5. E. Rosen and R. Tegman, "Solid, liquid, and gas phase equilibria in the system sodium monosulfide–sodium polysulfide–sulfur," Chem. Scr., 2, 221 (1972).
6. M. Hansen and A. Anderko, Constitution of Binary Alloys, McGraw-Hill, New York (1958).

ELECTROCHEMICAL REACTIONS RESULTING IN THE ELIMINATION OF ATOMIC HYDROGEN ON A MERCURY ELECTRODE UNDER CONDITIONS FOR THE SPECIFIC ADSORPTION OF AN ELECTROLYTE

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The photocurrents on a Hg electrode in solutions of KCl, KBr, and KI containing H^+ ions (0.001-0.1 N) and the tetrabutylammonium cation (TBA^+) have been investigated. The electrochemical desorption (ECD) reaction in the range of concentrations investigated mainly involves water molecules. The local values of the ψ' potential for the ionization and ECD reactions are different, this potential being more negative in the former case. The adsorption of TBA^+ results in inhibition of the ionization reaction.

Atomic hydrogen, which appears near the electrode surface upon the photoemission of electrons into acidic solutions, is eliminated on mercurylike metals in two parallel reactions, viz., ionization and electrochemical desorption (ECD) [1]. On a mercury electrode the rate of the former reaction depends on the potential, while the latter reaction, in all likelihood, has a zero activation energy in the range of potentials investigated, and its rate does not depend on the potential. In [2, 3] it was shown that the specific adsorption of iodine ions significantly accelerates the ionization of hydrogen atoms in comparison to the ECD reaction, as a result of which the "hydrogen drop" in the photocurrent appears at more negative potentials than in solutions not containing iodide. The interpretation of such an influence of the specific adsorption of I^- on the basis of the ψ' effect may be ambiguous. 1) In the presence or absence of specific adsorption, the ECD reaction involves mainly water molecules. Then the shift of the ψ' potential in the negative direction caused by the adsorption of I^- accelerates only the ionization of atomic hydrogen and does not influence the rate of ECD, since the latter reaction has a zero activation energy. 2) If mainly hydrogen ions participate in the ECD reaction, as is the case, in particular, in sufficiently acidic ($c_{H^+} > 0.1$ N [2]) solutions, the observed acceleration of the ionization of atomic hydrogen may be attributed to the fact that charge is transferred to different points in the two parallel reactions, i.e., the sites of the H_3O^+ ions formed in the ionization reaction and of the H_3O^+ ions participating in the ECD reaction are different. Then, different values of the ψ' potential appear in the corresponding kinetic equations. If the H_3O^+ ion formed upon the ionization of H atoms is closer to the electrode than the ion participating in ECD, i.e., if the corresponding ψ' potential is more negative, despite the increase in the concentration of hydrogen ions in the layer next to the electrode, displacement of the ψ' potential in the negative direction can result in acceleration of the ionization reaction in comparison to the ECD reaction.

In this context it would be of interest to investigate the mechanism of the ECD reaction under conditions for the specific adsorption of iodine ions and other adsorbed particles which alter the concentration of hydrogen ions next to the electrode. This question was investigated for the mercury electrode in the present work, where measurements of the photoemission currents in KCl, KBr, and KI solutions containing hydrogen ions, whose concentration was varied from 0.001 to 0.1 N, were carried out.† The influence of the tetrabutylammonium

†Measurements could not be carried out in iodide solutions at higher acidity due to the photooxidation of the I^- ions, which causes strong distortion of the measured photocurrents.

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cation (TBA^+) on the kinetics was simultaneously investigated in the KCl and KI solutions. Intensity-modulated ultraviolet light (the wavelength was 365 nm) was used for the photocurrent measurements.

