# INFLUENCE OF IONIC STRENGTH ON THE EFFICIENCY OF CHARGE SEPARATION

BRYSON L. GORE, ANTHONY HARRIMAN and MARIE-CLAUDE RICHOUX

*Davy Faraday Research Laboratory, The Royal Institution, 21 Albemarle Street, London W1X 4BS (Gt. Britain)*
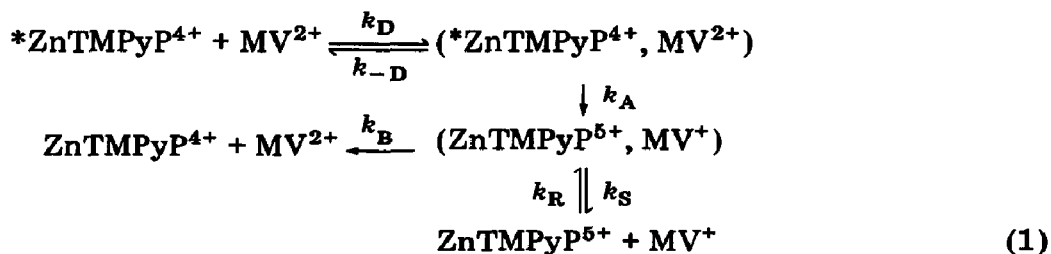
## Summary

Photoinduced electron transfer from the triplet excited state of zinc tetramethylpyridylporphyrin to methyl viologen in aqueous solution involves the intermediate formation of a triplet ion pair which can dissociate either to ground state reactants or to redox products. The yield of redox products decreases when the ionic strength of the background electrolyte exceeds 0.1 M and this effect can be explained in terms of a modified Fuoss equation.

Currently, there is intense interest in the development of systems capable of the collection and storage of solar energy in the form of chemical potential. Although there are many approaches to this ideal, the photodissociation of water into hydrogen and oxygen remains one of the most promising schemes for the construction of a practical solar energy storage device. If the photodissociation of water into hydrogen and oxygen is to be realized in homogeneous solution, a photosensitizer must be employed and, for the system to possess any real practical applications, the sensitizer must be capable of harvesting a large fraction of the solar spectrum and must give a high yield of primary photoredox products. In this respect water-soluble zinc(II) porphyrins appear to be quite attractive photosensitizers since they can collect some 30% of the energy available in sunlight and they undergo facile photoredox processes. However, we have shown previously [1] that the nature of the group used to assist the solubility of the porphyrin in water plays a very important role in determining the yield of primary redox products and strong electrostatic repulsion between the reagents favours the formation of separated ion products. Thus irradiation of zinc tetramethylpyridylporphyrin (ZnTMPyP$^{4+}$) in the presence of methyl viologen (MV$^{2+}$) results [1] in the formation of redox products with a quantum efficiency of about 0.75, whilst under similar experimental conditions the quantum yield of redox products from the zinc(II) *meso*-tetra(4-sulphophenyl)-porphine (ZnTSPP$^{4-}$)–MV$^{2+}$ system is less than 0.01. Since these reactions

$$R \equiv \quad \underset{}{\overset{}{-\hexagon N^+ -CH_3}} \qquad ZnTMPyP^{4+}$$

$$-\hexagon -SO_3Na \qquad ZnTSPP^{4-}$$
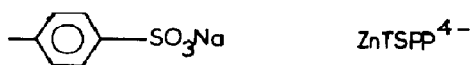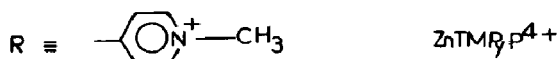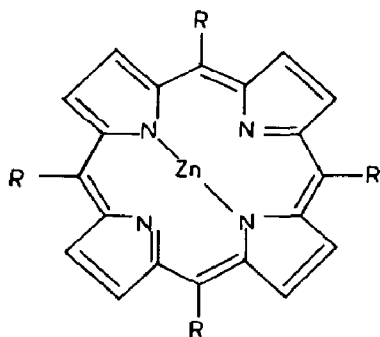
involve ionic species, the rate constants for the individual steps and thus the overall yield of the redox products should depend upon the background electrolyte, and in this paper we report on the influence of ionic strength upon the yield of primary redox products from the $ZnTMPyP^{4+}$–$MV^{2+}$ system. It should be noted that at the concentrations of $ZnTMPyP^{4+}$ employed in this work nuclear magnetic resonance studies have shown that there is no evidence for dimerization, even at the highest ionic strengths used.

