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Electrochemical behaviour of iron-complexes in presence of competitive ligands: A strategy for optimization of current density

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Abstract

Triethanolamine and D-gluconate both form alkali stable complexes with iron(III)- and iron(II)-ions. The redox behaviour of solutions containing one type of ligand is compared with solutions containing both ligands in excess compared with the iron(III)-concentration. Spectrophotometric investigations and experiments with cyclic voltammetry yield information about follow-up reactions proceeding during the cathodic reduction of the iron(III)-triethanolamine complex when D-gluconate is present in addition. The results indicate that the Fe(III)-triethanolamine complex is the predominant species as long as *c*(triethanolamine) exceeds *c*(Fe(III)) and thus the cathodic current density is mainly determined by the concentration of this complex. When the concentration of triethanolamine is lowered to 20% of the iron concentration then iron(III)–D-gluconate is the major species present in the solution. Then, besides ligand exchange reactions, an increase in cathodic current density indicates a redox reaction between Fe(II)-triethanolamine and Fe(III)–D-gluconate similar to the E_{cat}-type in cyclic voltammetry. Such conditions are of particular interest for the optimization of mediator systems with regard to the current density attainable at given iron(III)-concentration. The results show that a combination of different ligands can lead to an addition of the specific advantages of each metal-complex mediator.

1. Introduction

Alkali stable iron(II/III)-complexes are of interest for the indirect cathodic reduction of textile dyes in different textile dyeing processes [1]. Depending on the type of dyeing process and on the consumption of reducing agent necessary for complete dyestuff reduction, a cell current from 100 A up to more than 3000 A is required for full technical scale application. For these purposes multicathode cells have been used successfully. A maximum cell current of 1000 A was applied for continuous dyeing with indigo and for exhaustion dyeing with vat dyes a 45 A electrolyser has been tested [2–5].

At present nonregenerable reducing chemicals (e.g., $Na_2S_2O_4$), organic sulphoxylates or hydroxyacetone are used. The application of alkali stable iron(II)-complexes as regenerable reducing agents offers economic and ecological advantages. Improved process stability and more accurate control of process conditions will be of particular interest to the dyer [1, 5]. For the introduction of indirect electrolysis into textile dyehouses the development of a suitable electrolyser and the optimization of mediator systems with regard to maximum current density are both of decisive importance [2–4].

In aqueous alkaline solution amino compounds and sugar-acids are appropriate complexing agents for Fe(II)- and Fe(III)-ions [6–12]. Although stability constants for D-gluconate and related compounds are given in the literature the corresponding data for Fe(III)-triethanolamine complexes in alkaline solution have not yet been determined [6–9, 13]. The electrochemical behaviour of the Fe(III)-triethanolamine complex has been studied by different groups [6, 9, 14]. The reversible cathodic reduction of the Fe(III)-triethanolamine complex is observed at $E_p = -1050$ mV [9, 15]. The ratio iron(III):triethanolamine in the complex is assumed to be 1:1 with an pH-dependent amount of coordinated OH^--ions [6, 13, 14].

Iron–amino complexes (e.g., Fe(III)-triethanolamine) offer relatively high current density and sufficient negative redox potential at pH above 12 as required for proper reduction of all vat dyes in use today [6, 16]. A problem arises from the limited stability of the Fe(II)- and Fe(III)–TEA complexes at pH values below 12. In the textile dyeing process a rinsing step follows the dyeing procedure and as a result a decrease in the pH occurs. Under such conditions the precipitation of iron hydroxides from the dilute dyebath must be avoided [5].

The limited stability of such complexes at pH below 12 favours iron–sugar acid complexes (e.g. Fe(III)–

D-gluconate) for applications at pH 10–12, despite the lower achievable cathodic current density and the less negative redox potential in comparison to iron–amino complexes [1, 6, 8–12].

For an optimized mediator complex a combination of the advantages of each redox couple would be of distinct technical value, so investigations were performed to obtain information about the electrochemical behaviour of mediator solutions containing mixtures of triethanolamine (TEA) and D-gluconate (DGL). The complex mixtures were studied by spectrophotometric methods and with cyclic voltammetry. The results indicate the possibility of optimizing the composition of a mediator system with respect to maximum current density and chemical stability.

