J Appl Electrochem (2009) 39:1025–1031
DOI 10.1007/s10800-008-9750-9

ORIGINAL PAPER

Ferric-oxalate-gluconate based redox mediated electrochemical system for vat dyeing

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Received: 29 June 2008 / Accepted: 5 December 2008 / Published online: 23 December 2008

Abstract The voltammetric behaviour of the ferric-oxalate-gluconate system is investigated along with some electrochemical dyeing results. The results are compared with the conventional ferric-triethanolamine-gluconate system on a glassy carbon electrode. The ferric-triethanolamine redox system is stable and exhibits quasi-reversible redox behaviour in alkaline medium. The ferric-oxalate system undergoes hydrolysis and precipitates above pH 8. Vat dyeing requires the stability of the redox system in alkaline solutions. The ferric-oxalate redox system alone cannot satisfy this requirement. However, in the presence of excess gluconate, both systems exhibit stability in alkaline media. Mechanistic studies indicate the formation of ferrous-gluconate as the reducing agent for vat dyeing from these mediator systems. Electrochemical dyeing was also carried out in the mediator system under investigation. Colour depth was characterized by the Kubelka-Munk value (K/S) and CIE Lab-coordinates for the dyed fabrics and was found to be comparable with samples dyed using sodium dithionite as the reducing agent.

Keywords Cyclic voltammetry · Indirect electrolysis · Ferric-complex · Calcium gluconate · Oxalic acid · Vat dyes

1 Introduction

The negative environmental impacts of employing chemical reducing agents like sodium dithionite in vat and sulphur dyeing are well known. A variety of electrochemical approaches including the mediated redox catalytic approach are currently under investigation to evolve commercially viable industrial process for vat dyeing [1]. Comparative assessments of chemical and electrochemical approaches are also available [1–3]. Photochemical, electrochemical, biochemical and sonoelectrochemical approaches promise scope for environmentally benign vat dyeing technologies in the near future [4, 5].

Bechtold et al., have reported considerable progress in ferric-triethanolamine (Fe(III)-TEA) complex based electrochemical vat dyeing. The complexes are known to exhibit stability in alkaline media [6]. Insoluble micro particles of organic compounds including vat dye molecules were found to be electrochemically reducible in aqueous solutions with the aid of Fe(III)-TEA complexes [7, 8]. Cyclic voltammetric studies were employed to correlate the redox potential of vat dyes with the efficiency of reduction [9, 10]. Addition of calcium-gluconate to the Fe(III)-TEA mediator system was found to improve the efficiency of electrochemical vat dyeing [11]. This was presumed to be due to the formation of binuclear complexes involving Ca^{2+} and Fe^{3+} ions [12, 13]. The beneficial effects of gluconate as a competitive ligand have also been evaluated [14]. In the presence of excess gluconate, TEA content in the mediator system may be reduced to some extent, although Fe(III)-gluconte complex itself did not exhibit any distinct voltammetric redox response [15, 16]. Studies were also carried out with other hydroxyethyl group based ligands in place of TEA [17].

In a recent investigation from our laboratory the influence of various operating parameters on the overall improved efficiency of electrochemical vat dyeing was continuously monitored using a potentiometric approach [18]. In the present study efforts were made to identify an alternative

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ligand-based redox mediator which tends to be stable in alkaline media for this process. Both basic voltammetric investigations and laboratory scale vat dyeing experiments indicated that the Fe(III)-oxalate-gluconate system would be an alternative redox mediator for the process.

2 Experimental

2.1 Chemicals

Analytical grade ferric sulphate, TEA, Na-gluconate and NaOH with purity greater than 99% were procured from SRL (India) for voltammetric studies, whereas for electrochemical dyeing purposes only technical grade chemicals were used. Ca-gluconate, synthesised and characterised in our laboratory, was used. The dye systems investigated were technical product: Indanthrene Green-FFB (C. I. Name: VAT GREEN 1) and other dyestuffs, obtained from M/s. Fabricare organics (India). The pH of the solution was adjusted using NaOH. Except during study of pH effects, the pH of the solution was maintained at 13. The mediator solution was prepared by dissolving ferric sulphate in water and adding this solution to the separately prepared solution of TEA/oxalic acid/Ca-gluconate in sodium hydroxide under stirring [18]. This solution was mechanically stirred for 5 h and filtered through a 1.25 μm ceramic filter. The different compositions of the mediator solutions are given in Table 1.

