OVERVOLTAGE OF HYDROGEN ON MERCURY AT LOW CURRENT DENSITIES

III. INFLUENCE OF THE ACTIVITY OF WATER

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The overvoltage of hydrogen on mercury was investigated in acidified concentrated solutions of LiBr and NaBr, and the data on solutions of KI were supplemented. In the region of barrierless discharge, the nature of the anion, in full agreement with the theory, has no effect on the overvoltage. It was demonstrated that the activity coefficient of water does not influence the overvoltage, i.e., that the activity coefficient of the transition state depends upon the activity coefficient of water. This conclusion can be substantiated on the basis of the identity of the activated and final states for barrierless discharging.

In our previous communications [1,2] it was shown that the evolution of hydrogen on mercury at low overvoltages occurs by barrierless discharging of hydrogen ions (or under suitable conditions, of nondissociated acid molecules). A characteristic feature of barrierless discharge is equality of the activation energy and heat of the elementary event of the reaction; from this follow the values $\alpha = 1$ and the independence of the overvoltage in the discharging of H_3O^+ ions from the composition of the solution and structure of the double-layer [3].

The latter peculiarity permits the use of barrierless discharge for the solution of certain problems, practically inaccessible to experimental study under the conditions of the usual discharge. The most important among these seems to us to be the question of the influence of the activity of water – one of the two products of electrochemical conversion of the hydroxonium ion – upon the overvoltage. Appreciable deviation of the activity of water from 1 is observed only in extremely concentrated solutions of electrolytes, in which there may be large ψ_1-effects, associated with the specific adsorption of ions. An exact calculation of the ψ_1-potential in such solutions is practically impossible, while the errors in its approximate estimation are known to exceed the possible influence of the activity of water. Therefore, under the conditions of the usual discharge, it is practically impossible to make a more or less substantiated judgment of the role of the activity of water.

In the case of barrierless discharging, when the ψ_1-effect is absent, the change in the overvoltage in the transition to highly concentrated solutions can be estimated entirely on account of the change in the activity of water. In view of this, we investigated the overvoltage of hydrogen in acidified concentrated solutions of LiBr, as well as in certain other solutions.

EXPERIMENTAL SECTION

The experimental procedure was described in detail in [1]. Lithium and sodium bromides, distinguished by extremely high solubility, were recrystallized twice from double-distilled water, the solution was saturated at room temperature, and then the corresponding hydrate was frozen out at a temperature of about –60° in one case and about –20° in the other. Several different methods of purifying KI were tested. In [1], KI was recrystallized from a hot solution and used without further treatment. In this case, as a rule, we observed appreciable hysteresis in the region of the sharp rise of the polarization curve close to the point of zero-charge This hysteresis was explained by the presence of traces of some sort of impurities, adsorbed at a finite rate during slight charging of the electrode. This same phenomenon was also observed in earlier studies [4], and only Iofa and Tsa Chuang-hsin [5] have succeeded in obtaining a polarization curve without hysteresis in iodide solution close to the point of zero-charge. In this work, twice recrystallized potassium iodide was calcined for 1.5-2 h under vacuum. After such treatment, there was almost a complete coincidence of the curves of the forward and reverse processes, including in the region of the sharp rise close to the point of zero-charge; the divergence of the curves was random and did not exceed 3-5 mV as a rule. The same results are also obtained with noncalcined salt, if in its recrystallization the temperature

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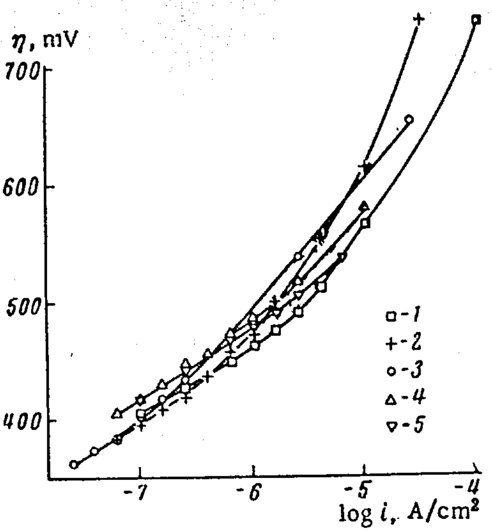

Fig. 1. Polarization curves in solutions of the following composition: 1) 3.1 KI + 0.4 HCl; 2) 3.3 KI + 0.15 HCl; 3) 6.6 NaBr + 0.85 HCl; 4) 11.8 LiBr + 0.018 HCl; 5) 11.6 LiBr + 0.040 HCl.

