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pH Dependent redox behaviour of Alizarin Red S (1,2-dihydroxy-9,10-anthraquinone-3-sulfonate) – Cyclic voltammetry in presence of dispersed vat dye

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ABSTRACT

The redox chemistry of Alizarin Red S (1,2-dihydroxy-9,10-anthraquinone-3-sulfonate) was studied as function of pH by photometry, potentiometric titration and cyclic voltammetry. Dependent upon solution pH three species of the oxidised form of Alizarin Red S are present. Electrochemical reduction of the anthraquinone group leads to 1,2,9,10-tetrahydroxy-anthracene-3-sulfonate. The four phenolic hydroxyl groups dissociate with increasing pH value, above pH 12 a tetra anion is the main species in solution. Cyclic voltammetry experiments in unbuffered solution indicate that the overall cathodic reduction contains electron transfer and pH-dependent protonation reactions. Above pH 12 dispersed Vat Yellow 1 could be reduced by indirect cathodic electron transfer using the fully deprotonated system as reversible redox couple. In cyclic voltammetry a reduction potential of $(E_p)_d = -900$ mV (vs. Ag/AgCl/3 M KCl) was observed, which is sufficiently negative to reduce Vat Yellow 1. No indication for an indirect cathodic reduction of Vat Yellow 46 could be registered.

1. Introduction

Due to their relevance in biological systems and technical use the redox behaviour of quinones has been studied extensively [1–5]. In neutral aqueous solution the electrochemical reduction of the quinone group is often considered as a model for an ECEC reaction (2 electron transfer reactions E/2 proton transfer reactions C) leading to the corresponding hydroquinone [6,7]. In unbuffered solution the electrochemical reduction of the quinone group and the following protonation reactions lead to a more complex reaction pathway, which depends on the acidity constants of the oxidised and reduced products.

Due to the widespread application of Alizarin Red S (1,2-dihydroxy-9,10-anthraquinone-3-sulfonic acid, $ALSH_2$ **1**) e.g. for histological staining, as a dye and for analytical purposes, research has been performed, to characterise the acid–base properties of the phenolic groups [8–10]. Dissociation constants for the two phenolic hydroxyl groups in $ALSH_2$ **1** were reported as pK_1(2-OH) = 5.49 and pK_2(1-OH) = 10.85 (25 °C, ionic strength 0.5 M) [8].

Electrochemical properties of $ALSH_2$ **1** have also been reported in the literature. Voltammetry has been used to study the cathodic reduction of $ALSH_2$ **1** on either mercury or graphite electrodes [11–14]. The solubility of hydroxy-9,10-anthraquinones in alkaline aqueous solution and the negative redox potential that can be achieved by cathodic reduction of the anthraquinone solution makes these compounds of interest for indirect reduction of dispersed organic compounds e.g. indigo and other vat dyes [5,12,13,15].

Direct electrochemical reduction of organic pigments can be achieved in cases where the dye microparticles have been attached to the surface of the electrode [16–19]. Reduction of dyestuff particles dispersed in the electrolyte can be achieved by means of a suitable organic redox system e.g. soluble anthraquinones [12,13,15]. $ALSH_2$ **1** is an important representative for this class of organic compounds and the electrochemical behaviour in strongly alkaline solution has been studied in detail [5,12,13]. Due to the pH-dependent dissociation of the phenolic hydroxyl groups and the corresponding hydroanthraquinones formed by cathodic reduction, complex redox behaviour is expected to occur for $ALSH_2$ **1** in the pH range between 3 and 12, which however has not been studied up to now. In this paper the pH-dependent cathodic reduction of $ALSH_2$ **1**

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has been studied by cyclic voltammetry. Photometric methods were applied to study the species distribution of $ALSH_2$ in the oxidised and reduced state as a function of pH. Using literature values for protonation constants and the computer programme BEST, species distribution of $ALSH_2$ **1** was calculated for comparison with experimental values [8,20]. Two different vat dyes CI Vat Yellow 1 and CI Vat Yellow 46 were used as a model to investigate the ability of reduced $ALSH_2$ **1** to transfer electrons to the dispersed pigment as function of solution pH.

2. Experimental

2.1. Materials

1,2-Dihydroxy-9,10-anthraquinone-3-sulfonate (Alizarin Red S, $ALSH_2$ **1**) was used as delivered by the supplier (Riedl-de-Haen, Seelze, Germany). The Alizarin Red S content was determined by potentiometric titration. Analytical grade NaOH, $K_3[Fe(CN)_6]$ were used for the experiments. CI Vat Yellow 1 (Indanthrene Yellow G, CAS 475-71-8, VY1) and CI Vat Yellow 46 (Indanthrene Yellow 5GF, CAS 12237-50-2, VY46) were commercial products (DyStar Textilfarben, Frankfurt a.M., Germany). The chemical structure of VY1 is shown in Scheme 1. At present the constitution and structure of Vat Yellow 46 is unknown.

2.2. Cyclic voltammetry

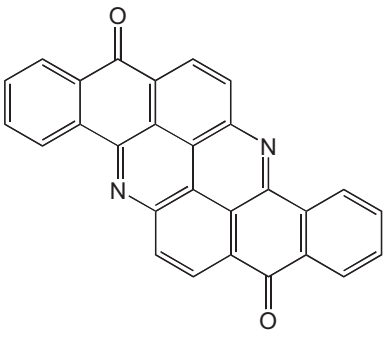
Cyclic voltammetric (CV) experiments were carried out employing a three-electrode configuration. The apparatus used for the experiments was an EG&G 264 A Potentiostat with a 303A HMDE (medium drop size, drop area 1.56×10^{-2} cm^2). A Platinum wire served as counter electrode. The cyclic voltammograms were recorded on a Rikadenki X-Y recorder. All potentials quoted are relative to a (Ag/AgCl, 3 M KCl) reference electrode. The test solutions were aerated for 8 min with He to eliminate interfering oxygen. All experiments were performed at room temperature.

pH-measurement of the electrolyte was made with a glass electrode and a potentiometer (Hamilton-flush-trode, Orion 720 A, Boston MA).

