

# Photoinduced electron transfer between triplet erythrosin dianion and highly charged ionic quenchers

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**Abstract** The lifetime of the lowest triplet state of the dianion erythrosin B depends on its concentration because of self-quenching. The self-quenching rate constants vary with the solution viscosity at room temperature. Dextrose was used to change the viscosity of aqueous solutions in the range  $1 \leq \eta \leq 5.31$  cP. Photoinduced electron transfer reactions between the triplet state of the erythrosin dianion and the highly charged ionic quenchers  $K_4[Fe(CN)_6]$  and  $K_4[Mo(CN)_8]$  were investigated in aqueous borate buffer solutions at pH 9.2 using flash photolysis. Electron transfer rates vary from  $3.0 \times 10^8$  to  $1.4 \times 10^8$   $M^{-1} s^{-1}$  depending on viscosity.

**Keywords** Photoinduced electron transfer · Triplet states self-quenching · Viscosity · Diffusion

## Introduction

Xanthene dyes are of both theoretical and practical interest because of their photophysical and photochemical properties and these dyes have therefore been widely studied [1–8]. Certain heterogeneous systems like polymer matrices [9], silica-gel glasses [10], intracellular reactions [6], and amorphous thin films of maltose and maltitol [11] were used to help understand the behavior of these dyes. Because xanthene dyes have wide applications in several

fields, such as solar energy conversion [12], laser dyes [6], biological markers, singlet oxygen photosensitizers [13], photoinitiators of polymerization [14], the interest in such compounds is still alive. Erythrosin B is well known for its high quantum yield of triplet formation by intersystem crossing [15–18]. In water, the  $T_1$  state is populated with nearly 100% efficiency [19–21] ( $\Phi_T \approx 1$ ). The main characteristics of erythrosin are: (1) high absorption coefficients in the visible region; (2) high efficiency of the intersystem crossing; (3) relatively low triplet energy ( $184$   $kJ mol^{-1}$ ) [22–24]; and (4) a tendency to transfer electrons in the excited state, yielding stable and long-lived radicals [25]. In the present study we therefore chose erythrosin for use in photoinduced electron transfer reactions with highly charged ionic quenchers in aqueous buffer solution [26]. Zakharova et al. [27] dealt with the electron transfer reactions of eosin and rose bengal with cyanide complexes of Mo, W, Ru, Fe, and Co. Braslavsky et al. [28] studied the photoinduced electron transfer reaction between the triplet state of erythrosin and metal cyanides in aqueous solutions by laser-induced optoacoustic spectroscopy. The aim of this paper is to support these studies by applying flash photolysis.

Using different solvents, Georges [29] and Duchowicz [20] found that the quenching rate constant depends on the solvent viscosity. We changed the viscosity by adding dextrose to the aqueous media [30, 31]. Quenching rate constants and electron transfer rate constants were obtained from Stern–Volmer plots.

## Results and discussion

At pH 9.2 [18] erythrosin exists only as dianion. As reported by Hasanein [32] the  $pK$  value of erythrosin is

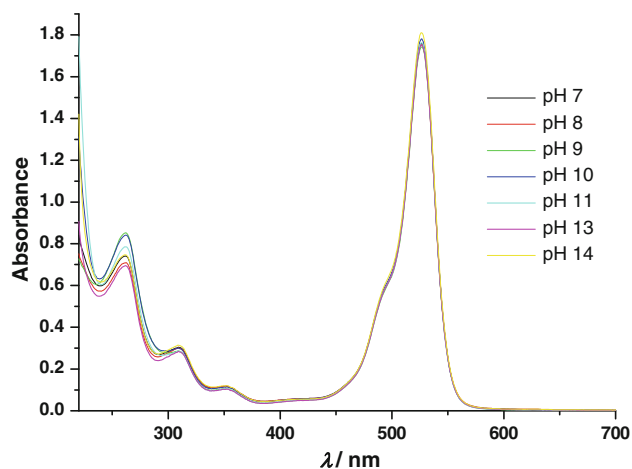
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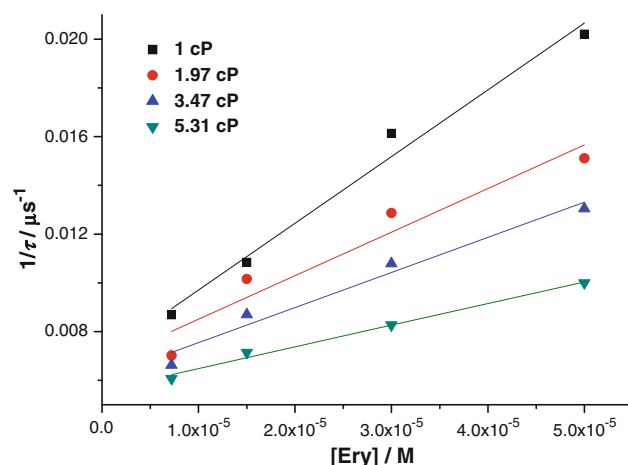
$4.18 \pm 0.15$ . To detect the effect of pH on the ionic state of erythrosin in alkaline media we measured its absorption spectra between pH 7 and 13 (Fig. 1). As there is no change in the position and intensities of the peak at 526.5 nm in the absorption spectra with changing the pH in this range erythrosin only exists in dianion form with the same pK value. The spectra show that under our experimental conditions, both in buffer solution and in water (with different viscosities) the predominant species present is the dianion [33]. At the low concentrations used in this work no evidence for dimer formation was found. Förster [34] reported that dimerization of the fluorescein dyes is unimportant for concentrations less than  $10^{-3}$  M.

