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Fe^{3+}-D-gluconate and Ca^{2+}-Fe^{3+}-D-gluconate complexes as mediators for indirect cathodic reduction of vat dyes – Cyclic voltammetry and batch electrolysis experiments

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Abstract

The indirect cathodic reduction of dispersed vat dyes CI Vat Yellow 1 and CI Vat Blue 5 was investigated by cyclic voltammetry and with batch electrolysis experiments. 0.01 mol L^{-1} solutions of the complexes Fe^{3+}-D-gluconate and Ca^{2+}-Fe^{3+}-D-gluconate were studied. The addition of dispersed dyestuff to the mediator solution lead to a catalytic current. While the cathodic peak currents of both complexes is comparable, Fe^{3+}-DGL shows higher enhancement factors, which are defined as quotient of catalytic peak current and cathodic peak current of the mediator system $(I_p)_c/(I_p)_d$. In the presence of 0.5 g L^{-1} of dispersed vat dye enhancement factors of 1.8 were determined at scan rates of 0.005–0.010 V s^{-1}. Galvanostatic batch reduction experiments with use of a laboratory multi-cathode cell confirmed the favourable properties of the Fe^{3+}-DGL in comparison to the binuclear Ca^{2+}-Fe^{3+}-DGL. With use of the Fe^{3+}-DGL mediator complete dyestuff reduction could be achieved. The batch reduction process was followed experimentally by photometry and redox potential measurement in the catholyte.

1. Introduction

The use of mediators for indirect cathodic dyestuff reduction in textile dyeing operations using vat dyes and indigo dye is a promising technique for substitution of non regenerable reducing chemicals [1–3]. A field of particular scientific interest is the use of soluble complexes as mediators for indirect electrochemical reduction of dispersed dyes.

Recently scale up of the technique has reached full scale operation in exhaust dyeing of yarn in package dyeing. In this system 100 kg of cellulose fibre yarn, mainly cotton, is dyed with vat dyes using a 500 A multi-cathode cell and iron(II/III)-complexes as mediators [3, 4].

Depending on the dyeing process and the dyestuff used, different pH and redox potential are required in the dyebath. For purposes of vat dyeing a redox potential more negative than −900 mV (vs. Ag/AgCl, 3 M KCl) has to be achieved in a dyebath of pH 13. For denim production with indigo dye (jeans) at pH 11.5 a redox potential more negative than −0.700 V has to be adjusted in the dyebath [3, 5].

Investigations on the properties of new soluble redox systems to serve as mediator for reduction of dispersed organic matter in alkaline solutions are of general scientific interest because only a few classes of redox couples have been studied in the past, e.g. iron-amino-complexes, anthraquinones [6–8]. In many cases the formal redox potential of Fe(II/III)-complexes is pH-dependent and shifts towards more negative values with increasing pH [9]. An important group of mediator complexes is based on complexes of $Fe^{3+/2+}$-D-gluconate (Fe^{3+}-DGL). As described in literature the uptake of Ca^{2+}-ions into the Fe^{3+}-D-gluconate complex causes a shift of the formal redox potential of the Fe(II/III)-complex towards more negative values which is due to the formation of a binuclear complex Ca^{2+}-Fe^{3+}-DGL [8].

While the complex chemistry and the cyclic voltammograms of this system have been studied in detail, no data for comparison of the ability of the mononuclear Fe^{3+}-D-gluconate (Fe^{3+}-DGL) and binuclear Ca^{2+}-Fe^{3+}-D-gluconate (Ca^{2+}-Fe^{3+}-DGL) complexes to serve as mediators for the indirect cathodic reduction of dispersed vat dyes have been reported.

This chemical class of iron-carbohydrate complexes, e.g. iron-gluconate complexes and mixed iron-calcium-gluconate complexes is of particular interest for indirect cathodic reduction of insoluble organic compounds because of its favourable chemical stability in alkaline baths and its ecological properties. However no investigations about changes in the mediator properties due to the uptake of Ca^{2+}-ions into Fe^{3+}-DGl complexes and formation of the binuclear Ca^{2+}-Fe^{3+}-D-gluconate complex are available at present.

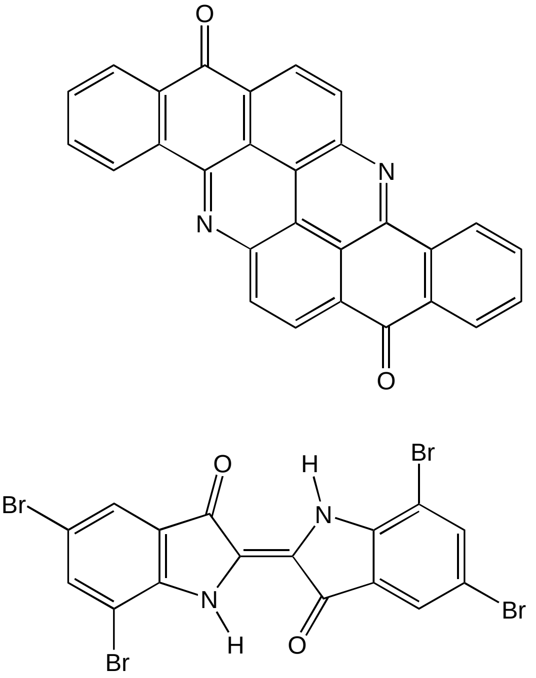
In this paper CV-studies and batch electrolysis experiments are presented to compare the performance of the Fe^{3+}-DGL system with the Ca^{2+}-Fe^{3+}-DGL complex. The data form a basic set of results describing the properties of representatives of two important groups of possible mediators. The analytical methods presented can be used as standard procedures for efficient characterisation of a chosen mediator complex.

