

Thionine Fluorescence Quenching by Metal Cations

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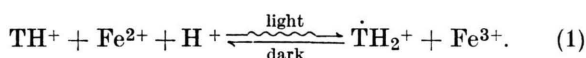
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The mechanism of the fluorescence quenching of aqueous thionine by various metal ions (Ce^{3+} , Fe^{2+} , Mn^{2+} , Mg^{2+} , Cs^+ and Na^+) was studied at $p_{\text{H}} = 2.5$. The following Stern-Volmer constants (K_{SV}) were determined: $K_{\text{SV}}(\text{Fe}^{2+}) = 1.13 \text{ dm}^3 \text{ mol}^{-1}$, $K_{\text{SV}}(\text{Mn}^{2+}) = 0.24 \text{ dm}^3 \text{ mol}^{-1}$, $K_{\text{SV}}(\text{Ce}^{3+}) = 0.24 \text{ dm}^3 \text{ mol}^{-1}$, $K_{\text{SV}}(\text{Cs}^+) = 0.03 \text{ dm}^3 \text{ mol}^{-1}$. At concentrations below $1 \text{ mol} \cdot \text{dm}^{-3}$ Na_2SO_4 and MgSO_4 are very weak quenchers ($K_{\text{SV}}(\text{Na}^+ \text{ or } \text{Mg}^{2+}) = 0.007$), but the influence on the fluorescence yield increases considerably at higher cation concentrations. This was attributed to the formation of ground state complexes between thionine and SO_4^{2-} ions. The salt concentration affects considerably the quenching rate of Fe^{2+} ions, but much less so that of the other cations. Fluorescence quenching mechanisms are discussed.

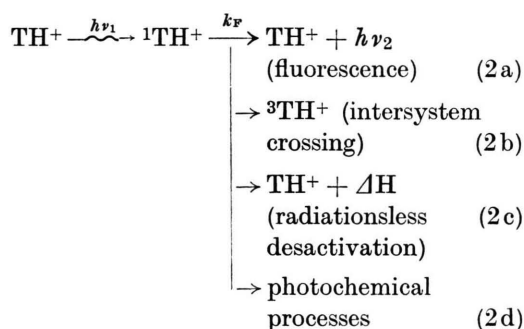
1. Introduction

The thionine-iron photogalvanic cell, first described by Rabinowitch [1], is a candidate for photochemical solar energy utilization. The overall forward reaction initiated by illumination and the back reaction in the dark can be summarized by:



A potential of 100–200 mV is obtained between the electrodes. The photoredox process proceeds thereby mainly from the triplet state of the thiazine dye (thionine or methylene blue) in acid aqueous solution. Furthermore, it was established that also the excited dye singlet state is involved in the reaction mechanism [2–15].

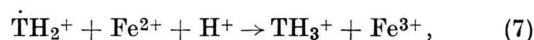
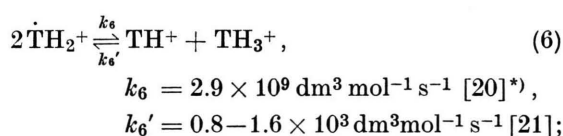
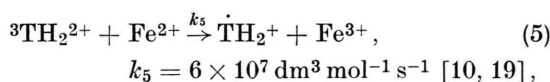
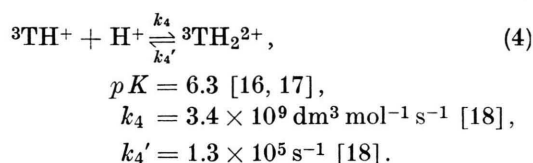
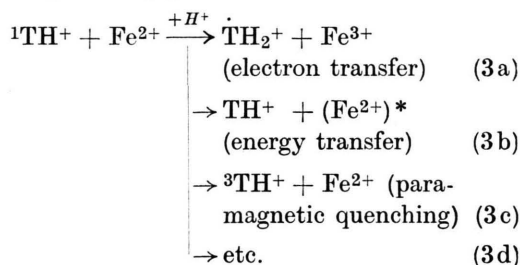
The processes induced by light absorption of the thiazine dye iron system are summarized in reactions (2) to (9)



where $k_F = 1.3 \times 10^8 \text{ s}^{-1}$ [5]; $Q_F = 0.047$ [12].

