Direct cathodic reduction of Leuco Sulfur Black 1 and Sulfur Black 1

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The electrochemical activity of Leuco Sulfur Black 1 in alkaline solution is shown by the means of voltammograms of the dyestuff recorded in a flow cell. The voltammograms indicate the possibility for further dyestuff reduction by cathodic electron transfer. In batch electrolysis experiments successful reduction of Leuco Sulfur Black 1 was achieved using a multi cathode cell. Applying similar experimental conditions cathodic reduction of the insoluble oxidized dyestuff Sulfur Black 1 was achieved. In a first step the dispersed Sulfur Black 1 is reduced to give an alkaline soluble form of the dyestuff that can be reduced further to yield Leuco Sulfur Black 1. Analogous to the electrochemical behaviour of technically produced Leuco Sulfur Black 1, which contains reducing agents, the solution of Leuco Sulfur Black 1 formed by electrolysis is able to undergo further cathodic electron transfer. The cathodic dyestuff reduction is of importance for the development of sulfur dyeing processes which do not require addition of reducing chemicals.

Keywords: *electrochemical reduction, sulfur dye, Sulfur Black 1, Leuco Sulfur Black 1, electrochemical cell*

1. Introduction

Sulfur dyes, particularly Leuco Sulfur Black 1 and Sulfur Black 1, hold a substantial part (20–25%) of the dyestuff market for cotton textiles [1] and about 70 000 tons of sulfur dyes were used in 1992 [2]. In the dyeing processes the addition of reducing agents is necessary to form the reduced dyestuff which is soluble in alkaline aqueous medium [3]. This reduced leuco-form of the dyestuff is reoxidized after diffusion into the fibre to give the insoluble oxidized dyestuff [4–6].

At this time a distinct amount of the reducing agent is added during the preparation of Leuco Sulfur Black 1 to obtain a liquid product easy to handle in the dye houses. When applying Leuco Sulfur Black 1 in the dyeing process an additional amount of reducing agent has to be added to achieve stable reduction conditions [4–6]. Typical reducing agents used are sulfides [7], glucose [8, 9] and hxdroxyacetone [10].

Sulfur Black 1 is present in the liquid formulation as dispersed pigment requiring the addition of higher amounts of reducing agent in the dye house because no prereduction has been performed during the preparation of the liquid product.

The possibility of achieving direct and indirect cathodic dyestuff reduction has been described [11–13] but little information on the electrochemistry of sulfur dyes is available [11–14].

In this paper the electrochemical behaviour of Sulfur Black 1 and Leuco Sulfur Black 1 are considered very important representative sulfur dyes. Voltammograms recorded in a flow cell and batch electrolysis experiments using a multicathode cell are given. The electrolysis experiments performed under various conditions with Leuco Sulfur Black 1 and with Sulfur Black 1 yield basic data for the reduction of the dyestuff molecule achieved by direct cathodic e^- transfer. Current efficiencies and cell voltages are given for different experimental conditions forming a set of basic data for further scale up of this electrochemical process.

2. Experimental details

2.1. *Construction of the electrochemical cells*

2.1.1. Flow cell with plane electrodes. The voltammograms were measured with a divided flow cell using plane electrodes (electrode area $100\,cm^2$) with a sintered glass frit (dia. 120 mm, thickness 10 mm, porosity D3) as separator. The cathode and the anode were manufactured from stainless steel. The catholyte flow was adjusted at $140\,ml\,min^{-1}$ by a peristaltic pump, corresponding a mean catholyte velocity of $0.17\,cm\,min^{-1}$. A more detailed description of this type of cell is given elsewhere [15].

The cell voltage was controlled as a function of cathode potential by an adjustable laboratory power supply (Farnell L30-1). All potential values given are related to a (Ag/AgCl, 3 M KCl) reference electrode and were measured using a potentiometer (Metrohm pH meter 654, Fa. Metrohm, Herisau, Switzerland).

2.1.2. Multicathode cell with three dimensional electrodes. The batch electrolysis experiments were performed using a multicathode cell. A scheme of the cell

is given in Fig. 1. Three cathodes were driven by separately adjustable electric power supplies connected to a common anode. Catholyte and anolyte were separated by a cation exchange membrane (Nafion$^{®}$). A solution of 1 mol dm^{-3} NaOH was used as anolyte and a stainless steel electrode (front area 100 cm^2, V4A-stainless steel) served as anode. The cathodes were three dimensional electrodes manufactured from stainless steel fabric (steel 1.4404, aperture size 0.325 mm, wire dia. 0.2 mm, open area 37%; Haver and Boecker, Oelde, Germany), each cathode unit exhibiting a front area 100 cm^2 and surface area 1440 cm^2, thus giving a full cathode area of 4320 cm^2. The cathode units were insulated from each other by three layers of PE fabric. A multicathode constructed in a similar manner is described in more detail elsewhere [16]. The catholyte circulation through the electrode was driven by a peristaltic pump and was adjusted at 150–250 ml min^{-1}. Assuming an equal flow and a porosity of about 40% in the cathodes, the average catholyte velocity through the electrodes can be calculated as 0.06 to 0.10 cm s^{-1}.

