TRANSIENT SPECTRA AND DECAY KINETICS OF SEMITHIONINE RADICALS IN SODIUM DODECYLSULPHATE MICELLAR MEDIA

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Summary

The transient spectra and decay kinetics of semithionine species produced by the photoreduction of thionine by ferrous ions were studied in sodium dodecylsulphate (SDDS) micellar media. The results were compared with data obtained for a homogeneous aqueous medium. It was found that, whereas in the homogeneous aqueous medium there is evidence for the interaction of the semithionine species with ferrous ions, particularly at higher pH values and high ferrous ion concentrations, this is not the case in the micellar medium. Further, the decay of the semithionine species which is a kinetically second-order dismutation process in the homogeneous aqueous medium becomes pseudo first order in the SDDS micellar medium and is attributable to re-oxidation of semithionine by ferric ions adsorbed on the same micelle surface. From a comparison of the spectra in the two media at different pH values it is inferred that the species is more likely to be the doubly protonated semithionine TH_3^{2+} form in the micelle in the pH range 0 - 2.5. Addition of high concentrations of electrolytes such as NaCl had no effect on the spectrum of the species in the micellar medium, but the decay reverted to second order. This has been interpreted in terms of displacement of the ferric ions from the micelle surface into the bulk aqueous phase such that dismutation becomes the only pathway available for semithionine decay. The dismutation rate was found to decrease with increases in the concentration of the micellized surfactant in qualitative agreement with the pseudophase model of micellar kinetics.

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1. Introduction

The importance of organized molecular assemblies such as micelles, bilayers and membranes in controlling the course of chemical reactions, particularly those of relevance to the problem of light energy conversion has been well recognized in the recent past [1]. The thionine–ferrous redox system has attracted considerable attention from the point of view of light energy conversion. Recent studies by Kamat *et al.* [2] have indicated that

the low power conversion efficiency in this system is mainly due to the fast re-oxidation of the photoproduced reduced thionine species in the bulk solution compared with their discharge at the electrode. The electroactive reduced species in this system has been recognized [2] to be leucothionine formed by the fast disproportionation of the initially formed semithionine species [3 - 6]. Obviously, therefore, any parameter that would affect the rate of this disproportionation could also influence the photogalvanic effect in the ferrous–thionine system. In view of the known influence of surfactant micelles on reaction rates [7], we undertook a study of the ferrous–thionine photoredox system in micellar media. Our preliminary results in sodium dodecylsulphate (SDDS) micellar media have been reported earlier [8]. The full details of this work are described in the present paper.

2. Experimental details

Thionine (Fluka; purity, 99% or more) and SDDS (Fluka; purity, 95% or more) were purified by methods described earlier [9]. All other chemicals used were the purest commercially available and were used as such. Ferrous solutions prepared from ferrous ammonium sulphate ($FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$) contained ferric ion as an impurity. This minimal ferric impurity was estimated to be 9.7×10^{-6} mol dm^{-3} in a 1.5×10^{-2} mol dm^{-3} ferrous solution. Experiments were normally carried out with such solutions containing minimal ferric impurity or, when required, with ferric externally added as ferric ammonium sulphate. Some experiments were also carried out with completely ferric-free solutions prepared by reduction with zinc under a completely inert atmosphere or by dissolution of AnalaR iron wire in deaerated aqueous H_2SO_4. Unless otherwise stated, the solutions contained 5×10^{-6} mol dm^{-3} of protonated thionine TH$^+$, 0.015 mol Fe^{2+} dm^{-3} and a minimal amount of Fe^{3+} and were acidified with H_2SO_4 to a pH of about 2.5. They were deaerated by bubbling oxygen-free argon through them for about 30 min and transferred to a Pyrex cell of 10 cm path length under an argon atmosphere before they were subjected to flash photolysis. The flash photolysis apparatus employed has been described previously [10].

3. Results and discussion

3.1. Transient spectra in homogeneous aqueous systems

The transient spectra recorded in homogeneous aqueous systems under various conditions are shown in Fig. 1. As previously reported [4, 10], at pH 2.5 these spectra, attributable to the photoproduced semithionine species TH$_2^+$, have a characteristic maximum around 760 nm. At lower Fe^{2+} concentrations the spectra are devoid of any structure. With increasing Fe^{2+} concentration there is a gradual increase in absorbance due to the increased extent of the photoreduction of thionine; in addition, a gradual appearance of a
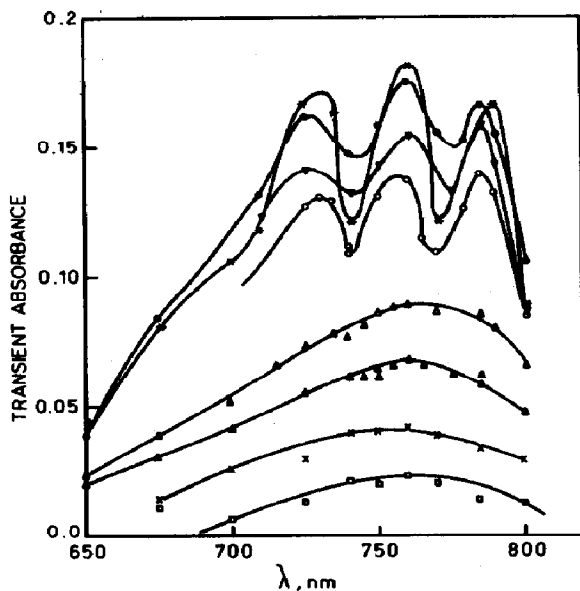
Fig. 1. Transient spectra of semithionine in the ferrous–thionine system in a homogeneous aqueous medium ($[TH^+] = 5 \times 10^{-6}$ mol dm^{-3}) at various Fe^{2+} concentrations (pH about 2.5) ($\square$, 1×10^{-4} mol dm^{-3}; $\times$, 2×10^{-4} mol dm^{-3}; $\blacktriangle$, 5×10^{-4} mol dm^{-3}; $\triangle$, 10^{-3} mol dm^{-3}; $\bigcirc$, 5×10^{-2} mol dm^{-3}) and at various pH values ($[Fe^{2+}] = 1.5 \times 10^{-2}$ mol dm^{-3}) ($\triangledown$, pH 2.7; $\bullet$, pH 3.2; $\star$, pH 3.8).

