# The Photoreduction of Thionine and Surfactant Thionine by Iron(II) in Anionic Micelles and Microemulsions

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*Colloides / Micelles / Photochemistry / Photoelectrochemistry*

The rate constants for the iron(II)-thionine and surfactant thionine system have been determined in aqueous solution, sodium dodecyl sulfate (SDS) micelles, and in a mineral oil-in-water microemulsion stabilized by sodium cetyl sulfate (SCS) and 1-pentanol. The triplet lifetimes are all in the range 7–9 μs. The rate constant for electron transfer quenching of triplet thionine by iron(II) is higher in the anionic media due to a higher local $Fe^{2+}$ concentration. However, the back reaction between semithionine and iron(III) is *not* similarly enhanced in the presence of micelles or microemulsion. The dismutation of semithionine is a little slower in microemulsion than in water, but over two orders of magnitude slower in SDS micelles. The quantum yield of thionine triplet formation, determined for surfactant thionine in SCS microemulsion, approaches unity.

## Introduction

The first use of organized media as photogalvanic cell fluids was recently reported [1]. The particular media employed were micelles and microemulsions. Such an application of micellar or other organized media was suggested by Calvin in 1973 [2]. It has now been shown that anionic micelles and microemulsion considerably enhance the output (power) of the classical iron(II)-thionine photogalvanic cell with respect to aqueous solution. Further, the use of a long alkyl chain thionine derivative was much superior to thionine, even in aqueous solution. The order of efficacy of the various fluids was microemulsion > micelle ≫ water. Two possible contributions of the surfactant media to the increased photogalvanic output were inhibition of thionine aggregation and increased adsorption of thionine on the illuminated tin oxide electrode. The former contributes because the thionine monomer is the photoactive species, and the latter because coating the electrode with thionine by various methods has been shown to increase electrode selectivity.

The question also arises as to the effect, if any, of these organized media on the rate constants of the reactions involved. While these have been investigated in aqueous [3] and acetonitrile solutions [4], no study in microheterogeneous media has been reported. Therefore, we have carried out a flash photolysis study in the same micellar and microemulsion media employed for the photogalvanic work.

## Experimental

The sodium dodecyl sulfate (SDS), 1-pentanol and paraffin (mineral) oil were from Fluka. The thionine hydrochloride (ThHCl), surfactant thionine ($C_{10}$ThHCl), and sodium cetyl sulfate were obtained as described in Ref. [1]. The SDS micellar solutions were 70 mM in SDS. The SCS microemulsion (μE) had the composition (% w/w); water 59.6, oil 8.8, 1-pentanol 19.2, and SCS, 12.4. All solutions were 5 mM in sulfuric acid. Iron(II) and (III) were used in the form of their sulfate salts.

The flash photolysis studies were carried out using a doubled Nd laser (530 nm) with a pulse duration of approximately 20 ns and a maximum pulse energy of about 100 mJ. A detailed description of the system has been published [5]. The solutions were all degassed by purging with argon for at least 15 minutes. The detection wavelengths employed were 404 and 616 nm. Interference filters of these wavelengths in combination with an infrared filter, were placed immediately after the Xenon spectroscopic lamp. This was necessary since the monochromator interfaced with the photomultiplier tube, and the direct Xe lamp beam caused extensive excitation of the sample. Absorption spectra were obtained on a Perkin Elmer-Hitachi-model 340 spectrophotometer. The thionine concentrations employed for the flash photolysis studies ranged from 2–20 μM.

The limits of error reported for values determined in this study represent one (*n*-1) standard deviation based on multiple (*n*) measurements.

The laser intensity for the triplet yield determination was measured by means of a bolometer, consisting of a model 172 joulemeter and a model 20 radiometer from Laser Instrumentation, Ltd., Chertsey, England.

