

Photoprocesses in sodium decyl sulphate micellar media

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MS received 16 December 1985

Abstract. The absorption and fluorescence behaviour of thionine dye in sodium decyl sulphate (SDS) medium has been studied in detail. The transient spectra and kinetics of decay of semithionine species produced by photoreduction of thionine by ferrous ions has been studied using flash photolysis technique. The results have been compared with those in neat aqueous medium and in sodium lauryl sulphate (SLS) media published earlier. It was found that the decay of semithionine which is kinetically second order in neat aqueous medium becomes pseudo first order as in the SLS medium; however unlike in the latter case, the pseudo first order rate decreases with increasing surfactant concentration at all concentrations of ferric ion. The effect of electrolyte concentration on transient semithionine spectra and decay kinetics has also been studied. It was found that with increasing NaCl concentration the transient absorbance decreases and the decay slowly reverts back to second order as in aqueous medium. In SDS medium as compared to SLS a much higher concentration of NaCl is needed for the reaction to become second order which is attributed to stronger binding of ferric ions to the SDS micelles.

Keywords. Photoprocesses; sodium decyl sulphate medium; thionine dye; dye-surfactant charge pair complex.

1. Introduction

The behaviour of dyes in organised assemblies such as micelles of surfactant molecules is important for understanding the thermal and light induced reactions in bio-membranes (Singhal *et al* 1970; Hevesi *et al* 1970). The relevance of these studies to light energy conversion has also been recognised (Kiwi *et al* 1982). In this connection the thionine (TH^+)-ferrous system is of considerable interest (Rabinowich 1940; Clark and Eckert 1975; Suda *et al* 1978; Kamat *et al* 1977, 1978). Reactions of photo-excited and free radical species occurring in this system show distinctly different behaviour in sodium lauryl sulphate (SLS) micellar medium as compared to that in a neat aqueous solution (Guha *et al* 1979, 1982 and 1985). There are changes in the absorption spectrum and decrease in fluorescence intensity at SLS concentrations below the critical micelle concentration (CMC). These changes have been attributed to the formation of a dye-surfactant charge pair complex (Guha *et al* 1982). At SLS concentrations above the CMC this charge pair complex breaks and the dye gets solubilized in the micellar Stern layer. The decay of semithionine radical (TH_2^+) formed by photoreduction, which is kinetically second order process in neat aqueous solutions, then becomes pseudo first order in the micellar medium. This has been attributed to the reoxidation of semithionine by ferric ions adsorbed on the same micelle surface (Guha *et al* 1985). In order to determine whether the different behaviour in the micellar system is dependent on the surfactant forming the micelle, detailed studies were undertaken in a sodium decyl sulphate (SDS) medium, the results of which are reported in this paper.

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2. Experimental

Thionine (Fluka, puriss grade) was purified as described earlier (Guha *et al* 1982). SDS was purified by repeated extraction of its aqueous solution with distilled diethyl ether, followed by evaporation and vacuum drying at slightly elevated temperature (50–60°C). Ferrous solutions prepared from $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (BDH 'AnalaR' grade) contained ferric ion as an impurity and this impurity level was $\approx 1.36 \times 10^{-5} \text{ mol dm}^{-3}$ in a $0.015 \text{ mol dm}^{-3}$ ferrous solution. In those experiments where the solutions contained more than this minimal ferric ion concentration the latter was adjusted by addition of calculated amounts of Fe^{3+} in the form of 'AnalaR' (BDH) ferric alum. For some experiments ferric free solutions were also used which were prepared by dissolving freshly polished, cleaned E Merck GR iron wire in deaerated 2 mol dm^{-3} H_2SO_4 . All other chemicals were the purest commercially available and were used as such. Stock solutions of SDS, thionine, ferrous and ferric (concentrations as required) were separately prepared in $8.9 \times 10^{-3} \text{ mol dm}^{-3}$ H_2SO_4 (pH 1.75). Required aliquots of these were mixed together (surfactant solution added last) and diluted to give a bulk pH of 2.5–2.7. Triple-distilled water was used for preparation of solutions and dilutions. Absorption spectra were recorded on a Hitachi Model 330 spectrophotometer and fluorescence measurements were carried out using an Aminco Bowman (Model 4-8202B) spectrofluorometer. The flash-photolysis apparatus and the method of deoxygenation of the solutions have been described earlier (Guha *et al* 1985). The decay of semithionine was monitored by following its absorbance near λ_{max} of 780 nm.

