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APPLIED ELECTROCHEMISTRY
AND CORROSION PROTECTION OF METALS

A Study of the Corrosion-Electrochemical Behavior of Mercury in Alkaline Solutions of Sodium Hypochlorite

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Abstract—Oxidation rate of mercury in solutions of potassium chloride and sodium hydroxide and hypochlorite was studied by measuring the polarization resistance.

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Hypochlorites (HCs) are strong oxidizing agents and find wide use in this respect, including that in demercurization processes [1]. It has been found that particular effective for this purpose is sodium HC [sodium oxochlorate(I)] [2, 3], which exhibits high oxidizing capacity in alkaline media due to the reversible process: $Cl_2 + 2NaOH \rightleftarrows NaOCl + NaCl + H_2O$. The interaction of mercury with alkaline solutions of HCs is a heterogeneous process characterized by a certain potential discontinuity at the metal–solution interface and by the formation of difficultly soluble compounds on the mercury surface, of which the most probable are mercury oxide and calomel. The rate of this oxidation process can be estimated by the known methods used to study the corrosion of metals. The potentiostatic method for recording of polarization curves is widely used to examine metals and alloys that can pass to the passive state. In this study, the method is employed to analyze the mercury oxidation rate in solutions of potassium chloride and sodium hydroxide and hypochlorite.

EXPERIMENTAL

A NaClO solution was prepared by passing chlorine through a carbonate-free solution of sodium hydroxide at temperatures of –5 to 0°C. Chlorine was obtained by reacting chemically pure hydrochloric acid with potassium permanganate [4]. The hypochlorite concentration was found iodometrically on the basis of the active chlorine. The pH value of the alkaline solution of HC remained nearly unchanged, irrespective of the duration and temperature of experiments, because of the excess amount of sodium hydroxide present in the HC solution. Solutions of potassium chloride and sodium hydroxide were prepared from reagents of chemically pure grade.

A preliminarily degreased mercury for electrodes was subjected to additional purification by multiple passing of a dispersed metal through a 5% solution of $Hg_2(NO_3)_2$ in 5% HNO_3 and the distillate.

The solution temperature was maintained with a UTU-2 ultrathermostat.

The polarization curves were measured with a PI-50 potentiostat.

The electrochemical cell *1* (Fig. 1) had the cathode and anode spaces separated by a porous glass partition *2*. A saturated silver chloride reference electrode *3* was placed in a side run-out, the end of whose capillary was situated near the working electrode. The experimentally found potential of the reference electrode was 0.203 V (s.h.e.) at 20°C. A platinum wire was introduced as a current lead into a tube with a diameter of 4 mm, sealed in the cell bottom. Prior to measurements, mercury serving as the working mercury electrode and having a 0.126-cm^2 surface area contacting with the solution was poured with a pipette into tube *4*. The auxiliary platinum electrode *5* was introduced into the separated cathode space. After the measurements, the solution under study and mercury were removed from the cell through a discharge pipe equipped with a cock *6*.

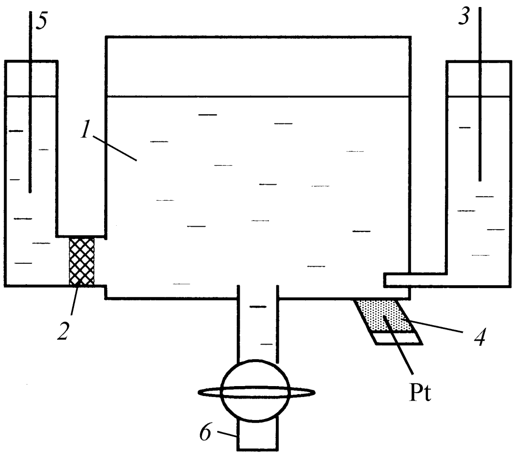

Fig. 1. Schematic of the electrochemical cell. For explanations, see text.

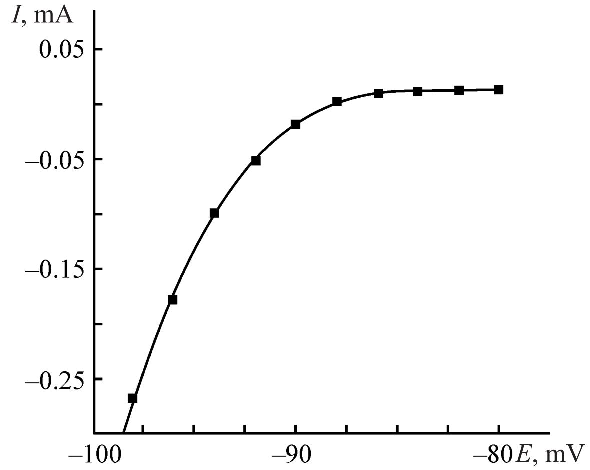

Fig. 2. Current–voltage curve obtained on the Hg electrode in 1 M NaClO. (I) Current and (E) potential. T 50°C, pH ~13.