## Results

The data were analyzed as described by Hatchard and Parker [3]. This analysis will be briefly discussed as the results are developed. The sequence of reactions and general order of rate constants were as in homogeneous solution. The reaction scheme (protons omitted) is given below ($S_0$ = thionine, $S_1$ = singlet excited thionine, T = triplet thionine, $S^\cdot$ = semithionine, L = (leucothionine).

$$\begin{aligned}
&S_0 \xrightarrow{h\nu} S_1 && \text{excitation and triplet formation with quantum yield } \phi_T\\
&S_1 \xrightarrow{\text{ISC}} T\\
&T \xrightarrow{k_T} S_0 && \text{triplet decay}\\
&T + \text{Fe(II)} \xrightarrow{k_q} S^\cdot + \text{FE(III)} && \text{reactive quenching}\\
&S^\cdot + S^\cdot \xrightarrow{k_d} S_0 + L && \text{dismutation of S}\\
&S^\cdot + \text{Fe(III)} \xrightarrow{k_b} S_0 + \text{Fe(II)} && \text{back reaction}\\
&L + \text{Fe(III)} \xrightarrow{k_L} S^\cdot + \text{Fe(II)} && \text{oxidation of L}
\end{aligned}$$

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Ber. Bunsenges. Phys. Chem. *89*, 526–530 (1985) – © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1985.
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## Extinction Coefficients

At higher laser powers in the absence of added iron, all of the thionine was converted to triplet. In this way, it was possible to determine the extinction coefficient of the triplet ($\varepsilon_T$) at 404 nm. At 404 nm, the triplet has a near maximal absorbance, while the thionine is essentially nonabsorbing. Semithionine also absorbs at 404 nm, and in the presence of high concentrations of Fe(II), again at higher laser power, all of the thionine was converted to semithionine permitting determination of its extinction coefficient ($\varepsilon_{S\cdot}$). It should be noted that, in accord with the observations of Hatchard and Parker [3], small amounts of Fe(III) must be present to prevent dark bleaching of the thionine by iron(II) in aqueous solution. In general, iron(III) concentrations of 0.1 – 0.2 mM were initially added. These concentrations were sufficiently low so that none of the processes involving Fe(III) occurred at an appreciable rate. In SDS micelles, and to an aven greater extent in SCS μE, the addition of Fe(II) does cause dark bleaching even in the presence of the Fe(III). In these cases, the actual equilibrium concentration of thionine was determined spectroscopically, and the calculation of $\varepsilon_S$ based on this value.

Ground state bleaching was followed at 616 nm. This wavelength is somewhat to the red of the absorption maximum (~ 600 nm). However, it was convenient for the thionine concentrations employed since the absorbance at 600 nm was in most cases too high. Also, at this wavelength both the triplet and semithionine have a very low absorbance (both can be taken as zero to a first approximation). Leucothionine is colorless. The pertinent extinction coefficients are given in Table 1.

## Triplet Yield

It has always been assumed that the triplet yield ($\phi_T$) was high, although no numerical values have been presented. We have estimated this yield by means of the method described by Lachish, Shafferman and Stein [6] for $C_{10}$ThHCl in the SCS microemulsion. In this method, the amount of triplet formed is measured as a function of laser power. The triplet was monitored at 404 nm, where thionine does not absorb. A plot of absorbance ($A_{404}$) vs. laser energy ($E$) is shown in Fig. 1. The solid line is a fit of the data to the equation $A = a\,[1 - \exp(-bE)]$. Here $a = \varepsilon_T \cdot c \cdot l$ is the absorbance when all of the thionine is converted to triplet. The thionine concentration is $c$, and the pathlength $l = 0.5$ cm. From the $a$ value derived from the fit in Fig. 1, a value of $\varepsilon_T^{404} = 6.8 \cdot 10^3$ $M^{-1}$ $cm^{-1}$ is obtained, in good agreement with the average value in Table 1. The parameter $b = \phi_T \sigma_e / s$, where $\sigma_e$ is the absorption cross section of the dye at the laser wavelength (here 532 nm) and $s$ is the cross-sectional area irradiated (here 0.3 $cm^2$). Using a value of $9.18 \cdot 10^3$ $M^{-1}$ $cm^{-1}$ for the extinction coefficient of $C_{10}$ThHCl in SCS μE at 532 nm, a value of $\phi_T = 1.0$ was obtained from the $b$ value of the data in Fig. 1. The fit of the data in Fig. 1 to the theoretical curve is far from perfect. In addition, there was about 12% degradation of the dye over the course of the experiment. Further, taking the absorbance at 532 nm and the triplet absorption into account, $\phi_T$ can be reduced to 0.8. In any event, it is clear that the triplet yield, as previously assumed, is quite high and is in all probability near unity.

