Steady state and dynamic quenching of zinc tetramethylpyridylporphyrin by methyl viologen ion pairs. Salt effects

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Received (in London, UK) 11th July 2002, Accepted 18th October 2002
First published as an Advance Article on the web 11th November 2002

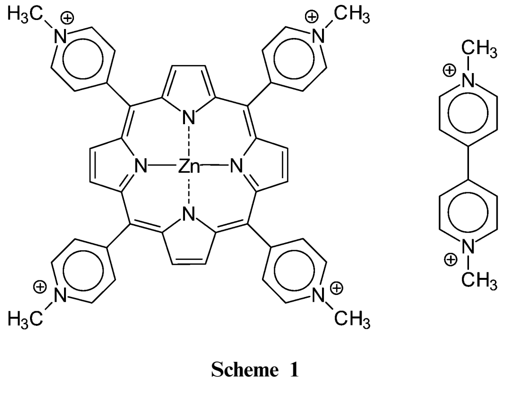
Quenching of the singlet and triplet excited states of Zn(II) *meso*-tetrakis(*N*-methylpyridinium-4-yl) porphyrin (ZnTMPyP^{4+}) by methyl viologen dichloride (MvCl$_2$) in aqueous solutions was studied using steady state fluorescence and laser flash photolysis techniques. External and inner salts added to the solution affect the photophysical properties of the ground and excited states of this ionic zinc porphyrin. The non-covalent association complex between zinc porphyrin and methyl viologen ion pairs can explain the electronic absorption spectral changes, which are enhanced in the presence of sodium chloride. The singlet and triplet excited states quenching experiments, at high quencher concentrations, show that the dynamic quenching is improved in the presence of sodium chloride and sodium sulfate, respectively. The photoinduced electron transfer (PET) process between zinc porphyrin triplet and methyl viologen, in the presence of sodium chloride, increases the triplet quantum yield. The efficiency of the corresponding ion pair radical production (from PET) is affected by the presence of salts being smaller for sodium chloride than for sodium sulfate. Good Arrhenius plots were obtained from the triplet decay quenching rate constant and radical ion formation at three different methyl viologen concentrations. The apparent activation energy (1.3–8.6 kcal mol^{-1}) increases with the quencher concentration until the diffusion activation energy in water is reached and is greater than the diffusion activation energy in ethylene glycol. The electron transfer process associated with the quenching reaction is analysed in terms of the contributions of free ions or ion pairs.

1. Introduction

Over the past years, substantial efforts have been directed to mimic photoinduced electron transfer and charge separation in photosynthetic reactions, aiming to understand the primary process in photosynthesis and to establish systems for solar energy conversion and storage.[1] Several molecules have been constructed with either covalent or non-covalently linked acceptor and donor chromophores.[2,3] Covalently linked systems are more difficult to obtain, however attention is focused on their synthesis because they enable some control of donor–acceptor separation as well as of their relative orientation. Non-covalent interactions in molecules have been used to investigate charge transfer in proteins and metalloproteins in order to understand mutagenic damage resulting from reaction between radical species and DNA[4,5] or to investigate the stacking ability of the DNA bases to facilitate charge transport.[6,7]

The thermodynamic driving force for the electron transfer reactions, the nature of intervening medium, the molecular structure and the distance and orientation between the donor and the acceptor affect the rate of the reactions.[2,3,8–10] In the case of energy storage the main goal is to use such parameters to produce radical ions of long lifetime usually obtained in self assembled systems such as micelles,[11–13] vesicles,[14–17] cyclodextrins,[18,19] zeolites[20–22] or supramolecules like dendrimers[23] and so to understand how these factors can affect the separation efficiency of radical ion pairs produced in photoinduced electron transfer. In the same way, strong electrolytes have been used in order to increase the ionic strength and/or specific interactions which can affect the efficiency of radical ion pair formation and recombination.[24,25]

Metalloporphyrins play an essential role in electron transport in natural systems.[2,3,26] Methyl viologen with a low reduction potential is a typical one-electron transfer acceptor unit producing the methyl viologen radical which cleaves water producing hydrogen (energy store) in the presence of catalysts in photochemical donor–acceptor systems.[26,27] The overall electron transfer between Zn(II) *meso*-tetrakis(*N*-methylpyridinium-4-yl)porphyrin (ZnTMPyP^{4+}) excited states and methyl viologen (Scheme 1) is affected by the strong electrostatic repulsion involved between radical ion pairs firstly produced in low quencher concentration.[25,28] In this paper, the effects of quencher (salt) concentration and the addition of other salts such as sodium sulfate and sodium chloride on the



Scheme 1

DOI: 10.1039/b206789g

electronic absorption and fluorescence properties of $ZnTMPyP^{4+}$ and on singlet and triplet excited state quenching processes are studied.

2. Experimental

2.1. Materials

The preparation of zinc porphyrin, $ZnTMPyP^{4+}$, was described previously.[29] Sodium sulfate pro analysis and analytical grade sodium chloride were purchased from Merck and Riedel-de Haën, respectively. Methyl viologen ($MvCl_2$) and ethylene glycol were purchased from Sigma-Aldrich and used without further purification. Water was bidistilled.

2.2. Equipment

The absorption spectra were recorded with a JASCO V-560 UV/VIS spectro-photometer. Fluorescence and excitation measurements were recorded with a Perkin Elmer LS 50B with the sample holder thermostated at 293 ± 0.5 K. Emission spectra were instrument corrected. A 2.0 mm pathway for the fluorescence cell was used for optical densities higher than 0.1 (10 mm) in order to reduce the filter effects. Fluorescence decays were measured by the time-correlated Single Photon Counting method using a Photon Technology International LS 100 with the sample holder thermostated also at 293 ± 0.5 K. The transient absorption spectra and the kinetics of the intermediates were carried out with laser flash photolysis equipment consisting of a Nd:YAG Quanta-Ray GCR-3 Spectra-Physics laser with the second harmonic (532 nm, 9 ns) as an excitation source. The probe light was filtered using a cut-off filter < 380 nm to avoid methyl viologen absorption. The detection of signals, digitisation and analysis (after 32 accumulations) are described elsewhere.[12] For transient experiments, the solutions were degassed with an argon flux for 30 minutes before carrying out the experiments.

3. Results and discussion

3.1. Steady state electronic absorption

The addition of $MvCl_2$ salt up to 0.05 M does not change the zinc porphyrin absorption and emission bands in the electronic absorption and fluorescence spectra. The fluorescence quantum yield and singlet excited state lifetime were also unaffected in agreement with the literature reports.[28] However, at higher methyl viologen concentrations, a red shift in the absorption bands is observed (Fig. 1). Similar behaviour is found in some dyad systems between porphyrin and viologen units.[30]

The differential absorption spectra in Fig. 1b show the changes in the porphyrin Q band region. These are a decrease of the absorption band around 565 nm and an increase in absorption around the 618 nm, 580 nm and > 500 nm regions with increasing methyl viologen concentration. In addition, there are at least two clear isobestic points at 535 nm and 572 nm. The porphyrins can aggregate as dimers at large salt concentrations; however, when zinc tetrakis(methylpyridyl)-porphyrin is present in solutions with strong electrolytes such as sodium sulfate and sodium chloride and in the absence of methyl viologen, no spectral absorption and emission changes are found.

The addition of sodium chloride to zinc porphyrin solutions (in the absence of methyl viologen) leads to a reduction of fluorescence intensity and singlet lifetimes (Fig. 2). This is probably due to the binding coordination exchange between the chloride ion and water molecule on the zinc metal ion and consequently the enhancement of the non-radiative channel of zinc porphyrin due to the chloride heavy atom effect. Irrespective of NaCl, the data clearly show a different and specific effect on zinc porphyrin ground state spectra in the presence of high concentrations of methyl viologen in the solution suggesting a porphyrin–methyl viologen complex association.

It is well known that methyl viologen can form ion pairs in water solution, which can be detected, by conductivity and spectroscopic measurements (references in Table 1).

