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Abstract

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THE ACTION OF RADIATION ON THE POTENTIAL OF A PLATINUM ELECTRODE IN A SULFURIC ACID SOLUTION

The appearance of products of water radiolysis under the action of ionizing radiation on a solution should lead to a change in the oxidation–reduction properties of the medium and affect the electrochemical and corrosion behavior of metals present in the irradiated solution. In those cases where the solution contains no substances entering into oxidative or reductive reactions with the products of water radiolysis, the radiolysis products may interact directly with the electrode, causing the establishment of a definite potential. V. I. Veselovskii and Ts. I. Zalkind first found that, upon irradiation of nitrogen-saturated solutions of H_2SO_4, a potential close to the reversible hydrogen potential is established on Pt, while on Au a potential of ~0.95 V is established. Thus, in the system Pt/solution of H_2SO_4 saturated with nitrogen/Au, a potential difference of ~0.9 V was obtained. These effects were explained by the authors as due to the selective interaction of Pt with the reducing components of water radiolysis (mainly H atoms), and of the gold electrode with the oxidizing components (mainly OH radicals) of water radiolysis ([1]). According to Clark' s data ([2]), a smooth Pt electrode is much more sensitive to the action of radiation than a platinized one, although in principle their behavior is similar.

Developing Allen' s idea concerning the onset of an equilibrium ratio of the concentrations of the oxidized and reduced forms of a substance during prolonged irradiation of a solution, Daynton and Collinson suggested that the state of equality of the rates of oxidation and reduction is characterized by an equivalent oxidation–reduction potential of irradiated water ([3]). Henderson et al. ([4]) found that, in the presence of an oxidation–reduction indicator (mainly KJ), the steady potential of a Pt electrode in an irradiated solution assumes a value of 0.85 V relative to the hydrogen electrode in the same solution. This value does not depend on the nature of the oxidation–reduction indicator, the dose rate, or the pH, and is taken by the authors to be equal to the oxidation–reduction potential of irradiated water.

In our work the aim was to determine the conditions under which the hydrogen potential and a potential close to 0.85 V are realized on Pt, and to evaluate the role of radical and molecular products in establishing the potential under

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

irradiation. The behavior of a smooth Pt electrode in an H_2SO_4 solution was studied over a wide range of radiation doses and dose rates. Irradiation was carried out with X-rays (voltage 80 kV, maximum current 200 mA) in glass cells of two types (Fig. 1, *I* and *II*), in which maximum dose rates of respectively $\sim 3 \cdot 10^{17}$ and $\sim 7 \cdot 10^{16}$ eV/cm$^3 \cdot$ sec could be attained. In cell *I*, owing to the large meniscus of the liquid and the small thickness of the solution layer (2–3 mm), the hydrogen formed during radiolysis could be removed from the solution during the experiment; in cell *II* the meniscus of the liquid is very small, and therefore the escape of hydrogen into the gas phase is hindered. In both cells it was possible to replace the solution during the experiment by forcing it from the reservoir vessel *B*, where it had previously been saturated with the corresponding gas. In some

In the experiments, the cell was a vertical thin-walled tube 7 mm in diameter, through which the solution flowed; a part of the cell 3 mm high, where the electrode was located, was exposed to a horizontal beam. Solutions of 0.8 N H_2SO_4 were prepared from twice-distilled H_2SO_4. Hydrogen and nitrogen for saturating the solutions were purified of traces of oxygen and impurities. Measurements of the potential were made with the aid of a cathode voltmeter; the reference electrode was either a hydrogen electrode or a mercury-sulfate electrode. The ignited Pt electrode was etched in hot aqua regia and washed in hot twice-distilled water; before the experiment the electrode was subjected to alternating cathodic and anodic polarization in the same or in a separate apparatus.

Fig. 1. Schematic representation of the cell for measurements. **A** —measuring vessel with the solution under investigation; **B** —auxiliary vessel for preliminary saturation of the solution with the required gas. The diagram does not show the inlet into the measuring cell for entry and exit of gas and the inlet for draining the solution from the cell, which is a thin tube reaching to the bottom, with a stopcock.

