THE POTENTIAL OF A PLATINUM ELECTRODE IN AN IRRADIATED SOLUTION OF SULFURIC ACID

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Abstract

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THE POTENTIAL OF A PLATINUM ELECTRODE IN AN IRRADIATED SOLUTION OF SULFURIC ACID

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We have previously shown ([1–4]) that the potential of a platinum electrode in an irradiated $0.8\,N$ sulfuric acid solution (radiation dose rate $2 \cdot 10^{15}$ eV/cm$^3 \cdot$ sec) assumes a value close to the potential of the hydrogen electrode in the same solution. Subsequently this was confirmed in works by other authors ([5,6]).

In the present communication we give some results obtained in studying the action of radiation of a substantially higher dose rate on the platinum/sulfuric acid solution system. The experiments were carried out on the Co^{60} source of the L. Ya. Karpov Physicochemical Institute ([7]); the radiation dose rate was $6.1 \cdot 10^{16}$ eV/cm$^3 \cdot$sec. The method of preparing and carrying out the experiments is described in papers ([2,3]).

Figure 1 gives the curve of the dependence of the potential of a platinum electrode in a deoxygenated $0.8\,N$ sulfuric acid solution on the duration of irradiation. As can be seen from the figure, at this dose rate as well there is the selectivity of the platinum electrode, previously established by us, with respect to the reducing products of water radiolysis, leading to the establishment of a potential of 10–20 mV. This potential value is maintained up to doses less than $2 \cdot 10^{20}$ eV/cm^3, after which it increases to 0.85 V.

The condition for stationarity of the electrode potential in an irradiated solution is equality of the rates of the processes occurring on it: oxidation of the reducing radiolysis products and, correspondingly, reduction of the oxidizing ones. The rates of these processes at the stationary potential may be written in the form

$$I_R = k_R[\mathrm{Red}] \exp\left(\frac{\alpha_R F \varphi_{\mathrm{st}}}{RT}\right), \tag{1}$$

$$I_{\mathrm{Ox}} = k_{\mathrm{Ox}}[\mathrm{Ox}] \exp\left(-\frac{\alpha_{\mathrm{Ox}} F \varphi_{\mathrm{st}}}{RT}\right). \tag{2}$$

It would be more correct to write

$$I_R = \sum_i k_{R_i}[\text{Red}]_i \exp\left(\frac{\alpha_{R_i} F \varphi_{\text{st}}}{RT}\right)$$

and correspondingly for I_{Ox}, but this would complicate the calculation without introducing anything essential into the final results.

Equations (1) and (2) may be written in the following form:

$$I_R = k'_R[\text{Red}] \exp\left(\frac{\alpha_R F \Delta\varphi_R}{RT}\right), \tag{1'}$$

$$I_{\text{Ox}} = k'_{\text{Ox}}[\text{Ox}] \exp\left(\frac{\alpha_{\text{Ox}} F \Delta\varphi_{\text{Ox}}}{RT}\right), \tag{2'}$$

where [Red] and [Ox] are the concentrations of the reducing and oxidizing radiolysis products, respectively; $\Delta\varphi_R = \varphi_{\text{st}} - \varphi^0_R$, $\Delta\varphi_{\text{Ox}} = \varphi^0_{\text{Ox}} - \varphi_{\text{st}}$.

($\varphi^0_R < \varphi_{\text{st}} < \varphi^0_{\text{Ox}}$); φ^0_R and φ^0_{Cx} are the corresponding equilibrium potentials; the remaining notation is conventional.

Using the stationarity condition $I_R = I_{\text{Ox}}$, we obtain

$$\frac{k'_R[\text{Red}]}{k'_{\text{Ox}}[\text{Ox}]} = \frac{\exp\left(\frac{\alpha_{\text{Ox}} F \Delta\varphi_{\text{Ox}}}{RT}\right)}{\exp\left(\frac{\alpha_R F \Delta\varphi_R}{RT}\right)}, \tag{3}$$

which, after taking logarithms, gives

$$\ln \frac{k'_R[\text{Red}]}{k'_{\text{Ox}}[\text{Ox}]} = \frac{F}{RT}(\alpha_{\text{Ox}}\Delta\varphi_{\text{Ox}} - \alpha_R \Delta\varphi_R). \tag{4}$$

Under conditions where no current passes through the system and all radiolysis products remain in solution, [Red] = [Ox], and

$$\ln \frac{k'_R}{k'_{\text{Ox}}} = \frac{F}{RT}(\alpha_{\text{Ox}}\Delta\varphi_{\text{Ox}} - \alpha_R \Delta\varphi_R). \tag{5}$$

If $k'_R \gg k'_{\text{Ox}}$, which is a measure of the selectivity of one process with respect to the other, the bracket on the right-hand side of the equation must be

Fig. 1. Dependence of the potential of a platinum electrode on irradiation time ($0.8\,N$ sulfuric acid, electrode surface 6 cm^2, solution volume 10 cm^3, gas-phase volume 50 cm^3)

Figure 1 and Figure 2: plots of electrode potential and polarizing current versus irradiation time.

Figure 1: Figure 1 and Figure 2: plots of electrode potential and polarizing current versus irradiation time.