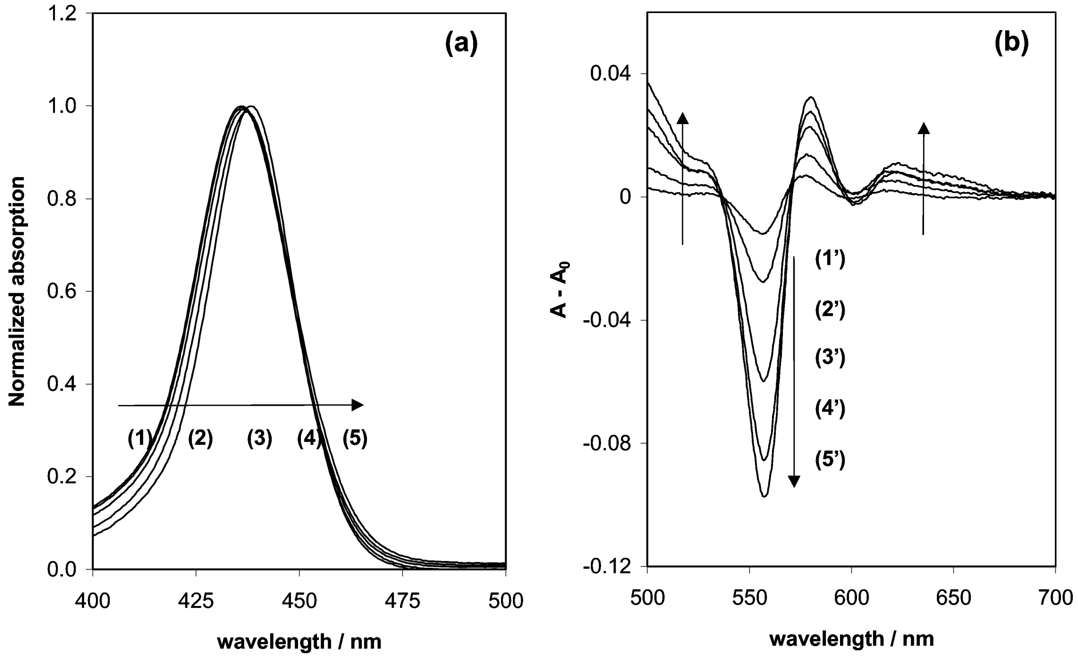


Fig. 1 a) The normalised absorption spectra at Soret region with methyl viologen concentrations of 0 M (1), 0.05 M (2), 0.1 M (3), 0.2 M (4) and 0.4 M (5); and b) the absorption and differential absorption spectra of zinc porphyrin with methyl viologen concentrations of 0.05 M (1′), 0.1 M (2′), 0.2 M (3′), 0.3 M (4′) and 0.4 M (5′).

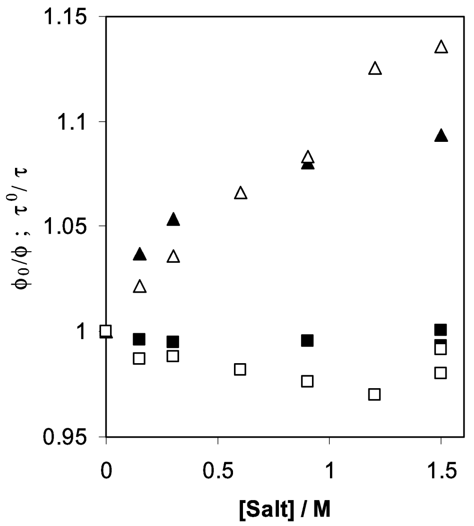


Fig. 2 Salt effect on fluorescence quantum yield (open symbols) and excited state singlet lifetime (close symbols). Na_2SO_4 (□) and NaCl (△).

$$\mathrm{MvCl_2} \rightleftharpoons \mathrm{MvCl^+} + \mathrm{Cl^-}$$
$$[\mathrm{MvCl_2}] = K_{a1} \cdot [\mathrm{MvCl^+}] \cdot [\mathrm{Cl^-}] \tag{1a}$$
$$\mathrm{MvCl^+} \rightleftharpoons \mathrm{Mv^{2+}} + \mathrm{Cl^-}$$
$$[\mathrm{MvCl^+}] = K_{a2} \cdot [\mathrm{Mv^{2+}}] \cdot [\mathrm{Cl^-}] \tag{1b}$$

The equilibrium constants found in the literature for such associations in ion pairs have a broad range (Table 1). In the Fuoss[36] equation (eqn. 2) the equilibrium constants depend on the solution ionic strength, I.

$$K_a = \frac{4\pi N_a R_{PQ}^3}{3000} e^{\frac{|z_P z_Q| r_C}{R_{PQ}(1+\kappa R_{PQ})}}$$
$$r_C = \frac{e_0^2}{\varepsilon k_B T} \text{ and } \kappa = \left(\frac{8\pi N_a r_C}{1000}\right)^{1/2} \times I^{1/2} \tag{2}$$

where κ is known as the ionic atmosphere radii reciprocal or the inverse Debye length. N_a is the Avogadro number, $z_P z_Q$ is the species charge product and ε is the static dielectric constant of the medium corrected in the presence of external salt by the relation $\varepsilon = \varepsilon_w + 2\delta^* c$. ε_w is the dielectric constant of pure water, δ^* is the average of molar dielectric constant depression coefficients of the electrolyte at 25 °C, and c is the molar concentration of the salt.[37] The static dielectric constant decreases with temperature increase and the respective values in water and ethylene glycol (see later) are taken from the literature.[38] The parameter R_{PQ} is the shortest distance between the zinc porphyrin and methyl viologen centres R_{PQ} (Å) = 10.3 ($R_{\mathrm{ZnTMPyP^{4+}}}$ = 7 Å and $R_{\mathrm{Mv^{2+}}}$ = 3.3 Å).

The ion concentrations depend on equilibrium constants thus the calculation of such constants by eqn. 2 is self-consistent until the differences between the species concentrations from one cycle to the next do not change. According to the calculated values, the association constants depend on the methyl viologen concentration range and this may be the reason for the disparity of values found in the literature. The values described in Table 1 are the average ones for the range of concentrations used in this work.

Table 1 Association constants for methyl viologen and chloride ion pairs

K_{a1}/M^{-1}	K_{a2}/M^{-1}	Ref.
10	—	31
1.5	—	32
—	0.21	33
—	> 0.2	34
0.39	2	35
1.32	1.44	this work

The presence of methyl viologen ion pairs can explain the zinc porphyrin spectroscopic properties, as observed before, and can affect the photoinduced electron transfer (see later). However, due to the complexity of the system studied, some assumptions were made: a) only 1:1 association complexes are taken into account; b) the zinc porphyrin, at much lower concentration than methyl viologen, is associated as an ion pair with chloride ions present in solutions; c) the association complexes involving zinc porphyrin are uncharged and d) ion pairs formed with external salt added are not taken into account. These assumptions are based on the concentration ranges of the experiment with the most important type of associations calculated with the Fuoss equation (2).

The results presented so far suggest complex formation between porphyrin and methyl viologen ion pairs (eqn. 3). The non-covalent interactions in such complexes can be long range electrostatic interactions and/or π–π interactions and they have been observed in similar systems.[39,40] It is interesting to note in Fig. 1b the absorption increases around 618 nm with methyl viologen concentration. It is well known that methyl viologen in the reduced form has a characteristic absorption in the 395 and 610 nm regions where the latter band is broader.[41] Unfortunately, at high methyl viologen concentrations the spectrum at 400 nm has a strong absorption due to the presence of ion pairs.[33] However, the good comparison at the 600 nm region is an indication of the charge transfer band in the association complex between porphyrin and methyl viologen ion pairs.

$$\mathrm{ZnTMPyPX}_m^{(4-m)+} + \mathrm{MvX}_n^{(2-n)+} \rightleftharpoons (\mathrm{ZnTMPyPX}_m^{(4-m)+}, \mathrm{MvX}_n^{(2-n)+}) \tag{3}$$

Although no specific changes were observed in the differential spectra in the presence and/or in the absence of strong electrolytes (NaCl and Na_2SO_4) the association constants, K_a, between porphyrin and methyl viologen ion pairs can be obtained from the Hildebrand–Benesi type relationship[42] (eqn. 4) for the 1:1 association complex.

$$\frac{A_0}{A - A_0} = (\varepsilon_r - 1)^{-1} \times \left(1 + \frac{1}{K_a[\mathrm{MvCl_2}]_0}\right) \tag{4}$$