fine structure is also evident, which becomes prominent at Fe^{2+} concentrations above about 0.015 mol dm^{-3} with maxima at 730, 760 and 785 nm. An identical spectrum was also observed in solutions containing high concentrations of Fe^{2+} from which Fe^{3+} had been completely eliminated. Also, in solutions with low Fe^{2+} concentrations in which a structureless spectrum is observed, externally added Fe^{3+} ions did not cause the appearance of the structure. These observations rule out the possibility that Fe^{3+} ions are responsible for this structural feature. It may be noted that our data reported earlier [10] at higher Fe^{2+} concentrations did reveal such a structure, although a smoothed curve had been drawn through the experimental points, thus ignoring the structure. The results of other studies cited by Solar and Getoff [11] in which the Fe^{2+} ion was used as the photoreductant also indicate a "scatter" of the experimental points in this region; this scatter has been explained [11] in terms of either the presence of a mixture of different acid–base forms of semithionine or the overlapping of the spectrum of the semithionine with that of the electron donor or its oxidized form. In the present work, we confirmed that the structured feature is genuine and not just a scatter and, further, that it becomes more prominent at higher pH values and high Fe^{2+} concentrations (see Fig. 1). As the reported pK_a of semithionine for

$$\overset{\centerdot}{TH}_3^{2+} \underset{\rule{0pt}{0.9em}}{\overset{K_{a1}}{\rightleftharpoons}} \overset{\centerdot}{TH}_2^+ + H^+ \tag{1}$$

is approximately unity [11] the contribution of the acid form to the spectrum observed at pH 3.8 should be negligible; also neither Fe^{2+} nor Fe^{3+} ions have absorption in the 600 - 800 nm region. Interference from the absorption spectrum of triplet thionine is also unlikely as, at the high Fe^{2+} concentration used, the reaction

$$^3\dot{T}H_2{}^{2+} + Fe^{2+} \longrightarrow \dot{T}H_2{}^+ + Fe^{3+} \tag{2}$$

($k_2 = 3 \times 10^7 \, dm^3 \, mol^{-1} \, s^{-1}$ [4]) is expected to be complete within the flash duration of 100 μs. It is therefore reasonable to assume that the excess Fe^{2+} ions in the system interact with the semithionine species giving rise to the fine structured spectrum. However, the decay of the species was found to be second order and the rate constants were found to be comparable both at low concentrations of Fe^{2+} ions (a condition giving the structureless spectrum) and at high concentrations of Fe^{2+} ions (a condition giving rise to the structured spectrum). This would indicate that the ferrous–semithionine interaction may be a complex formation according to the equilibrium

$$[Fe(TH)]^{2+} + H^+ \overset{K_3}{\rightleftharpoons} Fe^{2+} + \dot{T}H_2{}^+ \tag{3}$$

If the equilibrium is predominantly in favour of dissociation of the complex, i.e. $K_3 \gg 1$, and the latter has an appreciably higher extinction coefficient compared with that of the uncomplexed $\dot{T}H_2{}^+$, we can expect to find that the spectrum is affected by high concentrations of Fe^{2+}. When, in our experiments, the decay of the semithionine transient species is followed by monitoring the change in absorbance A at a selected wavelength λ with time, we can write

$$-\frac{dA}{dt} = k_c \epsilon_c l C_c{}^x + k_u \epsilon_u l C_u{}^y \tag{4}$$

where the subscripts c and u denote respectively the complexed and the uncomplexed species, k and ϵ are the corresponding decay constants and extinction coefficients, l is the cell path length and x and y represent the orders of the corresponding reactions involving the two species. In all previous studies [4, 5, 10] the decay of semithionine has been found to be a second-order ($y = 2$) dismutation reaction:

$$\dot{T}H_2{}^+ + \dot{T}H_2{}^+ \overset{k_5}{\longrightarrow} TH_3{}^+ + TH^+ \tag{5}$$
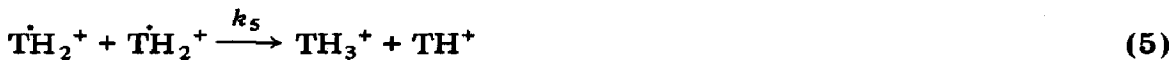
The same can be expected for the complexed species, in which case we expect $k_c \lesssim k_u$ owing to greater charge repulsion. On the assumption that equilibrium in reaction (3) is established *fast* compared with reaction (5) and with use made of the fact that $[Fe^{2+}]$ and $[H^+]$ are of the same order of magnitude and are much greater than the total $\dot{T}H_2{}^+$ concentration, eqn. (4) takes the form

$$-\frac{dA}{dt} = l C_u{}^2 \left(\epsilon_u k_u + \frac{\epsilon_c k_c}{K_3{}^2} \right) \tag{4a}$$

