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Electrode kinetics of photoinduced redox reactions: phenazine dye–EDTA aqueous systems at different pH

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Abstract

The photogalvanic effect in phenazine dye–EDTA aqueous systems was studied at different pH. The photovoltage growth and decay curves follow the functional forms related to the relaxation times. Under the experimental conditions, the inverse of the relaxation time or the rate of electrode reaction is pH dependent. The rate constants k of forward and backward reactions at 25 °C were calculated. From the plot of log k vs. pH catalytic constants for H^+ and OH^- were determined. The thermodynamic properties and the possible mechanism of the cells are discussed. © 1997 Elsevier Science S.A.

Keywords: Electrode kinetics; Redox reactions; Phenazine dye

1. Introduction

The redox system phenosafranin (PSF)–EDTA has been studied extensively for the generation of a fairly large photovoltage in aqueous solution [1–3] as well as in the solid polycrystalline state [4]. Simultaneously, other phenazine dyes, i.e. safranin-O (saf-O) [3,5], safranin-T (saf-T) [3] with EDTA had been studied and the systems generate large photovoltages. Recently, we have reported the cell characteristics of phenazine dyes (i.e. PSF, saf-O, saf-T and neutral red (NR)) and EDTA with different inorganic redox couples separated by a pyrex-sintered glass membrane [6]. The triplet state photochemistry of PSF and its interaction with EDTA, studied using flash photolysis and cyclic voltammetry of the reduction of PSF by EDTA, have been reported [7,8]. Mukherjee et al. [9] suggested the possible mechanism at the illuminated electrode for this system. Bhowmik and coworkers improved the SEE and storage capability for this system using coated electrodes [10] and glass membrane [11]. It is interesting to mention that the growth and decay of the photovoltage of PSF and EDTA in aqueous solution follow the functional forms of Eqs. (1) and (2), as reported earlier [12]:

$$V_t = V_0[1-\exp(-t/\tau_1+z_1)] \qquad (1)$$

$$V_t = V_0\exp(-t/\tau_2+z_2) \qquad (2)$$

Where V_t is the open-circuit photovoltage at time t, V_0 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 the kinetics of chemical reactions. The role of H^+ concentration, i.e. pH, is also found to be a vital factor in photochemical reactions dealing with phenazine or thiazine dyes and reducing agents. Bonneau et al. [13,14] studied thiazine dyes and EDTA by dye laser flash techniques at different pH. They reported that the degree of protonation of the triplet excited dye and the photoproduction quantum yield are dependent on the pH and the variation of pH depends on the acid–base equilibrium of semithionine ($pK_s=8.2$). They also mentioned that the fully deprotonated species of EDTA, i.e. Y^{4-}, is a better reducing form than HY^{3-} and gave the acid–base equilibrium of EDTA as

$$H_2Y^{2-} \rightleftharpoons HY^{3-}+H^+, \quad pK_3=6.16 \qquad (3)$$

$$HY^{3-} \rightleftharpoons Y^{4-}+H^+, \quad pK_4=10.22 \qquad (4)$$

In the case of phenazine dye PSF, the absorption spectra is pH independent but the photovoltage generation in the PSF–EDTA system is pH dependent [12]. So it is interesting to see whether the rate-determining step in the phenazine dye–EDTA system is affected by the change in pH. An attempt has now been made to study the electrode kinetics of phenazine dye–EDTA aqueous systems at 25 °C employing relax-

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ation times for the growth and decay of the photovoltage at different pH from 3 to 12.

2. Experimental details

The phenazine dyes used in this study were obtained from Sigma Chemicals and Fluka. These were Phenosafranin (3,7-diamino-5-phenyl phenazinium chloride), safranin-O (3,7-diamino-2,8-dimethyl-5-phenyl phenazinium chloride), safranin-T (3,6-diamino-2,7-dimethyl-5-phenyl phenazinium chloride) and neutral red (3-amino-6-dimethyl amino-2-methyl-phenazine hydrochloride). These were doubly recrystallized from ethanol–water. EDTA (disodium salt, dihydrate) and all other chemicals were of AR grade supplied by BDH and Merck and were used without further purification. All the solutions were prepared in doubly distilled water.

