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Fluorescence quenching of safranine T by inorganic ions in aqueous polyethylene glycol (PEG) medium

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Abstract

The fluorescence quenching of the dye safranine T by inorganic ions ($[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, Cu^{2+}, Co^{2+}, Ni^{2+} and Mn^{2+}) in aqueous polyethylene glycol (PEG) medium (four different molar masses of 200, 300, 400 and 600) has been investigated. The ions influence the process to different extents; the medium efficiency follows the order PEG 600 > PEG 400 > PEG 300 > PEG 200 > water. The efficiencies of the ions for quenching the fluorescence of safranine T in aqueous and aqueous PEG media are in the order $[Fe(CN)_6]^{3-} > [Fe(CN)_6]^{4-} > Cu^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+}$. The photophysical process is not governed by an electron transfer mechanism between the ions and the dye. The process involves collisional quenching and is essentially influenced by the viscosity of the medium; a configurational contribution of PEG to the process is absent. The Stern–Volmer constants of the quenching process are presented and rationalization of the results has been attempted. © 1997 Elsevier Science S.A.

Keywords: Fluorescence; Polyethylene glycol; Quenching; Safranine T; Viscosity

1. Introduction

The spectral behaviour of dyes depends on their environment and is reflected in their visible and fluorescence spectra [1–10]. The photoinduced electron transfer process of fluorescence in surfactant medium is important for efficient energy conversion and storage because surfactant micelles help to achieve the separation of the photoproducts by means of hydrophilic–hydrophobic interactions of the products at the micellar interface [11–15]. It has been reported from photophysical studies that the dye safranine T (ST) interacts with surfactants to form 1 : 1 complexes with micelles of both non-ionic and ionic types [3], i.e. Tweens, Triton X, cetyltrimethylammonium bromide (CTAB) and sodium dodecylsulphate (SDS). The fluorescence quenching of ST in aqueous medium and in non-ionic micellar solutions of Triton X-100 and Tweens (20, 40, 60 and 80) by inorganic ions has also been investigated [16]. It has been reported that the quenching phenomenon is not guided by the transfer of electrons from the quencher to the dye molecule, but is controlled by collisional quenching. To understand the effect of the polyethylene oxide (PEO) headgroup of Tweens on the charge transfer process between ST and Tween micelles, ground and excited state spectral studies of ST in aqueous solutions of polyethylene glycol (PEG) (average molecular weights of 200, 300, 400, 600 and 1000) have been made [1]. The efficiency of the interaction has been found to depend on the number of ethylene oxide (EO) residues in PEG; the polarity of the medium systematically decreases with an increase in the number of EO residues in PEG. As an extension of this study, an investigation of the fluorescence quenching of ST by different inorganic ions in PEG medium has been performed. This provides a better understanding of the photophysical phenomena affected by PEO groups. In this paper, we present the results of a detailed study on the fluorescence quenching of ST in PEG medium with average molecular weights of 200, 300, 400 and 600. Rationalization of the data has been attempted.

2. Experimental details

PEG 200, 300, 400 and 600 were BDH (UK) products of a quality reported previously [1]. The number corresponds to the average molar mass. ST (E. Merck) was recrystallized from ethanol–water medium. Doubly distilled conductivity water was used for solution preparation. The salts of quencher ions and urea were of BDH (UK) Excellar grade.

Absorption spectra were recorded on a Shimadzu (Japan) UV–visible 160 A spectrophotometer with a matched pair of

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silica cuvettes (path length, 1 cm). Fluorescence spectra were measured using a Fluorolog F III A spectrofluorometer (Spex Inc., NJ, USA) with a slit width of 2.0 nm. The excitation wavelength was 520 nm. All the spectral measurements were duplicated in a constant-temperature water bath (accuracy, ±0.1 °C) and the mean values were considered for data analysis. The viscosity of the solutions was measured using a calibrated Ostwald viscometer.

The concentration of ST used in the solutions was of the order of 10^{-5} mol dm^{-3}. In the fluorescence quenching measurements with $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$, the quencher concentrations were varied in the range 10–90 mmol dm^{-3}, and with Co^{2+}, Cu^{2+}, Ni^{2+} and Mn^{2+}, the concentrations were varied in the range 0.1–0.8 mol dm^{-3}. The fluorescence spectra of the dye were recorded at a constant PEG concentration with varying quencher concentration. All measurements were taken at 27 ± 0.1 °C.