2.2 Cyclic voltammetry

The instrument used for recording the cyclic voltammetric experiments was a BAS IM6 Electrochemical Analyser, USA with Thales 3.18-USB soft ware. In a conventional three electrodes system, glassy carbon (GC, 6 mm diameter) procured from Bio Analytical System, USA and a platinum foil were used as the working and counter electrodes, respectively. All potentials were recorded against a Hg/HgO/OH^- reference electrode. Prior to the experiments, glassy carbon was polished with 4/0 emery sheets using alumina gel (0.05 micron) and washed with distilled water. The electrode was sonicated for 5 min to remove adsorbed alumina. The test solutions were deaerated at least 30 min with N_2 to eliminate dissolved oxygen. All experiments were performed at 300 ± 2 K.

2.3 Electrochemical dyeing

2.3.1 Dyeing procedure

A PVC based rectangular divided cell with 400 mL anolyte and 1,000 mL catholyte capacity was employed for galvanostatic studies. A Nafion 423 membrane was used as a separator. A stainless steel plate (area of 30 cm^2) and a copper plate (area of 423 cm^2) were used as anode and cathode, respectively. External circulation was employed to homogenise the dye bath.

The electrolysis was carried out under galvanostatic conditions. During the electrolysis the conversion of ferric ions was estimated by iodometric titration at different times. After achieving maximum conversion of ferric ions (no further increase in Fe(II) concentration with time), the required quantity of selected dye was added to the catholyte. The electrolysis was continued for another 30 min for solubilisation of the dye molecules. Then the pre-treated fabric sample was introduced into the bath. Both electrolysis and electrochemical dyeing were carried out at 300 ± 2 K. Experiments were carried out at relatively

Table 1 Composition of solutions investigated with cyclic voltammetry

Mediator	c(Fe^{3+})/ mol L^{-1}	c(TEA)/ mol L^{-1}	c(Ca-Gluconate)/ mol L^{-1}	c(Na-Gluconate)/ mol L^{-1}	c(Oxalic acid)/ mol L^{-1}	c(NaOH)/ mol L^{-1}
Mediator A	0.03	0.345	–	–	–	0.45
Mediator B	0.03	–	0.05	–	–	0.5
Mediator C	0.03	–	–	0.05	–	0.5
Mediator D	0.03	0.175	0.01	–	–	0.5
Mediator E	0.03	0.175	0.02	–	–	0.5
Mediator F	0.03	0.175	0.03	–	–	0.5
Mediator G	0.01	–	–	–	0.25	0.5
Mediator H	0.015	–	–	–	0.25	0.5
Mediator I	0.02	–	–	–	0.25	0.5
Mediator J	0.03	–	–	–	0.25	0.5
Mediator K	0.01	–	0.05	–	0.1	1
Mediator L	0.02	–	0.05	–	0.1	1
Mediator M	0.03	–	0.05	–	0.1	1

large liquor ratio (1:80). The dyeing was carried out by the exhaustion method for 30 min with constant stirring. After completion of dyeing the fabric sample was washed with cold water and exposed to air, for oxidation/fixation of dye molecules. Then the fabric was soaped under boiling, rinsed with cold water and air dried.

Colour depths of the dyed fabrics were characterised by colour measurement in the form of K/S value and colour coordinates CIE L*, a*and b*. A sphere spectrophotometer (SP b2 X-Rite, USA) was used along with a D65 (daylight) light source with 10° viewing angle. Dyed samples were also evaluated for washing fastness properties (Source IS 764: 1979).

3 Results and discussion

3.1 Voltammetric studies of Ferric-TEA-Gluconate complex

Voltammetric studies on the Fe(III)-TEA redox systems were carried out by Bechtold et al., on mercury electrode with 0.005 mol L^{-1} Fe(III) concentration and around 0.1 mol L^{-1} TEA concentration using Ag/AgCl, 3 M KCl reference electrode [17]. In our earlier studies on electrochemical dyeing, a slightly higher concentration of Fe(III) (0.030 mol L^{-1}) as well as TEA (0.345 mol L^{-1}) was employed [18]. Figure 1 illustrates the cyclic voltammogram recorded under these conditions using a glassy carbon working electrode. Ferric TEA displays a quasi-reversible cyclic response versus Hg/HgO/OH^-. The peak currents were found to increase linearly with square root of sweep rate confirming diffusion control nature of the redox process (Eq. 1).