2. Experimental

2.1. *Chemicals*

The $Ca(NO_3)_2 \cdot 4H_2O$, NaOH, $Fe(NO_3)_3 \cdot 9H_2O$ were analytical grade chemicals, Na-D-gluconate (DGL, $C_6H_{11}O_7Na$) with purity greater than 99% was used (Merck, Riedl-de-Haen).

In the batch electrolysis experiments technical grade chemicals and products were used: $FeCl_3$, NaOH, $CaCl_2$, Na-D-gluconate, Colour Index (CI) Vat Yellow 1 (VY1, Indanthrene Yellow G, DyStar, Frankfurt a.M., Germany), Colour Index Vat Blue 5 (VB5, Brilliantindigo 4B-D fl., DyStar, Frankfurt a.M., Germany). The chemical structure of the dyes is given in Scheme 1.



VY1

VB5

Scheme 1.

2.2. *Electrochemical experiments – Cyclic voltammetry*

The CV-experiments were performed at a HMDE-electrode (EG&G potentiostat 264A with 303A polarographic analyser EG&G, Princeton, NJ). The potential values are related to a Ag/AgCl, 3 M KCl reference electrode. The samples were deoxygenated for at least 8 min with He. The experiments were performed at room temperature. The cyclic voltammograms were recorded on a Rikadenki X–Y recorder.

The composition of the solutions investigated is given in Table 1. In addition to the solutions given in Table 1 blank solutions without Fe^{3+} were investigated for comparison.

The pH of the solutions was measured with a glass electrode and a potentiometer (Hamilton-flush-trode, Orion 720A, Orion Research Inc. Boston, MA).

2.3. *Batch electrolysis experiments*

The galvanostatic reduction experiments were performed in a laboratory scale multi-cathode electrolyser [9, 10] (volume of catholyte 1 L, volume of anolyte 0.3 L, anolyte: c(NaOH) 1 mol L^{-1}; cathode material: stainless steel, cathode area 4320 cm^2, separator: cation exchange membrane 100 cm^2 area, stainless steel anode 100 cm^2 area; cell current 0.3–0.9 A, cathodic current density 0.07–0.2 mA cm^{-2}). The redox potential in the catholyte was measured outside the cell in the catholyte reservoir using a Pt-electrode and a potentiometer (Orion 720A, Orion Research Inc. Boston, MA). The potential values given are related to a Ag/AgCl, 3 M KCl reference electrode.

The composition of the solutions investigated is given in the results and discussion section (Table 4). The temperature range of each experiment is given with the other experimental data.

The catholyte circulation through the electrode was driven by means of a peristaltic pump and was adjusted to a volume flow of 0.150 L min^{-1}, which results in an average catholyte velocity of 0.025 cm s^{-1}, inside the three dimensional cathode unit of 0.065 cm s^{-1}. The absorbance was measured at 405, 445, 495, 585, 620 and 660 nm using a one-beam filter-photometer (Merck SQ 300) equipped with a flow through cuvette (path length 1 mm).

Table 1. Composition of solutions investigated with cyclic voltammetry

No.	$c(Fe^{3+})$ /M	$c(Ca^{2+})$ /M	c(DGL) /M	c(VY1) /g L^{-1}	c(VB5) /g L^{-1}	c(NaOH) /M	pH
1	0.01	–	0.02	–	–	0.2	13.0
2	0.01	–	0.02	0.5	–	0.2	13.0
3	0.01	–	0.02	1.0	–	0.2	13.0
4	0.01	–	0.02	–	1.0	0.2	13.0
5	0.01	0.01	0.02	–	–	0.2	13.0
6	0.01	0.01	0.02	0.5	–	0.2	13.0
7	0.01	0.01	0.02	1.0	–	0.2	12.9
8	0.01	0.01	0.02	–	1.0	0.2	12.9

For comparison solutions without addition of Fe^{3+} were investigated in CV experiments.

3. Results and discussion

3.1. *CV-experiments – indirect reduction of dispersed dye*

The indirect cathodic reduction of dispersed dyes CI Vat Yellow 1 (VY1) and CI Vat Blue 5 (VB5) was investigated with cyclic voltammetry on a HMDE in alkaline aqueous solution at pH 13. The CV-experiments were recorded with the complex Fe^{3+}-DGL (solutions 1–4) using a solution containing a stoichiometric ratio of Fe:DGL 1:2. The complex Ca^{2+}-Fe^{3+}-DGL (solutions 5–8) was studied using a solution with the stoichiometric composition Ca:Fe:DGl 1:1:2. The scan rate v was varied from 0.005 to 0.10 V s^{-1}. A pH of 13 was chosen for the experiments because at this pH a rapid dissolution of the reduced dyestuff occurs following the reduction step.

For reduction of VY1 a redox potential of −0.520 to −0.550 V has to be achieved by the mediator, while for VB5 a redox potential of −0.490 to −0.590 V is required to reduce the dyestuff.

