

Electrode Kinetics of Phenosafranine-EDTA System Using Illuminated Semiconductor Electrode

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The photogalvanic effect in the phenosafranine (PSF)-EDTA system in the solid polycrystalline state has been studied using illuminated semiconductor SnO_2 electrode and dark platinum foil counter electrode. The photovoltage growth and decay curves follow the functional forms related to the relaxation time. The measured relaxation time is a function of composition. At 2:1 composition of PSF and EDTA respectively, the photovoltage is 326 mV and relaxation times of growth and decay are 10.6 and 75.0 sec respectively. The calculated free energy of electron transfer across the electrode/electrolyte interface is about $-4.90 \text{ kJ mol}^{-1}$.

In recent papers from our laboratory Rohatgi-Mukherjee and coworkers^{1,2} studied the triplet state photochemistry of phenosafranine (PSF) and its interaction with EDTA using flash photolysis, and cyclic voltammetry of the reduction of PSF by EDTA. The photogalvanic effect of PSF and EDTA system has also been studied in aqueous solution using platinum electrodes, both in the light and the dark compartments³. The photovoltage reported was 615 mV at 25°C and it was found to be a function of temperature; the value increased from 543 mV at 20° to 870 mV at 49°C. When PSF in the solid polycrystalline state was pressed into a pellet and placed between a semitransparent conducting glass (coated with SnO_2) and a platinum foil, photovoltage to the extent of 90 mV was obtained⁴. This value increased to 326 mV when a pellet of an intimate mixture of PSF and EDTA in the ratio of 2:1 was used. It is interesting to mention that the photovoltage growth and decay of PSF and EDTA system in the solid polycrystalline state follow the functional forms (1) and (2) respectively,

$$V_t = V_o [1 - \exp(-t/\tau_1 + z_1)] \quad \dots (1)$$

$$V_t = V_o \exp(-t/\tau_2 + z_2) \quad \dots (2)$$

In Eqs (1) and (2) 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. So an attempt has now been made to study the electrode kinetics of PSF and EDTA system employing relaxation times for growth and decay of various compositions. The results are presented here.

Materials and Methods

Phenosafranine (3,7-diamino-5-phenylphenazinium chloride, PSF) (Sigma Chemicals) was recrystallized

from water. EDTA (disodium salt dihydrate) was of AR grade (BDH).

The photoelectrochemical cell and the details of the experimental set-up for the measurements of photovoltage were described earlier⁴.

Results and Discussion

On illumination of the cell *in vacuo*, a photovoltage developed and attained a maximum value within a few seconds. When the illumination was stopped, the photovoltage decreased gradually and attained almost the original dark value. The growth and decay of photovoltage for various compositions of PSF and EDTA are shown in Fig. 1 at 25°C. The open-circuit photovoltage was found to vary with the compositions of PSF and EDTA mixtures. The value of photovoltage varied from 90 mV in the pure PSF, attaining a maximum value of 326 mV at 0.67 mol fraction of PSF, and then decreasing gradually to zero. The plots of $\ln (v_o - v_t)/v_o$ versus time for growth (Fig. 2A) and of $\ln v_o/v_t$ versus time for decay (Fig. 2B) for all the compositions of PSF and EDTA mixtures were linear and the relaxation times for growth and decay were calculated from the slopes of these plots, respectively. The values at various compositions are given in Table I along with the maximum open-circuit photovoltage generation. Since the inverse of relaxation time represented the rate of chemical reaction, an attempt was made to calculate the rate constant by plotting the inverse of relaxation time against $[\text{PSF}]^m [\text{EDTA}]^n$ taking different values of m and n . But when $m=2$ and $n=1$, a linear relation was obtained as shown in Fig. 3. The rate constants were calculated from the slopes of these plots which were 0.624 s^{-1} and 0.088 s^{-1} respectively for growth and decay. It is interesting to mention that at different compositions of PSF and EDTA, the steady state open-circuit photovoltage, relaxation times for growth