The photoelectrochemical (PEC) cell employed to study the photogalvanic effect of the phenazine dyes–EDTA system has been described previously [6]. The illuminated (anode) compartment consisted of phenazine dyes and EDTA deoxygenated aqueous solution, and the dark (cathode) compartment consisted of an aqueous solution of iodine in iodide, separated by a pyrex-sintered glass memberne (porosity G-4).

The light source was a tungsten projector lamp (300 W, 220 V) focused at an intensity of 30 mW cm^{-2}. The photovoltage was measured with a Keithley (model 642) digital electrometer. The pH values of the solutions were adjusted with dilute acid (HCl) and dilute alkali (NaOH) and checked with a Digisun pH meter (DI-707).

3. Results and discussion

On illumination of the anode compartment of the cell, consisting of PSF (2×10^{-5} mol dm^{-3}) and EDTA (0.1 mol dm^{-3}) deoxygenated aqueous solution, a photovoltage develops which attains a maximum value V_{oc} within a few minutes (15–25 min). When the illumination is stopped, the photovoltage decays very slowly and 2–3 days are required for the photovoltage to reach close to the original dark value. The growth and decay of the photovoltage with time of irradiation of the anode compartment consisting of a fixed concentration of saf-O–EDTA aqueous solution at various pH values are shown in Fig. 1 at 25 °C. The growth and decay of the photovoltage of the cell consisting of other phenazine dye–EDTA aqueous solutions in the anode compartment behave similarly. The plots of $\ln(V_0 - V_t)/V_0$ vs. time for growth and of $\ln(V_0/V_t)$ vs. time for decay for phenazine dye–EDTA systems at various pH values were found to be linear for each pH, and the relaxation times for growth and decay were calculated from the slopes of these plots respectively. In the case of the saf-O–EDTA system, these plots are shown in Fig. 2, where the constants z_1 and z_2 are almost zero.

The inverse of relaxation time which represents the rate of chemical reaction was found to vary with the change in pH of the solution. The non-linear plots of rate vs. pH of the solutions give two maxima for the forward reaction with concomitant minima for the backward reaction in all cases except the NR–EDTA system, where one maximum–one minimum is obtained. However, the plots of logarithm of rate for both forward and backward reactions vs. pH of the solutions show a sharp change in slope from negative to positive value with an increase in pH. Both these plots of saf-O–EDTA and NR–EDTA are shown in Figs. 3 and 4 respectively. It is evident from the plots that rate of electrode kinetics is influenced by the change of pH (3–12). The rate constants k for both forward and backward reactions were calculated with the help of Eq. (5) at different pH values:

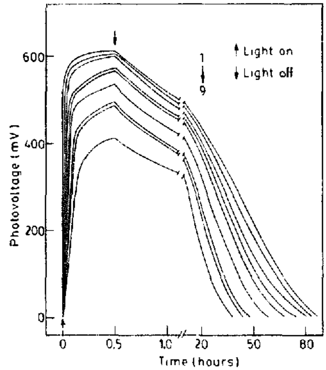

Fig. 1. Growth and decay of photovoltage induced by illumination of the anode compartment consisting of fixed concentrations of saf-O–EDTA in aqueous solution at different pH values: (1) 7.2, (2) 9.2, (3) 7.5, (4) 5.6, (5) 10.0, (6) 8.1, (7) 4.5, (8) 11.0 and (9) 3.6, at 25 °C.

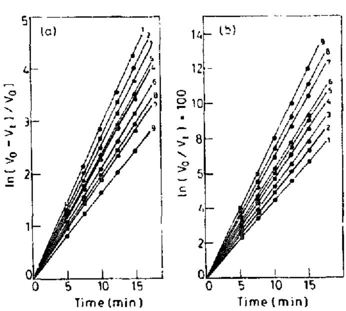

Fig. 2. (a) Plots of $\ln(V_0 - V_t)/V_0$ against t for growth and (b) plots of $\ln V_0/V_t$ against t for decay for the saf-O–EDTA aqueous system at fixed concentrations of reactants and varying pH of the solution: (1) 7.2, (2) 9.2, (3) 7.5, (4) 5.6, (5) 10.0, (6) 8.1, (7) 4.5, (8) 11.0 and (9) 3.6.