The triplet state of the erythrosin dianion  ${}^3\text{Ery}^{2-}$  exhibits an absorption spectrum extending from about 450 to 700 nm [29, 35] with a maximum around 620 nm in borate buffer [18]. For the timescale of our measurements (some microseconds after the excitation) only  $T_1$  excited species remain in solution, as relaxation of excited triplet state ( $T_2$ ) is pretty fast with a rate constant of the order of  $10^{11} \text{ s}^{-1}$  [21]. The erythrosin triplet ( ${}^3\text{Ery}^{2-}$ ) lifetime in degassed borate buffer at pH 9.2 is  ${}^3\tau_0 = 49 \pm 1 \text{ } \mu\text{s}$  measured from the 620 nm decay. The energies of excited state singlet and triplet of erythrosin are  $E(S_1) = 212 \text{ kJ mol}^{-1}$  and  $E(T_1) = 184 \text{ kJ mol}^{-1}$  [24, 36].

The erythrosin dianion triplet state  ${}^3\text{Ery}^{2-}$  can relax by energy transfer to oxygen in solution. This process is fast (diffusion controlled) and produces singlet oxygen which then relaxes back to triplet oxygen [29]. Vanderkooi et al. [37] first noted that the kinetics of the  $T_1$  emission is concentration dependent because of self-quenching by ground state molecules. The pseudo-first-order decay ( $1/{}^3\tau$ ) varied linearly with the erythrosin concentration according to Eq. 1 [13, 29] and is shown in Fig. 2.



**Fig. 1** Absorption spectra of erythrosin ( $2 \times 10^{-5}$  M) in  $\text{H}_2\text{O}$  at different pH values



**Fig. 2** Variation of pseudo-first-order decay time of erythrosin triplet state versus initial dye concentration in aqueous solvent at different viscosities

$$\frac{1}{{}^3\tau} = \frac{1}{\tau_{C \rightarrow 0}} + k_s [\text{Ery}^{2-}] \quad (1)$$

Here  $\tau_{C \rightarrow 0}$  (s) is the triplet state lifetime for  $[\text{Ery}^{2-}] \rightarrow 0$ . The intrinsic rate  $k_s$  is the bimolecular self-quenching rate constant given in Table 1.

The value of bimolecular self-quenching rate ( $k_s$ ) in water is close to that given by Georges [29] ( $3.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) for the self-quenching of the erythrosin triplet. This self-quenching is typically a diffusion-controlled process. It is of the utmost importance that oxygen is carefully removed from the solution because of its comparable rate constant for quenching of the triplet state of the erythrosin dianion.

As donor and acceptors are both charged species, the diffusion constant has to be calculated from the Debye equation, Eq. 2 [38].

$$k_{\text{diff}} = 4\pi(D_A + D_B)d_{AB} \left( \frac{\frac{z_A z_B e_0^2}{4\pi\epsilon_0 \epsilon_s d_{AB} k_B T}}{\left[ \exp\left(\frac{z_A z_B e_0^2}{4\pi\epsilon_0 \epsilon_s d_{AB} k_B T}\right) \right] - 1} \right) N_L$$

$$D_A + D_B = \frac{kT}{6\pi\eta} \left( \frac{1}{r_A} + \frac{1}{r_B} \right) \quad (2)$$

For self-quenching, both  $r_A$  and  $r_B$  are the radii of erythrosin.  $\eta$  denotes the viscosity of the solution, and  $D_A$  and  $D_B$  are the corresponding diffusion coefficients.