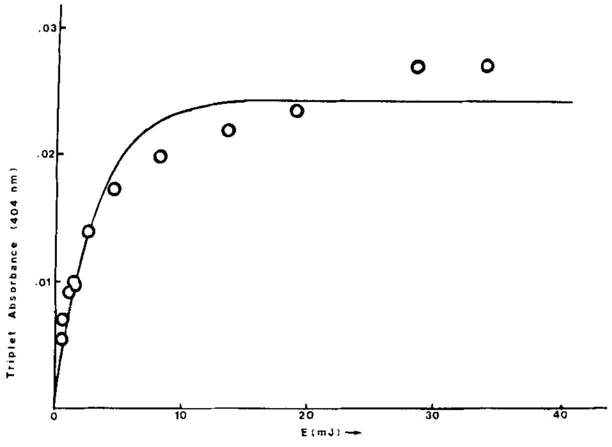

Fig. 1

Triplet absorbance at 404 nm ($A_{404}$) vs. laser energy ($E$) for $C_{10}$ThHCl in SCS microemulsion. The points are the experimental data and the solid curve is a best fit of the data to the equation $A = a\,[1 - \exp(-bE)]$. Here, $a = 0.0245$ and $b = 0.318$

## Rate Constants

As mentioned above, the analysis of the flash photolysis data employed to determine the rate constants was that of Hatchard and Parker [3]. The rate constant for triplet decay ($k_T$) was measured by following the change in absorbance at 404 nm with only thionine present (Fig. 2a). Upon addition of iron(II), there is a rapid decay due to additional quenching of the triplet by electron transfer from iron(II) forming semithionine, and a slower decay due to dismutation of the semithionine (Fig. 2b). The first order rate constant ($k_{obs}$) is obtained from the fast decay by subtracting a constant baseline from the start of the slow decay. Then the rate constant for quenching of dye by ferrous ion ($k_q$) is given by $k_q = (k_{obs} - k_T)/[Fe(II)]$. Varying the Fe(II) concentration yielded the same value of $k_q$ within experimental error (± 20%). Also, the integrated rate equation yields $A_0/A_\infty = (\varepsilon_T/\varepsilon_{S\cdot})\,(1 + k_T/k_q\,[Fe(II)])$, where $A_0$ and $A_\infty$ are the absorbances at the maximum (time "zero") and at the plateau (start of the slow decay). Values of $k_q$ obtained in this manner agreed with those obtained from $k_{obs}$. The value of the dismutation rate constant ($k_d$) was obtained from the decay of the absorbance at 404 nm in the presence of higher concentrations of iron(II), i.e. from the "slow" decay on a longer time scale (Fig. 2c). A second-order plot ($A^{-1}$ vs. $t$) yields $k_d/\varepsilon_S^{404}\, l$ as the slope, and using $l = 0.5$ cm and the value of $\varepsilon_{S\cdot}^{404}$ from Table 1, $k_d$ is evaluated.

Table 1

Extinction Coefficients[a] of thionine (ThHCl) and $C_{10}$ thionine ($C_{10}$ ThHCl) in Various Media

| Solvent | Dye | $\lambda_{max}$[b] | $\varepsilon_{max} \cdot 10^{-4}$ | $\varepsilon_{S0}^{616} \cdot 10^{-4}$ | $\varepsilon_T^{404} \cdot 10^{-3}$ | $\varepsilon_{S\cdot}^{404} \cdot 10^{-3}$ |
|---|---|---|---|---|---|---|
| Aqueous | ThHCl | 597[c] | 5.76[c] | 3.1 | 5.7 | 6.3[d,e] |
| Aqueous | $C_{10}$ThHCl | 598[c] | 3.54[c] | 1.5 | 4.1 | 4.5[d] |
| SCS μE | ThHCl | 604[c] | 5.70[c] | 3.7 | 5.8 ± 0.4 | 6.4 ± 0.3 |
| SCS, μE | $C_{10}$ThHCl | 604[c] | 6.56[c] | 4.0 | 7.0 ± 0.5 | 7.6 ± 0.4 |
| SDS micelles | ThHCl | 599 | 6.8 | 3.9 | 7.3 ± 0.8 | 8.0 ± 0.9[d] |

[a] $M^{-1}$ $cm^{-1}$.