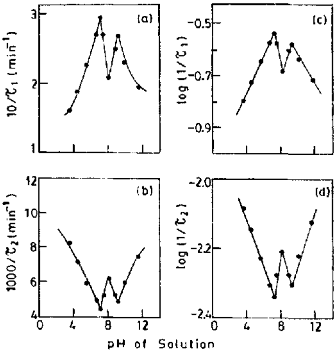

Fig. 3. Plots of rate (a, growth; b, decay) as well as log of rate (c, growth; d, decay) against pH of the solution for the saf-O–EDTA aqueous system.

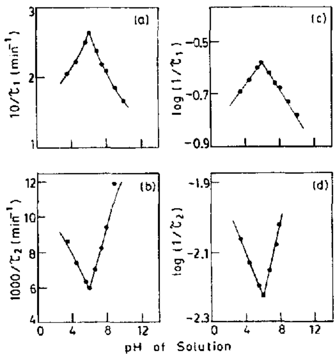

Fig. 4. Plots of rate (a, growth; b, decay) as well as log of rate (c, growth; d, decay) against pH of the solution for the NR–EDTA aqueous system.

$$k = [\text{Phenazine dye}]^{-1}[\text{EDTA}]^{0}\,\tau^{-1} \qquad (5)$$

It has already been confirmed [12] that the rate of electrode reaction in the PSF–EDTA aqueous system is first and zero order with respect to [PSF] and [EDTA] respectively. All the characteristics such as maximum photovoltage, relaxation times and rate constants of phenazine dye–EDTA systems at different pH values are presented in Tables 1–4.

The plot of log k against pH of the saf-O–EDTA system is shown in Fig. 5 and the curve shows the regions of catalysis by H^+ and OH^-, separated by a region in which the catalysis is unimportant in comparison with the spontaneous reaction. Under this circumstance, the rate constant k (both forward and backward) is therefore given by Eq. (6):

$$k = k_0 + k_{H^+}[H^+]^m + k_{OH^-}[OH^-]^n \qquad (6)$$

In Eq. (6), k_0 is the rate constant of the spontaneous reaction. k_{H^+} and k_{OH^-} are the catalytic constants for H^+ and OH^- respectively, and m and n represent the order in $[H^+]$ and $[OH^-]$ respectively. At lower pH, Eq. (6) becomes $k = k_0 + k_{H^+}[H^+]^m$ and at higher pH it is $k = k_0 + k_{OH^-}[OH^-]^n$; in the pH range 7–8 both H^+ and OH^- contribute to the catalytic effect and Eq. (6) holds good. The values of k_{H^+}, k_{OH^-}, m and n for both forward and backward reactions were determined from the lower and higher pH ranges of the curves in Fig. 5. With the help of these, the value of k_0 was calculated; the same value is obtained when it is calculated separately at both lower and higher pH ranges. The plot of log k vs. pH for other phenazine dye–EDTA systems is of same nature as Fig. 5. So, the above parameters of these systems can be calculated with the help of Eq. (6). All these values are inserted in Tables 1–4. The equilibrium constant K of the electrode reaction, the free energy change at the electrode–electrolyte interface $\Delta G_{\rm I}^{0}$ and at maximum photovoltage $\Delta G_{\rm II}^{0}$ of these systems were calculated at 25 °C. These thermodynamic properties of the cells are presented in Table 5. Owing to the difference in free energy change, direct electron transfer is not possible and as a result low effeciency of the cells has been observed.