Representative reactions for the indirect cathodic dyestuff reduction can be formulated according to Equations 1–4. In Equations 1 and 2 the indirect reduction of VY1 by the Fe^{3+}-DGL system is shown, while in Equations 3 and 4 the reduction of VB5 is formulated for the Ca^{2+}-Fe^{3+}-DGL mediator. The given stoichiometry of the complexes of the Fe^{3+}-form present at pH 13 is in agreement with other studies; thus a complex Fe:DGL 1:2 for the Fe^{3+}-DGL complex and Ca:Fe:DGL 1:1:2 for the Ca^{2+}-Fe^{3+}-DGL complex form the mediator complexes [8, 11–14].

$$[\mathrm{Fe^{III}H_{-4}(DGL)_2}]^{3-} + e^- \rightleftharpoons [\mathrm{Fe^{II}H_{-4}(DGL)_2}]^{4-} \tag{1}$$

$$2[\mathrm{Fe^{II}H_{-4}(DGL)_2}]^{4-} + (\mathrm{VY1}) \rightleftharpoons (\mathrm{VY1})^{2-} + 2[\mathrm{Fe^{III}H_{-4}(DGL)_2}]^{3-} \tag{2}$$

$$[\mathrm{CaFe^{III}H_{-5}(DGL)_2}]^{2-} + e^- \rightleftharpoons [\mathrm{CaFe^{II}_{-5}(DGL)_2}]^{3-} \tag{3}$$

$$2[\mathrm{CaFe^{II}H_{-5}(DGL)_2}]^{3-} + (\mathrm{VB5}) \rightleftharpoons (\mathrm{VB5})^{2-} + 2[\mathrm{CaFe^{III}H_{-5}(DGL)_2}]^{2-} \tag{4}$$

As active intermediates Fe^{2+}-complexes are formed cathodically. In Equations 1–4 possible changes in protonation of the Fe^{2+-}complexes prior to the electron transfer to the dispersed dye were not taken into account.

The data for the cathodic peak potential $(E_p)_d$ and cathodic peak current $(I_p)_d$ for the Fe^{3+}-DGL complex (solution 1) and the Ca^{2+}-Fe^{3+}-DGL complex (solution 5) are given in Tables 2 and 3.

In accordance to the data for pH of 8–12, at pH of 13 the CV of the complexes do not follow the criteria for diffusion limited reversible redox reactions; e.g. both the cathodic peak potential $(E_p)_d$ and the anodic peak potential $(E_p)_a$ shift towards more negative/positive potential with increasing scan rate [8, 16, 17].

Table 2. Peak potential and peak current of solutions 1–4 in cyclic voltammetry at various scan rates (0.005, 0.010, 0.020, 0.050 0.100 V s^{-1}) and corresponding enhancement factors e.f. = $(I_p)_c/(I_p)_d$

No.	V /V s^{-1}	(E_p) /V	(I_p) /μA	$(E_p)_a$ /V	$(I_p)_a$ /μA	e.f. $(I_p)_c/(I_p)_d$
		$(E_p)_d$	$(I_p)_d$			
1	0.005	−1.150	2.4	–	–	–
	0.010	−1.250	3.0	–	–	–
	0.020	−1.350	4.0	−0.670	–	–
	0.050	−1.380	6.2	−0.630	1.0	–
	0.100	−1.410	8.7	−0.630	2.2	–
		$(E_p)_c$	$(I_p)_c$			
2	0.010	−1.370	4.0	−0.510	0.1	1.33
	0.020	−1.330	5.2	−0.500	0.3	1.30
	0.050	> −1.350	8.9	−0.475	1.2	1.44
	0.100	−1.370	11.9	−0.475	1.5	1.36
3	0.005	−1.310	4.3	−0.510	0.1	1.79
	0.010	−1.320	5.3	−0.510	0.4	1.77
	0.020	−1.330	6.7	−0.500	0.8	1.68
	0.050	−1.350	9.2	−0.490	2.2	1.48
	0.100	−1.360	12.1	−0.480	2.4	1.39
4	0.005	−1.380	3.2	–	–	1.33
	0.010	−1.370	4.0	–	–	1.66
	0.020	−1.370	5.2	–	–	1.30
	0.050	−1.380	7.2	−0.480	0.1	1.16
	0.100	−1.410	11.0	−0.480	0.3	1.26

The cathodic peak current $(I_p)_d$ shows good linearity with square root of scan rate (Figure 1).

The formation of the reduced Fe^{2+}-form can be observed in the voltamogramms with anodic peaks at $(E_p)_a$ of −0.670 to −0.630 V (Fe^{3+}-DGL, solution 1) and $(E_p)_a$ −0.930 to −0.830 V (Ca^{2+}-Fe^{3+}-DGL).

Under the same experimental conditions the CVs of the complexes were recorded in the presence of 0.5 or 1 g L^{-1} VY1, or 1 g L^{-1} VB5.

When dispersed dyestuff is added to the complex solution an indirect cathodic reduction of the pigment occurs according to Equations 1–4 and distinct changes are observed in the voltammogramms. The influence of added dyestuff on the voltammograms can be seen in Figures 2a and b and 3a and b. The added dispersed dyestuffs do not exhibit significant electrochemical activity [6–8].