Life time of S_1 : $\tau_F = 365 \text{ ps}$ ($p_{\text{H}} = 2.5$;
HCl [12]),
 $\tau_F = 345 \text{ ps}$ ($p_{\text{H}} = 2.5$;
0.1 M K_2SO_4 [12]).

Possible quenching processes:



*) Note added in proof: This value is in very good agreement with $k_6 = 2.8 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ determined by pulse radiolysis very recently [34].

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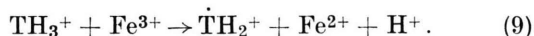
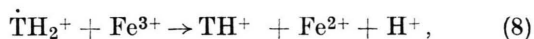


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The superscripts on the left indicate the multiplicity of the excited dye state; TH^+ and $\dot{\text{T}}\text{H}_2^+$ denote the semiquinone and its protonated form, TH_3^+ the leuco-dye.

Very recently Guha *et al.* [22] studied the effect of Fe^{2+} and Fe^{3+} ions on the formation and decay of semithionine in acid aqueous solution by flash photolysis. They observed an increase of the $\dot{\text{T}}\text{H}$ yield parallel to the concentration of Fe^{2+} up to $\text{Fe}^{2+} = 10^{-2} \text{ mol dm}^{-3}$, but it decreases at higher concentrations. The latter effect was explained by dynamic and/or static quenching of $\dot{\text{T}}\text{H}^+$. This excludes, however, singlet quenching by a charge transfer process.

It should be mentioned that the TH^+ - Fe^{2+} -system is not stable enough for practical use at a prolonged illumination, especially when illuminated with light of $\lambda < 500 \text{ nm}$. A similar instability was observed for the MB^+ / Fe^{2+} -system, excited at 292–313.4 nm. This effect was attributed to an energy transfer from the excited dye to Fe^{2+} (reaction 3b), occurring additionally in this wavelength range, which results in an electron ejection with $Q(e_{\text{aq}}^-) = 1.4 \times 10^{-5}$ [15]. It seems therefore to be of importance to learn more about the behaviour of the excited states of thiazine dyes in order to overcome this problem. The aim of the present investigations was to obtain information on the extent and the mechanisms of fluorescence quenching of thionine by various cations (Fe^{2+} , Mn^{2+} , Ce^{3+} , Mg^{2+} , Na^+ , Cs^+) in acid aqueous solution. Special attention was paid to the effects of SO_4^{2-} ions on this processes.

2. Experimental Procedures

All substances ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, Na_2SO_4 , Cs_2SO_4 and thionine) were of reagent grade (E. Merck) and were used without further purification. The thionine purity was checked by quantitative absorption spectroscopy. The obtained value for the molar extinction coefficient at 598 nm $\epsilon = 54.800 \text{ M}^{-1} \text{ cm}^{-1}$ is in very good agreement with that for high purity thionine $\epsilon_{598} = 55.00$ [7]. The absorption spectra were measured with a spectral-photometer "Coleman 565" (Perkin Elmer). The

fluorescence setup was previously described [23]. The solutions were prepared using at least four times distilled water and were saturated with high purity nitrogen (Messer Griesheim, Vienna) for about 1 hour, in order to prevent any eventual influence of oxygen. The $\text{pH} = 2.5 \pm 0.1$ was adjusted with perchlorid acid.

3. Results and Discussion

The influence of the salt concentration on the thionine absorption and fluorescence spectra was studied. An increasing the concentration of magnesium sulfate a red shift of the absorption maximum occurs (Figure 1). In the presence of $2 \text{ mol dm}^{-3} \text{ MgSO}_4$, λ_{max} moves from 598 nm to 605 nm and the extinction coefficient drops slightly from $5.48 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ to $5.25 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. When adding the above quoted cations in a concentration up to 2 mol dm^{-3} no spectral change of the fluorescence ($3 \times 10^{-6} \text{ mol dm}^{-3} \text{ TH}^+$, $\lambda_{\text{exc}} = 560 \text{ nm}$, $\lambda_{\text{em}} = 650 \text{ nm}$) could be detected.