3. Results

The fluorescence of ST in different PEG media is quenched by $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, Cu^{2+}, Co^{2+}, Ni^{2+} and Mn^{2+} ions. The Stern–Volmer quenching constants K_{sv} were obtained from the intercepts of the plots according to Eq. (1), where F_0 and F are the fluorescence intensities in the absence and presence of quencher ions (Q) respectively in aqueous (Fig. 1) and in different PEG (Fig. 2) media

$$\log(F_0/F-1)=\log K_{sv}+\log[Q] \qquad (1)$$

In PEG medium at low quencher concentration, a plot of F_0/F vs. [Q] also produces a good linear correlation according to Eq. (2)

$$F_0/F=1+K_{sv}[Q] \qquad (2)$$

At higher quencher concentrations, a deviation from the Stern–Volmer equation occurs (Fig. 3). In aqueous medium, the results obtained from Eq. (1) and Eq. (2) are in agree-

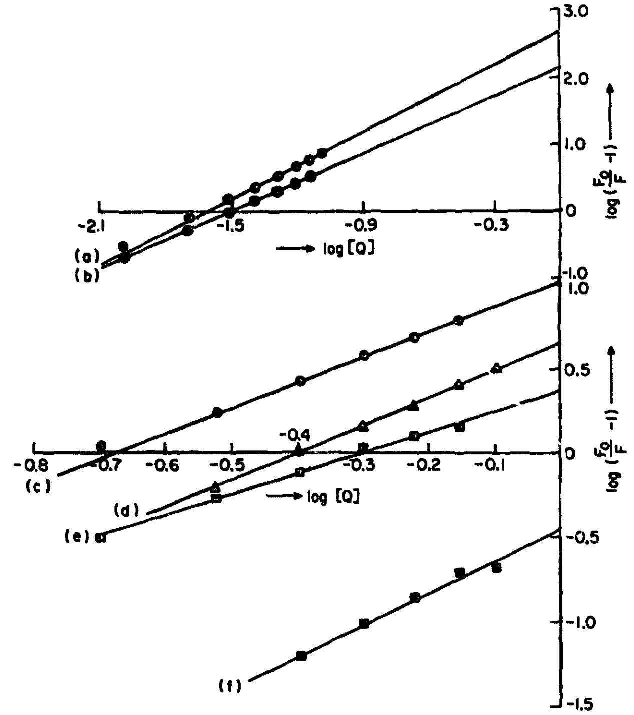

Fig. 1. Plot of $\log(F_0/F-1)$ vs. log [Q] in aqueous medium at 300 K: (a) $[Fe(CN)_6]^{3-}$; (b) $[Fe(CN)_6]^{4-}$; (c) Cu^{2+}; (d) Co^{2+}; (e) Ni^{2+}; (f) Mn^{2+}.