3. Results and discussion

3.1 Absorption and fluorescence behaviour

The results of both absorbance and fluorescence intensity measurements for $10^{-5} \text{ mol dm}^{-3}$ thionine at different SDS concentrations are given in figure 1. The general pattern of spectral changes with surfactant concentrations is as reported earlier in the case of SLS (Guha *et al* 1982). Thus from figure 1 it can be seen that the disappearance of the thionine absorption band at 598 nm is accompanied by the appearance of new bands at 515 nm and 635 nm. At surfactant concentrations beyond CMC these bands at 515 nm and 635 nm disappear and the band at 598 nm reappears with enhanced extinction coefficient. The CMC value for SDS derived from the plot of absorbance at 598 nm (λ_{max} of TH^+ in aqueous solution at pH ~ 2.5) versus SDS concentration is $\approx 3.0 \times 10^{-2} \text{ mol dm}^{-3}$. No significant variation of the CMC value was observed in HCl, H_2SO_4 and neutral media. Considering the fact that the use of a dye probe gives a somewhat lower value for CMC (Mukherjee and Mysels 1955) this CMC value is in good agreement with the reported value of $3.2 \times 10^{-2} \text{ mol dm}^{-3}$ for SDS (Fendler and Fendler 1975). For the SDS system the extent of formation of dye-surfactant complex is maximal at surfactant concentration of $8\text{--}9 \times 10^{-3} \text{ mol dm}^{-3}$, as inferred from the maxima and minima in figure 1. As with SLS the restoration of the 598 nm band and characteristic TH^+ fluorescence at SDS concentration well above CMC indicates that the dye-surfactant complex is unstable in the micellar environment. This could be explained as follows. In the pre-micellar region there are free surfactant

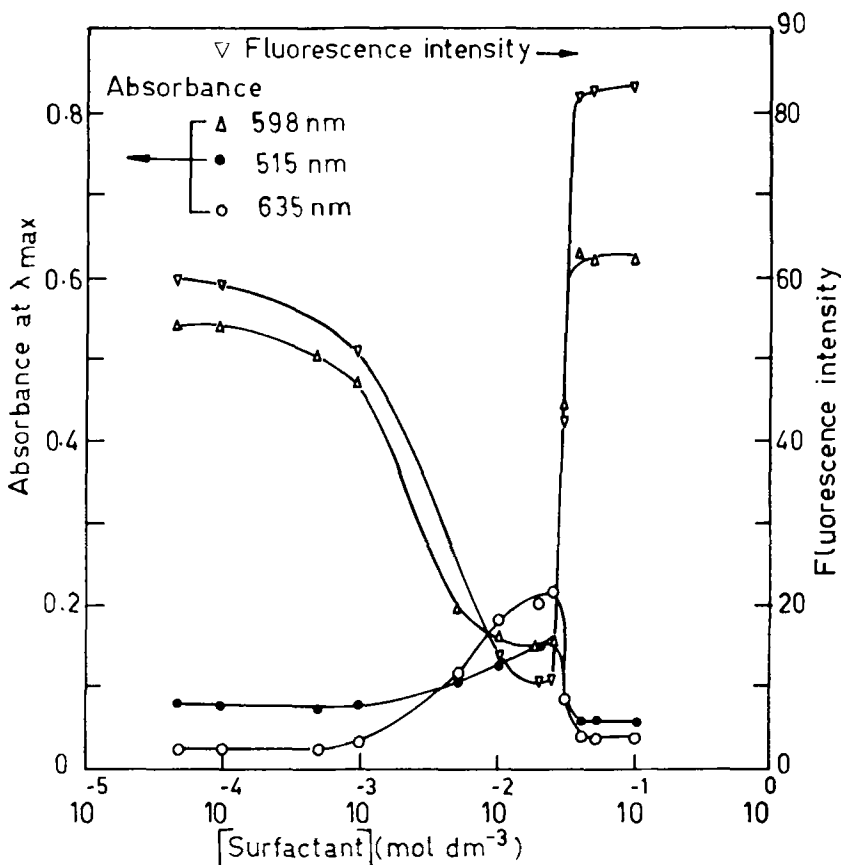


Figure 1. Effect of SDS concentration on thionine absorbance and fluorescence ($TH^+ = 1 \times 10^{-5} \text{ mol dm}^{-3}$, $\text{pH} \sim 2.7$).