Figure 2 shows the dependence of the potential of the Pt electrode on the time of action of the radiation at different dose rates. As is seen from the figure, the potential of Pt in a solution saturated with nitrogen, under the action of radiation, first shifts in the negative direction (section *a*) and reaches values close to the reversible hydrogen potential (section *b*). However, the hydrogen potential on Pt is not stable, since with continued irradiation the potential again shifts in the positive direction (section *b*) to values of ~0.85 V.

Figure 3

Figure 3: Figure 3

Figure 4

Figure 4: Figure 4

Fig. 2. Dependence of the potential of a platinum electrode on the time of action of radiation at different dose rates (in eV/cm^3 · sec). 1 —$2 \cdot 10^{17}$, 2 —$5 \cdot 10^{16}$, 3 —$2 \cdot 10^{16}$. Solution 1 saturated with nitrogen. ↓ —irradiation switched on, ↑ —irradiation switched off. Measurements in cell I.

During irradiation the potential reaches hydrogen values at an absorbed dose of 3—$5 \cdot 10^{18}$ eV/cm^3, independently of the dose rate*. If the yield of molecular hydrogen in 0.8 N H_2SO_4 is taken to be 1.0 molecule/100 eV [5], the concentration of molecular hydrogen in the solution at a dose of $4 \cdot 10^{18}$ eV/cm^3 will be

$$1.0 \cdot 4 \cdot 10^{18} \cdot 10^3/100 \cdot 6 \cdot 10^{23} = 6.6 \cdot 10^{-5} \text{ mol/l.}$$

The concentration of hydrogen in H_2SO_4 solution when the solution is saturated with hydrogen at atmospheric pressure and room temperature is ~$6 \cdot 10^{-4}$ mol/l. Since in our experiments the Pt potential during irradiation did not reach the equilibrium hydrogen potential by 10—40 mV, and the temperature of the solution during irradiation rose to 40°, we believe that the observed value of the potential corresponds to the concentration of molecular hydrogen formed during radiolysis. This conclusion is confirmed by the following observations.

1. If irradiation is interrupted when the most negative value of the potential has not yet been reached, the potential continues to shift in the neg—

* Approximately the same dose is required according to the data of Ts. I. Zalkind and V. I. Veselovskii with γ-radiation from Co^{60}, in whose experiments the dose rate was $2 \cdot 10^{15}$ eV/cm^3 · sec.

in the negative direction; analogous phenomena had previously been observed in our laboratory in nitrate solutions (6). In cell *I* the potential then shifts to 0.85 V, whereas in cell *II* the potential remains near the hydrogen value for a long time. This indicates that the potential is established in accordance with the concentration of the molecular hydrogen being formed, and that the stationary state at the electrode is not established instantaneously.

Fig. 3. Dependence of the Pt potential on time during irradiation of a flowing solution (flow rate 0.2 cm^3/sec, linear velocity 0.42 cm/sec). The solution is saturated with nitrogen. At point *A* the flow of the solution was stopped; at point *B* it was switched on again

Fig. 4. Dependence of the potential of a Pt electrode in 0.8 N H_2SO_4 solution on the concentration of H_2O_2: **1**—a nitrogen-saturated H_2O_2 solution is added to a hydrogen-saturated H_2SO_4 solution; **2**—H_2O_2 is formed during irradiation of a nitrogen-saturated H_2SO_4 solution

2. Addition to a solution of H_2SO_4 or $HClO_4$ of an active radical acceptor ($4 \cdot 10^{-3}$ mole/l KBr), which lowers the concentration of H atoms by ~10^3 times, does not change the dependence of the potential on dose in comparison with a solution of pure acid.

3. When the solution flows through the cell, i.e., under conditions in which, during irradiation, the stationary concentration of the molecular products of radiolysis is significantly reduced, while the stationary concentration of radicals changes little in comparison with a quiescent solution, irradiation does not cause a shift of the potential in the negative direction. When the flow is stopped, the potential under irradiation changes according to the same law as in cell *II* (Fig. 3).