For dynamic fluorescence quenching a linear relationship between the inverse of the fluorescence yield and the concentration of the quencher c_q should hold (Stern-Volmer-equation):

$$I_F^0/I_F - 1 = K_{\text{SV}} c_q, \quad (10)$$

$$K_{\text{SV}} = \tau_F k_q. \quad (11)$$

Herein I_F^0 is the fluorescence yield in the absence of a quencher and k_q the rate constant for the quenching process.

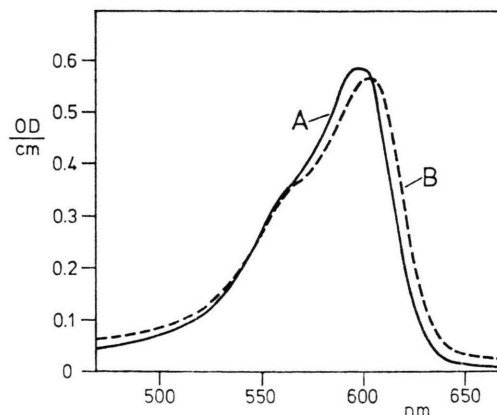


Fig. 1. Absorption spectra of an acid aqueous solution of $3 \cdot 10^{-6} \text{ mol dm}^{-3} \text{ TH}^+$ ($\text{pH} = 2.5$) in the absence (A) and in the presence of $2 \text{ mol dm}^{-3} \text{ MgSO}_4$ (B).

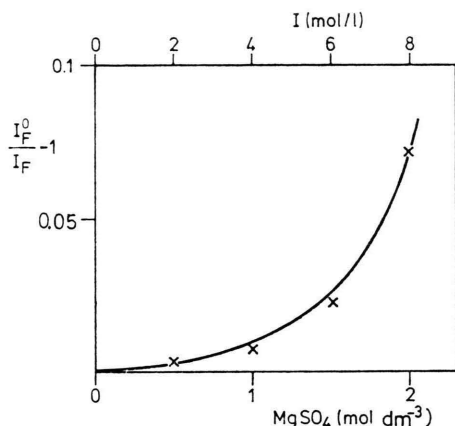


Fig. 2. Influence of MgSO_4 on the thionine fluorescence (solution: $3 \cdot 10^{-6} \text{ mol dm}^{-3} \text{ TH}^+$, $\lambda_{\text{exc}} = 560 \text{ nm}$, $\lambda_{\text{em}} = 650 \text{ nm}$, $p_{\text{H}} = 2.5$).

From Fig. 2 it is obvious that Mg^{2+} , as a representative of the group of light cations, causes not only dynamic fluorescence quenching. In the presence of Na_2SO_4 and MgSO_4 in concentrations of $\leq 1 \text{ mol dm}^{-3}$ only a very small fluorescence quenching effect, $K_{\text{SV}} = 0.007$, was obtained. However, on increasing the cation concentration a stronger reduction of the I_{F} -value occurs. This effect is due to the formation of a ground state complex, as indicated by a shift of the absorption maximum (Figure 1). It can be assumed that TH^+ associates with the SO_4^{2-} ions, since the influence of salt concentration was observed independently of the kind of the cation. The tendency of TH^+ to form complexes with several ions was previously proposed [3, 20, 24]. In this context it should be mentioned that the observed concentration effect on the reduction rate of the triplet excited dye was also attributed to an association of the positively charged reactive ions with sulfate anions [24].

The fluorescence quenching of thionine by the cations Fe^{2+} , Mn^{2+} , Ce^{3+} and Cs^+ obeyed relation (10) when the SO_4^{2-} concentration (ionic strength I) of the solutions was kept constant. The Stern-Volmer Plot for Fe^{2+} as quencher of thionine fluorescence at constant $[\text{MgSO}_4]$ is shown in Figure 3.