monomer anions $[\text{SO}_4^--(\text{CH}_2)_9-\text{CH}_3]$ and hence greater probability of forming a complex species such as is shown in chart 1. On the other hand in the micellar medium

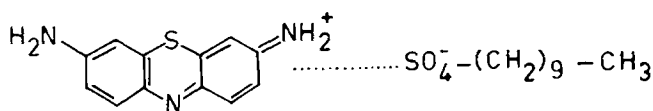


Chart 1.

there is less chance of formation of such a complex as the more hydrophobic part of the thionine molecule tries to penetrate into the hydrophobic core of the micelle, the positively charged amino group being held by the electrostatic field of the negatively charged headgroups of the surfactant molecules. Assuming a spherical structure for the micelle, the situation can be visualised as in chart 2. Thus in the post-micellar region, when almost all the surfactant molecules are in the micellar phase, the dye-surfactant

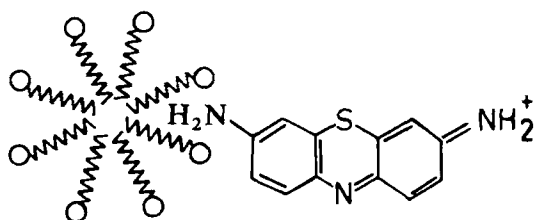


Chart 2.

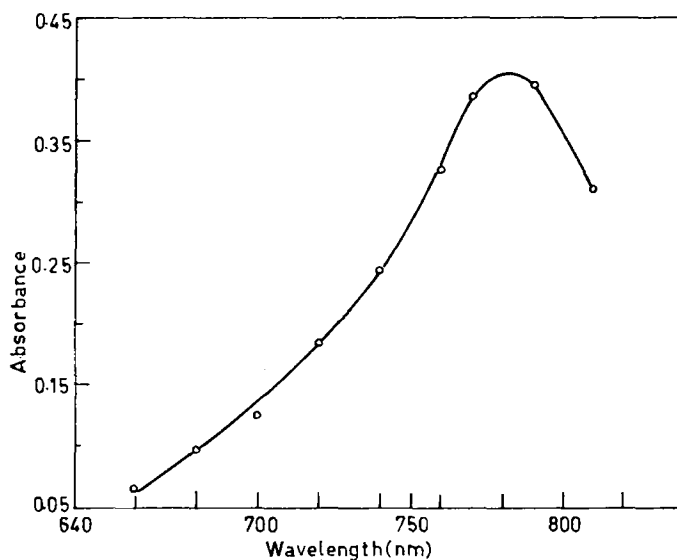


Figure 2. Transient spectrum of semithionine in SDS micellar medium at pH ~ 2.7 (concentrations in mol dm⁻³: TH⁺ = 5 × 10⁻⁶; SDS = 0.05; Fe²⁺ = 0.015; Fe³⁺ = minimal).

complex band disappears and the dye band reappears. The increased absorption and fluorescence in the micellar region may be attributed to the fact that the dye in the micellar environment has a different extinction coefficient and radiative life-time as compared to the pure aqueous environment (Guha *et al* 1985). From a correlation of the change in extinction coefficient of thionine with the medium polarity, the dielectric constant of the SDS micellar environment around thionine was evaluated to be 57. This is comparable with the value of 56 estimated earlier in the case of SLS (Guha *et al* 1982).

3.2 Transient spectra in SDS medium

The basic photoprocesses occurring in the thionine ferrous system are well known (Hatchard and Parker 1961; Ferreira and Harriman 1977). The transient semithionine spectrum observed in a micellar solution of SDS (surfactant concentration = 0.05 mol dm⁻³) is given in figure 2. At higher surfactant concentrations there is no qualitative change in the nature of the spectrum. As in the case of SLS micellar media