The methods described permit a rapid evaluation of improvements expected from a combination of two ligands in a mixed mediator system.

2. Experimental details

2.1. *Chemicals*

The composition of the solutions investigated is given in Table 1. The $Fe_2(SO_4)_3 \cdot (5\text{–}6)\ H_2O$, NaOH, triethanolamine TEA (tris-(2-hydroxy-ethyl)-amine) were analytical grade chemicals, Na–D-gluconate DGL ($C_6H_{11}O_7Na$) with purity greater than 99% was used (Merck, Riedl-de-Haen). For the experiments given in Table 2 and in Figure 7 technical grade $Fe_2(SO_4)_3 \cdot (5\text{–}6\ H_2O)$ was used.

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

Table 1. Composition and pH-value of the investigated complex solutions

Solution	$c(Fe^{3+})$ /mol dm^{-3}	c(TEA) /mol dm^{-3}	c(DGL) /mol dm^{-3}	c(NaOH) /mol dm^{-3}	pH
1	0.01	0.06	–	0.175	12.87
2	0.01	–	0.02	0.175	12.88
3	0.01	0.06	0.02	0.175	12.87
4	0.01	0.03	0.02	0.175	12.88
5	0.01	0.02	0.02	0.175	12.86
6	0.01	0.015	0.02	0.175	12.86
7	0.01	0.01	0.02	0.175	12.86
8	0.01	0.0075	0.02	0.175	12.86
9	0.01	0.004	0.02	0.175	12.86
10	0.01	0.002	0.02	0.175	12.86

Table 2. Cathodic peak potential and current measured with solution 1 at different scan rates

Scan rate /mV s^{-1}	$(E_p)_c$ /mV	$(E_{p/2})_c$ /mV	$(I_p)_c$ /μA	$(I_p)_a/(I_p)_c$	n
10	−1015	−955	12.0	0.94	0.91
100	−1015	−955	33.1	0.98	0.93
1000	−1025	−965	99.3	0.97	0.88

2.2. *Spectrophotometric experiments*

The spectrophotometric experiments were performed with a diode array photometer (Zeiss CLH 500/MCS 521 UV–vis, Carl Zeiss (Jena), Germany). A quartz glass cuvette with 10 mm path length was used.

The preparation of mixtures was started with formation of the Fe(III)DGL and subsequent addition of TEA. The spectra were measured after 16 h at room temperature to give sufficient time for equilibration between the different complexes.

2.3. *Electrochemical experiments*

The apparatus used was an EG&G 264A potentiostat with a 303A HMDE (drop size small, drop area 0.96×10^{-2} cm^2). A platinum wire served as the counter electrode. All potentials were measured against an Ag/AgCl 3 M KCl reference electrode. The test solutions were aerated for at least 8 min with N_2 or He to eliminate interfering oxygen. The cyclic voltammograms were recorded on a Rikadenki X–Y recorder or with personal computer based 16 bit acquisition instrument (National Instruments).

All experiments were performed at room temperature.

3. Results and discussion

3.1. *Cyclic voltammograms of Fe(III)TEA and Fe(III)DGL complexes*

3.1.1. *Fe(III)TEA*

The cyclic voltammograms of the Fe(III)TEA complex and of the Fe(III)DGL complex were recorded at different scan rates in the potential region −600 to −1300 mV to obtain basic results for a comparison of the behaviour of solutions containing mixtures of both ligands.

In Figure 1 voltammograms of the alkaline solution 1 containing the Fe(III)TEA complex recorded at different scan rates are given. The voltammograms show the expected characteristics of a reversible redox couple.

The ratio of the anodic peak current to the cathodic peak current $(I_p)_a/(I_p)_c$ is close to 1, $(I_p)_c$ is proportional to the square root of the scan rate and the cathodic peak potential $(E_p)_c$ is independent of the scan rate. From the difference between the cathodic half peak potential $(E_{p/2})_c$ and the cathodic peak potential E_p the electron transfer number was calculated as one [17]. Basic data describing the voltammograms obtained with solution 1 are presented in Table 2.