To simulate technical conditions the experiments were not performed under inert atmosphere.

2.2. Chemicals and analytical procedures

The NaOH, Na$_2$CO$_3$ and Na$_2$SO$_4$ used for the preparation of the ground electrolytes were analytical grade chemicals. Leuco Sulfur Black 1 (Diresul RDT liq.) and Sulfur Black 1 (Diresul 4G-EV liq.) are technical products which were used as delivered from the supplier (Clariant Ltd, Muttenz, Switzerland).

The dyestuff reduction was monitored by redox titration of samples of the catholyte with I$_2$-solution (c(eq) = 0.1 mol dm^{-3}) by means of a titroprocessor (Orion 960 Autochemistry System, Boston, MA). From the titration results the reduction capacity of the catholyte can be calculated as consumption of equivalents iodine per dm^3 of catholyte.
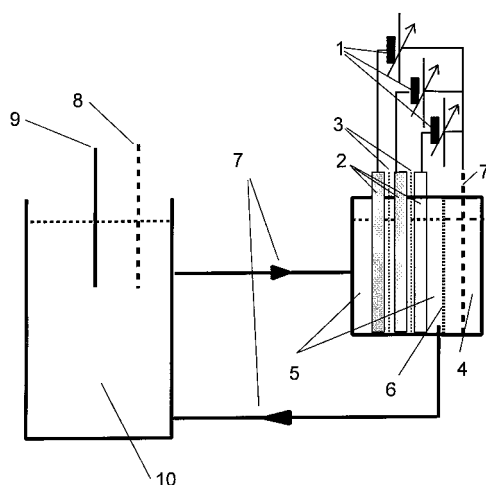

Fig. 1. Scheme of the multicathode cell for batch electrolysis experiments for the cathodic reduction of Leuco Sulfur Black 1 and Sulfur Black 1. Key: (1) current supply, (2) cathode unit, (3) porous insulator, (4) anolyte, (5) catholyte, (6) separator, (7) catholyte circulation, (8) redox electrode, (9) pH electrode, (10) catholyte batch.

In the case of Leuco Sulfur Black 1 the pH of the catholyte was maintained at a fixed value (e.g., pH 12 to avoid disturbing effects caused by undesired oxidation of the reducing chemicals present in the technically produced Leuco Sulfur Black 1.

Disturbing changes in pH of the catholyte are of minor importance in experiments with Sulfur Black 1 which contains no organic reducing agents. Here an increase in the titration results has to be considered only in experiments running with low current efficiency and without pH control. The NaOH formed from the reduction of water can cause an increased consumption of J$_2$-solution during the redox titration. In such experiments the current efficiency calculated from the titration results is estimated to be about 10 to 15% higher than actually reached by electrolysis (e.g., experiment F, Table 3). This effect is of minor importance in experiments performed at fixed pH or running with a current yield of 80% or higher.

An additional complication arises from the distinct tendency of Sulfur Black 1 to settle in the cell particularly at the beginning of the electrolysis, so the titration results vary somewhat due to inhomogenities in the dyestuff concentration in the catholyte.

The redox titrations were performed under nitrogen atmosphere to avoid the disturbing effect of oxygen intake.

3. Results and discussion

3.1. Voltammograms of Leuco Sulfur Black 1

At the beginning of the experiment the cathode compartment and the anode compartment were filled with ground electrolyte. After recording the voltammogram of the ground electrolyte dyestuff was added stepwise to give a solution containing 10 ml dm^{-3}, 20 ml dm^{-3} and 30 ml dm^{-3} dyestuff.

Typical voltammograms of Leuco Sulfur Black 1 recorded with plane electrodes are given in Figs 2 and 3.