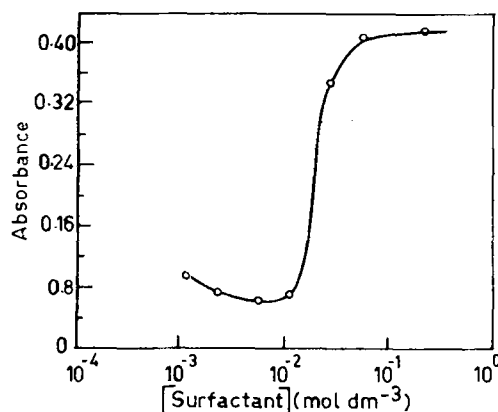


Figure 3. Effect of SDS concentration on the absorbance of semithionine at 785 nm (pH \sim 2.7; concentrations in mol dm⁻³; TH⁺ = 5×10^{-6} ; Fe²⁺ = 0.015; Fe³⁺ = minimal).

(Guha *et al* 1985) there is a shift in the λ_{\max} of about 25 nm compared to the spectrum in the neat aqueous medium and also no evidence of the fine structure. Thus semithionine ferrous interaction is suppressed in the SDS micellar medium also. The plot of semithionine absorbance versus surfactant concentration is given in figure 3. It can be seen that with increasing surfactant concentration the transient absorbance first decreases to a minimum at about $8-9 \times 10^{-3}$ mol dm⁻³ and thereafter increases sharply. This compares very well with changes in the absorbance of ground state thionine. Thus it seems that only uncomplexed thionine is involved in the photo-reduction by Fe²⁺ to form the semithionine species.

3.3 Decay kinetics

As reported earlier (Guha *et al* 1979) in homogeneous aqueous solutions semithionine decays by a second order process, attributed to its dismutation, with a rate constant of 2.4×10^9 dm³ mol⁻¹ sec⁻¹. In SDS solutions the behaviour is found to be different. At SDS concentrations near the CMC, the decay deviates from pure second order, and could be resolved into a first order and a second order component.

At surfactant concentrations above the CMC, the decay was found to be slower and purely first order. However, unlike in the case of SLS (Guha *et al* 1985) the first order rate constant (k_1) was found to decrease with increasing concentration of surfactant. The experiments carried out under ferric-free conditions prepared by the dissolution of AnalaR iron wire in deaerated H₂SO₄ and at higher concentration of ferric ion (1×10^{-4} mol dm⁻³) show similar behaviour as in minimal ferric solutions. The results of these are shown in figure 4. To see whether the decrease is due to increase in viscosity with increasing surfactant concentration, viscosity measurements were made. For a diffusion controlled reaction, the rate constant is directly proportional to the sum of the diffusion coefficients of reacting species, while the diffusion coefficients are inversely proportional to the viscosity of the medium. Hence the rate constant should be inversely proportional to viscosity (η) or k_1/η should be constant. As can be seen from the data given in table 1, the rate constant variation does not conform to the behaviour expected for a diffusion controlled reaction.

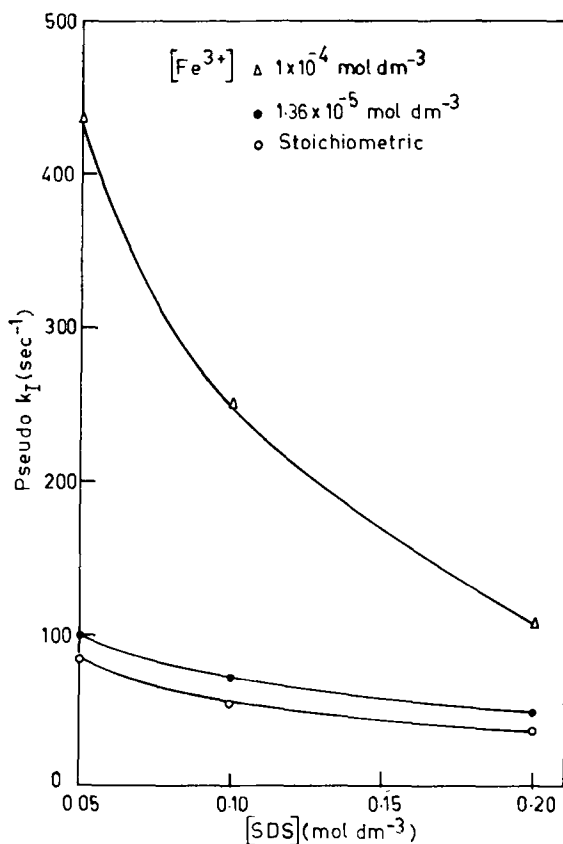


Figure 4. Effect of SDS concentration on pseudo first order rate at different Fe^{3+} concentrations (pH \sim 2.7; concentrations in mol dm^{-3} : $\text{TH}^+ = 5 \times 10^{-6}$; $\text{Fe}^{2+} = 0.015$).