Under the experimental conditions the Fe(II/III)TEA redox system forms a reversible redox couple which is well suited to serve as a mediator for the reduction of insoluble organic molecules [1, 9, 15].

As the structure of the complexes is not fully known at this time, the redox reaction is written in more general form according to Equation 1 in Scheme 1.

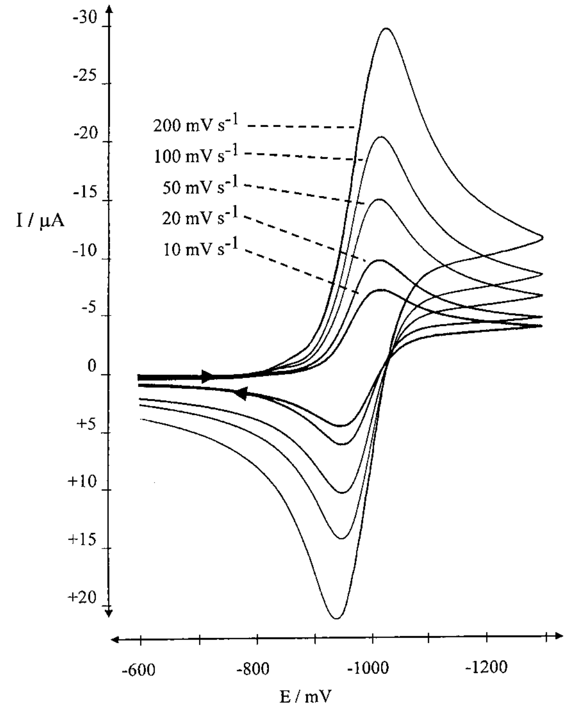

Fig. 1. Cyclic voltammograms of a solution 1 containing 0.01 mol dm^{-3} Fe^{3+}, 0.06 mol dm^{-3} TEA and 0.175 mol dm^{-3} NaOH at different scan rates.

3.1.2. *Fe(III)DGL*

Despite the fact that Fe(III)DGL complexes have been known for a long time and [$C_6H_8O_7Fe^{III}$]Na was isolated from aqueous alkaline solution by Traube, the chemistry of the Fe(III)DGL complexes in alkaline solution is still not fully understood. Different suggestions for possible complexes have been proposed; therefore the presentation of the redox couple in Scheme 1 has been simplified according to Equation 2 [7, 8, 10, 18].

Cyclic voltammograms of solution 2 at different scan rates are shown in Figure 2. No distinct cathodic peak for the reduction of Fe(III)DGL is observed during the cathodic scans. The reoxidation of the formed Fe(II)DGL is indicated during the reverse scan at about −600 mV.

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

$$\mathrm{Fe(III)DGL} + e^- \rightleftharpoons \mathrm{Fe(II)DGL} \quad (2)$$

$$\mathrm{Fe(II)TEA} + \mathrm{DGL} \rightleftharpoons \mathrm{TEA} + \mathrm{Fe(II)DGL} \quad (3)$$

$$\mathrm{Fe(II)TEA} + \mathrm{Fe(III)DGL} \rightleftharpoons \mathrm{Fe(II)TEA} + \mathrm{Fe(II)DGL} \quad (4)$$

$$\mathrm{Fe(III)GLC} + \mathrm{TEA} \rightleftharpoons \mathrm{Fe(III)TEA} + \mathrm{DGL} \quad (5)$$

Scheme 1. Possible reactions proceeding during the voltammetry of Fe(III)TEA/Fe(II)TEA and Fe(III)DGL/ Fe(II)DGL complexes.

At the same concentration of Fe(III)-complex the observed cathodic current for the reduction of Fe(III) DGL is much lower than the current measured with Fe(III)TEA.

