SHORT COMMUNICATIONS

Studies on Photo-polarography. IV. Solvent Effect on Photocurrents

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The photoelectric effect at a metal-electrolyte interface has recently attracted attention in relation to the formation of the solvated electron and its reaction with the scavenger.[1-3] The solvent effect on this process, however, has not yet been reported. The authors have investigated the solvent effect on the photocurrent of nitrate in aqueous-organic solvent solutions containing 0.2 M KCl. The dropping mercury electrode was irradiated by the polychromatic light from a xenon lamp (250—350 mμ with a Toshiba UV-D25 filter), and the photocurrent was produced by the reaction of e_{aq}^- with NO_3^- to form NO_3^{2-} as the intermediate.[4]

The quadratic relationship[2] of the field effect on the photocurrent was proved in the potential region from −1.0 to −1.6 V *vs.* SCE. At a given potential the photocurrent was proportional to the square root of the nitrate concentration (0.1—10 mM) in good accordance with Barker's theory.[1]

According to the Barker model of the process, the photoelectrically emitted electrons are thermalized at around a distance, δ, away from the electrode surface, and are then hydrated (*cf.* Fig. 1). At the distance, δ, the coulombic energy (image force) is in balance with the thermal energy of the electron, *i. e.*,

$$\frac{e^2}{\varepsilon\delta} = kT \tag{1}$$

where ε is the static dielectric constant of the medium and the other symbols are of their usual significance. It is noteworthy that in Eq. (1) δ is inversely proportional to ε. Our experimental evidence shows that log i_p (i_p, the photocurrent) is proportional to $1/\varepsilon$ as is shown in Fig. 2, *i. e.*,

$$\log i_p = K_1\left(\frac{1}{\varepsilon}\right) + K_2 \tag{2}$$

where K_1 and K_2 are the constants. Assuming the exponential distribution of emitted electrons along the r axis, equation (3) can be derived as follows;

$$i_p \propto \int_\delta^\infty e^{-r}\mathrm{d}r = -e^{-\delta} = -e^{-\frac{e^2}{\varepsilon kT}} \tag{3}$$

Detailed investigation is now in progress in our laboratory.

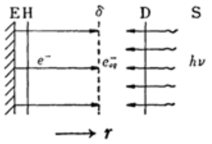

Fig. 1. Schematic representation of irradiated electrode surface.
E: Electrode D: Diffuse double layer
H: Helmholtz plane S: Solution
δ: Deposition plane

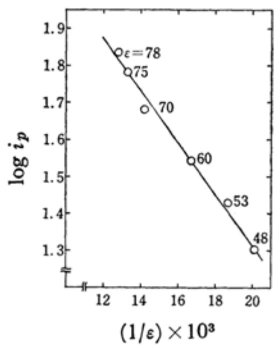

Fig. 2. Variation of log i_p with $1/\varepsilon$.
Solution; ethanol-water mixture containing 0.2 M KCl.
Scavenger of e_{aq}^-; 5 mM NO_3^-.
Applied potential; −1.6 V *vs.* SCE.
The measurements were carried out without altering at all the optical alignment. The values of ε were not corrected for the effect of the electric field and electrolyte.

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[1] G. C. Barker, A. W. Cardner and D. C. Sammon, *J. Electrochem. Soc.*, **113**, 1182 (1966).

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

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

[4] M. Ottolenghi and J. Rabani, *J. Phys. Chem.*, **72**, 593 (1968).