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Photoemission and Solvation Free Energies of Electrons in Polar Solvents

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The red limit potential of electron photoemission was measured in various polar solvents, and the apparent solvation free energies of the electrons were estimated. The energy state and transformation of photoemitted electrons in solution were discussed as regards the role of dry or damp electrons as an intermediate species. A proportionality between the intermediate solvation free energy and the energy quantum of the optical absorption band maximum of solvated electron in various polar solvents is pointed out.

In polar solvents the electrons produced by high energy radiation are localized or trapped by the surrounding solvent molecules in a delicate balance of short- and long-range interactions.[1] Such a solvated electron can also arise in photo-electrochemical processes, where the photoemission from a cathode under suitable conditions of illumination is measured as the cell current flowing due to the homogeneous electron capture process.[2] The dependence of the photocurrent on the square root of the scavenger concentration and rate constant of a scavenging reaction has been proved by the theory based on the semi-infinite diffusion equation.[3] The red limit potential or threshold potential, which can be estimated from the photoelectrochemical process, is related to the estimate of the work function of the electron from a metal into solution. The interaction of photoemitted electron with solvent molecules can be expressed in terms of the difference between the work function of the electron from a metal into vacuum and that from the metal into solution, when the Volta potential difference is taken into account. The values estimated for water from this relationship, however, show a fairly remarkable discrepancy from the hydration free energy of the electron obtained by radiation chemical studies.[4,5] Schiffrin[6] extensively discussed the difference, attributing it to the contribution of the solvent reorganization energy. On the other hand, Pleskov and his co-workers[7,8] interpreted the difference by assuming free or delocalized electrons.

In this paper precise data of the red limit potential in various polar solvents are presented. The physical meaning of the energy value estimated as an interaction energy of emitted electrons with solvent molecules prior to the electron capture reaction is discussed.

Experimental

The apparatus is shown in Fig. 1. A lock-in amplifier (Model LI-572B, NF Circuit Design Block Co.) with a light chopper, Model CH-352, was used at a *ca.* 20 Hz frequency. A three-electrode cell, equipped with a water jacket to control the temperature, was used. The potential of the working electrode (a mercury pool electrode renewed by spilling mercury in each run; illuminated area *ca.* 0.3 cm^2) was controlled with a potentiostat (Shimadzu Model PS-2). A 500 watt super high pressure mercury lamp (Ushio Type USH 500D) was used for illumination through a monochrometer or color filters. The wavelength of the incident light was 365 nm. When gas bubbles are evolved by a scavenging reaction, *e. g.* N_2 from N_2O or H_2 from H_3O^+, it is preferable to measure under a small current density. Since the current signal is very small, an electrode with wide illumination area gives more accurate measurements.

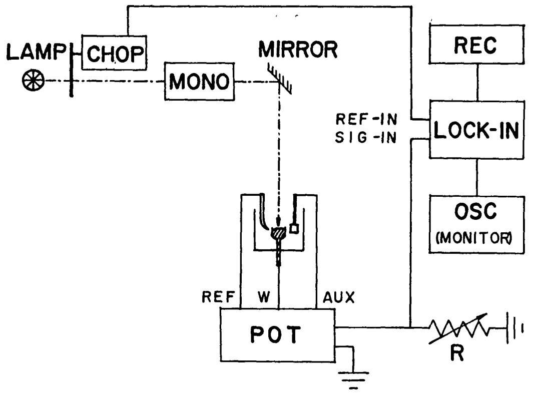

Fig. 1. Apparatus used for experimental measurements of photocurrents.
LAMP, super high pressure mercury lamp; CHOP, chopper; MONO, monochrometer; POT, potentiostat; REC, recorder; LOCK-IN, lock-in amplifier; OSC, oscilloscope; R, decade resistance.

All the solvents were purified by the usual methods.[9] Measurements were carried out at 25 °C.

Results and Discussion

Estimation of Intermediate Solvation Free Energy of Electron from Red Limit Potential. The dependence of photoemission current, I_e, on the quantum energy of incident light, $h\nu$, and the field strength or electrode potential, ϕ, under sufficiently high electrolyte concentration is given by[10]

$$I_e = A(h\nu - h\nu_0 - e\phi)^{5/2}, \tag{1}$$

where A is a constant depending upon the properties of the metal, h the Planck constant, and ν_0 the threshold frequency at the potential of zero charge, ϕ_{pzc}. All the potential values are referred to ϕ_{pzc}. The relationship known as the law of five halves, was derived as an approximate solution of a theoretical equation postulating the transmission of electrons through the energy barrier at the electrode-solution interface. The equation was verified experimentally to hold not only in aqueous solutions,[7,10] but also in non-aqueous solutions.[11] Figure 2 shows the linear relationship between $i_p^{0.4}$ and ϕ in hexamethylphosphoramide (HMPA) solution saturated with nitrous oxide, where i_p is the photocurrent measured in experiments. The extrapolation of $i_p^{0.4}$-ϕ straight line to $i_p=0$ gives the red limit potential of -0.42 V *vs.* Ag/0.01 M $AgClO_4$