To prepare the solution for the CV experiments of an $ALSH_2$ **1** solution was acidified with HCl (0.05 M, 10 mL) to obtain a solution of $ALSH_2$ **1** (4 mM, 100 ml). The solution pH was adjusted by addition of 1 M NaOH. The actual concentration of $ALSH_2$ **1** then was calculated on the basis of the final volume of solution.

2.3. Potentiometric titration of ALS

To record the potentiometric titration curve an amount of 0.4 mmol of $ALSH_2$ **1** was dissolved in water, acidified with (0.05 M, 10 mL HCl) and titrated with 0.05 M NaOH. A titroprocessor equipped with a glass electrode was used to record the titration curves (Orion 960 autochemistry system, Boston MA).



Scheme 1. Structure of the Vat Yellow 1.

2.4. Photometry of $ALSH_2$ 1 as function of pH

To record the absorbance spectra of $ALSH_2$ **1** as function of pH a 0.004 M $ALSH_2$ **1** solution was prepared. 100 mL of solution were acidified with HCl (0.05 M, 10 mL). The absorbance of the solution was measured by circulating the solution through a flow-through cuvette with 0.1 mm path length and measurement of absorbance with a diode array spectrophotometer (Zeiss CLH 500/MCS521 UV-Vis, Carl Zeiss (Jena) Germany). Then the solution pH was increased stepwise by addition of 0.05 M NaOH solution. In a second experiment 1 M NaOH was used, to reach higher pH values.

Photometry of reduced $ALSH_2$ **1** as function of pH was performed with a titroprocessor equipped with a glass electrode (Orion 960 autochemistry system, Boston MA), coupled to a flow-through electrode and a diode array spectrophotometer. First a 0.8 mM solution of $ALSH_2$ **1** was reduced at 60 °C in alkaline solution (0.2 M NaOH) by addition of 8.6 mmol $Na_2S_2O_4$. After a few minutes reaction time 40 mL of the reduced solution were titrated with 1 M HCl under Ar atmosphere. Absorbance as a function of pH was measured in a flow-through cuvette with 0.1 mm path length.

2.5. Voltammograms in a flow cell

A flow cell with parallel plate geometry was used to record voltammograms [21]. Catholyte and anolyte were separated by a cation exchange membrane (Nafion type). A Cu-cathode with 100 cm^2 area was used (Cu-foil, Merck, Darmstadt, Germany). The anode was made from stainless steel.

The catholyte was circulated by a peristaltic pump through the catholyte compartment with a flow of 140 mL min^{-1}, which corresponds to an estimated average catholyte flow in the cell of 0.15–0.20 cm s^{-1}. Total volume of catholyte was 800 mL. NaOH solution (1 M, 400 mL) was used as the anolyte. In the catholyte 0.1 M NaOH served as ground electrolyte.

The cell voltage was controlled by means of an adjustable power supply. The voltammograms were recorded by stepwise adjustment of the cathode potential and registration of the cell current. All potential values are given in relation to a (Ag/AgCl, 3 M KCl) reference electrode and were measured using a potentiometer (Metrohm pH meter 654, Fa. Metrohm, Herisau, Switzerland). The experiments were recorded at ambient temperature.

3. Results and discussion

3.1. Species distribution of $ALSH_2$ 1 and $ALSH_4$ 7 as function of pH

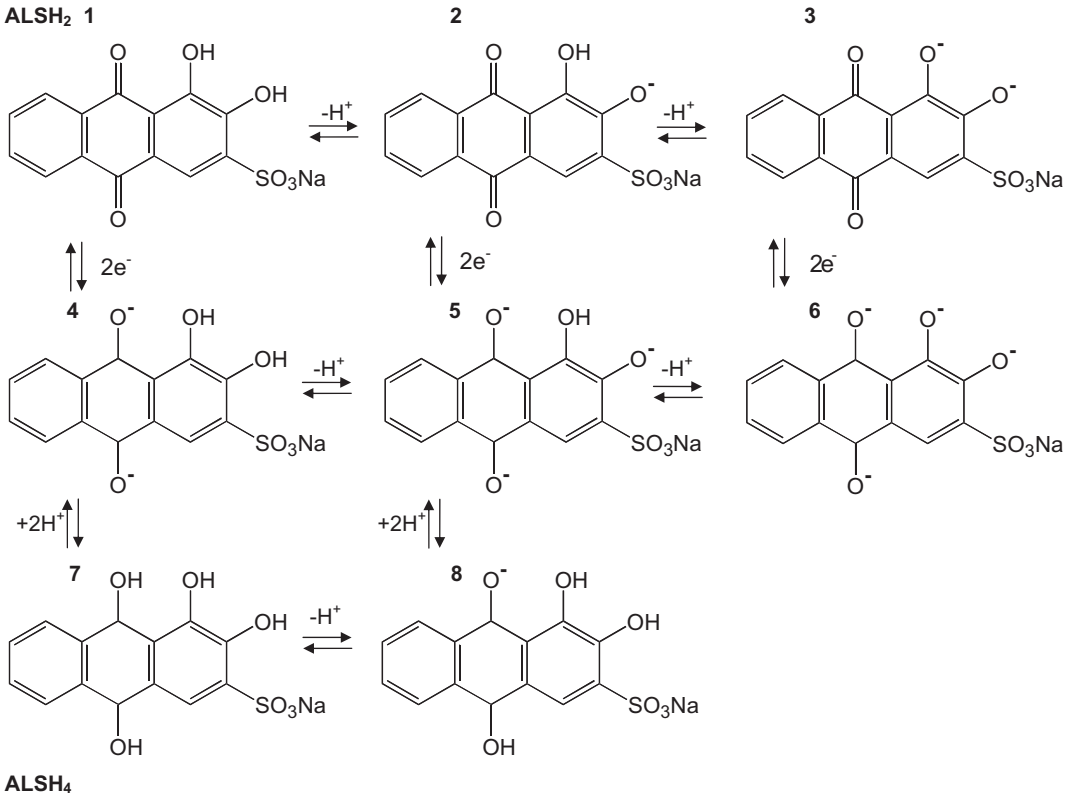
The species of oxidised $ALSH_2$ **1** and reduced $ALSH_4$ **7** present as function of experimental conditions are shown in Scheme 2.