**Table 1** Rate constants for quenching of triplet erythrosin ( ${}^3\text{Ery}^{2-}$ ) by ground state erythrosin ( $\text{Ery}^{2-}$ ) at different viscosities

| $\eta$ (cP) | $k_s$ ( $10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) | $\tau_{C \rightarrow 0}$ ( $\mu\text{s}$ ) <sup>a</sup> | $k_{\text{diff}}$ ( $10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) |
|-------------|--|---|--|
| 1           | 2.7  | 144   | 4.6  |
| 1.97        | 1.8  | 149   | 2.3  |
| 3.47        | 1.4  | 164   | 1.3  |
| 5.31        | 0.89   | 179   | 0.87   |

<sup>a</sup> From the intercept of Fig. 7

The quenching efficiency should depend mainly on the diffusion coefficient which is related to temperature and viscosity by the Stokes–Einstein equation. The energy gap between  $S_1$  and  $T_1$  in erythrosin is small ( $28 \text{ kJ mol}^{-1}$ ) [28, 33] and a reverse intersystem crossing is possible as a thermally activated process, with  $k_{TS1} = 6.5 \times 10^7 \text{ s}^{-1}$  for erythrosin B in aqueous solution [11]. But the interesting observation is that the activation energy for  $T_1$  to  $S_0$  is less than  $0.4 \text{ kJ mol}^{-1}$  [20] and so the decrease in self-quenching rate with increasing viscosity is not due to a high rate of intersystem crossing but simply the diffusion step becoming slower and eventually quenching becoming slower. Thus, there are fewer chances for back intersystem crossing from  $T_1$  to  $S_1$ . The decrease in the triplet lifetime with an increase in concentration is due to self-quenching of the excited triplet state by the ground state molecules. In order to check the effect of ionic strength on this process, we tried to work at higher ionic strength. But increasing the ionic strength increased the physical quenching.

#### Photoinduced electron transfer

The Rehm–Weller expression (Eq. 3) is applied to calculate the free energy changes involved in the excited state electron transfer [39]. It states the fundamental thermodynamic condition for spontaneous electron transfer.

$$\Delta G_{\text{el}}^{\circ} (\text{kJ mol}^{-1}) = 96.48 [E^{\circ}(\text{D}^+/\text{D}) - E^{\circ}(\text{A}/\text{A}^-)] - w_{\text{P}} + w_{\text{R}} - \Delta E_{\text{oo}} \quad (3)$$

where  $E^{\circ}(\text{D}^+/\text{D})$  is the oxidation potential of the electron donor,  $E^{\circ}(\text{A}/\text{A}^-)$  the reduction potential of the electron acceptor,  $E_{\text{oo}}$  is the excitation energy for the corresponding excited state of erythrosin, and  $w_{\text{P}}$  and  $w_{\text{R}}$  represent the coulombic work terms for reactants and products, respectively.

$$w_i = (z_A z_B e^2 N_L) / (8\pi \epsilon_0 \epsilon_s d_{AB}) \quad (4)$$

$d_{AB}$  is the reaction distance, normally approximated as  $d_{AB} = (r_A + r_B)$ ,  $z_A$ ,  $z_B$  are the charge numbers, and  $\epsilon_s$  is the static dielectric constant of water. The physical parameters of erythrosin,  $\text{Fe}(\text{CN})_6^{4-}$ , and  $\text{Mo}(\text{CN})_8^{4-}$  for calculations based on Eqs. 3 and 4 are summarized in Table 2. The reduction potential of erythrosin obtained by cyclic voltammetry in borate buffer at pH 9 is  $E^{\circ} = 0.719 \text{ V}$  versus saturated calomel electrode (SCE) and is consistent with the literature values [40, 41]. Sufficiently negative  $\Delta G_{\text{el}}$  is prerequisite for photoinduced electron transfer to excited triplet state with favorable thermodynamic conditions, see Table 3.

