

Electrochemical and Photochemical Investigations of the Iron–Thionine System in Micellar Sodium Dodecyl Sulfate Solution

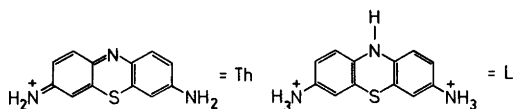
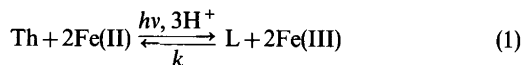
W. RICHARD BOWEN*

Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

The organic dye thionine (3-imino-3*H*-phenothiazin-7-amine) is effectively solubilised in aqueous sodium dodecyl sulfate (NaLS) solutions. Solubilisation leads to a reduction in the electrochemical rate constant for the thionine/leucothionine couple. Koutecky-Levich plots show that there is also an additional potential independent step introduced in the electrode reactions. The electrode kinetics of the Fe(II)/Fe(III) couple were unaffected by the presence of NaLS in the solution.

The iron–thionine photogalvanic system was studied in NaLS solution using the transparent rotating disc electrode technique. The usefulness of this technique was confirmed, the efficiency of formation of leucothionine and the rate of its destruction being determined.

This paper describes an investigation of the electrochemical and photochemical properties of the iron–thionine photogalvanic system in micellar solution. The photochemistry of this system has been investigated by numerous techniques.^{1–4} The overall reaction may be written as eqn. (1), where Th is



thionine and L is leucothionine, in the protonation states relevant to this study. Absorption of radiation by thionine and the subsequent electron transfer reaction to excited thionine molecules from

Fe(II) generates leucothionine and Fe(III). Power may be extracted when the products of this photochemical process react at electrodes, at the same time regenerating the initial reactants.⁵

A severe hindrance in the use of the iron–thionine system in practical photogalvanic cells is the low solubility of the thionine dye. This leads to two problems. Firstly, the radiation cannot be absorbed closely enough to the electrode to allow the photogenerated product to react at the electrode.⁵ Secondly, the photogenerated intermediates are generated over too wide a region of space to allow them to find each other and form leucothionine by a dismutation reaction.⁴

Micelles are molecular aggregates formed in solutions of surfactants—molecules in which a non-polar hydrocarbon “tail” is joined to a polar head group.^{6–8} At low concentrations in water, surfactants exist mainly as monomers. Above a certain critical concentration (CMC), numbers of them aggregate, with the hydrocarbon groups forming a core and the polar groups pointing outward. An outstanding property of such micellar solutions is their ability to solubilise organic compounds.⁸

The electrochemistry⁹ and photochemistry¹⁰ of micelle-solubilised materials are relatively new fields. In the present work electrochemical measurements were made at a platinum rotating disc electrode (RDE). The new technique of the transparent rotating disc electrode (TRDE)^{11–14} was utilised for photochemical measurements.

EXPERIMENTAL

The TRDE apparatus and technique have been previously described.^{11–14} Light is shone directly through the electrode, giving a high concentration

* Present address: Materials Development Division, AERE Harwell, Oxfordshire, OX11 0RA, England.

of photoproducts close to the electrode surface. Electrode rotation establishes a genuine steady state and gives a precisely calculable flux of photoproducts toward the electrode, where they may react. In these experiments the light source was a 250 W tungsten halogen lamp and the electrode was of platinum.

Sodium dodecyl sulfate (also called sodium lauryl sulfate, NaLS) of *puriss* grade was obtained from Fluka. Experiments were carried out at 25 °C. Viscosities (ν) were determined using an Ostwald Viscosimeter. Electrode potentials are reported with respect to the saturated calomel electrode, and all currents are regarded as positive.