From the literature values for the pKs of $ALSH_2$ **1** the species distribution between Alizarin Red S mono sodium salt $ALSH_2$ **1** and the deprotonated forms $ALSH^-$ **2** and ALS^{2-} **3** can be calculated as function of pH value, according Eqs. (1) and (2).

$$ALSH_2 + OH^- \rightleftarrows ALSH^- + H_2O \quad (1)$$

$$ALSH^- + OH^- \rightleftarrows ALS^{2-} + H_2O \quad (2)$$

The species distribution of $ALSH_2$ **1** shown in Fig. 1 was calculated as function of pH using the programme BEST and dissociation constants for the two OH groups from literature [8,20].



Scheme 2. Species of $ALSH_2$ **1** and $ALSH_4$ **7** formed in solution as function of pH.

As can be seen from Fig. 1 below pH 4 $ALSH_2$ **1** represents the main species, $ALSH^-$ **2** prevails in the pH region of 5.5–10.5 and ALS^{2-} **3** will be the relevant species above pH 12.

This result is in accordance with the potentiometric curves obtained by neutralisation of an acidified $ALSH_2$ **1** solution with NaOH (Fig. 2). Two equivalent points can be observed in the titration curve, the first equivalent point indicates the dissociation of $ALSH_2$ **1** to $ALSH^-$ **2** and the second equivalent point indicates the neutralisation of $ALSH^-$ **2** to ALS^{2-} **3**.

Due to the presence of two phenolic hydroxyl groups $ALSH_2$ **1** shows a pH-dependent deprotonation with parallel change of colour [9,10]. The absorbance spectra of a 0.004 M $ALSH_2$ **1** solution as function of solution pH and added volume of 0.05 M NaOH are given in Fig. 3. Three different species can be detected in solution, undissociated $ALSH_2$ **1**, a mono-phenolate form $ALSH^-$ **2** and the fully dissociated diphenolate ALS^{2-} **3**.

Potentiometric titration of the reduced form ALS^{4-} **6** obtained by chemical reduction of ALS^{2-} **3** using $Na_2S_2O_4$ was used to identify the different reduced species formed. Due to the presence of excess reducing agent, reaction by-products and the similar pKs-values of the four phenolic groups no separated equivalent points could be detected in the potentiometric titration curves. The presence of dissociated species of $ALSH_4$ **7** formed as function of pH during the titration with 1 M HCl, was monitored by photometry.

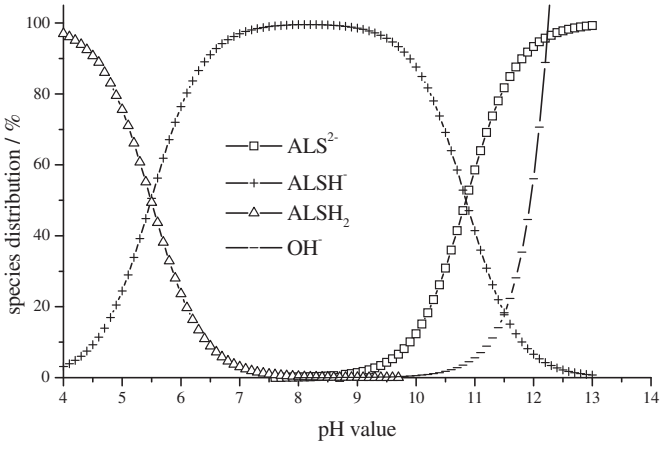


Fig. 1. Species distribution of 0.02 M $ALSH_2$ **1** as function of pH value (pK_1(2-OH) = 5.49 and pK_2(1-OH) = 10.85, 25 °C, ionic strength 0.5 M).

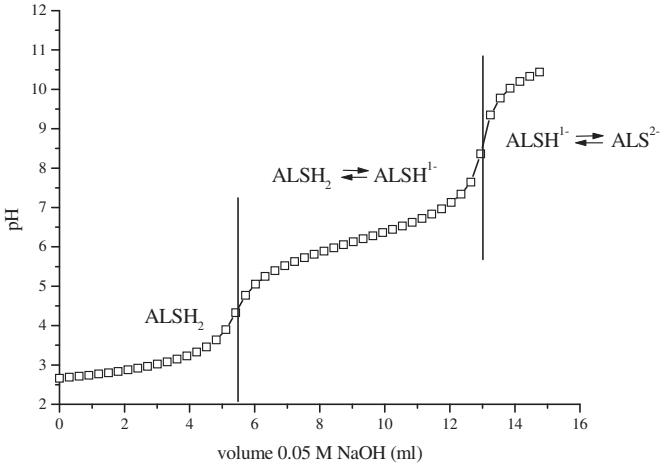


Fig. 2. Potentiometric titration of acidified 0.004 M $ALSH_2$ **1** solution with 0.05 M NaOH solution.

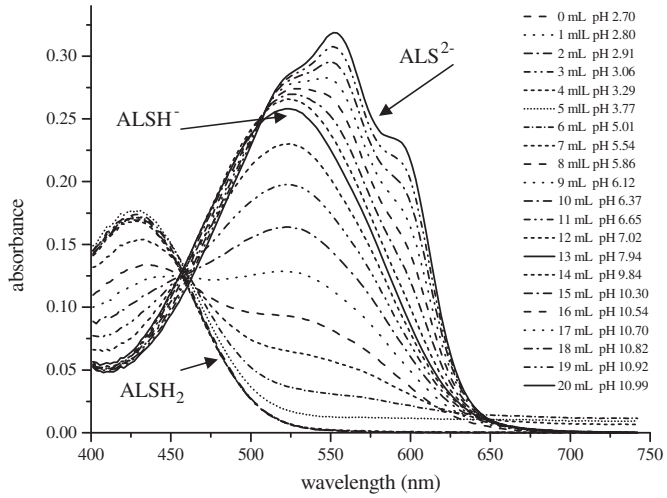


Fig. 3. Change in absorbance of a 0.004 M $ALSH_2$ **1** solution as function of pH after addition of 0.05 M NaOH.