There is no overlap between the absorption spectra of the erythrosin dianion ( $\text{Ery}^{2-}$ ) and the ionic quenchers

**Table 2** Radii and reduction potentials of erythrosin and the ionic quenchers

|                               | $r$ (Å)           | $E$ (V vs. SCE) |
|-------------------------------|-------------------|-----------------|
| Erythrosin                    | 7.0 <sup>a</sup>  | 0.719           |
| $\text{Fe}(\text{CN})_6^{4-}$ | 3.32 <sup>b</sup> | -0.115          |
| $\text{Mo}(\text{CN})_8^{4-}$ | 4.8 <sup>c</sup>  | -0.60           |

<sup>a</sup> Reference [18] with approximation for the long axis of the elongated erythrosin

<sup>b</sup> Reference [47]

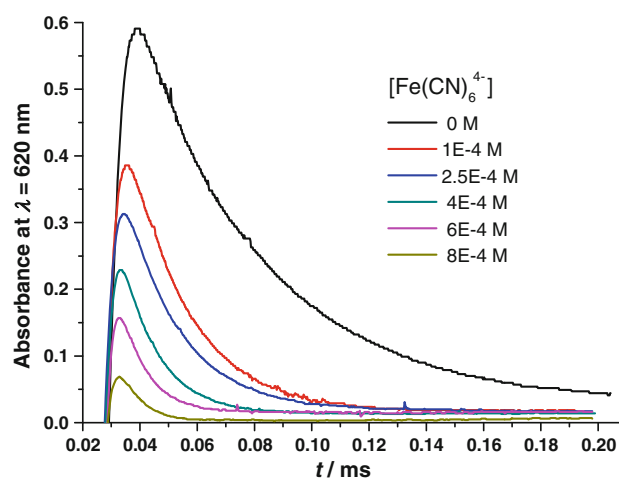
<sup>c</sup> Reference [48]

**Table 3** Calculated driving forces for electron transfer reactions of  ${}^3\text{Ery}^{2-}$

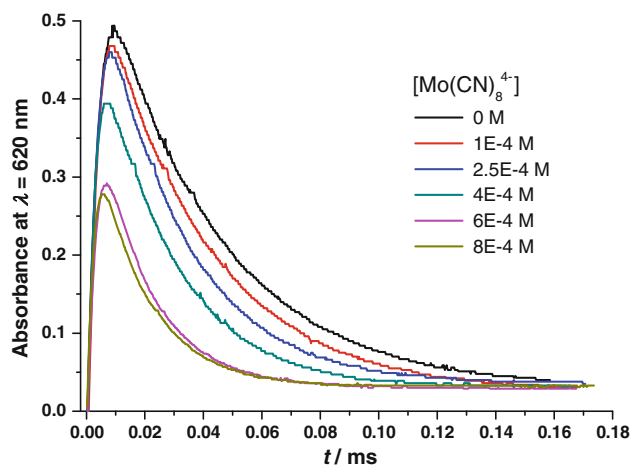
|   | $\Delta G_{\text{et}}^{\circ}$ (kJ mol <sup>-1</sup> ) |
|---|--|
| ${}^3\text{Ery}^{2-} + \text{Fe}(\text{CN})_6^{4-}$ | -83  |
| ${}^3\text{Ery}^{2-} + \text{Mo}(\text{CN})_8^{4-}$ | -63  |

used, like  $\text{K}_4[\text{Fe}(\text{CN})_6]$  [26] and  $\text{K}_4[\text{Mo}(\text{CN})_8]$ . Transient absorbance spectra measured upon flash excitation of a solution of erythrosin in buffer in the presence of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  or  $\text{K}_4[\text{Mo}(\text{CN})_8]$  showed that the triplet absorption of  ${}^3\text{Ery}^{2-}$  at 620 nm is strongly quenched, as shown in Figs. 3 and 4.