[b] ± 1 nm.

[c] Ref. [1].

[d] Calculated from $\varepsilon_{S\cdot} = 1.1\,\varepsilon_T$ at 404 nm, based on SCS μE results.

[e] In 0.1 N $H_2SO_4$, Ref. [3], a value of $\sim 6 \cdot 10^3$ $M^{-1}$ $cm^{-1}$ was obtained.

Table 2
Rate Constants for the Thionine and Alkyl Thionine-Iron System in Various Media (vide text)

| System | $k_T$ $[s^{-1} \cdot 10^{-5}]$ | $k_q$ $[M^{-1}\,s^{-1} \cdot 10^{-8}]$ | $k_d$ $[M^{-1}\,s^{-1} \cdot 10^{-8}]$ | $k_b$ $[M^{-1}\,s^{-1} \cdot 10^{-5}]$ | $k_L$ $[M^{-1}\,s^{-1} \cdot 10^{-2}]$ |
|---|---|---|---|---|---|
| ThHCl/SCS μE | 1.3 ± 0.1 | 1.1 ± 0.2 | 6.8 ± 0.3 | 1.2 ± 0.5 | 6 ± 2 |
| $C_{10}$ThHCl/SCS μE | 1.3 ± 0.1 | 1.3 ± 0.2 | 4.3 ± 0.2 | 5.6 ± 0.5 | 10 ± 2 |
| ThHCl/SDS micelle | 1.1 ± 0.3 | 4.8 ± 0.9 | 0.09 ± 0.03 | 1.9 ± 0.6 | [a] |
| $C_{10}$ThHCl/aqueous | 1.1 ± 0.1 | 0.24 ± 0.08 | 41 ± 11 | 6 ± 2 | 3.4 ± 0.2 |
| ThHCl/aqueous | 1.4[b] ± 0.1 | 0.2[c] | 12[d] | 0.8[e] – 9[f] | 2.6[e] – 4.2[f] |

[a] The value of $k_L$ could not be determined in this case due to (i) a small value of $k_d$ with respect to $k_b$, and thus very little lencothionine formed, and (ii) the inability of SDS to accommodate a high Fe(III) concentration.

[b] A value of $k_T = 1.3 \cdot 10^{-5}\ s^{-1}$ was reported in Ref. [4].

[c] A value of $k_q = 0.6 \cdot 10^8\ M^{-1}\ s^{-1}$ was reported in Ref. [4].

[d] A value of $k_d = 24 \cdot 10^8\ M^{-1}\ s^{-1}$ was reported in Ref. [3].

[e] Ref. [3].

[f] Ref. [4].

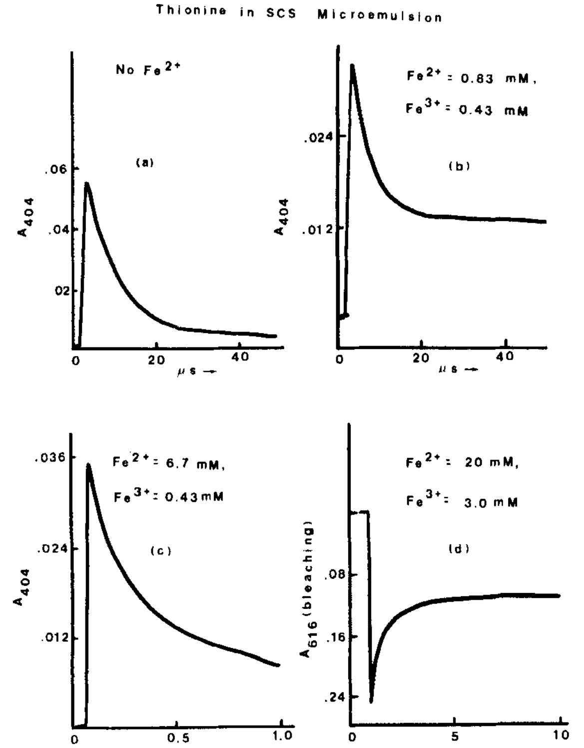

Fig. 2
Flash photolysis data for thionine in SCS microemulsion.
a) Dye only;
b) Dye + 0.83 mM Fe(II) and 0.43 mM Fe(III);
c) Dye + 6.7 mM Fe(II) and 0.43 mM Fe(III);
d) Dye + 20 mM Fe(II) + 3.0 mM Fe(III)

