Photogalvanic and Cyclic Voltammetric Studies of the Effect of Complexing Agents on Aqueous Iron(II)—a New Methylene Blue System

Adurthy S. N. Murthy* and Konda S. Reddy
Department of Chemistry, Indian Institute of Technology, New Delhi, 110 016, India

The effect of complexing agents KH_2PO_4, NH_4HF_2, and EDTA on the photopotential and photocurrents of a few Fe^{II}-dye photogalvanic systems has been examined. The photogalvanic outputs have been found to be enhanced in the presence of KH_2PO_4. The conclusions are supported by detailed cyclic voltammetric studies.

The photogalvanic effect arising out of photochemical redox reactions in solution has been utilized for solar energy conversion. Most of the work so far reported in the literature is concerned with the Fe^{2+}-thionine system.[1,2] The photo-outputs and efficiencies of this system are rather low owing to the recombination of the photochemically produced active species, non-selectivity of electrode reactions, and low solubility of the dye in aqueous medium. Ti Tien and Mountz[3] have reported an improved photopotential for the Fe^{2+}-thionine system in the presence of sodium acetate. The behaviour in water-acetonitrile solvent mixtures[4] and micellar solutions[5] has also been examined in order to improve the photogalvanic cell performance.

The function of the Fe^{2+}-thionine photogalvanic cell is based on reactions (1)—(4) occurring in aqueous acidic media.[1]

$$\mathrm{Th} + \mathrm{Fe}^{2+} + \mathrm{H}^+ \overset{\text{light}}{\xrightleftharpoons[\text{dark}]{k_1}} \mathrm{S} + \mathrm{Fe}^{3+} \quad (1)$$

$$2\mathrm{S} + \mathrm{H}^+ \xrightleftharpoons{k_2} \mathrm{L} + \mathrm{H}^+ \quad (2)$$

$$\mathrm{S} + \mathrm{Fe}^{3+} \xrightleftharpoons{k_3} \mathrm{Th} + \mathrm{Fe}^{2+} + 2\mathrm{H}^+ \quad (3)$$

$$\mathrm{L} + \mathrm{Fe}^{3+} \xrightleftharpoons{k_4} \mathrm{S} + \mathrm{Fe}^{2+} + 2\mathrm{H}^+ \quad (4)$$

Detailed kinetic considerations by Brokken-Zijp and his co-workers[6,7] have demonstrated that a decrease of the rates of reactions (3) and (4) would increase the open-circuit photovoltage and power output of the Fe^{2+}-thionine system. It has been suggested that addition of small amounts of complexing agents which preferentially bind Fe^{3+} may decrease k_3 and k_4 by an order of magnitude: this would possibly increase the overall performance of the photogalvanic cell. Archer and his co-workers[8] have indeed shown that fluoride ion increases the photocurrent but decreases the open-circuit voltage of the Fe^{2+}-thionine system.

Murthy and his co-workers[9-13] have examined the photogalvanic effect and cyclic voltammetry of a series of systems with reversible and irreversible reducing agents. It has been observed that of all the phenothiazine dyes, New Methylene Blue (NMB) yields higher photo outputs with Fe^{2+} in aqueous acidic medium and it was considered that the Fe^{2+}-NMB system is well suited to examine the effect of some complexing agents on its photogalvanic effect. In this paper, the effect of some complexing agents (which form strong complexes with Fe^{3+}) on the photogalvanic output of the Fe^{2+}-NMB system are reported. The stability constants[14] for the formation of Fe^{3+} complexes with the complexing agents studied are larger than those with Fe^{2+}. The electrochemical behaviour of the Fe^{2+} system in the presence of complexing agents has also been investigated in detail by cyclic voltammetry.