The influence of the ionic strength on the kinetic constant, K_{SV} , is demonstrated for Fe^{2+} as fluorescence quencher in Figure 4. The K_{SV} -value rises by increasing the SO_4^{2-} concentration. For comparison, two values obtained with Cl^- and NO_3^- are also

given in Figure 4. They are in good agreement with the values obtained in $\text{HSO}_4^-/\text{SO}_4^{2-}$ -medium. The K_{SV} values are extrapolated to $I = 0$, and then k_{q} was calculated (Table 1). As can be seen, this value

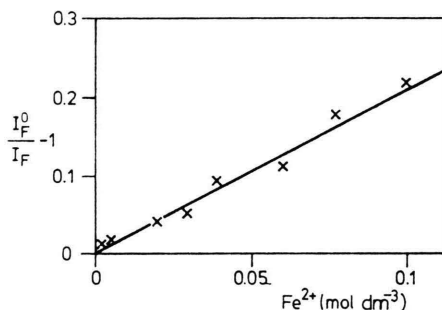


Fig. 3. Fluorescence quenching of thionine by Fe^{2+} ions (solution: $3 \cdot 10^{-6} \text{ mol dm}^{-3} \text{ TH}^+$, $\lambda_{\text{exc}} = 560 \text{ nm}$, $\lambda_{\text{em}} = 650 \text{ nm}$, $p_{\text{H}} = 2.5$; the total SO_4^{2-} concentration was kept constant: $\text{FeSO}_4 + \text{MgSO}_4 = 1.5 \text{ mol dm}^{-3}$).

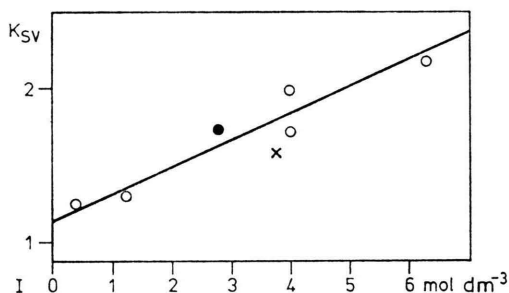


Fig. 4. Effect of the ionic strength (I) on the Stern-Volmer constant K_{SV} for the fluorescence quenching of thionine (solution: $3 \cdot 10^{-6} \text{ mol dm}^{-3} \text{ TH}^+$). (\circ) MgSO_4 (\bullet) KCl (\times) KNO_3 ($\lambda_{\text{exc}} = 560 \text{ nm}$, $\lambda_{\text{em}} = 650 \text{ nm}$, $p_{\text{H}} = 2.5$).

Table 1. Kinetic constants for the fluorescence quenching of $3 \cdot 10^{-6} \text{ mol dm}^{-3}$ thionine ($p_{\text{H}} = 2.5$) by various cations at constant ionic strength (I).

Quencher	K_{SV} (1 mol^{-1})	τ_{F}^* 10^{-12} s	k_{q} $10^9 \text{ l mol}^{-1} \text{ s}^{-1}$	I mol/l^{**}
FeSO_4	1.13	365	3.1	0
			2.9*	0
	1.24	345	3.6	0.4
			3.5*	0.4
	2.15	—	—	6.5
MnCl_2	0.24	365	0.65	0
	0.29	—	—	10
CeCl_3	0.24	365	0.65	0.4
CsSO_4	0.03	365	0.082	no influence

* Taken from (12). ** Adjusted with MgSO_4 .

is in very good agreement with that obtained from measurements of the fluorescence lifetime in the ps-range [12]. From this it is concluded that the fluorescence quenching process proceeds by a bimolecular reaction. The obtained k_q -value is very near to $k = 3.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [12], the rate constant for the diffusion controlled ionic reaction, calculated from [25]

$$k = 4\pi r_{AB} D_{AB} L \delta / (e^\delta - 1), \quad (12)$$

$$\delta = Z_A Z_B e^2 / \varepsilon k T r_{AB}, \quad (13)$$

where r_{AB} , the distance between the reaction partners A and B , is assumed to be 1 nm and D_{AB} , the relative diffusion coefficient for A and B , is taken to be $10^{-5} \text{ cm}^2 \text{ s}^{-1}$. L = Avogadro's number, Z_A, B = charge of A , B , ε = dielectric constant, k = Boltzmann constant, T = temperature.