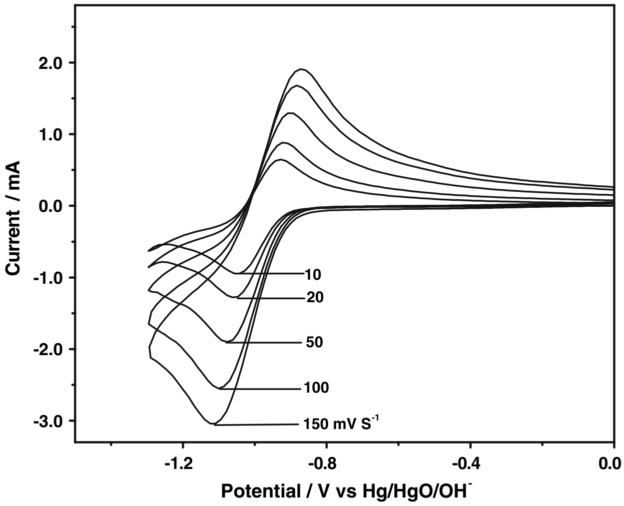

Fig. 1 Cyclic voltammograms of the Fe(III)-TEA complex 0.03 mol L^{-1} Fe^{3+} and 0.345 mol L^{-1} TEA in 0.45 mol L^{-1} NaOH at different scan rates 10, 20, 50, 100 and 150 mV s^{-1}

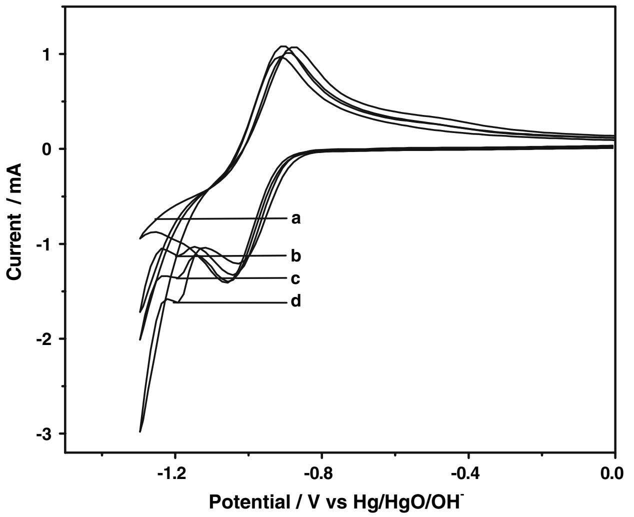

Fig. 2 Cyclic voltammograms of the Fe(III)-TEA complex 0.03 mol L^{-1} Fe^{3+} and 0.345 mol L^{-1} TEA in 0.45 mol L^{-1} NaOH (a) mediator alone and in presence of C·I. Vat green 1 dye concentrations; (b) 0.4 × 10^{-3} mol L^{-1}; (c) 0.8 × 10^{-3} mol L^{-1}; and (d) 1.2 × 10^{-3} mol L^{-1} at scan rate 25 mV s^{-1}

$$\text{Fe(III)-TEA} + 1e^- \rightleftharpoons \text{Fe(II)-TEA} \tag{1}$$

The ΔEp values observed on glassy carbon in the present work (110 mV at 10 mV s^{-1} and 230 mV at 150 mV s^{-1}) are significantly higher when compared to the same values on a mercury electrode reported earlier, indicating a relatively slower electron transfer on glassy carbon.