As a result of electron transfer from both  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Mo}(\text{CN})_8^{4-}$  to  ${}^3\text{Ery}^{2-}$ , radicals are formed. A new transient absorption at 410 nm [18] is indicative of the formation of the  $\text{Ery}^{3-}$  radical. The quantum yield of free radical formation is quite high provided that geminate recombination is relatively less efficient than the escape of the redox products. In such bimolecular photoinduced electron



**Fig. 3** Time-resolved absorption spectra of erythrosin ( $5 \times 10^{-5} \text{ M}$ ) with quencher  $\text{K}_4[\text{Fe}(\text{CN})_6]$  in borate buffer ( $5 \times 10^{-4} \text{ M}$ ) at pH 9.2



**Fig. 4** Time-resolved absorption spectra of erythrosin ( $5 \times 10^{-5}$  M) with quencher  $K_4[Mo(CN)_8]$  in borate buffer ( $5 \times 10^{-4}$  M) at pH 9.2

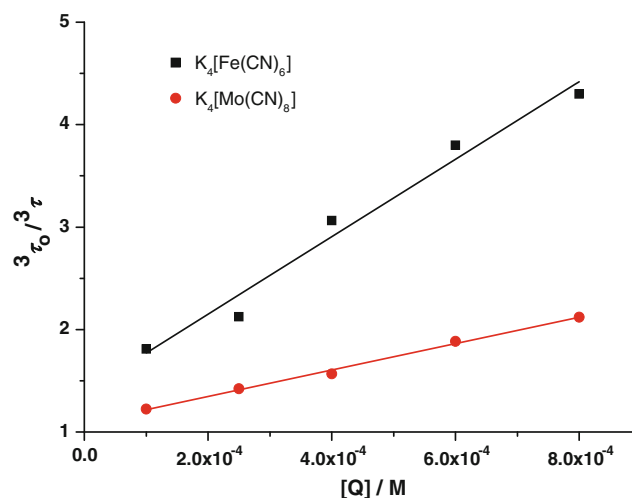
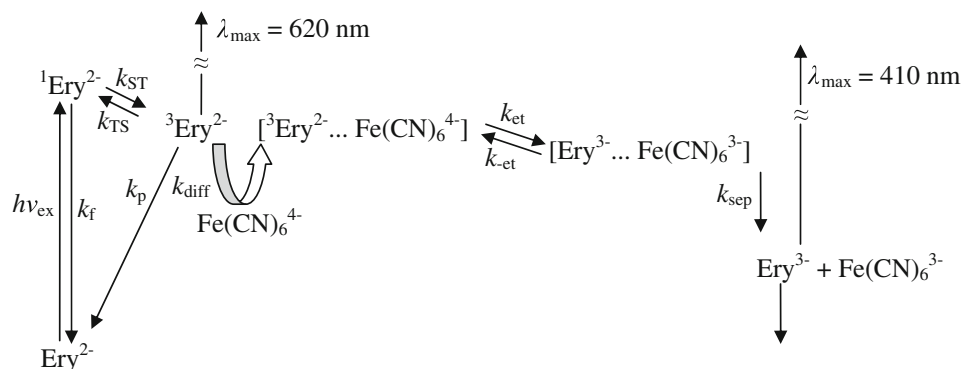
transfer the redox products live for several milliseconds before collapsing to the original system [18, 28].

A mechanism (Scheme 1) similar to one given by Braslavsky et al. [26] is proposed for photoinduced electron transfer and describes the various steps involved.

Erythrosin obeys monoexponential decay. The observed quenching reactions are of second order. The obtained Stern–Volmer plots show a linear behavior within the used range of quencher concentration, see Fig. 5. Rate constants for the bimolecular quenching ( $k_q$ ) are given in Table 4. The values of  $k_q$  for the quencher  $K_4[Mo(CN)_8]$  are in good agreement with those obtained by Braslavsky et al. [26] ( $6.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) using laser-induced optoacoustic spectroscopy.

To get the electron transfer rates, the quenching rates  $k_q$  must be corrected according to diffusion. Diffusion rate constants were calculated from the Debye equation (Eq. 2), as donor and acceptor have different radii (see Table 1) and charges. From Scheme 1, assuming that  $k_{\text{sep}} \gg k_{\text{et}}$ , the quenching rate constant, the diffusion rate constant, and the bimolecular electron transfer rate constant  $k_{\text{et}}$  are related by:

**Scheme 1**



**Fig. 5** Stern–Volmer plots of  ${}^3\text{Ery}^{2-}$  ( $5 \times 10^{-4}$  M) with ionic quencher  $K_4[Fe(CN)_6]$  (filled squares) and  $K_4[Mo(CN)_8]$  (filled circles) in borate buffer ( $5 \times 10^{-4}$  M) at pH 9.2

$$\frac{1}{k_{\text{et}}} = \frac{1}{k_q} - \frac{1}{k_{\text{diff}}} \quad (5)$$