Due to catalytic currents the cathodic current of the Fe-complexes $(I_p)_c$ increases while the anodic reoxidation peak disappears and is replaced by the anodic reoxidation of the dissolved reduced dyestuff at $(E_p)_a$ of −0.530 to −0.430 V depending on scan rate.

The data for the catalytic peak potential $(E_p)_c$ and the catalytic peak current $(I_p)_c$ are given in Tables 2 and 3. In experiments at a scan rate of 0.020–0.100 V s^{-1} reoxidation of the reduced dyestuff can be detected during the reverse scan with an anodic peak potential at $(E_p)_a$ of −0.430 to −0.530 V. In such experiments the anodic peak potential $(E_p)_a$ and the peak current $(I_p)_a$ are given in Tables 2 and 3.

In Figure 2a and b the cyclic voltammograms of 0.01 M Fe^{3+}-DGL complex in the presence of 0, 0.5 and

Table 3. Peak potential and peak current of solutions 5–8 in cyclic voltammetry at various scan rates (0.005, 0.010, 0.020, 0.050, 0.100 V s^{-1}) and corresponding enhancement factors e.f. = $(I_p)_c/(I_p)_d$

No.	v /V s^{-1}	$(E_p)/V$	(I_p) /μA	$(E_p)_a$ /V	$(I_p)_a$ /μA	e.f. $(I_p)_c/(I_p)_d$
		$(E_p)_d$	$(I_p)_d$			
5	0.005	−1.220/ −1.450	1.6/2.6	−0.930	1.2	–
	0.010	−1.270/ −1.470	2.0/3.0	−0.950	1.1	–
	0.020	−1.250/ −1.450	2.8/4.6	−0.920	1.6	–
	0.050	−1.280/ −1.460	4.3/6.2	−0.840	2.2	–
	0.100	−1.300/ −1.480	5.8/8.2	−0.830	3.2	–
		$(E_p)_c$	$(I_p)_c$			
6	0.005	−1.350/ −1.450	3.0/3.7	–	–	1.42
	0.010	−1.370/ −1.430	3.9/4.2	−1.140/ −0.500	–/0.1	1.40
	0.020	−1.400/ −1.440	5.1/5.6	–/−0.480	–/0.3	1.21
	0.050	–/−1.480	–/6.8	–/−0.460	–/1.4	1.10
	0.100	–/−1.490	–/11.1	–/−0.430	–/2.8	1.37
7	0.005	−1.310/ −1.380	3.4/4.0	−1.160/ −	–/–	1.54
	0.010	−1.300/ −1.360	4.5/4.8	−1.140/ −0.530	–/0.1	1.60
	0.020	−1.320/ −1.360	6.1/6.4	–/−0.510	–/0.6	1.39
	0.050	–/−1.370	–/9.6	–/−0.510	–/2.3	1.54
	0.100	–/−1.390	–/12.4	–/−0.510	–/3.6	1.53
8	0.005	−1.350/–	2.3/3.4	–	–	1.31
	0.010	−1.370/ −1.510	3.0/3.9	−1.130/–	–	1.30
	0.020	−1.320/ −1.540	4.0/4.7	−1.150/ −0.500	0.15	1.02
	0.050	−1.330/ −1.520	6.3/7.0	–/−0.470	0.65	1.13
	0.100	–/−1.530	–/9.4	–/−0.430	0.90	1.16

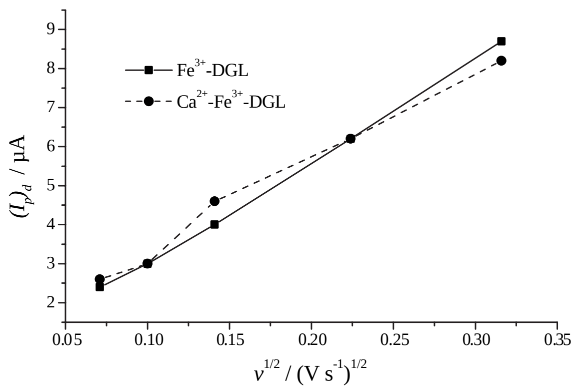


Fig. 1. Cathodic peak current $(I_p)_d$ as function of square root of scan rate $v^{1/2}$ for Fe^{3+}-DGL (solution 1) and Ca^{2+}-Fe^{3+}-DGL (solution 5).