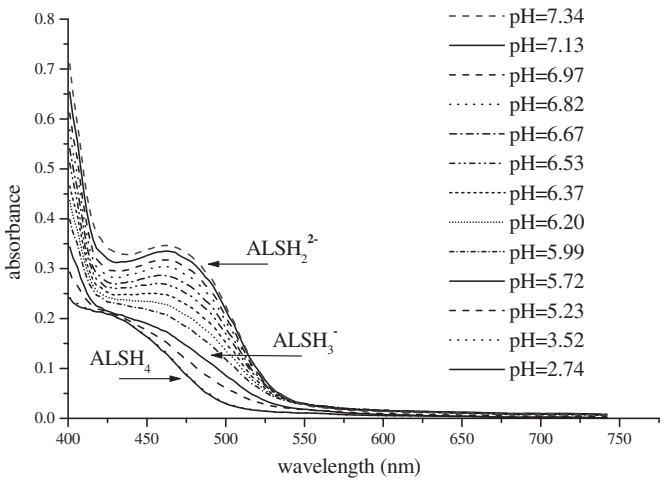


Fig. 5. Absorbance spectra obtained during potentiomentric titration of 0.8 mM $ALSH_4$ **7** in 1 M NaOH, with 1 M HCl. pH range 7.33–2.74.

As expected, five species $ALSH_4$ **7**, $ALSH_3^-$ **8**, $ALSH_2^{2-}$ **4**, $ALSH^{3-}$ **5** and ALS^{4-} **6** could be detected during titration of the reduced alkaline solution of ALS^{4-} **6** with 1 M HCl.

The absorbance spectra given in Figs. 4 and 5 allow identification of the expected five species. Fig. 4 shows the absorbance spectra in the pH range between 12.37 and 7.13 where neutralisation of ALS^{4-} **6** to $ALSH^{3-}$ **5** and $ALSH_2^{2-}$ **4** is observed. In Fig. 5 absorbance curves in the pH range 7.33–2.74 are shown. In this pH range $ALSH_2^{2-}$ **4**, $ALSH_3^-$ **8** and $ALSH_4$ **7** are present.

From the results it can be derived that $ALSH_4$ **7** is present as the main species up to pH 3.5. In the range of pH 3.5 to 5.7 the first phenolic group dissociates and $ALSH_3^-$ **8** is present as the main species at pH 5.7. $ALSH_2^{2-}$ **4** is the main species at pH 7.3, which dissociates to $ALSH^{3-}$ **5** in the pH range of 7.3–8.5. Above pH 11.6 $ALSH^{3-}$ **5** is fully dissociated and ALS^{4-} **6** is present in the alkaline solution above pH 12.0.

3.2. Cyclic voltammetry of $ALSH_2$ 1 as function of pH

Cyclic voltammetry is a very sensitive method for the characterisation of anthraquinoids with regard to their electrochemical properties [6,7,11–14].

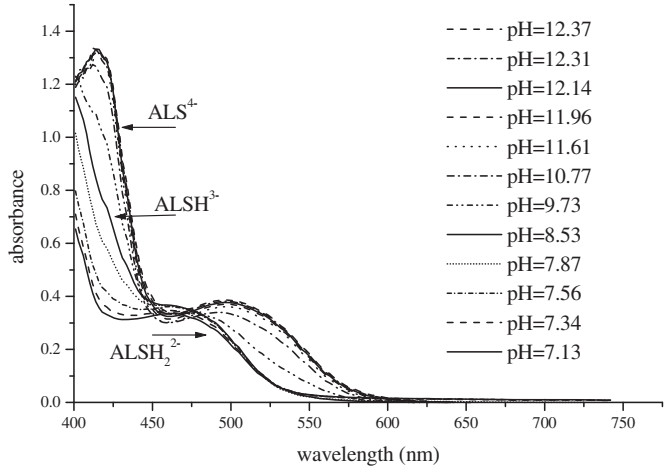


Fig. 4. Absorbance spectra obtained during potentiomentric titration of 0.8 mM $ALSH_4$ **7** in 1 M NaOH, with 1 M HCl. pH range 12.37–7.13.

In alkaline solution the reduction of ALS^{2-} **3** proceeds via a consecutive series of two rapid one electron transfer reactions according Eqs. (3) and (4). Formation of the reduced product ALS^{4-} **6** is the result of a second electron transfer (Eq. (4)) or of a disproportionation of the radical anion (Eq. (5)) [1,6,11]. At high pH e.g. 12 all of the formed phenolic groups remain in dissociated state and no following protonation reaction occurs. At lower pH consecutive protonation steps are involved and as a result reduced species of the form $ALSH_4$ **7** to $ALSH^{3-}$ **8** are formed.

$$ALS^{2-} + e^- \rightleftarrows ALS^{\bullet 3-} \quad (3)$$

$$ALS^{\bullet 3-} + e^- \rightleftarrows ALS^{4-} \quad (4)$$

$$2ALS^{\bullet 3-} \rightleftarrows ALS^{2-} + ALS^{4-} \quad (5)$$

The CVs of the system $ALSH_2$ **1**, $ALSH^-$ **2** and ALS^{2-} **3** recorded with a HMDE electrode in unbuffered solution at different pH values are shown in Figs. 6–9. Voltammograms in the presence of VY1 and VY46 are shown in Figs. 10 and 11.