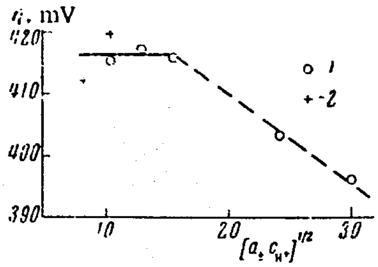

Fig. 2. Dependence of the overvoltage in solutions of LiBr upon the conditional average activity of the acid: 1) LiBr concentration about 11.8 M; 2) lower LiBr concentrations.

did not exceed 40°.* The data of [1] in a region sufficiently far removed from the point of zero-charge, i.e., in a region where no hysteresis were observed, entirely coincide with the results of this work.

In bromide solutions, with the procedure of purification of the salts described above, we observed no discrepancy of the forward and reverse processes, exceeding 3-5 mV.

It should be recalled that the methods of purification ensuring the absence of hysteresis on the polarization curves also led to quite reproducible data on the temperature dependence. Figure 1 gives some typical polarization curves. More complete characteristics are presented in Table 1.

DISCUSSION OF RESULTS

As was noted above, in this work we succeeded in obtaining quite reproducible data in solutions of KI in the region close to the point of zero-charge, which permits us to consider this region in greater detail, as we have done earlier [1]. As can be seen from Fig. 1, close to the point of zero-charge there is a sharp rise in the polarization curve, and as the distance from it increases, the slope decreases and approaches the value of about 120 mV, characteristic of normal discharging. Such a picture was described long ago in the literature [4,5]. It is important for us to note that the further sharp decrease in the slope as we pass to b ≃ 60 mV already occurs after a value b ≃ 120 mV, constant within some interval of current densities, has been established, i.e., after substantial changes in the structure of the double-layer, occurring close to the point of zero-charge, have been completed. Thus, the appearance of a slope of about 60 mV can in no way be related to the influence of the ψ_1-potential, a circumstance which we had already noted earlier [1]. Moreover, if the slope of 60 mV were related, as was proposed in [6], to a rearrangement of the double-layer, then the absence of an influence of the concentration of I^- ions upon the absolute value of the overvoltage, which we had observed previously [1] and also observed in this work, would be entirely incomprehensible.

In bromide solutions (LiBr and NaBr), the shape of the polarization curves is the same as in iodide solutions.† The virtual coincidence of the overvoltage in the region with slope about 60 mV in iodide and bromide solutions is especially interesting.‡ The absence of an influence of the nature of the adsorbed anion, i.e., the absence of an influence of the ψ_1-potential, entirely corresponds to the picture predicted by the theory of barrierless discharge. The main purpose of this work was to investigate the question of the kinetic factor of activity, more accurately, of the role of the activity coefficient of water.

In 1944, Frumkin and Iofa [7] found that the overvoltage of the evolution of hydrogen from acid concentrated solutions of chlorides at constant concentrations of acids and Cl^- ions, i.e., according to [7] at practically constant ψ_1-potential, is not changed by the replacement of the Li^+ cation by K^+, although the activity coefficient of hydrogen ions γ_{H^+} in these solutions unquestionably varies substantially. From this it was concluded that when γ_{H^+} is varied, the activity coefficient of the activated complex $\gamma^{\neq}$ also varies, which leads to the corresponding

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*Evidently at increased temperature the iodide peptizes (or dissolves) some sort of impurities, which are then entrapped by the precipitate.

†It should be mentioned that the transition from b ≃ 100-120 mV to b ≃ 60 mV occurs not in a jump, but gradually, within a rather narrow interval of potentials, about 50 mV.