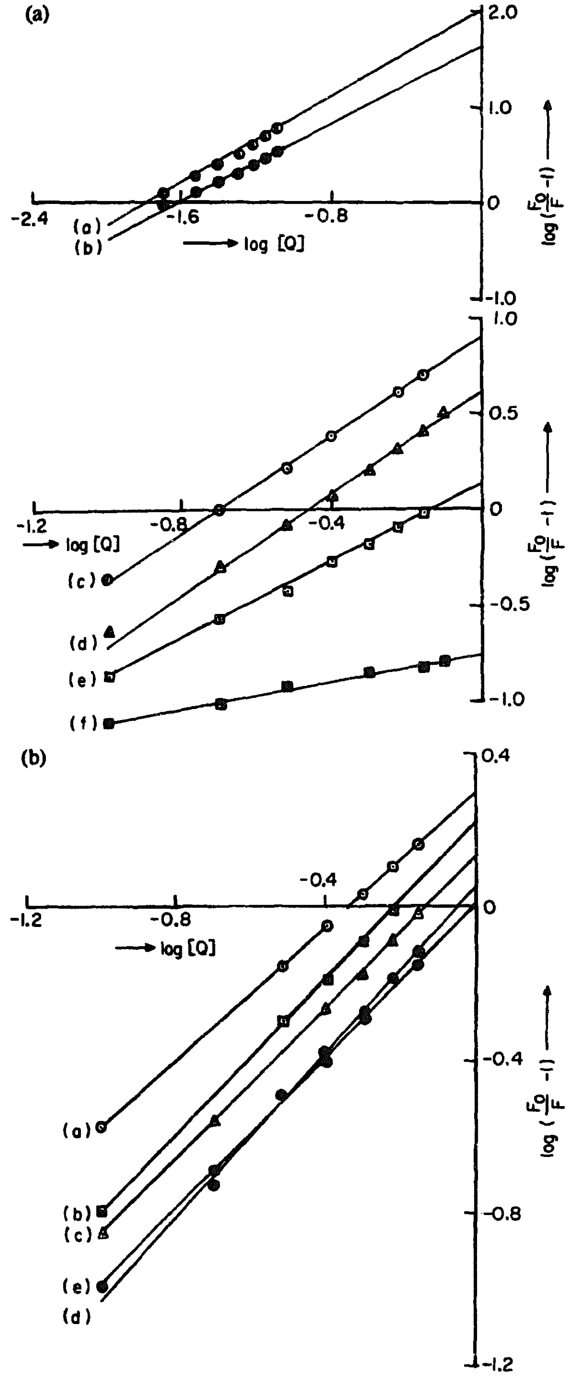

Fig. 2. (i) Plot of $\log(F_0/F-1)$ vs. log [Q] in PEG 300 medium at 300 K: (a) $[Fe(CN)_6]^{3-}$; (b) $[Fe(CN)_6]^{4-}$; (c) Cu^{2+}; (d) Co^{2+}; (e) Ni^{2+}; (f) Mn^{2+}. (ii) Plot of $\log(F_0/F-1)$ vs. log [Q] in different media with Ni^{2+} as quencher at 300 K: (a) aqueous; (b) PEG 200; (c) PEG 300; (d) PEG 400; (e) PEG 600.

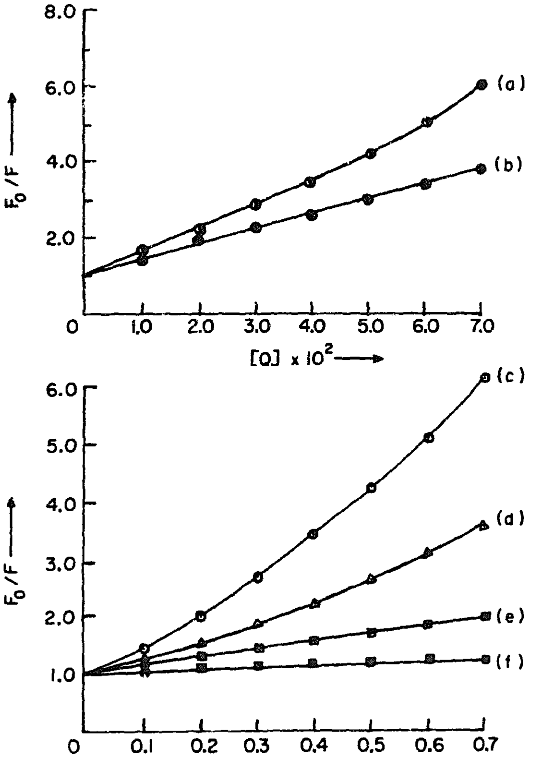

Fig. 3. Plot of F_0/F vs. [Q] according to Eq. (2) in PEG 300 medium: (a) $[Fe(CN)_6]^{3-}$; (b) $[Fe(CN)_6]^{4-}$; (c) Cu^{2+}; (d) Co^{2+}; (e) Ni^{2+}; (f) Mn^{2+}.

ment. In aqueous PEG medium, plots of $\log(F_0/F-1)$ vs. log [Q] are linear (Fig. 2, (i) and (ii)), but all the slopes (Table 1) are not equal to unity. The rate constants (k_q) of quencher–ST interaction have been calculated from the relationship, $K_{sv}=k_q\tau_0$, where τ_0 is the singlet state lifetime of ST. The k_q values are lower in PEG medium than in aqueous medium. $[Fe(CN)_6]^{3-}$ acts as a strong quencher and Mn^{2+} acts as a weak quencher. The trend of the quenching efficiency of the different quenchers is the same in aqueous as well as in PEG medium. However, the quenching process is hindered in PEG medium. The k_q value decreases with increasing molar mass of PEG.