Within the Marcus model,  $k_{\text{et}}$  is given by  $k_{\text{et}} = K_A k_{\text{el}}$ , where  $k_{\text{el}}$  denotes the rate of unimolecular electron transfer forming the successor complex.  $k_{\text{el}} = \kappa_{\text{el}} \nu_n \exp(-\Delta G^*/RT)$  with  $\kappa_{\text{el}}$  as an electronic transmission factor and  $\nu_n$  an effective nuclear frequency factor [42].  $k_{\text{el}}$  values are  $4.6 \times 10^{10} \text{ s}^{-1}$  for  $[{}^3\text{Ery}^{2-}/\text{Fe(CN)}_6^{4-}]$  and  $4.0 \times 10^{10} \text{ s}^{-1}$  for  $[{}^3\text{Ery}^{2-}/\text{Mo(CN)}_8^{4-}]$ . The bimolecular rate constants for the activated electron transfer calculated from Eq. 5 are listed in Table 4.

$K_A$  is the association constant given according to Sutin, Eq. 6 [42]:

$$K_A = 4\pi N_L d_{\text{AB}}^2 \delta d \exp\left(\frac{-w(d)}{RT}\right) \quad (6)$$

The reaction zone thickness  $\delta d$  is approximated as  $0.8 \text{ \AA}$  [42].

A thermodynamically favored electron transfer occurred which might lead to solvent-separated ion pairs  $\text{Ery}^{3-}$  and  $\text{Fe(CN)}_6^{3-}$  and  $\text{Mo(CN)}_8^{3-}$ , respectively.

**Table 4** Quenching rate constant, diffusion rate constant, association constants, bimolecular electron transfer rate constants, and first-order electron transfer rate constant in the complexes

| pH 9.2  | $k_q$ ( $10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) | $K_A$ ( $10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) | $k_{\text{diff}}$ ( $10^{-3} \text{ M}^{-1}$ ) <sup>a</sup> | $k_{\text{et}}$ ( $10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) |
|---|--|--|---|--|
| ${}^3\text{Ery}^{2-} + \text{Fe}(\text{CN})_6^{4-}$ | 7.6  | 1.6  | 2.6   | 1.4  |
| ${}^3\text{Ery}^{2-} + \text{Mo}(\text{CN})_8^{4-}$ | 2.7  | 2.6  | 6.6   | 2.6  |

<sup>a</sup> From Eq. 6

### Triplet lifetime and electron transfer rates as a function of solvent viscosity

The decay of the triplet state to ground state by phosphorescence is sensitive to temperature, solvent, and viscosity. For the erythrosin triplet it is known that temperature affects the back intersystem crossing rate as the singlet–triplet energy gap is small. The decay of erythrosin triplet to ground state becomes slower when the viscosity of the solution is increased by adding dextrose, as given in Table 5.

It is generally observed that the quenching rate constant decreases with increasing viscosity of the solution, and a similar trend was observed for the quenching of erythrosin triplet by  $\text{Fe}(\text{CN})_6^{4-}$  (Table 6). For an efficient excited state quencher, the quenching rate constant  $k_q$  is expected to vary with temperature and viscosity according to Eq. 7 [20]:

$$\frac{\tau_o}{\tau} = 1 + \tau_o A \frac{T}{\eta} \quad (7)$$

where  $A$  is a constant that includes the dye concentration and  $\eta$  is the bulk viscosity of the solution. Figure 6 shows Stern–Volmer plots at different viscosities and Fig. 7 shows that  ${}^3\tau_o f^3 \tau$  varies linearly with  $T/\eta$  at constant temperature ( $T = 298 \text{ K}$ ) for different concentrations of ionic quencher  $\text{K}_4[\text{Fe}(\text{CN})_6]$ .