The mechanism of the ECD reaction could be evaluated from the potential φ^*, at which the rates of the two parallel reactions, i.e., ionization and ECD, are equal to one another. Following the method described in [2], from the material balance we obtain

$$\frac{j}{2j_0-j}=\frac{k_1c_{H^+}e^{-\alpha\varphi}e^{-(1-\alpha)\psi_1'}+k_{10}e^{-\alpha'\varphi}e^{-\alpha'\psi_{10}'}}{k_2e^{\beta\varphi}e^{-\beta\psi_2'}}. \quad (1)$$

Here j is the measured photocurrent; j_0 is the emission current; k_1 and k_{10} are the rate constants of the electrochemical desorption reactions involving hydrogen ions and water molecules; α, α' and ψ_1', ψ_{10}' are the transfer coefficients and ψ' potentials for these reactions; k_2, β, and ψ_2' are the parameters for the ionization reaction; φ is the electrode potential; c_{H^+} is the hydrogen-ion concentration. All the potentials are given in units of RT/F. Under the conditions $\alpha = \alpha'$ and $\psi_1' = \psi_{10}'$ Eq. (1) is simplified, and the potential φ^* can be found from it [it corresponds to the equality $j/(2j_0 - j) = 1$]:

$$\varphi^*=\frac{1}{\alpha+\beta}\ln\frac{k_1c_{H^+}e^{-(1-\alpha)\psi_1'}+k_{10}e^{\alpha\psi_1'}}{k_2e^{-\beta\psi_2'}}. \quad (1a)$$

In the special case of $\alpha = 0$,

$$\varphi^*=\frac{1}{\beta}\ln\frac{k_1c_{H^+}e^{-\psi_1'}+k_{10}}{k_2}+\psi_2'. \quad (1b)$$

Let us consider two limiting cases in which only water molecules and only hydrogen ions participate in the ECD reaction. In this case, from (1) we have

$$\varphi^*=\frac{1}{\alpha'+\beta}\ln\frac{k_{10}}{k_2}+\frac{\alpha'}{\alpha'+\beta}\psi_{10}'+\frac{\beta}{\alpha'+\beta}\psi_2' \quad (2a)$$

and

$$\varphi^*=\frac{1}{\alpha+\beta}\ln\frac{k_1c_{H^+}}{k_2}-\frac{1-\alpha}{\alpha+\beta}\psi_1'+\frac{\beta}{\alpha+\beta}\psi_2'. \quad (2b)$$

Since the signs of the changes ψ_1' and ψ_2' coincide, from Eq. (2a) it follows that the shift of φ^* in the case of the ECD reaction involving water has the same sign as the shift of the ψ' potential. In this case, if $\alpha' \to 0$, the change in φ^* equals the change in ψ_2'. When the participation of hydrogen ions in the ECD reaction is predominant, different cases are possible. If $\varphi_1' = \psi_2'$, i.e., the H_3O^+ ion participating in the ECD reaction is found in the same place as the ion formed upon the ionization of H, with consideration of the experimentally observed relation $\alpha + \beta = 1/2$ [2] we have

$$\varphi^*=2\ln\frac{k_1c_{H^+}}{k_2}-\psi'. \quad (2b')$$

Here $\Delta\varphi^*$ is opposite in sign to $\Delta\psi'$. The same sign is observed in the shifts of φ^* and ψ' only when the condition $|(1-\alpha)\psi_1'| \ll |\beta\psi_2'|$ is fulfilled, i.e., if we take into account that $\alpha \simeq 0$, when the condition $|\psi_1'| \ll |\psi_2'|$ is fulfilled.

