Cyclic Voltammetric Study of Reduction of Phenosafranine by EDTA

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The cyclic voltammetric study of the reduction of phenosafranine (PSF) in the presence of EDTA indicates that PSF is adsorbed on the electrode surface before it is reduced. A prepeak appears at [E_{pc} = 325 mV and E_{pa} = 275 mV]. In the presence of EDTA the reduction of PSF is facilitated and it is reduced at lower potential region (E_{pc} = −506 mV, E_{pa} = −453 mV) than in absence of EDTA [E_{pc} = −723 mV, E_{pa} = −635 mV]. It is concluded that PSF forms charge transfer complex with EDTA which gets adsorbed before it undergoes electrochemical reactions at the electrode surface.

Phenosafranine (PSF) - EDTA redox system has been observed to give high open circuit photovoltage in a photogalvanic cell[1], similar to the observations of Kaneko and Yamada[2] for tolusafranine-EDTA system. Certain characteristics of the cell point to adsorption of PSF on the electrode surface and possible formation of charge transfer (CT) complex with EDTA. The formation of a weak CT complex between PSF and EDTA in solution has been confirmed by spectrophotometric studies[3]. Cyclic voltammetry is a useful technique to study electrode surfaces modified by attachment of polymeric films[4] and ligands with anchored redox system[5]. The cyclic voltammetric study of this reaction has therefore now been taken up to provide a mechanistic base for the interpretation of this reaction.

Materials and Methods

The voltammograms were obtained with a Wenking potentiostat (model ST 72) coupled with a Wenking voltage scan generator (model VSG 72) and a Houston X-Y recorder (model 2000). The redox system, PSF + EDTA was taken in a cell using platinum wire as working electrode, platinum foil as counter electrode and SCE as reference electrode. KCl was used as the supporting electrolyte. The dc potential (E) was applied at a given scan rate (V), in the form of a triangular wave. The current-potential curves were obtained using three electrode configuration as indicated above. The electrodes were static and the solutions were unstirred. Therefore the mass transfer was mainly controlled by diffusion. The solutions were deaerated by bubbling for 15 min commercial grade nitrogen purified and dried before use. Doubly distilled water was used as a solvent. EDTA (AR, Glaxo Laboratories) was used as such. PSF (George T. Gurr Ltd, London) was purified by chromatography.

Results and Discussion

The voltammograms of PSF and EDTA alone and of mixtures of PSF and EDTA at two different mol ratios are presented in Figs 1 and 2 respectively. There is a definite shift of the reduction potential peak of PSF in the presence of EDTA towards the lower potential region (Fig. 2). On the other hand, EDTA alone (Fig. 1B and Table 1) gives only oxidation peak around −525 mV, indicating that it is oxidised irreversibly.

PSF exhibits typical adsorption prepeak[6] on the cathodic scan (Figs 1 to 4) characteristic of a system in which the product of the electrode reaction is adsorbed. This peak is not symmetrical about the peak
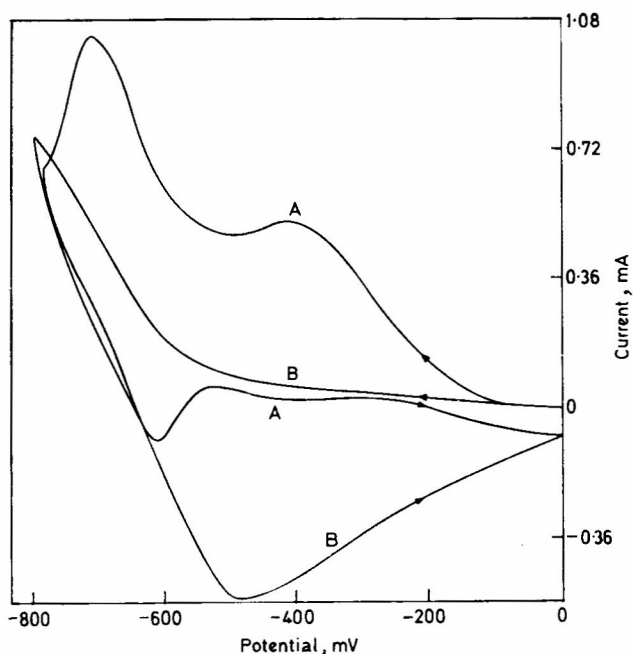