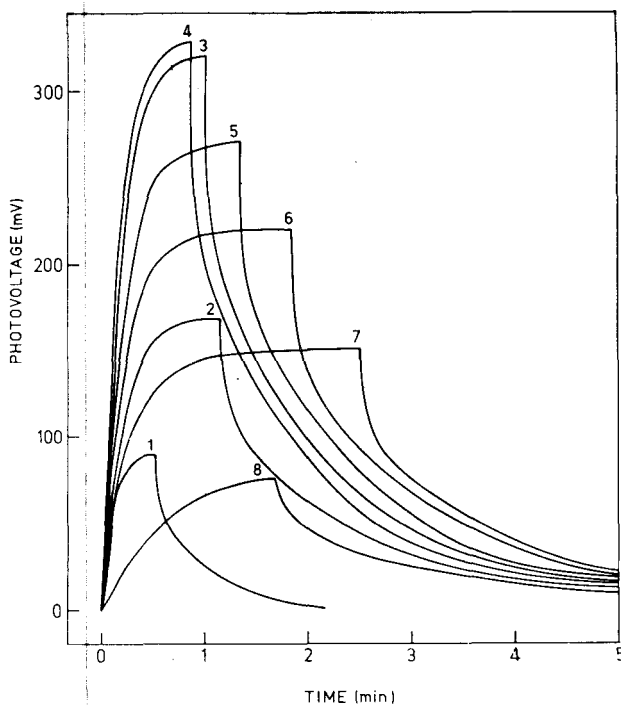


Fig. 1—Growth and decay of photovoltage induced by illumination of various compositions of PSF and EDTA [Mol fraction of PSF: (1) 1.00, (2) 0.80, (3) 0.70, (4) 0.67, (5) 0.60, (6) 0.50, (7) 0.40 and (8) 0.20. Each curve represents the average of 5-6 measurements with a mean deviation of 5%.]

and decay were found different, but the rate constant of the reaction calculated with the help of Eq.(3) $k = [\text{PSF}]^{-2} [\text{EDTA}]^{-1} \tau^{-1}$... (3)

remained unchanged within the limit of experimental 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. The value of K in case of PSF alone was about 4.60 but it was about 7.13 in the presence of EDTA at all compositions. The free energy of electron transfer at the electrode for PSF-EDTA system was about $-4.90 \text{ kJ mol}^{-1}$ whereas in the cell reaction it varied with the composition of PSF and EDTA; the value at 2:1 ratio of PSF and EDTA was $-31.46 \text{ kJ mol}^{-1}$.

This type of functional form of growth and decay of photovoltage generation which has been used for the measurement of relaxation time also finds a mention in the literature⁵ for electrode reaction in the case of electrodeposition. Here, rate-determining step in electrodeposition is based on charge transfer (CT) interaction. Similar behaviour of functional forms of the growth and decay of photovoltage in the case of pigmented bilayer lipid membranes has also been shown⁶.

In the present system, SnO_2 -coated glass is an n -type semiconductor electrode whereas PSF behaves as a p -

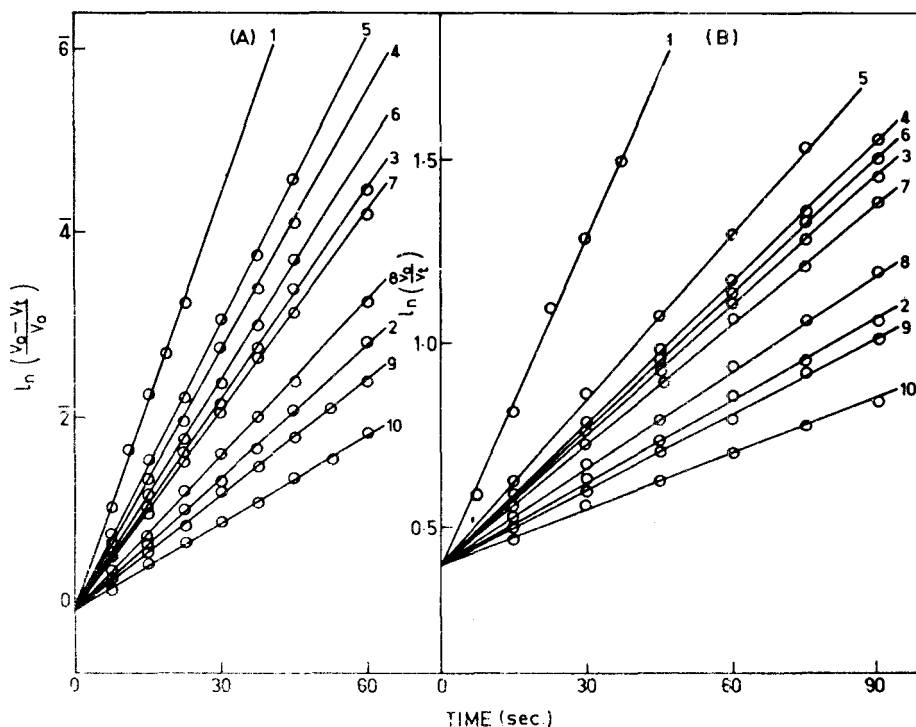


Fig. 2 - (A) Plots of $\ln(V_0 - V_t / V_0)$ against t and (B) plots of $\ln(V_0 / V_t)$ against t [Different curves represent the various compositions of PSF and EDTA in both the cases. Mol fraction of PSF: (1) 1.00, (2) 0.90, (3) 0.80 (4) 0.70, (5) 0.67, (6) 0.60, (7) 0.50, (8) 0.40, (9) 0.30 and (10) 0.20]

