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Electrochemical characteristics and dyeing properties of selected 9,10-anthraquinones as mediators for the indirect cathodic reduction of dyes

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ABSTRACT

Substituted 9,10-anthraquinones were characterised using cyclic voltammetry for their potential to serve as mediators for the indirect cathodic reduction of dispersed sulphur dyes, vat dyes and indigo. Besides characterisation of the electrochemical behaviour, the compounds were assessed in model dyeing experiments for chemical stability and staining of cotton fabric. 1,2-, 1,4- and 1,8-dihydroxy-9,10-anthraquinones exhibited negative mid-point potential $((E_p)_d + (E_p)_a)/2$ of −713 to −820 mV (vs. Ag/AgCl, 3 M KCl). Under model dyebath conditions staining of cotton fabric occurred. 9,10-anthraquinone-1,5-disulfonate and 9,10-anthraquinone-2,6-disulfonate both imparted low staining to cotton; their mid-point potentials (−698 mV and −475 mV, respectively) limit their applicability to the reduction of sulphur dyes. Dihydroxy substituted 9,10-anthraquinone-sulfonates exhibited low staining owing to their good solubility. The mid-point potentials of 1,4-dihydroxy-9,10-anthraquinone-2-sulfonate and 5,8-dihydroxy-9,10-anthraquinone-2-sulfonate were only −618 mV and −675 mV respectively. Of the 9,10-anthraquinoids studied, 1,2-dihydroxy-9,10-anthraquinone-3-sulfonate (C.I. Mordant Red 3) could be identified as the most promising reversible redox couple, displaying a mid-point potential of −848 mV, low staining of cotton fabric and sufficient chemical stability under dyebath conditions.

1. Introduction

The indirect cathodic reduction of vat dyes, including indigo, has been shown to offer substantial potential to replace reduction techniques [1–4] employing reductants such as $Na_2S_2O_4$, hydroxyacetone or glucose. After use the oxidised products of these chemicals cannot be transformed to their reduced form and regeneration is thus not possible. In an electrochemical reduction process, a non-regenerable reducing agent is replaced with a dissolved redox couple which can be reactivated by cathodic electron transfer [5–8]. Such soluble and electrochemically active redox systems are called mediators. A mediator system comprises an electrochemically regenerable reducing agent, which is required to establish an appropriate redox potential in the dyebath [9–12]. For successful reduction of vat dyes the reduction potential in solution should be more negative than the leuco potential of the dyes, a value <−950 mV (vs. Ag/AgCl, 3 M KCl) being required. For the reduction of indigo, a redox potential <−750 mV and for sulphur dye reduction a redox potential <−600 mV are sufficient to achieve stable, reduction dyebath conditions [6,13–16].

To be applicable as a mediator for indirect cathodic dye reduction, a redox couple has to exhibit stability under dyebath conditions and must be able to undergo several cycles of cathodic regeneration without decomposition. Different chemical concepts have been proposed as soluble mediator systems, the two most important groups being:

- iron-complexes such as those with amino compounds or sugar acids (e.g. D-gluconic acid) as ligands [8–11]. This type of mediator is of particular interest when negative redox potentials have to be achieved (e.g. −950 mV vs. Ag/AgCl, 3 M KCl).
- anthraquininoid compounds such as hydroxy-anthraquinones and anthraquinone-sulfonic acids. These compounds are of interest when by-products present in commercial dye samples cause the risk of precipitate formation, as exemplified by iron sulfide in the case of sulphur dyes [17,18].

The electrochemical properties of selected 9,10-anthraquinones (AQ) have been determined in detail using cyclic voltammetry and other electrochemical methods [19–26]. In particular, different dihydroxy-9,10-anthraquinones and 9,10-anthraquinone-sulfonic acids have been studied with regards their potential to serve as mediators for cathodic dye reduction [17,18,27]. The use of 1,8-dihydroxy-9,10-anthraquinone to enhance cathodic indigo reduction,

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reduction by glucose and bacterial indigo reduction, has been reported [27–30]. Soluble 9,10-anthraquinoids such as lawsone also have been applied as mediators for indirect cathodic indigo reduction [31].

Depending on substituents, anthraquinone (AQ) compounds are also dyes, as represented by alizarin, which is a major constituent of the natural colorant madder [32–34] and provide a very wide range of synthetic disperse dyes [35]. In case of their application as mediators for vat dye or sulphur dye reduction, the AQ should not exhibit significant adsorption on the cellulosic substrate as this will influence the shade of a dyeing. Problems of staining due to the uncontrolled adsorption of an anthraquininoid mediator used in sulphur dyeing already have been reported [17].

Besides low substantivity towards cellulosic fibres, AQs should also display sufficient stability in the alkaline, vat and sulphur dyebaths. Repetitive cathodic electron transfer to the oxidised form of the AQ should be possible without decomposition, so as to regenerate the reduced form of the AQ, which is required as a reducing agent for the dispersed dyestuff.

Whilst selected AQs have been studied for their electrochemical behaviour or in electrochemical dyeing experiments, no systematic study has been undertaken to determine the suitability of a wider range of technically available compounds.

In this work, a series of AQs were studied for suitability to act as a mediator for indirect dye reduction. Cyclic voltammograms were employed to study the electrochemical properties of the AQs under alkaline dyebath conditions with regards their possible application in the reduction of vat dyes, indigo or sulphur dyes. Photometry was used to characterise the stability of the AQs under dyebath conditions and the substantivity of selected AQs towards cellulose fibres was determined using model dyeing experiments.

2. Experimental

2.1. Materials

Dyeings were carried out using desized, scoured and bleached cotton fabric (satin weave, mass per area 116.2 g m^{-2}, warp yarn density 50 y cm^{-1}, weft yarn density 32 y cm^{-1}; Getzner Textile AG, Bludenz, Austria). Analytical grade NaOH was used for the electrochemical experiments and technical grade 50% w/w NaOH solution (Deuring, Hoerbranz, Austria) was used for the dyeing experiments. Technical grade nitrilo-triacetic acid sodium salt (NTA, Trilon A, BASF, Ludwigshafen, Germany), and analytical grade ethylene-diamine-tetraacetic acid disodium salt dihydrate (EDTA, Titriplex III, Merck, Darmstadt, Germany) were used as complexing agents in the dyeing experiments.

The AQs listed in Table 1 were used as delivered by the supplier (Riedl-de-Haen, Seelze, Germany; DyStar, Frankfurt a.M., Germany; Merck-Suchart, Hohenbrunn, Germany; Serva Biochemica, Heidelberg, Germany; Bayer, Leverkusen, Germany); the chemical structure of the AQs is shown in Scheme 1.

2.2. Cyclic voltammetry

Cyclic voltammetry was carried out employing a three-electrode configuration using an EG&G 264 A Potentiostat equipped with a 303A HMDE (small drop size, drop area 0.96×10^{-2} cm^{-2}); a Pt wire served as counter electrode. Cyclic voltammograms were recorded on a Rikadenki X–Y recorder. All potentials given were measured vs. a (Ag/AgCl, 3M KCl) reference electrode. The test solutions were aerated for 8 min with He/Ar (inert gas) to eliminate interfering oxygen. All experiments were performed at room temperature.

2.3. Stability under dyebath conditions

Conditions of the stability tests were derived from technical recommendations for a pale/medium shade vat dyeing using IN-type vat dyes [13]. A solution containing 0.05 g L^{-1} of the respective AQ in aq 0.1 M NaOH was kept at 60 °C in a water bath for 160–200 min (Julabo SW21, Julabo, Seelbach, Germany). The absorbance of the solution was measured at regular time intervals in the range 350–730 nm (10 mm cuvette, Zeiss CLH 500/MCS 521 UV–VIS, Carl Zeiss Jena, Jena Germany). The extent of stability was monitored at λ_{max}, which was determined for each AQ at the beginning of an experiment. For the AQs studied the respective λ_{max} values are shown in Table 1.