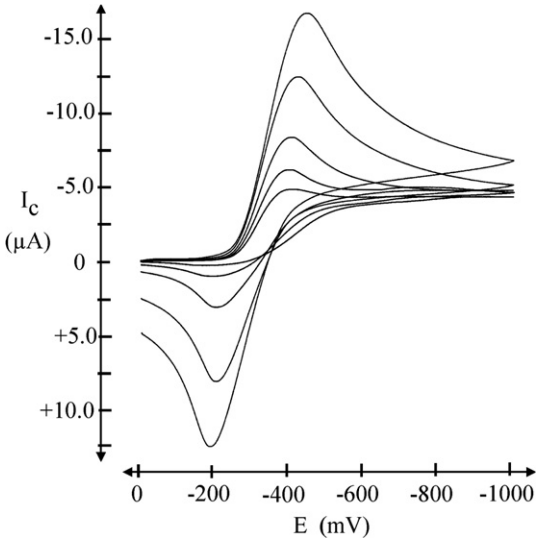


Fig. 6. Cyclic voltammogram of 3.940 mM $ALSH_2$ **1** on a HMDE at pH 2.66 at different scan rates of 5, 10, 20, 50, 100 mV s^{-1} (ground electrolyte 0.05 M NaCl).

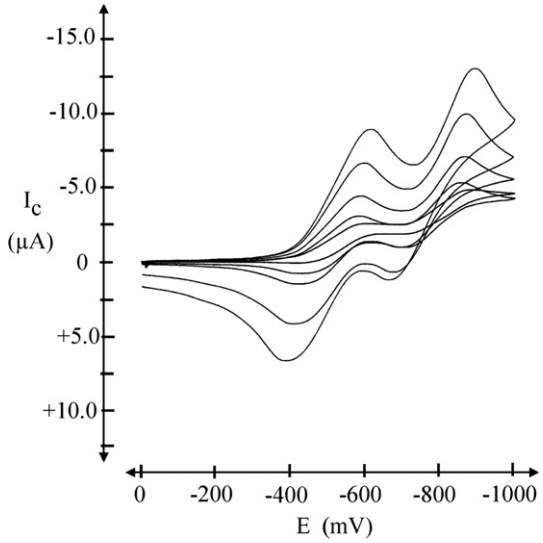


Fig. 7. Cyclic voltammogram of 3.927 mM $ALSH_2$ **1** on a HMDE at pH 5.02 at different scan rates of 5, 10, 20, 50, 100 mV s^{-1} (ground electrolyte 0.05 M NaCl).

The voltammograms at pH 2.7 show a cathodic peak potential of $(E_p)_c = -390$ to -450 mV. From the species distribution and photometric analysis of the reduced species, the overall redox reaction corresponds to Eq. (6). Due to consumption of protons in the reactions consecutive to the cathodic electron transfer, the pH in the cathodic diffusion layer increases and the main reduced species formed in unbuffered solution will be $ALSH_3^-$ **8**.

$$ALSH_2 + 2e^- + H^+ \rightleftarrows ALSH_3^- \quad (6)$$

At pH 5 two cathodic and two anodic current peaks are observed in unbuffered solution. In the first phase of the cathodic scan $ALSH^-$ **2** present in the diffusion layer is reduced to form $ALSH^{3-}$ **8** as the first product (Eq. (7)). As a result of the protonation, the pH in the boundary layer increases and a second cathodic peak, attributed to reduction of ALS^{2-} **3**, is observed. The corresponding anodic peak

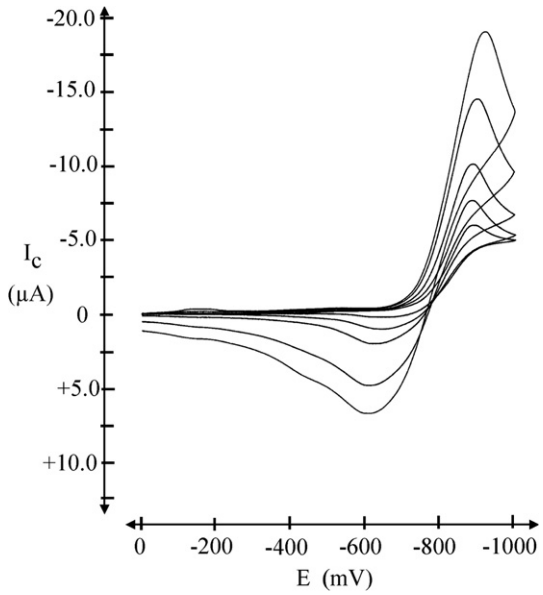


Fig. 8. Cyclic voltammogram of 3.911 mM $ALSH_2$ **1** on a HMDE at pH 10.53 at different scan rates of 5, 10, 20, 50, 100 mV s^{-1} (ground electrolyte 0.05 M NaCl).

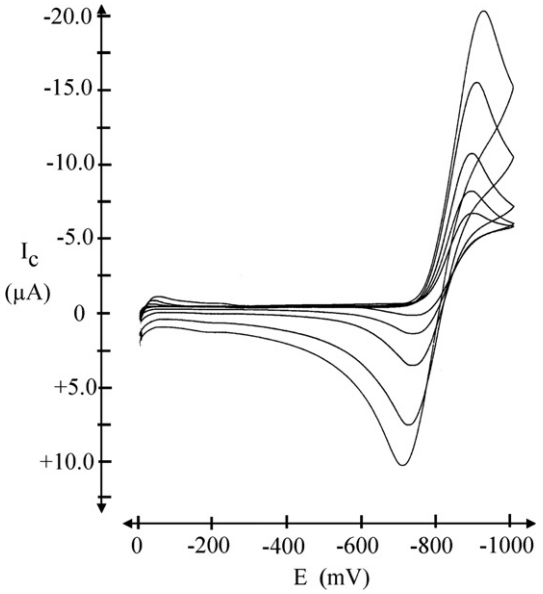


Fig. 9. Cyclic voltammogram of 3.844 mM $ALSH_2$ **1** on a HMDE at pH 12.10 at different scan rates of 5, 10, 20, 50, 100 mV s^{-1} (ground electrolyte 0.05 M NaCl).

at -700 mV can be attributed to oxidation of $ALSH^{3-}$ **8**, while the first peak at -400 mV indicates the oxidation of $ALSH_2^{2-}$ **4** (Eq. (8)).