$A - A_0$ is the differential absorption at the methyl viologen initially added concentration $[\mathrm{MvCl_2}]_0$ and $\varepsilon_r = (\varepsilon_{\mathrm{complex}}/\varepsilon_{\mathrm{porphyrin}})$ the ratio of absorptivities at 565 nm. Instead of straight lines through data points in Fig. 3, non-linear relationships were found. As the points converge at high values of methyl viologen concentration, it seems that the non-linearity in eqn. 3 is related to the association equilibrium constant. Under the assumptions described above for this complex system there are many species involved in the equilibrium, as described in eqn. 3. It is important to note that application of eqn. 4 serves only to summarize the majority of associations which are important to understand the system taking into account the spectroscopic results. The K_a values between ion pairs and zinc porphyrin species, in water solution, are strongly influenced by the ion concentrations (eqn. 5), and by the activity coefficients, in accordance with the Debye–Hückel theory[37,43] (eqn. 6).

$$K_a = \frac{a_{IP}}{a_{A+}a_{B-}} = \frac{c_{IP}}{c_{A+}c_{B-}} \times \frac{\gamma_{IP}}{\gamma_{A+}\gamma_{B-}} = \frac{c_{IP}}{c_{A+}c_{B-}} \times \frac{\gamma_{IP}}{\gamma_\pm^2} \tag{5}$$

$$\ln \gamma_\pm^2 = -|z_P z_Q| r_C \times \frac{\kappa}{1 + \kappa\sigma} \tag{6}$$

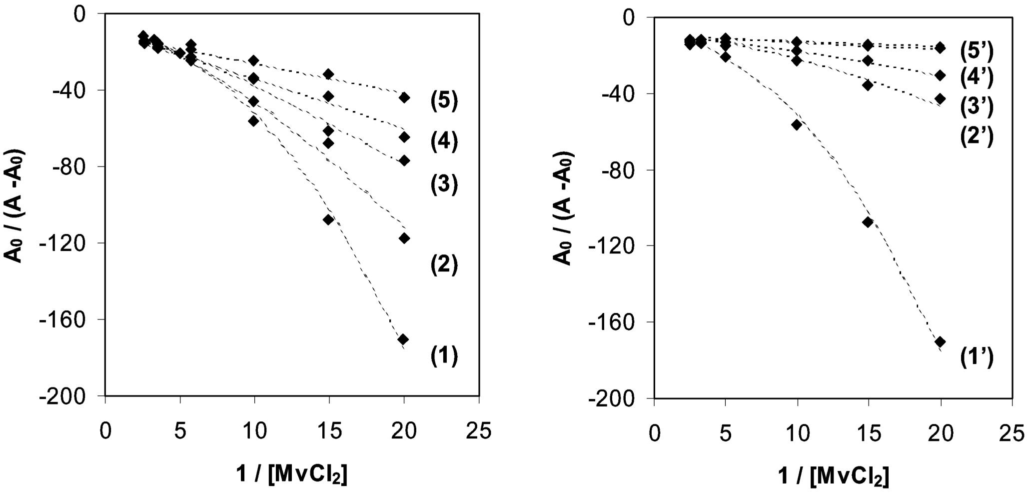


Fig. 3 Benesi–Hildebrand type plot for association between zinc porphyrin and methyl viologen at 0 M (1), 0.05 M (2), 0.15 M (3), 0.3 M (4) and 0.5 M (5) of Na_2SO_4 and 0 M (1′), 0.15 M (2′), 0.3 M (3′), 0.9 M (4′) and 1.5 M (5′) of NaCl. The dotted lines are fitted curves.

The presence of ion pairs reduces the ionic strength of the medium. Then, the ionic strength at high methyl viologen concentrations, in the absence or presence of sodium chloride, is calculated through the interactive process described before. In the case of sodium sulfate, a literature value was introduced for the association with methyl viologen (0.98 M^{-1}).[44] The presence of the sulfate anion reduces the concentration of $MvCl^+$ and $MvCl_2$ ion pairs. Once the ionic strength values are corrected for the presence of methyl viologen ion pairs, these values are used in the calculation of the activity coefficient described by eqn. 6. Mean activity coefficients ($\gamma_\pm$) are used in the K_a calculation because it was assumed that the association complexes where the zinc porphyrin is involved are uncharged species ($\gamma_{IP} = 1$). Therefore the equilibrium constant for the association equilibrium (eqn. 3) under the Debye–Hückel theory is:

$$\ln K_a = \ln K_a^0 + |z_P z_Q| r_C \times \frac{\kappa}{1 + \kappa\sigma} \tag{7}$$

where K_a^0 is the value for zero ionic strength. The σ value is taken as the lowest mean radius between the zinc porphyrin and methyl viologen, in other words, σ (Å) $= R_{PQ}/2$. After global analysis of all the data, the fitting curves in Fig. 3 were obtained, with K_a^0 equal to 0.038 M^{-1} and ε_r equal to 0.89. The results show that association complexes of zinc porphyrin and methyl viologen ion pairs in the presence of NaCl and Na_2SO_4 salts have average charge products that decrease with increasing electrolyte concentration (Fig. 4). This can be interpreted as production of more methyl viologen ion pairs, reflecting the tendency of more uncharged methyl viologen ion pairs involvement in association with zinc porphyrin (eqn. 3). Another conclusion which can be taken from Fig. 3 is the difference between the type of salt added to the solutions. The effect of sodium sulfate is smoother than that of sodium chloride. In other words, in the case of sodium sulfate the association seems to be closer to the system without salt (only methyl viologen), while with sodium chloride the data are almost linearly correlated with the inverse of methyl viologen concentration. This indicates that the interaction between zinc porphyrin and methyl viologen ion pairs involves the chloride ion to a larger extent than the sulfate ion.

3.2. Steady state fluorescence quenching

The fluorescence quenching of the singlet excited state was not observed at low methyl viologen concentration in agreement with earlier studies.[28] However, at high quencher concentration, a reduction in fluorescence emission was observed. This reduction cannot be simply accounted for by the static contribution of the association complex. Furthermore, besides the steady state quenching, a much less efficient dynamic quenching was also observed (Fig. 5a) and the quenching rate constant obtained was $k_q = 8.1 \times 10^8$ M^{-1} s^{-1}. This value is lower than the diffusion limited rate constant in water at 25 °C ($k_d = 7.6 \times 10^9$ M^{-1} s^{-1}) for neutral species at the Smoluchowski limit, and close to the limit when the charges are included in the estimation of the diffusion limited rate constant.[45] At such high quencher concentration, the Perrin process must be considered where there is a contribution from the non-equilibrium statistical distribution of the quencher molecules. Then, the fluorescence quenching can be adjusted by eqn. 8:

$$\frac{\Phi^0}{\Phi} = (1 + K_{SV} \times [Q]) \cdot (1 + K_a \times \varepsilon_r \times [Q]) \cdot \exp(V_R \cdot [Q]) \tag{8}$$

K_a and ε_r values were determined previously, and for methyl viologen the dynamic quenching ($K_{SV} = k_q \times \tau^0$) was also known, therefore the active volume V_R was obtained from the fitting of eqn. 8 and, finally the radius of the active sphere was calculated from eqn. 9 assuming the zinc porphyrin radius,

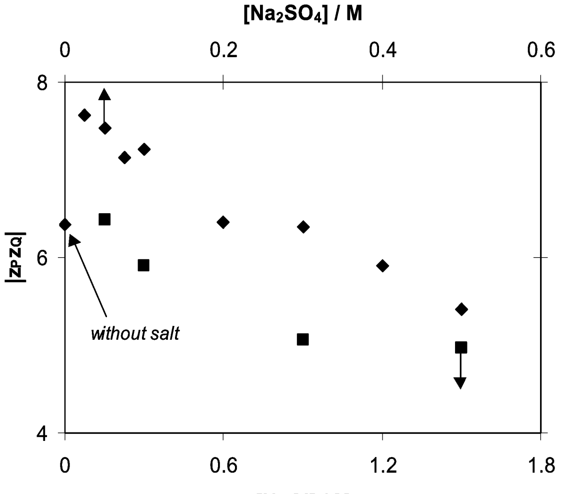


Fig. 4 Charge product values for the fitting using eqn. 7 with sodium sulfate (◆) and sodium chloride (■).