The addition of the dyestuff in its reduced form causes a rapid change in the potential of the solution to the redox potential of the reduced dyestuff. Below this potential the dyestuff is oxidized to form insoluble products of increased molecular mass. Therefore, the voltammograms in the presence of Leuco Sulfur Black 1 were started at the potential of the solution (about −560 mV) to avoid oxidation of the dyestuff at the cathode thereby forming an insoluble coating of oxidised dyestuff at the cathode surface. The voltammograms in Figs 2 and 3 indicate the electrochemical activity of the dyestuff. Above about −750 mV a current plateau was recorded, which appears different to the current plateau recorded with reversible redox systems under diffusion limited transport conditions. In contrast to the well defined plateau measured in this cell, for example with the Fe(II/III)-triethanolamine redox couple [10], the current increases with increasing potential due to an increased number of e$^-$-transfer steps becoming possible with increasing cathode potential.
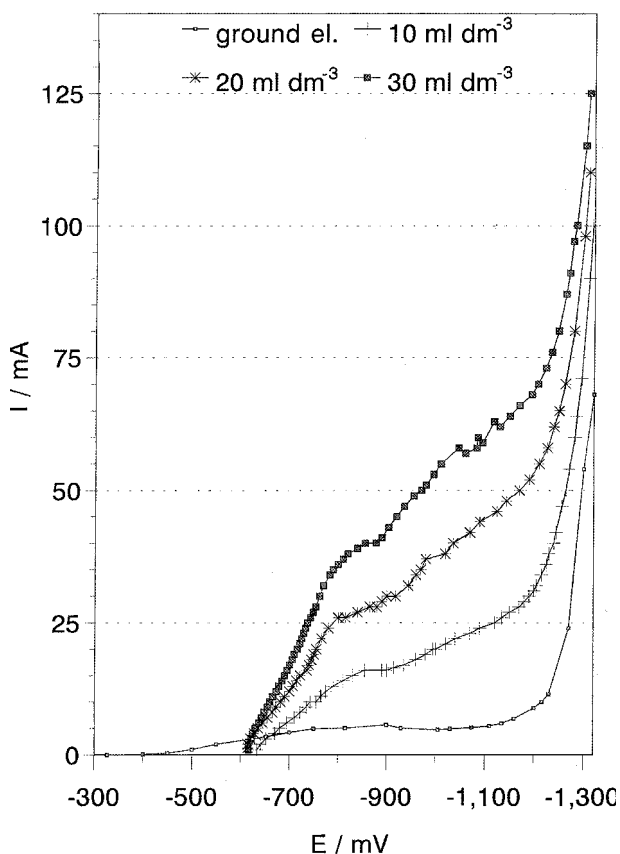
Fig. 2. Voltammograms of Leuco Sulfur Black 1 (10 ($+$), 20 ($*$) and 30 ($\blacksquare$) ml dm^{-3}) in 0.5 mol dm^{-3} NaOH ground electrolyte ($\square$) at room temperature. Mean catholyte flow 0.17 cm s^{-1}.
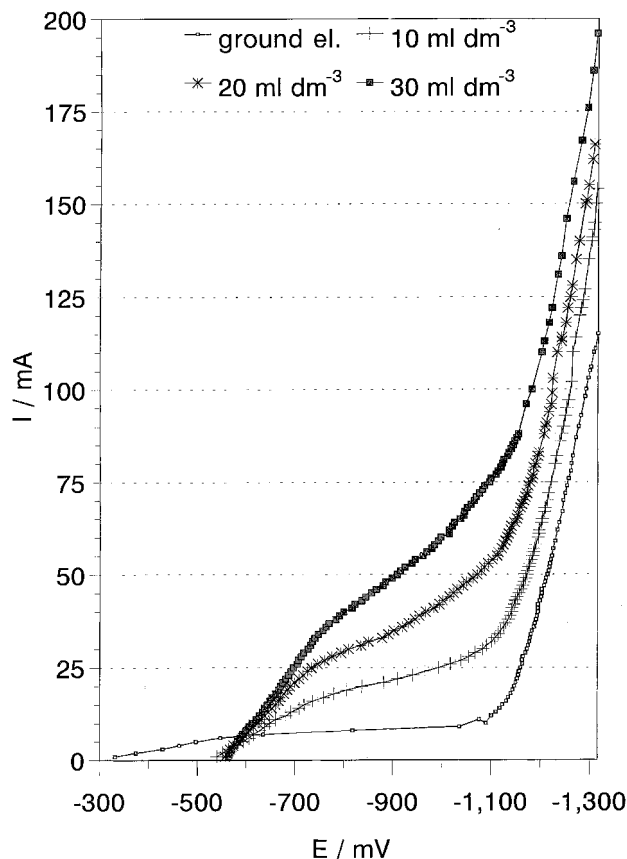
Fig. 3. Voltammograms of Leuco Sulfur Black 1 (10 ($+$), 20 ($*$) and 30 ($\blacksquare$) ml dm^{-3}) in 9.4×10^{-2} mol dm^{-3} Na$_2$CO$_3$ ground electrolyte ($\square$) at room temperature. Mean catholyte flow 0.17 cm s^{-1}.

Figure 4 gives a reaction scheme of the assumed redox reactions. First, Sulfur Black 1 which is initially present in the insoluble oxidized form, is reduced to Leuco Sulfur Black 1 (step A). These molecules can be reduced to a higher state of reduction characterised by determining the redox equivalents present in the catholyte at a given dyestuff concentration (step B). Leuco Sulfur Black 1 offers a number of reducible sites yielding redox products with similar reduction potentials, so a dyestuff molecule is able to enter into a consecutive series of reduction steps at the cathode. Disulfide groups and quinoneimine groups are reduced at the cathode and the reductive cleavage of the disulfide groups, in addition, yields molecules with lower molecular weight. The voltammograms prove the possibility of achieving an additional reduction of Leuco Sulfur Black 1 by cathodic electron transfer, despite the fact that the molecules are already present in an alkaline soluble reduced state at the beginning of the experiment. The experiments show that a technical product with a reduction state well suited for dyeing processes can be reduced further electrochemically, resulting in a higher state of reduction. Table 1 gives the measured current densities of a solution of 20 ml dm^{-3} Leuco Sulfur Black 1 at cathode potentials from -700 mV to -1000 mV in various ground electrolytes.

