

PHOTOGALVANIC CELLS XIII: NEW METHYLENE BLUE NN

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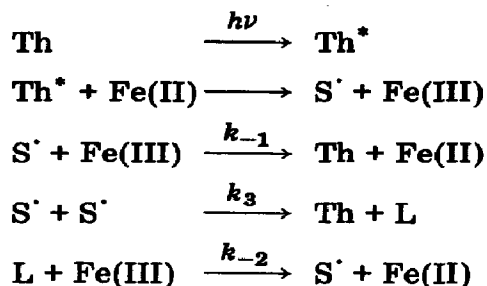
Summary

The suitability of new methylene blue *NN* as a dye for a photogalvanic cell for solar energy conversion is investigated. At concentrations as low as 10^{-4} mol dm $^{-3}$ there is extensive dimerization; however, the action spectrum shows that the photoredox reaction is only driven by the monomer. Data for the photoelectrochemical quantum efficiency in the concentration range 10 - 25.0 μ mol dm $^{-3}$ are explained by dimerization together with diffusion-controlled self-quenching by both monomers and dimers. These results show that new methylene blue *NN* is unsuitable and that self-quenching may be a serious problem for other iron-thiazine systems.

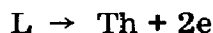
1. Introduction

A photogalvanic cell consists of two electrodes separated by approximately 0.1 mm with a thin layer of photogalvanic solution between them. One of the electrodes is transparent to allow the light to pass into the solution where it is absorbed by a dye. The dye, excited by the light, reacts with a quencher to produce energetic electron transfer products; these then react at the electrodes, generating electrical power and regenerating the dye and the quencher.

The iron-thionine system [1 - 5] has been much studied as a possible system for photogalvanic cells for solar energy conversion. This work is concerned with the related system where the dye is new methylene blue *NN* (NMB). The reaction scheme is as follows:



illuminated electrode



dark electrode



The structure of Th is given in Fig. 1. S^{\cdot} is the one-electron reduction product and L is the fully reduced leuco form.

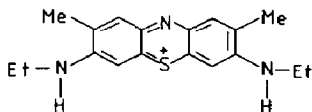


Fig. 1. The structure of Th.

Theoretical considerations of photogalvanic cells [6 - 8] have shown that for an efficient cell the light must be absorbed in a thin layer very close to the illuminated electrode. This necessitates a very soluble dye and so thionine, with a maximum solubility in aqueous solution of approximately 10^{-3} M, will never produce an efficient cell. Nevertheless, the iron-thionine system does have many features which are essential, namely relatively slow back-reaction kinetics, good quantum efficiency and a large extinction coefficient. Also the necessary electrode selectivity can be achieved by using the thionine-coated electrode [9 - 11].

NMB is a commercially available thiazine dye which is soluble up to approximately 10^{-1} M in aqueous solution [12] and therefore possesses the necessary solubility for an efficient photogalvanic cell. In this work we investigate NMB as a possible constituent of a photogalvanic cell. The technique used is that of the transparent rotating disc electrode [13 - 15]. By using solutions containing NMB and Fe(II) with no added Fe(III) the back reactions described by rate constants k_{-1} and k_{-2} are negligible and thus we can study the forward photochemical reactions and their quantum efficiencies. In particular the effects of the dimerization of the dye [16, 17] can be investigated.

2. Experimental

The apparatus and technique for the transparent rotating disc electrode have been described previously [13, 15]. The diffusion coefficient of NMB was measured using the method of Hitchman and Albery [18]. The spectra and absorbance measurements were made using a Cary 14 spectrophotometer with 1 mm, 1 cm and 10 cm cells. All chemicals were of AnalaR grade except for NMB which was used as supplied by Aldrich. All solutions were made with doubly distilled water and all experiments were carried out at 25 °C in 50 mM H_2SO_4 . The transparent rotating disc electrode experiments were performed at $[Fe(II)] = 10^{-2}$ M. All potentials are reported with respect to a saturated calomel electrode.