ELECTROLYTE PROPERTIES

Solubilisation in micellar solutions depends on the nature of the surfactant and its concentration. The negatively charged dodecyl sulphate ion was chosen as being a surfactant likely to significantly solubilise thionine. For example, thionine solubility 0.1 M NaLS/0.05 M H₂SO₄ was $\sim 3 \times 10^{-3}$ M compared to $\sim 10^{-4}$ M in 0.05 M H₂SO₄. Furthermore, even at high thionine concentrations, the absorption spectrum in NaLS solutions was essentially that of the monomeric form of the dye.

It was found that the addition of NaLS up to 0.1 M caused no apparent change in the pH of 0.05 M or 0.5 M H₂SO₄ solutions. Electrochemical measurements were made with NaLS concentration in the range 0.01–0.1 M, that is, above the CMC,⁷ and with either 0.05 M or 0.5 M H₂SO₄. Cyclic voltammograms at a Pt electrode in aqueous NaLS/H₂SO₄ solutions showed characteristics similar to those in non-surfactant solutions of the same pH. Peaks were recorded due to the formation and destruction of the surface oxide as well as two distinct hydrogen adsorption and two distinct hydrogen desorption peaks. In the surfactant solutions the anodic limit was shifted about 0.2 V in the positive direction.

ELECTROCHEMISTRY OF Fe(II)/Fe(III)

Current-voltage curves were measured for the Fe(II)/Fe(III) couple in aqueous H₂SO₄ solutions containing up to 0.1 M NaLS and compared to those in non-surfactant solutions at the same pH. The surfactant caused no change in the formal potential (E'), and in all cases the couple showed reversible electrode kinetics ($k'_0 > 30 \text{ cm ks}^{-1}$, where k'_0 is the standard electrochemical rate constant at the formal potential). The limiting currents (i_{lim})

obeyed the Levich equation ($i_{\text{lim}} \propto W^{\frac{1}{2}}$, where W is the electrode rotation speed in Hz), showing that they were diffusion controlled. Appreciable changes did, however, occur in the diffusion coefficients. For example, it was found from the Levich plots that in 0.05 M H₂SO₄, $D_{\text{Fe(II)}} = 6.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $D_{\text{Fe(III)}} = 5.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, whereas in 0.05 M H₂SO₄/0.1 M NaLS, $D_{\text{Fe(II)}} = 2.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $D_{\text{Fe(III)}} = 1.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

ELECTROCHEMISTRY OF Th/L

Current-voltage curves for the reduction of thionine in NaLS/H₂SO₄ solutions were recorded, and the rotation speed dependence of the limiting currents was measured. It was found that a Levich plot was not linear, and that the limiting currents were below the transport limited values. This shows that an additional rate limiting step is present in the reduction. The limiting current in such a case is described by the Koutecky-Levich equation.¹⁵ For an RDE, this predicts that a plot of i_{lim}^{-1} vs. $W^{-\frac{1}{2}}$ should be linear, Fig. 1. The intercept of the Koutecky-Levich plot gives the apparent rate constant of the additional limiting step ($k'_{\text{M,Th}}$). The oxidation of leucothionine also showed such a step ($k'_{\text{M,L}}$).

The dependence of $k'_{\text{M,Th}}$ and $k'_{\text{M,L}}$ on the concentration of NaLS is shown in Fig. 2. Also shown in the figure is the corresponding dependence of k'_0 . The formal potential (E') was 0.254 V and the apparent cathodic transfer coefficient about 0.2. Both were independent of the concentrations of NaLS and Th in the measured ranges. It was found that at

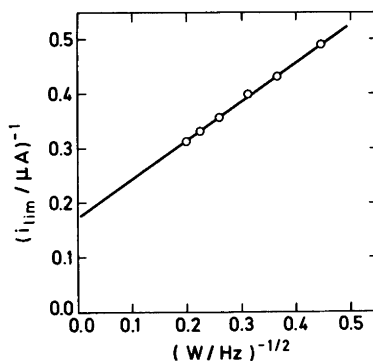


Fig. 1. Typical Koutecky-Levich plot for cathodic reduction of thionine in NaLS solution. [Th] = 2×10^{-4} M, [NaLS] = 0.1 M, [H₂SO₄] = 5×10^{-2} M. Electrode area = 0.12 cm².