Vat dyes like C·I. Vat green 1 employed in the study are insoluble in alkaline solution. However, the electro-generated Fe(II) complex reduces the dye molecule in a two step process leading to the formation of alkali stable leuco form.

$$\text{Fe(II)-TEA} + \text{Dye} \rightleftharpoons \text{Fe(III)-TEA} + \text{Dye}^- \tag{2}$$

$$\text{Dye}^- + \text{Fe(II)-TEA} \rightleftharpoons \text{Dye}^{2-} + \text{Fe(III)-TEA} \tag{3}$$

$$2\text{Dye}^- \rightleftharpoons \text{Dye}^{2-} + \text{Dye} \tag{4}$$

The cyclic voltammograms recorded for the Fe(III)-TEA system in the absence and presence of 0.4, 0.8 and 1.2 × 10^{-3} mol L^{-1} C·I. Vat green 1 dyes are shown in Fig. 2. The catalytic reduction of insoluble dye molecule in the initial stages is not significant and hence the first cathodic peak current does shows no enhancement in the presence of insoluble dye molecules. In fact, a small reduction in cathodic peak current is noticed, probably due to the surface blocking by partial adsorption of insoluble dye molecules. However, the slow formation of soluble leuco forms leads to a second cathodic peak around −1.2 V vs Hg/HgO/OH^-. This cathodic peak current increases with increasing dye concentration (Fig. 2).

The electro-generated Fe(II)-TEA species reduces the insoluble dye slowly, even after the completion of the

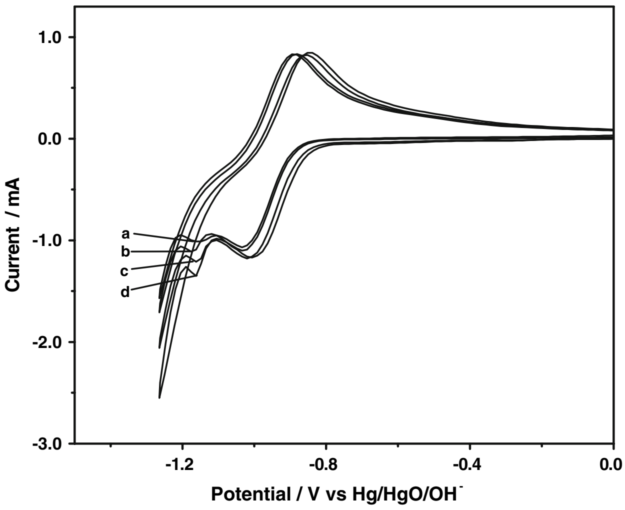

Fig. 3 Cyclic voltammograms of the Fe(III)-TEA complex 0.03 mol L^{-1} Fe^{3+} and 0.345 mol L^{-1} TEA in 0.45 mol L^{-1} NaOH at scan rate 20 mV s^{-1} at different time intervals (a) 3; (b) 6; (c) 9; and (d) 12 mins

voltammetric cycle. This is confirmed by monitoring the cyclic voltammetric responses for the same Fe(III)-TEA-dye system at regular intervals of 3 min between each potential cycle and is shown in Fig. 3. It is noticed that in subsequent voltammetric runs, the cathodic peak currents in the first and second peak potential regions increase significantly. These processes are due to the cathodic reduction (Eq. 2) and direct leuco form reduction (Eqs. 3 and 4), respectively, of the dye molecule.

As reported by Bechtold et al., it is very difficult to reduce the Fe(III)-gluconate system electrochemically [15]. A typical cyclic voltammogram obtained for Fe(III) in the presence of the Ca-gluconate system is shown in Fig. 4a.

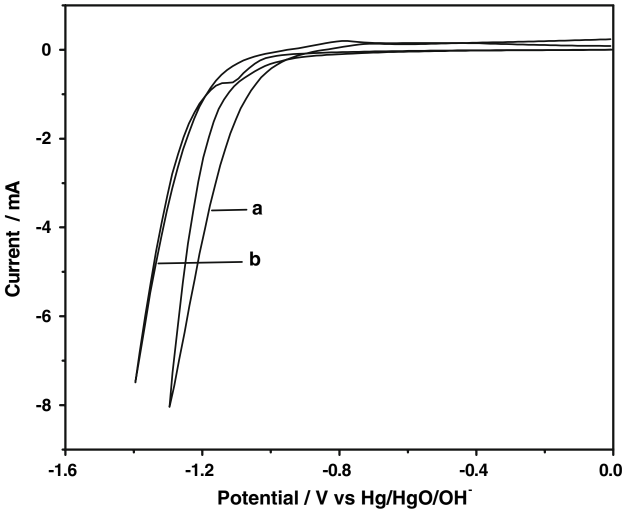

Fig. 4 Cyclic voltammograms of the Fe(III)-gluconate complex containing 0.03 mol L^{-1} Fe^{3+}, (a) 0.05 mol L^{-1} Ca-gluconate; and (b) 0.05 mol L^{-1} Na-gluconate in 0.5 mol L^{-1} NaOH at scan rate 40 mV s^{-1}

