KINETIC ISOTOPE EFFECT IN THE CATHODIC EVOLUTION OF HYDROGEN ON MERCURY–GALLIUM ALLOYS

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In the present work, we have investigated the kinetic protium–tritium isotope effect in the electrolytic evolution of hydrogen from acid solutions on mercury–gallium alloys. The experimental method and also the relation between the kinetic isotope effect and the mechanism and elementary act of the hydrogen evolution process have been reported in previous works [1-3]. The experimental results are given in Fig. 1. For comparison, Fig. 1 also gives data for mercury and gallium [4]. The plots of hydrogen-isotope separation factor (S) versus electrode potential obtained in the experiment were transformed into plots of S versus q (the charge on the electrode surface) using the data in [5]. It can be seen from Fig. 1 that both in all the cases studied previously [1, 3, 4] and in the case of the Hg–Ga alloys, the kinetic effect associated with hydrogen evolution from acid solutions decreases as the negative charge of the electrode surface increases. Within the limits of experimental error, our polarization curves are in agreement with the data in [6], in which the hydrogen overvoltage was observed to increase monotonically at constant current as the alloy composition changed from pure gallium to mercury. It can be seen from Fig. 1 that at low mercury concentrations (x_{Hg}) in the alloy, the isotope effect is the same as on pure gallium. At intermediate x_{Hg} values, the isotope effect is not only greater than that on mercury but also exceeds the effect observed on gallium (at the same surface charges), while S decreases when $x_{Hg} > 0.0024$ atomic fraction. The isotope effect on the 2.14% alloy is practically the same as that on mercury and gallium, since we were able to measure it only at high surface charges, at which the separation factors on mercury and gallium are the same. The maximum separation factor was observed at $x_{Hg} = 0.0024$ atomic fraction (curve 4).

The nonmonotonic dependence of the separation factor and the monotonic dependence of the overvoltage on the composition of the alloy can be explained on the basis of the following hypothesis. As is known [7], the mercury in mercury–gallium alloys is surface active, and the positive mercury adsorption for the 0.24% alloy is $1.5 \cdot 10^{-9}$ mole/cm^2, i.e., close to a monolayer. As can be estimated from the data in [7], the limiting mercury adsorption is approximately twice this value. Although the detailed picture of the composition distribution in the vicinity of the alloy surface is unknown, we can nevertheless state that a considerable proportion of the surface of the 0.24% alloy is covered with mercury. Since the atomic radius of gallium is 0.2 Å less than that of mercury [8], we can assume that H_3O^+ ions cannot approach as closely to the gallium atoms in the alloy as they can in the case of a surface not covered with mercury. This will lead to an increase in the proton jump distance and consequently to an increase in the isotope effect [1, 3] on the gallium atoms in the alloy compared with pure gallium (or alloys with a low mercury concentration). At a given potential, the rate of hydrogen evolution on gallium is approximately 400 times that on mercury [9]. Consequently, the fraction of the current due to discharge on the gallium atoms in the alloy may be greater than the fraction of the current due to discharge on the mercury atoms, and since the isotope effect on the gallium atoms in the alloy is greater than that on pure gallium, the total isotope effect on the alloy may be greater than that on pure gallium. As the concentration of mercury in the alloy increases, its concentration on the surface also increases [7], so that the contribution of the current due to discharge on the mercury atoms to the isotope effect increases, resulting in a decrease in the observed separation factor as the mercury content of the alloy increases.

The observed dependence of the overvoltage on the alloy composition can be explained in the same way as the dependence of S on x_{Hg}: An increase in mercury concentration will lead to a simultaneous decrease in the number of gallium atoms on the surface and to an increase in the proton jump distance, i.e., to a decrease in the probability of discharge on the gallium atoms and an increase in the probability of discharge on the mercury atoms. This will increase the overvoltage at a given current. In the limiting case of high x_{Hg} values,

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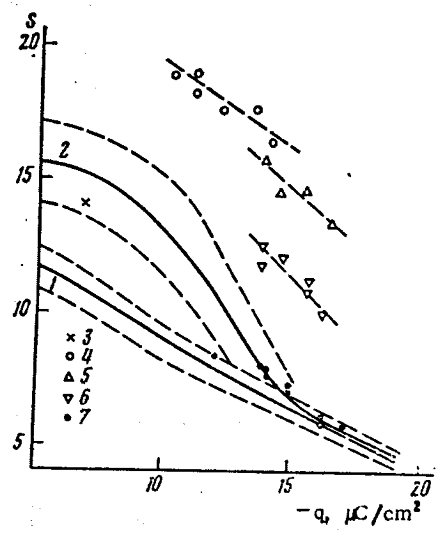