The quencher ions have no effect on the absorption spectrum of ST in aqueous and PEG media. The hexa-aquo cobalt(II) ion exhibits a weak maximum at 510 nm which overlaps with the absorption band of ST. The absorption spectrum of ST does not change with the addition of Co^{2+}; thus they do not undergo interaction in the ground state.

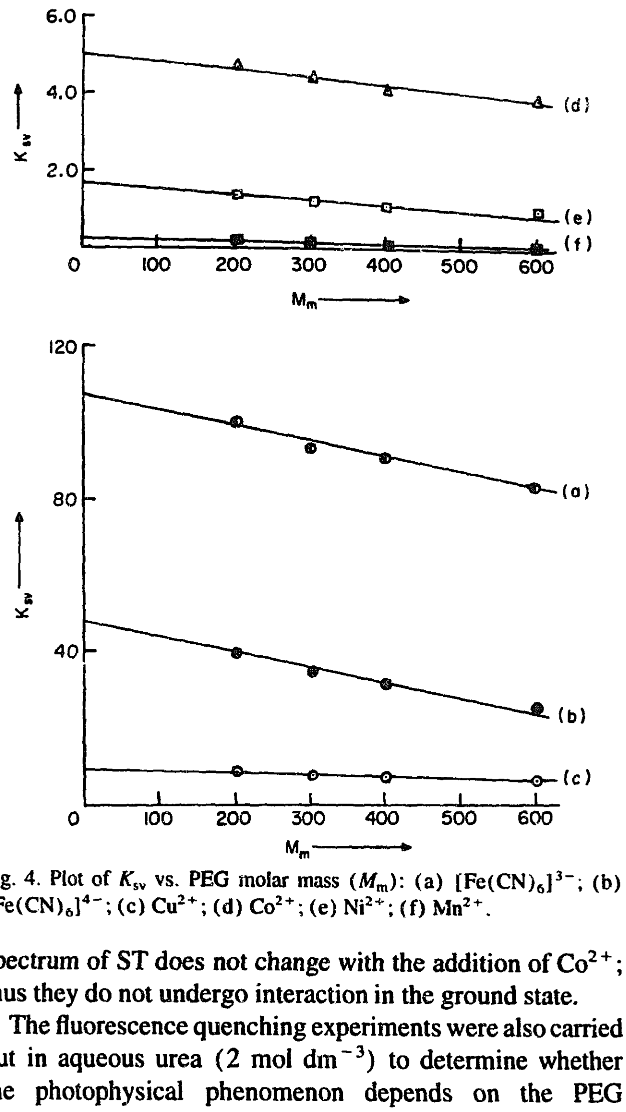

Fig. 4. Plot of K_{sv} vs. PEG molar mass (M_m): (a) $[Fe(CN)_6]^{3-}$; (b) $[Fe(CN)_6]^{4-}$; (c) Cu^{2+}; (d) Co^{2+}; (e) Ni^{2+}; (f) Mn^{2+}.

The fluorescence quenching experiments were also carried out in aqueous urea (2 mol dm^{-3}) to determine whether the photophysical phenomenon depends on the PEG configuration.

4. Discussion

The inorganic ions quench the fluorescence of ST in both aqueous and aqueous PEG media following the trend $[Fe(CN)_6]^{3-}$ > $[Fe(CN)_6]^{4-}$ > Cu^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+}. The quenching interaction was assessed in the light

Table 1
K_{sv} and slopes of Eq. (1) for the quenching process between inorganic ions and ST in aqueous PEG medium at 300 K

Quencher ion	Aqueous	PEG [a] 200	PEG [a] 300	PEG [a] 400	PEG [a] 600
$[Fe(CN)_6]^{3-}$	107.20 (1.25)	100.0 (1.17)	93.32 (1.10)	91.20 (1.10)	83.12 (1.09)
$[Fe(CN)_6]^{4-}$	47.86 (1.10)	39.8 (1.10)	34.67 (0.93)	31.62 (0.9)	25.12 (0.9)
Cu^{2+}	9.77 (1.35)	8.51 (1.33)	7.94 (1.29)	7.69 (1.25)	6.76 (1.22)
Co^{2+}	5.01 (2.0)	4.78 (1.2)	4.42 (1.45)	4.17 (1.2)	3.89 (1.0)
Ni^{2+}	2.0 (0.9)	1.40 (1.2)	1.35 (1.0)	1.12 (1.0)	1.02 (1.0)
Mn^{2+}	0.48 (2.5)	0.22 (2.3)	0.17 (0.37)	0.08 (2.25)	0.01 (0.80)

[a] [PEG] = 0.1 mol dm^{-3}.