If it is assumed that $\epsilon_c/K_3 \ll \epsilon_u$, and since $k_c \lesssim k_u$, eqn. (4a) can be approximated as

$$-\frac{dA}{dt} \approx k_u \epsilon_u l C_u^2 \tag{4b}$$

Also, with the above assumption, the absorbance of the solution will be given approximately by $\epsilon_u l C_u$, and eqn. (4b) becomes

$$-\frac{dA}{dt} \approx \frac{k_u A^2}{\epsilon_u l} \tag{6}$$

Therefore the rate constant evaluated from a linear plot of $1/A$ versus t would be close to that of the uncomplexed species. Thus we expect the observed rate constant to be nearly the same at both high and low Fe^{2+} concentrations as found experimentally.

Whereas, as mentioned above, the fine structure in the semithionine spectrum was more prominent at high pH, highly acidic (0.1 N H_2SO_4 and above) solutions gave a structureless spectrum even at high Fe^{2+} concentrations. This observation, together with the value of pK_{a1} of about unity, is consistent with equilibria (1) and (3); thus at low pH, dissociation of the $[Fe(TH)]^{2+}$ complex is favoured to give free semithionine which, in turn, becomes protonated to TH_3^{2+} under this condition. This acid form has been produced by Solar and Getoff [11] by hydrogen atom reduction of thionine in highly acidic solutions in pulse radiolysis experiments. It does not exhibit any structure and has a λ_{max} at 790 nm. However, we could not verify this in our experiments because of the dark bleaching of thionine solutions due to thermal reduction by Fe^{2+} ions at acidities greater than about 0.1 N H_2SO_4. Nevertheless, in the pH region 2.5 - 1, λ_{max} showed a progressive red shift with increasing acidity, reaching about 785 nm at 0.1 N H_2SO_4. This is in the direction expected on the basis of the finding of Solar and Getoff that $\lambda_{max} = 790$ nm for the acid form TH_3^{2+}.

3.2. Transient spectra in surfactant solutions

The transient semithionine spectra observed in micellar solutions of SDDS at two different Fe^{2+} concentrations and at a bulk pH of 2.5 are shown in Fig. 2. It is seen that the spectra remained qualitatively unchanged, with a λ_{max} at about 785 nm and with no evidence of fine structure indicated even at an Fe^{2+} concentration high enough to show fine structure in the homogeneous aqueous medium. The semithionine—ferrous interaction thus appears to have been suppressed in the micellar environment. Our previous work on ground state thionine [9] has revealed that this molecule is adsorbed on the Stern layer of anionic micelles such as those of SDDS, wherein it experiences a considerably lower dielectric constant than that of bulk water. The suppression of the ferrous—semithionine interaction is then understandable in view of the greater like-charge repulsion in an environment of lower dielectric constant. In agreement with this we have found that the transient semithionine spectra observed in the flash photoreduction of
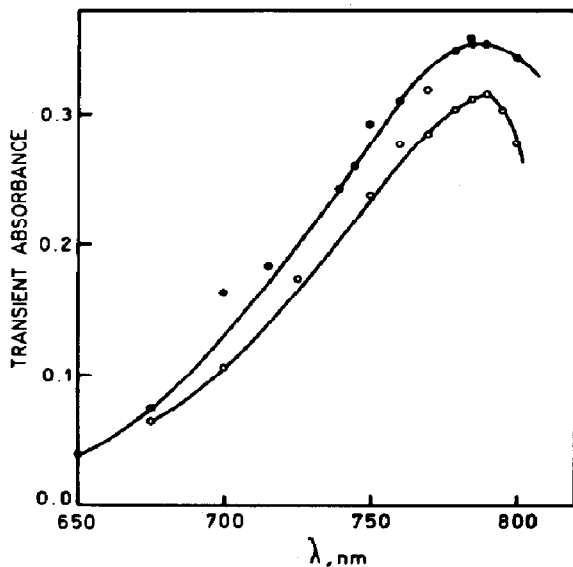
Fig. 2. Transient spectra of semithionine in an SDDS micellar medium at different Fe^{2+} concentrations ($[TH^+] = 5 \times 10^{-6}$ mol dm^{-3}; $[SDDS] = 4.5 \times 10^{-2}$ mol dm^{-3}; pH 2.5): $\circ$, 10^{-3} mol dm^{-3}; $\bullet$, 1.5×10^{-2} mol dm^{-3}.