In the potential region of -800 to -900 mV a current density of 0.25–0.35 mA cm^{-2} can be achieved in the presence of 20 ml dm^{-3} Leuco Sulfur Black 1.

The composition of the catholyte is of minor importance for the current density recorded at the diffusion limited plateau, which is of interest for the wide use of the electrochemical reduction process under the different conditions applied in dyeing processes.

3.2. Batch electrolysis experiments of Leuco Sulfur Black 1 and Sulfur Black 1

A series of batch electrolysis experiments was performed with Leuco Sulfur Black 1 and Sulfur Black 1 to investigate the possibility of achieving enhanced
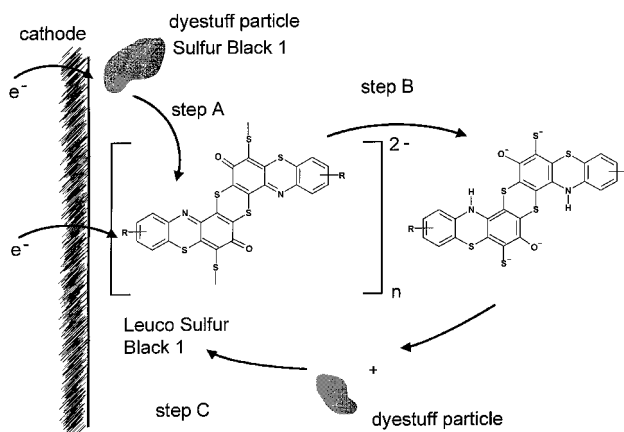

Fig. 4. Reaction scheme for the cathodic reduction of dispersed Sulfur Black 1 and dissolved Leuco Sulfur Black 1.

Table 1. Voltammetric current densities measured at selected potential values with Leuco Sulfur Black 1 ($20\,ml\,dm^{-3}$) in various ground electrolytes

Ground electrolyte	Dyestuff conc. /ml dm^{-3}	Current density at different potentials/mA cm^{-2}			
		$-700\,mV$	$-800\,mV$	$-900\,mV$	$-1000\,mV$
NaOH	0	0.04	0.05	0.06	0.05
0.5 mol dm^{-3}	10	0.06	0.14	0.16	0.20
	20	0.12	0.26	0.30	0.37
	30	0.17	0.36	0.43	0.54
NaOH	0	0.06	0.08	0.08	0.09
0.25 mol dm^{-3}	10	0.07	0.14	0.17	0.20
	20	0.13	0.26	0.32	0.39
	30	0.18	0.36	0.45	0.55
NaOH	0	0.07	0.08	0.085	0.09
0.13 mol dm^{-3}	10	0.06	0.14	0.17	0.20
	20	0.13	0.25	0.30	0.36
	30	0.17	0.35	0.43	0.53
Na$_2$CO$_3$	0	0.08	0.08	0.09	0.09
9.4×10^{-2} mol dm^{-3}	10	0.14	0.19	0.22	0.25
	20	0.21	0.30	0.35	0.43
	30	0.26	0.40	0.49	0.60
Na$_2$CO$_3$	0	0.08	0.08	0.09	0.09
4.7×10^{-2} mol dm^{-3}	10	0.13	0.18	0.22	0.25
NaCl	20	0.16	0.28	0.34	0.43
8.5×10^{-2} mol dm^{-3}	30	0.30	0.40	0.49	0.62

dyestuff reduction to substitute conventional reducing chemicals added to the dyebath today. In the case of Sulfur Black 1 tests were performed to assess the possibility for successful cathodic dyestuff reduction when the electrolysis is started with the dispersed oxidised pigment.

3.2.1. Leuco Sulfur Black 1. Leuco Sulfur Black 1 is present in reduced alkaline soluble form at the beginning. Some of the disulfide groups are reduced by reducing agents added during the preparation of the product.

A solution of 0.14 mol dm^{-3} Na$_2$SO$_4$ was chosen as ground electrolyte. A batch of 1.3 dm^3 volume catholyte was electrolysed at a current of 1.2 A (0.4 A per cathode unit) at room temperature and at 50 °C. The dyestuff concentration was varied from 10 to 40 ml dm^{-3} Leuco Sulfur Black 1. The reduction experiments were monitored by titration of catholyte samples with I$_2$-solution to determine the current efficiency.

The pH was held constant by addition of small quantities of NaH$_2$PO$_4$ to minimise the influence of pH variations on the iodometric determination of the current yield. Results describing the performance of the electrolysis and the experimental conditions applied are given in Table 2.

Figure 5 shows the build up of the reduction capacity during electrolysis as a function of transported charge for the experiments A–E given in Table 2. The graphs in Fig. 5 have been normalised with respect to the start of the electrolysis so that solutions containing different concentrations of dyestuff can be compared directly. The graphs of experiment D and E with a dyestuff concentration of 40 ml dm^{-3} Leuco Sulfur Black 1 show a higher slope in comparison to curves registered with 20 or 10 ml dm^{-3}.