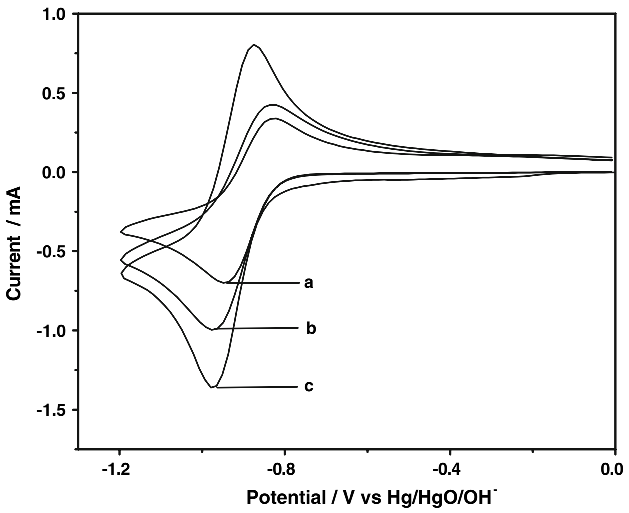

Fig. 5 Cyclic voltammograms of the Fe(III)-TEA-gluconate complex 0.03 mol L^{-1} Fe^{3+}, 0.15 mol L^{-1} TEA and varying the concentration of Ca-gluconte (a) 0.01 mol L^{-1}; (b) 0.02 mol L^{-1}; and (c) 0.03 mol L^{-1} in 0.5 mol L^{-1} NaOH at scan rate 20 mV s^{-1}

No distinct cathodic reduction peak was observed. However, a small concentration of Fe(III)-gluconate is probably reduced along with hydrogen evolution as evidenced by the appearance of a small and broad anodic peak during the reverse sweep. Similar voltammetric responses were obtained for sodium gluconate (compare Fig. 4a, b), except for the shift of the background current towards more negative region by about 100 mV. This suggests that Ca^{2+} and Na^{+} ions do not influence the electro reduction process significantly. Between the two ligands, namely TEA and gluconate, the gluconate complex appears to be more stable. The ligand exchange process in Eq. 5 appears to be favourable for the forward reduction.

$$\text{Fe(III)-TEA} + \text{Gluconate} \rightleftharpoons \text{Fe(III)-Gluconate} + \text{TEA} \quad (5)$$

With increasing concentration of gluconate, the redox peak current for the Fe(III)-TEA complex is found to decrease significantly, as shown in Fig. 5. This is due to the decrease in concentration of Fe(III)-TEA according to Eq. 5.

3.2 Voltammetric studies of ferric-oxalate-gluconate system

Conventionally, industrial vat dyeing is preferably carried out above pH 12 and very few Fe(III) complexes are stable in such alkaline conditions. Many well-known complexes like Fe(III)-oxalate, precipitate out in such alkaline medium [19]. During the preliminary experiments, when ferric sulphate was added to 1 mol L^{-1} NaOH and 0.1 mol L^{-1} oxalic acid, a brown precipitate was obtained. The Fe(III)-oxalate complex was found to be stable at pH values less than or equal to 8. Typical cyclic voltammograms of