The rate constant for the back reaction ($k_b$) of semithionine with iron(III) was obtained from the bleaching at 616 nm (Fig. 2d). The concentration of iron(II) was kept high and constant to ensure complete conversion to semithionine, and the ratio of the maximum bleaching ($A_0$) to that at the plateau ($A_\infty$) was measured as a function of iron(III) concentration. The plateau is actually a slow decay due to the oxidation of leucothionine by iron(III) (*vide infra*). Since the bleaching is due to both the dismutation and back reaction, the integrated rate equations yield $(1 - 2A_\infty/A_0) = X \ln(1 + 1/X)$. Here, $X = [\mathrm{Fe(III)}]\, k_b/2k_d[\mathrm{S}]$, and $\varepsilon_{S_0}^{616}$ has been taken equal to zero (*vide supra*). The concentration of semithionine (S˙) is calculated from $A_0/l\varepsilon_T^{616}$. The value of $\varepsilon_{S_0}^{616}$ is given in Table 1. Using these data and the previously determined value of $k_d$, $k_b$ is evaluated.

The oxidation of leucothionine by iron(III) is considerably slower than all of the other reactions. However, by using high Fe(III) concentrations, the "plateau" mentioned above could be seen to be a slow decay. It was difficult to obtain accurate data on these very slow decays using the flash photolysis apparatus and associated electronics employed in this study. In particular, only a relatively small fraction of the decay could be obtained, and it was not possible to reliably determine the order. However, Osif, Lichtin and Hoffman have shown that this decay is pseudo first order with respect to thionine [7]. Therefore, we have evaluated $k_L$ from $k_l = k_L\,[\mathrm{Fe(III)}]$, where $k_l$ is the first order rate constant for (slow) decay of the bleaching at 616 nm. It should be noted that the oxidation of leucothionine, and possibly semithionine, by iron(III) has been shown to likely involve the formation of an association complex [7]. This was not investigated in the present study and $k_L$ would then be a product of the association constant and actual rate constant for electron transfer. A summary of the rate constants is given in Table 2.

## Discussion

### Triplet Lifetime

It is clear that the various media have little effect on the triplet lifetime of thionine, and that alkylation of the thionine also does not affect the lifetime. The former observation is in accord with the reported insensitivity of $k_T$ to a change in acid from trifluoromethylsulfuric to sulfuric or to a change in solvent from water to 50 $V/V$ % aqueous acetonitrile [4]. The latter might be expected since alkylation of the amine group has little effect on the visible absorption spectrum [1].

### Quenching

The observed values of $k_q$ are qualitatively in accord with what would be expected on the basis of micelle or microdroplet surface charge. For SDS micelles, an effective surface potential ($\Psi$) may be determined with respect to water by means of Eq. (i),

$$k_q^{\mathrm{SDS}}/k_q^{\mathrm{aq}} = \exp(e\Psi/kT) \qquad \text{(i)}$$

where $k$, $e$ and $T$ are Boltzman's constant, the electronic charge and the absolute temperature, respectively. A value of $\Psi \approx 80$ mV is obtained from the data in Table 2. This value is somewhat low compared with values (~ 130 mV) obtained from other rate constants [8]. However, it may be that the thionine is partitioned to some extent between the aqueous phase and the micelle. The thionine is likely all in the microdroplet in the microemulsion, however, as indicated by the same value of $k_q$ for both ThHCl and $C_{10}$ThHCl in SCS microemulsion. This is consistent with the observation that substances which are partitioned in micelles are not partitioned in microemulsions [9], probably due to the higher phase volume and larger regions of varying polarity. The value of $\psi$ calculated for the SCS μE is about 45 mV. This seems reasonable when compared with values obtained by other means [10], although effective surface potentials in microemulsions are best computed with reference not to water but to a comparable nonionic microemulsion [8]. In any event, the higher values of $k_q$ in SDS micelles and SCS microemulsion will yield a higher initial yield of semithionine. If $\phi^0_{S\cdot}$ is the quantum yield of semithionine produced initially as a result of quenching of the triplet by iron(II), then it is given by Eq. (ii)