thionine by Fe^{2+} ions in water–ethanol mixtures (pH 2.5) are also devoid of fine structure and red shifted. Related to the dielectric constant of the micelle Stern layer is also its apparently higher acidity compared with that of the bulk aqueous phase [12]. Probe molecules such as proflavin [13] and thionine [14] exhibit positive pK_a shifts as high as 3.0 units and 2.4 units respectively in SDDS micellar media compared with those in aqueous solutions. This apparent increase in pK_a is attributable to an increase in the local H^+ concentration in the micelle Stern layer. The binding of H^+ ions to the Stern layer of anionic micelles has been considered [15] as a partition of these ions and the surfactant counter-ions between the micellar pseudophase and the aqueous bulk phase. For SDDS the number m of H^+ ions per micellized surfactant head group has been found to be given by the empirical relation [15]

$$m = \frac{0.82[H^+]}{[H^+] + [Na^+]}$$

where $[H^+]$ and $[Na^+]$ are the total (analytical) concentrations of these two ions in the system. The volume of the Stern layer of SDDS micelles has been estimated to be 0.14 dm^3 per mole of Stern layer head groups [16]. From these we can compute a value of about 0.25 for the pH of the Stern layer in a 0.1 mol dm^{-3} SDDS solution at an analytical pH of 2.5 (corresponding to the total analytical concentration of H^+). Thus, under these conditions, a pK_a shift of at least 2.25 units is expected. Hence, at a bulk pH of 2.5 micellar-bound semithionine is likely to be largely in the conjugate acid form TH_3^{2+} which, as discussed before, is not complexed by Fe^{2+} ions. In

addition to these two factors of greater like-charge repulsion in an environment of lower polarity and higher acidity, preferential binding of both semithionine and Fe^{2+} to the surfactant head groups in the micelle could be an additional factor favouring the dissociation of the ferrous—semithionine complex in the micelle Stern layer. In essence, we may infer that micellar-bound semithionine in media with a bulk pH of about 2.5 is largely in the uncomplexed conjugate acid form $\overset{.}{T}H_3^{2+}$. Both the absence of fine structure and the red shift of λ_{max} (*cf.* Figs. 1 and 2) are in good agreement with this inference. With increasing acid concentration, λ_{max} shows a further red shift (Fig. 3) to 790 nm, the absorption maximum of the fully protonated $\overset{.}{T}H_3^{2+}$ form.
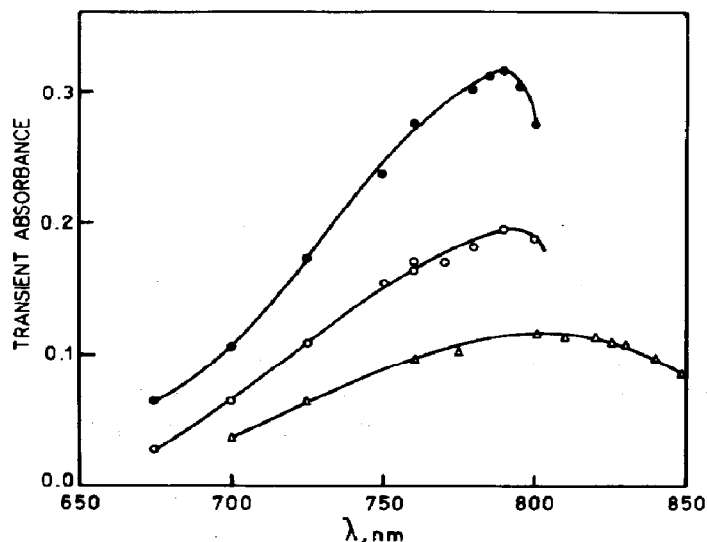

Fig. 3. Transient semithionine spectra in SDDS micellar media ($[TH^+] = 5 \times 10^{-6}$ mol dm^{-3}; $[Fe^{2+}] = 10^{-3}$ mol dm^{-3}; $[SDDS] = 4.5 \times 10^{-2}$ mol dm^{-3}): ●, pH 2.5; ○, 0.1 N H_2SO_4; △, 1 N H_2SO_4.