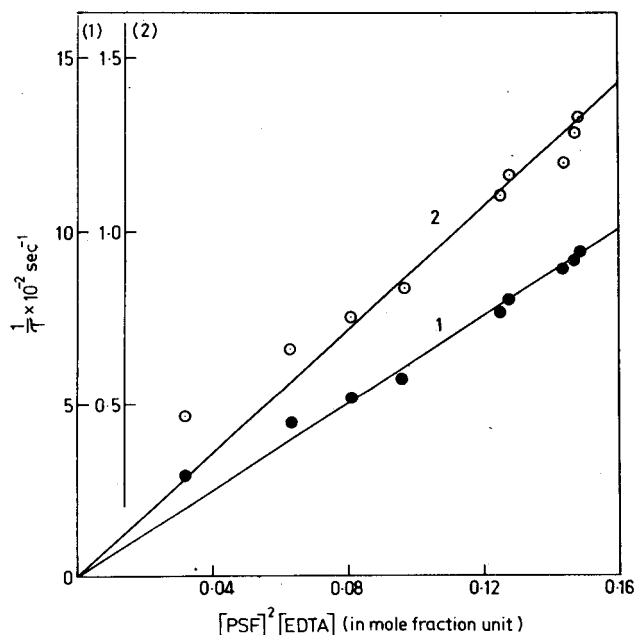


Fig. 3—Plots of $1/\tau$ versus $[\text{PSF}]^2[\text{EDTA}]$ for various compositions of system

Table 1—Photovoltage Generation and Relaxation Times at Different Compositions of PSF and EDTA in Solid Polycrystalline State

Composition of system (PSF mol fraction)	Photo-voltage (mV)	Relaxation time (s)		Rate constant (s^{-1})	
		Growth	Decay	Growth	Decay
1	90	7.50	34.5	—	—
0.9	130	19.50	133.5	0.633	0.092
0.8	170	12.50	88.5	0.625	0.088
0.7	320	10.85	78.0	0.627	0.087
0.67	326	10.60	75.0	0.637	0.090
0.6	270	11.25	84.2	0.617	0.082
0.5	220	13.00	91.5	0.615	0.087
0.4	150	17.50	119.0	0.595	0.088
0.3	100	22.00	151.5	0.722	0.105
0.2	75	33.50	213.0	0.933	0.147
0	—	—	—	—	—

type semiconductor electrode as measured by Hall effect. An illuminated *p-n* junction always exhibits the photovoltaic effect⁷ by creating excess electron-hole pairs in both the regions. The photovoltage of 90 mV develops when PSF pellet is illuminated in a sandwich cell. The addition of EDTA to PSF increases the photovoltage generation by donating electron to the hole left on excitation of PSF and therefore, blocks recombination of the excited electrons. The rate as well as photovoltage generation indicates that there is an interaction between PSF and EDTA in the mol ratio of 2:1 respectively. In the solid state, the formation of complexes with 2:1 stoichiometry is not too unusual while in solution, 1:1 complexes are common⁸. Phenothiazine, analogous to PSF, is reported to form

complexes of compositions other than 1:1 in the solid state⁹. In the solid state, the crystalline forces help to stabilize the complex in a 1:2 mode.

The visible absorption spectrum of PSF in dilute aqueous solution ($\sim 1 \times 10^{-6} M$) exhibits absorption maximum at 521 nm which is blue-shifted to 500 nm in the solid polycrystalline state. If the absorption maximum at 500 nm is due to aggregation (mainly dimerization) of PSF, the stabilization energy of PSF aggregation is about 806 cm^{-1} (9.62 kJ mol^{-1}). The visible absorption maximum of PSF in aqueous solution is shifted to 523 nm in the presence of EDTA with slight increase in intensity. This slight perturbation of PSF absorption spectrum in the presence of EDTA may be due to very weak CT interaction between PSF as an electron acceptor and EDTA as an electron donor in the ground state. Both the excitation and emission (fluorescence) spectra of PSF in the presence of EDTA suggest the formation of weak complex between PSF and EDTA in the excited state as there is red-shift in both the cases accompanied by increase in intensity. PSF shows excitation and emission maxima at 523 and 585 nm respectively which are shifted to 527 and 589 nm respectively in the presence of EDTA.

Thus the analysis of growth and decay curves of photovoltage generation in PSF and EDTA system helps to calculate the free energy of electron transfer across the electrode/electrolyte interface and to know the rate-determining step. In this case, the rate-determining step may be the weak electron donor-acceptor complex of dimer PSF and EDTA, i.e. $(\text{PSF})_2 \dots \text{EDTA}$ complex and it is in the mol ratio of 2:1.

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