Photogalvanic Cells. Part 14.† The Synthesis and Characterization of Disulphonated Thionines

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Two reasons for the poor performance of the iron–thionine photogalvanic cell are first the low solubility of thionine, which means that the incident solar radiation is absorbed too far from the illuminated electrode, and secondly the formation of dimers which do not undergo the desired photoredox reaction. The synthesis and photoelectrochemical characterization of several isomeric disulphonated thionines are reported. All the isomers examined are sufficiently soluble to absorb solar radiation close to the illuminated electrode of a photogalvanic cell and show no evidence of dimerization *via* stacking interactions at concentrations up to 10^{-3}M. Using the following techniques, the transparent disc electrode, flash photoelectrolysis, and stopped flow, the kinetic parameters have been determined to see how well the conditions needed for an efficient photogalvanic system are met. The 4,6-isomer of disulphonated thionine is the only isomer that fulfills the required kinetic constraints.

As yet very low efficiencies ($<0.1\%$) [1,2] have been found for solar energy conversion using the iron–thionine system in a photogalvanic cell (see Figure 1). Theoretical considerations [3-5] indicate that efficiencies as high as 18% could be obtained. To improve the efficiency it is essential that the light should be absorbed within *ca.* 10^{-4} cm of the illuminated electrode. This constraint arises because the unstable electron-transfer products must be generated close to the illuminated electrode to avoid thermal back reaction in the bulk and so allow them to reach the electrodes.

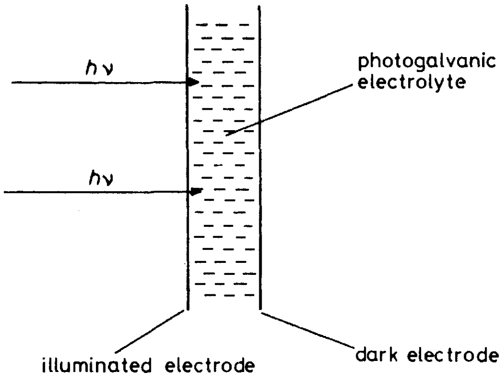

FIGURE 1 A typical photogalvanic cell

The iron–thionine system has many features which are essential for the efficient cell,[6] relatively slow back-reaction kinetics, high quantum efficiency, and a large extinction coefficient well placed with respect to the solar spectrum. In addition there exists a selective electrode [7,8] at which the thionine couple can react but the Fe^{II}–Fe^{III} couple is blocked. However, the low solubility of the dye means that most of the light is absorbed too far from the illuminated electrode to be of any use.

In this paper we report the synthesis and characterisation of disulphonated derivatives of thionine, which are more soluble, and examine the extent to which the modified dyes retain the desirable features of the thionine system. For their characterisation as photogalvanic dyes we use the approach developed with thionine,[6] namely the techniques of the transparent rotating-disc electrode, flash electrolysis, stopped flow, and the study of electrochemical parameters using conventional rotating-disc electrode techniques.

Preparation of Disulphonated Thionines (*DSTS*).—We first attempted to prepare disulphonated thionines by the direct introduction of sulphonic acid groups into the thionine nucleus. A wide variety of reaction conditions were investigated but the reaction consistently led to complex mixtures of mono and higher sulphonated products which proved impractical to separate. We have therefore developed synthetic methods which make the phenothiazine nucleus with the required substituents.

Thionine (Lauth's Violet) can be easily prepared in high yield by the oxidative coupling of two molecules of *p*-phenylenediamine (1a) in the presence of hydrogen sulphide [9-11] (Scheme 1; X = H). However, when we performed the same experiment with the corresponding sulphonated derivative (1b) (2,5-diaminobenzenesulphonic acid), the coupling of the two monomeric units did not proceed efficiently and led to very low yields of phenothiazine products (Scheme 1; $X = SO_3H$). An insoluble red product was formed; this is probably similar to 'Aniline Black' which is a minor product when X = H.

A more successful approach was to modify Bernthsen's classical synthesis [12-15] for Methylene Blue [3,5-bis(dimethylamino)phenothiazonium hydrochloride].[16] The oxidative coupling in aqueous acetic acid solution of 2,5-diaminobenzenesulphonic acid (1b) and aniline-2-sulphonic acid (4) in the presence of sodium thiosulphate and aluminium sulphate (Scheme 2) afforded a reasonable yield of a very soluble blue material, $\lambda_{max.}$ (H_2O) 580—585 nm, which was found to be a 1 : 10 mixture of two isomeric disulphonated thionines, DST-1, $\lambda_{max.}$ (H_2O) 585 nm, and DST-2, $\lambda_{max.}$ (H_2O) 580 nm. The two isomers were separated by extensive column chromato-