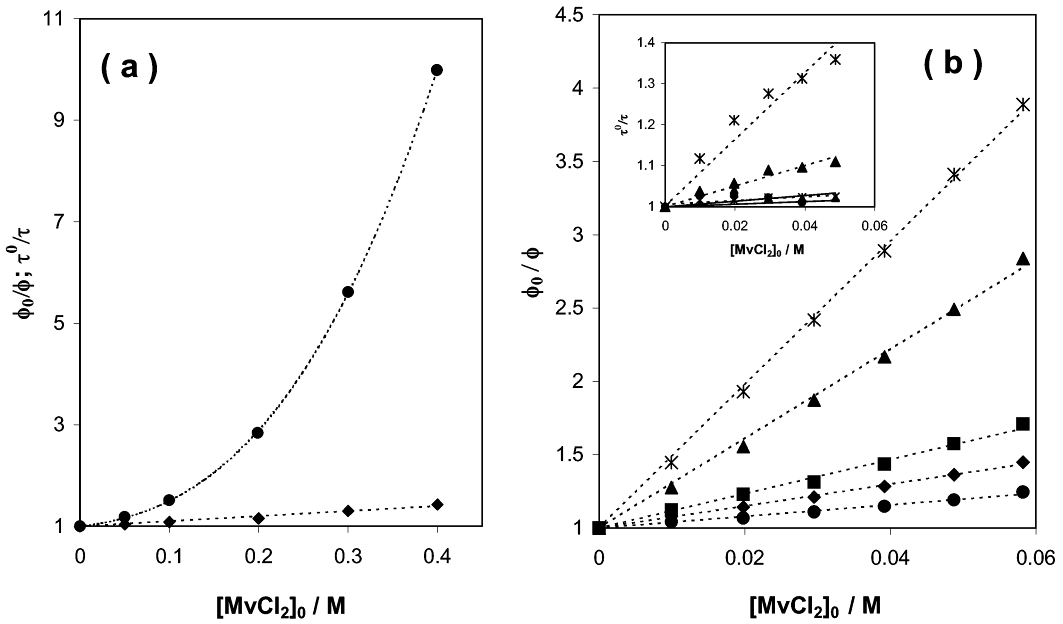


Fig. 5 The quenching of zinc porphyrin excited singlet by methyl viologen. (a) Fluorescence quantum yield (●) and excited state singlet lifetime (◆), and (b) salt effect on fluorescence quenching quantum yield with 0 M (●), 0.15 M (◆), 0.3 M (■), 0.9 M (▲) and 1.5 M (*) of NaCl. Inset: Dynamic part of fluorescence quenching of zinc porphyrin excited singlet state by methyl viologen recovered. All the dotted lines are the fitting curves.

R_P, is equal to 7 Å.

$$R = \left(\frac{3000 \times V_R}{4 \times \pi \times N_a} + R_P^3\right)^{1/3} \tag{9}$$

From eqn. 8 the static and dynamic contributions of the fluorescence quenching were known and thus residual quenching can be attributed to the non-equilibrium proximity between the excited zinc porphyrin and the quencher molecules. The active volume of 2.12 M^{-1} found corresponds to the maximum distance of 10.6 Å between the centre of the quencher and the zinc porphyrin molecules, which is close to the values attributed to the R_{PQ}.

When external salts were added to the solution, the zinc porphyrin fluorescence quenching process occurred more efficiently (Fig. 5b). The differences between the types of salt added, where the quenching is more affected by sodium chloride than sodium sulfate, can also be seen. Although good linear correlations are obtained from the data (Fig. 5b) the quenching rate constants calculated are somewhat higher than the diffusion limited values. Discounting the static contribution and assuming that the active Perrin volume is independent of the presence of external salts, the quenching process can be corrected to recover the dynamic part (Fig. 5b, inset). Reasonable results could be taken only at highest ionic strength. For sodium sulfate and sodium chloride at concentrations lower than 0.3 M and 0.9 M respectively, the dynamic part of the quenching process is indistinguishable from that in the absence of any salt. Data from fluorescence decays in the presence of salt could not be obtained because of the very low quantum yield and changes in lifetimes were not significant. However, besides these problems, it is important to note that the dynamic contribution of zinc porphyrin fluorescence quenching by methyl viologen increases in the presence of salts. The estimated quenching rate constants are shown in Table 2.

3.3. Triplet quenching

The triplet lifetime of zinc porphyrin in aqueous solution has a wide range of values in the literature: 655 μs to ~3.0 ms depending on the experimental conditions such as the amount of oxygen present and ionic strength.[45] In our studies in aqueous solution, $ZnTMPyP^{4+}$ triplet lifetimes range between 850 μs and 3.0 ms and the decays follow first order kinetics. However, the triplet decays became faster and non-exponential with small variations of the zinc porphyrin concentration in aqueous solutions with non-zero ionic strength.

The effect of the ionic strength on the triplet decay rate constant is important in second order processes like triplet–triplet annihilation and self-quenching by the ground state.[46] Our results confirm the presence of radical ions produced (around 400 nm) in the second order process. The results obtained from numerical analysis of $ZnTMPyP^{4+}$ triplet state decays (probed at 470 nm) at different concentrations (varying zinc porphyrin concentration and laser energy excitation) confirm such processes at fixed ionic strength. Therefore, the kinetics involved besides the natural triplet decay (k_T) included a triplet bimolecular process such as triplet quenching by the ground state ($k_{TG} = 2.1 \times 10^7$ M^{-1} s^{-1}) and T–T annihilation ($k_{TT} = 3.9 \times 10^8$ M^{-1} s^{-1}) whose rate constants values are close to the reported values.[46]

In the presence of sodium chloride or sodium sulfate, the triplet decays deviate from exponentiality and a transient absorption appears around 400 nm. As in phosphate buffer solution, the zinc porphyrin triplet undergoes bimolecular self-quenching. The reactant molecules are charged; therefore, the ionic strength can affect the radical ion production in bimolecular processes. At the same ionic strength, the zinc porphyrin triplet decay rate constant at 470 nm is more affected in the presence of sodium chloride than in sodium sulfate (Fig. 6a, b). Furthermore, the presence of sodium sulfate practically does not modify the transient absorptions at 395 nm and 470 nm. However,

Table 2 The k_q values of zinc porphyrin quenching by methyl viologen in the presence of external salts

Salt	$k_q/10^9$ M^{-1} s^{-1}
NaCl (0.9 M)	2.0
NaCl (1.5 M)	6.7
Na_2SO_4 (0.3 M)	2.7
Na_2SO_4 (0.5 M)	2.6

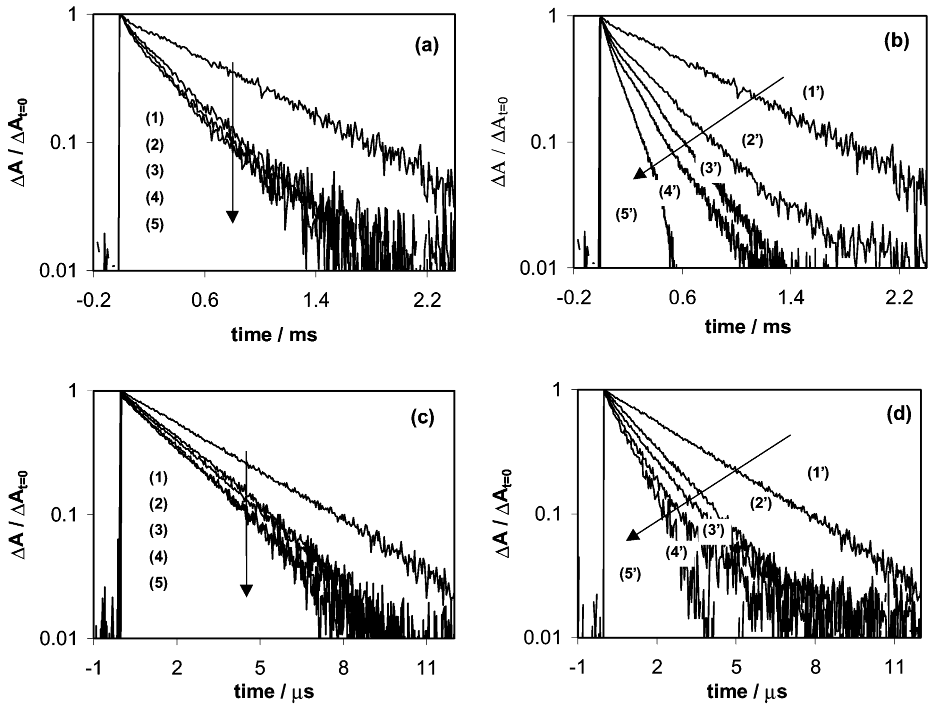


Fig. 6 Zinc porphyrin triplet decays without methyl viologen at different salt concentrations of (a) 0 M (1), 0.05 M (2), 0.15 M (3), 0.3 M (4) and 0.5 M (5) of Na_2SO_4 and (b) 0 M (1′), 0.15 M (2′), 0.3 M (3′), 0.9 M (4′) and 1.5 M (5′) of NaCl; and with 0.05 M of methyl viologen and Na_2SO_4 (c) and NaCl (d).