Fig. 1. Dependence of the protium−tritium separation factor on the surface charge of the electrode (32°C, 1 N H_2SO_4): 1) on mercury [1, 3, 4]; 2) on gallium [3, 4]; and on their alloys with Hg contents (atomic fractions) of: 3) 0.0011; 4) 0.0024; 5) 0.0065; 6) 0.0112; 7) 0.0214. The dotted lines for curves 1 and 2 indicate the limits of the spread of the experimental data.

the surface of the alloy will probably be completely covered with mercury and the participation of the gallium atoms in the evolution of hydrogen will become insignificant. This is why the overvoltages measured on the alloy with x_{Hg} = 0.0214 atomic fraction and on pure mercury are equal [6].

The temperature dependence of the kinetics of hydrogen evolution on a gallium−mercury alloy with x_{Hg} = 0.0214 atomic fraction has been investigated in [9]. It was found that although the hydrogen overvoltages on pure mercury and the alloy are close at room temperature, the calculated values of the preexponential factor and activation energy of the reaction on the alloy differ considerably from those on mercury. Thus, the calculated preexponential factor for the alloy is ~ 10^4 times higher than for mercury. Such an increase in the preexponential factor should be accompanied by an appreciable decrease in isotope effect [3], but this is not confirmed experimentally: The isotope effects on the alloy and mercury are practically the same (see Fig. 1, curves 1 and 7). It seems to us that the temperature dependence of the kinetics of hydrogen evolution on the alloys may be distorted to a considerable extent by the temperature dependence of the surface state of the alloy. Thus, it is known that the solubility of mercury in gallium increases by a factor of 1.5 when the temperature is increased from 32 to 80°C [10], and this is the temperature range in which the kinetics of hydrogen evolution on the alloy containing 0.0214 atomic fraction of mercury were studied in [9]. An alloy with this concentration will be saturated at room temperature; at higher temperatures, it will not be saturated and it is reasonable to assume that the surface coverage of the alloy with mercury atoms will decrease, i.e., the proportion of the current due to discharge on gallium atoms, on which the overvoltage is lower than on the sections covered with mercury, will increase. It is probably this effect which leads to $|d\eta/dT|$ being too high, i.e., to overestimation of the calculated activation energy and preexponential factor of the reaction.

When the relative variation in solubility with temperature is slight, the distortion of the temperature dependence of the kinetics of hydrogen evolution will probably also be slight. Such systems include, in particular, amalgams of indium and thallium [10]. The results of temperature measurements of the kinetics of hydrogen evolution on these [11] can be regarded as being more reliable than those on mercury−gallium alloys.

LITERATURE CITED

1. V. M. Tsionskii and L. I. Krishtalik, Élektrokhimiya, 5, 1184 (1969).
2. L. I. Krishtalik, Élektrokhimiya, 6, 1456 (1970).
3. L. I. Krishtalik and V. M. Tsionskii, J. Electroanalyt. Chem., 31, 363 (1971).
4. V. M. Tsionskii and L. I. Krishtalik, Élektrokhimiya, 9, 810 (1973).
5. N. S. Polyanovskii and A. N. Frumkin, Élektrokhimiya, 3, 1129 (1967).
6. L. M. Dubova, N. B. Grigor'ev, and I. A. Bagotskaya, Élektrokhimiya, 8, 1359 (1972).
7. N. S. Polyanovskii and T. V. Kalish, Élektrokhimiya, 5, 455 (1969).
8. Chemist's Handbook [in Russian], Vol. 1, Goskhimizdat, Moscow (1962), p. 380.
9. E. N. Potapova, L. I. Krishtalik, and I. A. Bagotskaya, Élektrokhimiya, 10, 49 (1974).
10. M. N. Gavze, Reaction of Mercury with Metals and Alloys [in Russian], Nauka, Moscow (1966), p. 89.
11. J. N. Butler and A. C. Makrides, Trans. Faraday Soc., 60, 1665 (1964); J. N. Butler, E. A. Barron-Apps, and M. L. Meehan, Trans. Faraday Soc., 61, 2509 (1965).