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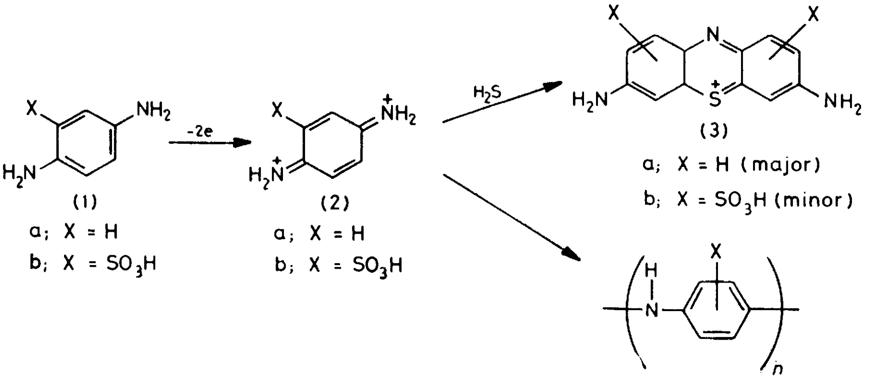
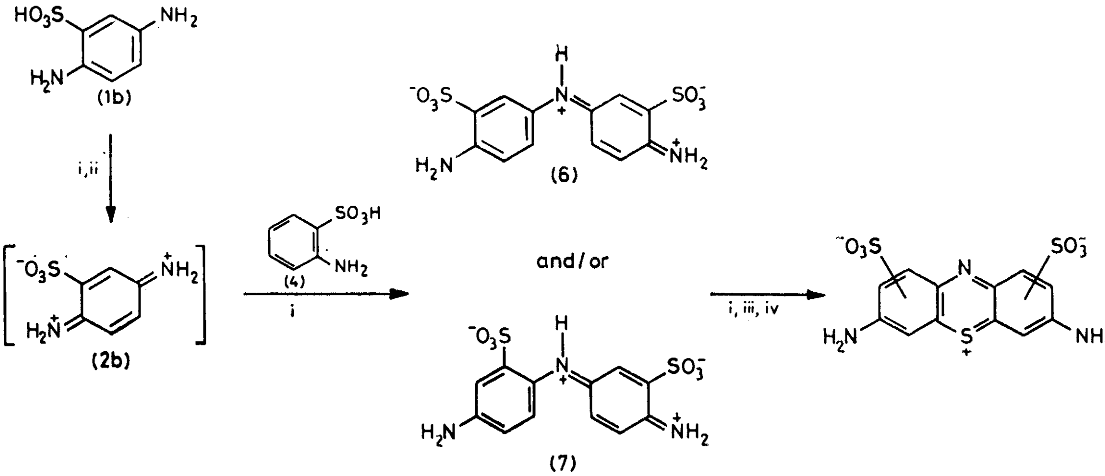
† Part 13 is ref. 32.

graphy,* the fast-running fraction (DST-1) being the minor component of the mixture. In this manner we obtained a sufficient quantity of each isomer (DST-1 <1 mg, DST-2 *ca.* 10 mg) to enable us to carry out their photoelectrochemical characterisation.

We obtained the n.m.r. spectrum of DST-2 but owing to cross-ring coupling it was impossible to make a definitive structural assignment. We therefore determined the position of the sulphonate groups in these isomers by the following argument.



SCHEME 1



SCHEME 2 Reagents: i, $Na_2Cr_2O_7$; ii, $H_2O-CH_3CO_2H$; iii, $Na_2S_2O_8$; iv, $Al_2(SO_4)_3$

The synthesis in Scheme 2 can only produce isomers which are disulphonated with one sulphonate group in each ring; there are six such isomers but because of the structures of the two isomeric indamines [(6) and (7) in Scheme 2] only five can be formed. To determine which indamine produces DST-1 and DST-2 we synthesised disulphonated thionines which can only be formed from indamine (7) according to Scheme 3. Aromatic nucleophilic displacement of chloride ion[17] from 2-chloro-5-nitrobenzenesulphonic acid (8) (prepared from *p*-chloronitrobenzene)[18] by 2,5-diaminobenzenesulphonic acid (1b) in water at 100 °C in the presence of base afforded a 90% yield of a single nitrodiphenylamine (9) which was isolated and characterized spectroscopically as the barium salt. We assign structure (9) to this compound since the coupling of *ortho*-substituted anilines is unfavourable and requires much more vigorous reaction conditions. The ^{1}H n.m.r. spectrum of the barium salt (D_2O-[$^{2}H_6$]DMSO) is also consistent with our postulated assignment. When the nitrophenylamine (9) was reduced to the diamine (10) with Zn–dilute H_2SO_4 followed by oxidative ring closure *under the same reaction conditions* used for DST-1 and DST-2 (Scheme 2), two *different* isomeric disulphonated thionines (DST-3 and DST-4) were obtained in a ratio of 1 : 1 000 (Scheme 3). This proves that DST-1 and DST-2 are produced through the intermediacy of indamine (6) and that the structures possible for these