3. Results and discussion

Absorption spectra for three different concentrations of NMB are shown in Fig. 2. The change in the relative heights of the peaks suggests that the dye forms dimers or possibly higher polymers; the existence of an isosbestic point together with analysis at other wavelengths show that there are only two predominant forms of the dye in the solution, suggesting that we need only consider dimerization. Figure 3 shows the variation of the optical density (OD) at 632 nm (the maximum of the low concentration or monomer peak) with the total concentration c_T of NMB. Assuming that the other form of the dye is a dimer,



then

$$OD = (\epsilon_M c_M + \epsilon_D K c_M^2) l \quad (1)$$

where

$$c_M = \{(1 + 8Kc_T)^{1/2} - 1\} / 4K \quad (2)$$

and

$$c_T = c_M + 2c_D \quad (3)$$

ϵ_M is the decadic molar extinction coefficient of the monomer and c_M is its concentration; ϵ_D is the decadic molar extinction coefficient of the dimer and c_D is its concentration; c_T is the total concentration of dye and l is the

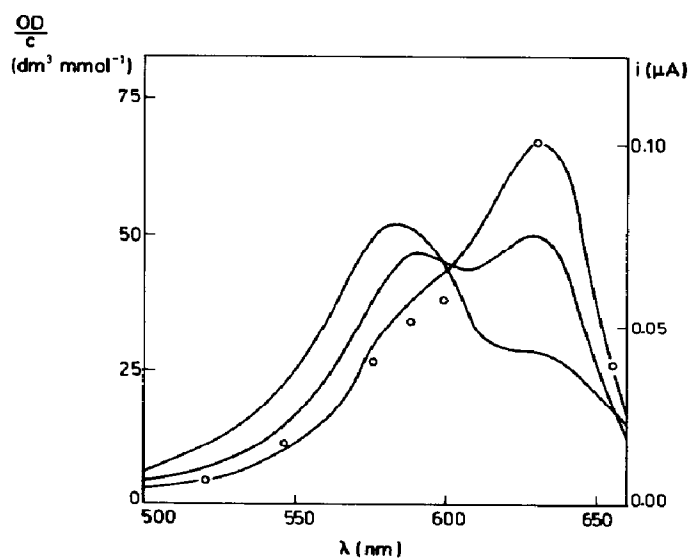


Fig. 2. Normalized spectra of NMB at three different concentrations ($c = 1.5, 15$ and $150 \mu\text{mol dm}^{-3}$) together with the action spectrum of the photocurrent (\circ). The action spectrum corresponds to the monomer spectrum observed at the lowest concentration.

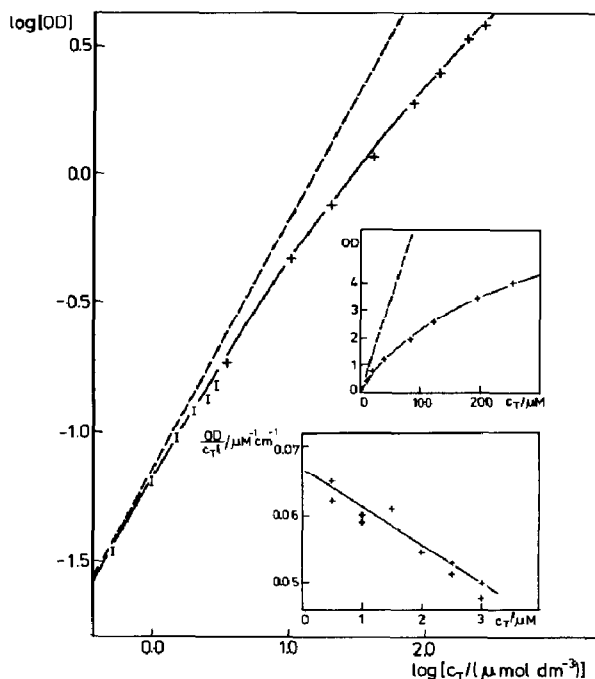


Fig. 3. The variation of the optical density at $\lambda = 632$ nm with the total concentration of NMB. The main plot is a logarithmic plot. The upper inset shows how the points at high concentration deviate from the line established at low concentration: ---, expected absorption for the monomer; —, absorption calculated using eqn. (1) and the values in eqns. (5) - (7). The lower inset shows the plot of eqn. (4) for the data at low concentration to find ϵ_M .

path length in centimetres. At low concentrations of dye where $c_D < 0.1c_T$ we can show that

$$OD/lc_T \approx \epsilon_M + (\epsilon_D - 2\epsilon_M)Kc_T \quad (4)$$

The inset in Fig. 3 shows a plot of this equation from which we obtain

$$\epsilon_M = (6.7 \pm 0.1) \times 10^7 \text{ cm}^2 \text{ mol}^{-1} \quad (5)$$