The potential φ^* was found experimentally in the following manner. The photocurrents for nitrous oxide $j(N_2O)$ were measured simultaneously with the photocurrents for hydrogen ions $j(H^+)$ in the KCl, KBr, and KI solutions. Then the dependence of $j(H^+)/j(N_2O)$ on the potential was plotted (Fig. 1). At negative potentials it is a straight line parallel to the potential axis, and at more positive values of φ it deviates downward. The independence of the ratio between the photocurrents at $\varphi < -0.9$ V indicates that atomic hydrogen par-

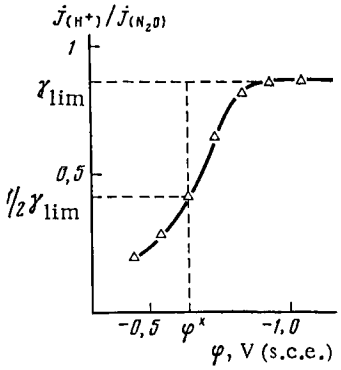

Fig. 1

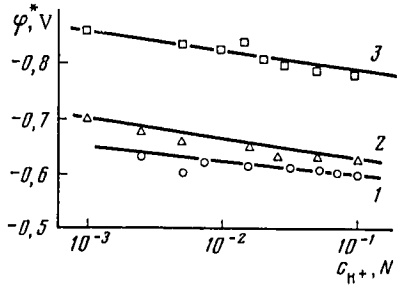

Fig. 2

Fig. 1. Dependence of the ratio $j(H^+)/j(N_2O)$ on the potential for 0.5 N KCl + $1.7 \cdot 10^{-2}$ N HCl and 0.5 N KCl + N_2O solutions.

Fig. 2. Dependence of φ^* on c_{H^+} for three solutions: 1) (0.5 − X) N KCl + X N HCl; 2) (0.5 − X) N KBr + X N HCl; 3) (0.5 −X) N KI + X N HCl.

ticipates in only one reaction, viz., ECD, in this range, while the ionization of H atoms may be neglected. In other words, here the photocurrent for hydrogen ions is equal to emission current with accuracy to a factor which is not dependent on the potential, as is the case in solutions of nitrous oxide [1].†

The potential φ^* corresponds to a value of $j(H^+)/j(N_2O)$ equal to half of its limiting constant value at negative potentials. The values of φ^* found for different hydrogen-ion concentrations for three background solutions are given in Fig. 2, from which it is seen that an increase in c_{H^+} by two orders of magnitude is accompanied by the displacement of φ^* in the positive direction. The dependence of φ^* on log c_{H^+} is linear with a slope equal to 25-30 mV in a first approximation. Within the range of accuracy of the determinations, this is consistent for the range of hydrogen-ion concentrations given with the previously found dependences [2]. At one particular hydrogen-ion concentration φ^* is shifted in the negative direction along the series Cl^-, Br^-, I^-. The displacement of φ^* in the negative direction in comparison to the data for KCl amounts to 195-210 mV in the KI solutions and 30-50 mV in the KBr solutions. This practically coincides with the displacement of the hydrogen overvoltage and, therefore, with the displacement of the ψ' potential at the site of the discharged H_3O^+ ion in 1 N KX + 0.1 N HCl (180 and 55 mV, respectively [4]) and in 2 N KX + 1 N HCl (180-190 and 60-70 mV [5]).

From Fig. 2 it follows that both water molecules and hydrogen ions simultaneously undergo the electrochemical desorption reaction in all the solutions in the range of hydrogen-ion concentrations given, the fraction of the participation of the latter being smaller than that of the former. Only at $c_{H^+} \simeq 0.1$ N do the rates of the two parallel ECD reactions become commensurate. At higher acid concentrations the slope of the φ versus log c_{H^+} dependence increases to ∿100 mV (φ^* in 1 N HCl is equal to −0.5 V as opposed to −0.6 V in 0.5 N KCl + 0.1 N HCl). This corresponds to a predominant contribution of the reaction involving H_3O^+ ions (similar data are given in [2]).