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* Column chromatography was carried out under a positive pressure (2—5 lb in^{-2}) of high purity nitrogen gas. Brockman neutral alumina, (activity I) (eluent ethanol–aqueous acidic methanol) gave the best separations but the elution of fractions was rather slow. Merck t.l.c. silica gel (type G) (eluant ethanol) was less satisfactory, but gave quicker separations. Each pure isomer gave a single spot on t.l.c. (Merck silica gel plates, 0.25 mm, 2 × 7 cm; solvent system butanol-propanol–conc. ammonia–water 4 : 4 : 1 : 1). All volatile organic materials were removed in vacuum, the last traces co-distilled with double distilled water several times, and the resulting solution subjected to ion-exchange chromatography (Dowex 50 in the Na$^+$ form).

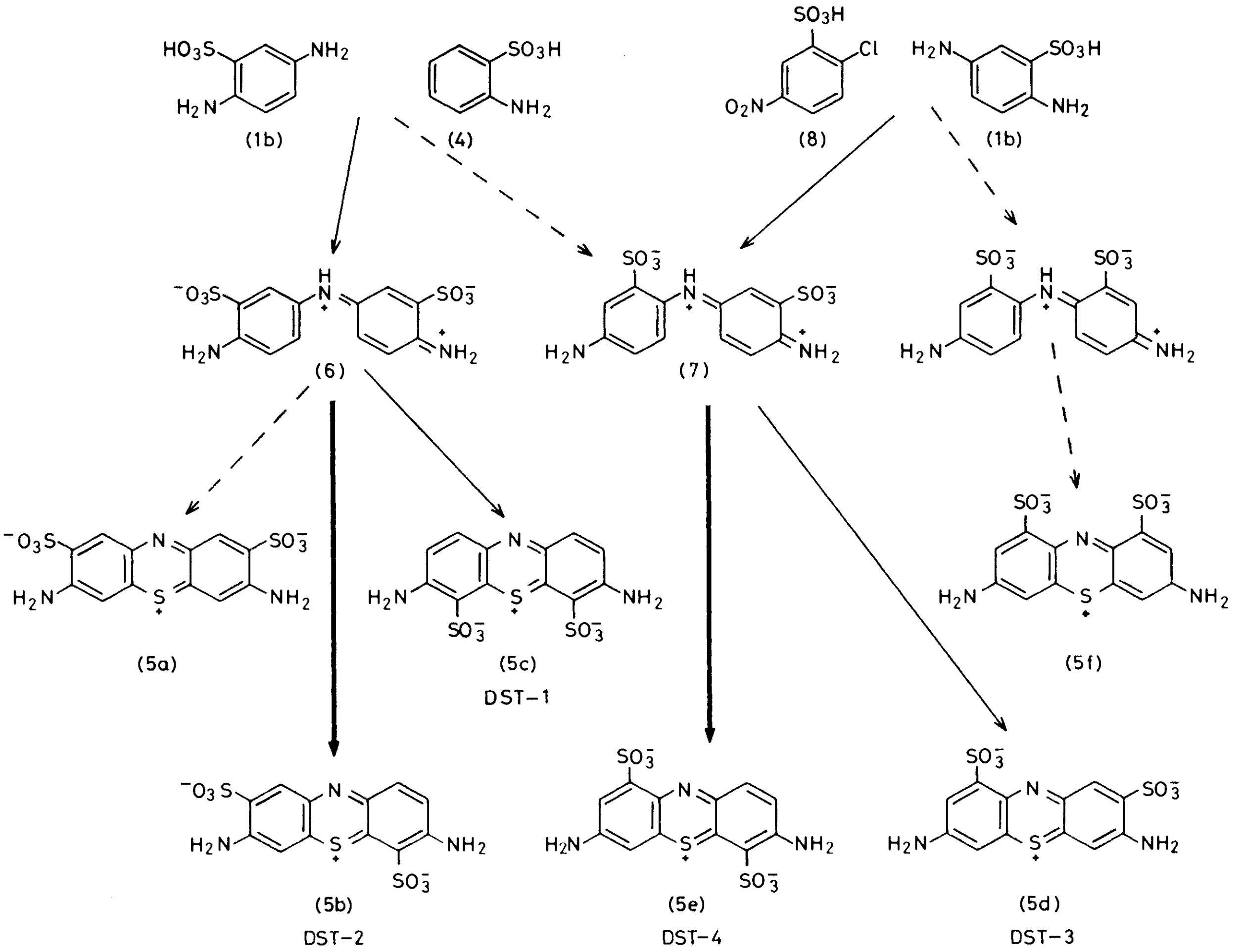
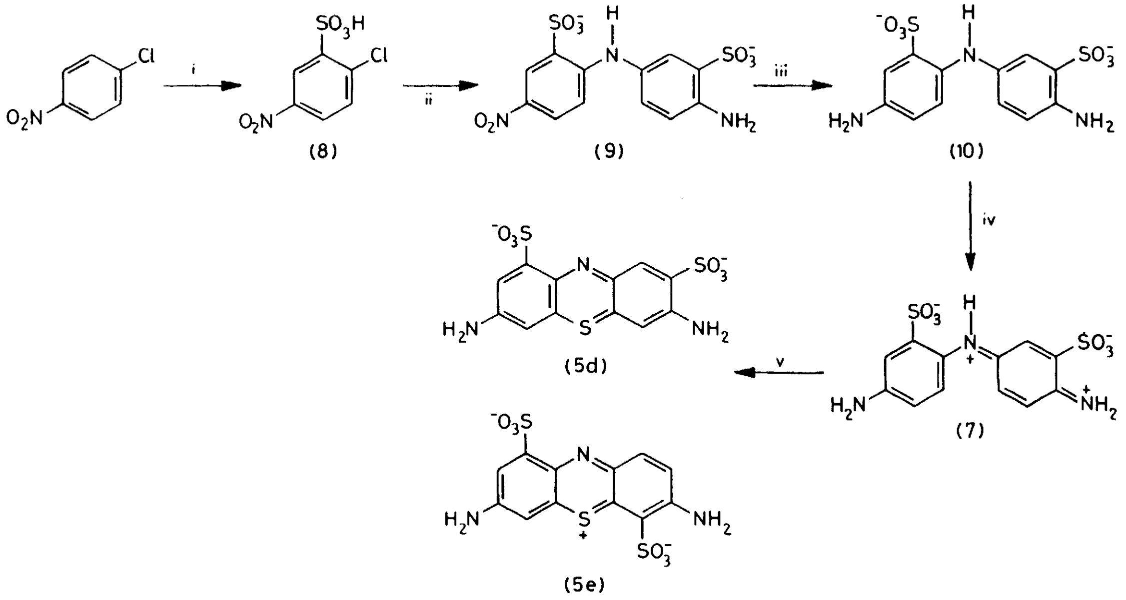