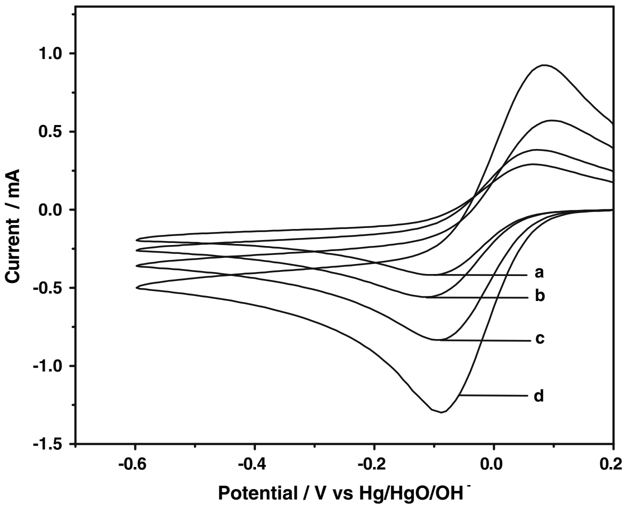

Fig. 6 Cyclic voltammograms of the complex containing 0.25 $\mathrm{mol\ L^{-1}}$ oxalic acid and different concentrations of $\mathrm{Fe^{3+}}$ (a) 0.01 $\mathrm{mol\ L^{-1}}$; (b) 0.015 $\mathrm{mol\ L^{-1}}$; (c) 0.02 $\mathrm{mol\ L^{-1}}$; and (d) 0.03 $\mathrm{mol\ L^{-1}}$ in 0.5 $\mathrm{mol\ L^{-1}}$ NaOH at pH 8 at scan rate 20 $\mathrm{mV\ s^{-1}}$

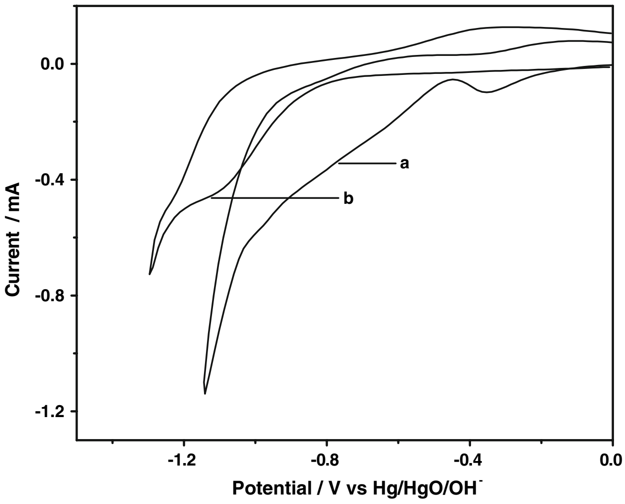

Fig. 7 Cyclic voltammograms of the complex containing 0.1 $\mathrm{mol\ L^{-1}}$ oxalic acid, 0.03 $\mathrm{mol\ L^{-1}}$ $\mathrm{Fe^{3+}}$ and 0.05 $\mathrm{mol\ L^{-1}}$ Ca-gluconate at two different pH (a) 8; and (b) 13 at scan rate 40 $\mathrm{mV\ s^{-1}}$

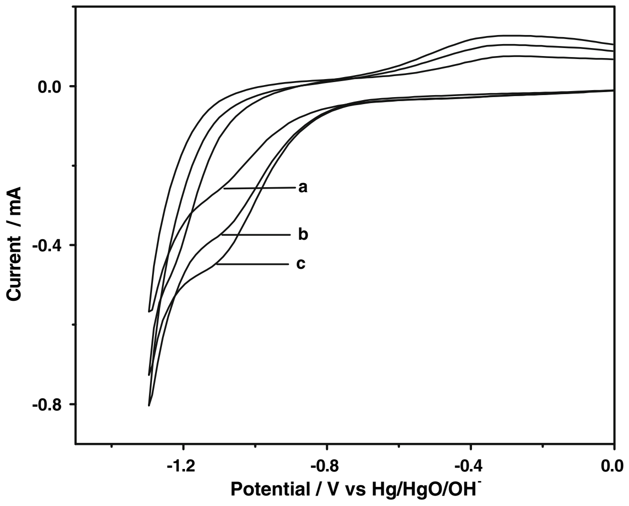

Fig. 8 Cyclic voltammograms of the complex containing 0.1 $\mathrm{mol\ L^{-1}}$ oxalic acid and 0.05 $\mathrm{mol\ L^{-1}}$ Ca-gluconate in 1 $\mathrm{mol\ L^{-1}}$ NaOH increasing the concentration of $\mathrm{Fe^{3+}}$ (a) 0.01; (b) 0.02; and (c) 0.03 $\mathrm{mol\ L^{-1}}$ at scan rate 40 $\mathrm{mV\ s^{-1}}$

Fe(III)-oxalate at different Fe(III) concentrations at pH 8 are shown in Fig. 6. This redox system also gives rise to well defined quasi reversible diffusion controlled voltammograms. The peak current increases with increasing concentration of Fe(III) ions. However, the redox potential, and the pH value is too low to be of any use for vat dyeing.