The results of experiments performed at different surfactant concentrations are depicted in Figs. 4 and 5. It is seen that, with increasing SDDS concentration, the transient absorbance first decreased to a minimum at about 5×10^{-5} mol dm^{-3} and thereafter increased accompanied by a marked red shift of λ_{max}. The effect is similar to that reported [9] for ground state thionine and shown in Fig. 5 for comparison. From the second inflection point of the curve shown for the ground state molecule, the critical micelle concentration (CMC) of SDDS in the presence of 1.5×10^{-2} mol $FeSO_4(NH_4)_2SO_4$ dm^{-3} and 1.5×10^{-3} mol H_2SO_4 dm^{-3} (pH 2.5) can be inferred to be 2×10^{-4} mol dm^{-3}. This is considerably lower than the value of 8.1×10^{-3} mol dm^{-3} reported in the literature [7] for two reasons. The CMC derived from spectral changes of the dye molecules used as probes are generally lower than those determined by means of physical methods such as light scattering and conductivity because of the formation of dye-induced micelles
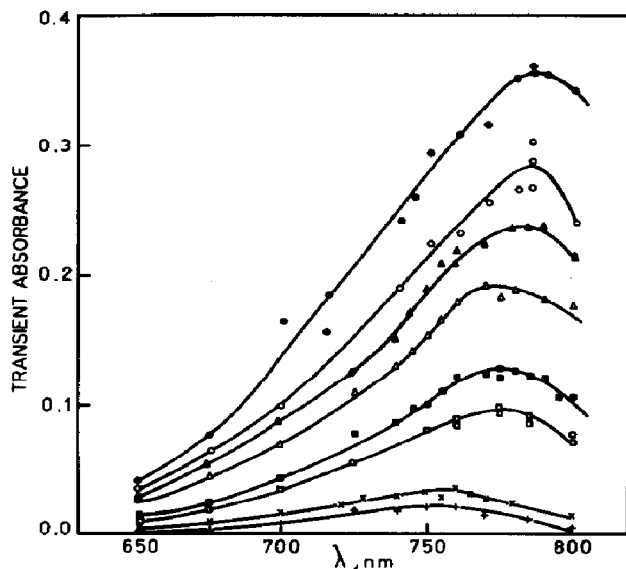
Fig. 4. Effect of various SDDS concentrations on the transient semithionine spectrum ($[TH^+] = 5 \times 10^{-6}$ mol dm^{-3}; $[Fe^{2+}] = 1.5 \times 10^{-2}$ mol dm^{-3}; about pH 2.5): +, 0.05 × 10^{-3} mol dm^{-3}; ×, 0.16 × 10^{-3} mol dm^{-3}; □, 0.65 × 10^{-3} mol dm^{-3}; ■, 1.0 × 10^{-3} mol dm^{-3}; △, 2.0 × 10^{-3} mol dm^{-3}; ▲, 3.0 × 10^{-3} mol dm^{-3}; ○, 10.0 × 10^{-3} mol dm^{-3}; ●, 25.0 × 10^{-3} mol dm^{-3}.

[17]. The presence of electrolytes also lowers the CMC of surfactants [18]. The decrease in thionine absorbance at surfactant concentrations below the CMC has been attributed to charge pair complex formation between TH$^+$ and the surfactant anion [9]. As the complex so formed is a poor absorber of light, the extent of photoreduction and hence the transient absorbance decrease with increasing surfactant concentration in this region. At and above the CMC, when micelles are formed, the complex has been found to break up and the dye incorporated in the Stern layer where it exhibits an absorption spectrum similar to that which it exhibits in the homogeneous aqueous medium and also undergoes photoreduction by Fe^{2+} ions with the same quantum yield as that in the homogeneous aqueous medium. As will be seen later, the decay of the product semithionine species gradually slows down with increasing SDDS concentration. Since the transient absorbance values shown in Fig. 5 are not corrected for any decay during the flash (the correction is of a larger magnitude at lower surfactant concentrations where the decay is faster), the curve of transient absorbance *versus* surfactant concentration does not exhibit as steep a rise as does that for ground state thionine for a surfactant concentration of around the CMC. The transient absorbance eventually reaches a plateau at surfactant concentrations well above the CMC.

3.3. Decay kinetics

As mentioned before, in homogeneous aqueous solutions, semithionine undergoes dismutation according to equation (5) with a second-order rate
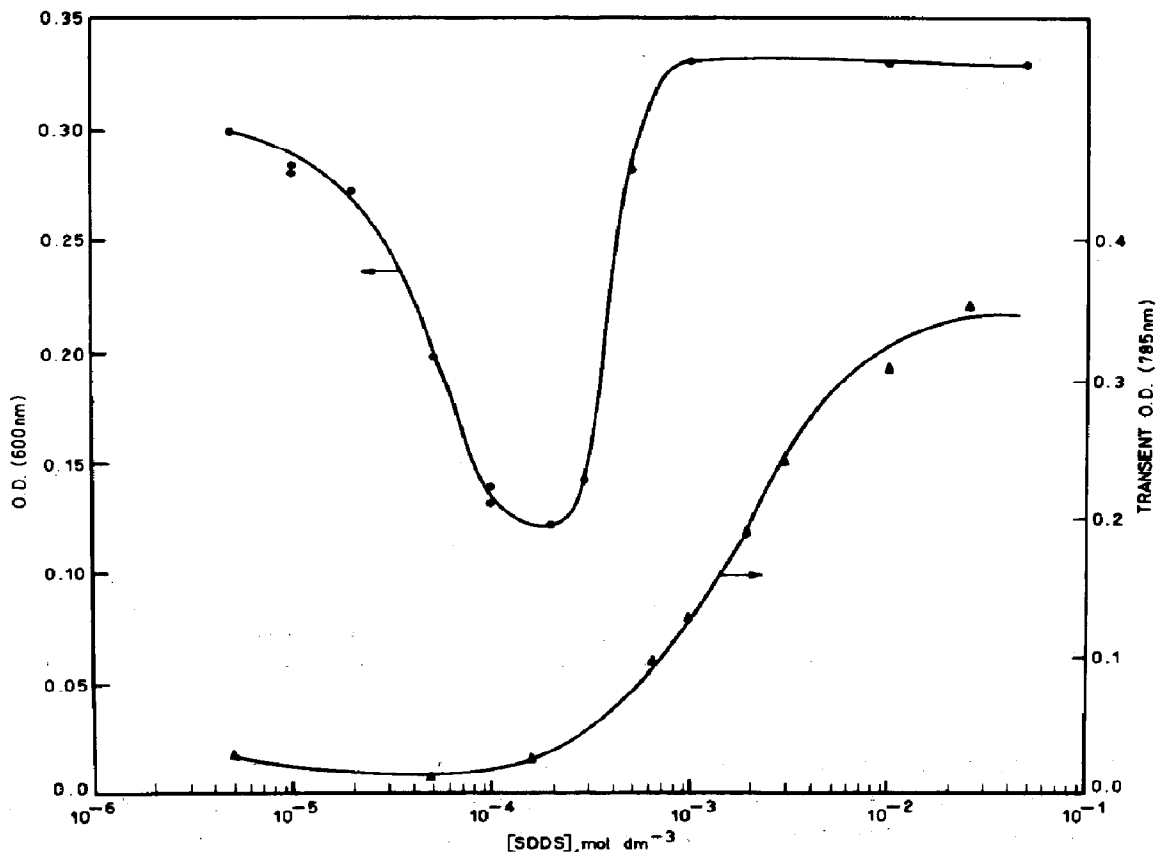
Fig. 5. Effect of the SDDS concentration on the absorbance of thionine at 600 nm (●) and semithionine at 785 nm (▲).

