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Electrode Kinetics of Photoinduced Redox Reactions: Phenosafranin - EDTA Aqueous System

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The photogalvanic effect in the phenosafranin-EDTA aqueous system has been studied using different concentrations of redox couple. The photovoltage growth and decay curves follow the functional forms related to the relaxation times. Under the experimental conditions, the inverse of relaxation time or the rate of electrode reaction is first order with respect to [phenosafranin] and independent of [EDTA]. The rate constants of forward and backward reactions at 25°C are: $k_1 = 2.0 \times 10^3$ mol^{-1} dm^3 min^{-1} and $k_2 = 4.15 \times 10^3$ mol^{-1} dm^3 min^{-1}. The calculated free energy of electron transfer across the electrode/electrolyte interface is about -3.92 kJ mol^{-1}.

Phenosafranin (PSF)-EDTA system has been found to generate fairly large photovoltage in aqueous solution[1,2] as well as in the solid polycrystalline state[3]. The triplet state photochemistry of PSF, study of its interaction with EDTA by flash photolysis, and the cyclic voltammetry of the reduction of PSF by EDTA have been reported[4,5]. An attempt has also been made to suggest the mechanism of reaction of this system at the illuminated electrode[6]. The solar energy efficiency as well as the storage capability of this system have been improved further employing coated electrodes[7] and glass membrane[8]. But it is interesting to mention that the photovoltage growth and decay of PSF-EDTA system in aqueous solution follow the functional forms (1) and (2) respectively, as mentioned earlier[2];

$$V_t = V_0[1 - \exp(-t/\tau_1 + z_1)] \quad \text{... (1)}$$

$$V_t = V_o \exp(-t/\tau_2 + z_2) \quad \text{... (2)}$$

where V_t is the open-circuit photovoltage at time t, V_o is the steady state open-circuit photovoltage, τ_1 and τ_2 are the relaxation times for growth and decay respectively, and z_1 and z_2 are constants for this system. The relaxation time plays an important role in kinetics of chemical reactions (inverse of relation time represents rate of reaction). Recently, we have reported[9] the electrode kinetic studies, based on the measurement of relaxation times of PSF-EDTA system in the solid polycrystalline state using illuminated semiconductor (SnO_2) electrode. The formation of 2:1 molecular complex between PSF and EDTA prior to photovoltage generation has been concluded from these studies. In the solid state the semiconducting properties of PSF, which is a *p*-type semiconductor[3], play an important role in generating photovoltage during illumination of PSF and PSF-EDTA mixture using *n*-type semiconductor (SnO_2)[10] electrode. On the other hand, photoinduced redox reaction between PSF and EDTA in aqueous solution creates electroactive species for the generation of photovoltage. Obviously, the mechanisms of photovoltage generation in both solid state and aqueous solution are different. So to find the rate-determining step in the latter, an attempt has now been made to study the electrode kinetics of PSF-EDTA aqueous system by measuring the relaxation times for growth and decay of photovoltages at various concentrations of the redox couples. The results are presented here.

Materials and Methods

Phenosafranin (3,7-diamino-5-phenylphenazinium chloride, PSF) (Sigma Chemicals) was recrystallized from ethanol-water. EDTA (disodium salt dihydrate) was of AR grade (BDH).

The photoelectrochemical cell and the details of the experimental set-up for the measurement of photovoltage have been described earlier[11].

Results and Discussion

On illumination of the cell under deoxygenated condition a photovoltage developed and attained a maximum value within a few minutes. When the illumination was stopped, the photovoltage decreased gradually and attained almost the original dark value. The growth and decay of photovoltage for different concentrations of PSF and a fixed concentration of EDTA are shown in Fig.1 at 25°C. The open-circuit photovoltage (V_{oc}) was found to increase with increase in the concentration of PSF upto 2×10^{-5} mol dm^{-3} beyond which slight decrease in V_{oc} was observed due to aggregation of PSF in aqueous solution. The plots of $\ln(V_0 - V_t)/V_0$ versus time for growth (Fig. 2A) and of