there is an increased triplet absorption at 470 nm with increasing sodium chloride concentration, while the 395 nm absorption remained the same. Therefore, there is a specific effect from the sodium chloride which is different from that of the sodium sulfate salt. Again, the ability of chloride to coordinate at the zinc metal on the metalloporphyrin can be responsible for such differences. It seems that the chloride anion induces the formation of more triplet states. However, the production of radical ions by the self-quenching reactions is not affected by both anions. As observed before, the singlet lifetime decreases with the amount of sodium chloride added (Fig. 2) with the increase of the triplet absorption at 470 nm. This means that the singlet state quenching by chloride anion enhances the formation of the zinc porphyrin triplet state.

The triplet lifetime shortens when $MvCl_2$ concentration increases (Fig. 7). Also, fast formation of the methyl viologen radical ion can be followed by the absorptions at 390–400 nm and at 600–610 nm. These regions are almost the same for radical ions formed by the zinc porphyrin self-quenching reaction in the absence of methyl viologen.

The external salt affects the efficiency of triplet self-quenching of zinc porphyrin to produce the radical ions. Such processes become secondary when good electron acceptors, such as methyl viologen, are present in solutions where the triplet quenching efficiency is improved (Fig. 6c, d). However, the radical ion quantum yield (proportional to the ratio between the radical ion and triplet state absorptions) decreases when additional salts are present and the effect is more pronounced

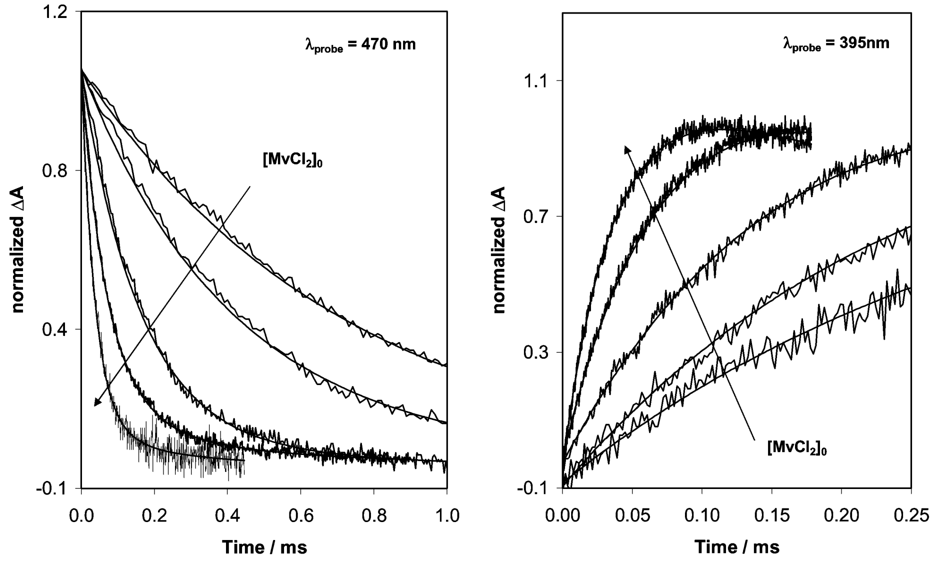


Fig. 7 Zinc porphyrin triplet decays at 470 nm and production of methyl viologen reduced form at 395 nm in different methyl viologen concentrations.

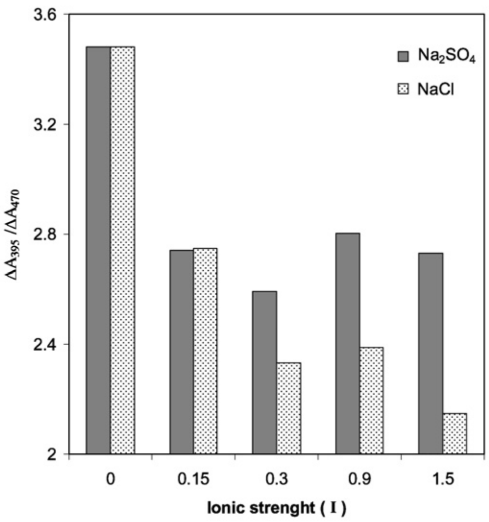


Fig. 8 Production of methyl viologen reduced efficiency from zinc porphyrin triplet at different salt concentrations.

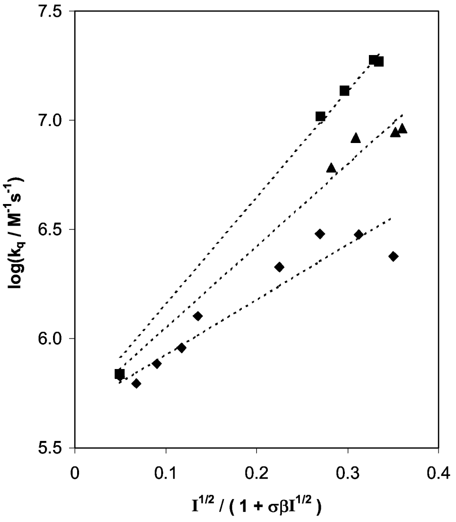


Fig. 9 Debye–Hückel–Bronsted plot for the quenching decay rate constants of zinc porphyrin triplet: in the absence of salt (◆), in sodium sulfate (▲) and in sodium chloride (■).

in sodium chloride (Fig. 8). It is possible that sodium chloride improves the triplet quenching by the methyl viologen and improves the radical ion recombination, once the electrostatic repulsions are reduced in such high ionic strength media.

3.3.1 Debye–Hückel–Bronsted analysis.

The effect of ionic strength on ionic species reaction rate constants is described by eqn. 10 based on the Debye–Hückel–Bronsted[47] model.

$$\log k = \log k^0 + \frac{2Az_Pz_Q\sqrt{I}}{1+\sigma\beta\sqrt{I}} \tag{10}$$

where k^0 is the rate constant at zero ionic strength, $A = 0.51$ $l^{1/2}$ $mol^{-1/2}$ and $\beta = 3.29 \times 10^9$ $l^{1/2}$ $mol^{-1/2}$ m^{-1} at 25 °C; the parameter σ was defined earlier. This equation is similar to the one used above for the association equilibrium (eqn. 7). When this model is applied to the bimolecular reaction studied, the rate constant for zero ionic strength is equal to 4.7×10^5 M^{-1} s^{-1}, which is close to the value found in the literature.[28] The charge product of ionic species responsible for the quenching in the absence of external salt is equal to 2.5. In the presence of salt, charge products are increased to 3.8 and 4.9 for sodium sulfate and sodium chloride, respectively. The charge product values are smaller than expected for free ion reactants ($z_Pz_Q = 8$) which may mean, on average, that zinc porphyrin or methyl viologen or both are present as ion pairs. Although reasonable linear correlations were found by fitting (Fig. 9), some care has to be taken; it has been observed, in a similar system but with the opposite charged reagents that the collisional distance, at the diffusion controlled limit, becomes smaller with increasing ionic strength, leading to the vanishing of the Coulombic interaction between the reactants.[48] The size parameter, σ, was not changed here and used in the model for the collisional domain. Therefore, the absolute values of charge products obtained from the fitting have to be viewed carefully. Even so, the variation of quenching rate constant with the ionic strength in Fig. 9 shows again the differences caused by the addition of sodium chloride and sodium sulfate.