When hydroxonium ions are discharged, the 180-mV decrease in the overvoltage is caused by displacement of the ψ' potential by the same amount in the negative direction. Such a shift corresponds to an increase in the surface concentration of the discharged ions by three orders of magnitude. This is sufficient for the concentration of H_3O^+ in the plane of the discharged ions in an iodide solution to correspond over the entire range of concentration studied to a bulk acidity > 1 N in the chloride solution. If the H_3O^+ ions taking part in the ECD reaction are in the same plane, the ECD reaction involving hydrogen ions should have been sharply predominant in the iodide solution. This, in turn, would result in displacement

†In both solutions these factors are not equal to one another and depend mainly on the rate constants for electron capture by the acceptors (H^+ and N_2O) and the concentrations of the latter. Therefore, the ratio $j(H^+)/j(N_2O)$ is not equal to unity in the general case.

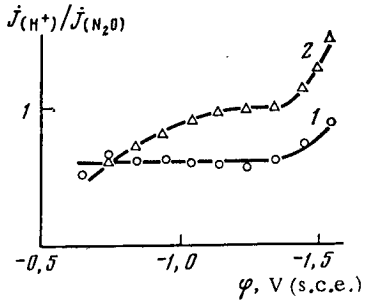

Fig. 3. Dependence of $j(H^+)/j(N_2O)$ for two pairs of solutions: 1) 0.5 N KCl + $5\cdot10^{-3}$ N HCl + 10^{-3} N TBAOH and 0.5 N KCl saturated with N_2O + 10^{-3} N TBAOH); 2) 0.5 N KI + $5\cdot10^{-3}$ HCl + 10^{-3} N TBAOH and 0.5 N KI saturated with N_2O + 10^{-3} N TBAOH.

of φ^* in iodide solutions in the positive direction according to Eq. (2b). Neither this nor the other conclusion was confirmed experimentally.

The displacement of φ^* by an amount on the order of $\Delta\psi'$ (in the case of the discharging of hydrogen ions) suggests that ψ_2' is close to the ψ' for discharging and that $|\psi_1'| \ll |\psi_2'|$ [see (2b)]. Thus, the position of the H_3O^+ ions formed as a result of the ionization of H, on the one hand, and participating in the ECD reaction, on the other hand, differ significantly, i.e., in the former case, they are found close to the inner Helmholtz plane, and in the latter case, they are nearer the outer plane. The potentials of the outer Helmholtz plane for the solutions of interest to us were determined in [6, 7]. From these data it follows that the ψ° potential in 0.5 N KI is more negative than that in 0.5 N KCl by 34-42 mV (the values of ψ° at the potentials corresponding to φ^* in the solutions under discussion were compared). Such a shift in ψ° corresponds to an increase in the surface concentration by 0.6-0.7 orders of magnitude, i.e., at least three experimental points for the KI solution should have been compared to a KCl solution in which the acidity was above 0.1 N. Therefore, assuming that $\psi_1' = \psi^\circ$, we should expect a transition to predominance of the ECD reaction with the participation of H_3O^+, which does not occur. This may mean that the ion participating in the electrochemical desorption is located further from the electrode than the outer Helmholtz plane.

Figure 3 shows the influence of the specific adsorption of the TBA^+ cation on the rate of the elimination of atomic hydrogen. In a 0.5 N KCl solution the ratio $j(H^+)/j(N_2O)$ remains constant at potentials from −0.6 to −1.3 V. The increase in this ratio at more negative potentials is due to the occurrence of the desorption of TBA from the mercury surface and the associated increase in the concentration of H^+ in the diffuse double layer, which results in more complete capture of the hydrated electron. In KI solutions the independence of the ratio $j(H^+)/j(N_2O)$ with respect to the potential is observed over a narrower range (−1.0 to −1.3 V). At positive values of φ a decrease is observed in the ratio due to the occurrence of the oxidation of atomic hydrogen.† From the figure it is seen that the specific adsorption of the TBA^+ cation practically complety stops the oxidation of hydrogen atoms in KCl solutions due to the shift of the ψ' potential in the positive direction.