Table 1. Effect of SDS concentration on the viscosity of the medium and the rate constant for semithionine decay. (Minimal $[\text{Fe}^{3+}]$).

[SDS] (mol dm^{-3})	Observed rate constant k_1 (sec^{-1})	Viscosity η (cp)	$k_1 \cdot \eta$
0.05	0.983×10^2	0.91	0.90×10^2
0.1	0.700×10^2	0.95	0.66×10^2
0.2	0.495×10^2	1.04	0.51×10^2

At a fixed concentration of surfactant (0.05 mol dm^{-3}) the first order rate constant was found to increase with increasing concentration of added Fe^{3+} ions as observed in the case of SLS earlier. The plot of $\log k_1$ vs $\log [\text{Fe}^{3+}]$ was found to be linear (figure 5) indicating that k_1 is proportional to Fe^{3+} ion concentration. Hence the reaction with which semithionine disappears seems to be pseudo first order with respect to Fe^{3+} in the SDS micellar medium also and is inferred to be the reoxidation of semithionine by

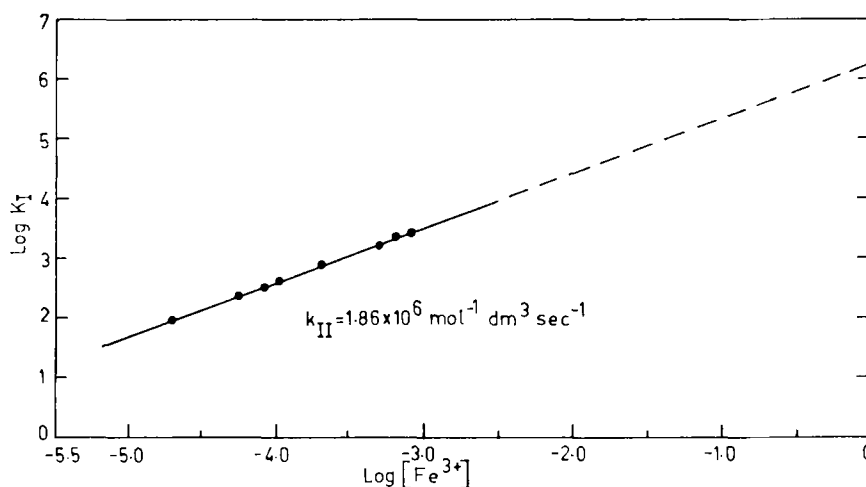


Figure 5. Dependence of first order decay rate of semithionine in SDS micellar solution on Fe^{3+} concentration (pH \sim 2.7; concentrations in mol dm^{-3} : SDS = 0.05, Fe^{2+} = 0.015, TH^+ = 5×10^{-6}).

ferric ions:



In the case of SLS micellar medium this has been confirmed by observing the recovery of the photobleaching of thionine with the same rate constant as for the decay of semithionine (Guha *et al* 1985). The intercept of the linear plot in figure 5 gives a value of $k_{II} = 1.86 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ for the rate constant of this reoxidation reaction as compared to a value of $6 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ deduced in the case of the SLS micellar medium (Guha *et al* 1985). It may be noted that these rate constants are not true bimolecular rate constants as applicable to a homogeneous medium, but must be interpreted as representing the probability of occurrence of reaction between species adsorbed or solubilized in the micelle. The value for this rate constant in a homogeneous aqueous solution is an order of magnitude higher: $7 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ (Ferreira and Harriman 1977). Although the values are of the same order of magnitude in the SLS and SDS micellar media it is appreciably smaller in the latter. This would imply that the semithionine and Fe^{3+} are more tightly bound in the SDS micelle as compared to the SLS one. The same conclusion is reached from a study of the effect of electrolytes (see §3.4).