2.4. Dyeing experiments

A sample of cotton fabric was dyed using a liquor ratio of 1:100 using a solution containing 1 g L^{-1} of the respective AQ in a solution of 0.19 M NaOH in deionised water. The samples were treated for 30 min in a shaking water bath at 145 rpm at ambient temperature. After dyeing, the samples were rinsed three times for 10 min. For the first rinse bath, different compositions were tested namely deionised water, the addition of 1 g L^{-1} NTA or 1 g L^{-1} EDTA as well as 1 g L^{-1} technical grade citric acid. For the second and third rinse stages, deionised water was employed. The final pH of the rinse

Table 1
Anthraquinones (AQ) investigated, source and colour of solution in 0.1 M NaOH.

Code	Name	Source	Quality	Colour	Max. abs. nm
DA1,2	1,2-Dihydroxy-9,10-anthraquinone, (Alizarin)	Fluka	p.a.	Violet	565
DA1,4	1,4-Dihydroxy-9,10-anthraquinone (Chinizarin)	Merck	synth.	Violet	560
DA1,8	1,8-Dihydroxy-9,10-anthraquinone	Merck	p.a.	Red	500
TA	1,2,5,8-Tetrahydroxy-9,10-anthraquinone	Merck	p.a.	Violet	571
PA	1,2,4,5,8-Pentahydroxy-9,10-anthraquinone	DyStar	techn.	Dark blue	610
HA	1,2,4,5,6,8-Hexahydroxy-9,10-anthraquinone	DyStar	techn.	Violet	586
ADS1,5	9,10-anthraquinone-1,5-disulfonic acid hydrate sodium salt	Aldrich Chemie	95%	Colourless	459
ADS2,6	9,10-anthraquinone-2,6-disulfonic acid disodium salt	Aldrich	p.a.	Colourless	401
DAS1,2	1,2-Dihydroxy-9,10-anthraquinone-3-sulfonic acid sodium salt (Alizarin Red S)	Riedel-de Haen	p.a.	Violet	556
DAS1,4	1,4-Dihydroxy-9,10-anthraquinone-2-sulfonic acid	Bayer	techn.	Blue	589
DAS5,6	5,6-Dihydroxy-9,10-anthraquinone-1-sulfonic acid sodium salt	DyStar	techn.	Violet	582
DAS5,8	5,8-Dihydroxy-9,10-anthraquinone-2-sulfonic acid potassium salt	DyStar	techn.	Violet	605
TAC	1,3,4-Trihydroxy-9,10-anthraquinone-2-carbonic acid	DyStar	techn.	Red	545
AAC	1-Amino-9,10-anthrachinone-2-carbonic acid	Bayer	techn.	Red	496
AAS	1–Amino-9,10-anthraquinone-2-sulfonic acid	Bayer	techn.	Orange	474
DDD	4,8-diamino-1,5-dihydroxy-9,10-anthraquinone-2,6-disulfonic acid tetrasodium salt	DyStar	techn.	Violet	623

bath was monitored and the samples were air dried at ambient temperature. The extent of staining of the cotton samples was characterised using CIELab coordinates.

2.5. Colour measurement

The CIE-L*a*b* values of the dyed fabric were measured using four layers of material, on a Minolta Chroma-Meter CR 200 (geometry d/0°, sample diameter 8 mm); the mean of two measurements were taken. The colour difference between the undyed and dyed specimens was calculated (the colour change of the cotton substrate as a result of 60 °C treatment in 0.1 M NaOH was negligible).

3. Results and discussion

3.1. Cyclic voltammetry(CV)

Under highly alkaline conditions, the reduction of an AQ proceeds via a consecutive series of two, rapid, single-electron transfer reactions as described in equations (1) and (2). Usually the formation of the radical anion is not observed in aqueous solution and so the overall reaction is two-electron transfer, with the formation of the AQ dianion. Formation of AQ^{2-} can result both from transfer of a second electron to the radial anion (equation (2)) or from disproportionation of the radical anion according to equation (3).

$$AQ + e^- \rightleftarrows AQ^{\bullet -} \tag{1}$$

$$AQ^{\bullet -} + e^- \rightleftarrows AQ^{2-} \tag{2}$$

$$2AQ^{\bullet -} \rightleftarrows AQ + AQ^{2-} \tag{3}$$

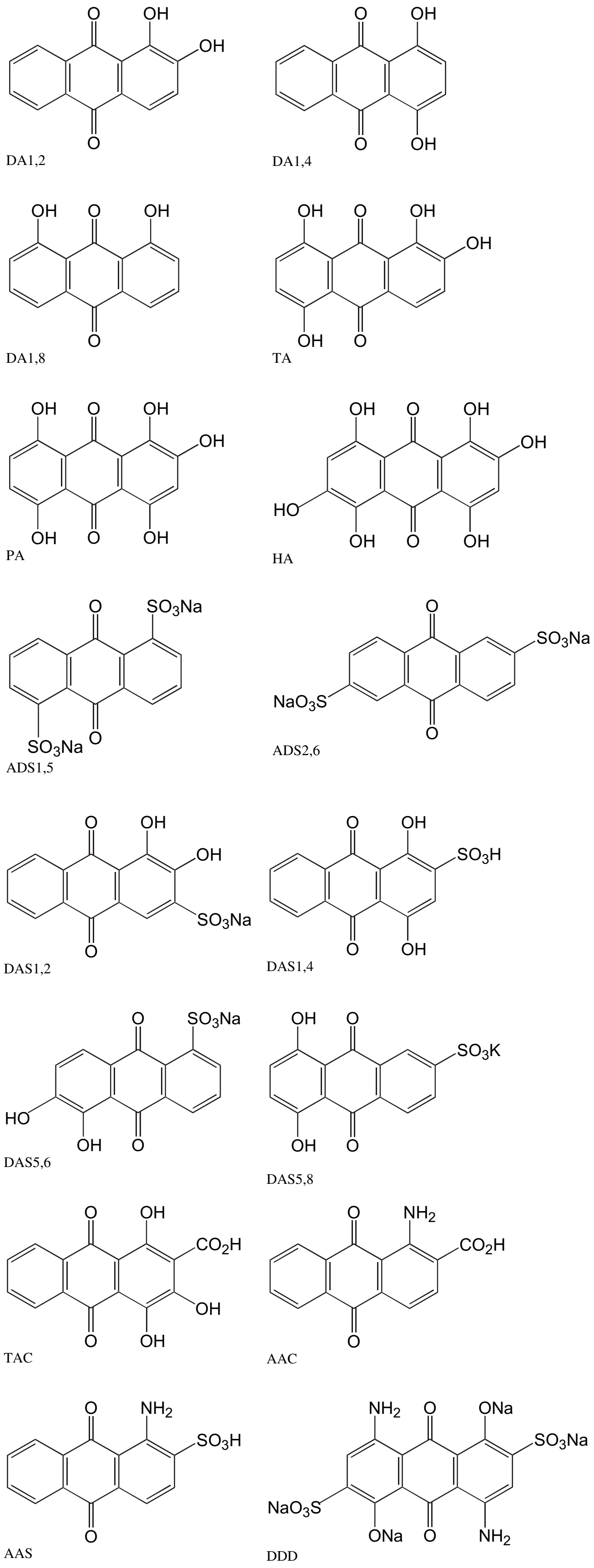
$$AQ^{2-} + \mathrm{dye} \rightleftarrows AQ + \mathrm{dye}^{2-} \tag{4}$$

If a sufficiently negative redox potential can be established in solution by the redox couple AQ/AQ^{2-}, the dispersed dye will be reduced according to equation (4) and the oxidised form of the AQ is regenerated.

As shown in the literature, cyclic voltammetry is well suited to characterise AQs with regard to their electrochemical properties in the context of alkali soluble mediators [17,18,27,31]. From voltammograms, information about the suitability of a chosen AQ can be obtained.