Experimental

NMB, Methylene Blue, and Azur-A (Aldrich) were twice recrystallized from doubly distilled water. Analytical grade $FeSO_4(NH_4)_2SO_4,6H_2O$, ethylenediaminetetra-acetic acid (EDTA), KH_2PO_4, and NH_4HF_2 were used without further purification. Prepurified nitrogen gas was used for deaeration of solutions. The pH of the solution was adjusted with either dilute H_2SO_4 or NaOH using an expanded-scale pH meter (ELICO). Cyclic voltammetric experiments were carried with a Wenking (POS-73) potentiostat along with an X–Y recorder. A digital multimeter (Apalab model 1003) was used to measure the photopotentials and currents. A water-cooled 500 W tungsten lamp was used for illuminating the photogalvanic cell. The intensity of the illuminated light was *ca.* 25 mW cm^{-2}. A typical arrangement for photogalvanic studies consist of an H-shaped[15] cell with two thin foils of electrochemically treated platinum (*ca.* 1 cm^2 area) as electrodes and saturated calomel as a reference electrode. The distance between the two platinum electrodes was *ca.* 3.5 cm. Cyclic voltammetric experiments[15] were carried out employing a three-electrode configuration consisting of platinum wire (0.346 cm^2 area) as a working electrode, saturated calomel electrode (s.c.e.) as reference, and a platinum foil as counter electrode.

Results and Discussion

It was shown[13] that the optimum photogalvanic effect for any Fe^{2+}-dye system could be observed in a solution consisting of 7.5×10^{-5} mol dm^{-3} dye and 5×10^{-2} mol dm^{-3} Fe^{2+}. Employing these concentrations of NMB and Fe^{2+}, the Fe^{2+}-NMB photogalvanic cell has been examined in the presence of potassium dihydrogen phosphate and the results are shown in

Table 1. Effect of KH_2PO_4 on Fe^{2+}-NMB photogalvanic system. [NMB] 7.5×10^{-5} mol dm^{-3}; [Fe^{2+}] 5.0×10^{-3} mol dm^{-3}; electrode area 1.0 cm^2

[KH_2PO_4]/ mol dm^{-3}	Potential *versus* s.c.e. (mV)		V_{oc}/mV	I_{sc}/μA
	Dark	Illuminated		
	262.0	137.0	125.0	3.2
1.0×10^{-4}	292.0	181.0	111.0	4.0
1.0×10^{-3}	291.0	172.0	119.0	4.3
1.0×10^{-2}	274.0	125.1	148.9	6.4
2.5×10^{-2}	267.0	107.7	159.3	6.9
5.0×10^{-2}	259.0	115.2	143.8	6.4
7.5×10^{-2}	254.0	117.8	136.2	5.6
1.0×10^{-1}	251.0	150.9	100.1	4.1