Findings considerably at variance with ours have been reported in a recent paper (Mackay and Grätzel 1985). These are: the reoxidation reaction is not enhanced in the SLS micellar medium and the semithionine decay as monitored at 404 nm is second order. In the light of this report we performed a set of experiments exactly under the conditions given in their paper with respect to pH and the concentrations of thionine, ferrous and ferric, as well as the monitoring wavelength. Even under these conditions we obtained the same result as reported here and in the previous publication (Guha *et al* 1985). In this connection we wish to add that the results of experiments in micellar systems are very sensitive to the presence of impurities (Guha *et al* 1982) as also to the

Table 2. Electrolyte effect on semithionine absorbance in SDS micellar media.

[NaCl] (mol dm ⁻³)	Absorbance at 770 nm
0	0.42
1.0	0.44
1.5	0.35
1.8	0.31
2.0	0.25
2.5	0.22

method of preparing the reaction mixture. These have been meticulously controlled in our work as detailed in the experimental section.

3.4 Effect of electrolytes

In the presence of NaCl, the transient semithionine spectrum in SDS micellar medium did not exhibit any change in λ_{\max} though there was a decrease in absorbance with increasing NaCl concentration (table 2). This can be explained as due to the effect of electrolytes on the structure of the ionic micelles and the phenomenon of ion exchange occurring on the micellar Stern layer (Ikeda *et al* 1981; Quina and Chaimovich 1979; Cuccovia and Chaimovich 1982; Kishore and Moorthy 1983). Thus on addition of high concentrations of NaCl we expect the adsorbed Fe²⁺ ions to be displaced from the Stern layer by the cations of the added electrolyte. Consequently the concentration of Fe²⁺ ions available for photoreduction of excited thionine decreases, leading to a decreased extent of photoreduction, and hence, the decrease in the absorbance of semithionine with increasing NaCl concentration.

A second effect of the addition of NaCl to the SDS micellar system is that the decay of the semithionine reverts back to second order. As inferred in the case of SLS, this is due to the displacement of Fe³⁺ ions from the micelle surface by Na⁺ ions as a result of which the reoxidation of semithionine by Fe³⁺ ions is not possible any more and the dismutation of semithionine becomes dominant. However, in the SDS case, as compared to SLS, we need much higher concentrations of electrolyte for the reaction to become second order. This would point to a tighter binding of Fe³⁺ ions in the former case. It is also observed that the second order slope ($k_{II}/\epsilon \cdot I$) increases with NaCl concentration. This variation is given in table 3. In the system there are two possible effects which can be expected to cause variation in the reaction rate. As the ionic strength of solution increases with increasing NaCl concentration the rate of the reaction between two like-charged species is expected to increase, but at the same time with increasing NaCl concentration there is also observed an increase in the viscosity of solution which brings down the rate of diffusion controlled reactions. The fact that the observed rate constant increases with increasing NaCl concentration seems to indicate that the effect of ionic strength dominates over that of viscosity. A more detailed account of these effects is being published separately.

Table 3. Variation of 2nd order slope for semithionine decay with NaCl concentration in SDS micellar media.

[NaCl] (mol dm ⁻³)	Second order slope × 10 ⁻³ (sec ⁻¹)
1.0	1.56
1.5	3.13
1.8	6.20
2.0	9.02
2.5	12.1

3.5 Pseudophase model of kinetics in micellar media

The micellar effects on the kinetics of reactions have been recently explained on the basis of the pseudophase model (Bunton *et al* 1977; Bunton 1979). The applicability of this model to the reactions of semithionine has been discussed previously in the case of SLS medium (Guha *et al* 1985). In the SDS micellar system, as in the case of SLS, the reoxidation of semithionine by Fe³⁺ is an order of magnitude slower than in the neat aqueous medium. Therefore on the basis of the pseudophase model, there is expected to be a monotonous decrease in the rate of this reaction with increase in SDS concentration due to the pseudophase dilution effect. This was hardly noticeable in the case of SLS with no externally added Fe³⁺, but is definitely seen in the SDS system (figure 4). However, in both cases the effect is quite marked in presence of added Fe³⁺ ions. Similarly, in presence of added NaCl when the dismutation of semithionine dominates over its reoxidation by Fe³⁺, the pseudophase dilution effect is again clearly discernible.

Acknowledgements

The authors are grateful to Dr R M Iyer and Dr K N Rao for their encouragement and support of this work, and to Shri S N Guha for helpful discussions and suggestions.

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