Consequently, the quenching of thionine fluorescence by Fe^{2+} ions seems to be diffusion controlled, without strong thermal activation.

The rate parameters for the fluorescence quenching by the other cations were obtained in a similar way and are compiled in Table 1. Mn^{2+} , Ce^{2+} and Cs^+ are considerably weaker quenchers than Fe^{2+} .

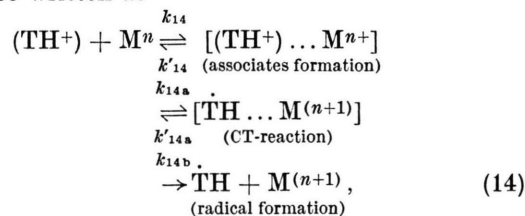
For all these cations it can be concluded that no energy transfer process (3b) from $^1\text{TH}^+$ to the cation quencher for excitation with light $\lambda > 500 \text{ nm}$ does occur. This is because none or only very weak absorption bands (for Fe^{2+}) of the cations exist in this wavelength range. Since the $^5\text{T}_{2g} \rightarrow ^5\text{E}_g$ transition for the aquo complexes $\text{Fe}^{2+} \cdot 6\text{H}_2\text{O}$ is Laporte forbidden [26] and since the overlapping of this absorption with the thionine emission is very weak, resonance energy transfer is very unlikely to occur.

The fluorescence quenching by Cs^+ ions can be explained by an enhanced singlet-triplet intersystem crossing due to the heavy atom effect. The obtained k_q -value (Table 1) is far below the diffusion limit (k).

Two reaction mechanism can be responsible for the fluorescence quenching by Fe^{2+} , Ce^{3+} and Mn^{2+} ions. Firstly, an electron transfer under formation of semiquinone can take place (reaction 3a) and secondly, intersystem crossing could be enhanced, e.g. by the paramagnetic moment of these ions ($\mu(\text{Fe}^{2+}) = 4.9 \text{ BM}$; $\mu(\text{Mn}^{2+}) = 5.92 \text{ BM}$ [27], see also reaction 3c). At higher cation concentrations, necessary for efficient singlet quenching, the triplet lifetime becomes very short [10]. Therefore, measurements of the triplet yield by conventional flash photolysis

could not be performed. To decide whether the first or second mechanism is mainly involved in the quenching, model calculations for CT processes can be carried out.

If one assumes for the charge transfer reaction (3a) an "outer sphere" mechanism similar to the CT-process between aromatic molecules [28, 29], it can be written as



where $k_{14} \dots k_{14b}$ are rate constants of the individual reaction steps, k_{14} represents the rate constant for the diffusion controlled process of an encounter complex, M^n is the quencher molecule and $\dot{\text{T}}\text{H}$ the radical before protonation.

From reaction scheme (14) the rate constant (k_q) for the quenching process can be deduced:

$$k_q = k_{14} \cdot \left(1 + \frac{k'_{14}}{k_{14a}} \exp(\Delta G/RT) + \frac{k'_{14}}{k_{14a}} \exp(\Delta G^*/RT) \right)^{-1}, \quad (15)$$

ΔG is the free energy change for the electron transfer.

The activation free energy of the second reaction step can be estimated as follows ($\Delta G^*(0)$ is ΔG^* for $\Delta G = 0$) [28, 29]:

$$\Delta G^* = \frac{\Delta G}{2} + \left[\left(\frac{\Delta G^2}{2} \right) + (\Delta G^*(0))^2 \right]^{1/2}. \quad (16)$$