constant $k_5 = 2.4 \times 10^9 \, dm^3 \, mol^{-1} s^{-1}$ [4, 5, 10]. Re-oxidation of semithionine according to

$$\overset{\bullet}{T}H_2^+ + Fe^{3+} \xrightarrow{k_7} TH^+ + Fe^{2+} + H^+ \tag{7}$$

is a much slower process as $k_7 = 7 \times 10^7 \, dm^3 \, mol^{-1} \, s^{-1}$ [19]. Under the conditions of our experiment, i.e. $[\overset{\bullet}{T}H_2^+] = [TH^+] = 5 \times 10^{-6} \, mol \, dm^{-3}$ (complete photoreduction of thionine) and $[Fe^{3+}] \approx 9 \times 10^{-6} \, mol \, dm^{-3}$, (see Section 2) $k_7[Fe^{3+}] \ll k_5[\overset{\bullet}{T}H_2^+]$, and hence the re-oxidation reaction cannot compete with the dismutation. This is true even in the presence of added Fe^{3+} ions up to an Fe^{3+} concentration as high as about $10^{-4} \, mol \, dm^{-3}$.

In the SDDS solutions, however, the kinetics of semithionine decay were found to be quite different. Thus, at surfactant concentrations not far above the CMC, as the SDDS concentration increased the transient decay deviated from pure second order and could be resolved into a first-order and a second-order component. Analysis of the observed mixed-order decay according to the linearizing method of Matheson and Dorfman [20] gave a first-order component independent of the SDDS concentration and a second-order

TABLE 1

Effect of the sodium dodecylsulphate concentration on the first- and second-order rate constants for semithionine

[SDDS] ($\times 10^{-3}$ mol dm^{-3})	k_5 ($\times 10^8$ dm^3 mol^{-1} s^{-1})	$k_{I(obs)}$ ($\times 10^2$ s^{-1})
1	6.1	2.4[a]
1.3	5.0	1.9[a]
2	3.3	2.0[a]
2.5	2.2	1.4[a]
3	2.0	1.4[a]
5	—	1.9[b]
10	—	1.5[b]
25	—	1.8[b]
40	—	1.9[b]
60	—	2.6[b]
80	—	1.8[b]
100	—	1.9[b]
200	—	1.4[b]

[a] At $[Fe^{3+}] = 0.97 \times 10^{-5}$ mol dm^{-3}; derived from a mixed-order decay analysis.
[b] At $[Fe^{3+}] = 1.6 \times 10^{-5}$ mol dm^{-3}; purely first-order decay and hence there are no data for k_5.

component which decreased with increasing SDDS concentration (Table 1). At a given surfactant concentration, the first-order rate constant was found to increase with increasing concentration of added Fe^{3+} ions. At SDDS concentrations well above the CMC, the decay was found to be much slower and purely first-order [8] and the decay constant was independent of the SDDS concentration (Table 1), but increased with the concentration of added Fe^{3+} ions. A log–log plot of the observed first-order rate constant $k_{I(obs)}$ *versus* the concentration of Fe^{3+} was found to be linear with a slope of unity (Fig. 6), thus indicating that $k_{I(obs)}$ is proportional to $[Fe^{3+}]$. Hence the corresponding reaction can be inferred to be pseudo first order with respect to Fe^{3+} ions, and can be identified with the re-oxidation reaction

$$\dot{T}H_3^{2+} + Fe^{3+} \longrightarrow TH^+ + Fe^{2+} + 2H^+ \qquad (7a)$$

in the micellar phase. This conclusion is further supported by the observation that the recovery of the photobleaching of thionine monitored at λ_{max} (598 nm) was also first order with the same rate constant as that of the decay of semithionine. From the intercept of the plot in Fig. 6 a value of 6×10^6 dm^3 mol^{-1} s^{-1} is inferred for the rate constant of reaction (7a).