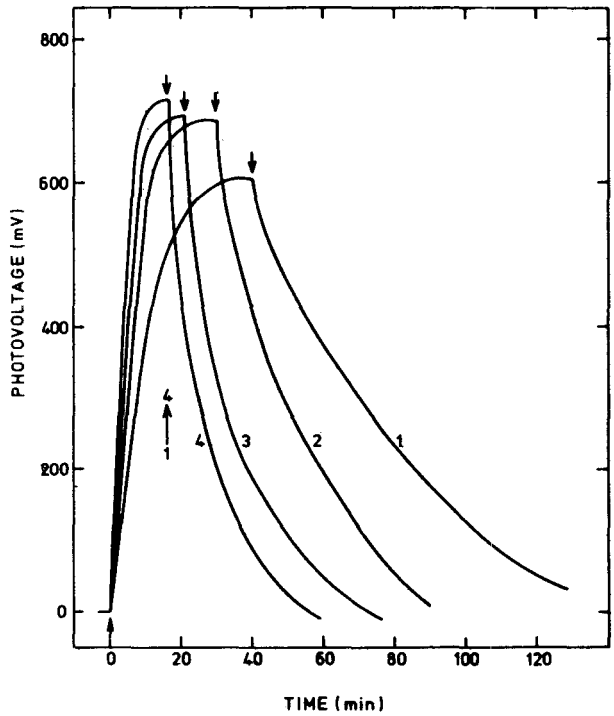

Fig. 1—Growth and decay of photovoltage induced by illumination of PSF-EDTA aqueous system using varying concentrations of PSF and fixed concentration of EDTA (2.0×10^{-3} mol dm^{-3}) [Concentrations of PSF in mol dm^{-3}; (1) 0.5×10^{-5} (2) 1.0×10^{-5} (3) 1.5×10^{-5} and (4) 2.0×10^{-5}. ↑ : Light on; ↓ :light off]

$\ln(V_o/V_t)$ versus time for decay (Fig.2B) at different concentrations of PSF and a fixed concentration of EDTA were linear and the relaxation times for growth and decay were calculated from the slopes of these plots, respectively. The same procedure was followed using another fixed concentration of EDTA and different concentrations of PSF. The values at various concentrations of PSF and EDTA are given in Table 1, alongwith the maximum V_{oc} generation. An attempt was made to calculate the rate constant by plotting the inverse of relaxation time against $[PSF]^m$, by taking different values oF m. But when $m=1$, a linear relationship was obtained as shown in Fig.3 for two sets of experiments consisting of different concentrations of PSF with a fixed concentration of EDTA in each set. The rate constants, calculated from the slopes of these plots, were 2.0×10^4 and 4.15×10^3 mol^{-1} dm^3 min^{-1} respectively for growth and decay and the values were independent of EDTA concentration. It is interesting to mention that at different concentrations of PSF and EDTA, the steady state V_{oc}, relaxation times for growth and decay were found different, but the rate constant of the reaction calculated with the help of Eq.(3)