The voltammogram at pH 10.5 (Fig. 8) shows the cathodic reduction of ALS^{2-} **3** to $ALSH^{3-}$ **5** (Eq. 8) and the voltammogram at pH 12.10 (Fig. 9) shows the reduction of ALS^{2-} **3** to ALS^{4-} **6** without involvement of consecutive protonation reactions (Eq. 9).

$$ALSH^- + 2e^- + H^+ \rightleftarrows ALSH_2^{2-} \quad (7)$$

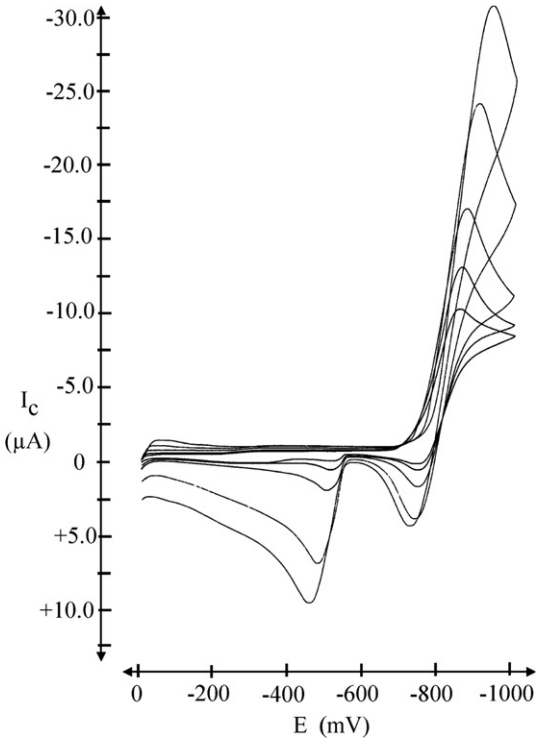


Fig. 10. Voltammograms of 3.844 mM $ALSH_2$ **1** in presence of 5 g L^{-1} VY1 on a HMDE at pH 11.945 at scan rate of 5, 10, 20, 50, 100 mV s^{-1} (ground electrolyte 0.05 M NaCl).

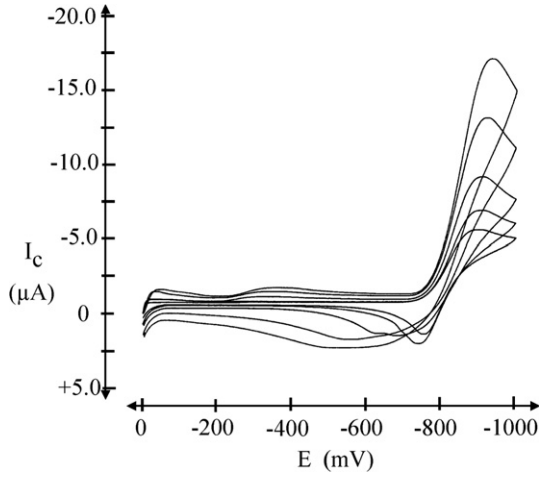


Fig. 11. Voltammograms of 3.826 mM $ALSH_2$ **1** in presence of 5.024 g L^{-1} VY46 on a HMDE at pH 11.937 at scan rate of 5, 10, 20, 50, 100 mV s^{-1} (ground electrolyte 0.05 M NaCl).

$$ALS^{2-} + 2e^- + H^+ \rightleftarrows ALSH^{3-} \quad (8)$$

$$ALS^{2-} + 2e^- \rightleftarrows ALSH^{4-} \quad (9)$$

The respective diffusion controlled cathodic peak potentials $(E_p)_d$ and cathodic peak currents $(I_p)_d$ of the system $ALSH_2$ **1** at different pH values are shown in Table 1.

3.3. Cyclic voltammetry of $ALSH_2$ *1* in the presence of dispersed dyestuff

For successful indirect cathodic reduction of dispersed vat dyes two basic requirements have to be fulfilled. The soluble redox couple has to be able to achieve negative redox potentials in sufficient height to achieve electron transfer to the dispersed pigment (Eq. 10). Secondly the pH value has to be high enough to ensure rapid dissolution of the leuco-form of the reduced vat dye. In the case of slow dissolution the surface of the particle will be covered with reduced dyestuff and the indirect reduction will be stopped. As a result, incomplete dyestuff reduction or no electron transfer at all will be observable in the CV.

$$ALS^{4-} + dye \rightleftarrows ALS^{2-} + dye^{2-} \quad (10)$$

When a dispersed vat dye present in the diffusion layer of the cathode then is reduced, the oxidised form of the anthraquinone is regenerated. The regeneration of the electroactive species leads to an increase in the respective cathodic current.

The overall reaction scheme then is similar to an electrode reaction with catalytic regeneration of the oxidised form of the electroactive component [22]. In Eqs. (11) and (12) O and R represent the oxidised and corresponding reduced form of the anthraquinone, Z corresponds to the dispersed vat dye and P stands for the leuco-vat dye.

$$\begin{array}{ccc} O + n\,e^- & \rightleftharpoons & R \\ \uparrow & & \downarrow \\ R + Z & \rightleftharpoons & O + P \end{array} \quad (11 \text{ and } 12)$$

A successful indirect cathodic reduction of dispersed organic substances can be detected in the CV by different diagnostic criteria.

- In the case of successful indirect reduction the cathodic peak current of the anthraquinoid mediator system increases, as oxidised anthraquinone is formed within the diffusion layer of the cathode as result of the coupled redox reaction. A description of the catalytic activity can be obtained by calculation of so-called enhancement factors *e.f.* $= (I_p)_c/(I_p)_d$ [23].
- The anodic peak of the mediator systems disappears, as the reduced form of anthraquinone has been consumed by the coupled reduction of dispersed vat dye.
- An additional anodic peak appears at a potential characteristic for the oxidation of the reduced vat dye.

