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Studies on Photo-polarography. V. Theory of Photo-current and Reaction of Aquated Electrons with Scavenger[1]

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The existence of trapped electrons in gamma irradiated glass was directly substantiated by ESR studies[2]. The ESR technique, however, can not be applied to such a transient entity as solvated electrons in solution. On the other hand, the possible existence of free solvated electrons in solution at reasonably close proximity to the parent ion was suggested by spectrophotometric studies[3] using a matrix isolation technique. From kinetics and mass-transport studies[4,5] the reactive but transient entity of an electron in solution is known to be solvated. Accordingly, photo-detached electrons emitted into an aqueous electrolyte solution from an electrode irradiated by ultra-violet light are reasonably assumed to be aquated at a certain distance apart from the electrode surface, where electrons are thermalized. The aquated electrons $\mathrm{e}_{\mathrm{aq}}^-$ then react with scavenger ions or molecules in solution, producing the photo-current in an electrolytic cell circuit.

The electrolytic photo-current is controlled by the diffusion of $\mathrm{e}_{\mathrm{aq}}^-$ and its reaction rate with a scavenger. Barker *et al.*[6] gave an equation for the photo-current, but without details. A more generalized solution of this semi-infinite diffusion problem is presented in this paper on the basis of Hatta's theory on the absorption of gases in a reactive solution[7]. The validity of our theory was proved by the dependence of the photo-current on the scavenger concentration and by the Brønsted theory on an ionic reaction with special regard to the solvent effect on the rate process.[8]

Theory

According to Barker's model of the reaction the electrons emitted from the irradiated electrode partly return to the electrode by attraction. Some electrons, however, have sufficient kinetic energy to overcome the attraction,[9] and are thermalized at a distance δ where the attraction is equal to the thermal energy of an electron $\boldsymbol{kT}$. In this process water molecules are repelled by a thermalized electron, and the liquid is dilated so that a cavity is created in the solution. The electron is then held in the cavity as an aquated electron (Eq. (1)), and enters into the chemical reaction with a scavenger ion or molecule S, as shown in Eq. (2). In this reaction it is assumed that the aquated electrons are wholly depleted through Reaction (2) except the self-decay (Reactions (3) and (4)).

These reactions are schematically shown in the following:

$$\mathrm{e}^- + n\mathrm{H_2O} \rightleftarrows \mathrm{e}_{\mathrm{aq}}^- \tag{1}$$

$$\mathrm{e}_{\mathrm{aq}}^- + \mathrm{S} \xrightarrow{k_{\mathrm{s}}} \mathrm{S}^- \tag{2}$$

$$\mathrm{e}_{\mathrm{aq}}^- \rightarrow \mathrm{H}_{\mathrm{aq}} + \mathrm{OH}_{\mathrm{aq}}^- \tag{3}$$ [13]

$$2\mathrm{e}_{\mathrm{aq}}^- \rightarrow \mathrm{H}_2 + 2\mathrm{OH}_{\mathrm{aq}}^- \tag{4}$$ [13]

When the self-decay of $\mathrm{e}_{\mathrm{aq}}^-$ can be neglected in comparison with the rate of the scavenging reaction, the semi-infinite diffusion equation for the process given by Eqs. (1) and (2) is expressed as follows:

$$\frac{\partial C_\mathrm{e}}{\partial t} = D_\mathrm{e}\frac{\partial^2 C_\mathrm{e}}{\partial x^2} - k_\mathrm{s}C_\mathrm{e}C_\mathrm{s} \tag{5}$$

where C_e and D_e are the concentration and diffusion coefficient of the aquated electron, respectively, k_s the rate constant of Reaction (2), and C_s the scavenger concentration. Under a sufficiently high concentration of scavenger, C_s the scavenger concentration. Under a sufficiently high concentration of scavenger, $C_{\mathrm{s}(t=0,x)} = C_{\mathrm{s}(t=t,x)}$, we have

$$k_\mathrm{s}C_\mathrm{e}C_\mathrm{s} = kC_\mathrm{e} \tag{6}$$

Thus, Reaction (2) can be approximated as a pseudo-first order reaction.

At the stationary state of the diffusion and scavenging process $\partial C_\mathrm{e}/\partial t = 0$, and we have from Eq. (5)

$$D_\mathrm{e}\frac{\partial^2 C_\mathrm{e}}{\partial x^2} = kC_\mathrm{e} \tag{7}$$

The boundary conditions for Eq. (7) are

$$\left.\begin{aligned} &\text{at} && x=0,\ C_\mathrm{e}=C_\mathrm{e}^\delta \\ &\text{and at} && x=r,\ \frac{\mathrm{d}C_\mathrm{e}}{\mathrm{d}x}=0, \end{aligned}\right\} \tag{8}$$

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1) This paper was presented at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, April 1969. For Part IV see, This Bulletin, **42**, 578 (1969).