The electrochemical behaviour of the different AQs in aqueous 0.1 M NaOH was recorded over the potential range −500 mV to −1200 mV at different scan rates ranging from 5 mV s^{-1} to 100 mV s^{-1}. From the voltammograms the diffusion controlled cathodic and anodic peak potential, $(E_p)_d$, $(E_p)_a$ and the mid-point potential $((E_p)_d + (E_p)_a)/2$ were determined. In Table 2 representative data obtained at a scan rate of 50 mV s^{-1} are shown. The cathodic and anodic peak currents $(I_p)_d$ and $(I_p)_a$ measured at 50 mV s^{-1} scan rate also are shown in Table 2. For better comparison of the cathodic peak currents, the concentration independent factor $(I_p)_d/c$ is provided in Table 2.

Based on the assumption of a diffusion-controlled, rapid, two-electron transfer reaction, chemical reversibility can be studied by comparison of the anodic peak current $(I_p)_a$ with the cathodic peak current $(I_p)_d$ via the factor $(I_p)_a/(I_p)_d$. In Table 2 the values of $(I_p)_a/(I_p)_d$ obtained from the CV experiments at 50 mV s^{-1} are shown. The presence of a cathodic reduction peak and anodic reoxidation peak of the reduced AQ in the voltammogram together with a reversibility factor of $(I_p)_a/(I_p)_d = 1$ indicates stability in the



Scheme 1. Chemical structure of the AQs studied.

Table 2
CV-characteristics of AQ solutions on 0.1 M NaOH, measured at a scan rate of 50 mV s^{-1}. Peak potentials $(E_p)_d$, $(E_p)_a$, mid-point potential $((E_p)_d + (E_p)_a)/2$ and peak currents $(I_p)_d$, $(I_p)_a$ and ratio $(I_p)_a/(I_p)_d$.

Code	Name	Conc. mM	$(E_p)_d$ mV	$(E_p)_a$ mV	$((E_p)_d+(E_p)_a)/2$ mV	$(I_p)_d$ μA	$(I_p)_d/c$ μA/mM	$(I_p)_a$ μA	$(I_p)_a/(I_p)_d$
DA1,2	1,2-dihydroxy-9,10-anthraquinone (Alizarin)	0.36	−880	−820	−845	1.93	5.36	1.60	0.83
DA1,4	1,4-dihydroxy-9,10-anthraquinone (Chinizarin)	0.44	−735	−690	−713	2.40	5.52	2.06	0.86
DA1,8	1,8-dihydroxy-9,10-anthraquinone	0.39	−780	−720	−750	2.29	5.88	1.85	0.81
TA	1,2,5,8-tetrahydroxy-9,10-anthraquinone	0.34	−880	−845	−863	1.02/1.13[a]	3.00	1.25	–
PA	1,2,4,5,8-pentahydroxy-9,10-anthraquinone	0.56	−820	–	–	1.18	2.12	–	–
HA	1,2,4,5,6,8-hexahydroxy-9,10-anthraquinone	0.52	−810	–	–	n.d	–	–	–
			−900	−850					
			−1170	−1100					
ADS1,5	9,10-anthraquinone-1,5-disulfonic acid hydrate sodium salt	0.38	−735	−680	−698	1.48	4.00	1.53	1.03
ADS2,6	9,10-anthraquinone-2,6-disulfonic acid disodium salt	0.52	−515	−435	−475	1.45	2.78	1.51	0.95
DAS1,2	1,2-dihydroxy-9,10-anthraquinone-3-sulfonic acid sodium salt (Alizarine Red S)	0.41	−875	−820	−848	1.54	3.77	1.45	0.94
DAS1,4	1,4-dihydroxy-9,10-anthraquinone-2-sulfonic acid	0.54	−645	−590	−618	2.10	3.86	1.98	0.94
DAS5,6	5,6-dihydroxy-9,10-anthraquinone-1-sulfonic acid sodium salt	0.54	−940	−770	−855	0.45	0.83	0.40	0.89
DAS5,8	5,8-dihydroxy-9,10-anthraquinone-2-sulfonic acid potassium salt	0.52	−700	−645	−675	1.29	2.48	1.35	1.05
TAC	1,3,4-trihydroxy-9,10-anthraquinone-2-carbonic acid	0.54	−760	−620	−690	0.63	1.16	0.25	0.40
			−1010	−900	−955	0.90		0.79	0.88
AAC	1-amino–9,10-anthraquinone-2-carbonic acid	0.52	−815	−720	−768	2.08	1.75	2.00	0.96
AAS	1—amino-9,10-anthraquinone-2-sulfonic acid	0.58	−715	−620	−668	1.95	3.61	2.00	1.03
DDD	4,8-diamino-1,5-dihydroxy-9,10-anthraquinone-2,6-disulfonic acid tetrasodium salt	0.52	−715	−645	−680	1.34	3.76	0.98	0.73

[a] Two cathodic current peaks.

cases of both forms, AQ and AQ^{2-}, within the time scale of the CV experiment. In case that both oxidised and reduced form of the AQ are chemically stable, the mid-point potential $((E_p)_d + (E_p)_a)/2$ indicates the redox potential, which can be generated by the AQ/AQ^{2-} redox couple under alkaline dyebath conditions.

For AQs which showed well defined cathodic and anodic current peaks, electrochemical reversibility was determined by analysis of $(I_p)_d$ as a function of the square root of scan rate $v^{1/2}$ for linearity (Figs. 1–3) [36].

From Figs. 1–3 it can be seen that most AQs tested exhibited a linear relationship between $(I_p)_d$ and square root of scan rate, which demonstrates electrochemical reversibility of the electron transfer reaction. Visible deviation from linearity was observed for DA1,2 (1,2-dihydroxy-anthraquinone), DAS5,6 (5,6-dihydroxy-9,10-anthraquinone-2-sulfonic acid), DAS5,8 (5,8-dihydroxy-9,10-anthraquinone-2-sulfonic acid), the second cathodic current peak of TAC (TAC 2 in Fig. 3) and AAS (1-amino-9,10-anthraquinone-2-sulfonic acid).

According to the diagnostic criteria available for interpretation of CV data, the non-linear increase of $(I_p)_d$ with square root of scan rate can be attributed to the complex, reduction cathodic mechanism already shown in equations (1)–(3) [36].

The height of the cathodic peak current measured for a given concentration can be taken as a measure for the maximum current that can be achieved under diffusion limited conditions. To correct for different concentrations of AQ used in the CV experiments the normalised quotient $(I_p)_d/c$ has been calculated (Table 2). The suitability of the different AQs for cathodic dyestuff reduction can be discussed on the basis of the electrochemical parameters as a function of scan rate (Tables 3–6).

3.2. Hydroxy-9,10-anthraquinones

Dihydroxy-9,10-anthraquinones DA1,2, DA1,4 and DA1,8 show mid-point potentials between −713 mV (DA1,4) and −845 mV (DA1,2) (Table 3). The mid-point potential of −713 mV makes DA1,

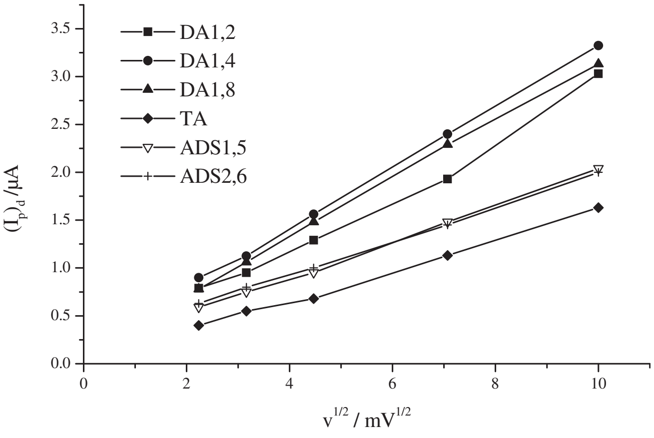


Fig. 1. Cathodic peak current $(I_p)_d$ as function of square root of scan rate for dihydroxy-anthraquinones DA1,2; DA1,4; DA1,8 and 9,10-anthraquinone-disulfonic acids ADS1,5 and ADS2,6.