**Table 5** Triplet state lifetime ( ${}^3\tau_o$ ) of erythrosin ( $5 \times 10^{-5} \text{ M}$ ) in aqueous solution at different viscosities

| $\eta$ (cP) | ${}^3\tau_o$ ( $\mu\text{s}$ ) |
|-------------|--------------------------------|
| 1           | 49.5                           |
| 1.97        | 74.3                           |
| 3.47        | 105.8                          |
| 5.31        | 119.8                          |

**Table 6** Quenching, diffusion, and electron transfer rate constants at different viscosities for  $\text{Ery}^{2-} + \text{Fe}(\text{CN})_6^{4-}$ 

| $\eta$ (cP) | $k_q$ ( $10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) | $k_{\text{diff}}$ ( $10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) | $K_A$ ( $10^{-3} \text{ M}^{-1}$ ) | $k_{\text{et}}$ ( $10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) |
|-------------|--|--|------------------------------------|--|
| 1           | 7.6  | 16   | 2.5                                | 1.4  |
| 1.97        | 5.6  | 8.3  | 2.5                                | 1.7  |
| 3.47        | 3.9  | 4.8  | 2.5                                | 2.3  |
| 5.31        | 2.8  | 3.1  | 2.5                                | 3.0  |

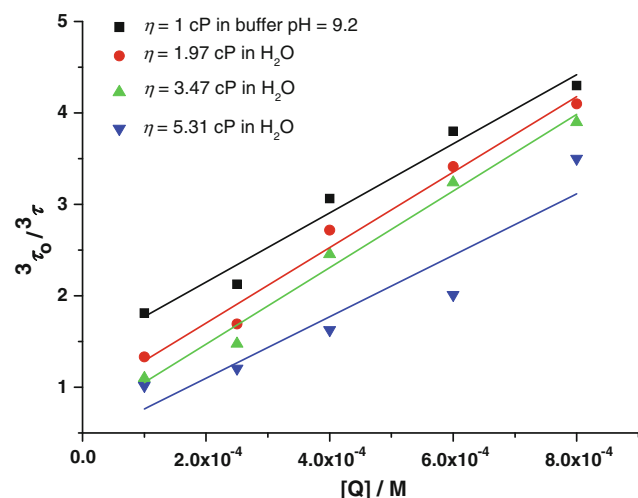
Increasing the viscosity slowed down the deactivation of triplet states by the quencher. For the erythrosin triplet it was observed that there was a large shift in absorption maximum as a function of solvent which was interpreted as being due to preferential solvation [33, 43]. We proved that dextrose changes only the viscosity of the aqueous solution and does not produce any triplet quenching. As mentioned earlier there are fewer chances for back intersystem crossing, so the decrease in electron transfer rate with increasing viscosity is not due to a high rate of intersystem crossing but simply the diffusion step becomes slower and eventually electron transfer becomes slower.

### Conclusion

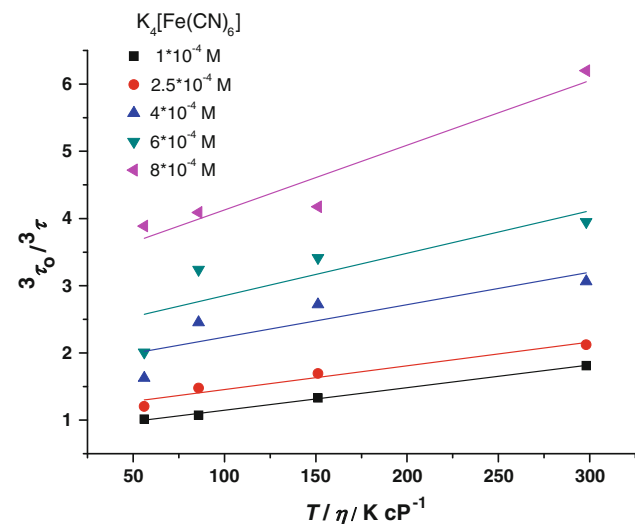
In argon-saturated solutions the lifetime of the triplet state is found to be dependent upon erythrosin concentration because of self-quenching, and the rate constants of self-quenching are close to diffusion rate constants.  $\text{Fe}(\text{CN})_6^{3-}$  and  $\text{Mo}(\text{CN})_8^{4-}$  proved to be efficient ionic quenchers of the erythrosin triplet by photoinduced electron transfer reactions. First-order decay kinetics were observed for quenching of the triplet erythrosin by ground state quencher molecules. Changing the viscosity of solvent changed the triplet lifetime and changed quenching rate constants. Increasing viscosity lowers the electron transfer rate constants because diffusion of reactants became slower. Changing ionic strength increased the physical quenching of triplet erythrosin.