$$\phi^0_{S\cdot}/\phi_T = \tau_T/(\tau_T + \tau_q)\,. \tag{ii}$$

Here, $\tau_T$ is the triplet lifetime and $\tau_q^{-1} = k_q$ (II)]. Using a value of $\phi_T = 1$ (*vide supra*) and an iron(II) concentration comparable to that employed in photogalvanic cells (0.01 M), $\phi^0_{S\cdot} = 0.60$ (aqueous), 0.90 (SCS μE), and 0.98 (SDS micelles).

## Dismutation

The range of $k_d$ values is quite striking, varying over more than two orders of magnitude from aqueous solution to SDS micelles. It might be expected that the dismutation rate be slowed somewhat in micellar solution since no micelle contains more than one thionine at the concentrations employed [11]. However, the concentration of both micelles and microdroplets is ~ 1 mM [12], but the rate constant in microemulsion is only about half that in water. In order to understand these results, a previously developed solubilization model was employed [13]. The overall scheme is presented by Eqs. (iii)–(vi)

$$S_w^{\boldsymbol{\cdot}} + M \underset{k_1}{\overset{k_2}{\rightleftharpoons}} M_1 \tag{iii}$$

$$S_w^{\boldsymbol{\cdot}} + M_1 \underset{2k_1}{\overset{k_2}{\rightleftharpoons}} M_2 \tag{iv}$$

$$2S_w^{\boldsymbol{\cdot}} \xrightarrow{k_d^w} \text{products} \tag{v}$$

$$M_2 \xrightarrow{k_e} \text{products} + M\,. \tag{vi}$$

Here $S_w^{\boldsymbol{\cdot}}$ is aqueous semithione, M, $M_1$ and $M_2$ are micelles containing 0, 1, and 2 semithionine molecules, respectively, $k_d^w$ is the dismutation rate constant in water, and $k_e$ is the intramicellar (intraparticle) first order rate constant for the dismutation of two semithionine molecules in the same micelle. A number of studies have shown that the entrance rate constant ($k_2$) is diffusion controlled (~ $10^9-10^{10}$ $M^{-1}$ $s^{-1}$) while the exit rate constant ($k_1$) generally varies from ~ $10^2-10^7$ $s^{-1}$, depending on the solute [14]. Values of $k_e$ are usually on the order of $10^6-10^7$ $s^{-1}$ (14c, f.). In this study, (M) ≈ $10^{-3}$ M and (S) ≈ $10^{-5}$ M (*vide supra*). Using a Poisson distribution [14], $(M_1) \approx (S)$, $(M_2) \approx (S)^2/2(M) \approx 5 \cdot 10^{-8}$ M, and at equilibrium, $(S)_w = (S)/[1 + K(M)] \approx 10^{-7}$ M, where $K = k_2/k_1$. The value of $k_d^w$ is ≈ $10^9$ (Table 2). Using the above values in conjunction with the rates derived from Eqs. (iii)–(vi), it is clear that the concentrations ($S_w$) and ($M_1$) are given by their equilibrium values in the absence of reaction, irrespective of whether reaction takes place in the micellar phase, aqueous phase, or both [15]. Thus, the steady state approximation can be applied to $M_2$ irrespective of the relative values of $k_e$ and $k_1$. If, in addition, as the above estimates indicate, reaction in the aqueous phase is negligible, it is easily shown that the observed dismutation rate constant ($k_d$) is given by Eq. (vii)

$$k_d = k_2k_e/(2k_1 + k_e)\,[1 + K(M)]\,. \tag{vii}$$

In microemulsion, if $k_1 = 10^6$ $s^{-1}$ and $k_e = 10^6-10^5$ $s^{-1}$, $k_d = 3-5 \cdot 10^8$ $M^{-1}$ $s^{-1}$ (observed value $= 6 \cdot 10^8$, Table 2). However, in the SDS micelle, $k_d \approx 10^7$ $M^{-1}$ $s^{-1}$. Based on the above scheme, either the exit rate is slow (e.g. $k_1 = 10^4$ $s^{-1}$ yields $k_d \approx 10^7$) or $k_e$ is very low. If $k_e$ is sufficiently low ($\leq 10^3$ $s^{-1}$), then the rate of dismutation will be controlled by reaction in the aqueous phase, and $k_d$ will be given by Eq. (viii)