FIGURE 2 The overall reaction scheme for the synthesis of the four isomers of disulphonated thionine. The relative widths of the arrows indicate the major and minor product; broken arrows show routes to products that were formed in insignificant proportions



SCHEME 3 Reagents: i, H_2SO_4–25% SO_3–3 h–110 °C; ii, (1b)–aqueous base–100 °C; iii Zn–H_2SO_4; iv, $Na_2Cr_2O_7$; v, $Na_2S_2O_3$–$Al_2(SO_4)_3$

two isomers are (5a—c) as shown in Figure 2. The exclusive formation of indamine (6) in Scheme 2 can be rationalised in terms of the electronic effect of the sulphonic acid group in *p*-quinonedi-imine (2b) which directs the attack of orthanilic acid (4) to take place at the *meta*-nitrogen [producing intermediate (6)] rather than at the *ortho* [leading to intermediate (7)]. Similar considerations explain the exclusive formation of indamine (7) in Scheme 3.

Further evidence for the structures of DST-1 and DST-2 was obtained from the ^{1}H n.m.r. spectrum (Fourier transform; 100 MHz) of DST-2, which is the only pure isomer we could produce free from transition-metal ions in sufficient quantity to allow recording of its ^{1}H n.m.r. spectrum. The spectrum shows a set of four different aromatic signals and, although it does not allow a first-order signal assignment due to cross-ring coupling, it is consistent only with structure (5b).

Based on electronic effects,[19] we suggest that the addition of sodium thiosulphate to the indamines (6) and (7) (Schemes 2 and 3) to give corresponding thiosulphonic acids should take place exclusively at those positions *ortho* to the sulphonate groups. Subsequent ring closure to the thiazine nucleus should then be expected to lead to DST-1 [structure (5c) in Figure 2] as the major product of the reaction from indamine (6). However, in this case there is considerable steric crowding of the sulphonates in the transition state for ring closure, and DST-2 (5b) is therefore the preferred product. None of structure (5a) is found since the directing effect of both sulphonates is unfavourable. Applying the same considerations to reactions in Scheme 3 leads us to assign structures (5d and e) respectively to DST-3 and DST-4 (Figure 2) with DST-4 being the major product.