According to the data in [8], the shift of the ψ' potential upon the addition of 10^{-3} N TBA to 1 N HCl amounts to ∿170 mV. In the case of such a shift under the conditions of the experiment shown in Fig. 3, φ^* should have been −0.46 V, i.e., shifted to a potential sig-

†Since the photocurrents $j(H^+)$ and $j(N_2O)$ in Fig. 3 were measured under not completely identical conditions (in particular, under different light intensities), this ratio has a nominal character. However, we are interested in the nature of the dependence of $j(H^+)/j(N_2O)$ on the potential, rather than its absolute value.

nificantly more positive than those investigated experimentally. This explains why the oxidation of H atoms was practically not observed in KCl solutions with an addition of TBA.

In KI solutions the oxidation of H atoms does not disappear in the presence of TBA, but it is slower than in pure KI solutions. Evaluation of φ^* from Fig. 3 yields a value of −0.6 −0.7 V, while in a 0.5 N KI solution without TBA at the same acidity $\varphi^* = -0.88$.

The shift of the overvoltage in 2 N KI + 2 N HCl upon the addition of $4.5 \cdot 10^{-4}$ N TBA^+ amounts to ~−30 mV according to the data in [9]. In the experiment illustrated by curve 2 in Fig. 3 we observe, however, a shift of φ^* in the positive direction, rather than in the negative direction, as might have been expected on the basis of the similarity to all the other cases. The reason for this is not entirely clear. The structure of the double layer in the case of the combined adsorption of two ions differing strongly in size is very complex; therefore, the interpretation of the picture as a whole is difficult. It is possible that the shielding effect of the TBA^+ ions combined with adsorbed iodide ions in the form of ion pairs causes the H atoms to approach the electrode at points relatively more distant from the I^- ions, making the local ψ' potential more positive, while a purely electrostatic effect, i.e., a tendency for an increase in the local concentration of the H_3O^+ ions near the adsorbed anion, is significant in the case of the discharging of these ions.

The conclusion drawn in the present work that the difference between the ψ potentials for the ionization and electrochemical desorption reactions is significant calls for a discussion of the possible reasons for this phenomenon. Let us first assume that adsorbed hydrogen atoms participate in both reactions. Then the proton formed upon ionization should be added to the nearest water molecule, i.e., to a molecule in the first monolayer. In this case, a hydroxonium ion, whose center of gravity is close to the inner Helmholtz plane, is formed. The same position of hydroxonium is optimal for its discharging, whence follows the experimentally found equality $\psi_2' \simeq \psi_{dis}'$. If an H_3O^+ ion participating in ECD must approach the adsorbed atom in such a manner that the $H_{ads}\ldots H\!-\!O$ grouping of atoms is on one line, according to purely geometric arguments the hydroxonium O atom, i.e., the center of charge, is further from the electrode than are the O atoms of water molecules in the first monolayer. Hence it follows that $|\psi_1'| < |\psi_2'|$, as was observed in the experiment.

This explanation is not, however, completely satisfactory. In fact, the dimensions of the H atom are small in comparison to a water molecule. Therefore, the factor under discussion cannot cause the ejection of the hydroxonium into the second monolayer or even beyond its limits (especially if we take into account the high probability of the adsorption of H in interstitital positions, in which case the "surface" of the H atom does not project beyond the boundary of the "surface" of the Hg atoms). Therefore, the finding that $|\psi_1'| \leqslant |\psi^\circ|$ could hardly be explained in this manner. This relationship is easily explained, if it is assumed that the cathodic reaction is the reaction of a dissolved H atom occurring at a certain distance from the electrode, rather than the desorption of adsorbed hydrogen. There are no fundamental impediments to the realization of this reaction, since electron-transfer reactions with the participation of particles located in the outer Helmholtz plane or even beyond it are well known. Then the proton donor (H_3O^+, H_2O) can be located either in the outer sheet of the double layer or beyond it. We note that for the observation of the equality $\psi_2' \simeq \psi_{dis}'$ there is no need at all for the H atom being ionized to be adsorbed. An H atom located within the second monolayer of water molecules (or between the first and second monolayers) will be added after ionization in the form of a proton predominantly to water molecules of the first monolayer, since in this case, the H_3O^+ ion is formed at a more negative ψ' potential, i.e., at an energetically more favorable position. Thus, the equality $\psi_2' \simeq \psi_{dis}'$ can be fulfilled for the ionization of both adsorbed and free H atoms.