‡The small increase in the overvoltage in the most concentrated solutions is associated with the decrease in the molar fraction of water (see next page).

TABLE 1

Composition of solution, moles/liter	Value of η(mV) at i = 10^{-7} A/cm^2	Slope of curve, b, mV	Integral $-\log i$ corresponding to b = 0.06 V
3,1KI +0,4 HCl	402	59	5,8--7,0
3,3KI +0,15 HCl	396	60	6,6--7,2
4,1KI +0,4 HCl	(402)	(60)	6,0--6,2
4,3KI +0,3 HCl	(396)	(60)	6,2--6,4
6,0KI +0,55 HCl	(404)	57	5,4--6,6
6,6NaBr+0,85 HCl	(396)	60	7,2--7,6
7,0NaBr+0,85 HCl	402	60	7,0--7,4
6,5LiBr +0,9 HCl	412	60	6,8--7,4
7,5LiBr +0,7 HCl	420	55	6,8--7,4
10,5LiBr +0,28 HCl	392	54	5,8--7,2
11,8LiBr +0,018HCl	415	60	6,8--7,2
11,8LiBr +0,028HCl	417	58	6,0--7,4
11,6LiBr +0,040HCl	416	60	6,0--7,0
11,8LiBr +0,10 HCl	403	57	5,8--7,0
11,9LiBr +0,15 HCl	396	51	5,8--7,0

Note: The extrapolated values of η and the values of b obtained within a narrow interval of current densities are indicated in parentheses.

TABLE 2

Item No.	Concentration and nature of salt	Number of independent experiments	Average value* of η at 10^{-7} A/cm^2	Shift of η(mV) in comparison with No. 1		
				Calculated according to		Experimental
				a_{H_2O}	x_{H_2O}	
1	3 — 4,3 KI	10	403,5 (±5)	0	0	0
2	6KI	9	404,5 (±2,5)	10	3,5	1
3	6,5—7,5 NaBr, LiBr	4	407,5 (±8,5)	18	4	4
4	11,8 LiBr	3	416 (±1)	60	8	12,5

*The average deviations from the mean value are indicated in parentheses.

compensation. Thus, the ratio $\gamma^{\beta}_{H^+}/\gamma^{\neq}$, which enters into the equation for the usual decelerated discharge, is a constant. Since all the activity coefficients approach 1 when the solution is diluted, the ratio $\gamma^{\beta}_{H^+}/\gamma^{\neq} = \text{const} = 1$.

However, strictly speaking, the kinetic factor of the activity is not reduced only to the ratio $\gamma^{\beta}_{H^+}/\gamma^{\neq}$. The equation of a discharge, both normal and barrierless, contains both the coefficient α and the value of the equilibrium potential, which is a linear function of $\ln a_{H_2O}$. Consequently, ultimately the equation includes the activity of water to the exponent α. Therefore, the complete expression for the kinetic factor of the activity is equal to $\gamma^{\beta}_{H^+}\gamma^{\alpha}_{H_2O}/\gamma^{\neq}$. Usually γ_{H_2O} is close to 1, so that this correction has no significant influence upon the accuracy of calculation of the kinetic factor. However, it is of great theoretical importance, since the results of Frumkin and Iofa were later generalized by Temkin [8] for the case of variation of the temperature.*

As was noted in the introduction, a strict experimental evaluation of the effects associated with the activity of water for the usual discharge seems virtually unfeasible. For barrierless discharging, for which the ψ_1-effect is absent, the conditions are extremely favorable for detecting the influence of the activity of water. The greatest effects in this case might be expected, for example, in highly concentrated solutions of LiBr, in which the activity coefficient of water is reduced to values close to 0.1 [9].

We had earlier demonstrated that in acidified solutions, in the presence of sufficiently great acidity of the solution, the discharging of nondissociated acid molecules becomes appreciable [2]. In concentrated solutions of LiBr,

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*Problems associated with the temperature dependence of the overvoltage will be discussed in our following communication.

the average ionic activity coefficient of the electrolyte is so high that one might expect the appearance of nondissociated acid molecules even at a relatively low acidity of the solution. Therefore, in order to ascertain that our data pertain to the discharging of H_3O^+ ions and are not distorted by the participation of HBr molecules, we studied the dependence of the overvoltage in concentrated LiBr upon the acid concentration.