Interestingly, in the presence of excess gluconate, the Fe(III)-oxalate complex did not lead to any hydrolysis or precipitation. The pH of the Fe(III)-oxalate-gluconate system could be raised beyond 13. As shown in Fig. 7, the reduction peak below 0.5 V was found to decrease with increasing pH and gluconate concentration. Another broad peak was observed at more negative potentials. Typical cyclic voltammograms of the Fe(III)-oxalate-gluconate system recorded at two different pH values of 8 and 13 are shown in Fig. 7a, b respectively. At pH 13, abroad cathodic as well as anodic peak currents were found to increase with increasing Fe(III) concentration, as shown in Fig. 8. All these observations suggest that Fe(III) is stable in such a medium containing oxalate and gluconate ligands. The following dynamic equilibrium probably substantiates the above fact (Eq. 6).

$$\text{Fe(III)-Gluconate} + \text{Oxalate} \rightleftharpoons \text{Fe(III)-Oxalate} + \text{Gluconate} \qquad (6)$$

Fe(III)-gluconate is probably more stable. However, a small concentration of Fe(III)-oxalate would still be available for electrochemical reduction (Eq. 7).

$$\text{Fe(III)-Oxalate} + 1\mathrm{e}^- \rightleftharpoons \text{Fe(II)-Oxalate} \qquad (7)$$

A decrease in the concentration of Fe(III)-oxalate due to electro reduction at the interface will shift equilibrium (Eq. 6) towards the right ensuring continuous availability of former species at the electrode surface. The redox peaks due to Fe(III)-oxalate-gluconate complex was found to increase with increasing concentrations of insoluble dye molecule as shown in Fig. 9. In this system, only one cathodic peak is observed. No separate reduction peak due to the solubilised organic intermediate was observed (compare Figs. 2, 3 and 9). The cathodic peak current in the presence of dye, however, was found to increase with increasing dye concentration. This is probably due to a small catalytic influence by the mediator. Typical voltammetric results in the absence and presence of dye molecules including peak current enhancement factor $((\mathrm{Ip})_c/(\mathrm{Ip})_d)$ are summarised in

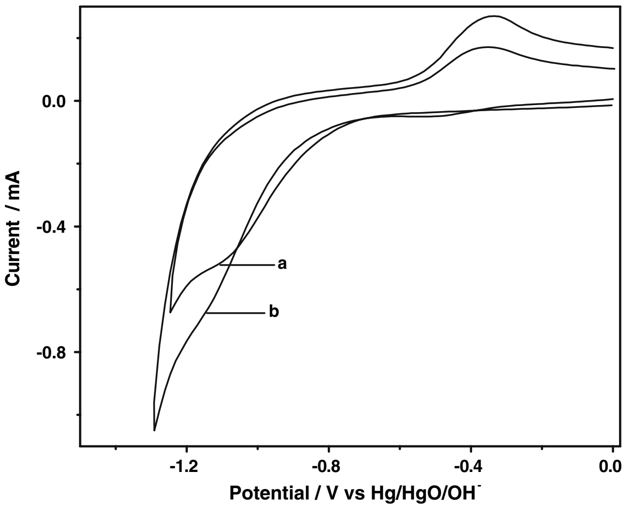

Fig. 9 Cyclic voltammograms of the complex containing 0.1 mol L^{-1} oxalic acid, 0.05 mol L^{-1} Ca-gluconate and 0.03 mol L^{-1} Fe^{3+} in 1 mol L^{-1} NaOH in presence of C·I. Vat green 1 dye concentrations (a) 0.8×10^{-3} mol L^{-1}; and (b) 1.2×10^{-3} mol L^{-1} at scan rate 40 mV s^{-1}

Table 2. Similar enhancement factors have also previously been reported for the Fe(III)-TEA-gluconate system [15]. It is therefore likely that a similar catalytic influence occurs by the formation of Fe(II)-gluconate from Fe(II)-oxalate, as well as Fe(II)-TEA species.

$$\text{Fe(II)-TEA} + \text{Fe(III)-Gluconate} \rightleftharpoons \text{Fe(III)-TEA} + \text{Fe(II)-Gluconate} \quad (8)$$

$$\text{Fe(II)-Oxalate} + \text{Fe(III)-Gluconate} \rightleftharpoons \text{Fe(III)-Oxalate} + \text{Fe(II)-Gluconate} \quad (9)$$

$$\text{Fe(II)-Gluconate} + \text{Insoluble dye} \rightleftharpoons \text{Fe(III)-Gluconate} + \text{Soluble leuco dye} \quad (10)$$

Hence in both these media, the ultimate reducing agent for the dye molecule is Fe(II)-gluconate (Eqs. 8–10). This is probably responsible for substantial similarities between the Fe(III)-TEA-gluconate system and the Fe(III)-oxalate-gluconate system. Studies relating to the type of complex formation in both ferrous and ferric states and the mechanism of vat dye reduction are in progress.