EXPERIMENTAL

The apparatus and technique for the transparent rotating-disc electrode has been described previously.[6,20] The irradiance of the light passing through the electrode was measured using a Metrologic Radiometer. The diffusion coefficients of the sulphonated thionines were measured using the method of Hitchman and Albery.[21] The stopped-flow experiments were carried out using a Nortech SF2A stopped flow spectrometer. The u.v.–visible spectra of the new dyes were measured using a Cary 14 spectrophotometer. All chemicals and solutions, except the disulphonated thionines, were prepared as described previously.[22] All experiments were carried out at 25 °C in 50mM-H_2SO_4.

RESULTS AND DISCUSSION

The reaction scheme for the iron–thionine system is [5,6,22-26] shown in Scheme 4, where Th is the thiazine dye, S· its one-electron reduction radical product, and L its fully reduced leuco-form. The variation of the photocurrent with irradiance, rotation speed, and [Fe^{III}] showed that the mechanism for the disulphonated thionines was the same as that for thionine. We now outline the experiments typically performed on each new dye to be characterized and describe how the kinetic parameters can be obtained from the experimental data.

The u.v.–visible spectra of all four isomers are similar to that of thionine with maxima in the range 580—593 nm with the important exception that there is no evidence for dimerisation up to concentrations of 10^{-3}M. This is in marked contrast to thionine,[27-31] Methylene Blue [27,30] and other commercially available thiazine dyes such as New Methylene Blue NN.[32] This is a satisfactory feature because the dimers are photoelectrochemically inactive as they do not undergo the photoredox reaction.[29,33] Furthermore, the solubility of all the isomers is $>10^{-2}$M and therefore is much closer to the ideal value of 10^{-1}M than the corresponding figure for thionine (*ca.* 10^{-3}M).

$$\mathrm{Th} \xrightarrow{h\nu} \mathrm{Th}^*$$

$$\mathrm{Th}^* \xrightarrow{k_t} \mathrm{Th}$$

$$\mathrm{Th}^* + \mathrm{Fe(II)} \xrightarrow{k_q} \mathrm{S}^{\cdot} + \mathrm{Fe(III)}$$

$$\mathrm{S}^{\cdot} + \mathrm{Fe(III)} \xrightarrow{k_{-1}} \mathrm{Th} + \mathrm{Fe(II)}$$

$$\mathrm{S}^{\cdot} + \mathrm{S}^{\cdot} \xrightarrow{k_3} \mathrm{Th} + \mathrm{L}$$

$$\mathrm{L} + \mathrm{Fe(III)} \xrightarrow{k_{-2}} \mathrm{S}^{\cdot} + \mathrm{Fe(II)}$$

Illuminated electrode

$$\mathrm{L} \longrightarrow \mathrm{Th} + 2\mathrm{e}$$

Dark electrode

$$\mathrm{Fe(III)} + \mathrm{e} \longrightarrow \mathrm{Fe(II)}$$

SCHEME 4

As a result of the much increased solubility of the sulphonated dyes it is difficult to obtain pure solid samples for direct determination of the extinction coefficient, ε. Here we present a method for determining the concentration of the dye and hence its extinction coefficient by a combination of electrochemical measurements. The method of Hitchman and Albery [21] allows the determination of the diffusion coefficient of an electroactive substance independent of the concentration and the number of electrons transferred. The technique consists of the exhaustive electrolysis of a known volume of solution at a rotating-disc electrode. The decay of limiting current with time obeys first-order kinetics and a plot of $\ln|i_L|$ *versus* t has a slope given by equation (1) where A is the electrode area, W is the rotation speed in Hz, ν is the kinematic viscosity, and V is the volume of solution. A typical plot of $\ln|i_L|$ *versus* t is shown in Figure 3.

$$|\mathrm{slope}|_{\mathrm{HA}} = 1.554\, A W^{1/2} D^{2/3} / \nu^{1/6} V \qquad (1)$$

Using this value of D and assuming two electrons are transferred (as is the case for thionine) we can obtain c_∞, the concentration of the dye, from the slope of a plot of i_L *versus* $W^{\frac{1}{2}}$ using the Levich equation [34] (2). A typical Levich plot is shown in Figure 4. Knowing c_∞, if the absorbance of this solution is measured then a value for the extinction coefficient, ε, can be obtained. Values

$$|\mathrm{slope}|_{\mathrm{L}} = 1.554 A F \nu^{1/6} D^{2/3} n c_\infty \qquad (2)$$