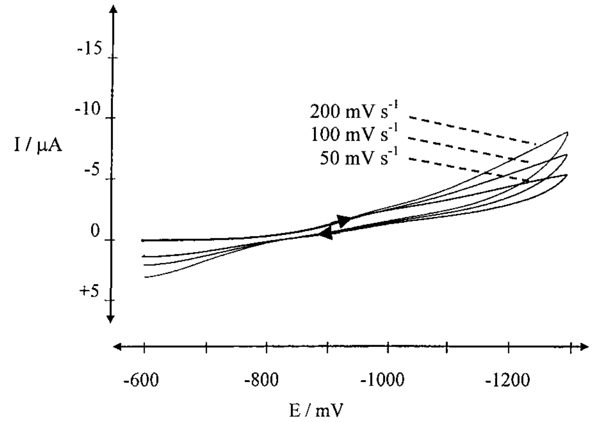

Fig. 2. Cyclic voltammograms of a solution 2 containing 0.01 mol dm^{-3} Fe^{3+}, 0.02 mol dm^{-3} DGL and 0.175 mol dm^{-3} NaOH at different scan rates.

3.2. *Spectrophotometric investigations*

When both TEA and DGL ligands are used in concentrations that exceed the minimum amount required for complexation the most stable complex is formed preferably. In the case of TEA and DGL this complexation can be observed by means of photometric measurements. In Figure 3 the light absorption of the solutions between 350 nm and 550 nm is shown.

The Fe(III)TEA complex shows low absorption at 430 nm compared Fe(III)DGL, so the extinction at 430 nm can be used as a quantitative indicator of the concentration of Fe(III)DGL in solution. Assuming that no mixed complexes, containing both ligands, are formed, then the residual amount of Fe(III)-ions not complexed by DGL is present as Fe(III)TEA complex. The presence of Fe(II)-complexes need not to be considered because the investigated solutions were prepared from the Fe(III)-sulphate and thus no significant amounts of Fe(II)-complex are present in solution.

In Table 3 the extinction of solutions 1–10 measured at 430 nm and the estimated concentrations of Fe(III) complexes are given. It can be seen that TEA is the stronger ligand and a stoichiometric amount of Fe(III)-ions is bound by TEA. When the amount of TEA is lowered beneath a Fe(III)-concentration of 0.01 mol dm^{-3} the detected concentration of Fe(III) DGL corresponds to the residual amount of Fe(III)-ions. This indicates an iron:triethanolamine ratio of 1:1 in the Fe(III)TEA complex.

3.3. *Cyclic voltammograms of mixed systems*

In addition to the cathodic electron-transfer reactions (Reactions 1 and 2 shown in Scheme 1), follow-up reactions can proceed in solution when both ligands are present at the same time (Equations 3–5). Redox reaction (4) or ligand exchange reactions (3) and (5) without a change in the oxidation state of the Fe(II/III)-ion must be considered. The observation of these reactions is dependent on properties of the ligands used

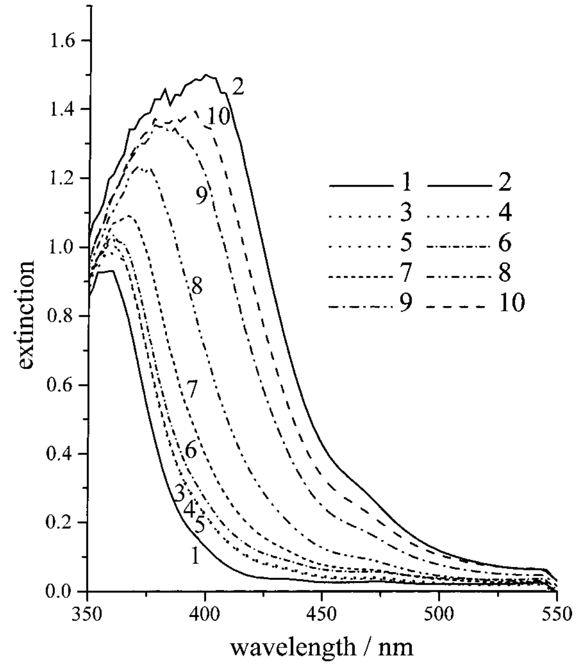

Fig. 3. Extinction of the solutions 1–10 between 350 nm and 550 nm (path length 10 mm).