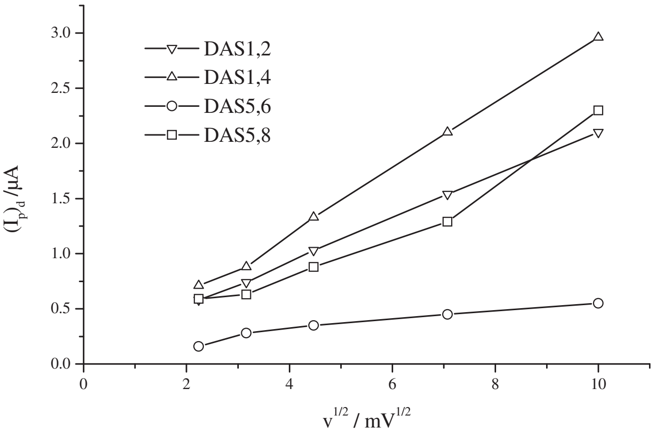


Fig. 2. Cathodic peak current $(I_p)_d$ as function of square root of scan rate for dihydroxy-9,10-anthraquinone-sulfonic acids DAS1,2; DAS1,4; DAS5,6; DAS5,8.

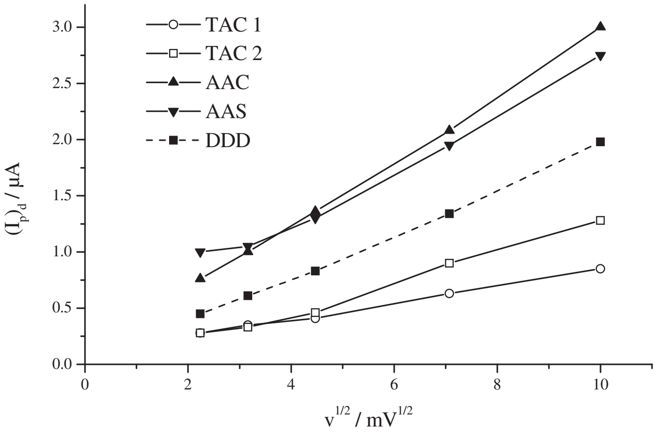


Fig. 3. Cathodic peak current $(I_p)_d$ as function of square root of scan rate for first cathodic current peak (TAC 1) and second cathodic current peak (TAC 2) of TAC (1,3,4-trihydroxy-9,10-anthraquinone-2-carbonic acid) and substituted amino-anthraquinones AAC, AAS, and DDD.

4 suited for sulphur dye reduction. DA1,8 and DA1,2 exhibit sufficient negative potential for reduction of dispersed indigo. All three dihydroxy-9,10-anthraquinones show sufficient chemical stability within the time scale of the CV experiment. Reoxidation of the reduced AQ could be observed during the anodic scan and values for $(I_p)_a/(I_p)_d$ of 0.81–0.86 indicate chemical reversibility of the couple AQ/AQ^{2-}. Both cathodic and anodic peak current of these AQs are comparable and $(I_p)_d/c$ of 5.36–5.88 was calculated for these compounds. Thus for a given concentration, these components permit to achieve relative high diffusion limited current density. While the mid-point potentials are almost independent for different scan rates, the values of $(E_p)_d$ shift 5–10 mV more negatively and the value for $(E_p)_a$ shift 5–10 mV more positively with increasing scan rate. At a scan rate of 100 mV s^{-1} the difference $(E_p)_d - (E_p)_a$ is between 55 and 65 mV, which corresponds within the experimental accuracy the value expected for a reversible one electron transfer [36].

The AQs bearing 4–6 hydroxyl groups, TA, PA and HA did not exhibit electrochemical or chemical reversibility in the CV experiments. Reduction peaks were observed at potential values more negative than −800 mV however the presence of several current peaks during the cathodic and anodic scan of the CV indicate that these compounds undergo several reduction steps, possibly with parallel chemical reactions.

As a representative, TA showed two reduction waves and one oxidation peak in the CV. Both waves show comparable cathodic current height, which could indicate a series of two consecutive one-electron transfer steps. The anodic oxidation peak current shows the height of one cathodic peak. Due to the complicated electrochemical processes the reversibility parameter $(i_p)_a/(i_p)_d$ was not calculated for TA, PA or HA.

3.3. 9,10-Anthraqinone-sulfonic acids

Two 9,10-anthraquinone-sulfonic acids were studied in this work ADS1,5 and ADS2,6. Both AQs are stable in reduced and oxidised form and exhibit chemically reversible redox behaviour, thus the factor $(I_p)_a/(I_p)_d$ equals 1. Detailed data are given in Table 4. The mid-point potential $((E_p)_d+(E_p)_a)/2$ is around −700 mV for ADS1,5, which permits an application for sulphur dyeing only, which is in agreement with the literature [17]. The mid-point potential of ADS2,6 of −480 mV is the least negative among the AQs studied. For ADS1,5 $(E_p)_d$ and $(E_p)_a$ are almost independent of scan rates and the

Table 3
CV-characteristics of 0.36 mM DA1,2, 0.44 mM DA1,4, 0.39 mM DA1,8 solutions on 0.1 M NaOH, measured at a scan rate of 5–100 mV s^{-1}. Peak potentials $(E_p)_d$, $(E_p)_a$, mid-point potential $((E_p)_d+(E_p)_a)/2$ and peak currents $(I_p)_d$, $(I_p)_a$ and ratio $(I_p)_a/(I_p)_d$.

Code	v mV s^{-1}	$(E_p)_d$ mV	$(E_p)_a$ mV	$((E_p)_d+(E_p)_a)/2$ mV	$(I_p)_d$ μA	$(I_p)_a$ μA	$(I_p)_a/(I_p)_d$
DA1,2	5	−880	−825	−853	0.79	0.68	0.86
	10	−870	−830	−850	0.95	0.75	0.79
	20	−880	−825	−853	1.29	1.13	0.87
	50	−880	−820	−845	1.93	1.60	0.83
	100	−880	−820	−845	3.03	2.13	0.70
DA1,4	5	−735	−690	−713	0.90	0.76	0.84
	10	−730	−695	−713	1.13	1.02	0.90
	20	−735	−690	−713	1.56	1.39	0.89
	50	−735	−690	−713	2.40	2.06	0.86
	100	−745	−680	−713	3.33	2.78	0.83
DA1,8	5	−770	−730	−750	0.78	0.68	0.87
	10	−770	−730	−750	1.06	0.88	0.82
	20	−775	−725	−750	1.48	1.26	0.86
	50	−780	−720	−750	2.29	1.85	0.81
	100	−775	−720	−748	3.13	2.53	0.81

Table 4
CV-characteristics of 0.37 mM ADS1,5 and 0.52 mM ADS2,6 in 0.1 M NaOH, measured at a scan rate of 5–100 mV s^{-1}. Peak potentials $(E_p)_d$, $(E_p)_a$, mid-point potential $((E_p)_d+(E_p)_a)/2$ and peak currents $(I_p)_d$, $(I_p)_a$ and ratio $(I_p)_a/(I_p)_d$.