The first-order rate constant was found to be independent of the SDDS concentration over a wide range, whereas, as mentioned before, the second-order component as derived from an analysis of the mixed-order decay at the lower surfactant concentration decreased with increasing surfactant concentration (Table 1). As the decay is purely first order at surfactant concentrations well above the CMC, we can only derive an upper limit for
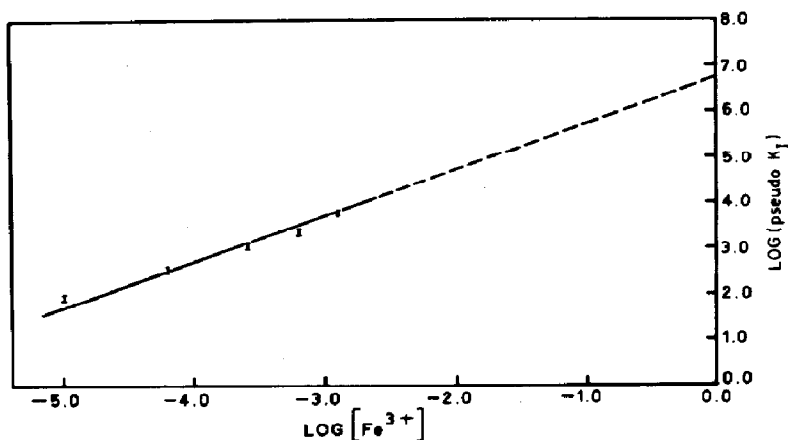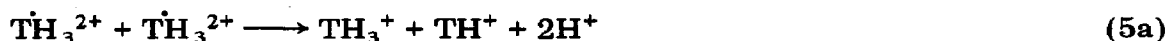
Fig. 6. Dependence of the observed first-order decay rate of semithionine in SDDS micellar media on the Fe^{3+} concentration (in order to span a wide range of concentration a log–log scale is employed) (slope, unity; [SDDS] = 0.025 mol dm^{-3}).

the second-order component, *i.e.* the rate constant attributable to the reaction

$$\overset{\bullet}{TH}_3{}^{2+} + \overset{\bullet}{TH}_3{}^{2+} \longrightarrow TH_3{}^+ + TH^+ + 2H^+ \tag{5a}$$

Even in the absence of any externally added Fe^{3+} ions, the reaction was first order with a rate constant of about 90 s^{-1}. Assuming that reaction (5a) is about 10 times slower and using the above value for k_{7a} we can give this upper limit as 2×10^6 dm^3 mol^{-1} s^{-1}. Thus compared with the homogeneous aqueous phase the anionic micellar system stabilizes the semithionine species against dismutation. Stabilization of radical cations on anionic micelles has also been reported previously [13, 21]. The Stern layer of anionic micelles is known to bear a residual negative charge [22] and is hence capable of binding cations. The semithionine $TH_3{}^{2+}$ and Fe^{3+} ions are therefore expected to be bound to the micelle surface. Such binding is a dynamic process represented by

$$\text{micelle} + S_{aq} \underset{k_{ex}}{\overset{k_{en}}{\rightleftharpoons}} S_{micelle} \tag{8}$$

where S_{aq} and $S_{micelle}$ represent respectively the aqueous and micelle-bound forms of the solute S, and the ratio of the entry rate constant k_{en} to the exit rate constant k_{ex} gives the binding constant K_S. The binding constants of several cations on SDDS micelles have been reported in the past [7] and are generally quite high (10^3 dm^3 mol^{-1}). For thionine itself, the value is 10^4 dm^3 mol^{-1} [9]; a similarly high value can also be expected for semithionine. At the concentrations of thionine and SDDS employed in the present experiments the probability of multiple occupancy of the micelles (*i.e.* each micelle contains more than one semithionine) is negligible. Therefore the only pathways available for reaction between semithionine species are either diffusion and collision of semithionine-carrying micelles or initial exit of the

species from the micelle followed by reaction in the aqueous medium. The first pathway is expected to be hindered as a result of both the bulkiness of the micelles and the repulsion between approaching like-charged micelles (as only part of the charge on the micelles is neutralized by bound counter-ions [16]). For the second pathway, the exit rate constants of bound species from anionic micellar surfaces are rather low, of the order of 10^6 dm^3 mol^{-1} s^{-1} [23, 24]; in addition, there is a high probability that the semithionine species will encounter an Fe^{3+} ion produced simultaneously in the photoreduction step before it exits from the micelle. This is particularly true in the micellar medium where the micelle essentially "cages" the two species formed in the photoreduction step [25]. Since such a reaction between the caged pairs does not require bimolecular diffusional collisions, it is expected to be first order. This was in fact observed to be the case; in completely Fe^{3+}-free solutions, where Fe^{3+} can be formed only by the photoreduction process in concentrations stoichiometrically equal to that of the semithionine, the decay of the semithionine was found to be clearly first order in the micellar system with a rate constant of about 90 s^{-1}. Under this condition, the reaction should have been kinetically second order if it occurred via free diffusion of the two reactant species. Thus the re-oxidation reaction (7a) in the anionic micellar medium is intramicellar, occurring between semithionine and Fe^{3+} adsorbed on the same micelle. Increasing the Fe^{3+} concentration above the stoichiometric value by external addition increases the concentration of adsorbed Fe^{3+} ions on the individual micelles, thereby contributing to an increase in the rate of this re-oxidation reaction and hence to the observed pseudo-first-order kinetics.