3.3 Electrochemical dyeing on cotton fabric

Dyeing of fabric in the Fe(III)-oxalate-gluconate system was carried out with an MLR value of 1:80. The dye intensity of dyed cloth was measured by means of the K/S value, which was found to be reasonably good. For 0.8 wt% shade of C. I. Vat Green 1 on pre-treated cotton fabric, a K/S value of 2.27 was achieved. Apart from C. I. Vat Green 1 dye, four other dyestuffs were also evaluated for their overall dyeing efficiency. K/S values and CIE Lab coordinates for all these dyes are shown in Table 3. Fairly good K/S values were obtained. In general a variety of vat dyes could be effectively dyed using the same Fe(III)-oxalate-gluconate mediator system. The dyed fabrics also show good washing fastness properties.

4 Conclusion

The present study shows that the Fe(III)-oxalate system can be stabilised in alkaline media in the presence of excess gluconate. This approach also offers further scope for choosing other redox complexes, for electrochemical vat dyeing. Voltammetric investigations indicate that the Fe(II)-TEA-gluconate system, as well as the Fe(II)-oxalate-gluconate system, catalyse the electrochemical vat dyeing system through the Fe(II)-gluconate intermediate. The same redox mediator can also be used for dyeing a number of vat dyes such as Vat Green 1, Vat Violet 1, Vat Brown 1, Vat Yellow 2 and Vat Black 27.

Table 2 Peak potential and peak current of mediator ferric-oxalate-gluconate (concentrations are same as shown in Figure 9) system and corresponding enhancement factors at different sweep rates

Sl. No	Solution	Sweep rate/mV s^{-1}	$(Ep)_a$/V	$(Ip)_c$ or $(Ip)_d$/mA	$(Ep)_c$/mV	$(Ip)_c/(Ip)_d$
1	Ferric-Oxalate-Gluconate system	20	−1.337	−284	−492	–
		40	−1.335	−420	−492	–
		80	−1.335	−653	−427	–
		160	−1.349	−781	−325	–
2	Ferric-Oxalate-Gluconate system + 0.8 mM dye	20	−1.341	−381	−577	1.34
		40	−1.357	−543	−577	1.29
		80	−1.383	−754	−549	1.15
		160	−1.412	–	−533	–
3	Ferric-Oxalate-Gluconate system + 1.2 mM dye	20	−1.377	−393	−547	1.38
		40	−1.393	−555	−544	1.32
		80	−1.418	−794	−534	1.21
		160	−1.444	–	−517	–

Table 3 Effect of different colors of vat dyes with the Ferric-oxalate-gluconate system (mediator composition: 0.02 mol L^{-1} $Fe_2(SO_4)_3$, 0.05 mol L^{-1} Ca-gluconate and 0.1 mol L^{-1} oxalic acid in 1.0 mol L^{-1} NaOH)

Ex. No.	C·I. Name of dye	Percent shade (%)	K/S Value	L^*	a^*	b^*	Washing fastness	
							Staining	Shading
1	Vat Green 1	0.8	2.27	34.19	−43.10	1.29	4–5	4
2	Vat Violet 1	0.8	2.05	29.70	28.19	−30.86	4–5	3–4
3	Vat Brown 1	0.8	3.00	45.14	9.02	3.85	4–5	3–4
4	Vat Yellow 2	0.8	1.24	75.89	9.04	33.88	4–5	4
5	Vat Black 27	0.8	1.65	53.41	−2.43	6.52	4–5	4

0.8 wt% shade of dye was produced on the pretreated fabric

Acknowledgments The authors thank the Department of Science and Technology, India for financial support to carry out this work. The authors also thank Prof. A. K. Shukla, Director, CECRI, for his support and encouragement.

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