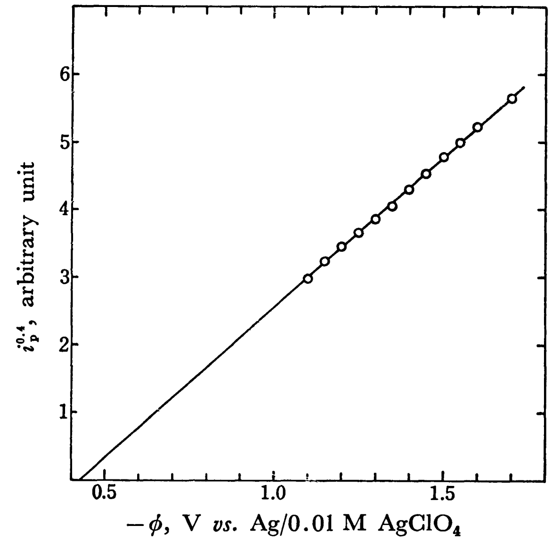

Fig. 2. Dependence of $i_p^{0.4}$ on ϕ for 0.2 M $NaClO_4$ HMPA solution saturated with N_2O.

electrode. According to the definition of the red limit potential, ϕ_0, Eq. 1 leads to

$$h\nu_0 = h\nu - e\phi_0 \tag{2}$$

The energy quantum, $h\nu_0$, can be replaced by the work function, W_{m-s}, of the electron emission from a metal into solution as given by

$$W_{m-s} = h\nu - e\phi_0. \tag{3}$$

A tentative energy cycle was proposed from a comparison of the electron photoemission in solution with that *in vacuo* (the work function; W_{m-v}).[12] However, there is a discrepancy between the data obtained by this method and those by radiation chemical studies. A modification of the energy cycle can be deduced by taking the discrepancy into consideration. The modified energy cycle involves two stages of the electron-solvent interaction, namely an intermediate state[6] of solvation (a quasi-solvated state) and fully solvated state as shown in Fig. 3. The symbols, e^-_{q-s} and e^-_{f-s}, represent the quasi-solvated and fully solvated electrons, respectively, ΔG the free energy change for respective solvation process, and $\Delta\Delta G_s$ the difference between ΔG_{f-s} and ΔG_{q-s}. The energy balance in routes (1) and (2) lead to the following expressions.

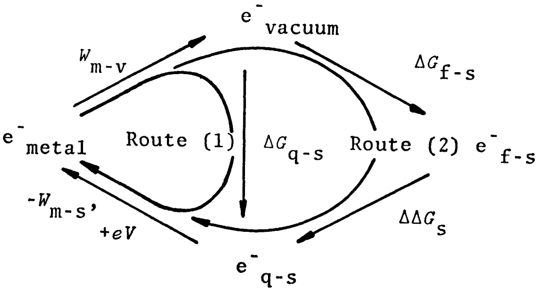

Fig. 3. Modified energy cycle of the electron.

$$-\Delta G_{q-s} = W_{m-v} - W_{m-s} + eV_{m-s}$$
$$= W_{m-v} - h\nu + e(\phi_0 + V_{m-s}) \tag{4}$$
$$-\Delta G_{f-s} = -\Delta G_{q-s} + \Delta\Delta G_s, \tag{5}$$

where V_{m-s} is the Volta potential difference between a metal and solution.

Taking $W_{Hg-vacuum}=4.52$ eV, $h\nu=3.40$ eV corresponding to $\lambda=365$ nm, $e\phi_0=0.26$ eV for saturated-N_2O aqueous solution containing 0.2 M KCl, and $eV_{Hg-aq}=-0.26$ eV, which is evaluated from the data obtained by Randles[13] and Grahame *et al.*,[14] we obtain $-\Delta G_{q-s}=1.14$ eV from Eq. 4. This value coincides with previous estimates,[3,6,7] the value of $-\Delta G_{f-s}$ estimated in radiation chemical studies being

Table 1. Values of threshold potentials, quasi-solvation free energies of electrons and transition energies for the optical absorption maxima of solvated electrons in various polar solvents

Solvent	ϕ_0/V	ϕ_{pzc}/V	V_{m-s}/V	$\Delta G_{q-s} + eV_{m-s}$/eV	ΔG_{q-s}/eV	λ_{max}/nm	$h\nu_{max}$/eV	ε
HMPA	-0.42_2	-0.30		-1.01		2250[d)]	0.55	30
MeOH	-0.36_2	-0.78_6	-0.53[a)]	-1.55	-1.02	630[e)]	1.97	32.6
DMF	-0.54	-0.68	-0.63[b)]	-1.27	-0.64	1680[f)]	0.74	36.7
						650[g)]	1.91	
MeCN	-0.46_8	-0.62		-1.28		690[h)]	1.80	38
DMSO	-0.76_5	-0.59_4		-0.96				48.9
PC	-1.03	-1.24		-1.34				64.4
H_2O	-0.18_5	-0.44	-0.26[c)]	-1.40	-1.14	720[i)]	1.72	78.5

HMPA, hexamethylphosphoramide; MeOH, methanol; DMF, *N*,*N*-dimethylformamide; MeCN, acetonitrile; DMSO, dimethylsulfoxide; PC, propylene carbonate; Scavenger, N_2O; Supporting electrolyte, 0.2 M $NaClO_4$ (0.2 M KCl in the case of water); Reference electrode, Ag/0.01 M $AgClO_4$ (SCE in the case of water).