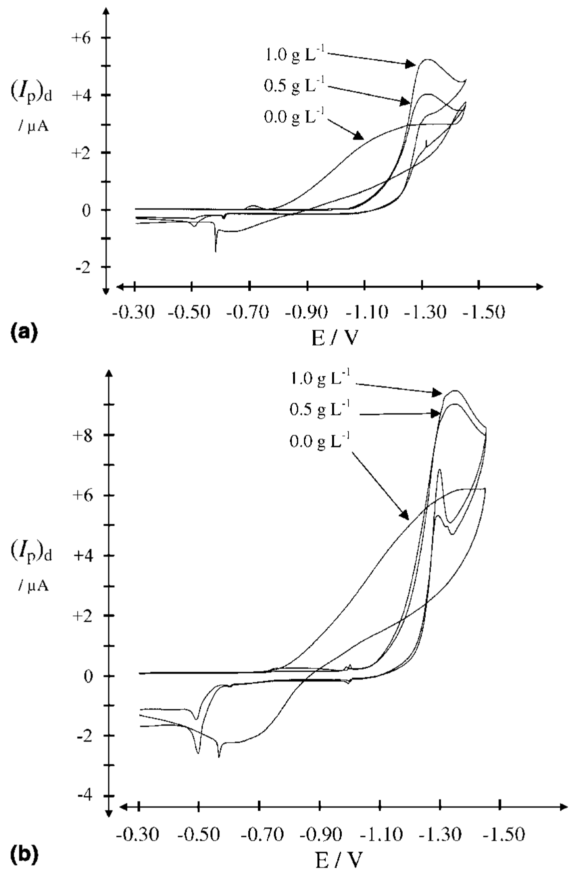


Fig. 2. Cyclic voltammograms of solutions 1, 2 and 3 Fe^{3+}-DGL (0, 0.5, 1 g L^{-1} VY1) in the potential interval of −0.300 to −1.450 V, scan rate: (a) 0.010 V s^{-1}, (b) 0.050 V s^{-1}.

1.0 g L^{-1} VY1 are shown for scan rates of 0.010 V s^{-1} (Figure 2a) and 0.050 V s^{-1} (Figure 2b).

In Figure 3a CVs of the Ca^{2+}-Fe^{3+}-DGL complex at scan rates from 0.005 to 0.100 V s^{-1} are shown. In Figure 3b the voltammograms in presence of 1 g L^{-1} VY1 are given. The increase in the cathodic peak current $(I_p)_c$ in the presence of dispersed dye is accompanied by a distinct change in the shape of the voltammogram.

Similarly to the CV given in Figure 2a and b for Fe^{3+}-DGL the addition of dispersed dyestuff causes a shift in peak potential toward more negative values and an increase in cathodic peak current $(I_p)_c$ is observed. Due to the presence of dispersed dyestuff as oxidant for the cathodically formed Fe(II)-complex, the shape of the voltammograms differs from the catalytic current plateau observed with homogenous conditions.

Determination of the enhancement factor (e.f.) as quotient of the catalytic current in the presence of dyestuff $(I_p)_c$ divided by the cathodic peak current of the mediator system $(I_p)_d$ is used to describe the effectiveness of a mediator/dye system [1, 6, 7, 15]. For the Fe^{3+}-DGL system $(I_p)_d$ was measured at $(E_p)_d$ of the pure complex solution (solution 1). The CV of the binuclear complex Ca^{2+}-Fe^{3+}-DGL shows two current peaks which indicate the presence of two complex species. In case of the Ca^{2+}-Fe^{3+}-DGL the e.f. were calculated on the basis of the total cathodic current $(I_p)_d$ measured for the second cathodic peak at $(E_p)_d$ of −1.450 to −1.480 V (solution 5).

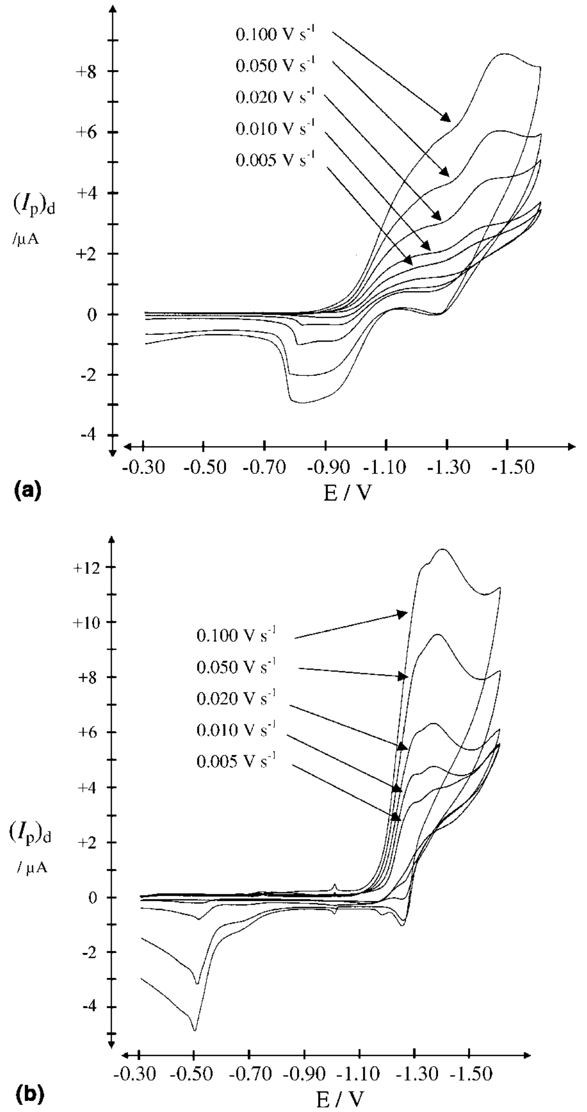


Fig. 3. (a) Cyclic voltamogramms of solution 5 (Ca^{2+}-Fe^{3+}-DGL complex) in the potential range of −0.300 to −1.600 V at various scan rate of 0.005, 0.010, 0.020, 0.050, 0.100 V s^{-1}. (b) Cyclic voltamogramms of solution 7 (Ca^{2+}-Fe^{3+}-DGL complex and 1 g L^{-1} VY1) in the potential range of −0.300 to −1.600 V at various scan rate of 0.005, 0.010, 0.020, 0.050, 0.100 V s^{-1}.