Code	v mV s^{-1}	$(E_p)_d$ mV	$(E_p)_a$ mV	$((E_p)_d+(E_p)_a)/2$ mV	$(I_p)_d$ μA	$(I_p)_a$ μA	$(I_p)_a/(I_p)_d$
ADS1,5	5	−740	−685	−713	0.59	0.51	0.87
	10	−740	−685	−713	0.75	0.68	0.90
	20	−735	−685	−710	0.95	1.00	1.05
	50	−735	−680	−708	1.48	1.53	1.03
	100	−735	−670	−703	2.04	2.08	1.02
ADS2,6	5	−505	−435	−470	0.63	0.60	1.04
	10	−505	−445	−475	0.80	0.75	1.07
	20	−535	−435	−485	1.00	1.00	1.00
	50	−515	−435	−475	1.45	1.51	0.95
	100	−515	−445	−480	2.00	2.13	0.94

Table 5
CV-characteristics of 0.41 mM DAS1,2, 0.54 mM DAS1,4, 0.54 mM DAS5,6 and 0.52 mM DAS5,8 solutions in 0.1 M NaOH, measured at a scan rate of 5–100 mV s^{-1}. Peak potentials $(E_p)_d$, $(E_p)_a$, mid-point potential $((E_p)_d+(E_p)_a)/2$ and peak currents $(I_p)_d$, $(I_p)_a$ and ratio $(I_p)_a/(I_p)_d$.

Code	v mV s^{-1}	$(E_p)_d$ mV	$(E_p)_a$ mV	$((E_p)_d+(E_p)_a)/2$ mV	$(I_p)_d$ μA	$(I_p)_a$ μA	$(I_p)_a/(I_p)_d$
DAS1,2	5	−875	−820	−848	0.58	0.53	0.91
	10	−870	−820	−845	0.74	0.70	0.95
	20	−870	−820	−845	1.03	0.98	0.95
	50	−875	−820	−848	1.54	1.45	0.94
	100	−885	−820	−853	2.10	1.99	0.95
DAS1,4	5	−640	−600	−620	0.71	0.70	0.98
	10	−640	−595	−618	0.88	0.95	1.09
	20	−640	−600	−620	1.33	1.30	0.98
	50	−645	−590	−618	2.10	1.98	0.94
	100	−645	−580	−613	2.96	2.80	0.95
DAS5,6	5	−910	−770	−840	0.16	0.29	0.57
	10	−910	−775	−843	0.28	0.18	0.64
	20	−920	−775	−848	0.35	0.28	0.79
	50	−940	−770	−855	0.45	0.40	0.89
	100	−960	−770	−865	0.55	0.51	0.93
DAS5,8	5	−725	−655	−690	0.59	0.68	1.15
	10	−710	−655	−683	0.63	0.88	1.32
	20	−700	−655	−678	0.88	1.08	1.23
	50	−700	−650	−675	1.29	1.35	1.05
	100	−705	−645	−675	2.30	2.50	1.09

Table 6
CV-characteristics of 0.54 mM TAC, 0.52 mM AAC, 0.58 mM AAS and 0.52 mM DDD solutions on 0.1 M NaOH, measured at a scan rate of 5–100 mV s^{-1}. Peak potentials $(E_p)_d$, $(E_p)_a$, mid-point potential $((E_p)_d+(E_p)_a)/2$ and peak currents $(I_p)_d$, $(I_p)_a$ and ratio $(I_p)_a/(I_p)_d$.

Code	v mV s^{-1}	$(E_p)_d$ mV	$(E_p)_a$ mV	$((E_p)_d+(E_p)_a)/2$ mV	$(I_p)_d$ µA	$(I_p)_a$ µA	$(I_p)_a/(I_p)_d$
TAC	5	−740	−660	−700	0.28	0.28	1.00
		−1040	−910	−960	0.28	0.21	0.75
	10	−750	−655	−703	0.35	0.20	0.57
		−1010	−900	−955	0.33	0.35	1.06
	20	−750	−650	−700	0.41	0.24	0.58
		−1000	−900	−950	0.46	0.43	0.93
	50	−760	−620	−690	0.63	0.25	0.40
		−1010	−900	−955	0.90	0.79	0.88
	100	−760	−610	−685	0.85	0.30	0.35
		−1010	−890	−950	1.28	1.10	0.86
AAC	5	−810	−710	−760	0.76	0.81	1.07
	10	−810	−720	−765	1.00	1.03	1.03
	20	−805	−725	−765	1.36	1.34	0.98
	50	−815	−720	−768	2.08	2.00	0.96
	100	−825	−710	−768	3.00	2.75	0.92
AAS	5	−750	−615	−683	1.00	1.05	1.05
	10	−720	−620	−670	1.05	1.18	1.12
	20	−710	−620	−663	1.30	1.55	1.19
	50	−715	−620	−668	1.95	2.00	1.03
	100	−710	−610	−660	2.75	2.73	0.99
DDD	5	−700	−660	−680	0.45	0.40	0.89
	10	−710	−660	−685	0.61	0.52	0.86
	20	−715	−650	−683	0.83	0.68	0.82
	50	−715	−645	−680	1.34	0.98	0.73
	100	−720	−640	−680	1.98	1.28	0.65

distance $(E_p)_d - (E_p)_a$ is between 55 and 65 mV as expected for a one electron transfer step (equation (1)). For ADS2,6 a higher value for $(E_p)_d - (E_p)_a$ is measured with 70–100 mV which indicates quasi reversible behaviour [36].

3.4. Hydroxy-9,10-anthraquinone-sulfonic acids

The electrochemical behaviour of four dihydroxy-9,10-anthraquinone-sulfonic acids DAS1,2, DAS1,4, DAS5,6 and DAS5,8 is summarised in Table 5. DAS1,2 exhibits scan rate independent cathodic and anodic peak potentials and a mid-point potential of −850 mV, which indicates suitability of DAS1,2 to serve as mediator for indirect cathodic reduction of indigo including selected vat dyes with moderate reduction potential [13–15]. The distance between $(E_p)_d$ and $(E_p)_a$ of 50–65 mV corresponds to the value expected for a one electron transfer step. The factor $(I_p)_a/(I_p)_d$ of 0.91–0.95 indicates chemical reversibility of the couple AQ/AQ^{2-}.

In the voltammogram of DAS1,4 a mid-point potential of −613 mV to −620 mV is observed (Fig. 4). The mid-point potential makes DAS1,4 suitable to serve as mediator for sulphur dye reduction. The distance between $(E_p)_d$ and $(E_p)_a$ increases with scan rate from 40 mV at 5 mV s^{-1} to 65 mV at 100 mV s^{-1}. At high scan rate the first one electron transfer, according to equation (1), determines the shape of the CV curve.

The factor $(I_p)_a/(I_p)_d$ of 0.94–1.09 indicates chemical reversibility of the couple AQ/AQ^{2-}. Small shoulders observed at the cathodic peak can be attributed to the presence of electro-active impurities.

The voltammogram obtained with DAS5,6 showed several reduction and reoxidation peaks with a strong signal at $(E_p)_d = -940$ mV accompanied by an adsorption peak. During reoxidation two signals at $(E_p)_a = -770$ mV and $(E_p)_a = -670$ mV are observed in the anodic scan of the voltammogram. Detailed analysis of the voltammogram would require further experiments, which would exceed the scope of the present work.