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LITERATURE CITED

1. Yu. V. Pleskov and Z. A. Rotenberg, "Photoemission of electrons from metals into electrolyte solutions as a method for investigating double-layer and electrode kinetics," in: Advances in Electrochemistry and Electrochemical Engineering, Vol. 11, Wiley, New York (1978), pp. 1-124.
2. Z. A. Rotenberg, V. I. Lakomov, and Yu. V. Pleskov, "Kinetics of the electrochemical conversion of atomic hydrogen on a mercury electrode," Élektrokhimiya, 6, 515 (1970).

3. Z. A. Rotenberg, V. I. Lakomov, and Yu. V. Pleskov, "Electron photoemission as a new method for studying the electric double layer structure and the kinetics of electrochemical reactions," J. Electroanal. Chem., 27, 403 (1970).
4. Z. Iofa, B. Kabanov, E. Kuchinskii, and F. Chistyakov, "Overvoltage on mercury in the presence of surface-active electrolytes," Zh. Fiz. Khim., 13, 1105 (1939).
5. Ch'uang-Hsin Tsa and Z. A. Iofa, "Influence of adsorbed anions on the overvoltage of hydrogen," Dokl. Akad. Nauk SSSR, 126, 1308 (1959).
6. D. C. Grahame, "Components of charge and potential in non-diffuse region of the electrical double layer: potassium iodide solutions in contact with mercury at 25°," J. Am. Chem. Soc., 80, 4201 (1958).
7. D. C. Grahame and R. Parsons, "Components of charge and potential in the inner region of the electrical double layer: aqueous potassium chloride solutions in contact with mercury at 25°," J. Am. Chem. Soc., 83, 1291 (1961).
8. E. P. Andreeva, "Overvoltage of hydrogen on a mercury electrode in acidic solutions containing surface-active organic compounds," Zh. Fiz. Khim., 29, 699 (1955).
9. Ch'uang-Hsin Tza and Z. A. Iofa, "Combined effect of organic cations of halide anions on the evolution of hydrogen on a mercury electrode," Dokl. Akad. Nauk SSSR, 125, 1065 (1959).

DIFFERENTIAL CAPACITANCE OF A MERCURY ELECTRODE IN DILUTE 1:1 ELECTROLYTES

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Measurements of the capacitance of the double layer in dilute solutions of 1:1 electrolytes at infrasonic frequencies have been carried out. The results obtained attest to the applicability of the Gouy–Chapman theory in solutions of electrolytes in the 10^{-3}–10^{-5} M concentration range.

The modern ideas on the diffuse part of the electrical double layer are based on the Gouy–Chapman theory, according to which [1] its capacitance equals

$$C_d = |z| f A \operatorname{ch}\left(\frac{1}{2}|z| f \psi'\right), \quad (1)$$

where z is the charge of the anion or cation, f = F/RT, $A = \sqrt{\frac{RT\varepsilon c}{2\pi}}$, ε is the dielectric constant of the solvent, c is the concentration of the solution, and ψ' is the potential drop in the diffuse part of the double layer.

Fundamental testing of this theory was carried out by Grahame [2], who approximated the double layer by a model of two capacitors connected in series:

$$\frac{1}{C} = \frac{1}{C_d} + \frac{1}{C_c}, \quad (2)$$

where C is the capacitance of the double layer, and C_c is the capacitance of the compact part, which is dependent on the charge of the electrode. Grahame discovered good agreement between the theory and experiment for the capacitance of the mercury electrode in solutions of 1:1 electrolytes at concentrations above 10^{-3} M.

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