### Materials and methods

Erythrosin B (extra bluish) was purchased from Fluka and used without further purification.  $\text{K}_4[\text{Mo}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$  was

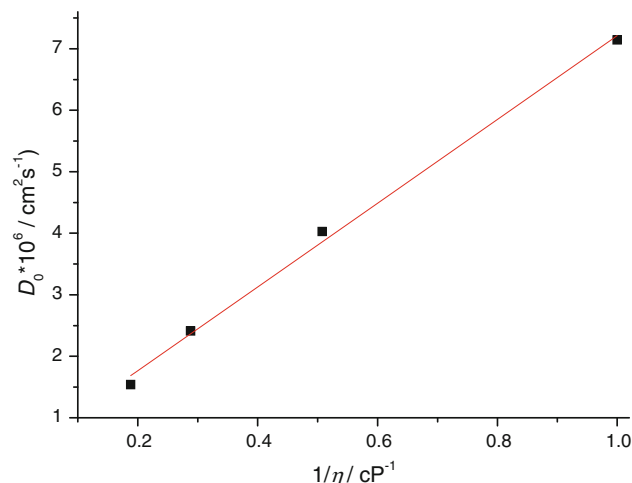


**Fig. 6** Stern–Volmer plots of  ${}^3\text{Ery}^{2-}$  ( $5 \times 10^{-5}$  M) with quencher  $\text{K}_4[\text{Fe}(\text{CN})_6]$  at different viscosities at  $T = 295$  K



**Fig. 7** Plots of  ${}^3\tau_0/{}^3\tau$  vs.  $T/\eta$  for erythrosin ( $5 \times 10^{-5}$  M) with different concentrations of quencher  $\text{K}_4[\text{Fe}(\text{CN})_6]$  at  $T = 298$  K

prepared as described [44].  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  (p.a., Fluka) and boric acid  $\text{H}_3\text{BO}_3$  (99% pure, Fluka) were used as received. Doubly distilled water was used. A borate buffer concentration of 0.5 mM at pH 9.2 (20 °C) was used for all experiments to any avoid ionic strength effect. The triplet state lifetime ( ${}^3\tau_0$ ) of the erythrosin dianion ( $5 \times 10^{-5}$  M) does not change with buffer concentration ranging from  $5 \times 10^{-4}$  to  $5 \times 10^{-3}$  M. For recording of the absorption spectra at different pH values, we used phosphate buffer (pH 7–8, 10–12), borate buffer (pH 9), and KCl/NaOH (pH 13). The viscosity of the aqueous solution was increased from 1 to 5.31 cP by adding inactive pure dextrose. Although the viscosity changed by



**Fig. 8** Plot of the diffusion coefficient  $D$  as a function of the reciprocal viscosity  $1/\eta$  for dextrose-containing aqueous solutions [31]

almost five times, the corresponding change in the dielectric constant is relatively small. Figure 8 shows that the diffusion coefficient [31] depends linearly on the reciprocal viscosity (at 22.5 °C).

The molar absorption coefficient of erythrosin in aqueous solution is  $\epsilon_{526} = 90,000 \text{ M}^{-1} \text{ cm}^{-1}$  [45], and the literature value of the molar absorption coefficient for the triplet state of the erythrosin dianion ( ${}^3\text{Ery}^{2-}$ ) is  $\epsilon_{580} = 11,000 \text{ M}^{-1} \text{ cm}^{-1}$  [46]. The erythrosin concentration used was  $5 \times 10^{-5}$  M and remained constant in all quenching and viscosity experiments, except for measurement of the dependence of excited state lifetime on dye concentrations of  $5 \times 10^{-5}$  to  $7.2 \times 10^{-6}$  M. All solutions were bubbled for 20 min with purified argon, followed by freeze–pump–thaw cycles (4 times) prior to use for transient absorbance measurements in order to avoid quenching by oxygen [29].

Absorption spectra were recorded with a Shimadzu UV-3101-PC and a Perkin Elmer Lambda 12 spectrometer. Transient absorption spectra were obtained with flash photolysis equipment consisting of a R928 photomultiplier tube and a digital oscilloscope (HAMEG HM 205-2) for data storing. Two flash lamps were simultaneously driven by the discharge energy of around 160 J (condenser capacity,  $C = 1 \mu\text{F}$ ,  $U = 18 \text{ kV}$ , flash lifetime FWHM = 2.4  $\mu\text{s}$ ). A homemade kinetic computer program (KINCALC4) was used for analysis of the data. Cyclic voltammograms were obtained by using a conventional three-electrode cell arrangement, comprising a Au working electrode and a Pt counter electrode together with an SCE reference electrode.

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