$$k = [PSF]^1 [EDTA]^\circ \tau^{-1} \quad \ldots (3)$$

remained unchanged within the limit of experimental

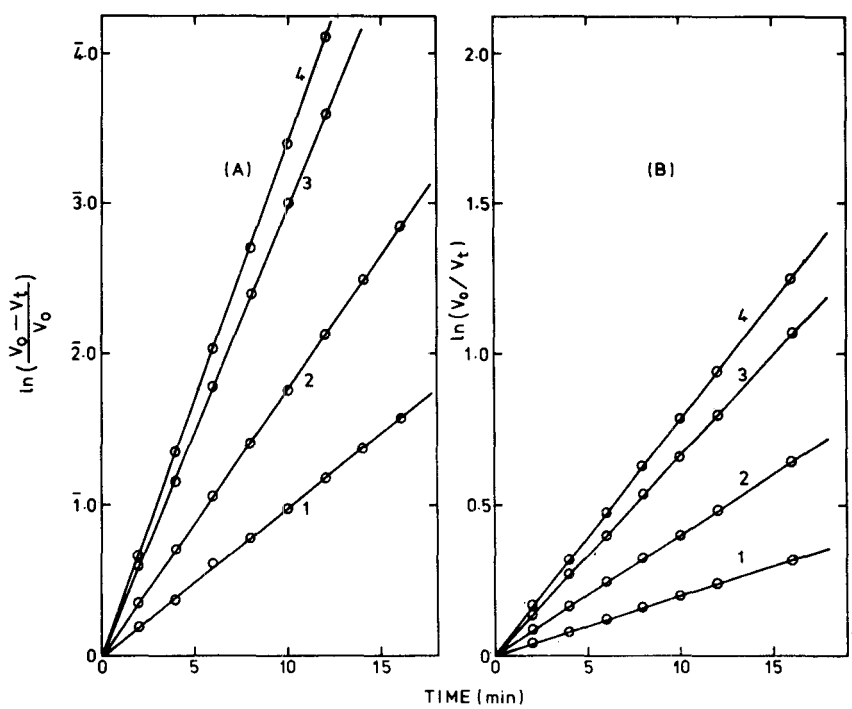

Fig. 2—(A) Plots of $\ln(V_0 - V_t)/V_0$ against t for growth and (B) Plots of $\ln(V_0/V_t)$ against t for decay for PSF-EDTA aqueous system at fixed EDTA concentration (2.0×10^{-3} mol dm^{-3}) and varying concentrations of PSF [Concentrations of PSF in mol dm^{-3}: (1) 0.5×10^{-5} (2) 1.0×10^{-5} (3) 1.5×10^{-5} (4) 2.0×10^{-5}]

Table 1— Photovoltage Generation, Relaxation Times and Rate Constants at Different Concentrations of PSF as well as EDTA in PSF-EDTA Aqueous System

Conc. of PSF × 10^5 (mol dm^{-3})	Photovoltage (mV)	Relaxation time (min)		Rate constant (mol^{-1} dm^3 min^{-1})	
		Growth	Decay	Growth (k_1 × 10^{-4})	Decay (k_2 × 10^{-3})
		EDTA conc. = 0.001 mol dm^{-3}			
0.5	355	9.52	45.45	2.10	4.41
1.0	437	4.84	23.02	2.07	4.34
1.5	560	2.97	14.10	2.24	4.73
2.0	577	2.38	11.80	2.10	4.23
		EDTA conc. = 0.002 mol dm^{-3}			
0.5	625	10.11	52.63	1.98	3.80
1.0	645	5.61	26.61	1.78	3.76
1.5	699	3.33	16.00	2.00	4.17
2.0	713	2.96	13.07	1.69	3.83

k_1 for two sets, 2.13 × 10^4 and 1.86 × 10^4 mol^{-1} dm^3 min^{-1} with average 2.00 × 10^4 mol^{-1} dm^3 min^{-1}

k_2 for two sets, 4.42 × 10^3 and 3.88 × 10^3 mol^{-1} dm^3 min^{-1} with average 4.15 × 10^3 mol^{-1} dm^3 min^{-1}

Equilibrium constant (K), i.e. k_1/k_2 is 4.82; ΔG° at electrode/electrolyte interface is −3.92 kJ mol^{-1} and ΔG° of the cell (V_{oc}, 713 mV) is −68.8 kJ mol^{-1}.

error (Table 1). The equilibrium constant (K) of the electrode reaction, both for growth and decay, was calculated from the slopes of the plots in Fig.3. For all concentrations of PSF and EDTA, the value of K is about 4.82. The free energy of electron transfer at the electrode for PSF-EDTA system is about −3.92 kJ mol^{-1} whereas in the cell reaction it varies with the composition of PSF and EDTA, the value corresponding to maximum V_{oc} is about −68.8 kJ mol^{-1}.