3.3.2 Arrhenius treatment.

The proposed mechanism for the zinc porphyrin triplet quenching can be summarised as depicted in Scheme 2. (P,Q)* is the encounter pair caged by the solvent molecules formed by the diffusion of P* and Q. Using the steady state approximation the k_q measured in the experiments is:

$$k_q = \frac{k_d \times k_{et}}{k_{-d} + k_{et}} \tag{11}$$

where k_d and k_{-d} are the diffusion and dissociation rate constants, and k_{et} is the electron transfer rate constant.

Unlike the singlet state, the triplet state has a long enough lifetime and since the concentration of this diffusional encounter pair is larger, this increases the probability that the intrinsic reaction will occur. Therefore, the quenching rate constant for the electron transfer reaction will depend on the lifetime of the encounter complex. The parameters k_d and k_{-d} can be estimated with eqn. 12–14.[49]

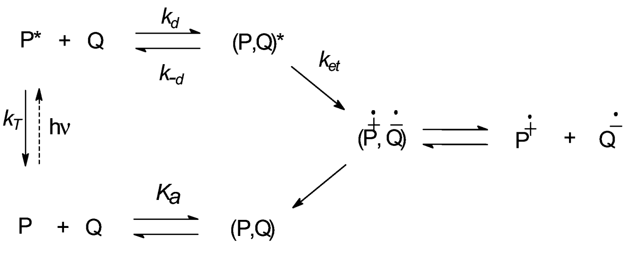
$$k_d = \frac{2 \cdot N_a \cdot k_B T}{3000 \cdot \eta} \cdot \left(\frac{R_P}{R_Q} + \frac{R_Q}{R_P} + 2\right) \times \frac{1}{R_{PQ}\int_{R_{PQ}}^{\infty} r^{-2}\exp[w(r,I)/k_B T]\mathrm{d}r} \tag{12}$$

$$k_{-d} = \frac{k_B T}{2\pi \times \eta \times R_{PQ}^2} \cdot \left(\frac{1}{R_Q} + \frac{1}{R_P}\right) \times \frac{\exp[w(R_{PQ},I)/k_B T]}{R_{PQ}\int_{R_{PQ}}^{\infty} r^{-2}\exp[w(r,I)/k_B T]\mathrm{d}r} \tag{13}$$

where $w(r,I)$ is the work required to bring the charged reactants to the separation distance r in the presence of an ionic atmosphere based on ionic strength I calculated by:

$$w(r,I) = \frac{z_Pz_Q.e^2}{2 \cdot \varepsilon \cdot r}\left[\frac{\exp(\kappa \cdot \sigma_P)}{1+\kappa \cdot \sigma_P} + \frac{\exp(\kappa \cdot \sigma_Q)}{1+\kappa \cdot \sigma_Q}\right] \times \exp(-\kappa \cdot r) \tag{14}$$

k_B is the Boltzmann constant, η the solvent viscosity. σ_P and σ_Q are the sum of respective reagent molecular radius plus



Scheme 2

Table 3 Arrhenius parameters from the triplet zinc porphyrin quenching by methyl viologen ($r^2 = 0.909$–0.991)

[MvCl$_2$]/M	$A/10^9$ M^{-1} s^{-1}	E_a/kcal mol^{-1}
0.005	0.014	1.3
0.05	0.079	1.6
0.20	2.47	3.5
0.033^a	1169	8.6

^{a} In ethylene glycol.

the dominant counter-ion radius in the ionic atmosphere, in the case of chloride, 1.67 Å.[49] The other parameters have already been defined (in eqn. 2). In our work, we integrated numerically by Simpson's method, eqns. 12 and 13, in the range $R_{PQ} = 10.3$ to 5000 Å. Depending on the k_{-d} and k_{et} values, the reaction assumes different kinetics.

A good Arrhenius correlation between the triplet quenching rate constant and the formation rate constant of reduced methyl viologen with the reciprocal of temperature was found. Table 3 shows the Arrhenius parameters in different media.

Bimolecular reactions have an intrinsic energy of diffusion. In water, the activation energy value, calculated from the temperature dependence of the solvent viscosity,[38,50,51] is 4.0 kcal mol^{-1} and in ethylene glycol it is 6.7 kcal mol^{-1}. The viscosity is also changed in the presence of ions,[37,52] *e.g.* the activation energy in 0.5 M of magnesium dichloride water solution[52] (from Arrhenius correlation) is 3.7 kcal mol^{-1}, a value close to the bulk of water. From the results obtained (Table 3), only in ethylene glycol is there an exception where the activation energy of the electron transfer reaction between the zinc porphyrin triplet state and methyl viologen is higher than the solvent diffusion activation energy, in the other cases they are lower. It is known that when the activation energy is smaller than the diffusion energy, this provides evidence for some complex formation before the intrinsic reaction occurs.[53] Therefore, the diffusional mechanism in aqueous solution is unlikely to be the controlling quenching process because the activation energy is less than the energy necessary for the diffusion of reactant molecules.

The values for diffusion rate constants and diffusional dissociation rate constants can be calculated for the zinc porphyrin charged as 4+ and methyl viologen charged as 2+ and using the experimental results, k_q, the k_{et} values can be obtained using eqn. 11. From the results shown in Table 4, the k_{-d} values are around two orders of magnitude higher than k_{et}, which means that the activation energy for the reaction is independent of the diffusion of species. The pre-equilibrium can be assumed for the formation of the encounter pair where $k_q \sim K_D \times k_{et}$, where K_D is calculated by eqn. 15.

Table 4 Diffusion rate constants, diffusional dissociation rate constants and electron transfer rate constants from eqn. 11 for free ion reactants

[MvCl$_2$]/M	$k_d/10^9$ M^{-1} s^{-1}	$k_{-d}/10^9$ s^{-1}	K_D/M^{-1}	$k_{et}/10^7$ s^{-1}
0.001	0.4	16.6	0.02	2.6
0.002	0.6	16.2	0.03	2.5
0.004	0.8	15.8	0.05	2.6
0.005	0.9	15.5	0.06	2.5
0.007	1.2	15.1	0.08	2.2
0.011	1.5	14.5	0.10	2.4
0.050	3.8	10.7	0.35	1.2
0.100	5.2	8.6	0.59	1.0
0.200	6.4	6.9	0.92	0.6
0.400	7.2	5.6	1.28	0.4

$$K_D\,(\mathrm{M}^{-1}) = \frac{k_d}{k_{\text{-}d}} = \frac{4\pi}{3} \cdot 1000 \cdot R_{PQ}^3 \cdot N_a \cdot \exp\left[\frac{-w(R_{PQ}, I)}{k_B T}\right] \quad (15)$$

Therefore, if the Arrhenius relation is applied, the apparent or observed activation energy, E_a, can be defined as:

$$E_a = E_a^0 + \Delta H_D(R_{PQ}, I) \quad (16)$$

where $\Delta H_D(R_{PQ}, I)$ is the enthalpy of the encounter pair formation obtained from the van't Hoff plot of eqn. 15, since $w(R_{PQ}, I)$ is also temperature dependent. Using the same parameter values for the results in Table 4, the K_D values for each example in Table 3 are calculated. The intrinsic barrier, E_a^0, values were very close to the apparent activation energies. The small negative values found for $\Delta H_D(R_{PQ}, I)$ are due mainly to the ionic strength attenuating the Coulombic repulsions, which increase with temperature.

The electrostatic interaction can also contribute to the pre-exponential values obtained from Arrhenius plots (Table 3) that are proportional to $\exp(\Delta S_C^{\ddagger}/k_B)$. The electrostatic contribution to the entropy of activation $\Delta S_C^{\ddagger}$ at constant pressure can be calculated by the temperature gradient of the electrostatic free energy contribution that can be estimated from $w(R_{PQ}, I)$. The $\Delta S_C^{\ddagger}$ values show an increase when the concentration of ionic quencher increases. The same trend is observed in the pre-exponential values (Table 3).