Vat dyes then can be used to probe the reduction properties of reduced Alizarin Red S at different pH. Two different vat dyes were used as representatives, Vat Yellow 1 and Vat Yellow 46. According to literature data the reduction of Vat Yellow 1 proceeds in the range of −520 mV to −550 mV while for reduction of Vat Yellow 46 an approximately 200 mV more negative redox potential has to be established for successful dyestuff reduction [24]. The reduced dyestuff, the so-called leuco dye is formed at the surface of the dispersed particles and dissolves under sufficiently alkaline conditions.

The voltammograms of $ALSH_2$ **1** alone and in presence of Vat Yellow 1 or Vat Yellow 46 were recorded at different pH values between pH 2.6 and 12 with scan rates of 5–100 mV s^{-1} (Figs. 10 and 11).

In Table 2 the cathodic peak potential and cathodic peak current of $ALSH_2$ **1**, $ALSH^-$ **2** and ALS^{2-} **3** in presence of VY 1 are shown.

In Fig. 12 the *e.f.* $(I_p)_c/(I_p)_d$ for both combinations $ALSH_2$ **1**/VY1 and $ALSH_2$ **1**/VY46 are shown.

For VY 1 a distinct increase in *e.f.* is observable at pH 12, while for VY46 all values for *e.f.* remain below unity. Besides an increase in $(I_p)_c$, the cathodic peak potential of the soluble anthraquinone, the formation of reduced VY1 can be observed during the reverse scan. The oxidation of dissolved leuco-VY1 can be recognised at an oxidation peak with an anodic peak potential $(E_p)_a$ of −450 mV.

From the *e.f.* in Fig. 12 indirect cathodic reduction of VY1 can be proven at pH 12. From the *e.f.* in the range of pH 5.8–10.0 some dyestuff reduction could be expected, however CV experiments do

Table 1
Cathodic peak potential and cathodic current peak of $ALSH_2$ **1**, $ALSH^-$ **2** and ALS^{2-} **3** as function of pH and scan rate.

pH	c($ALSH_2$) mM	Scan rate mV s^{-1}	$(E_p)_d$ mV	$(I_p)_d$ μA
2.66	3.940	5	−390	5.0
		10	−390	6.3
		20	−410	8.5
		50	−430	12.5
		100	−450	16.8
5.02	3.927	5	−590/−860[a]	2.8/2.4
		10	−580/−860	3.5/3.0
		20	−590/−870	4.3/3.8
		50	−590/−890	6.5/5.0
		100	−630/−900	8.8/6.5
10.53	3.911	5	−900	5.8
		10	−890	7.3
		20	−880	10.0
		50	−910	14.3
		100	−910	18.8
12.10	3.844	5	−890	6.0
		10	−890	7.5
		20	−880	10.5
		50	−910	15.5
		100	−920	19.8

[a] Two peaks.

Table 2
Cathodic peak potential and cathodic current peak of $ALSH_2$ **1**, $ALSH^-$ **2** and ALS^{2-} **3** and in presence of VY1 or VY46 as function of pH and scan rate.

pH	c($ALSH_2$) mM	Scan rate mV s^{-1}	$(E_p)_d$ mV	$(I_p)_d$ μA	c(dyest) g L^{-1}
VY1					
3.07	3.940	5	−620[a]	6.0	5.014
		10	−490[a]	6.8	5.014
		20	−430	8.0	5.014
		50	−440	12.0	5.014
		100	−470	15.5	5.014
5.79	3.927	5	−550/−850	1.4/4.8	5.058
		10	−560/−850	2.0/5.5	5.058
		20	−540/−850	2.5/7.3	5.058
		50	−560/−900	4.3/9.6	5.058
		100	−580/−920	5.8/11.8	5.058
10.03	3.911	5	−840	7.6	5.090
		10	−850	9.4	5.090
		20	−850	13.0	5.090
		50	−890	17.8	5.090
		100	−910	22.0	5.090
11.95	3.844	5	−860	9.5	5.034
		10	−860	12.3	5.034
		20	−880	16.0	5.034
		50	−890	23.8	5.034
		100	−930	29.8	5.034
VY46					
3.59	3.950	5	−440/−520[b]	4.5	5.072
		10	−440/−520[b]	6.0	5.072
		20	−450/−530[b]	7.25	5.072
		50	−450/−530[b]	10.5	5.072
		100	−480/−560[b]	15.8	5.072
5.36	3.938	5	−530/−900	2.0/2.8	5.036
		10	−530/−900	2.3/3.5	5.036
		20	−530/−890	3.3/4.0	5.036
		50	−550/−890	5.0/6.3	5.036
		100	−550/−890	6.8/8.3	5.036
9.80	3.920	5	−880	5.3	5.016
		10	−880	6.8	5.016
		20	−880	8.5	5.016
		50	−900	13.0	5.016
		100	−890	18.4	5.016
11.94	3.826	5	−900	4.8	5.024
		10	−910	6.1	5.024
		20	−910	8.3	5.024
		50	−930	12.1	5.024
		100	−925	15.9	5.024

[a] Plateau.
[b] Second peak on −440 mV plateau.

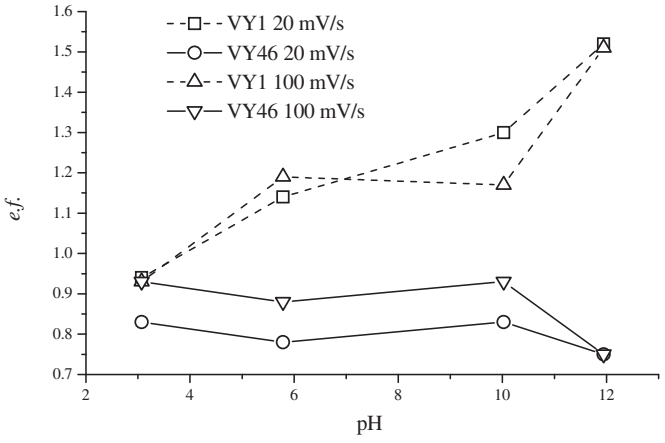


Fig. 12. *e.f.* as function of pH, at scan rates of 20 mV s^{-1} and 100 mV s^{-1} in presence of VY1 or VY46.