2) D. C. Walker, *Quart. Rev., London.* **21**, 79 (1967). F. S. Dainton, in Gomberg Centenary Volume, Butterworth, London (1967). J. Zimbrick and L. Kevan, *J. Amer. Chem. Soc.*, **89**, 2483 (1967).

3) M. Anbar and E. J. Hart, *J. Phys. Chem.*, **69**, 1244 (1965).

4) W. C. Gottschall and E. J. Hart, *J. Phys. Chem.*, **71**, 2102 (1967).

5) K. H. Schmidt and W. L. Buck, *Science*, **151**, 70 (1966).

6) G. C. Barker, A. W. Gardner and D. C. Sammon, *J. Electrochem. Soc.*, **113**, 1182 (1966).

7) S. Hatta, *Technol. Reports Tohoku Univ.*, **10**, 916 (1939).

8) For experimental techniques see K. Yamashita and H. Imai, This Bulletin, **41**, 1339 (1968), **42**, 578 (1969).

9) The energy barrier for the emission of electrons in an electrolyte solution has been discussed by Delahay and Srinivasan[10], Brodski and Gurevich[11], and Sharma *et al.*[12]

10) P. Delahay and V. S. Srinivasan, *J. Phys. Chem.*, **70**, 420 (1966).

11) A. M. Brodski and Yu. Ya. Gurevich, *Electrochim. Acta*, **13**, 1254 (1968).

12) V. P. Sharma, P. Delahay, G. G. Susbielles, and G. Tessari, *J. Electroanal. Chem.*, **16**, 285 (1968).

13) Whether the decay is to proceed in the first order reaction (Reaction (3)) or in the bimolecular decay depends upon the concentration of the aquated electrons formed on the deposition plane. For a review see F. S. Dainton, "The Chemistry of the Electron," Nobel Symposium 5, ed. by S. Claeson, Interscience Publishers, New York, N. Y. (1967), pp. 185—209.

where r denotes the distance where e_{aq}^-s are depleted.

The solution of Eq. (7) is given by Hatta[7] as in the following:

$$\frac{C_e}{C_e^\delta} = \frac{\cosh\left\{\sqrt{\frac{k}{D_e}}r\left(1-\frac{x}{r}\right)\right\}}{\cosh\left(\sqrt{\frac{k}{D_e}}r\right)} \tag{9}$$

The rate of electron depletion, v, through the scavenging reaction is expressed by the number of electrons diffusing away from the deposite plane during unit time, *i.e.*,

$$v = -D_e\left(\frac{dC_e}{dx}\right)_{x=0} \tag{10}$$

Thus, the photo-current can be expressed as follows:

$$i_p = -FD_e\left(\frac{dC_e}{dx}\right)_{x=0} = FD_eC_e^\delta\sqrt{\frac{k}{D_e}}\tanh\left\{\sqrt{\frac{k}{D_e}}r\right\} \tag{11}$$

When the reaction rate is sufficiently high, then $\sqrt{k/D_e}\cdot r \rightarrow \infty$, and $\tanh(\sqrt{k/D_e}\cdot r)$ can be approximated as unity. Thus, Eq. (11) leads to

$$i_p = FD_eC_e^\delta\sqrt{\frac{k}{D_e}} = FC_e^\delta\sqrt{k_sC_sD_e} \tag{12}$$

On the contrary, when the diffusion is sufficiently high in comparison with the reaction rate, the rate will be expressed simply as

$$v' = kC_e^\delta r \quad \text{and} \quad i_p' = FC_e^\delta k_sC_sr \tag{13}$$

It is noteworthy that Eq. (12) coincides well with the Barker equation[6].

Results and Discussion

In the following the validity of Eq. (12) is proved in relation to the dependence of photo-current on the scavenger concentration, ionic strength of the solution and on the static dielectric constant of the solution.

Field Effect on i_p. The field effect on the photo-current was first pointed out by Barker *et al.*[6] Delahay and Srinivasan applied Fowler's theory of photo-detached electrons *in vacuo* to the solution medium in question, and a quadratic relation of i_p to the electrode potential E was proved in the scavenging of e_{aq}^- by the hydrogen ion. Brodski and Gurevich[10] proposed an improved theory and proved a better linear relationship between i_p and $E^{5/2}$. In our experiment using polychromatic light (250—350 mμ) and nitrate as the e_{aq}^- scavenger[14] a better linear relationship of i_p *versus* $E^{5/2}$ was obtained as shown in Fig. 1.

Dependence of i_p on C_s. Eq. (12) shows a linear relationship between the photo-current and the square root of the scavenger concentration. The photo-current measured at the electrode potential of −1.6 V *vs.* S. C. E. showed a good linearity against the square root of the nitrate concentration as shown in Fig. 2. Even in 44% ethanol-water mixture the linearity was excellent in accordance with Eq. (12).