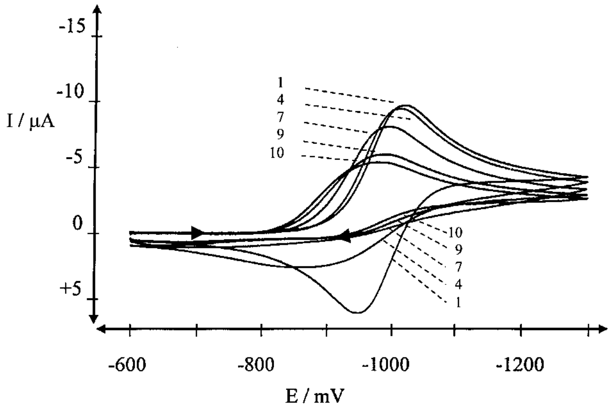

Fig. 4. Cyclic voltammogram of solutions 1, 4, 7, 9, 10 at a scan rate of 20 mV s^{-1} in the potential region between −600 to −1300 mV.

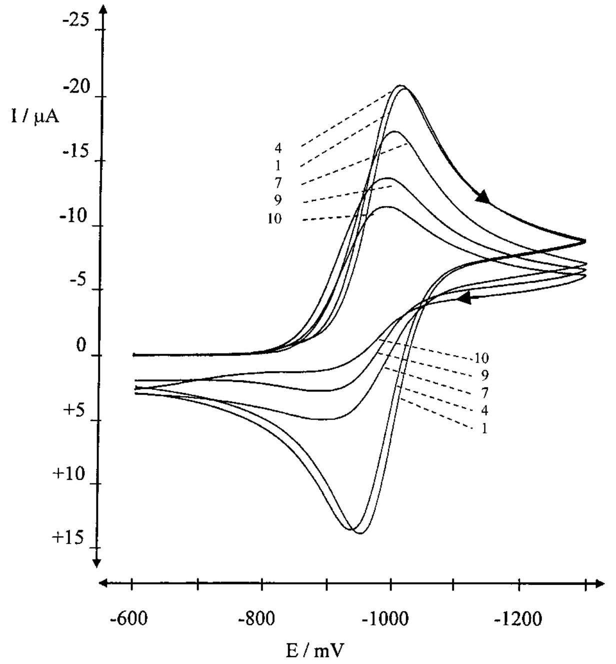

Fig. 5. Cyclic voltammogram of solution 1, 4, 7, 9, 10 at a scan rate of 100 mV s^{-1} in the potential region between −600 to −1300 mV.

and on the applied experimental conditions. In Figures 4 and 5 cyclic voltammograms of the Fe(II/III)TEA redox couple and of mixed systems in the potential region −600 to −1300 mV recorded at scan rates of 20 mV s^{-1} and 100 mV s^{-1} are shown. A presentation of the cathodic peak current $(I_p)_c$ at different scan rates for the investigated mixtures is given in Table 4. From the concentration of TEA present in a solution a theoretical value for the cathodic peak current $(I_p)_{th}$ can be calculated assuming that the whole TEA present in solution forms the Fe(III)TEA complex as long as $c(\text{TEA}) \leq c(\text{Fe(III)})$. The ratio of $(I_p)_c/(I_p)_{th}$ is also given in Table 4. This factor can be used as an additional indicator for follow-up reactions.

From the spectrophotometric investigations it is know that Fe(III)TEA is the predominant complex as long as c(TEA) exceeds c(Fe(III)). A comparison of the voltammograms recorded at a scan rate of 100 mV s^{-1} in solutions 1 and 4 shows only slight changes in the voltammograms. At low scan rates (e.g., 20 mV s^{-1}), the cathodic part of the voltammogram is almost unchanged in shape while the anodic part is different. The current observed during the cathodic scan with solution 4 is determined by Reaction 1 but in the presence of DGL a slow follow-up reaction, according to Equation 3, removes part of the Fe(II)TEA to give Fe(II)DGL. Reactions 4 and 5 are not of importance for solution 4 because Fe(III)DGL is required for these steps. Both the photometric data and the reverse scan in the voltammogram of solution 4 at a scan rate 100 mV s^{-1} indicate that only minor amounts of Fe(III)DGL are present in solution; only a reaction according Equation 3 in Scheme 1 can be used to explain this finding.