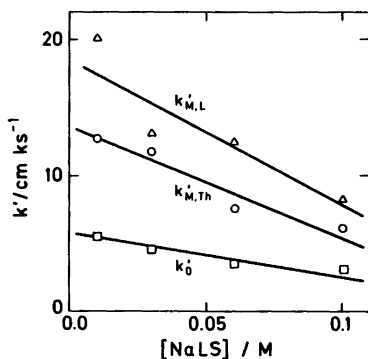


Fig. 2. The dependence of $k'_{M,Th}$ (○), $k'_{M,L}$ (△) and k'_0 (□) on NaLS concentration. $[Th] = [L] = 2 \times 10^{-4}$ M, $[H_2SO_4] = 0.5$ M.

the same thionine concentration (2×10^{-4} M), D_{Th} decreased from 1.0×10^{-6} cm² s⁻¹ in 0.01 M NaLS to 8.2×10^{-7} cm² s⁻¹ in 0.1 M NaLS. D_L decreased from 1.3×10^{-6} to 9.4×10^{-7} cm² s⁻¹ over the same range. The values for non-surfactant solutions are $k'_0 > 30$ cm ks⁻¹, $E' = 0.172$ V, $D_{Th} = D_L = 5.6 \times 10^{-6}$ cm² s⁻¹, and there is no step corresponding to k'_M .

The dependence of $k'_{M,Th}$ and k'_0 on the concentration of Th is shown in Fig. 3. It was found that at the same NaLS concentration (0.1 M) D_{Th} decreases from 8.2×10^{-7} cm² s⁻¹ at $[Th] = 2 \times 10^{-4}$ M to 6.3×10^{-7} cm² s⁻¹ at $[Th] = 2 \times 10^{-3}$ M.

The most interesting result is the measurement of the additional rate determining step. As a recent survey of the field has shown,⁹ it has been generally found that electrochemically active, solubilised species give diffusion limited currents. It is not possible to describe the nature of this step, as too

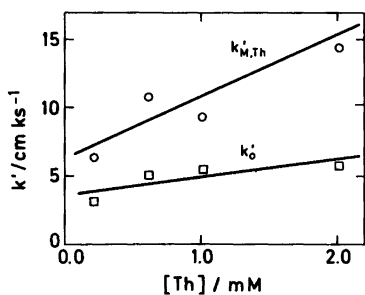


Fig. 3. The dependence of $k'_{M,Th}$ (○) and k'_0 (□) on thionine concentration. $[NaLS] = 0.1$ M, $[H_2SO_4] = 0.5$ M.

little is known about the position of thionine molecules in the micelles or about the details of electrochemical processes in micellar systems. It has been speculated¹⁶ that diffusion of the solubilised species from the micelle interior, or a distortion of the micelle itself, so as to release solubilised material, may be important steps.

The decreasing value of k'_0 with increasing NaLS concentration is in accordance with the findings¹⁶ that the reversibility of azobenzene reduction decreased with increasing surfactant concentration. The decreasing value of D with increasing NaLS concentration and increasing thionine concentration is in accordance with findings⁹ for anthraquinone dyes. These results were taken to indicate that the diffusing "particle" from the bulk solution to the electrode is the micelle with the dye. The size of this "particle" may increase with increasing concentrations of NaLS and Th.

PHOTOELECTROCHEMISTRY

A current-voltage curve and a photocurrent (i_p)-voltage curve for the iron-thionine system at a platinum TRDE is shown in Fig. 4. The photocurrent has been taken as the difference between the currents measured under illumination and in the dark. The dependence of i_p on light intensity (I) and rotation speed were studied by potentiostating the electrode in the region of almost zero dark current at a potential where photochemically produced leucothionine is oxidized and photochemically produced Fe(II) is reduced at their limiting rates.