$$k_d = k_d^w/[1 + K(M)]^2\,. \tag{viii}$$

A value of $k_1 = 10^6$ $s^{-1}$ gives $k_d = 10^7$ $M^{-1}$ $s^{-1}$. Of these two possibilities, the former seems more likely since, for ex., the intramicellar dismutation of $(Ag)_2^+$ occurs within 1–2 μs while the intermicellar reaction occurs on a $10^{-4}-10^{-2}$ s time scale [16].

In order to provide a definitive answer to the dismutation mechanism in the SDS micellar solution, a detailed study is required. Specifically, $k_d$ should be measured as a function of (M), and $k_1$' $k_2$ and $k_e$ should be obtained. It may be possible to measure the exit and entrance rates by the use of suitable water and oil quenchers of the thionine triplet state [13], assuming that thionine and semithionine behave similarly in this regard. The value of $k_e$ may possibly be estimated from the fast-decay component of an oil soluble quencher or by means of triplet-triplet annihilation at higher thionine concentrations. The use of the $C_{10}$-thionine in SDS micelles should also result in a lower exit rate.

It should be noted that the value of $k_d$ for aqueous $C_{10}$-thionine is higher than that for aqueous thionine. This may be a result of increase of aggregation of the former in water [1]. The slightly lower value of $k_T$ is consistent with this observation.

## Back Reaction

Perhaps the most remarkable feature of the variation of $k_b$ with the medium is the lack of variation. It might be expected that $k_b$ change in the same fashion as $k_q$, for the same reasons (*vide supra*). In fact, Fe(III) should, if anything, be more strongly bound to the anionic micelle or microdroplet than Fe(II). A possible, and likely, explanation for this is a negative shift in reduction potential of the iron 2+/3+ couple from water to microemulsion (and micelle). In effect, the back reaction is slowed down because the (negative) free enthalpy difference between reactants and products is decreased, which compensates for the increased local concentration of Fe(III). There are two observations which support this hypothesis. First, negative shifts of 200 mV are often observed for aqueous ions such as Cd(II) on going from water to anionic microemulsion, and a shift as high as 900 mV has been observed for Cu(II) [17]. Second, as noted earlier, when Fe(II) is added to solutions of thionine in micelles or microemulsion containing small amounts of Fe(III), a dark bleaching of the color is observed. The extent depends upon the relative concentrations of Fe(II) and Fe(III) and is somewhat greater in SCS microemulsion than in SDS micelles. Under comparable conditions, no bleaching is observed in aqueous solution.

In any event, the net result is that while an anionic assembly increases the quenching rate, it does not increase the rate of the back reaction. Of course, if the above explanation is correct, this happy state of affairs is being paid for by an unhappy decrease in maximum realizable potential.

### Leucothionine Oxidation

The rate constant in microemulsion is about 2–3 times greater than in water, and the same considerations should apply here as were discussed above. The value of $k_L$ could not be determined for SDS micelles in the present study for the reasons given in Table 2. It is interesting to note that in the case of SDS micelles, since $k_d$ is so small, very little leucothionine is formed. It may then be in this case that semithionine is also functioning as an electrode-active species, since SDS micelles give a good photogalvanic output relative to water [1].

This work was partially supported by the Office of Basic Energy Sciences, U.S. Department of Energy. One of us (R.M.) also wishes to thank Drexel University for their support of his leave, and Professor Michael Grätzel and the Ecole Polytechnique Fédérale de Lausanne for their support of his stay in Lausanne. Many thanks are also due to Dr. P. P. Infelta for his many kindnesses and much valuable discussion, and without whose assistance this work could not have been performed.