3.3.3 Electron transfer.

The value of k_{et}, in eqn. 11, can be calculated from the classical description of nonadiabatic rate constant electron-transfer reactions:[9,54]

$$k_{et} = v \exp\left(-\frac{\Delta G^*}{k_B T}\right) \quad (17)$$

where

$$v = \frac{4\pi^2 V^2}{h(4\pi\lambda k_B T)^{1/2}} \quad (18)$$

and

$$\Delta G^* = \frac{(\lambda + \Delta G^0)^2}{4\lambda} \quad (19)$$

h is the Planck constant and V is the electronic coupling related to vibration of reacting species and λ, the free energy of reorganisation. ΔG^0 is the energy determined by the redox potentials of the reacting species from the excited state, equal to 0.003 eV,[28] plus the work terms ($w_P - w_R$) calculated by eqn. 14 with the inclusion of ionic strength effect.[10]

According to eqns. 17–19 the intrinsic activation energy in zinc porphyrin triplet quenching by methyl viologen is the free-energy barrier ΔG^*. Using the linear form of eqn. 17, the relationship between $\ln(T^{1/2} \times k_{et})$ and T^{-1} should be observed. Indeed, ΔG^* is obtained (0.07–0.39 eV) directly from the slope in the good linear fitting curves in Fig. 10a. λ is calculated with eqn. 19 (0.27–1.57 eV) and, finally, V is obtained from intercept values of the curve fittings and λ (0.0002–0.082 eV). Different values for k_d and k_{-d} (for the two limit cases of free ion and ion pair reactants) will result in different values for k_{et} and consequently different values for the electron transfer parameters. Although the λ values obtained here are in the range of typical values, they are on average smaller than the values obtained from similar systems with non charged reactants (1.1–1.3 eV).[55]

The solvent reorganisation energy, λ_S, can be calculated (eqn. 20) using the dielectric continuum model of Marcus,[54,56] where n is the index of refraction of the solvent of dielectric constant ε_S and the rest of the parameters are as previously defined.

$$\lambda_S = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{2R_P} + \frac{1}{2R_Q} - \frac{1}{R}\right)\left(\frac{1}{n^2} - \frac{1}{\varepsilon_S}\right) \quad (20)$$

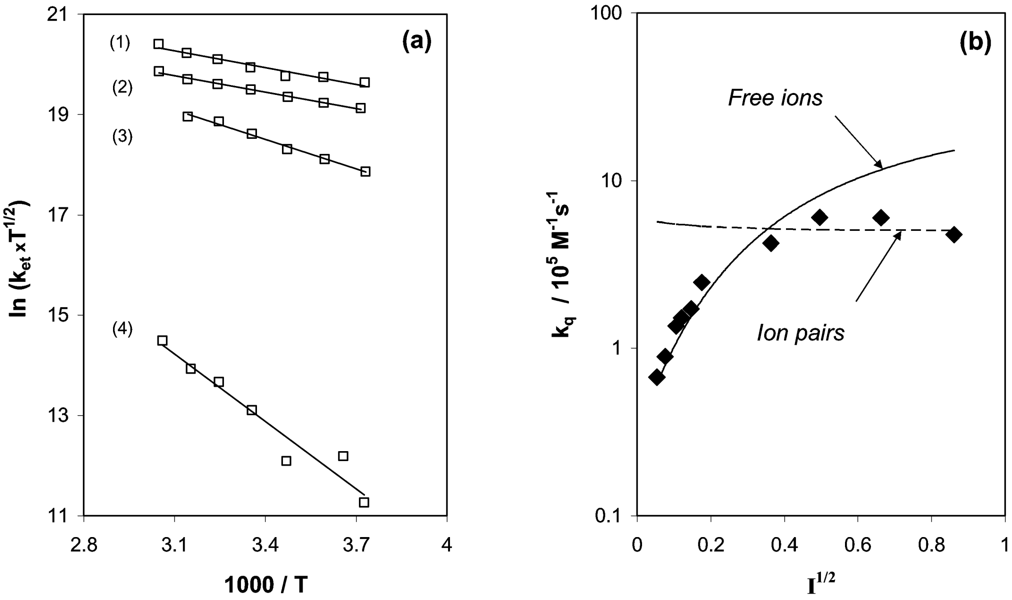


Fig. 10 (a) The ln($T^{1/2} \times k_{et}$) and T^{-1} plot, where k_{et} is the electron transfer rate constant after correction of diffusion and dissociation rates in MvCl$_2$ concentration equal to (1) 0.005 M, (2) 0.05 M and (3) 0.2 M in water and (4) 0.033 M in ethylene glycol. (b) Ion concentration effect in zinc porphyrin triplet quenching rate constants for experimental points (◆). The theoretical curves are for the cases in aqueous solution at 0.05 M concentration of MvCl$_2$ (—) $Q_R = +8$, $Q_P = +5$, $R_{PQ} = 10.3$ Å, $\lambda = 0.41$ eV and $\nu = 5.83 \times 10^8$ s^{-1} (free ions); (---) $Q_R = 0$, $Q_P = -1$, $R_{PQ} = 20.3$ Å, $\lambda = 0.33$ eV and $\nu = 6.2 \times 10^6$ s^{-1} (ion pairs).

Therefore, the solvent reorganisation energy, λ_S, for $R = R_{PQ} = 10.3$ Å and bulk water is 1 eV.

Besides λ_S there are two other small contributions to λ; the contribution of the inner sphere arising from the activation of frequency modes within the precursor complex, and the contribution of the ionic atmosphere which surrounds each charged reactant.[56] If these effects are computed the total reorganisation energy estimated for λ will be higher than the values obtained.

The distance R considered for the calculation of λ_S is normally the geometric distance between the centres of the donor and acceptor assuming the reactant molecules are spheres and the medium is a continuous dielectric. However, there are cases reported where the effective distance of the electron transfer is quite different from the sum of the reactant radii.[57] Electron transfer at such small distances has also been observed in a porphyrin–viologen dyad system.[58]

Although such corrections in the overestimated λ_S have been reported,[57,59] it is important to regard the effect of high concentration of methyl viologen where the presence of ion pairs can alter the potential energies of the reacting species.

The possibility that reactant ion pairs are involved in the electron transfer process has been included for methyl viologen in aqueous solution and for the low dielectric constant medium ethylene glycol. The results show that except for methyl viologen at 0.005 and 0.05 M, the λ values are higher than λ_S estimated using the contact radii (including the counter ions radii). In this case accounted for by the ion pairs, the internal reorganisation free energy can be relevant.

3.3.4 Simulation curves for k_q. It is clear that the values of electron transfer rate constants obtained from eqn. 11 depend on the models and approximations used to calculate the diffusion and dissociations rate constants, k_d and k_{-d}. Therefore, all the other parameters obtained from Marcus theory for the electron transfer in eqns. 17–20 within the temperature experiments are also dependent on the previous models. However, if such parameters and approximations are applied to predict the quenching rate constant of the zinc porphyrin triplet state by the methyl viologen in aqueous solution at 298 K, a very nice agreement is observed. In Fig. 10b, the experimental values of k_q agree with the calculated ones at quenching concentrations lower than 0.05 M when the parameters used apply to free ion reactants. In this situation the electron transfer parameters change little and the intrinsic electron transfer rate constant ranges within 1.2–2.8 × 10^7 s^{-1}. Therefore, the quenching rate constant reaction has a larger contribution from k_d and k_{-d} (because of electrostatic repulsion). In the high concentration region, the experimental points are below the predicted curve. However, this was expected since the ion pair associations become important ($Q_R = 0$, $Q_P = -1$) and occur in two likely cases: (i) methyl viologen concentration higher than 0.05 M in water and (ii) low dielectric solvents (ethylene glycol). In such cases, the electrostatic repulsion between the reactants is absent and therefore, the contribution of intrinsic electron transfer rate constant to the k_q values is more significant.

4. Conclusions

In this work, the effect of ionic strength caused by high quencher (salt) concentration or external salt (sodium sulfate and sodium chloride) was studied in the association of two charged species, zinc porphyrin and methyl viologen. It was observed that the addition of salts improves the association between the ion pairs. In addition, a specific effect caused by the chloride ion due to its zinc coordination ability was observed causing a reduction in zinc porphyrin excited state (singlet or triplet) lifetime and an enhancement in the quenching reaction by methyl viologen. However, the yield of radical ions produced in this reaction is reduced when the salts are present, notably for the case of sodium chloride. In such a complex system the electron transfer process in the quenching reaction was analysed in two extremes cases (free ions and ion pairs) resulting in parameter values that have to be considered carefully due to the assumptions and models applied.