From the gradient of eqn. (4) and from the data at higher concentrations we obtain the following values for ϵ_D and K :

$$\epsilon_D = 1.0 \times 10^7 \text{ cm}^2 \text{ mol}^{-1} \quad (6)$$

$$K = 5.0 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \quad (7)$$

The good fit between the data and values of the OD calculated from eqns. (1) - (7) is shown in Fig. 3 and proves that a monomer-dimer equilibrium is adequate to describe the behaviour observed. In the range of concentration studied, trimers and higher polymers need not be considered. Dimerization is much more extensive for NMB ($K = 5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$) than for other thiazine dyes such as methylene blue [19, 20] ($K = 5 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$) or thionine itself [20] ($K = 10^3 \text{ dm}^3 \text{ mol}^{-1}$). We now consider the effect that

this increased dimerization has on the photoelectrochemical behaviour of NMB.

Current-voltage curves at a rotating disc electrode [21, 22] show that NMB is reduced in a reversible two-electron process with $E_{1/2} = 136$ mV. This value may be compared with $E_{1/2} = 208$ mV for thionine [10]; the electron-releasing groups attached to the aromatic nucleus are no doubt responsible for this shift in potential. Such a shift is desirable for a photo-galvanic cell since the cell would develop more voltage.

Values of the mixed diffusion coefficient \bar{D} were obtained from the limiting current at different concentrations of NMB, and using the value of K given here we found

$$\bar{D} = D_M c_M / c_T + 2D_D c_D / c_T$$

where [23]

$$D_D = 2^{-0.6} D_M$$

and

$$D_M = 4.25 \pm 0.09 \text{ cm}^2 \text{ M s}^{-1} \quad (8)$$

Turning to the photoelectrochemistry, the photocurrents caused by the oxidation of photogenerated L were measured as a function of the rotation speed W , the irradiance, the concentration of NMB and the wavelength. The action spectrum of the photocurrent for $c_T = 45 \mu\text{M}$, where there is a significant concentration of dimer, is shown in Fig. 2. It can be seen that the action spectrum corresponds to that of the monomer and hence only the monomer undergoes the photoredox reaction. We next consider the variation of the photocurrent with the rotation speed. In all cases the photocurrents were found to be proportional to $W^{-1/2}$ and the irradiance. This shows [15] firstly that the photogenerated product is not being destroyed by homogeneous kinetics and secondly that the solution close to the electrode is not being bleached. Under these conditions the photocurrent measures the efficiency of the photochemical and homogeneous reactions leading to L. The photocurrent i_p should be given by [15]

$$i_p = 0.64AF\phi_1\Phi I_{\Phi=1}\epsilon_M c_M D_M^{1/3} \nu^{1/6} W^{-1/2} \quad (9)$$

where A is the area of the electrode, ϕ_1 is the quantum efficiency for the production of S' , Φ is the transmittance of the neutral density filter and $I_{\Phi=1}$ is the irradiance with $\Phi = 1$; $\epsilon_M c_M$ is used because only the monomer undergoes the photoredox reaction. The remaining terms arise from the Levich [21] equation for the diffusion length. In our experiments only a small fraction of the light is absorbed in the diffusion layer and hence the absorption by the dimers is unimportant.

Figure 4 shows how i_p/Φ varies with the concentration c_M of monomer when the total concentration of NMB is varied between 10 and 250 μM . Each point is the mean of four determinations with $\Phi = 0.18, 0.30, 0.48$ and 1.0. Equation (9) is not obeyed. We suggest that in addition to the dimeriza-