### References

[1] N. S. Dixit and R. A. Mackay, J. Phys. Chem. *86*, 4593 (1982).
[2] M. Calvin, in: "Proceedings of Photochemical Workshop on Solar Energy", N. N. Lichtin, Ed., Boston 1973.
[3] C. G. Hatchard and C. A. Parker, Trans. Faraday Soc. (London) *57*, 1073 (1961).
[4] P. D. Wildes, N. N. Lichtin, M. Z. Hoffman, L. Andrews, and M. Linschitz, Photochem. Photobiol. *25*, 21 (1977).
[5] G. Rothenberger, P. P. Infelta, and M. Grätzel, J. Phys. Chem. *83*, 1871 (1979).
[6] U. Lachish, A. Shafferman, and G. Stein, J. Chem. Phys. *64*, 4205 (1976).
[7] T. L. Osif, N. N. Lichtin, M. Z. Hoffman, J. Phys. Chem. *82*, 1778 (1978).
[8] R. A. Mackay, J. Phys. Chem. *86*, 4756 (1982).
[9] R. A. Mackay and C. Hermansky, J. Phys. Chem. *85*, 739 (1981).
[10] a) C. E. Jones, L. Weaver, and R. A. Mackay, J. Phys. Chem. *84*, 1495 (1980); b) R. A. Mackay, K. Jacobson, and J. Tourian, J. Colloid. Interface Sci. *76*, 515 (1980).
[11] Using an aggregation number of 65 for SDS (P. Lianas and R. Zara, J. Coll. Int. Sci. *84*, 100 (1982)) and a CMC of $\sim$ 8 mM, the concentration of micelles = (70-8)/65 $\approx$ 1 mM. The dye (thionine) concentration was $\leq 20\,\mu$M, so the dye to micelles ratio $\lesssim 0.02$.
[12] R. A. Mackay, in: "Microemulsions", I. D. Robb, Ed., Plenum Press: London 1982.
[13] A. Yekta, M. Aikawa, and N. J. Turo, Chem. Phys. Lett. *63*, 543 (1979).
[14] a) N. J. Turro, M. Grätzel, and A. M. Braun, Angew. Chem. Int. Ed. Engl. *19*, 675 (1980); b) M. Almgren, F. Grieser, and J. K. Thomas, J. Am. Chem. Soc. *101*, 279 (1979); c) P. Lranas, J. Lang, C. Strazlelle, and R. Zana, J. Phys. Chem. *86*, 1019 (1982); d) Y. Moroi, P. P. Infelta, and M. Grätzel, J. Am. Chem. Soc. *101*, 573 (1979); e) M.-P. Pileni and M. Grätzel, J. Phys. Chem. *84*, 1822 (1980); f) M. D. Hatlee, J. J. Kozak, G. Rothenberger, P. P. Infelta, and M. Grätzel, ibid *84*, 1508 (1980).
[15] Since these are thermodynamically single phase systems, the term "micellar phase" means the micellar "pseudophase".
[16] A. Henglein and Th. Proske, Ber. Bunsenges. Phys. Chem. *82*, 471 (1978).
[17] R. A. Mackay, N. S. Dixit, and R. Agarwal, "Inorganic Reactions in Microemulsions", ACS Symposium Series No. 177, S. L. Holt, Ed., 1982, pages 179–194.

(Eingegangen am 23. August 1984, E 5824
endgültige Fassung am 18. Januar 1985)

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# Intercalation of Graphite by Aluminum Chloride. Influence of Graphite Properties on Intercalation Rate

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*Chemical Kinetics / Gases / Intercalation / Materials Properties*

Kinetics of the intercalation of several well characterized graphites by aluminum chloride in the presence of chlorine were investigated in the 500 to 660 K temperature range. Temperature was the decisive parameter determining the stage of the intercalation compound. The intercalation rate depended on temperature, on graphite properties, and on partial pressures of aluminum chloride and chlorine. Crystalline perfection and amount of prismatic edges were found to be important graphite properties determining the intercalation rate. With all graphite types, the intercalation rate was linear with time in the early part of the intercalation, i.e. to about 50% of the saturation uptake. Intraparticle aluminium concentration profiles measured by electron microprobe exhibited no significant gradient of the intercalate in the intercalated region, indicating that the intercalation process was not limited by diffusion of the intercalate into the interspaces of the graphites.

Ber. Bunsenges. Phys. Chem. *89*, 530–538 (1985) – © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1985.
0005–9021/85/0505–0530 $ 02.50/0