Figure 6 shows a series of titration curves of the electrolysis experiment C (20 ml dm^{-3} dyestuff, 47–48 °C). The results of Fig. 5 show the change in reducing capacity in the catholyte due to the cathodic electron transfer. The corresponding titration curves in Fig. 6 characterize the reduction state of the dyestuff in more detail. The volume of I$_2$-solution consumed increases with the time but no significant change in the titration curves occurs with increased reduction capacity, indicating the formation of reduced products with similar redox potential.

Table 2. Electrolysis experiments with Leuco Sulfur Black 1 with Na$_2$SO$_4$ (0.14 mol dm^{-3}) ground electrolyte, catholyte batch volume 1.3 dm^3, cell current 1.2 A (0.4 A per cathode unit)

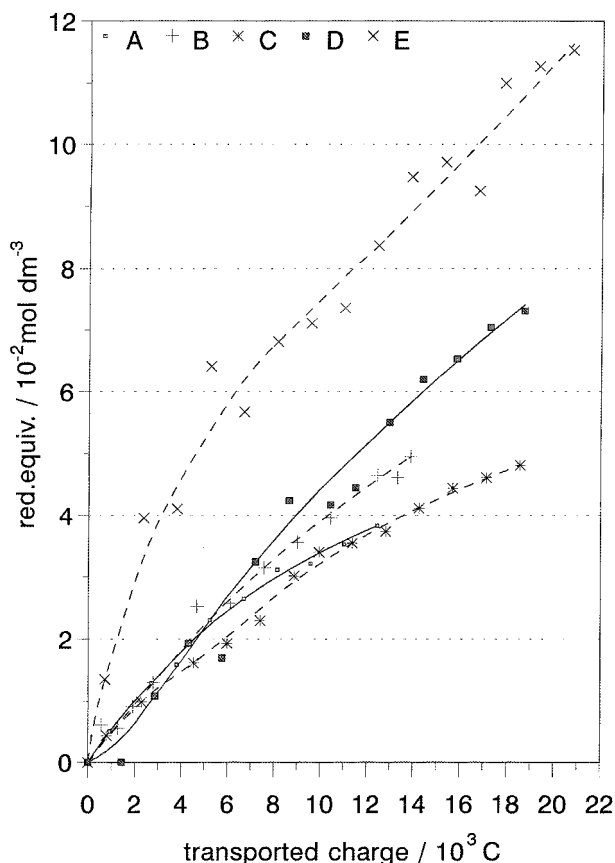| Exp.	Dyestuff conc. /ml dm^{-3}	Temp. /°C	Sample volume /ml	pH	Conc. of red. equiv.		Curr. eff. /%	Cell voltage in cathode unit		
					beginning /mol dm^{-3}	end /mol dm^{-3}		1 /V	2 /V	3 /V
A	10	22–25	20	11.6–11.9	0.033	0.064	49	3.47	4.13	4.37
B	20	20–25	10	12.1–12.3	0.087	0.114	47	3.28	3.77	3.91
C	20	47–48	10	11.1–11.2	0.088	0.128	44	2.98	3.28	3.38
D	40	22–26	5	12.0–12.1	0.176	0.231	58	3.34	3.73	3.84
E	40	50–55	5	11.2–11.6	0.192	0.231	61	2.61	2.74	2.70

Fig. 5. Increase in reduction capacity in the catholyte at different extent of transported charge for the experiments A–E (10–40 ml dm^{-3} Leuco Sulfur Black 1, experimental conditions given in Table 2).

but lowers the cell voltage, thus lowering the consumption of electric energy per kg of dyestuff. Typical values for the cell voltage of the three cathode units are also given in Table 2.

3.2.2. Sulfur Black 1. According to Fig. 4 with Sulfur Black 1 both reaction step A and reaction step B have to be performed successfully by cathodic electron transfer. First a small part of the dyestuff has to be reduced to such an extent that a small concentration of soluble dyestuff molecules is formed in the catholyte which is able to serve as a redox mediator for the residual part of the dispersed dyestuff (reaction step C). Although Sulfur Black 1 is an oxidized product the titration experiments indicate a certain small amount of reducible compounds at the beginning of the electrolysis (Table 3). The determined content of reduced compounds in Sulfur Black 1 corresponds to a reduction state of 15–25% in relation to Leuco Sulfur Black 1. The determination of the reduction state is difficult because part of reduced sites (reducing equivalents) are enclosed within the particles of Sulfur Black 1 and therefore cannot be determined with high accuracy by redox titration. During the proceeding of the electrolysis the particles begin to dissolve and thereby additional reducing equivalents are released from the interior of the dissolving pigments into the catholyte. The analytically determined current yield is increased by this phenomena to a certain extent which can be estimated to remain below 10–15%. In Table 3 the experimental conditions of a series of reduction experiments with Sulfur Black 1 are given.