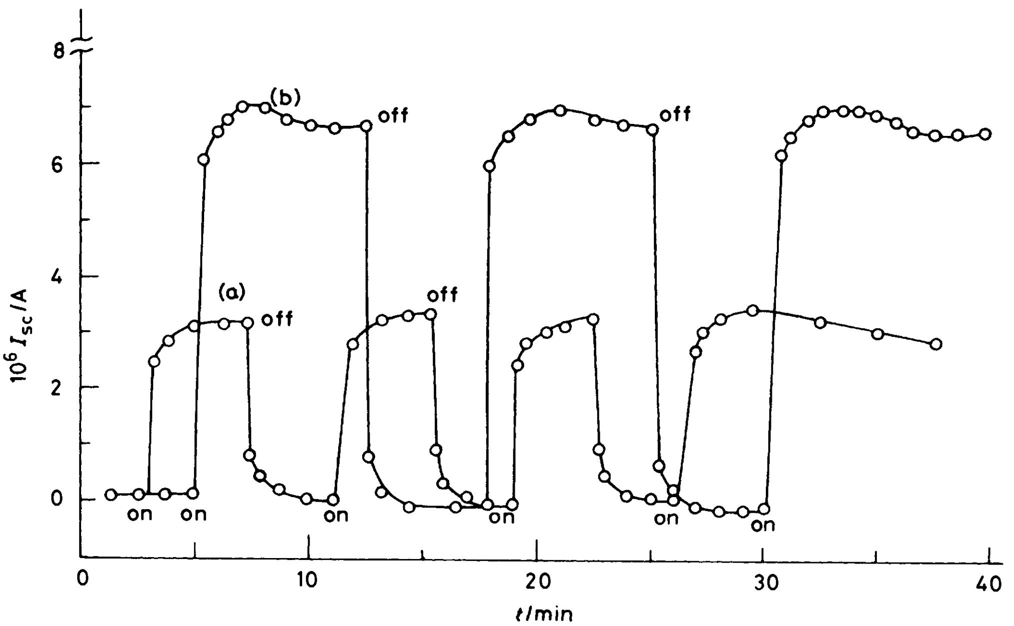

Figure 1. On–off reversible characteristics of (a) Fe^{2+}–NMB photogalvanic cell; (b) Fe^{2+}–NMB photogalvanic cell in the presence of KH_2PO_4. Electrode area *ca.* 1.0 cm^2

Table 2. Photogalvanic effect of a few Fe^{2+}–dye photogalvanic systems in the presence of complexing agents. [Fe^{2+}] 5.0 × 10^{-2} mol dm^{-3}; [Dye] 7.5 × 10^{-5} mol dm^{-3}; [EDTA] 1.0 × 10^{-4} mol dm^{-3}; [NH_4HF_2] 7.5 × 10^{-3} mol dm^{-3}; [KH_2PO_4] 2.5 × 10^{-3} mol dm^{-3}; Electrode area *ca.* 1.0 cm^2

Complexing agent	Fe^{2+}–NMB		Fe^{2+}–Methylene Blue		Fe^{2+}–Azur-A	
	V_{oc}/mV	I_{sc}/μA	V_{oc}/mV	I_{sc}/μA	V_{oc}/mV	I_{sc}/μA
	125.0	3.2	120.0	1.8	119.0	2.9
Na_2EDTA	128.0	3.3	122.5	3.1	121.2	3.1
KH_2PO_4	159.3	6.9	145.6	5.8	147.2	5.7
NH_4HF_2	152.9	6.2	139.2	5.1	135.4	4.9

Table 1. The optimum pH for this photogalvanic solution has been found to be 2.5. The maximum open-circuit photopotential and short-circuit photocurrents are obtained when the concentration of KH_2PO_4 is 2.5 × 10^{-2} mol dm^{-3}. The KH_2PO_4–Fe^{3+} complex does not reduce the dye in the dark.

Bifluoride ion is also another complexing agent which can preferentially bind Fe^{3+} ions. The results with NH_4HF_2 as the complexing agent show that the maximum photopotential could be obtained around pH 2—3 and, when the concentration of NH_4HF_2 is greater than 7.5 × 10^{-3} mol dm^{-3}, the photopotential decreases. This may be due to a process of salting out the dye at higher concentrations of ammonium hydrogen fluoride.

However, with EDTA, when the concentration is larger than 1.0 × 10^{-3} mol dm^{-3}, the dye gets reduced in the dark. This is possibly because the complex formed by Fe^{2+} with EDTA is a stronger reducing agent than Fe^{2+}. At an EDTA concentration of 1.0 × 10^{-4} mol dm^{-3}, where no reduction of dye occurs in the dark, the observed photopotential and currents (Table 2) are not significantly different from those without EDTA.