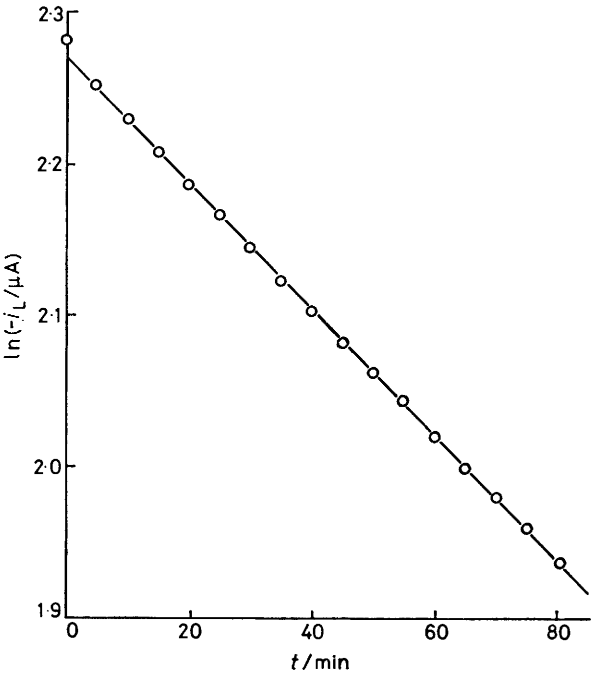


FIGURE 3 Typical variation of the limiting current with time to find the diffusion coefficient according to equation (1)

of D and ε are given in the Table along with values for the half-wave potentials $E_{\frac{1}{2}}$.

Stopped flow was used to measure k_{-2}, the rate constant for the reaction between Fe^{III} and the leuco-form of the dye. In all stopped-flow experiments the leuco-form was produced by electrochemical reduction of the parent dye. The same rate constant was determined using the complementary technique of flash electrolysis. The results are summarised in the Table. For DST-4 plots of $k_{obs.}$ *versus* [Fe^{III}] were curved.

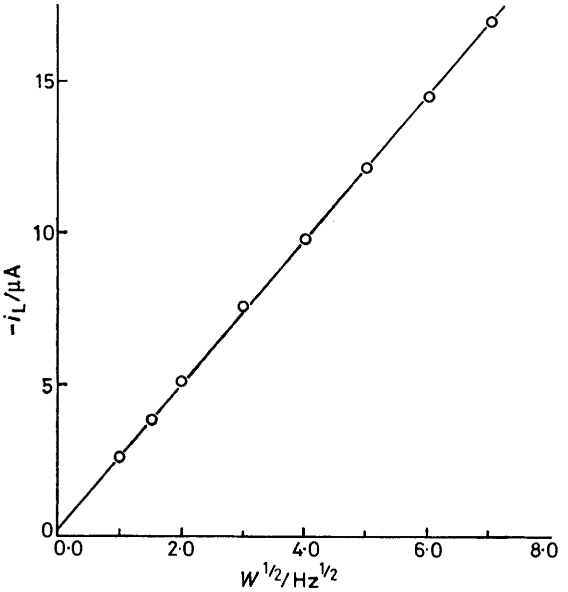


FIGURE 4 Typical variation of the limiting current with rotation speed to find the concentration of the disulphonated thionine according to equation (2)

Properties of disulphonated thionines

	DST-1	DST-2	DST-4	Thionine
$\lambda_{max.}$/nm	585	580	593	599
D/cm^2 Ms^{-1}	1.9	5.2		5.8
ϵ/cm^2 μmol^{-1} [a]	161	115		129
K_Q/mmol dm^{-3}	1.0	1.0		4
$(\phi_1)_\infty$ [b]	0.56	0.27		0.55
(k_{-1}^2/k_3)/dm^3 mol^{-1} s^{-1}	27	50		8
k_{-2}/dm^3 mol^{-1} ms^{-1}	0.80 [c]	2.0 [c]	10.8 [c,d]	0.43 [c]
	1.20 [e]	2.2 [f]	8.4 [f,d]	0.43 [f]
		2.5 [e]		0.56 [e]
k/s^{-1}			90	
			70	
$E_{\frac{1}{2}}$/mV [g]	188	177	145	208

[a] These values are natural rather than decadic extinction coefficients. [b] The quantum efficiency when [Fe^{II}] ≫ K_Q. [c] Measured by flash electrolysis. [d] Calculated from $k_{-2} = Kk$ with K/dm^3 mol^{-1} = 120. [e] Measured by transparent rotating-disc electrode. [f] Measured by stopped flow. [g] Measured with respect to a saturated calomel electrode.

This behaviour was attributed to complexation between L and Fe^{III} according to Scheme 5 for which we obtain equation (3). The results are shown in Figure 5 and values for k and K calculated from the gradient and intercept are reported in the Table.