Acknowledgements

This work was supported by CQE4/FCT and project POCTI/35398/QUI/1999. D. M. Togashi thanks FCT for the award of BPD 5739/2001.

References

1 T. J. Meyer, *Acc. Chem. Res.*, 1989, **22**(5), 163.

2 P. Piotrowiak, *Chem. Soc. Rev.*, 1999, **28**, 143.

3 T. Hayashi and H. Ogoshi, *Chem. Soc. Rev.*, 1997, **26**, 355.

4 S. Steenken, *Chem. Rev.*, 1989, **89**, 503.

5 S. R. Rajski, S. Kumar, R. J. Roberts and J. K. Barton, *J. Am. Chem. Soc.*, 1999, **121**, 5615.

6 B. Giese, *Acc. Chem. Res.*, 2000, **33**, 631.

7 M. Ratner, *Nature*, 1999, **397**, 480.

8 S. F. Nelsen, D. A. Trieber II, M. A. Nagy, A. Konradsson, D. T. Halfen, K. A. Splan and J. R. Pladziewicz, *J. Am. Chem. Soc.*, 2000, **122**, 5940.

9 P. F. Barbara, T. J. Meyer and M. A. Ratner, *J. Phys. Chem.*, 1996, **100**, 13 148.

10 N. Sutin, *Acc. Chem. Res*, 1982, **15**, 275.

11 P. L. Luisi, M. Giomini, M. P. Pileni and B. H. Robinson, *Biochim. Biophys. Acta*, 1988, **947**, 209.

12 S. M. B. Costa, P. L. Cornejo, D. M. Togashi and C. A. T. Laia, *J. Photochem. Photobiol. A*, 2001, **142**, 151.

13 A. Uehata, H. Nakamura, S. Usui and T. Matsuo, *J. Phys. Chem.*, 1989, **93**, 8197.

14 F. M. Menger and M. I. Angelova, *Acc. Chem. Res.*, 1998, **31**, 789.

15 J. H. Fendler, *Science*, 1984, **223**, 988.

16 P. J. G. Coutinho and S. M. B. Costa, *J. Photochem. Photobiol. A*, 1994, **82**, 149.

17 R. Rossetti, S. M. Beck and L. Brus, *J. Am. Chem. Soc.*, 1984, **106**, 980.

18 V. Ramamurthy and D. F. Eaton, *Acc. Chem. Res.*, 1988, **21**, 300.

19 S. Hamai and T. Koshiyama, *J. Photochem. Photobiol. A*, 1999, **127**, 135.

20 J. K. Thomas, *Chem. Rev.*, 1993, **93**, 301.

21 L. Persaud, A. J. Bard, A. Campion, M. A. Fox, F. E. Mallouk, S. E. Webber and J. M. White, *J. Am. Chem. Soc.*, 1987, **109**, 7309.

22 H. Ringsdorf, B. Schlarb and J. Venzmer, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 113.

23 F. Vögtle, S. Gestermann, R. Hesse, H. Schwierz and B. Windisch, *Prog. Polym. Sci.*, 2000, **25**, 987.

24 K. Kalyanasundaram and M. Neumann-Spallart, *Chem. Phys. Lett.*, 1982, **88**, 7.

25 B. L. Gore, A. Harriman and M.-C. Richoux, *J. Photochem.*, 1982, **19**, 209.

26 J. R. Darwent, P. Douglas, A. Harriman, G. Porter and M.-C. Richoux, *Coord. Chem. Rev.*, 1982, **44**, 83.

27 I. Okura, *Coord. Chem. Rev.*, 1985, **68**, 83.

28 M.-C. Richoux and A. Harriman, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 1873.

29 D. M. Togashi and S. M. B. Costa, *Phys. Chem. Chem. Phys.*, 2000, **2**, 5444.

30 I. Okura, N. Kaji, S. Aono and T. Nishisaka, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 1243.

31 J. R. Barnett, A. S. Hopkins and A. Ledwith, *J. Chem. Soc., Perkin Trans. 2*, 1973, 80.

32 T. W. Ebbesen, L. E. Manring and K. S. Peters, *J. Am. Chem. Soc.*, 1984, **106**, 7400.

33 D. Le Roux, J.-C. Mialocq, O. Anitoff and G. Folcher, *J. Chem. Soc., Faraday Trans. 2*, 1984, **80**, 909.

34 P. Douglas, G. Waechter and A. Mills, *Photochem. Photobiol.*, 1990, **52**, 473.

35 S. G. Bertolotti, J. J. Cosa, H. E. Gsponer and C. M. Previtali, *Can. J. Chem.*, 1987, **65**, 2425.

36 R. M. Fuoss, *J. Am. Chem. Soc.*, 1958, **80**, 5059.

37 R. A. Robinson and R. H. Stokes, *Electrolyte Sotutions*, 2nd edn., Butterworths, London, 1959.

38 D. R. Lide, *Handbook of Chemistry and Physics*, 72nd edn., CRC Press, Boca Raton, Boston, 1991.

39 K. Kano, T. Sato, S. Yamada and T. Ogawa, *J. Phys. Chem.*, 1983, **87**, 566.

40 E. Kaganer, E. Joselevich, I. Willner, Z. Chen, M. J. Gunter, T. P. Gayness and M. R. Johnson, *J. Phys. Chem. B*, 1998, **102**, 1159.

41 T. Watanabe and K. Honda, *J. Phys. Chem.*, 1982, **86**, 2617.

42 H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703.

43 J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry*, Plenum, New York, 1970, vol. 1, ch. 3.

44 P. M. S. Monk, N. M. Hodgkinson and R. D. Partridge, *Dyes Pigments*, 1999, **43**, 241.

45 D. M. Togashi and S. M. B. Costa, *Phys. Chem. Chem. Phys.*, 2002, **4**, 1141.

46 V. H. Houlding, K. Kalyansundaram, M. Grätzel and L. R. Milgrom, *J. Phys. Chem.*, 1983, **87**(17), 3175.

47 B. Perlmutter-Hayman, *Prog. React. Kinet.*, 1972, **6**, 239.

48 A. D. Scully, S. Hirayama, D. Hachisu and T. Tominaga, *J. Phys. Chem.*, 1992, **96**, 7333.

49 C. Chiorboli, M. T. Indelli, M. A. R. Scandola and F. Scandola, *J. Phys. Chem.*, 1988, **92**, 156.

50 L. H. Thomas, R. Meatyard, H. Smith and G. H. Davis, *J. Chem. Eng. Data*, 1979, **24**, 161.

51 J. V. Sengers and J. T. R. Watson, *J. Phys. Chem. Ref. Data*, 1986, **15**, 1291.

52 M. Afzal, M. Saleem and M. T. Mahmood, *J. Chem. Eng. Data*, 1989, **34**, 339.

53 U. Maharaj and M. A. Winnik, *J. Am. Chem. Soc.*, 1981, **103**, 2328.

54 R. A. Marcus, *J. Chem. Phys.*, 1956, **24**, 966.

55 T. Ohgushi, Z.-C. Li, F.-M. Li, T. Komatsu, S. Takeoka and E. Tsuchida, *J. Porphyrins Phthalocyanines*, 1999, **3**, 53.

56 C. D. Clark and M. Z. Hoffman, *Coord. Chem. Rev.*, 1997, **159**, 359.

57 N. Kitamura, H.-B. Kim, S. Okano and S. Tazuke, *J. Phys. Chem.*, 1989, **93**, 5750.

58 N. J. Head, J. Thomas, M. J. Shepard, M. N. Paddon-Row, T. D. M. Bell, N. M. Cabral and K. P. Ghiggino, *J. Photochem. Photobiol. A*, 2000, **133**, 105.

59 M. Morillo, C. Denk, P. Pérez, M. López, A. Sánchez, R. Prado and F. Sánchez, *Coord. Chem. Rev.*, 2000, **204**, 173.