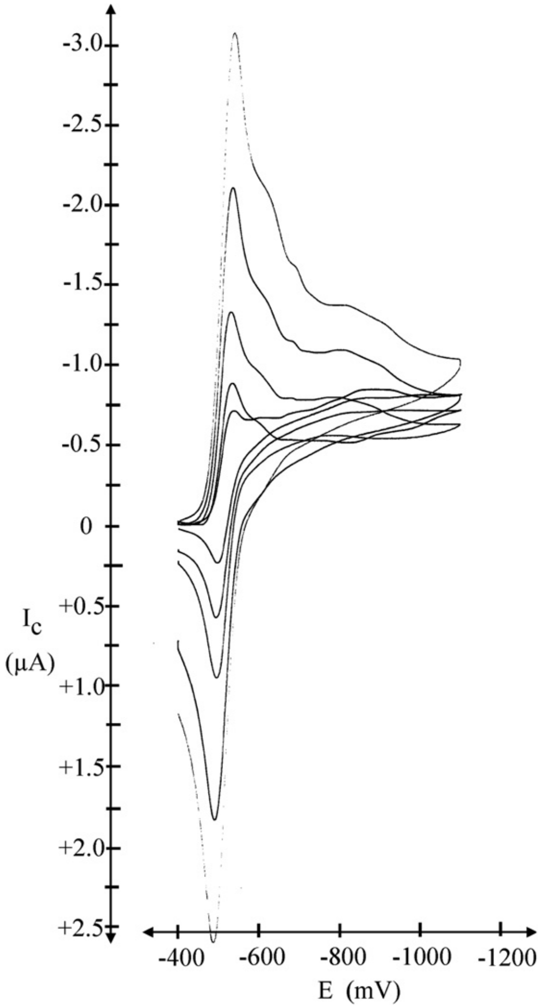


Fig. 4. Cyclic voltammograms of 0.543 mM DAS1,4 (1,4-dihydroxy-9,10-anthraquinone-2-sulfonic acid) solution in 0.1 M NaOH, in the potential range of −400 V to −1200 mV at the scan rates 5, 10, 20, 50, 100 mV s^{-1}.

The voltammogram of DAS5,8 shows non-linear relationship between cathodic peak current $(I_p)_d$ and $v^{1/2}$ indicating quasi-reversible behaviour. The CV curves of DAS5,8 are shown in Fig. 5. At scan rate of 100 mV the voltammogram of DAS5,8 exhibits a mid-point potential of −675 mV, indicating limited potential for application as mediator compound. The distance between $(E_p)_d$ and $(E_p)_a$ of 60 mV at a scan rate of 100 mV s^{-1} corresponds to a one-electron transfer step. While the anodic reoxidation peak exhibits the typical shape of a diffusion controlled electrode process, the broader shape of the cathodic peak at lower scan rates and the high value for $(I_p)_a/(I_p)_d$ at 5–20 mV s^{-1} of 1.15–1.32 indicate a more complex reaction pathway, occurring as a result of the cathodic electron transfer.

3.5. Trihydroxy-9,10-anthraquinone-carbonic acid and amino-9,10-anthraquinone acids

In the voltammogram of TAC two cathodic and anodic current peaks are observed (Fig. 6). The mid-point potential of the first peak is near −700 mV and thus not sufficient negative for reduction of dispersed indigo or other common vat dyes. Cathodic and anodic peak potentials shift with increasing scan rate (Table 6). The linearity of the cathodic peak current $(I_p)_d$ with scan rate demonstrates the reversibility of the cathodic electron transfer. With increase of scan rate from 5 mV s^{-1} to 100 mV s^{-1} the cathodic current peak potential $(E_p)_d$ shifts from −660 mV s^{-1} to −610 mV. The shape of the voltammogram indicates possible follow-up reactions during the cathodic reduction. The decreasing values of $(I_p)_a/(I_p)_d$ also support the assumption of a complex electrode reaction, including irreversible chemical steps.

The second cathodic peak exhibits a mid-point potential of −955 mV. The non-linear relation between $(I_p)_d$ and $v^{1/2}$ and the shape of this cathodic current peak again indicate complicated electrode reactions, most probably involving following chemical reactions and rearrangements.

AAC and AAS as amino group containing AQs exhibit a mid-point potential of −765 mV and −665 mV respectively. The CV of AAS is shown in Fig. 7. While the relation between $(I_p)_d$ and $v^{1/2}$ is linear for AAC, the sulfonic acid shows non-linear behaviour, indicating non-reversible electron transfer. While AAC could be expected to be useful as a mediator, the mid-point potential of AAS is not sufficient negative for indigo and vat dye reduction.

Both AQs exhibit a high potential difference between $(E_p)_d$ and $(E_p)_a$ which in the case of AAC ranges from 100 mV at 5 mV s^{-1} to 115 mV at 100 mV s^{-1}, corresponding values for AAS are 135 mV at 5 mV s^{-1} and 100 mV at 100 mV s^{-1}. The distance between $(E_p)_d$

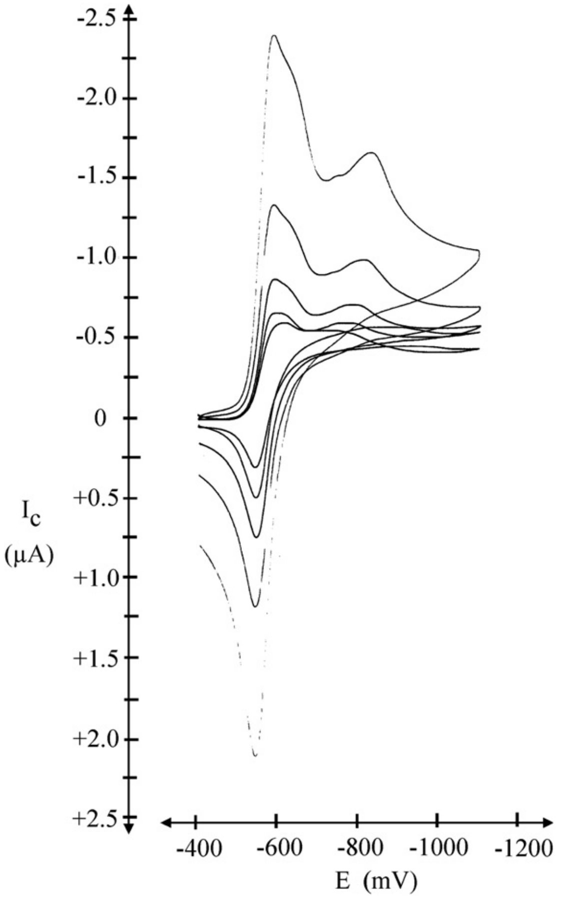


Fig. 5. Cyclic voltammograms of 0.541 mM DAS5,8 (5,8-dihydroxy-9,10-anthraquinone-2-sulfonic acid) solution in 0.1 M NaOH, in the potential range of −400 V to −1200 mV at the scan rates 5, 10, 20, 50, 100 mV s^{-1}.

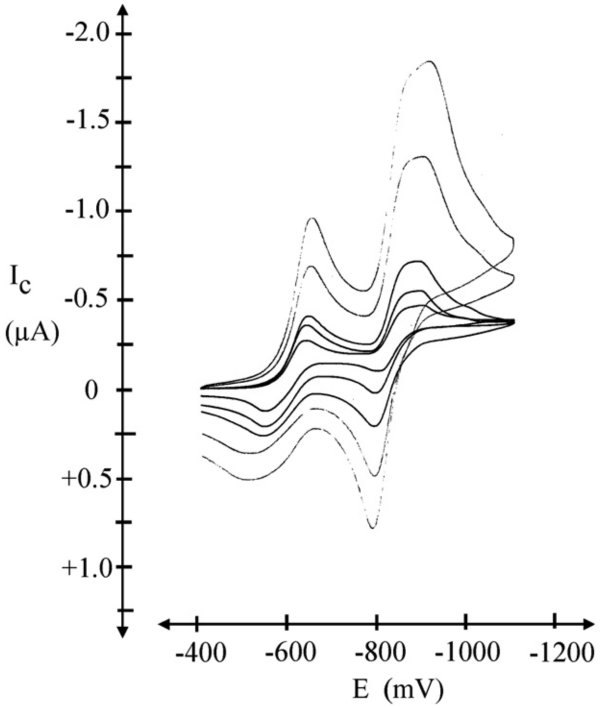


Fig. 6. Cyclic voltammograms of 0.541 mM TAC (1,3,4-trihydroxy-9,10-anthraquinone-2-carbonic acid) solutions on 0.1 M NaOH, measured at a scan rate of 5–100 mV s^{-1}.