Table 1

Photovoltage generation, relaxation times and rate constants of the PSF–EDTA system at different pH at 25 °C ($[\text{PSF}] = 2\times10^{-5}$ mol dm^{-3} and $[\text{EDTA}] = 0.1$ mol dm^{-3})

pH	Photovoltage (mV)	Relaxation time (min mol dm^{-3})		Rate constant k (min^{-1})		Specific constant values according to Eq. (6)		
		Growth	Decay	Growth × 10^{-3}	Decay × 10^{-2}	Growth		Decay
3.5	432	8.0	114.8	6.25	4.36		k_{H^+} (min^{-1})	
4.6	518	6.6	147.1	7.58	3.40	3.45×10^{3}		6.72×10^{2}
5.6	596	5.6	182.0	8.93	2.75		k_{OH^-} (min^{-1})	
6.8	620	4.5	233.6	11.11	2.14	3.72×10^{3}		6.92×10^{2}
7.0	608	4.8	199.5	10.42	2.51		m	
7.6	540	6.5	134.6	7.69	3.71	−0.07		0.08
8.0	580	5.8	160.3	8.62	3.12		n	
8.9	628	4.2	241.0	11.90	2.07	−0.10		0.10
10.0	584	5.7	185.9	8.77	2.69		k_0 (min^{-1})	
11.0	506	6.9	144.7	7.25	3.46	5.05×10^{2}		5.22×10^{1}

Table 2
Photovoltage generation, relaxation times and rate constants of the saf-O–EDTA system at different pH at 25 °C ([saf-O] = 2×10^{-5} mol dm^{-3} and [EDTA] = 0.1 mol dm^{-3})

pH	Photovoltage (mV)	Relaxation time (min mol dm^{-3})		Rate constant k (min^{-1})		Specific constant values according to Eq. (6)		
		Growth	Decay	Growth $\times 10^{-3}$	Decay $\times 10^{-2}$	Growth		Decay
3.6	412	6.2	121.4	8.10	4.12		k_H' (min^{-1})	
4.5	496	5.3	140.8	9.39	3.55	4.52×10^{3}		7.79×10^{2}
5.6	572	4.4	170.9	11.30	2.92		k_{OH} (min^{-1})	
6.7	604	3.7	203.2	13.55	2.46	4.89×10^{4}		7.94×10^{2}
7.2	612	3.4	222.2	14.86	2.25		m	
7.5	600	3.7	190.5	13.43	2.62	−0.06		0.10
8.1	536	4.8	162.6	10.39	3.07		n	
8.9	600	4.0	190.5	12.44	2.62	−0.09		0.15
9.2	604	3.7	203.0	13.55	2.46		k_0 (min^{-1})	
10.0	566	4.3	168.1	11.69	2.97	5.45×10^{2}		9.34×10^{1}
11.0	488	5.1	133.8	9.75	3.73			

Table 3
Photovoltage generation, relaxation times and rate constants of the saf-T–EDTA system at different pH at 25 °C ([saf-T] = 2×10^{-5} mol dm^{-3} and [EDTA] = 0.1 mol dm^{-3})

PH	Photovoltage (mV)	Relaxation time (min mol dm^{-3})		Rate constant k (min^{-1})		Specific constant values according to Eq. (6)		
		Growth	Decay	Growth $\times 10^{-3}$	Decay $\times 10^{-2}$	Growth		Decay
3.6	396	5.5	104.7	9.14	4.76		k_H' (min^{-1})	
4.5	484	4.9	129.8	10.10	3.84	6.53×10^{3}		11.43×10^{2}
5.6	554	4.4	165.9	11.29	3.03		k_{OH} (min^{-1})	
6.7	594	3.9	211.4	12.85	2.36	6.46×10^{4}		8.9×10^{2}
7.2	598	3.7	240.4	13.50	2.08		m	
7.5	586	4.0	200.0	12.53	2.50	−0.04		0.13
8.1	520	4.8	142.8	10.49	3.50		n	
8.9	584	4.5	192.7	11.04	2.60	−0.05		0.15
9.2	588	4.4	212.8	11.25	2.35		k_0 (min^{-1})	
10.0	552	4.7	160.3	10.64	3.12	5.53×10^{2}		9.41×10^{1}
11.0	472	4.9	113.5	10.09	4.40			