The cyclic voltammograms for Ca^{2+}-Fe^{3+}-DGL indicate the more negative formal redox potential due to the formation of the binuclear complex Ca^{2+}-Fe^{3+}-DGL [8].

Taking the formal redox potential as parameter determining the ability of a system to serve as a mediator for vat dye reduction, Ca^{2+}-Fe^{3+}-DGL should offer advantageous properties.

In Figures 4 and 5 the e.f. and the catalytic peak current $(I_p)_c$ of Fe^{3+}-DGL and Ca^{2+}-Fe^{3+}-DGL for indirect cathodic reduction of VY1 are given as a function of scan rate. Comparing the $(I_p)_c$ of the complexes no significant difference is observed.

On the basis of the e.f. the Fe^{3+}-DGL system seems more promising. At low scan rates e.f. of up to 1.8 are observed with Fe^{3+}-DGL in the presence of VY1 at scan rates of 0.005 and 0.010 V s^{-1}. The total catalytic current $(I_p)_c$ is higher for the Fe^{3+}-DGL system. Particularly at low scan rates the cathodic peak current $(I_p)_c$ of the Fe^{3+}-DGL system exceeds the current of the Ca^{2+}-Fe^{3+}-DGL approximately by 30–50%. Thus on the basis of e.f. as a measure for the effectiveness of a mediator system Fe^{3+}-DGL complexes will be favourable. At scan rates of 0.050–0.100 V s^{-1} the e.f. generally reduces to 1.1–1.3. This behaviour is similar to the results obtained with anthraquinone mediators and can be attributed to slow electron transfer between reduced mediator and dispersed dyestuff [1].

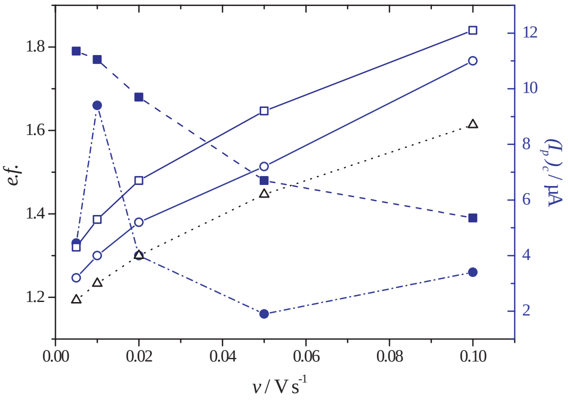


Fig. 4. Cathodic peak potential $(I_p)_c$ (respectively $(I_p)_d$) and corresponding enhancement factor e.f. ($(I_p)_c/(I_p)_d$) for Fe^{3+}-DGL (solution 1, 3, 4) as function of scan rate. (Δ) $(I_p)_d$ Fe^{3+}-DGL, (□) $(I_p)_c$, solution 3 (VY1), (○) $(I_p)_c$ solution 4 (VB5), (■) e.f. VY1, (●) e.f. VB5.

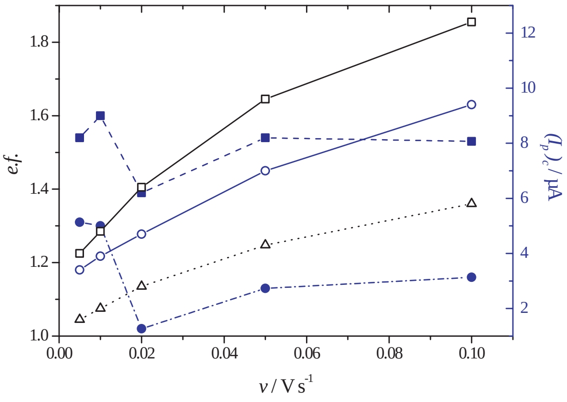


Fig. 5. Cathodic peak potential $(I_p)_c$ (respectively $(I_p)_d$) and corresponding enhancement factor e.f. ($(I_p)_c/(I_p)_d$) for Ca^{2+}-Fe^{3+}-DGL (solution 5, 7, 8) as function of scan rate. (Δ) $(I_p)_d$ Ca^{2+}-Fe^{3+}-DGL, (□) $(I_p)_c$ solution 7 (VY1), (○) $(I_p)_c$ solution 8 (VB5), (■) e.f. VY1, (●) e.f. VB5.

The effect of added dispersed dyestuff is detected more clearly at low scan rates (e.g. 0.010 V s^{-1}) which indicates a limited overall reaction rate for indirect cathodic dyestuff reduction. The observed e.f. with maximum values of 1.8 are low in relation to e.f. of 4 for iron-amino complexes [6, 7].

3.2. *Galvanostatic batch electrolysis*

To obtain further information for comparison of the two types of complexes galvanostatic batch electrolysis experiments were performed. The indirect reduction was monitored both by photometric observation of the dyestuff reduction and measurement of the redox potential in the catholyte.