In previous work [1] we have shown that the above reaction can be described by the following scheme in which the triplet excited state of $ZnTMPyP^{4+}$ donates an electron to ground state $MV^{2+}$ in aqueous solution at pH 5:

$$*ZnTMPyP^{4+} + MV^{2+} \xrightleftharpoons[k_{-D}]{k_D} (*ZnTMPyP^{4+}, MV^{2+})$$
$$\downarrow k_A$$
$$ZnTMPyP^{4+} + MV^{2+} \xleftarrow{k_B} (ZnTMPyP^{5+}, MV^+)$$
$$k_R \parallel k_S$$
$$ZnTMPyP^{5+} + MV^+ \qquad (1)$$

The essential features of this scheme involve the reversible formation of an encounter complex in which there is practically no binding energy between the reactants and the formation of a triplet ion pair which can dissociate to ground state reactants or separate into ion products. The quantum yield $\Phi_{ions}$ for the formation of ion products can be considered as the product of three probabilities:

$$\Phi_{ions} = \Phi_T \Phi_Q \Phi_S \tag{2}$$

where $\Phi_T$ is the quantum yield for formation of the triplet excited state of $ZnTMPyP^{4+}$ ($\Phi_T = 0.9$) and $\Phi_Q$ is the probability of quenching the triplet state of lifetime $\tau_T$ at any particular concentration of $MV^{2+}$:

$$\Phi_Q = \frac{k_Q[MV^{2+}]}{k_Q[MV^{2+}] + \tau_T^{-1}} \tag{3}$$

$$k_Q = \frac{k_D k_A}{k_A + k_{-D}} \tag{4}$$

The $\Phi_S$ term is the probability of the ion pair separating into ion products and can be formulated as

$$\Phi_S = \frac{k_S}{k_S + k_B} \tag{5}$$

Now, for an electron transfer reaction between ions of charges $Z_A$ and $Z_B$ in aqueous solution, $k_Q$ should depend upon the ionic strength $\mu$ of the medium according to the Debye–Hückel relationship [2]

$$\log k_Q = \log k_Q^0 + 1.02\, Z_A Z_B \frac{\mu^{1/2}}{1 + \mu^{1/2}} \tag{6}$$

and from our previous work [1] the rate constant $k_Q^0$ for quenching at zero ionic strength has a value of about $2 \times 10^5$ $M^{-1}$ $s^{-1}$. This relationship was used to calculate $k_Q$ as a function of ionic strength and the values derived were used to determine $\Phi_Q$ for a series of concentrations of $MV^{2+}$ throughout the ionic strength range 0.02 - 1.0 M (Fig. 1). It is seen that $\mu$ has a marked effect upon the calculated $\Phi_Q$ term when the concentration of $MV^{2+}$ is kept fairly low (less than $1 \times 10^{-3}$ M), but when high concentrations of quencher are employed (greater than $4 \times 10^{-3}$ M) the $\Phi_Q$ term approaches unity even at low ionic strengths.

For our work, we wanted to keep the concentration of $MV^{2+}$ fairly low in order to minimize the ionic strength in the absence of added electrolyte, but for the experimental measurements it was necessary to use sufficient $MV^{2+}$ to give a modest yield of redox products. Consequently we used a fixed quencher concentration of $4 \times 10^{-3}$ M and for this value Fig. 1 shows that $\Phi_Q$ should increase throughout the ionic strength range $0 < \mu < 0.1$ M but remain approximately unity at $\mu > 0.1$ M. However, it should be realized that the ionic strengths used in this work are above those normally associated with the Debye–Hückel equation [2] so that the exact application of this relationship may not be valid. Even so, it seems probable that under our experimental conditions $\Phi_Q$ approaches unity at ionic strengths greater than 0.1 M so that any observed changes in $\Phi_{ions}$ can be attributed to variations in $\Phi_S$.