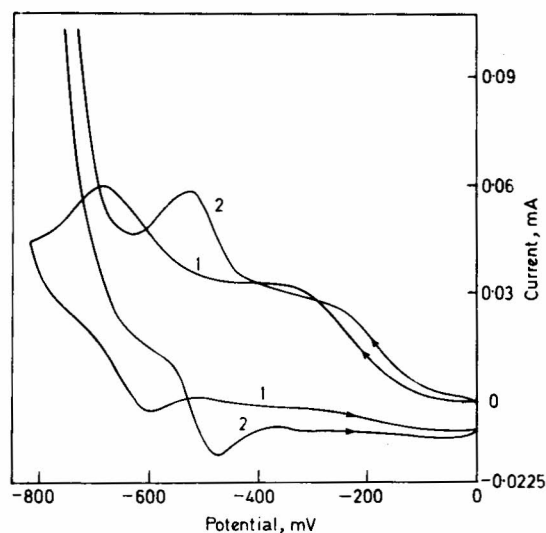Fig. 1—Cyclic voltammetry of (A) 10^{-4} mol dm^{-3} PSF and (B) 10^{-4} mol dm^{-3} EDTA [Scan rate 100 mV s^{-1}]

Fig. 2—Effect of varying of EDTA concentration on cyclic voltammetry of PSF at 100 mV s^{-1} scan rate [(1) 10^{-4} mol dm^{-3} PSF + 10^{-4} mol dm^{-3} EDTA; and (2) 10^{-4} mol dm^{-3} PSF + 5 × 10^{-3} mol dm^{-3} EDTA]

Table 1—Effect of Varying EDTA Concentration on Cathodic (E_{pc}) and Anodic (E_{pa}) Peaks Potentials

	[EDTA] × 10^4 mol dm^{-3}	[PSF] × 10^4 mol dm^{-3}	E_{pc} mV	E_{pa} mV
1.	1.0	0	—	−525
2.	0	1.0	−723	−630
3.	1.0	1.0	−700	−610
4.	5.0	1.0	−654	−586
5.	10.0	1.0	−567	−504
6.	25.0	1.0	−539	−480
7.	50.0	1.0	−506	−453
8.	100.0	1.0	−506	−453

potential and that for higher concentrations the adsorption prepeak current is independent of concentration of PSF (Fig. 3), in accordance with the theory of the strong adsorption of products[1,6,7]. At low concentration of PSF ($2 × 10^{-5}$ mol dm^{-3}), a decrease in the current is observed (Fig. 3). This is expected because adsorption becomes partially diffusion-controlled under this condition[7−9]. No effect of pH has been observed on the cathodic (E_{pc}) and anodic (E_{pa}) peak potentials. The values of E_{pc} (506 mV) and E_{pa} (453 mV) remain constant at different pH values (4.53, 7.02 and 9.12) under the conditions: [PSF] = $1 × 10^{-4}$ mol dm^{-3}; and [EDTA] = 5 × 10^{-3} mol dm^{-3}.

When the heterogeneous rate constant K_{sh}, is such that $K_{sh} \geqslant$ V we have reversible situation and the following relationships hold:

$$\Delta E_p = E_{pa} - E_{pc} = 57/n \qquad \ldots (1)$$
$$-i_{pa} = i_{pc} \qquad \ldots (2)$$
$$\text{and } \Delta i_p V^{\frac{1}{2}} = \text{constant} \qquad \ldots (3)$$