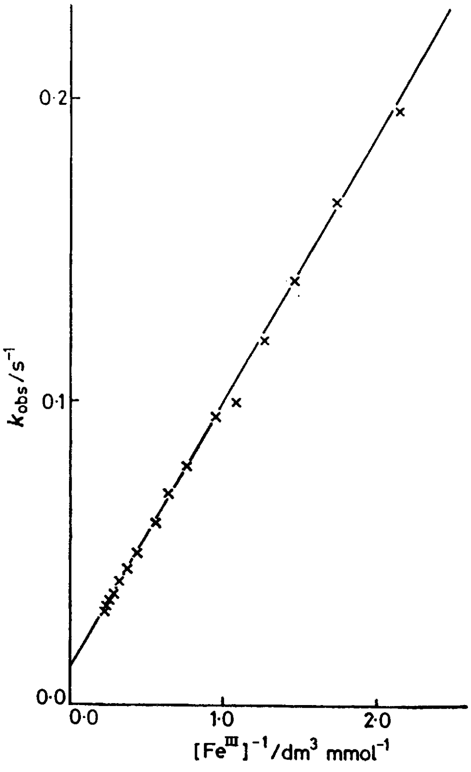


FIGURE 5 Plot of observed rate constant against [Fe^{III}] according to equation (3) to find K, which describes the formation of a complex between Fe^{III} and L

We now turn to the photoelectrochemical characterisation using the transparent rotating-disc electrode. Action spectra for the new dyes were measured and in all cases their shape was identical to the corresponding absorption spectrum. With no added [Fe^{III}] the kinetics of the back reactions are negligible. Then from the size of the photocurrent, which varies with $W^{-\frac{1}{2}}$, we can measure the efficiency of the photochemical production

$$\frac{1}{k_{\text{obs.}}} = \frac{1}{kK[\mathrm{Fe(^{III})}]} + \frac{1}{k} \tag{3}$$

$$\mathrm{Fe^{III}} + \mathrm{L} \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} \underset{\text{complex}}{[\mathrm{Fe^{III}{\cdot}L}]} \xrightarrow{k} \mathrm{Fe^{II}} + \mathrm{S^{\cdot}}$$

SCHEME 5

of leucothionine as given in equation (4). In this equation the characteristic lengths $X_{\mathrm{D},1}$, the diffusion length at $W = 1$ Hz, and X_ϵ the absorption length are given by equations (5) and (6) and the photon current, $i_{h\nu}$, by equation (7) in which $I_{\Phi=1}$ is the irradiance (in mol cm^{-2} s^{-1}) with no neutral density filter. Φ is the fraction of light transmitted by the neutral density filter, ϕ_1 is the quantum efficiency for the production of

$$i_{\mathrm{p}} = 2\phi_1\phi_2\Phi i_{h\nu}\frac{X_{\mathrm{D},1}}{X_\epsilon}W^{-\frac{1}{2}} \tag{4}$$

$$X_{\mathrm{D},1} = 0.64\ D^{1/3}\ \nu^{1/6} \tag{5}$$

$$X_\epsilon = (\varepsilon[\mathrm{Th}])^{-1} \tag{6}$$

$$i_{h\nu} = AF\,I_{\Phi=1} \tag{7}$$

semithionine in Scheme 4, and ϕ_2 is the fraction of semithionine that is converted to leucothionine; with no added [Fe^{III}] $\phi_2 = \frac{1}{2}$.[6] Typical results are plotted according to equation (4) in Figure 6.

The quantum efficiency ϕ_1, varies with [Fe^{II}] according to equation (8). Combining equations (4) and (8) we obtain (9). Typical results are shown in Figure 7 and values of the Stern–Volmer constant K_{Q}, which is equal to $k_{\mathrm{t}}/k_{\mathrm{q}}$ in Scheme 4, are given in the Table.

$$\phi_1^{-1} = (\phi_1)_\infty^{-1}\,(1 + K_{\mathrm{Q}}/[\mathrm{Fe^{II}}]) \tag{8}$$

$$\frac{\Phi}{i_{\mathrm{p}}W^{\frac{1}{2}}} = \frac{X\varepsilon}{(\phi_1)_\infty i_{h\nu}X_{\mathrm{D},1}}(1 + K_{\mathrm{Q}}/[\mathrm{Fe^{II}}]) \tag{9}$$