At the beginning of the experiments the current efficiency is low because the concentration of soluble partially reduced dyestuff molecules is small. After the formation of a certain amount of soluble reduction products the current yield of the cathodic reduction process increases due to an increasing
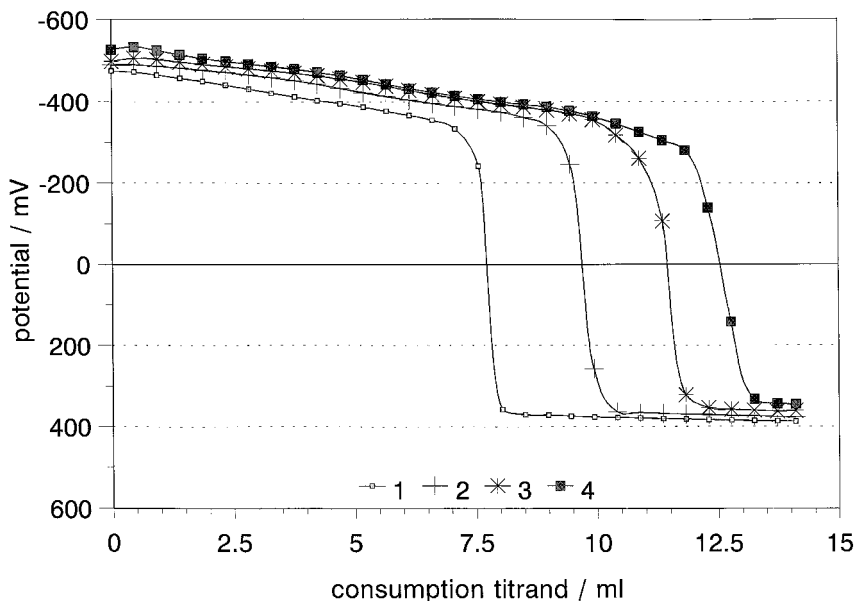
The mean current efficiency during a well defined build up of reduction capacity is also given in Table 2. At comparable stage of dyestuff reduction the current efficiency increases with the higher concentration of dyestuff. An increase in temperature offers no significant advantage for the current yield

Fig. 6. Titration curves registered during the electrolysis experiment C. Key: (1) 0 C, (2) 5.98 × 10^3 C, (3) 11.4 × 10^3 C, (4) 18.6 × 10^3 C.

Table 3. Electrolysis experiments with Sulfur Black 1

Exp.	dyest. conc. /ml dm^{-3}	Catholyte composition	Cath. volume /dm^3	Temp. /°C	Sample volume /ml	pH	Cell current /A	Conc. of red. equiv.		Curr. eff. /%	Cell voltage cathode unit		
								beginning /mol dm^{-3}	end /mol dm^{-3}		1 /V	2 /V	3 /V
F	20	0.14 mol dm^{-3} Na$_2$SO$_4$	0.7	50–55	10	11.0–12.7	1.2	0.016	0.154	53	2.69	2.79	2.86
G	20	0.14 mol dm^{-3} Na$_2$SO$_4$ 2 ml dm^{-3} wetting agent	0.7	50–60	10	11.6–12.7	1.2	0.022	0.163	81	2.67	2.85	2.96
H	20	0.14 mol dm^{-3} Na$_2$SO$_4$ 2 ml dm^{-3} wetting agent	1.0	21–25	10	11.8–12.2	1.2	0.011	0.023	<13	3.49	3.79	4.54
I	20	0.14 mol dm^{-3} Na$_2$SO$_4$ 2 ml dm^{-3} wetting agent	1.0	50–56	10	<11.4	1.2	0.028	0.048	<15	2.77	2.98	3.07
J	20	0.14 mol dm^{-3} Na$_2$SO$_4$ 3.8 × 10^{-2} mol dm^{-3} NaOH 2 ml dm^{-3} wetting agent	1.0	20–23	10	12.3	1.2	0.019	0.028	<20	3.55	4.31	4.63
K	20	0.14 mol dm^{-3} Na$_2$SO$_4$ 3.8 × 10^{-2} mol dm^{-3} NaOH 2 ml dm^{-3} wetting agent	1.0	30–60	10	11.3	1.2	0.028	0.068	45	2.54	2.71	2.80
L	200	7.5 × 10^{-2} mol dm^{-3} NaOH 2 ml dm^{-3} wetting agent	0.5	45–55	1	12.7	4.5	0.177	0.651	96	5.01	5.82	6.07
M	200	7.5 × 10^{-2} mol dm^{-3} NaOH 2 ml dm^{-3} wetting agent	0.6	45–60	1	11.2–12.2	4.5	0.231	0.571	97	4.72	5.32	5.42
N	200	7.5 × 10^{-2} mol dm^{-3} NaOH 2 ml dm^{-3} wetting agent	0.6	45–55	1	11.7	4.5	0.124	0.797	73	4.62	5.27	5.46
O	200	7.5 × 10^{-2} mol dm^{-3} NaOH 2 ml dm^{-3} wetting agent	0.6	45–55	1	11.7	4.5	0.797	1.379	56	3.62	3.85	3.90

contribution of reaction step C (Fig. 4). In a series of experiments with $20 \, ml \, dm^{-3}$ Sulfur Black 1 experimental conditions for the successful start of the electrolysis were evaluated; for example, in the experiments H, I and J the cathodic reaction proceeded with a current yield lower than 20%. At temperatures above $30 \, °C$ and also at pH above 11.5 the current yield was increased up to 81% (experiment G). The addition of $2 \, ml \, dm^{-3}$ wetting agent enhanced the removal of gaseous hydrogen out of the three dimensional cathode and supported the desired cathode reaction (experiments F and G). Based on these results experiments with $200 \, ml \, dm^{-3}$ Sulfur Black 1 were performed at a temperature of $45–55 \, °C$.