4. In cell *II* the rise of the potential to values of 0.85 V occurs at a higher dose than in cell *I*, in which the stoichiometric ratio of the concentrations of H_2 and H_2O_2 in the solution is disturbed in the direction of increasing H_2O_2.

All this indicates that atomic hydrogen does not play an essential role in establishing the hydrogen potential under irradiation. S. D. Levina and T. V. Kalish arrived at the same conclusion regarding the behavior of a Ni electrode under irradiation (7).

A potential of 0.85 V is the stable state of the Pt electrode in irradiated H_2SO_4 solution; moreover, the dose at which this value of the potential is reached depends somewhat on the state of the electrode surface and on how rapidly the gaseous products of radiolysis are exchanged between the solution and the gas phase. Attainment of a potential of 0.85 V in apparatus *I* occurs upon absorption of $3 \cdot 10^{19}$ eV/cm^3, and in apparatus *II* upon 2–$5 \cdot 10^{20}$ eV/cm^3, independently of dose rate*. After it has reached—

* The same dose as in cell *II* is required also in a cell of volume 6 cm^3, completely filled with nitrogen-saturated solution, in which the escape of hydrogen from the solution was eliminated.

···min, irradiation for an hour or more (dose rate $1 \cdot 10^{17}$ eV/cm$^3 \cdot$ sec) does not change its value. Termination of irradiation in this state also has almost no effect on the magnitude of the potential. Upon repeated irradiation of the same electrode in the same solution after a steady potential has been attained, the potential shifts in the negative direction by only 20-50 mV, and then the potential again returns to the steady value (Fig. 2, curve 2, start of irradiation —point *A*). If the solution is replaced by a fresh one, then under irradiation the potential again shifts toward the equilibrium hydrogen value (Fig. 2, curve 2, replacement of the solution—point *B*), and then to 0.85 V. Such phenomena are

repeated many times on the same electrode when the solution is replaced.

The shift of the potential from the hydrogen value in the positive direction is associated with the accumulation of H_2O_2 in the solution during irradiation. In Fig. 4, for comparison, curves are juxtaposed for the dependence of the Pt potential in H_2SO_4 solution on the concentration of H_2O_2. Curve 1 shows the change in the Pt potential when a solution of H_2O_2, saturated with nitrogen, is added to an H_2SO_4 solution saturated with hydrogen. The potential at first changes almost not at all, and at an H_2O_2 concentration of $\sim 2.4 \cdot 10^{-3}$ mol/l it shifts sharply in the positive direction to values of ~ 0.8 V. Curve 2 represents the dependence of the potential on dose at a dose rate of $7 \cdot 10^{16}$ eV/cm$^3 \cdot$ sec, recorded in cell II and recalculated as a dependence of the potential on the concentration of the H_2O_2 formed (taking the yield of H_2O_2 to be 0.8 molecule/100 eV). As is seen from Fig. 4, H_2O_2, irrespective of the manner in which it is introduced into the solution, causes a shift of the potential to values of ~ 0.8 V. The accumulation of H_2O_2 to a stationary concentration also explains the following results. The hydrogen potential at atmospheric hydrogen pressure does not change under prolonged irradiation. However, the Pt potential in H_2SO_4 solution at a hydrogen pressure of 0.1 atmosphere, under prolonged irradiation (dose $\sim 3 \cdot 10^{20}$ eV/cm^3), shifts to 0.85 V. In the first case, owing to the large exchange current of the hydrogen evolution-ionization reaction, accumulation of H_2O_2 to the stationary concentration is unable to shift the potential in the positive direction. When the hydrogen concentration is decreased by a factor of 10 and the hydrogen exchange current is correspondingly reduced, reduction of the H_2O_2 present in the solution at the stationary concentration shifts the potential in the positive direction.

Thus, the potential of a Pt electrode in 0.8 N H_2SO_4 solution under the action of radiation is determined by the molecular products of the radiolysis of water accumulating in the solution—hydrogen and hydrogen peroxide. Radical products play no appreciable role in establishing the potential on Pt; the greater part of them evidently recombines in the bulk of the solution and on the electrode surface.

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