3.4. Effect of electrolytes

In the presence of a high concentration (0.8 mol dm^{-3}) of an electrolyte such as NaCl, which is known [26] to increase the aggregation number of SDDS micelles and to change their shape from spherical to rod-like, we found that the transient spectrum in the micellar medium did not exhibit any change in λ_{max} or ϵ_{max}. However, the decay kinetics were significantly different. Thus, whereas the decay was pseudo first order with a rate constant of about 2×10^2 s^{-1} (no externally added Fe^{3+}) in the absence of NaCl, it reverted to second order in the presence of NaCl. The second-order decay constant decreased with increasing concentration of SDDS (Table 2) whereas, in the absence of NaCl, the pseudo first-order decay constant, as mentioned before, was independent of the SDDS concentration. The values of the second-order decay constant are of the same order of magnitude as the dismutation rate constant in the homogeneous aqueous medium, and the process occurring in the micellar medium in the presence of NaCl may also be attributed to dismutation of the semithionine species. It is known [26] that the counter-ionic atmosphere created by the addition of a large excess of electrolyte shields the electrostatic potential of the SDDS micelles, which therefore behave more like non-ionic micelles. As in non-ionic micelles, therefore, repulsion between colliding micelles can be expected to be less,

TABLE 2

Dependence of the semithionine dismutation rate constant on the sodium dodecylsulphate concentration in the presence of a fixed NaCl concentration (0.8 mol dm^{-3})

[SDDS] ($\times10^{-2}$ mol dm^{-3})	Dismutation rate constant k_5 [a] ($\times10^9$ dm^3 mol^{-1} s^{-1})
0.5	5.1
1.0	2.6
2.0	1.3
4.5	0.9

[a]Calculated on the assumption that the semithionine extinction coefficient is 2.2×10^4 dm^3 mol^{-1} cm^{-1} under this condition.

thereby allowing a closer approach of the interacting micelles [24]. In agreement with this it was found that the decay of semithionine (formed by photoreduction of thionine with Fe^{2+}) in neutral micellar media of Triton X-100 and Brij-35 was second order as for SDDS micellar media in the presence of NaCl (Table 2).

Addition of electrolytes to ionic micellar systems also gives rise to another effect, i.e. exchange of bound ions with those of the added electrolyte [27]. Thus, by employing the polarographic technique [28], it has been shown earlier that addition of an excess of NaCl to SDDS micelles containing adsorbed cations such as Cd^{2+} leads to displacement of the Cd^{2+} cations into the bulk aqueous phase. Similar polarographic experiments carried out separately with Fe^{3+} ions and thionine revealed that, whereas Fe^{3+} ions are driven out into the bulk aqueous phase on addition of NaCl, thionine continues to remain adsorbed on the micelle surface and the same may be expected for semithionine. This would imply that, in the presence of a high concentration of an electrolyte, the semithionine and Fe^{3+} ions formed by photoreduction in the SDDS micellar Stern layer do not remain caged therein as one of the species, i.e. Fe^{3+}, is displaced into the bulk. Under this condition, therefore, we do not expect the kinetically first-order intramicellar re-oxidation reaction observed in the absence of added electrolyte, and dismutation becomes the only route for semithionine decay.

3.5. Pseudophase model and the decay kinetics

The micellar effects on the kinetics of many reactions have recently been explained on the basis of the pseudophase model [16]. In this model the surfactant micelles are assumed to constitute a pseudomicrophase in equilibrium with the bulk aqueous phase and the reactants are assumed to be partitioned between the two phases. Detailed treatment of the kinetics of bimolecular reactions in the pseudophase distribution model [16] predicts an initial enhancement in the reaction rates at low concentrations of micellized surfactant due to the bringing together of the two reactants in the micellar pseudophase. However, as the concentration of the micellized

surfactant increases, the reactants eventually become "diluted" in the micellar pseudophase. Thus, in cases where the bimolecular rate constant in the aqueous medium is less than that in the micellar medium, the observed rate passes through a maximum with increasing concentration of the micellized surfactant. In contrast, in cases where the rate constant in the aqueous medium is higher, a monotonic decrease in the rate with increasing surfactant concentration is expected as a result of the dilution effect referred to above. The observed decrease in the dismutation rate constants of semi-thionine with increasing SDDS concentration both in the absence and in the presence of NaCl is qualitatively in agreement with the predictions of the pseudophase model (as shown by the k_5 values in Tables 1 and 2).

3.6. Photogalvanic effect in the micellar system

It has been shown earlier [2] that leucothionine is the electroactive reduced species responsible for the photogalvanic effect in the ferrous–thionine system. As the formation of this species is not favoured in the SDDS micellar system because of the preferred re-oxidation of semithionine rather than its disproportionation to give leucothionine, the photogalvanic effect is expected to be reduced in the micellar medium. On the basis of an electrochemical study Bowen [29] has also arrived at the same conclusion.

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