[b] Slopes are given in parentheses.

Table 2
Viscosity coefficients of different PEG media at 300 K, slopes (α), intercept values of Eq. (3), $[(K_{sv})_{Aq}-(K_{sv})_{PEG}]/(CH_2\text{–}CH_2\text{–}O)_n=P$ for different quencher ions at 300 K and Stokes radius (r) of the quencher ions

Medium	Viscosity η (cP)	Quencher ion	Slope × 10^4	Intercept	P	r (Å)
Aqueous	0.798	$[Fe(CN)_6]^{3-}$	400.0	107.0	1.78	4.44
PEG 200	0.949	$[Fe(CN)_6]^{4-}$	333.0	48.0	1.79	4.02
PEG 300	1.053	Cu^{2+}	66.7	9.5	0.25	3.89
PEG 400	1.082	Co^{2+}	18.0	5.0	0.08	4.07
PEG 600	1.210	Ni^{2+}	15.4	1.7	0.10	3.99
		Mn^{2+}	4.0	0.25	0.045	4.22

of the Stern–Volmer equation (Eq. (1)). The slopes of Eq. (1) are unity for $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$ and Ni^{2+}. For the rest of the quencher ions, the values mostly deviate from unity. This deviation is supported by duplicate experiments. For all the quencher ions, the K_{sv} values decrease with the molar mass (M_m) of PEG. The K_{sv}–M_m profiles show a linear dependence (Fig. 4) obeying the relation

$$(K_{sv})_{PEG}=(K_{sv})_{Aq}-\alpha M_m \qquad (3)$$

The α (slope) values of Eq. (3) are presented in Table 2; they vary in the same sequence as the order of the quenching efficiencies of the inorganic ions. A one hundredfold decrease in magnitude between $[Fe(CN)_6]^{3-}$ and Mn^{2+} has been observed. The strength of the quencher–ST interaction per unit molar mass of the polyoxyethylene group, $-(CH_2\text{–}CH_2\text{–}O)-$, falls into two categories; Co^{2+}, Ni^{2+} and Mn^{2+} interact weakly compared with the other ions.

The $[(K_{sv})_{Aq}-(K_{sv})_{PEG}]/(CH_2\text{–}CH_2\text{–}O)_n$ ratios (P) (where n stands for the number of repeat units (oxyethylene moiety)) for the different PEGs show more or less constant values (with a slight decreasing trend with increasing M_m of PEG). The averages for the quencher ions are given in Table 2. The sequence is not as straightforward as for K_{sv} (Table 1). $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ show equivalent activities; the other ions follow the trend $Cu^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$.

The quencher ions $[Fe(CN)_6]^{3-}$, Cu^{2+} and Ni^{2+} are in their maximum oxidation states. Their quenching activities are comparable with the other ions in their lower oxidation states. Therefore the process does not involve electron transfer between the quencher ion and ST. The trend of the quenching efficiencies of the ions is the same in both aqueous and aqueous PEG media. The phenomenon is considered to involve collisional quenching, as recently reported for aqueous micellar medium comprising non-ionic surfactants with polyoxyethylene groups [16].

The varying fluorescence quenching behaviour of ST in different PEG media may be related to the molecular configuration of the polymers and/or the medium viscosity. It is possible that, with an increase in the molar mass, the PEG molecules may undergo segmental folding trapping ST molecules and making them inaccessible to the quencher. Unfolding caused by a chemical agent such as urea (a hydrogen bond breaker and hydrophobic interaction weakener) may thus affect (increase) the quenching to alter the Stern–Volmer constant K_{sv}. However, measurements taken in 2 mol dm^{-3} aqueous urea medium yield the same quantitative information as those without urea. Therefore it can be concluded that the molecular configuration of PEG does not influence the fluorescence quenching process. The observed differences in the photophysical behaviour in the different PEG media may originate from the hydrodynamic (viscous) condition of the medium. At constant concentration, the viscosity coefficient (η) of the aqueous PEG medium increases with the molar mass of the polymer. For all the quencher ions, the K_{sv} values vary inversely and linearly with η (Fig. 5). The slopes of the lines and the viscosity coefficients at 300 K are presented in Table 2. The results indicate that, in all probability, the hydrodynamic condition of the PEG medium is