Table 3. Extinction of the investigated mediator solutions at 430 nm and calculated concentration of Fe(III)TEA and Fe(III)DGL

Solution	Extinction	10^3 c(TEA) /mol dm^{-3}	10^3 c(Fe(III) TEA)/mol dm^{-3}	10^3 c(Fe(III) DGL)/mol dm^{-3}
1	0.0372	60	10	–
2	0.8547	–	–	10
3	0.0727	60	>9.5	<0.5
4	0.0718	30	>9.5	<0.5
5	0.0768	20	9.5	0.5
6	0.1003	15	9.2	0.8
7	0.1386	10	8.8	1.2
8	0.2467	7.5	7.4	2.6
9	0.4989	4	4.4	5.6
10	0.6609	2	2.4	7.6

Reactions according Equation 4 become more important when c(TEA) is lower than c(Fe(III)). The voltammograms of solutions 7, 9 and 10 show a decrease in

Table 4. Cathodic peak current $(I_p)_c$ of mixed complexes at different scan rates and ratio of the experimental current $(I_p)_c$ to the corresponding theoretical value $(I_p)_{th}$ ($(I_p)_c$ of solution 1 with correction of the lower TEA concentration)

Scan rate Solution	10 mV s^{-1}		20 mV s^{-1}		50 mV s^{-1}		100 mV s^{-1}		200 mV s^{-1}	
	$(I_p)_c/\mu A$	$(I_p)_c/(I_p)_{th}$	$(I_p)_c/\mu A$	$(I_p)_c/(I_p)_{th}$	$(I_p)_c/\mu A$	$(I_p)_c/(I_p)_{th}$	$(I_p)_c/\mu A$	$(I_p)_c/(I_p)_{th}$	$(I_p)_c/\mu A$	$(I_p)_c/(I_p)_{th}$
1	6.8	–	9.5	–	14.8	–	20.5	–	29.8	–
3	7.3	1.07	9.6	1.01	14.8	1.00	20.4	0.99	28.5	0.96
4	7.1	1.06	9.5	1.00	14.4	0.98	20.8	1.01	28.5	0.96
5	6.8	1.00	9.1	0.96	14.3	0.97	19.8	0.96	27.5	0.92
6	6.3	0.93	8.5	0.89	13.3	0.90	19.0	0.93	26.5	0.89
7	5.8	0.85	7.8	0.82	12.0	0.81	16.8	0.82	24.0	0.81
8	5.3	1.04	7.3	1.02	11.3	1.02	15.8	1.02	22.1	0.99
9	4.3	1.57	6.0	1.57	9.5	1.61	13.5	1.65	18.5	1.55
10	3.8	2.78	5.3	2.76	8.1	2.75	11.3	2.74	14.8	2.48

$(I_p)_c$ with decreasing TEA concentration. Parallel to the lowering of *c*(Fe(III)TEA) the concentration of Fe(III)DGL increases and the redox reaction according to Equation 4 becomes more important. As a result the observed cathodic peak current with solution 10 is much higher than expected from the present Fe(III)TEA complex and the anodic peak around −900 to −950 mV further decreases. As the concentration of DGL remained constant in solution 2–10 the observed decrease in the anodic peak from solution 3 to 10 must be explained by reference to the effect of Reaction 4.

In Figure 6 the experimental cathodic peak current $(I_p)_c$ is shown as a function of the TEA concentration and for comparison the theoretical maximum value $(I_p)_{th}$ is shown. The extinction at 430 nm, which can be used as a measure for *c*(Fe(III)DGL), also is shown. The cathodic peak current decreases near *c*(TEA) 0.01 mol dm^{-3} but, particularly at low concentration of TEA, the experimental current is higher than expected from a simple cathodic reduction of the Fe(III)TEA complex in solution. An electrocatalytic mechanism according to Equation 4 causes this increased cathodic current at low TEA concentration [19].

On the assumption that *c*(TEA) = *c*(Fe(III)TEA) when *c*(TEA) < *c*(Fe(III)) a calculation of a theoretical voltammogram basing on Equations 1 and 2 is possible. In Figure 7 the voltammogram of 10 is compared with a curve calculated from the proportionate addition of the insulated voltammograms of solutions 1 and 2 (calc.). In the coupled system (exp.) an increase in cathodic current during the cathodic scan can be seen and the formation of additional amounts of Fe(II)DGL are detected during the anodic scan at a potential around −700 to −600 mV.