In the batch electrolysis experiments 0.01 M Fe^{3+}-DGL complex (solutions 9–14) or 0.01 M Ca^{2+}-Fe^{3+}-DGL (solution or 15–20) were reduced in the presence of 0.5 g L^{-1} VY1 or 0.5 g L^{-1} VB5. The cell current was held constant at 0.3, 0.6 or 0.9A, which corresponds to a current per single cathode unit of 0.1, 0.2 and 0.3 A respectively. Thus the average current density in the three dimensional cathodes was between 0.07 and 0.21 mA cm^{-2}. The catholyte flow through the electrode compartment reached 0.025 cm s^{-1} or 0.065 cm s^{-1} inside the porous electrode. The experiments were performed at ambient temperature, the exact temperature range for each experiment is given in Table 4. A total volume of 1.0 L catholyte was reduced per batch. No inert gas atmosphere was used.

The reduction of the dispersed dye was monitored by measurement of E_c, the redox potential, and the absorbance of the catholyte (CI Vat Yellow 1 at 620 nm, CI Vat Blue 5 at 445 nm). The reduction of the dispersed dyestuff can be observed by an increase in absorbance at 620 nm from 445 nm and by a shift in the redox potential in the catholyte to negative values, e.g., −0.650 to −0.750 V. The effect of increased cell current for VY1 can be seen in Figure 6. Indirect cathodic dyestuff reduction was detected in experiments 10 and 11 while insufficient reduction was observed in experiments 9 and 17. In experiments 9 and 17 the redox potential changed to more negative values, e.g., −0.450 to −0.580 V but no dyestuff reduction was observed by photometry.

In Figure 7 the suitability of the two complexes to reduce VB5 was compared at similar experimental conditions (solutions 13, 14 for Fe^{3+}-DGL, solutions 19, 20 for Ca^{2+}-Fe^{3+}-DGL). The batch electrolysis experiments indicate favourable electrochemical properties of the Fe^{3+}-DGL system, compared to the Ca^{2+}-Fe^{3+}-DGL complex. At similar electrolysis conditions

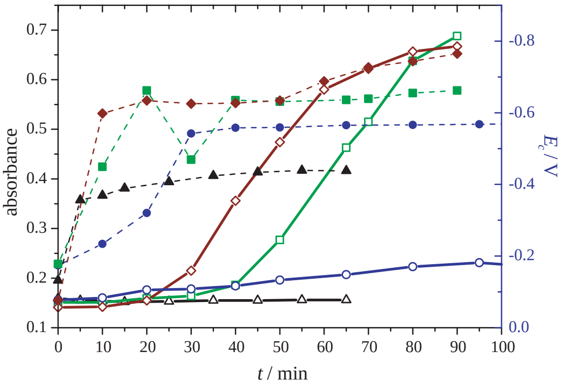


Fig. 6. Reduction of VY1 by Fe^{3+}-DGL at cell current 0.3, 0.6, 0.9 A and by Ca^{2+}-Fe^{3+}-DGL at 0.9 A). Absorbance (620 nm) and catholyte potential E_c as function of electrolysis time. (solutions 9, 10, 11, 17). (▲) E_c Fe^{3+}-DGL, 0.3 A, (■) E_c Fe^{3+}-DGL 0.6 A, (♦) E_c Fe^{3+}-DGL, 0.9 A, (●) E_c Ca^{2+}-Fe^{3+}-DGL, 0.9 A, (Δ) abs. Fe^{3+}-DGL, 0.3 A, (□) abs. Fe^{3+}-DGL 0.6 A, (◇) abs. Fe^{3+}-DGL, 0.9 A, (○) abs. Ca^{2+}-Fe^{3+}-DGL, 0.9 A.

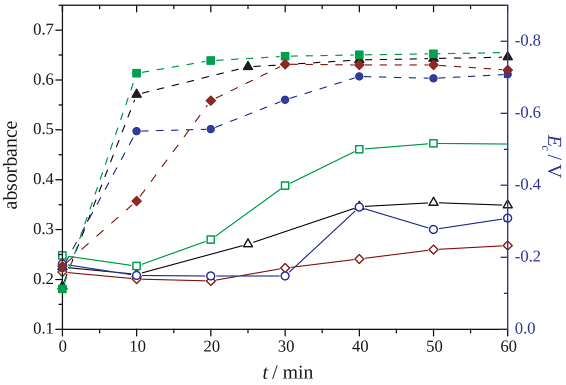


Fig. 7. Reduction of VB5 by Fe^{3+}-DGL (solution 13, 14) and Ca^{2+}-Fe^{3+}-DGL (solutions 19, 20) at 0.6 and 0.9 A cell current. Absorbance (445 nm) and catholyte potential E_c as function of electrolysis time. (▲) E_c Fe^{3+}-DGL, 0.6 A, (■) E_c Fe^{3+}-DGL 0.9 A, (♦) E_c Ca^{2+}-Fe^{3+}-DGL, 0.6 A, (●) E_c Ca^{2+}-Fe^{3+}-DGL, 0.9 A, (Δ) abs. Fe^{3+}-DGL, 0.6 A, (□) abs. Fe^{3+}-DGL 0.9 A, (◇) abs. Ca^{2+}-Fe^{3+}-DGL, 0.6 A, (○) abs. Ca^{2+}-Fe^{3+}-DGL, 0.9 A.