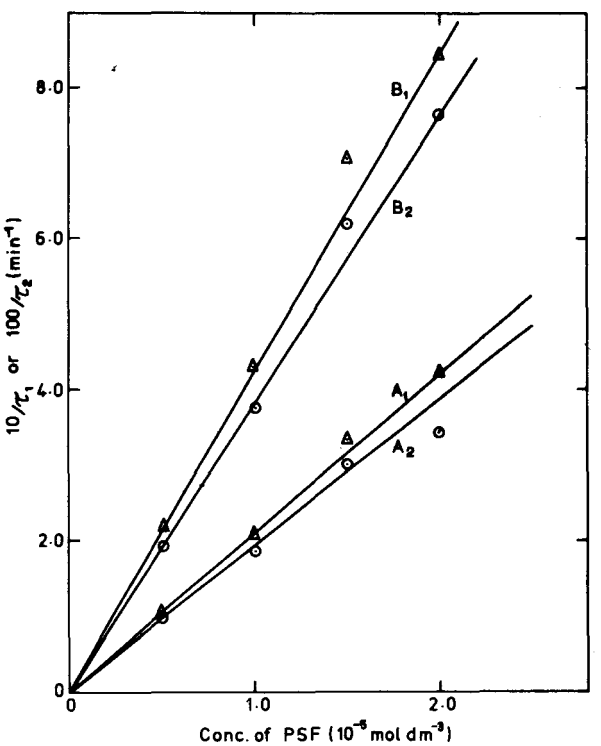

Fig. 3— Plots of $1/\tau$ versus [PSF], where [PSF] varies from 0.5 × 10^{-5} to 2.0 × 10^{-5} mol dm^{-3} for two different concentrations (1 × 10^{-3} and 2 × 10^{-3} mol dm^{-3}) of EDTA [The curves A_1 and A_2 represent the growth and B_1 and B_2 represent the decay for the two sets]

This type of functional forms of growth and decay of photovoltage generation which has been used for the measurement of relaxation time also finds a mention in the literature for electrode reaction in the case of electrodeposition[12] as well as in the case of pigmented bilayer lipid membrane[13].

In the solid state of this system[9], it has been concluded from the experimental results that the rate-determining step is the electron donor acceptor complex of dimer PSF and EDTA, i.e. $(PSF)_2$ ... EDTA complex. But in aqueous solution using low concentrations of PSF and EDTA, the rate depends on the concentration of PSF only, i.e., the electrode species generated by the reaction which takes place via kinetic encounter between a long-lived triplet state of the PSF molecule and a EDTA molecule. The mechanism of the photoredox reaction leading to the photovoltage generation in PSF-EDTA aqueous system has been shown earlier[6-8]. The mechanism at pH 4.55 is shown in Scheme 1

From the spectrophotometric studies, it has been found that the shift of visible absorption maximum of PSF in the presence of EDTA is about 70 cm^{-1} which indicates very weak interaction of PSF and EDTA in the ground state. The excitation and emission spectra of PSF and EDTA system shows shift of 150 cm^{-1} and 120 cm^{-1} respectively which suggest the formation of

$$D + h\nu \rightarrow {}^1D \rightarrow {}^3D$$

$${}^3D \underset{-H^+}{\overset{H^+}{\rightleftharpoons}} {}^3DH^+ \underset{-H^+}{\overset{H^+}{\rightleftharpoons}} {}^3DH_2^{2+}$$

$${}^3DH_2^{2+} + EDTA \rightleftharpoons ({}^3DH_2^{2+} \ldots EDTA) \rightleftharpoons$$

$$({}^3DH_2^{+} \ldots EDTA^+) \rightarrow DH_2^+ + EDTA^+$$

$$2DH_2^+ \rightleftharpoons DH_3^+ + DH^+$$

$$DH_2^+ \rightarrow DH^+ + H^+ + e^- \text{ (anode reaction)}$$

$$EDTA^+ + e^- \rightleftharpoons EDTA \text{ (cathode reaction).}$$

where D, DH^+, DH_2^{2+} & DH_3^+ represent PSF, protonated PSF, semi-PSF and leuco-PSF respectively.

Scheme 1

weak exciplex between PSF and EDTA. In the above mechanism the slowest step is the formation of triplet state of PSF and our results of electrode kinetics also support this. It is interesting to mention that Ainsworth[14] reported the kinetics of thionine-ferrous ion reaction. At low concentration of ferrous ion ($\leqslant 10^{-3}$ mol dm^{-3}) the reaction takes place via kinetic encounters between a long-lived triplet state of the thionine molecule and a ferrous ion and at higher ferrous ion concentration the reaction proceeds primarily through electron transfer within a thionine-ferrous complex. Our results in the aqueous system support the first mechanism, whereas the solid state support the second mechanism.

Thus the analysis of growth and decay curves of photovoltage generation in PSF-EDTA aqueous system helps to calculate the free energy of electron transfer across the electrode/electrolyte interface and to know the rate-determining step.

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