4. Conclusions

Under the investigated experimental conditions described in this work the Fe(II/III)TEA redox couple shows a reversible redox system behaviour and the current density of the electrode reaction is limited by diffusion. The Fe(II/III)DGL couple shows a more complex mechanism and so the measured lower current density is limited by the kinetics of the reactions proceeding in the diffusional layer, e.g. rearrangement

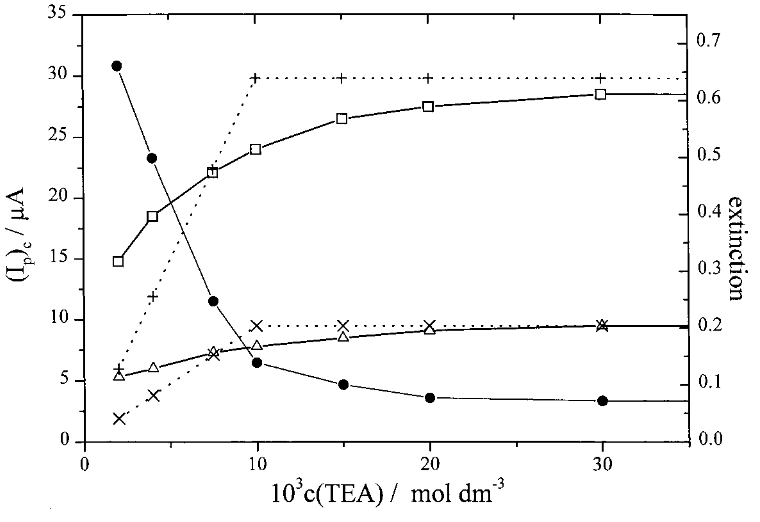

Fig. 6. $(I_p)_c$, $(I_p)_{th}$ and extinction of the complex solution at 430 nm as a function of *c*(TEA). Key: (+) 200 mV s^{-1} (theor.); (□) 200 mV s^{-1} (exp.); (×) 20 mV s^{-1} (theor.); (△) 20 mV s^{-1} (exp.); (●) extinc.

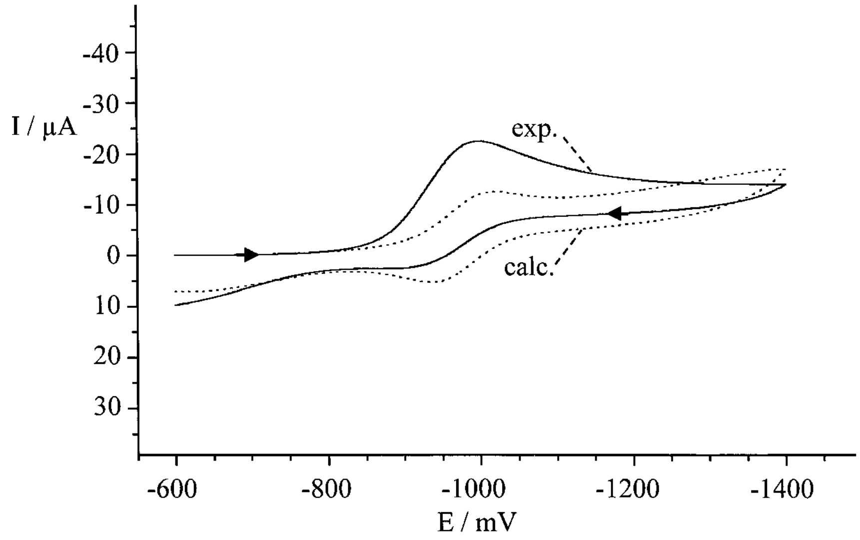

Fig. 7. Voltammogram recorded with solution 10 (exp.) in the potential interval from −600 to −1400 mV at a scan rate of 200 mV s^{-1} (HMDE, drop area 1.56×10^{-2} cm^2) and corresponding calculated voltammogram (calc.) resulting from proportionate addition of the voltammograms of solutions 1 and 2.

of the complex, dissociation of multi-center complexes and altered structure of the complex with change in oxidation number of the centre ion.