Table 4
Photovoltage generation, relaxation times and rate constants of the NR–EDTA system at different pH at 25 °C ([NR] = 2×10^{-5} mol dm^{-3} and [EDTA] = 0.1 mol dm^{-3})

pH	Photovoltage (mV)	Relaxation time (min mol dm^{-3})		Rate constant k (min^{-1})		Specific constant values according to Eq. (6)		
		Growth	Decay	Growth $\times 10^{-3}$	Decay $\times 10^{-2}$	Growth		Decay
3.5	250	4.9	116.2	10.25	4.30		k_H' (min^{-1})	
4.5	354	4.5	134.9	11.20	3.71	6.86×10^{3}		7.21×10^{2}
5.6	452	4.0	156.5	12.44	3.19		k_{OH} (min^{-1}	
6.0	472	3.8	167.8	13.00	2.98	6.07×10^{4}		9.62×10^{2}
6.8	420	4.2	141.3	11.86	3.53		m	
7.5	352	4.6	120.9	10.88	4.13	−0.04		0.09
8.0	316	4.8	105.9	10.35	4.72		n	
9.0	204	5.4	84.2	9.25	5.94	−0.03		0.06
							k_0 (min^{-1})	
10.0	108	6.0	75.8	8.29	6.59	5.87×10^{2}		9.63×10^{1}

The transient photochemistry of saf-O [15], a dye very similar to PSF, as a function of pH indicates that the order of reactivities of the three triplet species are $^3DH_2^{2+} > {}^3DH^+ > {}^3D$. The p$K_a$ values of EDTA (H_4Y) [16] are 2.1, 2.7, 6.2 and 10.3. Bonneau et al. [17] have shown that only the species HY^{3-} and Y^{4-} have a lone pair of electrons on nitrogen atoms which can be donated to suitable acceptors. Therefore EDTA will act as an efficient electron donor towards triplet dye above pH 6.0. While the triplet diprotonated dye ($^3DH_2^{+2}$) is a prominent electron acceptor

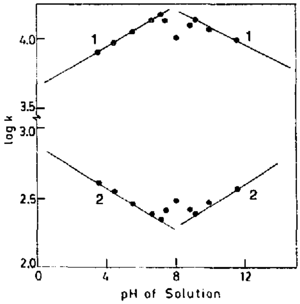

Fig. 5. Plots of log k for both growth and decay against pH of the solution for the saf-O–EDTA aqueous system (curves 1 and 2 for growth and decay respectively).

among the three triplet dye species, the fully ionized EDTA (Y^{4-}) is also expected to function as a strong electron donor among the different species of EDTA.

As mentioned earlier, the rate of phenazine dye–EDTA photoinduced redox reactions depends on [D] only, i.e. the electrode species generated by the reaction which takes place via kinetic encounter between a long-lived triplet state of dye molecule and EDTA molecule. If we consider the variation of photovoltage with pH of the systems from Tables 1–4, it is observed that the systems with dye PSF, saf-O and saf-T give two maxima at pH ~ 7 and pH ~ 9 respectively, but with NR the second maximum in the alkaline region (pH ~ 9) is not obtained. Considering the pK_a values of triplet species of PSF and saf-O [7,15] and studying the effect of pH on them, it can be concluded that the CT interaction occurs between ${}^3DH_2^{2+}$ and HY^{3-} at pH ~ 7 and that of ${}^3DH^+$ with Y^{4-} at pH ~ 9.0. Since structurally saf-T is similar to saf-O, two of three triplet species interact with EDTA and form CT complexes at pH 7.2 and 9.2 respectively. In the case of neutral red, it was reported [18] that two CT interactions occur between triplet species and EDTA at pH > 4.8 and pH < 9.5, but one CT interaction at pH 6.0 is observed from our study. This may be due to the limited solubility of NR above pH 7.0, and the decay of ${}^3DH^+$ is very fast compared with ${}^3DH_2^{2+}$. It is also interesting to mention that the maximum photovoltages are generated at pH corresponding to the pK_a values of dyes when the rate of forward reaction is maximum and the rate of backward reaction is minimum.