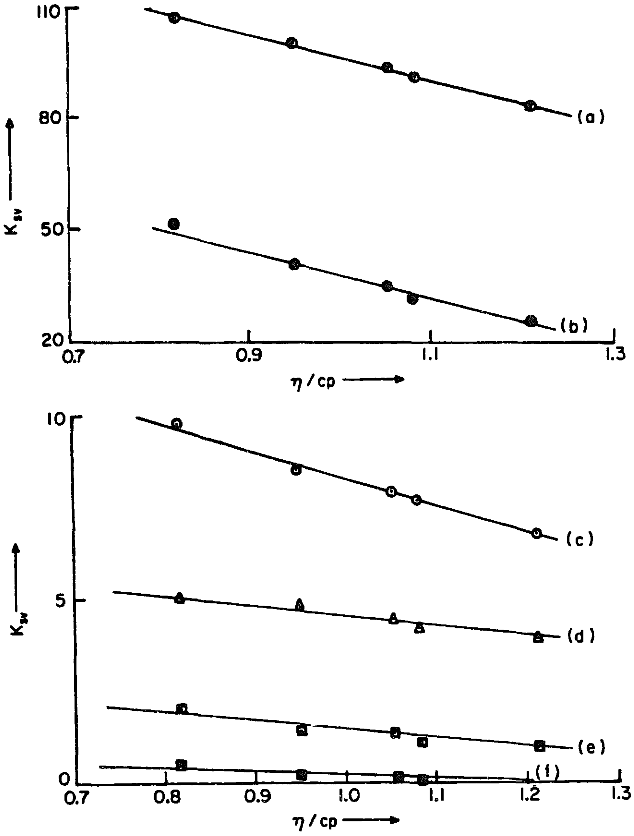

Fig. 5. Dependence of K_{sv} on η: (a) $[Fe(CN)_6]^{3-}$; (b) $[Fe(CN)_6]^{4-}$; (c) Cu^{2+}; (d) Co^{2+}; (e) Ni^{2+}; (f) Mn^{2+}.

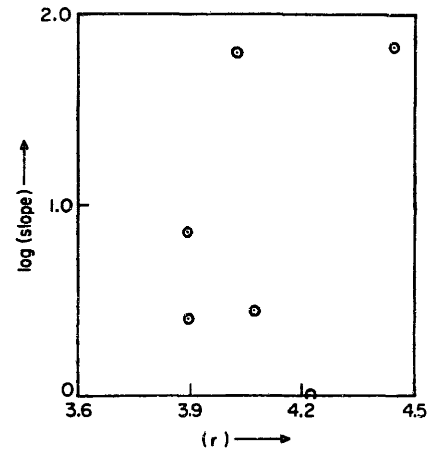

Fig. 6. Plot of the logarithm of the slopes of the K_{sv}–η lines vs. the Stokes radius (r) of the ions.

responsible for the altered fluorescence quenching of ST by the inorganic ions. The slopes follow the quenching efficiency order of the inorganic ions. The dependence of the slope on the type of ion may be ascribed to the hydrodynamic (or Stokes) radius. A higher Stokes radius leads to a lower diffusion of the ion and a reduced interaction with ST for quenching. The logarithm of the slopes of the K_{sv}–η lines is plotted vs. the Stokes radius of the ions in Fig. 6. An increasing trend of K_{sv} is observed with significant scatter. An overall hydrodynamic radius-dependent ionic quenching of ST fluorescence is envisaged.

5. Conclusions

1. The inorganic ions $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, Cu^{2+}, Co^{2+}, Ni^{2+} and Mn^{2+} quench the fluorescence of ST in aqueous PEG medium with decreasing efficiency.
2. The quencher ion-related Stern–Volmer constants (K_{sv}) at constant [PEG] follow the order $[Fe(CN)_6]^{3-} > [Fe(CN)_6]^{4-} > Cu^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+}$. For all the ions, K_{sv} decreases with increasing molar mass of PEG.
3. The phenomenon of collisional quenching is operative in the systems studied and is influenced by the viscosity of the medium.

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