Photometric investigations performed with mixtures of both ligands present in excess compared to the Fe(III)-concentration indicate that the Fe(III)TEA complex is the predominant species as long as *c*(TEA) exceeds *c*(Fe(III)). Cyclic voltammetry supports this finding and the measured cathodic current density is mainly dependent on the concentration of Fe(III)TEA. In the presence of additional DGL, a ligand exchange is observed and part of the Fe(II)TEA formed during the cathodic scan reacts with DGL to give Fe(II)DGL.

When *c*(TEA) is lower than *c*(Fe(III)), Fe(III)DGL is present in solution and a redox reaction between cathodically formed Fe(II)TEA and Fe(III)DGL is observed yielding Fe(III)TEA and Fe(II)DGL as products. At low *c*(TEA) this coupled redox reaction causes a catalytic current and an increase in current density is observed. In voltammetric experiments with a ratio *c*(TEA)/*c*(Fe(III)) of 0.2 an increase in cathodic current is achieved, which is 2.7 times the cathodic current of the simple Fe(III/II)TEA redox couple.

The results demonstrate the possibility of a successful combination of the advantages of two selected redox couples when using a mixture of both ligands which are in competition for a lower amount of centre ion.

Such complex mixtures are of particular interest for the indirect electrochemical reduction of vat dyes. In the example presented in this work the combined advantages are improved stability due to the presence of DGL at lowered pH values occurring in rinsing processes and an increased cathodic current density due to the addition of TEA which permits higher cell current in a technical electrolyser.

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References

1. T. Bechtold, E. Burtscher, G. Kühnel and O. Bobleter, *J. Soc. Dyers and Colourists* **113** (1997) 135.
2. T. Bechtold, E. Burtscher, O. Bobleter, W. Blatt and L. Schneider, *Chem. Eng. Technol.* **21** (1998) 877.
3. W. Blatt and L. Schneider, *Melliand Textilberichte* **80** (1999) 240.
4. T. Bechtold, E. Burtscher, A. Turcanu and O. Bobleter, *J. Appl. Electrochem.* **27** (1997) 1021.
5. T. Bechtold, E. Burtscher, A. Turcanu and F. Berktold, *Melliand Textilberichte* **81** (2000) 195.
6. J.G. Ibanez, C. Choi and R.S. Becker, *J. Electrochem. Soc.* **134** (1987) 8.
7. G.M. Escandar, F.H. Gandolfor and L.F. Sala, *Anal. Asoc. Quim. Argent.* **78** (1990) 37.
8. R.L. Pecsock and J. Sandera, *J. Am. Chem. Soc.* **77** (1955) 1489.
9. T. Bechtold, E. Burtscher, A. Amann and O. Bobleter, *J. Chem. Soc. Faraday Trans.* **89** (1993) 2451.
10. W. Traube and F. Kuhbier, *Chem. Ber.* **69** (1936) 2655.
11. B.J.J. Engbers, *Textilpraxis intern.* **47** (1992) 365.
12. C.L. Mehltretter, B.H. Alexander and C.E. Rist, *Ind. Eng. Chem.* **45** (1953) 2782.
13. P. Djurdevic, *J. Serb. Chem. Soc.* **60** (1995) 797.
14. D.S. Polcyn and I. Shain, *Anal. Chem.* **38** (1966) 376.
15. T. Bechtold, E. Burtscher, D. Gmeiner and O. Bobleter, *J. Electroanal. Chem.* **306** (1991) 169.
16. T. Bechtold, E. Burtscher, A. Turcanu and O. Bobleter, *J. Electrochem. Soc.* **143** (1996) 2411.
17. A.J. Bard and L.R. Faulkner, 'Electrochemical Methods' (J. Wiley & Sons, New York, 1980), p. 2655.
18. J. Gonzalez-Velasco, *Anales de Quimica* **76** (1980) 17.
19. R.S. Nicholson and I. Shain, *Anal. Chem.* **36** (1964) 706.