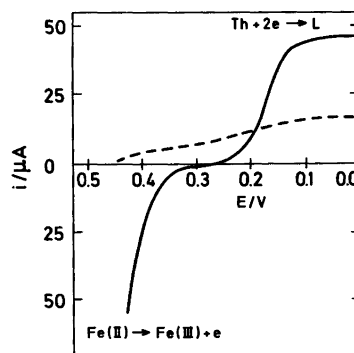


Fig. 4. Typical current-voltage curve (—) and photocurrent-voltage curve (---) for the thionine-iron system in NaLS solution at a TRDE. $[Th] = 2.5 \times 10^{-3}$ M, $[Fe(II)] = 1 \times 10^{-2}$ M, $[H_2SO_4] = 5 \times 10^{-2}$ M. Electrode area = 0.12 cm².

There is a net cathodic photocurrent because Fe(III) is reduced at a transport limited rate, whereas the oxidation of leucothionine is controlled by the slower additional step. If most of the light is absorbed within the diffusion layer distance (X_D), eqn. (2) may be given,¹⁴ where $i_p = i_{p,Fe(III)} - i_{p,L}$.

$$i_{p,Fe(III)} = i_p \left(1 + \frac{X_D k'_{M,L}}{D_L} \right) \quad (2)$$

Such corrected currents are plotted in Fig. 5.

It is found at the lowest rotation speeds that $i_{p,Fe(III)} \propto W^{1/6}$, and $i_{p,Fe(III)} \propto I^{2/3}$. It has been shown that these dependencies are diagnostic for the case of a photoproduct being destroyed by a second order process.¹² In the present case this is interpreted as being the back-reaction between photochemically produced Fe(III) and photochemically produced L. At the highest rotation speeds, it is found that $i_{p,Fe(III)} \propto W^{-1/2}$ and $i_{p,Fe(III)} \propto I$. The photoproducts now have a shorter distance to diffuse to the electrode and are stable on the time-scale of the experiment.¹¹

It may be shown¹¹ that, at the highest rotation speeds, the corrected photochemical flux at the electrode should be given by eqn. (3), where

$$j = gX_D \quad (3)$$

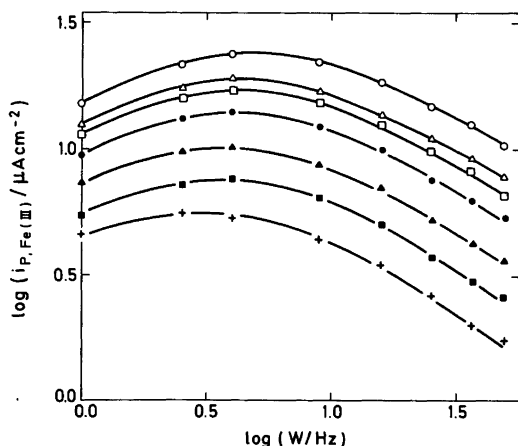


Fig. 5. The dependence of $i_{p,Fe(III)}$ on W and I . $[Th] = 2 \times 10^{-3}$ M, $[Fe(II)] = 1 \times 10^{-2}$ M, $[NaLS] = 0.1$ M, $[H_2SO_4] = 5 \times 10^{-2}$ M. Relative light intensities are, 1 (○), 0.72 (△), 0.60 (□), 0.47 (●), 0.30 (▲), 0.22 (■) and 0.14 (+). Light wavelength = 599 nm.