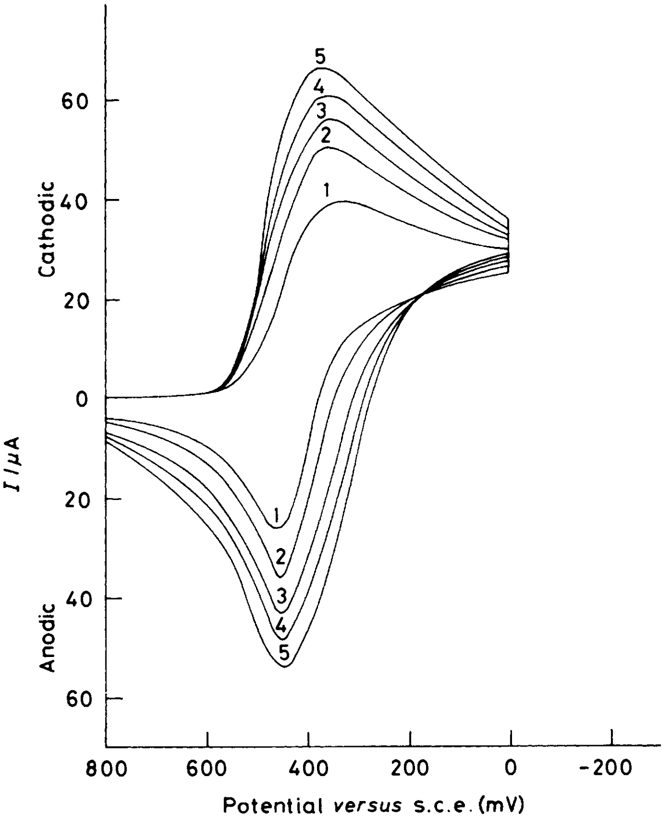

Figure 2. Cyclic voltammograms of Fe^{3+} in the presence of KH_2PO_4 in 0.1 mol dm^{-3} H_2SO_4 at different scan rates: (1) 20 mV s^{-1}; (2) 40 mV s^{-1}; (3) 60 mV s^{-1}; (4) 80 mV s^{-1}; (5) 100 mV s^{-1}. [Fe^{3+}] 5.0 × 10^{-3} mol dm^{-3}; [KH_2PO_4] 5.0 × 10^{-2} mol dm^{-3}. Electrode area 0.346 cm^2

The effect of these complexing agents on the photogalvanic effect of a few Fe^{2+}–dye systems (NMB, Methylene Blue, Azur-A) is shown in Table 2. The photogalvanic effect in all the systems shows a considerable enhancement in the presence of complexing agents with the exception of EDTA. Among the three complexing agents investigated, potassium dihydrogen

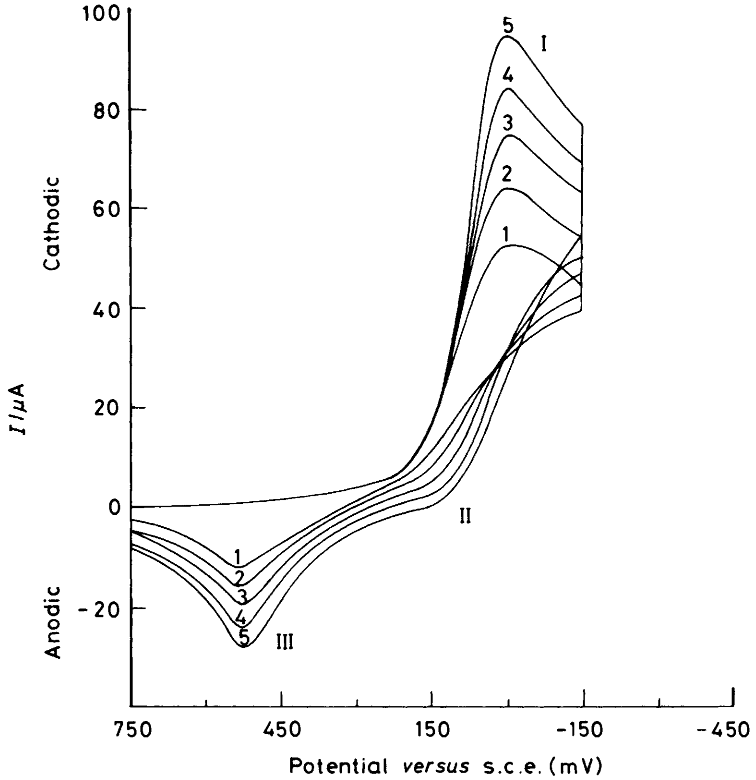

Figure 3. Cyclic voltammograms of Fe^{3+} in the presence of EDTA in 0.1 mol dm^{-3} H_2SO_4 at different scan rates: (1) 20 mV s^{-1}; (2) 40 mV s^{-1}; (3) 60 mV s^{-1}; (4) 80 mV s^{-1}; (5) 100 mV s^{-1}. Electrode area 0.346 cm^2