When Na_2SO_4 was used as ground electrolyte the pH of the catholyte increased at the beginning of the electrolysis and at a pH of 11.5 to 12.0 cathodic reduction of Sulfur Black 1 begins. In Fig. 7 the build up of the reduction capacity as a function of transported charge is shown for selected experiments with 20 and with $200 \, ml \, dm^{-3}$ Sulfur Black 1.

Depending on the reaction conditions good current yields of up to 90% could be observed.

At high dyestuff concentration the cell voltage depends particularly on the time of electrolysis because both the increasing concentration of Na^+ ions (counter ions of the thiolate groups) and of OH^- ions (due to losses in current yield) increase the conductivity of the catholyte, so the cell voltages given in Table 3 must be understood as typical average values.

With Sulfur Black 1 a catholyte potential of -100 to $-300 \, mV$ (depending on the ground electrolyte) is measured at the beginning which rises during the electrolysis up to $-800 \, mV$. The rise in catholyte potential and the increase of reducing equivalents as function of transported charge for an experiment with $200 \, ml \, dm^{-3}$ Sulfur Black 1 is shown in Fig. 8
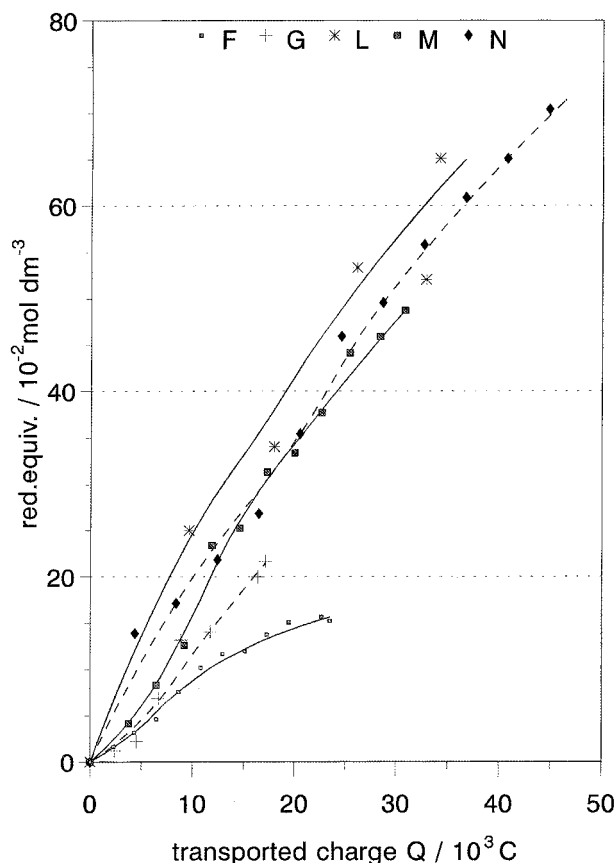

Fig. 7. Increase in reduction capacity of the catholyte as a function of transported charge for the experiments F, G, L, M, N (20 or $200 \, ml \, dm^{-3}$ Sulfur Black 1, experimental conditions given in Table 3).

$(200 \, ml \, dm^{-3}$ Sulfur Black 1, $7.5 \times 10^{-2} \, mol \, dm^{-3}$ NaOH and $2 \, ml \, dm^{-3}$ wetting agent, $45–55 \, °C$, pH 11.7). In Fig. 9 titration curves recorded at different time of the electrolysis are shown. At the beginning of the experiment molecules with high
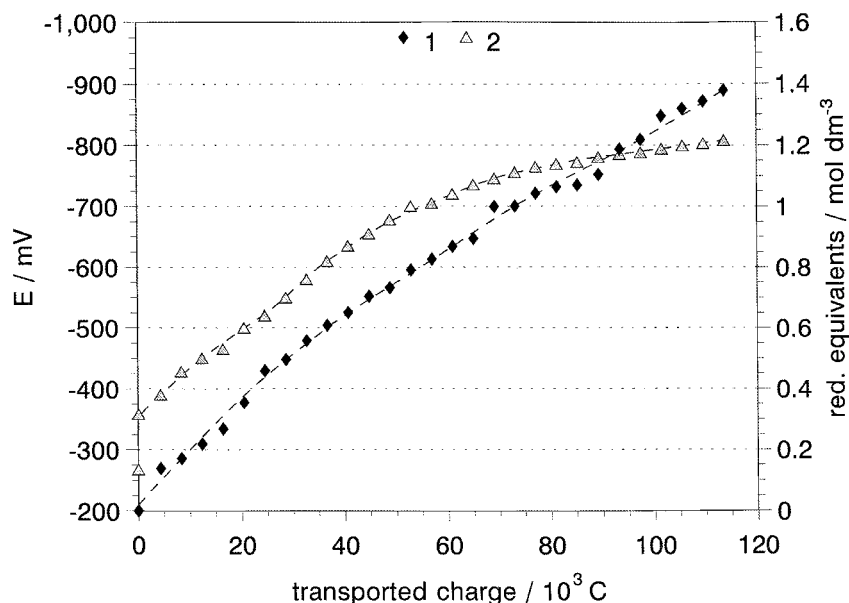