The mercury oxidation rate, equivalent to the corrosion current density i_{cor}, can be estimated using the results of measurements of the polarization resistance R_p [5]:

$$i_{\mathrm{cor}} = \frac{b_a b_k}{2.303\,(b_a + b_k)} \frac{1}{R_p}\ , \qquad (1)$$

where b_a and b_c are the coefficients of the Tafel equation for the anodic and cathodic processes.

Equation (1) can be represented as $i_{\mathrm{cor}} = B/R_p$, where constant B is applicable to a particular system and is determined experimentally. The value of b_a cannot be reliably found in experiments because of the rather limited range of active dissolution of mercury in the solutions under study. Therefore, B was calculated theoretically, with the Tafel coefficients of the anodic and cathodic processes taken to be 0.12 V, because the transfer of the second electron is commonly the rate-determining stage for two-electron reactions in oxidation. With this condition, $B = 0.026$ V and the corrosion current

$$I_{\mathrm{cor}} = 0{,}026/\,R_p. \qquad (2)$$

A somewhat different value of B was obtained in [6] by processing a large body of data by the least-squares method, to give the most probable value $B = 0.0209$ V. This value is a result of a comparison of the average value of R_p with the average value of the corrosion current, calculated from gravimetric data for various bivalent metals, including those readily passivated (Cu, Ni, stainless steel, etc.). Because of the pronounced difference between the coefficients, the corrosion current calculations were made for these two values of coefficient B.

The polarization resistance of the mercury electrode was calculated from polarization curves measured under potentiostatic conditions in the potential range $E_i = 0 \pm 10$ mV with a step of 2 mV. The results obtained were processed using the TC (Table Curve) software to find the equation that describes the dependence of the current I (mA) on the mercury electrode potential E (mV) and has the highest correlation coefficient and to determine the coefficients of this equation: b, c, and d. Upon differentiation of the resulting equation and substitution of the experimentally found steady-state potential into the expression for the derivative, the polarization resistance R_p was calculated.

Figure 2 shows as an example a current–voltage curve obtained on the Hg electrode in 1 M NaClO at a temperature of 50°C. Calculations of the polarization resistance demonstrated that the current–voltage dependence obtained at potentials close to the steady-state potential for the mercury electrode in an HC solution at all the temperatures studied is described by a third-order polynomial $I = a + bE + cE^2 + dE^3$ with a correlation coefficient $r = 0.9994$ and coefficients $b = 1.6087$, $c = 0.01947$, and $d = 7.8574 \times 10^{-5}$. Because the value of $E_I = 0$ experimentally found at $I = 0$ is –88.0 mV, the derivative $\mathrm{d}E/\mathrm{d}I = b + 2cE + 3dE^2 = 0.006747$ and $R = \mathrm{d}E/\mathrm{d}I = 148.21$ ohm. The polarization resistance $R_p = RS$, where S is the electrode area, is 18.67 ohm cm^{-2}.

The I–E dependence for the mercury electrode in NaOH and KCl solutions is described by a second-order polynomial with smaller correlation coefficients (0.98–0.97), which is due to the rather low currents measured in this case. The results of calculation of the polarization resistance of the Hg electrode in 1 M NaOH, KCl, and NaOCl solutions (pH 12) at various temperatures are listed in Table 1. The same table presents the corrosion current densities calculated by Eq. (1) with the use of two values of coefficient *B*.

It follows from these data that the mercury oxidation rate in the hypochlorite solution at 25°C, calculated from the results of measurements of the polarization resistance, is approximately 450 and 600 times that in NaOH and KCl solutions, respectively. Raising the temperature makes the polarization resistance lower, and the mercury oxidation rate in NaOH and KCl solutions, higher. By contrast, in an HC solution, the polarization resistance of mercury increases and the oxidation rate decreases with increasing temperature. The same behavior has been observed under potentiodynamic conditions [7]. The phenomenon can be explained as follows.