As shown in Fig. 2, the ionic strength does affect the magnitude of $\Phi_{ions}$, as measured by flash photolysis techniques, in that $\Phi_{ions}$ increases
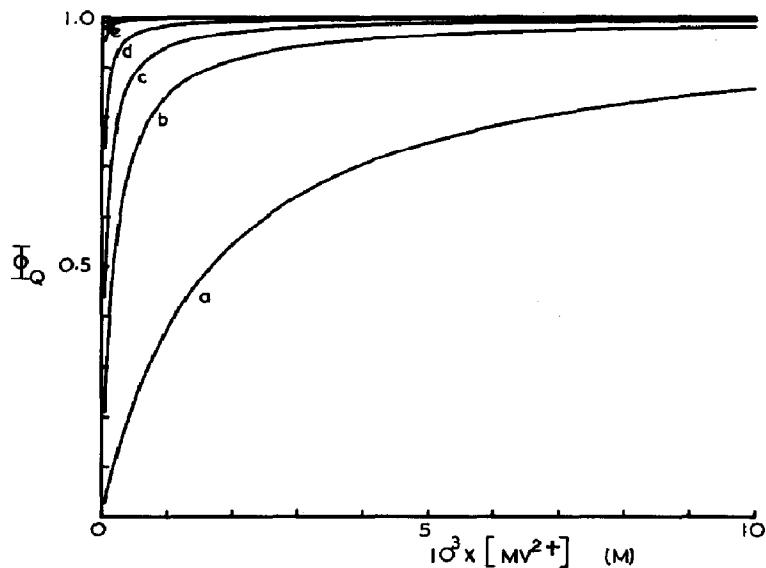
Fig. 1. The effect of ionic strength on the calculated $\Phi_Q$ term for a range of quencher concentrations: curve a, $\mu = 0.02$ M; curve b, $\mu = 0.05$ M; curve c, $\mu = 0.10$ M; curve d, $\mu = 0.20$ M; curve e, $\mu = 0.50$ M; curve f, $\mu = 1.00$ M.
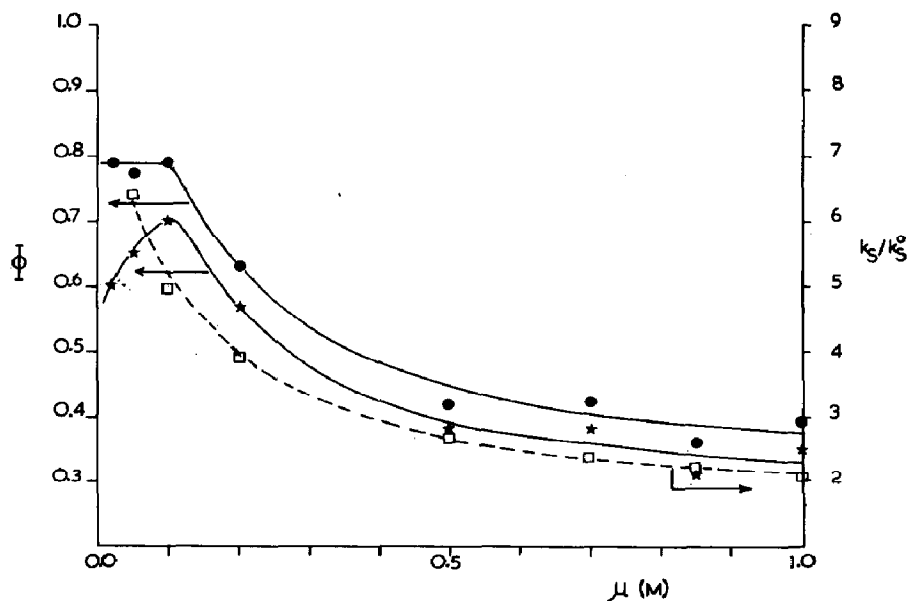


Fig. 2. The influence of ionic strength on the $\Phi_{ions}$ (*) and $\Phi_S$ (●) terms and on the calculated $k_S$ values.