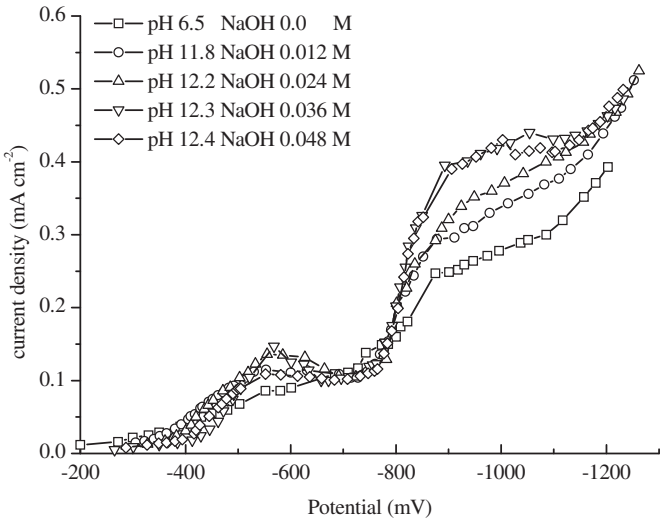


Fig. 13. Voltammogram of $ALSH_2$ **1** 0.0040 M in presence of 0 M NaOH (pH = 6.5), 0.012 M (pH = 11.8), 0.024 M (pH = 12.2), 0.036 M (pH = 12.3), 0.048 M (pH = 12.4).

not indicate successful reduction of the dispersed dyestuff. At pH 10 the cathodic peak potential of ALS^{2-} **3** is sufficiently negative to achieve reduction of the dispersed VY1 however slow dissolution and low solubility of reduced VY1 could be responsible for the absence of an anodic current peak for oxidation of reduced VY1.

In case of VY46 e.f. values below 1 do not indicate any redox reaction between the dispersed vat dye and the ALS. In the voltammograms in Fig. 11 lower anodic peak currents attributed for oxidation of ALS^{4-} **6** could indicate disappearance of the formed ALS^{4-} **6**. The absence of a clear anodic peak for oxidation of reduced VY46 does not support the assumption of a successful electron transfer from ALS^{4-} **6** to VY46. An explanation for these findings could be a slow dissolution reaction of reduced VY46, which then limits the rate of reduction. As a result only low amounts of dyestuff are reduced during the time scale of the CV-scan and no detectable amounts of dissolved reduced dyestuff are present in solution.

3.4. Voltammogramms in a flow cell

In alkaline solution neutralisation of $ALSH^-$ **2** to ALS^{2-} **3** should influence current density in voltammetry. Thus a series of voltammograms in a flow cell with increasing NaOH concentration in the catholyte were recorded. Fig. 13 shows voltammograms of 0.0040 M $ALSH_2$ **1** in presence of increasing concentrations of NaOH corresponding to pH 6.5 to 12.4.

The diffusion controlled cathodic current plateau, which is observed in the potential range of −850 to −1100 mV increases with pH as the concentration of ALS^{2-} **3** increases. Above pH 12.3 no further increase is observed. $ALSH_2$ **1** is present in the fully dissociated form ALS^{2-} **3** and the cathodic reduction leads to the reduced form ALS^{4-} **6** (compare Figs. 3 and 4).

4. Conclusions

From the CV experiments it can be deduced, that in the pH range of 2–11 the cathodic reduction of $ALSH_2$ **1** follows a pH-dependent series of electron transfer reactions and consecutive protonation reactions.

The oxidised form of Alizarin Red S is present as $ALSH_2$ **1**, $ALSH^-$ **2** or ALS^{2-} **3**, above pH 12 ALS^2 **3** is the prevailing species. Five different reduced species of Alizarin Red S $ALSH_4$ **7**, $ALSH_3^-$ **8**, $ALSH_2^{2-}$ **4**, $ALSH^{3-}$ **5** and ALS^{4-} **6** were detected by photometry.

In unbuffered solution, e.g. at pH 5, protonation of the reduced anthraquinone increases the pH value in the boundary layer of the cathode and as a result two cathodic and two anodic current peaks were observed during a CV-scan. The cathodic reduction of an anthraquinone group leads to a pH shift in the surrounding aqueous solution. Thus reduction of the anthraquinoid group in $ALSH_2$ **1**, $ALSH^-$ **2**, and ALS^{2-} **3** causes an increase in pH, while reoxidation will decrease the pH value. In alkaline solution above pH 12 both the oxidised form ALS^{2-} **3** and the reduced form ALS^{4-} **6** are the main species involved in the redox reaction thus the overall redox reaction can be formulated according Eq. 13.

$$ALS^{2-} + 2e^- \rightleftarrows ALS^{4-} \quad (13)$$

$$ALS^{4-} + VY1 \rightleftarrows ALS^{2-} + VY1^{2-} \quad (14)$$

The reduction potential of ALS^{2-} **3** is sufficiently negative to achieve rapid dyestuff reduction of VY1 (Eq. 14). In case of VY46 at pH 12 the redox potential of the ALS^{2-} **3**/ALS^{4-} **6** couple should be sufficiently negative to reduce VY46. However, no indirect reduction of VY46 was observed, which can be explained by rather slow dissolution of reduced dyestuff.

In CV experiments at pH 10 and lower no indication of a successful indirect cathodic reduction of dispersed dye was found. This can be explained both, with an insufficient negative potential of the anthraquinoid redox couple and with low solubility of leuco-vat dyes at pH values below 11.

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