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1.67[4] or 1.71[5] eV. Thus the value of $\Delta\Delta G_s$ is estimated to be 0.53—0.57 eV, *viz.*, the energy of the quasi-hydrated state is higher by 0.53—0.57 eV than that of the fully hydrated state.

The data of ΔG_{q-s} estimated similarly in various polar solvents and related values are summarized in Table 1.

Transformation of Emitted Electrons and the Succeeding Reaction. In the reaction sequence of the photoemitted electrons in solution containing a scavenger, it seems that the emitted electrons are thermalized and solvated, and then the solvated electrons are captured by scavengers, resulting in the photocurrent. At low concentrations of electron acceptor the mechanism was supported by the coincidence with a theory[2,3] based on the semi-infinite diffusion coupled with the scavenging reaction. The solvent effect on the rate of scavenging process was also confirmed experimentally.[3] At low scavenger concentrations the participation of the fully solvated electron in the reaction pathway seems to be predominant. In the present case, however, the experiment was carried out at relatively high scavenger concentrations, so that the emitted electrons may have been captured by the scavenger prior to full solvation. Hunt and his co-workers[15—17] developed a picosecond stroboscopic pulse radiolysis technique. They found that there are precursors called dry or damp electrons, around which solvent molecules relax to form the fully solvated electrons. This intermediate species might be quasi-solvated and reacts with a scavenger prior to full solvation. The life of the intermediate species is shown to be within the order of picoseconds in aqueous solutions and much longer in alcoholic media.[18]

Taking these findings into consideration, the transformation of photoemitted electrons and the reaction sequence in solution can be expressed as shown in Fig. 4.

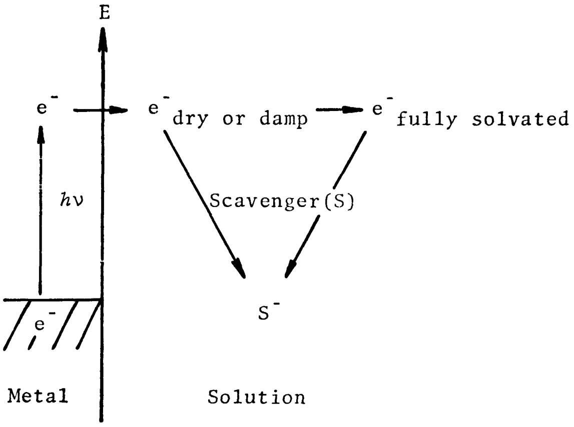

Fig. 4. Transformation of photoemitted electrons and the sequence of reactions.

Relationship between ΔG_{q-s} and $h\nu_{max}$ of Optical Absorption Band Maximum of Solvated Electron. A plot of ΔG_{q-s} *vs.* $h\nu_{max}$, the energy quantum of the optical absorption band maximum of solvated electrons, is shown in Fig. 5.

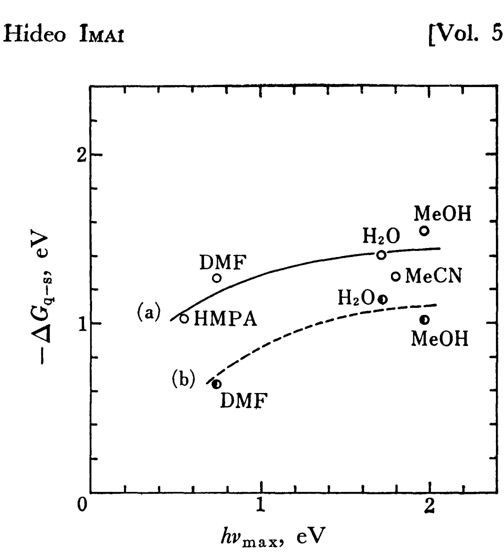

Fig. 5. Empirical correlation between quasi-solvation free energy of the electron and energy of optical absorption band maximum of the solvated electron.
(a) Values uncorrected for the Volta p. d.
(b) Values corrected for the Volta p. d.

The value of $-\Delta G_{q-s}$ increases with increase in $h\nu_{max}$. The solvents used have static dielectric constants ranging from 17 to 84 at room temperature. The optical absorption spectra[1] of the solvated electrons in hydroxy compounds including water are mostly in the visible or near-infrared region. The amides or amines are in the intermediate region 1400—2050 nm, and the ethers are in the infrared region 1800—2300 nm. Corresponding to this trend, it is expected that the free energy of fully solvated electrons decreases in the solvents in the order

hydroxy compounds>amides and amines>ethers,

since the transition energy, $h\nu_{max}$, for optical absorption maximum corresponds to the depth of the potential well of the solvated electron. It is noteworthy that the energy of quasi-solvated electrons also shows the same trend as shown in Fig. 5.

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