The Brϕnsted Theory Applied to the Reaction of e_{aq}^- with Nitrate. We assumed that the photo-current flows as a result of Reaction (2) which proceeds in the solution phase at a distance δ apart from the electrode surface (for the reaction model proposed hitherto, *cf.* Ref. 6, 15, 16). The validity of our reaction model, which coincides with the Barker model, can be proved by a solvent effect on the activity coefficient of the reacting species. Thus the Brϕnsted theory on an ionic reaction was treated, and in the modified expression of the theory a plot of $\log i_p$ *vs.* $\sqrt{\mu}/(1+\sqrt{\mu})$ (μ : the ionic strength) should yield a straight line with slope of $0.51\,Z_eZ_s$, provided C_e and D_e are not significantly varied with changing μ. These data are shown in Fig. 3, which indicates that the values of both Z_e (the charge of the aquated electron) and Z_s (the charge of the scavenger) are univalent and negative.

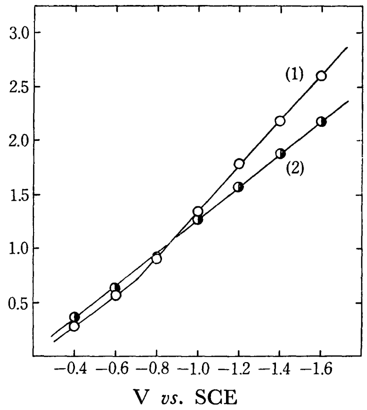

Fig. 1. Dependence of the photo-current on the electrode potential.
0.2 M KCl and 5 mM KNO_3 aq. solution.
(1) $i_p^{1/2}-E$, (2) $i_p^{2/5}-E$.

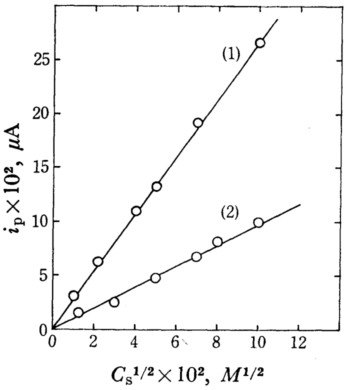

Fig. 2. Dependence of the photo-current on the scavenger concentration.
(1) 1 M KCl aq. solution.
(2) 0.2 M KCl and 44% ethanol aq. solution.
Scavenger, NO_3^-.

The effect of the static dielectric constant of a solvent on the rate of an ionic reaction can be discussed in the same way. By combining the Brϕnsted-Christiansen-Scatchard equation[17,18] and Eq. (12) a plot

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[14] The scavenging reaction seems to proceed as follows:
$e_{aq}^- + NO_3^- \rightarrow NO_3^{2-} + aq \rightarrow NO_2 + 2OH^-$
(or $HNO_3^- + OH^-$)

[15] H. Berg, *Electrochim. Acta*, **13**, 1249 (1968).

[16] M. Heyrovsky, *Nature*, **200**, 880 (1963), *Z. Physik. Chem. (Frankfurt)*, **52**, 1 (1967).

[17] G. Scatchard, *Chem. Rev.*, **10**, 229 (1932).

[18] B. Krishna and H. S. Singh, This Bulletin, **41**, 325 (1968).

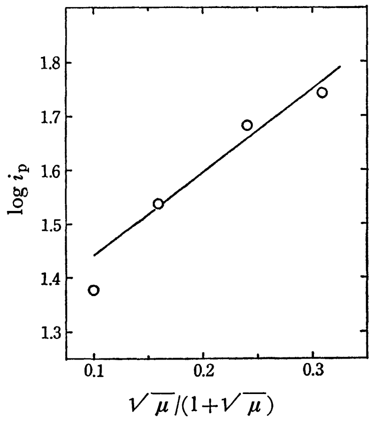

Fig. 3. Effect of the ionic strength on the photo-current. KCl and 5 mM KNO_3 aq. solution.

of $\log i_p$ *versus* $(\sqrt{\varepsilon}-\text{const})/\sqrt{\varepsilon^3}$ (ε : the static dielectric constant) should yield a straight line for solutions constant μ. The data are shown in Fig. 4. The value of D_e was not corrected for the charge of the solution media in this plot. Nevertheless, it gives a fairly good straight line in accordance with the theory. From the plot the charge of an aquated electron is evaluated to be negative, and the rate-determining step of the photo-current is a reaction of an aquated electron with nitrate in the reaction layer.

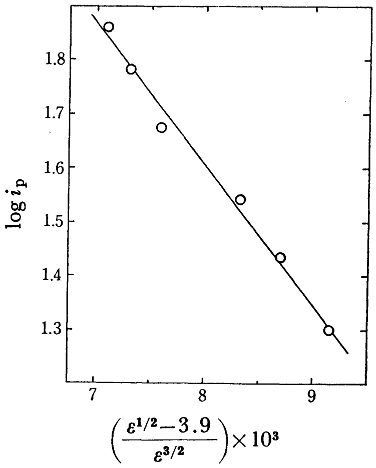

Fig. 4. Effect of the static dielectric constant on the photo-current.
Ethanol-water mixture containing 5 mM KNO_3 and 0.2 M KCl.