Fig. 8. Increase in reducing equivalents (1) and catholyte potential E (2) as function of transported charge ($200 \, ml \, dm^{-3}$ Sulfur Black 1, $7.5 \times 10^{-2} \, mol \, dm^{-3}$ NaOH, $2 \, ml \, dm^{-3}$ wetting agent, $45–55 \, °C$).
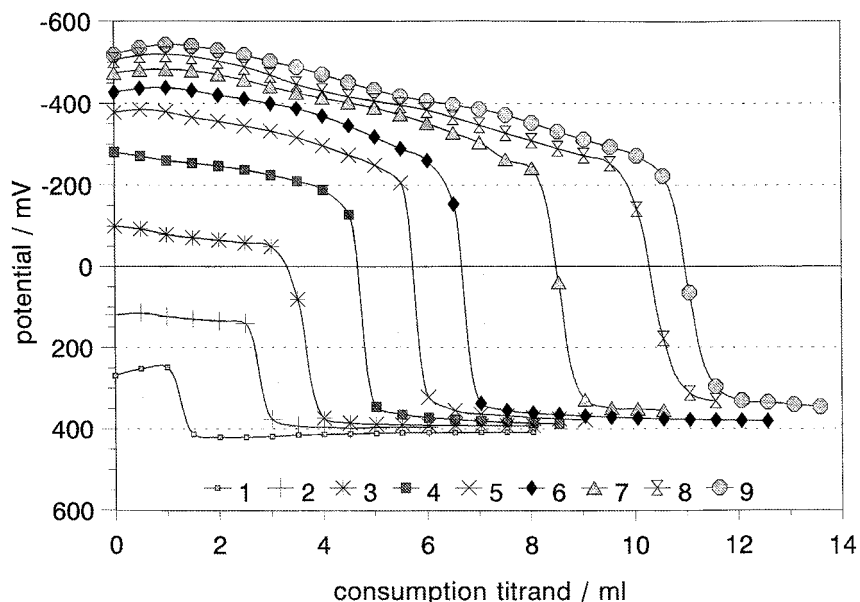
Fig. 9. Titration curves registered during the electrolysis experiment shown in Fig. 8 at different extent of transported charge. Key: (1) 0 C, (2) 16.5×10^3 C, (3) 20.5×10^3 C, (4) 24.6×10^3 C, (5) 32.7×10^3 C, (6) 40.8×10^3 C, (7) 57.0×10^3 C, (8) 69.1×10^3 C, (9) 81.3×10^3 C.

molecular mass and low solubility are present in the catholyte. With increased state of reduction the particles dissolve completely (completed reaction steps A and C in Fig. 4), the reduction process continues under homogeneous conditions (reaction step B in Fig. 4). At this time the cathodic reduction proceeds similarly to Leuco Sulfur Black 1 (cf Fig. 6).

4. Conclusions

Voltammograms of Leuco Sulfur Black 1 recorded in a flow cell demonstrate the possibility of achieving direct cathodic reduction of the dyestuff under conditions applied in textile dyebaths. The tendency to rapid sedimentation of a dispersion of Sulfur Black 1 and the insolubility of the dispersed dye prevent the measurement of useful voltammograms under the applied experimental conditions. In contrast a solution of Leuco Sulfur Black 1 is well suited for the recording of voltammograms but allows only a description of reduction step B shown in Fig. 4.

Using a multicathode cell Leuco Sulfur Black 1 and Sulfur Black 1 successfully were reduced in batch electrolysis experiments. In the case of Leuco Sulfur Black 1 the molecules are present in dissolved form and a higher stage of reduction can be achieved by reduction of disulfide groups. Current efficiencies of 50% were found at a dyestuff concentration from 10 to $40 \, \text{ml dm}^{-3}$ at $50 \, °C$.

With Sulfur Black 1 a start up of the reduction has to be achieved at first. A small amount of soluble dyestuff molecules has to be formed by cathodic reduction which support the electron transfer to the dispersed oxidized dyestuff by acting as a soluble redox mediator. Current efficiencies of 70–90% can be observed at dyestuff concentrations of $200 \, \text{ml dm}^{-3}$ Sulfur Black 1 at $60 \, °C$.

Both the electrolysed solutions of Leuco Sulfur Black 1 and Sulfur Black 1 accumulate concentrations of reducing equivalents comparable to the state realised today in dyebaths by the addition of reducing chemicals.

The direct electrochemical dyestuff reduction offers economic and ecological advantages because the production of reduced sulfur dyes without the addition of a reducing agent becomes possible.

Acknowledgements

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