phosphate has been found to be effective in giving enhanced outputs in Fe^{2+}–dye cells. The on–off curves (short-circuit photocurrent I_{sc} *versus* time) for the Fe^{2+}–NMB cell with and without KH_2PO_4 are shown in Figure 1. The I_{sc} value was measured when the incident light was switched on and off at 5 min intervals. When the light is switched on, the photocurrent rises to an equilibrium value in a few seconds and when the light is switched off the current becomes zero. On continuous illumination of the cell for 20 min, the I_{sc} value falls only by 1.0—0.5 µA, thereby indicating the relatively high stability of the cell. This is possibly because KH_2PO_4 forms a strong complex[14] with Fe^{3+} without reducing the dye in the dark. Salting out of the dye also does not occur in presence of KH_2PO_4. It may therefore be concluded that KH_2PO_4 exerts a positive influence on reactions (3) and (4), thereby enhancing the photogalvanic output.

It was considered interesting to examine the electrochemical behaviour of the Fe^{2+}–Fe^{3+} system in the presence of complexing agents used in the present study. The cyclic voltammograms of Fe^{3+} (5.0×10^{-3} mol dm^{-3}) in 0.1 mol dm^{-3} H_2SO_4 and in the presence of KH_2PO_4 (5.0×10^{-2} mol dm^{-3}) at different scan rates are shown in Figure 2. The anodic and cathodic peak potentials of the Fe^{2+}–Fe^{3+} couple shift to negative values in the presence of KH_2PO_4. The ΔE_p value is *ca.* 80 ± 2 mV, indicating the charge-transfer process is quasi-reversible. The redox potential of the Fe^{2+}–Fe^{3+} couple in presence of KH_2PO_4 has been found to be *ca.* 410 mV *versus* s.c.e., which is *ca.* 40 mV cathodic of the Fe^{2+}–Fe^{3+} couple without the complexing agent.

The cyclic voltammograms of the Fe^{2+}–Fe^{3+} couple in the presence of NH_4HF_2 showed that the charge-transfer process is highly irreversible, possibly because of the instability of the complexes formed by either Fe^{2+} or Fe^{3+} with NH_4HF_2. The redox potential of the Fe^{2+}–Fe^{3+} couple, however, did not change appreciably in the presence of NH_4HF_2 in acid medium.

The cyclic voltammograms of Fe^{3+} in the presence of EDTA and 0.1 mol dm^{-3} H_2SO_4 show interesting features (Figure 3). Three peaks designated I—III can be identified at the scan rates shown. Peak I is obviously due to a reduction of the Fe^{3+}–EDTA complex. Peak II may correspondingly be assigned to the oxidation of Fe^{2+}–EDTA complex, which appears to be weaker than the Fe^{3+}–EDTA complex. Peak III appears at 530 mV, which may be assigned to the oxidation of free Fe^{2+} ions: the free Fe^{2+} ions are obviously liberated by the dissociation of the less stable Fe^{2+}–EDTA complex in acid medium. Tha fact that a corresponding peak due to free Fe^{3+} ion is not observed is possibly due to the high stability of the Fe^{3+}–EDTA complex. The redox potential of the Fe^{2+}–EDTA/Fe^{3+}–EDTA couple is more negative than that of the dye–reduced dye couple. Hence the dye is reduced in the dark.

The cyclic voltammetric data thus conclusively proves that KH_2PO_4 is a better complexing agent than either NH_4HF_2 or EDTA for enhancing the photogalvanic output of the Fe^{2+}–dye systems. Cyclic voltammetry is thus a useful technique for choosing the appropriate complexing agents to enhance photogalvanic outputs. The reversible behaviour of dye couples, however, is not affected by the complexing agents.

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