When mercury is brought in contact with potassium chloride or sodium hydroxide solutions, Cl– and OH– anions present in the solutions passivate the mercury surface via formation of difficultly soluble compounds by the reactions

$$2Hg + 2Cl^- \leftrightarrow Hg_2Cl_2 + 2e \tag{3}$$

$$Hg + 2OH^- \leftrightarrow H_2O + HgO + 2e. \tag{4}$$

Calomel is deposited under the anodic polarization in the form of submonomolecular layer onto the surface of the mercury electrode. Mirceski, V. and Lovric, M. [8] assumed that there is no interaction between the deposited particles and regarded redox reaction (3) as an electrosorption reaction in which the Cl^- ligand is adsorbed on the electrode surface to give more or less polarized covalent bonds with mercury atoms [9]. If the amount of adsorbed ligands is smaller than that necessary for a monolayer to be formed, the substance adsorbed on the electrode surface behaves as a 2D gas. The adsorption constant of the ligand depends on the electrode potential:

$$K_{ads} = K^0_{ads} \exp(2F\,(E - E_{z.ch})/RT), \tag{5}$$

where $E_{z.ch}$ is the zero-charge potential.

Adsorbed ligands are removed from the electrode surface in cathodic polarization of the mercury drop. Raising the temperature must also lead to desorption of passivating Cl^- ions, with an increase in the diffusion rate of the reaction components at the electrode surface and in the solution bulk and a rise in the solubility of the calomel formed. All the factors mentioned above must, in the end, make the corrosion current higher.

Table 1. Results of calculation of the polarization resistance and corrosion current density

Solution, mol l^{-1}	t, °C	R_p, ohm cm^{-2}	I_{cor}, mA cm^{-2}, at indicated B = 0.0209 V	I_{cor}, mA cm^{-2}, at indicated B = 0.026 V
NaOH	22	3512	5.95×10^{-3}	7.40×10^{-3}
	30	3345	6.25×10^{-3}	7.77×10^{-3}
	40	1640	1.27×10^{-2}	1.59×10^{-3}
	50	1454	1.44×10^{-2}	1.79×10^{-2}
KCl	25	4803	4.35×10^{-3}	5.41×10^{-3}
	30	4236	4.93×10^{-3}	6.14×10^{-3}
	40	3797	5.50×10^{-3}	6.85×10^{-3}
	50	2790	7.49×10^{-3}	9.35×10^{-3}
NaOCl, pH 12	25	7.87	2.66	3.30
	30	13.13	1.59	1.98
	40	17.68	1.18	1.47
	50	18.68	1.12	1.39

In the alkaline medium, the reason why the metal passes to the passive state is that a chemisorbed layer of oxygen atoms or a phase oxide is formed on its surface. In the absence of free oxygen in solution, the hydroxide ion can enter into an interaction with mercury atoms by reaction (4) to give mercury oxide. The oxide film has a good electrical conductivity and acts as the cathode, whereas the anodic process occurs in pores under the action of the high current density, which creates conditions for metal ions with increased valence to be formed and transferred to solution in small amounts. As in the preceding case, raising the temperature leads to partial desorption of passivating ions from the metal surface and to an increase in the corrosion current.

The alkaline HC solution contains, in addition to OH^- and Cl^- ions, a high concentration of ClO^- ions, which are reduced on mercury with low overvoltage by the reaction

$$ClO^- + H_2O + 2e = Cl^- + 2OH^- \tag{6}$$

Table 2. Logarithm of the current density for the anodic dissolution of mercury

Solution, mol l^{-1}	Temperature, °C	I_η, μA	i_η, μA cm^{-2}	log i_η	$1/T$, K^{-1}
NaOH	22	0,7	5,5555	0,7447	0,00338
	30	1,0	7,9365	0,8996	0,00330
	40	1,5	11,9047	1,0757	0,00310
	50	2,1	16,6666	1,2218	0,00300
KCl	25	0.4	3.1746	0.5016	0.00335
	30	0.5	3.9682	0.5985	0.00330
	40	0.8	6.3492	0.8027	0.00310
	50	1.2	9.5238	0.9788	0.00300
NaOCl, pH 12	23	0.027	0.2142	–0.6690	0.00378
	30	0.019	0.1507	–0.8216	0.00330
	44	0.018	0.1428	–0.8450	0.00310
	50	0.014	0.1111	–0.9542	0.00300

and are depolarizers of the corrosion process. This reaction leads to a comparatively high rate of mercury corrosion in the HC solution. The decrease in the corrosion current on raising the temperature is probably due to a fall of the surface concentration of depolarizing ions (ClO^-), which is, in turn, caused by desorption of ClO^- ions from the mercury surface and by a decrease in their stability under heating.