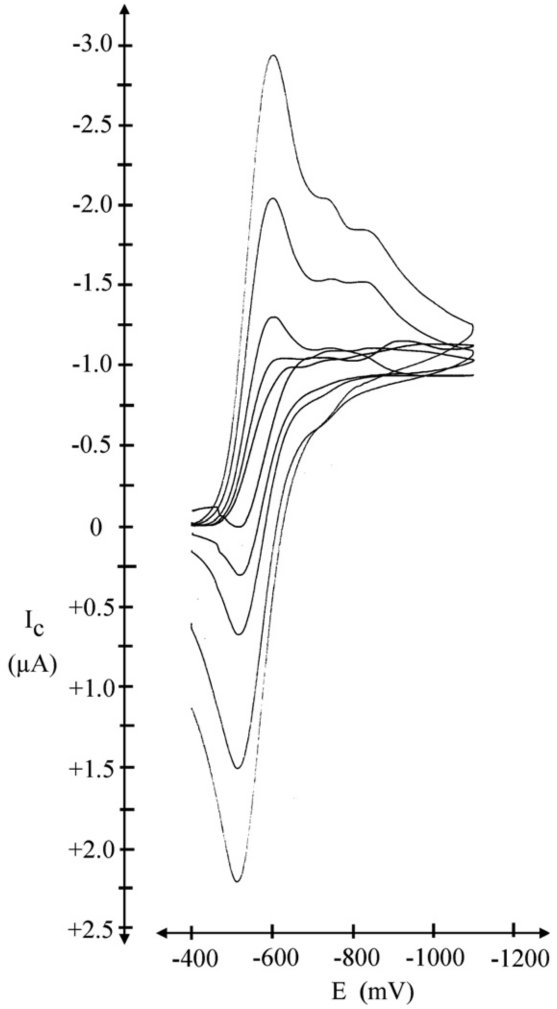


Fig. 7. Cyclic voltammograms of 0.576 mM AAS (1-amino-9,10-anthraquinone-2-sulfonic acid) solution in 0.1 M NaOH, in the potential range of −400 V to −1200 mV at the scan rates 5, 10, 20, 50, 100 mV s^{-1}.

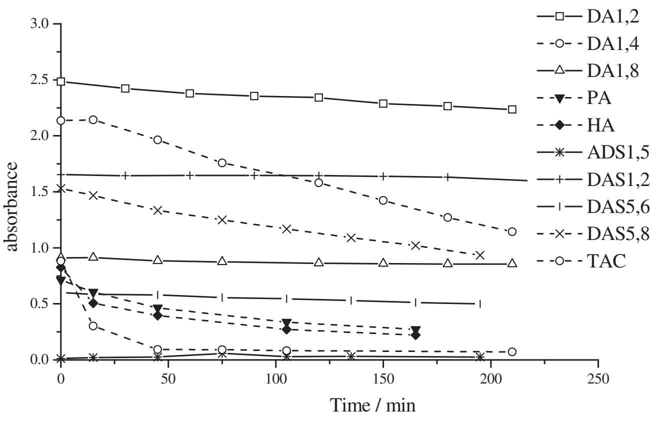


Fig. 8. Stability of AQ – Absorbance of a 0.05 g L^{-1} AQ solution in 0.1 M NaOH as function of time measured under dyebath conditions (60 °C, 0.1 M NaOH).

and $(E_p)_a$ supports the assumption of chemically non-reversible electrode processes including chemical rearrangements.

Both AAC and AAS show values for $(I_p)_a/(I_p)_d$ near unity. In case of AAS at a scan rate of 20 mV s^{-1} $(I_p)_a/(I_p)_d$ increases to 1.19, which supports the assumption of a complex electrode reaction.

Despite the rather complicated chemical structure of DDD (4,8-diamino-1,5-dihydroxy-9,10-anthraquinone-2,6-disulfonic acid tetrasodium salt) a well defined CV is observed in alkaline solution, with linear increase of $(I_p)_d$ with $v^{1/2}$. The mid-point potential is measured near −680 mV. The difference between $(E_p)_d$ and $(E_p)_a$ increases with scan rate from 40 mV at 5 mV s^{-1} to 80 mV at 100 mV s^{-1}, parallel the ratio of $(I_p)_a/(I_p)_d$ decreases from 0.89 to 0.65. Thus CV results indicate a complicated overall electrode process, which would require more detailed analysis.

3.6. Chemical stability

Besides the electrochemical properties, an AQ compound has to fulfil a number of basic requirements, defined by the dyeing procedure e.g. vat dyeing, indigo or sulphur dyeing.

The substance has to be soluble in alkaline solution, which can be achieved by presence of sulfonate or carboxylate substitutents, or phenolic hydroxyl groups. However it has to be considered that solubility of hydroxy-9,10-anthraquinones can be limited to the alkaline range of pH, where dissociation of the phenolic hydroxyl groups occurs. In this case, solubility increases with pH value. Limited solubility of an AQ-based mediator system at lower pH causes the risk of deposition of the AQ on the cellulosic fibres. As a result the electrochemically active system will be transported out of the process baths, which will lower the concentration of the electro-active system. Further many of the tested AQs are coloured compounds thus absorption on the fibre also has to be avoided to prevent in-acceptable colour changes of the dyeings.

Furthermore, in order to be applicable, the AQ has to be chemically stable under dyebath conditions. Decomposition or rearrangement in alkaline solution will decrease the concentration of electrochemically active mediator.

The stability tests were concentrated on AQs which exhibited negative mid-point potential in the CV of approximately −700 mV or lower.

To study the chemical stability, the oxidised form of the selected AQ was monitored at 60 °C in 0.1 M NaOH solution by means of spectrophotometry. In Fig. 8 the absorbance of the solutions, measured at the wavelength of maximum absorbance, is shown as function of time (Table 1). Accordingly to usual process time of dyeing, the duration of the stability experiment was defined with 3 h.

As can be seen from Fig. 8 several AQs exhibit insufficient chemical stability, indicated by a time dependent decrease in absorbance. Mainly oxidation reactions are supposed to occur at

Table 7
Adsorption of AQ on cotton: dyebath pH, colorimetric coordinates of undyed and dyed samples obtained using 1 g L^{-1} AQ solution in 0.19 M NaOH. Composition of the first rinse: water, NTA, EDTA, citric acid.

Name	pH	Water			NTA			EDTA			Citric acid		
	dyebath	L*	a* h°	b* C*	L*	a* h°	b* C*	L*	a* h°	b* C*	L*	a* h°	b* C*
Undyed sample	–	92.76	−2.04	0.58									
			164.1	2.12									
DA1,2	12.86	76.79	5.88	0.51	82.67	1.79	3.26	83.72	1.28	4.78	77.28	1.65	25.59
			5.0	5.90		61.2	3.72		75.0	4.95		86.3	25.64
DA1,4	13.16	80.02	7.69	20.79	90.46	0.36	17.54	89.28	−0.50	13.58	80.13	15.67	34.14
			69.7	22.17		88.8	17.54		92.1	13.59		65.4	37.56
DA1,8	12.57	87.31	−5.41	19.48	92.66	4.65	9.08	93.11	7.21	15.39	90.36	11.02	42.21
			105.5	20.22		62.9	10.20		64.9	17.00		75.4	43.62
TA	12.71	79.81	3.19	−4.22	83.86	2.24	−1.17	–	–	–	72.25	13.36	20.51
			307.1	5.29		332.4	2.53		–	–		56.9	24.48
PA	12.72	73.53	2.96	−3.71	77.43	2.74	−0.97	–	–	–	71.23	4.53	−2.04
			308.6	4.75		340.5	2.91		–	–		335.8	4.97
HA	12.72	87.84	2.11	0.09	79.41	2.86	5.48	88.47	2.85	0.08	80.05	8.59	4.75
			2.4	2.11		62.4	6.18		1.6	2.85		28.9	9.82
ADS1,5	13.16	92.95	−2.00	0.79	93.33	−2.04	0.54	93.43	−1.29	1.34	93.00	−2.03	0.46
			158.5	2.15		165.2	2.11		133.9	1.86		167.2	2.08
DAS1,2	12.60	87.40	2.20	0.80	89.55	0.17	1.11	90.35	−0.69	2.54	88.65	0.55	4.85
			19.98	2.34		81.29	1.12		105.2	2.63		83.53	4.88
DAS5,6	13.67	91.56	−0.66	0.14	92.45	−1.39	0.81	–	–	–	92.03	−2.23	3.24
			168.0	0.67		149.8	1.61		–	–		124.5	3.93
DAS5,8	13.55	88.89	−1.04	0.97	90.11	−0.98	0.31	–	–	–	88.14	−0.22	4.98
			137.0	1.42		162.5	1.03		–	–		92.5	4.98
TAC	nd	75.67	9.07	−2.13	84.24	3.87	−1.78	–	–	–	76.00	6.58	−2.68
			346.8	9.32		335.3	4.26		–	–		337.8	7.10
DDD	13.56	75.95	−4.13	−12.19	74.80	−4.68	−12.62	–	–	–	74.62	−4.66	−12.64
			251.3	12.87		249.7	13.46		–	–		249.8	13.47