Figure 2 presents the corresponding data. Since there is no information in the literature on the activity of acid in the corresponding solutions, as an arbitrary measure of it, in a first approximation characterizing the tendency to form nondissociated molecules, we took the square root of the product of the average ionic activity of LiBr and the hydrogen ion concentration $(a_{\pm}c_{H^+})^{1/2}$. Data on the activity of LiBr were taken from [9]. The points 1 denote the values pertaining to a practically constant LiBr concentration (about 11.8 M); the points 2 pertain to the other data. Although the discrepancy of the values of the overvoltage only slightly exceeds the possible experimental errors, still, just as in iodide solutions [2], there is a rather distinct tendency for a decrease in the overvoltage when the activity of the acid exceeds a definite limit. In any case, from the data of Fig. 2 we can conclude with full assurance that at the lowest acidities that we studied, only H_3O^+ ions are discharged, while the HBr molecules practically do not take part in the process. Consequently, these data can be used to consider the question of the role of the activity of water.

A comparison of all the data of this work and [1], combined according to groups of solutions of close composition, is given in Table 2. In this table, together with the experimental values of the overvoltage, we cite the calculated shifts of the overvoltage with respect to solutions of the first group (the most dilute solutions). In this case the calculation was performed in two variations, if the overvoltage were influenced by the activity of water (data on the activity of water are taken from [9]) and if only the molar fraction of water exerted a direct influence, i.e., if the change in the activity coefficients of water and the activated complex compensated one another. As can be seen from a comparison of the last three columns of the table, only the second assumption agrees with the experimental results within limits of the possible experimental errors; for the first variation of calculation, the discrepancy is larger than the experimental error. This is especially evident for the most concentrated solutions of LiBr, in which the expected effects are the largest. Actually, calculation according to the activity of water gives a value of the shift of 60 mV, and according to molar fraction, 8 mV, whereas the experimental value is 12.5 mV. The discrepancy between the experiment and the first variation of calculation undoubtedly lies beyond the limits of the possible errors; the agreement with the second variation may be considered quite satisfactory.

Thus, the data cited permit us to conclude that the activity coefficient of water has no influence upon the overvoltage of hydrogen in barrierless discharging. From this, reasoning analogously to Frumkin and Iofa, we arrive at the conclusion that $\gamma_{H_2O}/\gamma^{\neq} = 1$. Generalizing this result and the result of Frumkin and Iofa for the case of any process of discharging of hydrogen ions, we can write the following approximate equation $\gamma^{\neq} = \gamma_H^{\beta} + \gamma_{H_2O}^{\alpha}$ or

$$RT \ln \gamma^{\neq} = \beta RT \ln \gamma_{H^+} + \alpha RT \ln \gamma_{H_2O}. \quad (1)$$

For barrierless discharging, it is easy to ascertain that $\gamma^{\neq} \simeq \gamma_{H_2O}$. Actually, a peculiarity of barrierless discharging is the coincidence of the activated and final states; the highest point of the potential energy curve corresponds precisely to the final state. For the discharging of hydroxonium ions, the final state is the adsorbed hydrogen atom and the water molecule in the double-layer. The activity coefficient of adsorbed hydrogen at low degrees of coverage is equal to 1, and consequently, the activity coefficient of adsorbed water $\gamma_{H_2O(ads)} \simeq \gamma_{H_2O}$ should be taken as the activity coefficient of the transition state. Thus, on the basis of the identification of the final and activated states for barrierless discharging, we arrived at practically the same result as from a consideration of the experimental data on the overvoltage in highly concentrated solutions.

From the considerations cited, it follows that in all probability it is physically more justified to substitute the activity coefficient of the particles not in the volume, but on the surface into Eq. (1). However, the difference of the corresponding values is insufficiently large to cause effects susceptible to experimental detection.

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