogen at a liquid gallium cathode (30°C) from a 0.5 M H_2SO_4 + 1 M KI solution. All the reagents were redistilled or recrystallized not less than twice. Before an experiment, the solutions were cathodically polarized successively at platinized platinum and mercury for about 20 h with a current of 5 mA with constant flushing by hydrogen and stirring with a magnetic stirrer. The potentials were measured and were referred to a hydrogen electrode in the same solution. We used gallium containing not more than 0.00014% of impurities.

The parameters of the polarization curves of the cathodic evolution of hydrogen obtained in our experiments agree with those found by Bagotskaya and Khalturina [7]. Figure 1 shows the results of measurements of the distribution coefficient (S) in the absence of iodide [10] (curve 1) and in the presence of iodide (curve 2). It can be seen from a comparison of these curves that iodide decreases the isotope effect. Since the error in the determination of the isotope effect on gallium is considerable, as can be seen from the figure, it was necessary to make a comparison of the isotope effects in the presence of iodide and without it within the limits of a single experiment: the distribution coefficient was determined in the absence of iodide (points 3), after which iodide was added to the solution and the distribution coefficient was measured again at the same current (points 4). These changes are shown in the figure by arrows. As can be seen from the figure, the measurements in pure sulfuric acid agreed with our previous results, and the measurements of the distribution coefficient after the addition of iodide agreed with curve 2. Thus, there is no doubt that the addition of iodide to the solution decreases the isotope effect.

Let us assume that the influence of iodide on the kinetics of the evolution of hydrogen on gallium amounts exclusively to a ψ_1-effect. In this case, it must be assumed that the action of iodide is analogous to the action of the tetrabutylammonium cation on mercury, i.e., the increase in the overvoltage by 20-30 mV is due to a shift of the ψ_1-potential by the same amount in the positive direction. Then the potential jump in the dense part of the double layer becomes negative by the same amount. If, however, the distribution coefficient is, as in the case of adsorption of mercury, an unambiguous function of the potential jump in the dense part of the double layer, the displacement of curve 2 by 20-30 mV to the right relative to curve 1 would produce coincidence of these curves. However, as can be seen from the figure this requires a shift not of 30 mV but of some hundreds of mV. Thus, the observed decrease in the distribution coefficient, as also the rise in overvoltage, in the adsorption of iodide on gallium cannot be ascribed exclusively to the action of the ψ_1-effect.

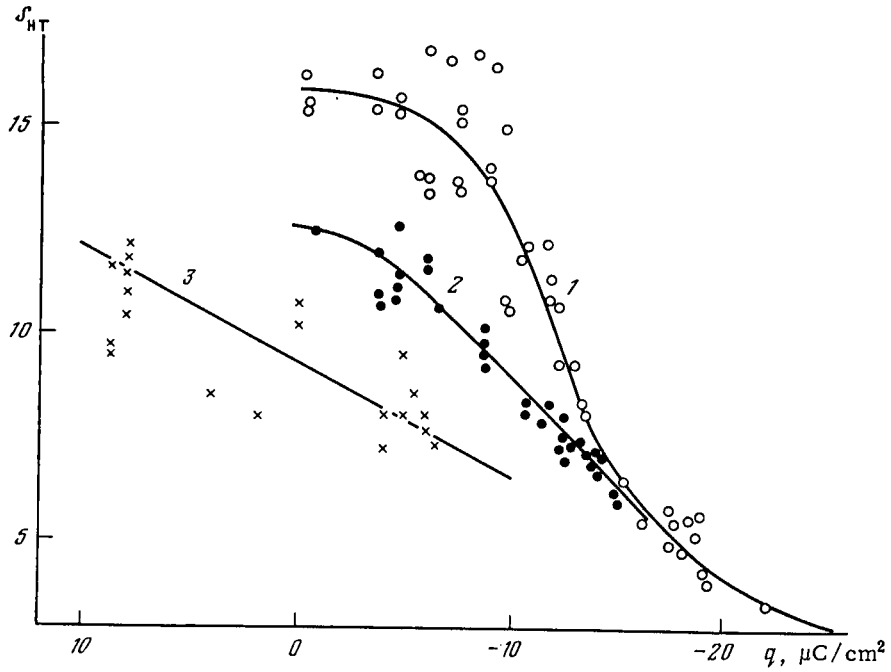

Fig. 2. Dependence of the distribution coefficient on the charge of the electrode: 1) Ga; 2) Hg; 3) Ga in the presence of iodide.