$g = I\epsilon a\theta_L$, ϵ is the extinction coefficient of Th at the wavelength of light used, a is the thionine concentration, θ_L is the overall quantum efficiency for the production of L, and $X_D = 0.643 W^{-1/2} \nu^{1/6} D^{1/3}$. Thus, a plot of j/I vs. $W^{-1/2}$ should give a straight line, the slope of which gives a value of θ_L . It is found that $\theta_L = 0.15$. It may also be shown¹² that the corrected photochemical flux at the lowest rotation speeds should be given by,

$$j = D^{2/3} g^{2/3} k_{-2}^{-1/3} X_D^{-1/3} \quad (4)$$

where k_{-2} is the rate constant for the second order destruction reaction. Thus, a plot of $jI^{-2/3}$ vs. $W^{1/6}$ should give a straight line. From the slope of this line, and using the above value of θ_L , it is found that $k_{-2} = 1 \times 10^6$ l mol⁻¹ s⁻¹.

Values for θ_L and k_{-2} for this system at the same pH in non-surfactant solution have previously been tabulated and discussed.¹⁴ Different methods gave values of θ_L in the range 0.27–0.3 and values of k_{-2} in the range 4.3×10^2 to 5.6×10^2 l mol⁻¹ s⁻¹. Thus, the effect of the surfactant has been to lower θ_L and to greatly increase k_{-2} .

CONCLUSION

Thionine was significantly solubilised in NaLS solution. The solubilised thionine had a lowered value of k'_o , and Koutecky-Levich plots showed that an additional potential independent rate limiting step was present in the electrode reaction. The electrode reactions of Fe(II)/Fe(III) were unaffected by the presence of NaLS. The diffusion coefficients of thionine, leucothionine, Fe(II) and Fe(III) were all diminished in NaLS solutions. The micellar solution reduced the efficiency of photochemical formation of leucothionine and greatly increased the rate of its destruction.

Thus, it is on balance unfavourable to use NaLS solutions for the solubilisation of thionine in photogalvanic cells. Besides clarifying this question, the present study elucidates the electrochemical behaviour of the Th/L and Fe(II)/Fe(III) couples in NaLS solution. The study has also confirmed the usefulness of the TRDE for measuring critical photochemical parameters.

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REFERENCES

1. Hatchard, C. G. and Parker, C. A. *Trans. Faraday Soc.* 57 (1961) 1093.
2. Hall, D. E., Clarke, W. D. K., Eckert, J. A., Lichtin, N. N. and Wildes, P. D. *Ceramic Bulletin* 56 (1977) 408.
3. Albery, W. J., Bowen, W. R. and Archer, M. D. *J. Photochem.* 11 (1979) 15.
4. Albery, W. J., Bowen, W. R., Archer, M. D. and Ferreira, M. I. *J. Photochem.* 11 (1979) 27.
5. Albery, W. J. and Archer, M. D. *Nature* 270 (1977) 399.
6. Mittal, K. L. *Solution Chemistry of Surfactants*, Plenum, New York and London 1979, Vols. 1 and 2.
7. Fendler, J. H. and Fendler, E. J. *Catalysis in Micellar and Macromolecular Systems*, Academic, New York 1977.
8. Menger, F. M. *Acc. Chem. Res.* 12 (1979) 111.
9. Shinozuka, N. and Hayano, S. p. 599 in Ref. 6 Vol. 2, and references therein.
10. Thomas, J. K. and Almgren, M. p. 541 in Ref. 6 Vol. 2, and references therein.
11. Albery, W. J., Archer, M. D. and Egdell, R. G. *J. Electroanal. Chem.* 82 (1977) 199.
12. Albery, W. J., Bowen, W. R., Fisher, F. S. and Turner, A. D. *J. Electroanal. Chem.* 107 (1980) 1.
13. Albery, W. J., Bowen, W. R., Fisher, F. S. and Turner, A. D. *J. Electroanal. Chem.* 107 (1980) 11.
14. Albery, W. J., Bartlett, P. N., Bowen, W. R., Fisher, F. S. and Foulds, A. W. *J. Electroanal. Chem.* 107 (1980) 23.
15. Koutecky, J. and Levich, V. G. *Zh. Fiz. Khim.* 32 (1956) 1565.
16. Westmoreland, P. G., Day, R. A. and Underwood, A. L. *Anal. Chem.* 44 (1972) 737.

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