the phenolic hydroxyl groups, the rate being dependent on the respective pattern of substitution. In-sufficient stability was attributed to AQs which showed a decrease in absorbance above 10% of their initial value. Significant decreases in absorbance was observed for five of the AQs, namely DA1,4, PA, HA, DAS5,8 and TAC. Sufficient stability was observed for DA1,2, DA1,8, DAS1,2 and DAS5,6. ADS1,5 showed very low absorbance, thus at the chosen experimental conditions stability of ADS could not be proven. However for ADS stability under dyebath conditions has been reported [17,18].

3.7. Dyeing behaviour – substantivity towards cellulosic fibres

An ideal anthraquinoid mediator system should be colourless or at least should not exhibit disturbing substantivity to cellulosic substrates. The major part of the AQs tested showed intensive colour in alkaline solution. The colour of the AQ in alkaline solution is given in Table 1. To avoid in-acceptable shifts in colour of the dyed goods, complete removal of the AQ from the dyed sample has to be achieved during the rinsing procedures following the dyeing step.

Model dyeing experiments were performed at ambient temperature to follow the usual procedure for indigo dyeing in denim production and to achieve maximum substantivity of the AQ. Time of immersion was extended to 30 min to permit sufficient time for AQ exhaustion and equilibration.

In the electrochemical experiments and for determination of the chemical stability, low concentrations of AQ were used, which were defined by the respective analytical technique. In the dyeing experiments a higher concentration of 1 g L^{-1} AQ was used. This concentration can be seen as lower concentration limit for the use of a certain AQ for indirect cathodic dyestuff reduction. Lower concentrations would be favourable, however stability of reduction conditions in the dyebath will become insufficient and dimensions of the electrolyser will be grown due to lower cathodic current density. Higher concentrations e.g. 10 g L^{-1} AQ will increase chemical consumption and costs due to increased losses of AQ in the textile processing.

In a series of dyeing experiments the sorption of AQs on cotton fabric was studied. Dependent on the pre-treatment of the fabric residual amounts of Ca^{2+} present on the fibres could bind dissolved hydroxy-9,10-anthraquinones e.g. alizarin under formation of insoluble complexes, yielding coloured samples [32,37,38]. Thus besides rinse operations with use of deionised water, experiments with addition of complexing agents NTA or EDTA to the first rinse bath were performed, to remove any Ca^{2+} from the dyed material. For comparison also the effect of an acid rinse with addition of citric acid was studied.

Table 8
CIE colour difference between undyed and dyed samples as a function of composition of the first rinse stage: water, NTA, EDTA, citric acid.

AQ	ΔE			
	Water	NTA	EDTA	Citric acid
DA1,2	17.83	11.12	10.51	29.64
DA1,4	25.80	17.28	13.55	39.99
DA1,8	19.96	10.82	17.46	43.70
TA	14.77	10.03	–	32.48
PA	20.33	16.13	–	22.66
HA	6.46	15.04	6.52	17.09
ADS1,5	0.29	0.57	1.26	0.27
DAS1,2	6.84	3.93	3.39	6.47
DAS5,6	1.88	0.76	–	2.76
DAS5,8	4.02	2.87	–	6.63
TAC	20.56	10.63	–	19.13
DDD	21.21	22.44	–	22.60

After drying at ambient temperature the samples were characterised by measurement of the CIELab and CIELh coordinates. In Table 7 the colorimetric parameters of cotton fabric samples obtained after different rinse operations are shown; the coordinates of the undyed material are also provided.

For interpretation of the final colour it has to be considered, that during the rinse operation the pH in the baths changes and thus the colour of the dyed samples can shift due to protonation of the phenolate groups in the AQ.

The colour difference between the undyed and dyed specimen is shown in Table 8.

The colour difference data shown in Table 8 indicate significant staining, which is independent of washing conditions in the cases of DA1,2, DA1,4, DA1,8, TA, PA, HA, TAC, and DDD. Lower colour difference (ΔE) values of 0.5 and 4 were observed for ADS1,5, DAS1,2, DAS5,6, and DAS5,8, which all contained sulfonate groups and thus exhibited higher solubility during the rinsing operation, particularly when the pH of the dyebath was lowered. As a general observation the first rinse in the presence of the complexing agents NTA or EDTA resulted in lowest staining, as such agents bind Ca^{2+}, and so lower sorption of AQ occurs [37]. As can be seen by the hue angle in Table 7, staining due to sorption of dihydroxy-anthraquinones DA1,2, DA1,4 and DA1,8 resulted in yellow shades, with a hue angle between 60 and 105. The colour of TA, PA and TAC stains were violet (h° of 305–350), whilst samples treated in DDD solution were of a blue colour with h^o values of approximately 250.

4. Conclusions

Substituted AQs can undergo reversible reduction/oxidation processes, which makes them an interesting class of compounds to be of potential value as mediators for indirect cathodic reduction of dispersed dyes e.g. sulphur dyes, indigo and vat dyes. Cyclic voltammetry is a very powerful method to assess the potential of a compound, to serve as mediator for indirect electrolysis. A considerable number of AQs tested exhibited promising electrochemical properties, to become applicable for indirect cathodic reduction of dispersed indigo, however reducing power is not sufficient negative, to achieve reduction of the major part of vat dyes technically used at present.

Among the different groups of AQs studied, hydroxy-9,10-anthraquinoids showed promising negative cathodic current peak potentials $(E_p)_d$ and mid-point potentials $((E_p)_d + (E_p)_a)/2$ however lack in chemical stability and tendency to stain cotton samples during the dyeing process makes successful application questionable.

The limited solubility of hydroxyl-9,10-anthraquinones in neutral aqueous solutions increases the risk of deposition of the coloured compounds on the cellulose material during the rinse operations. Presence of Ca^{2+} binding complexing agents in the first rinse bath lowers the staining, however still significant adsorption is observed.

Hydroxy-9,10-anthraquinone-sulfonic acids exhibit good solubility in neutral solutions thus risk of staining of cotton samples is low. Model dyeing experiments demonstrated the low substantivity of the substances to cotton fibres. The mid-point potential of the major part of these compounds is not sufficiently negative to be of interest for cathodic reduction of indigo or other vat dyes.

The most promising substituted AQ among the studied representatives was found to be DAS1,2 (1,2-dihydroxy-9,10-anthraquinone-2-sulfonic acid; Alizarin Red S) which offers a rather negative mid-point potential of −848 mV, good chemical stability under dyebath conditions and low staining of the dyed material.

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