Hydroxide ions passivate mercury brought in contact with the HC solution, and chlorine ions simultaneously act as passivators and depassivators of the metal surface. On the one hand, they form a crystalline calomel film, and on the other, compete in adsorption with oxygen and displace it from separate parts of the metal surface. Penetrating into the lattice of the oxide film and occupying sites originally belonging to O^{2-}, chlorine ions create in the film defects necessary for the ion motion [10]. In the process, intermediate formation of the soluble $HgCl_2$ is possible, which leads to an increase in porosity and to partial depassivation, with the protecting properties of the oxide film impaired. The simultaneous crystallization of calomel and chemisorption of oxygen on the mercury surface deteriorate the structure of the protective film, facilitate the oxidation of mercury at boundaries of dissimilar films, and diminish the corrosion resistance of mercury in the HC solution.

To determine the nature of the stage determining the rate of the electrochemical oxidation of mercury in the media under study, it was of interest to find the activation energy of these processes. The effective activation energy of the anodic dissolution of mercury was found from potentiostatic polarization curves at potentials close to the steady-state potential of the metal under the conditions in which a passivating film grows without forming a solid dense layer. The polarization curves were recorded at various temperatures at potentials in the range $E_{st} \pm 160$ mV. First, the mercury electrode was cathodically polarized at a potential $E = E_{st} - 160$ mV for 5–10 min until a constant value of the current was attained, and then a current–voltage curve was recorded with a step of 10 mV; at potentials $E = E_{st} \pm 40$ mV, the step was lowered to 2 mV. From the resulting curves, the current I_η, current density I_η, and dependence of log i_η on $1/T$ were determined for a constant overvoltage η (20 mV for KCl and NaOH solutions and 10 mV for NaOCl). These overvoltages were chosen because the region of active mercury dissolution in the sodium hypochlorite solution is less extended than that for the alkali and potassium chloride solutions. The results of determination of the anodic current at the overvoltages specified above are listed in Table 2.

The activation energies were calculated using the Arrhenius equation applied to description of electrochemical processes:

$$\log i_\eta = \log B - E_\eta/2.3RT,$$

where i_η is the current density at a certain overvoltage, and E_η is the effective activation energy of the electrode reaction.

The most probable values of the slope ratio and correlation coefficient were found using TC software. For NaOH and KCl solutions, the correlation coefficient $r > 0.98$, and for the NaOCl solution, $r \approx 0.95$. It should be noted that a current instability and poor reproducibility of measurement results are observed in the hypochlorite solution at temperatures higher than 30°C. This is probably due to an increase in the instability of HC ions at higher temperatures and stronger electrode polarizations.

The calculated activation energies of mercury dissolution are 22.4, 24.5, and –6.2 kJ mol^{-1} for 1 M NaOH, KCl, and NaOCl, respectively. The activation energies of the anodic dissolution of mercury in potassium chloride and sodium hydroxide solutions are approximately the same and close to the activation energy of diffusion processes.

For the hypochlorite solution at potentials close to the steady-state value, the anodic current decreases with increasing temperature. As shown above, the same dependence is characteristic of the corrosion current. The negative activation energy of the anodic dissolution of mercury in the HC solution can be attributed to a decrease in the concentration of depolarizing ClO^- ions at the phase boundary because of their desorption from the surface and partial decomposition at higher temperatures. As a result, the passivators Cl^- and OH^- are formed, which, in the end, leads to a decrease in the corrosion rate.

CONCLUSIONS

(1) The potentiostatic method was used to study the corrosion-electrochemical behavior of mercury in solutions of potassium chloride and sodium hydroxide and hypochlorite. It was shown that the mercury oxidation rate in the alkaline sodium hypochlorite solution at a temperature of 20°C is 450 and 600 times that in NaOH and KCl solutions, respectively.

(2) It was found that the activation energies of the anodic dissolution of mercury in potassium chloride and sodium hydroxide solutions, calculated from potentiostatic polarization curves, are close to the activation energy of diffusion processes and equal to 24.5 and 22.4 kJ mol^{-1}, respectively.

(3) It was demonstrated that, in a sodium hypochlorite solution, the rate of mercury corrosion decreases with increasing temperature, and the activation energy is negative, which is due to a decrease in the concentration of depolarizing ClO^- ions on the metal surface upon an increase in temperature.

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