Fig. 2. Dependence of the magnitude of the polarizing current on irradiation time at a platinum-electrode potential of 0.4 V (0.8 N sulfuric acid, electrode surface 6 cm^2, solution volume 10 cm^3, gas-phase volume 50 cm^3)

greater than 1, and $\Delta\varphi_{\text{Ox}} > \Delta\varphi_R$. Consequently, in this case the stationary potential of the electrode must be closer to the equilibrium potential of the reducing radiolysis products, as is the case for a platinum electrode because of its selectivity toward the process of hydrogen ionization. From equation (4), taking $\alpha_R = \alpha_{\text{Ox}} = \alpha$, one can obtain the following expression for the value of the stationary potential φ_{st}:

$$\varphi_{\text{st}} = \frac{\varphi^0_{\text{Ox}} + \varphi^0_R}{2} + \frac{RT}{2\alpha F} \ln \frac{k'_{\text{Ox}}[\text{Ox}]}{k'_R[\text{Red}]}. \tag{6}$$

If [Red] $\neq$ [Ox], i.e., if the stoichiometry between the oxidizing and reducing products of water radiolysis is disturbed, then the stationary potential of the electrode will have another value. In this connection it should be noted that the shift of the stationary potential associated with the inequality of concentrations may be greater than follows from equation (6), since the rates of the processes determining the magnitude of the stationary potential may, at certain potentials, be controlled by diffusion of substances to the electrode.

The results shown in Fig. 1 were obtained under conditions where the volume of the gas phase was approximately 5 times greater than the volume of the solution. The resulting

during the radiolysis hydrogen was distributed between the gas phase and the solution, and in the solution the stoichiometry between the oxidizing and reducing products of radiolysis was disturbed, i.e., [Red] < [Ox]. According to equation (6), this should lead to a shift of the potential in the positive direction, which is also observed at doses greater than $2 \cdot 10^{20}$ eV/cm^3. Measurement of the dependence of the depolarization currents on the irradiation time confirms this.

Figure 2 gives the curve of the dependence of the depolarization currents at a potential of 0.4 V on the irradiation time, characterizing the accumulation of radiolysis products. On this curve one observes at first a sharp increase in the current, then a slower increase, the attainment of a certain limiting value, and, finally, its decrease with time. Point A corresponds to removal of the source. Such a complex course of the curve is connected with the fact that at a potential

Figure 3

Figure 2: Figure 3

Figure 4

Figure 3: Figure 4

of 0.4 V both oxidation of hydrogen and reduction of hydrogen peroxide can occur. Owing to the selectivity of platinum for the process of hydrogen ionization, in the initial periods the process of hydrogen oxidation proceeds predominantly. However, as hydrogen peroxide accumulates in the solution (within an hour hydrogen peroxide accumulates to $1 \cdot 10^{-3}$ N in the solution) and hydrogen passes into the gas phase, the rate of reduction of hydrogen peroxide increases; the total current, equal to $I_{H_2} - I_{H_2O_2}$, begins to fall and, at doses greater than $2 \cdot 10^{20}$ eV/cm^3, assumes a negative value. A study was made of the dependence of the potential of the platinum electrode on the irradiation time under conditions excluding a disturbance of the equality [Red] = [Ox]. The space of the apparatus in which the electrode under test was located was completely filled with solution, i.e., there was no gas phase above the solution. This part of the apparatus was connected by means of thin capillaries with the parts of the apparatus in which the reference electrode and the auxiliary electrode for polarization were located, separated from the main electrode by stopcocks. The electrode under test was platinum foil rolled into a loose roll. Its surface was ~ 120 cm^2, and the volume of the solution was 9 cm^3.

Fig. 3. Dependence of the potential of a platinum electrode on irradiation time (0.8 N sulfuric acid, electrode surface 120 cm^2, solution volume 9 cm^3, no gas phase)

Figure 3 gives the curve of the change in the potential of a platinum electrode in such a system as a function of the time of action of the radiation. As can be seen, the potential rapidly assumes the value +20 mV, which is maintained throughout the entire experiment, ~ 20 h (the total dose was $3 \cdot 10^{21}$ eV/cm^3).

Fig. 4. Dependence of the magnitude of the polarizing current on irradiation time at a platinum-electrode potential of 0.4 V (0.8 N sulfuric acid, electrode surface 120 cm^2, solution volume 9 cm^3, no gas phase)

In the system described above, the ratio between the electrode surface and the solution volume is such that, when a positive current is passed, i.e., during the ionization of hydrogen, the equality of the concentrations of the oxidizing and reducing products of radiolysis is rapidly disturbed, since there is practically no "reservoir" from which the consumption of hydrogen at the electrode can be replenished. This disturbance of the equality of concentrations is observed,

as is seen on the curve in Fig. 4, already when recording the current–time curve itself at a potential of 0.4 V. The accumulation thereby occurring of oxidizing

radiolysis products at a higher concentration leads to a rapid drop in the current during irradiation and to a negative current after irradiation is stopped, despite the selectivity of platinum toward the process of hydrogen ionization.

If a second electrode is present in the irradiated solution, on which the selective process of reduction of the oxidizing radiolysis products can take place—for example, a gold electrode [3,4]—then the equality [Ox] = [Red] will be maintained when a current of a definite magnitude is passed throughout the entire irradiation time. The electrode potentials in this case will be determined only by the selectivity of the latter with respect to the products of water radiolysis.

Consequently, the process of ionization, on a platinum electrode, of the hydrogen formed during radiolysis of water can be carried out at a stationary potential only if, at the same time and at an equal rate, the process of reduction of the oxidizing radiolysis products proceeds on the same electrode (the total current is equal to zero) or on another electrode selective with respect to oxidizing products; in this case the corresponding current will flow in the external circuit.

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Note: Figure translations are in progress. See original paper for figures.