Table 4. Composition of solutions and experimental conditions of batch electrolysis experiments: I_{1-3} is the total cell current, I_i the current for single cathode unit, U_{1-3} the cell voltage of cathode 1 and 3 measured after 30 min electrolysis, T the temperature, absorbance (abs.) measured at experimental time = 0 and 60 min (VY1 620 nm, VB5 445 nm)

No.	$c(Fe^{3+})$ /M	$c(Ca^{2+})$ /M	c(DGL) /M	c(VY1) /g L^{-1}	c(VB5)/ g L^{-1}	c(NaOH) /M	I_{1-3} /A	I_i /A	U_{1-3} /V	T /°C	Abs. t = 0 min	Abs. t = 60 min
9	0.01	–	0.02	0.52	–	0.2	0.3	0.1	2.4–2.8	22.5–23.3	0.159	0.156
10	0.01	–	0.02	0.50	–	0.2	0.6	0.2	3.0–3.4	23.3–25.6	0.141	0.401
11	0.01	–	0.02	0.51	–	0.2	0.9	0.3	3.4–4.0	23.5–24.9	0.152	0.795
12	0.01	–	0.02	–	0.52	0.2	0.3	0.1	2.3–2.5	22.5–23.6	0.222	0.367
13	0.01	–	0.02	–	0.50	0.2	0.6	0.2	2.9–3.3	22.3–23.8	0.225	0.349
14	0.01	–	0.02	–	0.55	0.2	0.9	0.3	3.6–4.2	22.6–26.4	0.248	0.471
15	0.01	0.01	0.02	0.52	–	0.2	0.3	0.1	2.6–2.7	23.8–25.1	0.152	0.198
16	0.01	0.01	0.02	0.50	–	0.2	0.6	0.2	3.0–3.3	24.7–26.4	0.168	0.180
17	0.01	0.01	0.02	0.50	–	0.2	0.9	0.3	3.4–3.9	21.8–25.3	0.156	0.203
18	0.01	0.01	0.02	–	0.50	0.2	0.3	0.1	2.3–2.5	22.8–24.2	0.203	0.206
19	0.01	0.01	0.02	–	0.54	0.2	0.6	0.2	2.8–3.2	24.0–26.0	0.215	0.268
20	0.01	0.01	0.02	–	0.58	0.2	0.9	0.3	3.3–3.8	22.8–24.5	0.231	0.323

successful dyestuff reduction is observed with Fe^{3+}-DGL at a cell current of 0.9 A, while the Ca^{2+}-Fe^{3+}-DGL fails to permit complete and time stable dyestuff reduction (Figure 6). The curves in Figure 7 show stable reduction of VB5 in experiment 14, while unsatisfactory results are observed with Ca^{2+}-Fe^{3+}-DGL (experiments 19 and 20).

Detailed experimental data are given in Table 4. For both mediators a total cell current of 0.3 A does not achieve indirect dyestuff reduction in the experimental time scale. At a cell current of 0.9 A reduction of both VY1 and VB5 is possible using the Fe^{3+}-DGL mediator.

4. Conclusions

For indirect reduction of dispersed vat dyes with reduction potential in the range −0.500 to −0.600 V (vs. Ag/AgCl, 3 M KCl), e.g., Vat Yellow 1 or Vat Blue 5 various mediator complexes can be used [1–3, 6, 7]. Due to their excellent chemical stability the group of Fe^{3+}-sugar acid complexes is of particular interest.

The electrochemical properties of Fe^{3+}-DGL and Ca^{2+}-Fe^{3+}-DGL show distinct differences in the suitability to serve as mediator for indirect cathodic dyestuff reduction. The introduction of Ca^{2+}-ions into Fe^{3+}-DGL complexes leads to formation of a binuclear Ca^{2+}-Fe^{3+}-DGL complex and the formal redox potential shifts approximately −0.100 V more negatively values [8].

Experiments with cyclic voltammetry and batch electrolysis were performed at pH 13 with Fe^{3+}-DGL complex and Ca^{2+}-Fe^{3+}-DGL complex as mediators to compare the properties of the two complexes.

In the presence of dispersed reducible compounds (dyestuff) a catalytic current is observed in the CV-experiments when indirect cathodic dyestuff reduction is achieved. In cyclic voltammetry Fe^{3+}-DGL and Ca^{2+}-Fe^{3+}-DGL showed comparable cathodic peak currents $(I_p)_d$; the higher increase in catalytic peak current $(I_p)_c$ was observed in the presence of dispersed dyestuff with Fe^{3+}-DGL.

In the presence of reducible dispersed dyestuff enhancement factors $(I_p)_c/(I_p)_d$ of up to 1.8 were observed for Fe^{3+}-DGL, while e.f. remained below 1.6 using Ca^{2+}-Fe^{3+}-DGL as mediator.

The formation of dissolved reduced dyestuff was also observed during the reverse scan by an anodic current peak at $(E_p)_a$ of −0.530 to −0.430 V. This current can be attributed to the reoxidation of reduced dyestuff formed during the cathodic scan.

Galvanostatic batch electrolysis with a cell current of 0.3–0.9 A confirmed the results of the CV-experiments Under the experiment conditions studied, both CI Vat Yellow 1 and CI Vat Blue 5 were reduced at a current of 0.9 A by indirect cathodic reduction with Fe^{3+}-DGL. Under the same experimental conditions the Ca^{2+}-Fe^{3+}-DGL mediator failed to reduce of dispersed dye in the catholyte satisfactorily.

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