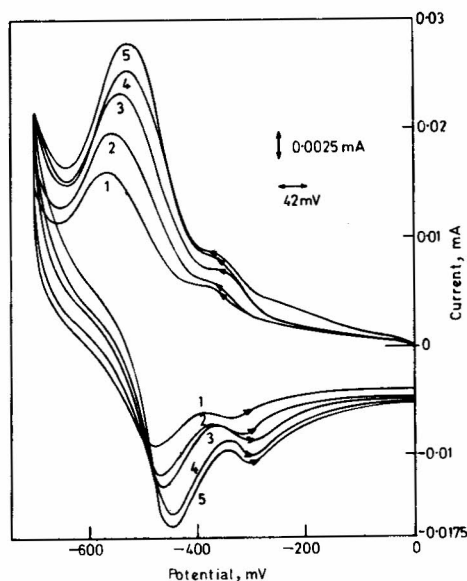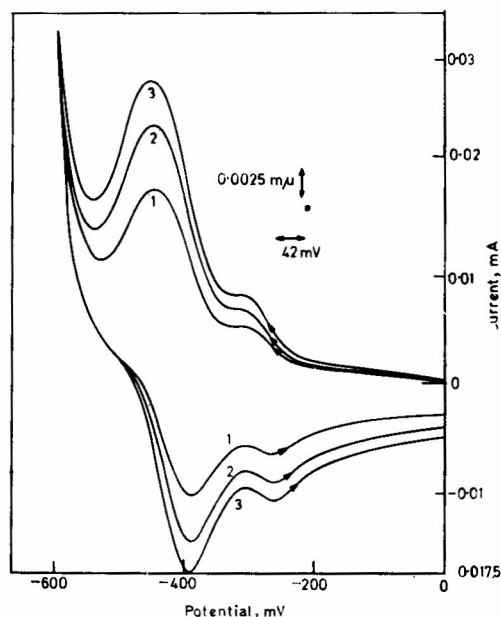Fig. 3—Effect of PSF concentration on cyclic voltammetry of PSF at pH 4.5 and scan rate 50 mV s^{-1} in the presence of $5 × 10^{-3}$ mol dm^{-3} EDTA [(1) $2 × 10^{-5}$ mol dm^{-3}; (2) $4 × 10^{-5}$ mol dm^{-3}; (3) 6 × 10^{-5} mol dm^{-3}; (4) $8 × 10^{-5}$ mol dm^{-3}; and (5) $10 × 10^{-5}$ mol dm^{-3}]

Fig. 4—Effect of varying scan rate on cyclic voltammetry of PSF (10 × 10^{-5} mol dm^{-3}) in the presence of $5 × 10^{-3}$ mol dm^{-3} EDTA at pH 4.5 [Scan rates: (1) 25 mV s^{-1}; (2) 40 mV s^{-1}; and (3) 50 mV s^{-1}

where i_{pa}, i_{pc} are peak currents corresponding to E_{pa} and E_{pc}. The cyclic voltammogram of PSF (C = 10 × 10^{-5} mol dm^{-3}) in the presence of EDTA ($5 × 10^{-3}$ mol dm^{-3}) at different scan rates are presented in Fig. 4. It is seen that ΔE_p is 63 mV at different scan rates, although one should expect a separation of 57 mV for one-electron reversible reaction[10].

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There are several mechanisms which can account for the observed anodic-cathodic peak potential separation (ΔE_p) of 63 mV. One of them is quasi-reversible charge transfer (CT) between the reactants adsorbed on the surface of the electrode. To establish this mechanism the scan rates for the measurement of peak current were varied from a range of 25 mVs^{-1} to 100 mVs^{-1}. If the charge transfer is quasi-reversible, the current function $[(i_{pc})/\sqrt{V}$ or $i_{pa}/i_{pc}]$ is expected to decrease[6] and the peak separation to increase with the increase in scan rate[10]. However, it is observed that peak separation increases with increase in the scan rate (Fig. 4) but the function $i_{pc}/\sqrt{V}$ also increases. This is most likely to be due to the adsorption of PSF and confirms the contention of Wopschall and Shain[6] for similar studies on the methylene blue system. Furthermore, i_{pa}/i_{pc} is not equal to unity suggesting that the system is not strictly reversible. Careful measurement of the differences between the peak potential (E_p) and the half-peak potential $(E_p)_{\frac{1}{2}}$ gives a value of 33.5 mV at the scan rates studied, which is in good agreement with the studies of Kemula[8]. For an ideal reversible reaction this value is 30 mV. The deviation from the ideal value may again be ascribed to adsorption[9]. In fact, the observed increase in peak separation with increase in scan rate (Fig. 4) suggests a CT mechanism[7] in the present system. That the peak appears at lower potentials in both cathodic and anodic processes (Table 1, Fig. 2) further corroborates a CT mechanism.

Therefore, it is concluded that the voltammetric reaction of PSF with EDTA is a one electron quasi-reversible transfer phenomenon and PSF is adsorbed before it is reduced. In presence of EDTA the reduction of PSF occurs more easily presumably due to formation of a CT complex between PSF and EDTA[1]. This corroborates the conclusion derived from the growth curve for open circuit photovoltage V_{oc} generation in photogalvanic experiments on the system as observed in our laboratory and communicated elsewhere[11].

References

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