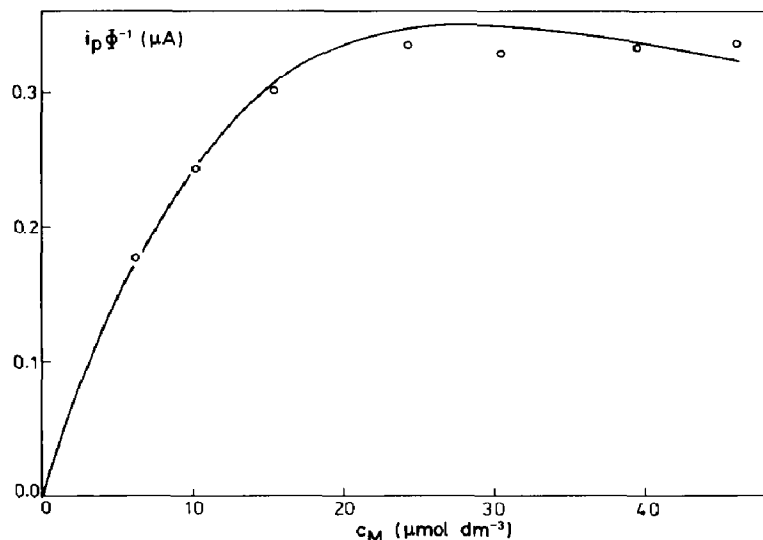


Fig. 4. The variation of photocurrent with concentration of monomer calculated from eqns. (2) and (7): —, calculated from eqns. (9) and (10).

tion reducing the efficiency of the photoredox process there must also be considerable self-quenching. Equation (9) is modified by writing

$$\phi_1 = (\phi_1)_0 \frac{k_q[\text{Fe(II)}]}{k_q[\text{Fe(II)}] + k_M c_M + k_D c_D} \quad (10)$$

where the rate constants describe the quenching of the triplet state by the three different species. We tested three hypotheses:

$$\text{self-quenching by monomer} \quad k_D = 0 \quad (\text{I})$$

$$\text{self-quenching by dimer} \quad k_M = 0 \quad (\text{II})$$

$$\text{self-quenching by both monomer and dimer} \quad k_M = k_D \quad (\text{III})$$

These hypotheses are tested in Fig. 5 which shows plots of ϕ_1^{-1} , calculated from eqns. (8) and (9), against c_M , c_D and $c_M + c_D$. It can be seen that hypotheses (I) and (II) give curved plots while hypothesis (III) gives a reasonable straight line. We therefore conclude that both the monomer and the dimer quench the triplet state. From the gradient and the intercept we find $k_M/k_q = 2.6 \times 10^2$. For thionine $k_q = 3 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [24] and assuming that the value for NMB is similar we find that, as might be expected, both k_M and k_D are rate constants for diffusion-controlled reactions. This justifies putting $k_M = k_D$ in hypothesis (III). Finally from eqn. (10) we also obtain a value for $(\phi_1)_0$ of 0.24, which is a factor of two less than the corresponding value for thionine [15].

These results for NMB show that because of dimerization, self-quenching and the low value of $(\phi_1)_0$ it is not a satisfactory dye for an efficient photogalvanic cell. The diffusion-controlled self-quenching reactions by both monomer and dimer are ominous for the development of these cells using

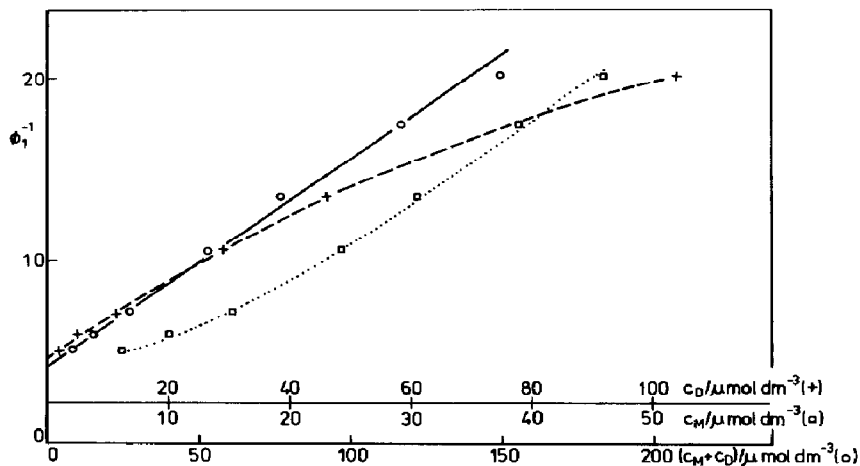


Fig. 5. The variation of ϕ_1^{-1} (calculated from eqns. (8) and (9)) plotted according to eqn. (10) for each of the three hypotheses: \square , \cdots , hypothesis (I); \times , $---$, hypothesis (II); \circ , $---$, hypothesis (III).

other thiazine dyes since to trap the light close to the electrode it is necessary to have concentrations of dye as large as $10^{-1} \text{ mol dm}^{-3}$.

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