Let us consider whether it is possible to explain the observed effects with the aid of an assumption of a change in the energy of adsorption of atomic hydrogen in the presence of adsorbed iodide. In order to determine the dependence of the distribution coefficient on the energy of adsorption of atomic hydrogen we must compare the isotope effects at the same distance of the proton jump, i.e., at the same force acting on the discharging H_3O^+ ion. For such a comparison it is possible to use either the charge on the surface or the potential jump between the discharging ion and the electrode. The latter could be calculated (to an accuracy corresponding to a constant) for a mercury electrode from the difference in the overvoltages in solutions with iodide and without it [3], but in our case this cannot be done since we assume that it is not only the change in the ψ_1 potential that affects S and the overvoltage. Figure 2 shows the dependence of S on the charge of the electrode. For gallium in 0.5 M H_2SO_4 and on mercury it was taken from [10], and for gallium in a solution containing iodide it was plotted on the basis of curve 2 of Fig. 1 and the dependence of the charge of a gallium surface in the presence of iodide on the potential from the results of Frumkin et al. [11], It can be seen from Fig. 2 that S is substantially less in the presence of iodide than in a solution containing no iodide. This means that the adsorption of iodide anions on gallium substantially lowers the energy of adsorption of atomic hydrogen and, judging from the positions of curves 2 and 3, makes it close to the energy of adsorption of hydrogen on mercury (and possibly even below it). The fall in E_{M-H} on the adsorption of iodide can be explained by the assumption that both iodide and atomic hydrogen are electron donors and their combined adsorption weakens the bond with the surface. A decrease in E_{M-H} should considerably raise the overvoltage of the evolution of hydrogen on gallium and, perhaps, even make it higher than on mercury. Nevertheless, the observed increase in overvoltage on the addition of iodide is much smaller than the difference in the overvoltages on mercury and gallium in solutions containing no iodide (this difference is close to 300 mV [12]). To all appearance, when iodide is adsorbed on gallium a competition takes place between the effect of the lowering of E_{M-H} (which we judge from the decrease in the KIE) and a shift of the ψ_1 potential in the negative direction, as is the case on mercury. Thus, the observed small (20 mV) increase in the overvoltage on gallium in the presence of iodide is the result of two large effects taking place in opposite directions.

It must be mentioned that it is possible to explain the change in the KIE solely by a change in E_{M-H} only on the assumption that, regardless of the adsorption of iodide the same distances of the proton jump correspond to the same charges of the surface. In principle, it is possible to explain the decrease in the KIE on gallium in the presence of iodide by a

decrease in the distance of the proton jump, which levels out the difference in the probability of the tunneling of isotopes of different masses. The decrease in the jump distance could be connected with a substantial change in the structure of the double layer in the presence of strongly adsorbed iodide and, in particular, with the approach of the inner Helmholz plane to the electrode. A decrease in the jump distance of the proton means an increase in the probability of its tunneling, i.e., a rise in the pre-exponential factor of the kinetic equation of the reaction. In any case, whether the proton jump distance or the ψ_1-potential or both these magnitudes change, the factor acting in the opposite direction and making a slight difference in the overvoltages on gallium with iodide and without is the decrease in E_{M-H} in the presence of iodide. It does appear possible to evaluate quantitatively to what extent the inhibition of the reaction through the decrease in E_{M-H} is compensated by the increase in the pre-exponential factor and the shift of the ψ_1-potential in the negative direction. However, it is quite obvious that the observed effect cannot be explained without taking influences in opposite directions into account.

LITERATURE CITED

1. A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa, and B. N. Kabanov, The Kinetics of Electrode Processes [in Russian], Izd. Mosk Univ., (1952).
2. L. I. Krishtalik, J. Electroanal. Chem., 35, 157 (1972).
3. V. M. Tsionskii and L. I. Krishtalik, Élektrokhimiya, 5, 1184 (1969).
4. Z. A. Iofa and Kam Fan Lyong, Élektrokhimiya, 7, 696 (1971).
5. K. E. Heusler and G. H. Cartledge, J. Electrochem. Soc., 108, 732 (1961).
6. T. Sh. Korkashvili, V. M. Tsionskii, and L. I. Krishtalik, Élektrokhimiya, 16, 886 (1980).
7. I. A. Bagotskaya and T. I. Khalturina, Elektrokhimiya, 5, 1085 (1969).
8. Ya. M. Kolotyrkin and L. A. Medvedeva, Zh. Fiz. Khim., 25, 1355 (1951).
9. Ya. M. Kolotyrkin and L. A. Medvedeva, Zh. Fiz. Khim., 29, 1477 (1955).
10. V. M. Tsionskii and L. I. Krishtalik, Élektrokhimiya, 9, 810 (1973).
11. A. N. Frumkin, N. B. Grigor'ev, and I. A. Bagotskaya, Dokl. Akad. Nauk. SSSR, 157, 957 (1964).
12. I. A. Bagotskaya, E. A. Preis, K. Sabo, and S. Raicheva, Élektrokhimiya, 2, 1209 (1966).

DETERMINATION OF THE DIFFUSION COEFFICIENTS OF SPARINGLY SOLUBLE COMPOUNDS BY THE TWIN CELL METHOD

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Thin-layer methods are extremely promising for the investigation of electrochemical processes. They are simple and convenient and permit working with very small amounts of substance (of the order of 10^{-9} mole). The essence of thin-layer procedure is that a very thin layer of electrolyte (10-50 μ) immediately adjacent to the electrode surface is subjected to electrolysis. In such a thin layer, the convective transfer of the reactants is practically excluded, and therefore the mathematical description of the processes taking place at the electrodes is considerably simplified. The most widely used method is thin-layer voltammetry [1, 2] in which a slow potential sweep is applied to the working electrode with the aid of an external auxiliary electrode placed beyond the limit of the thin-layer part of the cell and cyclic current—potential curves analogous in some degree to derivative polarographic waves are recorded. The method is used mainly to investigate reversible systems or, on the other hand, slow electrochemical reactions.

Another variant of the thin-layer method is the so-called twin-cell method [3] in which a difference of potentials is applied to plane-parallel electrodes and a steady-state diffusional flow of electro-active component is established in a thin layer; being reduced at one electrode it diffuses to the other, where it is oxidized. With the aid of an external aux-

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