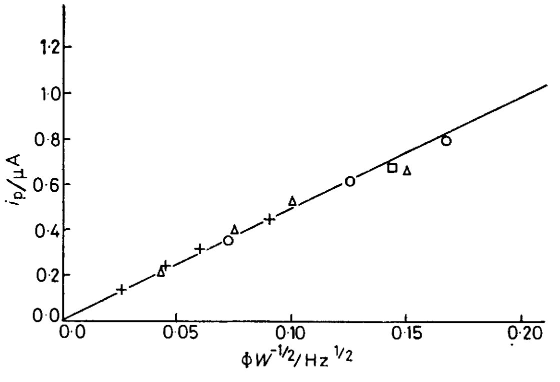


FIGURE 6 Variation of photocurrent with rotation speed W and irradiance Φ according to equation (4) where Φ is the transmittance of the neutral density filter used: values of Φ are ■, 1.0; ●, 0.50; ▲, 0.30; +, 0.18

Addition of iron(III) enables us to investigate the homogeneous back reactions of S$^{\cdot}$ and L in the manner described in Part 10.[6] In this way we obtain the parameters (k_{-1}^2/k_3) and k_{-2} which are given in the Table. Also included in the Table are the data for the parent compound thionine obtained previously.[6] Of the three new isomers the second-order rate constant for the back-reaction of DST-4 is too rapid to meet the criterion for the ideal cell that k_{-2}/dm^3 mol^{-1} ms^{-1} < 1. It is interesting that the formation of the complex between L and Fe^{III} means that the reaction is described by the first-order rate constant k at high concentrations of Fe^{III} and under these conditions the rate was not further increased with increasing [Fe^{III}]. However, this value of k/s^{-1} is also greater than the ideal value of 10. For these reasons no further characterisation of DST-4 was carried out. For other isomers the formation of a somewhat more stable complex may be an advantageous feature. Of the other two isomers DST-1 is preferred to DST-2 because its value of ϕ_1,k_{-2} and k_{-1}^2/k_3 are all significantly better, and in the case of k_{-2} and k_{-1}^2/k_3 just meet the criteria for the ideal cell. The only disadvantage of DST-1 is the lower value of its diffusion coefficient. The substitution of two sulphonate groups therefore appears more successful than thionine-1-sulphonic acid investigated previously.[35]

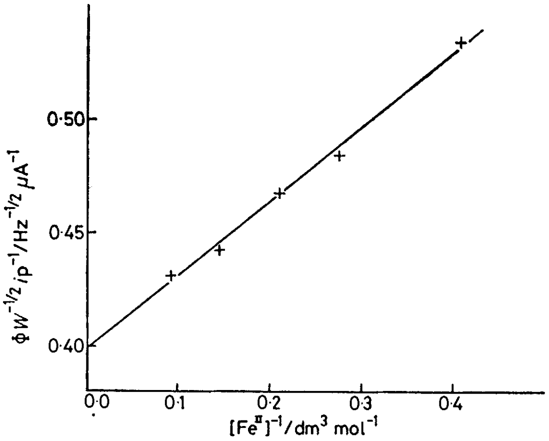


FIGURE 7 Variation of photocurrent with [Fe^{II}] plotted according to equation (9) to find the Stern–Volmer quenching constant K_{Q}

Turning finally to the electrochemistry of the isomers, current–voltage curves on a rotating platinum disc electrode show that the couples are almost completely reversible. Hence the values of $E_{\frac{1}{2}}$ reported in the Table are almost identical to the values of $E^\ominus$. Compared to thionine the shifts in voltage mean that a cell would develop somewhat larger voltages. But the increased thermodynamic driving force for the back reaction means that the values of the rate constant k_{-2} and k_{-1} also increase. Figure 8 shows a linear free energy relationship between log k_{-2} and $E_{\frac{1}{2}}$. A value of α for the reaction cannot be obtained because $E_{\frac{1}{2}} \simeq E^\ominus$ refers to the two-electron transfer whereas k_{-2} refers to only one step; also this step must involve proton transfer

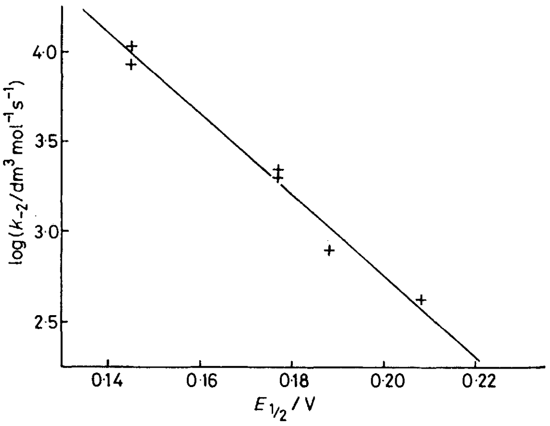


FIGURE 8 A linear free energy relationship between the rate constant for the back-reaction k_{-2} and the half-wave potential $E_{\frac{1}{2}}$ for different thiazine dyes

as well. However, the linear free energy relationship does underline one of the problems with developing these cells. Systems that produce a reasonable voltage will also have back-reactions that are too fast.

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