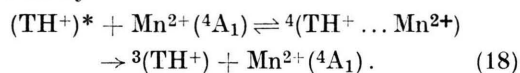
For charge transfer a relation between ΔG and the reduction potential of the dye, $E(\text{TH}^+/\dot{\text{T}}\text{H})$, as well as of the oxydation potential of the corresponding cation, $E(\text{M}^n/\text{M}^{(n+1)+})$, holds:

$$\Delta G = E(\text{M}^n/\text{M}^{(n+1)+}) - E(\dot{\text{T}}\text{H}/\text{TH}^+) - E(^1\text{TH}^+). \quad (17)$$

$E(^1\text{TH}^+)$ represents the excitation energy for the S_1 state of thionine. Taking $E(\text{TH}^+/\dot{\text{T}}\text{H}) = 0.49 \text{ V}$ [30], $E(\text{Fe}^{2+}/\text{Fe}^{3+}) = 0.77 \text{ V}$ [31], $E(^1\text{TH}^+) = 46 \text{ kcal mol}^{-1}$, $k'_{14}/k_{14a} \approx k'_{14}/k_{14a} \approx 0.25$ and $\Delta G^*(0) = 2 \text{ kcal mol}^{-1}$ [28–30], ΔG and the rate constant for the fluorescence quenching, k_q , can be derived. ΔG is found to be $-17 \text{ kcal mol}^{-1}$, which favours strongly the CT process, and k_q is therefore very

near to the limit of $k_{14}/1.25$. Quenching of the singlet state by Fe^{2+} can therefore be attributed mainly to a CT-process. This is confirmed by the fact that the yield of TH_2^+ , formed by flash photolysis, is independent of the Fe^{2+} concentration [13], but in contradiction to [22].

The evaluation of k_q for Mn^{2+} [$E(\text{Mn}^{2+}/\text{Mn}^{3+}) = 1.51 \text{ V}$ [31]] gives $\Delta G = 0.13 \text{ kcal mol}^{-1}$. This predicts k_q to be twice the observed value. However in this case and also for Ce^{3+} the calculated values for k_q are very sensitive to small variations of ΔG . Especially $E(^1\text{TH}^+)$ and $\Delta G^*(0)$ are only poorly known, so that the conclusion from the calculations are not clear cut. Since Mn^{2+} and Ce^{3+} ($E(\text{Ce}^{3+}/\text{Ce}^{4+}) = 1.44$ [31] giving $\Delta G = -1.5 \text{ kcal mol}^{-1}$) show equal quenching efficiency by different redox potentials, the quenching constant is not correlated to ΔG for these two ions. Similarly no correlation between k_q and ΔG was found previously for the fluorescence quenching by inorganic anions, when the electron donating ability becomes small [32, 33]. In this case, enhanced intersystem crossing was shown as origin for the fluorescence quenching [33]. Therefore it is assumed that the quenching by Mn^{2+} and Ce^{3+} leads mainly to an increased crossing to the triplets, probably called forth by the paramagnetic moment of these ions. The process can be described by



${}^4\text{A}_1$ indicates the ground state of Mn^{2+} in aqueous solution. The process is allowed according to Wig-

ner's spin conservation rule [27] and is determined by the formation of an exciplexstate.

The values plotted in Fig. 3 and listed in Table 1 show clearly the salt effect on the quenching processes. Added salt apparently suppresses the repulsive interactions between TH^+ and the metal ion. This can explain the twofold increase of the quenching by Fe^{2+} when the concentration of MgSO_4 is raised to 1.5 mol dm^{-3} . However, the Debye-Hückel treatment is obviously not applicable at the high ionic strengths studied here. Clearly there are specific ionic interactions in the thionine sulfate system which render a simple electrostatic interpretation of the results of little significance. In any event, the relatively small effect in the case of Mn^{2+} (20% increase for $\text{MgSO}_4 = 2.5 \text{ mol dm}^{-3}$) could support the interpretation that the quenching by Mn^{2+} is different in nature from the quenching by Fe^{2+} .

As a conclusion, it can be pointed out that the quenching of the thionine singlet state by Fe^{2+} proceeds mainly by an electron transfer process, similar to that observed for the triplet state. For Mn^{2+} a charge transfer effect cannot be excluded but it seems more likely that quenching leads to enhanced intersystem crossing.

Acknowledgements

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