slightly upon increasing $\mu$ from 0.02 to 0.1 M but further increases in $\mu$ result in a substantial decrease in $\Phi_{ions}$. When the calculated $\Phi_Q$ values from Fig. 1 are used, it is seen that the increase in $\Phi_{ions}$ at moderate ionic

strengths can be attributed to increases in $\Phi_Q$ associated with the triplet quenching rate constant $k_Q$, whilst viewed over the entire ionic strength range there is a sigmoidal decrease in the $\Phi_S$ term. This is an important finding since it is a primary requisite for any solar energy storage device that the $\Phi_{ions}$ term approaches unity and the above observation shows that the ionic strength of the background electrolyte can have a marked effect upon the efficiency of the overall photoredox reaction.

According to eqn. (5) the influence of ionic strength upon $\Phi_S$ may be due to $k_S$ and/or $k_B$ containing ionic-strength-dependent terms. However, $k_B$ refers to an electron transfer process within the ion pair and as such it should be virtually independent of ionic strength. In contrast, $k_S$ refers to charge separation from the ion pair, and it has been reported previously [3] that the dissociation of an ion pair into products does depend upon the ionic strength for high background electrolyte concentrations.

The specific rate of dissociation of the ion pair into ionic products can be calculated as

$$k_S = k_R/K \tag{7}$$

where the stability constant $K$ can be evaluated from the Fuoss equation [4] suitably modified to account for the high ionic strengths used in this work. Thus

$$k_S = \frac{k_S^0\{3Z_A Z_B Ne^2/4\epsilon rT(1 + \kappa r\sqrt{\mu})\}}{1 - \exp\{-Z_A Z_B Ne^2/\epsilon rT(1 + \kappa r\sqrt{\mu})\}} \tag{8}$$

where

$$\kappa = \left(\frac{8N^2 e^2}{10^3 \epsilon RT}\right)^{1/2} \tag{9}$$

and the radius $r$ of the activated complex is given a value of 1 nm. We have used the above equation to calculate $k_S$ as a function of ionic strength for the range $0.02 < \mu < 1.0$ M and the derived values are expressed as

$$k_S = k_S^0 \times \text{constant} \tag{10}$$

where $k_S^0$ is the rate constant for ionic separation in the absence of electrostatic forces. The calculated values predict that $k_S$ should decrease with increasing $\mu$ throughout this range (Fig. 2) in agreement with the experimental data. Consequently the observed decrease in $\Phi_{ions}$ found in aqueous solutions at high ionic strength can be attributed to a decrease in the rate of ionic separation from the ion pair.

In the lower ionic strength region studied here (0.1 M or less) the $\Phi_S$ term appears to attain a constant value of 0.8 and this is the maximum quantum yield of redox products that can be obtained from this system. The observed plateau for $\Phi_S$ is not predicted from eqn. (8), but this equation is valid only for high concentrations of background electrolyte and it reduces to simplified versions at lower ionic strengths. At zero ionic strength $k_S$ can be calculated directly from the Debye equation [5], and it seems plausible

that the levelling-off in the $\Phi_S$ term noted in our work reflects the point at which the coulombic potential energy for the ions within the ion pair is not perturbed by the surrounding ionic atmosphere.

The above model, which is very oversimplified since it treats all ions as spherical point charges and ignores specific effects and short-range ion–dipole interactions, predicts that every photoredox system involving ionic products should possess a maximum $\Phi_S$ term that is characteristic of the reactants and is not limited by the surrounding electrolyte solution. Presumably this maximum value is set by eqn. (5) and the maximum value that $k_S$ can attain is that given by the Debye equation [5] for ionic species at zero ionic strength. Therefore at a given ionic strength the $\Phi_S$ term will be increased for systems where there is strong electrostatic repulsion between the species and for solutions of high dielectric constant and low viscosity. However, even after maximizing these terms it is necessary to give some consideration to the $k_B$ term since if the rate of reverse electron transfer within the ion pair is very high then it is this rate constant that will determine the final $\Phi_S$ term.

## Acknowledgments

## References

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