The various steps of redox reaction initiated after light absorption by the dye for photovoltage generation in the PEC cell Pt | phenazine dye–EDTA ‖ I^-, I_2 | Pt at pH corresponding to low pK_a values of protonated phenazine dyes are given below:

$$D + h\nu \rightarrow {}^1D \rightarrow {}^3D \qquad \text{(i)}$$

$${}^3D \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} {}^3DH^+ \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} {}^3DH_2^{2+} \qquad \text{(ii)}$$

$${}^3DH^{2+} + HY^{3-} \rightleftharpoons ({}^3DH_2^{2+} \ldots HY^{3-})$$
$$\rightleftharpoons (DH_2^{+} \ldots HY^{2-})(\text{CT interaction}) \rightarrow DH_2^{+} + HY^{2-} \qquad \text{(iii)}$$

$$2DH_2^{+} \rightleftharpoons DH^{+} + DH_3^{+} \qquad \text{(iv)}$$

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

$$\tfrac{1}{2}I_2 + e^{-} \rightleftharpoons I^{-} \quad (\text{cathode reaction}) \qquad \text{(vi)}$$

$$HY^{2-} + I^{-} \rightleftharpoons HY^{3-} + \tfrac{1}{2}I_2 \ (\text{at junction}) \qquad \text{(vii)}$$

The overall forward (light) and backward (dark) reaction at the electrode is represented by Eq. (viii):

$$D + HY^{3-} + 2H^{+} \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} DH_2^{+} + HY^{2-} \qquad \text{(viii)}$$

Here D, DH^+, DH_2^+ and DH_3^+ represent dye, protonated dye, protonated semi- and leuco- dye respectively at pH ~ 7.0 whereas HY^{3-} represents triply ionized EDTA. Similarly, the photochemical and electrochemical reactions at pH ~ 9.0 corresponding to high pK_a values of protonated phenazine dyes are the same except the formation of ${}^3DH^+$ by Eq. (ii) and its CT interaction with Y^{4-} and the generation of electrode species DH and Y^{3-} which in turn react as shown in Eqs. (ix) and (x) while the cathode reaction remains the same:

$$DH \rightarrow D + H^{+} + e^{-} \quad (\text{anode reaction}) \qquad \text{(ix)}$$

$$Y^{3-} + I^{-} \rightleftharpoons Y^{4-} + \tfrac{1}{2}I_2 \ (\text{at the junction}) \qquad \text{(x)}$$

while the formation of protonated triplet dye in Eq. (ii) is favoured at low pH, the anode reactions Eqs. (v) and (ix) should be favoured at higher pH and the maximum photovoltage generation at pH ~ 7.0 and pH ~ 9.0 is the balance between the two. In the above mechanism, the slowest step is the protonation of the triplet state of the dye as is evident

Table 5
Thermodynamic properties of the PEC cell consisting of phenazine dye–EDTA redox systems

Phenazine dye	K $\left[\frac{k_0(\text{Forward})}{k_0(\text{Backward})}\right]$	ΔG_1^0 at the electrode–electrolyte interface (kJ mol^{-1})	ΔG_{11}^0 of cell corresponding to max. photovoltage (kJ mol^{-1})	pK_a values of the triplet dye species	
PSF	9.67	−5.66	−60.7	6.8	8.9
Saf-O	5.83	−4.40	−59.1	7.2	9.2
Saf-T	5.87	−4.41	−57.8	7.2	9.2
NR	6.09	−4.51	−45.6	6.0	—

from studies by Baumgartner et al. [15] and Marks et al. [18]. From this study, the pK_a values of phenazine dyes have been evaluated and are listed in Table 5.

Thus the results of the present work help us to calculate the free energy of electron transfer across the electrode–electrolyte interface and to determine the rate-determining step.

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