Time-resolved fluorescence spectroscopy of quinine dication free and bound to polymethacrylic acid

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Abstract

The fluorescence decay and quenching by halides of quinine dication (QS) and derivatives in hydrogenated form (QSH) and bound to polymethacrylic acid in aqueous solution at low pH are investigated by time-resolved and steady-state fluorescence measurements. QS and QSH have very similar bi-exponential decay surfaces indicating that the peripherical double bond of the quinuclidine group play no role in the excited state deactivation. Experiments with the free probe in water/ethylene glycol solvent mixtures show that the QS fluorescence decay depends strongly on the solvent viscosity. Solvent friction and polarization drive the interconversion rate between different conformers in excited state. When QS is bound to a compact polymer coil, the decay becomes three-exponential, and an additional lifetime component of about 10 ns is recovered. This decay component is ascribed to a fraction of the probe placed on a high local viscous medium.

The quenching process by halides follows the efficiency series $I^- > Br^- > Cl^-$ in all cases investigated. The quenching rate constants are higher for QS than for QSH or QS bound to polymer. In the case of iodide, there is a static quenching contribution which may be ascribed to a weak association between probe and quencher. The average free energy change in the association process is of the order of 2.5 kcal/mol. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Time-resolved fluorescence spectroscopy; Quinine; Polymethacrylic acid

1. Introduction

The photophysics of the fluorescence standard quinine sulfate has been the subject of several experimental investigations in time-resolved emission spectroscopy due to its more complex decay kinetics than a single exponential relaxation. The first evidence of a bi-exponential decay of the dication in water was reported by O'Connor et al. [1] by pulse decay measurements and later confirmed by Barrow and Lentz [2] using phase and modulation method. These results have promoted further experimental investigations by Pant and coworkers using quinine and its derivatives in several different conditions where solvent polarity and viscosity, protonation degree of the fluorophore, temperature, excitation and emission wavelength were changed [3–8]. For quinine dication, the bi-exponential behavior was ascribed to an interplay between two different emitting states formed by an intramolecular charge transfer from the 6-methoxy group to the quinoline ring upon excitation [7,8]. This process leads to changes in the charge distribu-

tion density and geometry of the fluorophore which combined with solvent relaxation gives a multi-exponential decay behavior.
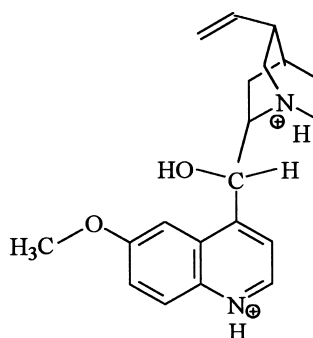
Quinine dication

Thus, solvent viscosity and polarity affect dramatically the fluorescence decay kinetics of quinine dication, since those factors drive the interconversion rate between the two main conformers in the excited state [8].

The quenching of the quinine dication by iodide, bromide and chloride has been reported [9–13]. This process has been

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explored for designing fluorescence optical sensors for halides [14], where in some situations the probe is loading in membranes or in sol–gel systems [15]. This fact may demand a more specific analysis of the photophysics behavior of the fluorophore in microheterogeneous systems or in high viscous media owing to its intrinsic multi-exponential decay in homogeneous acidic aqueous solution.

The photophysics of quinine (QS), hydrogenated quinine (QSH) and quinine dications bound to polymethacrylic acid (QS-MAA) in low pH aqueous solutions, and the quenching by halides are studied by time-resolved and steady-state fluorescence measurements. The effect of local solvent viscosity in QS-MAA system in the fluorescence decay kinetics due to the polymer coiling around the probe is compared to experimental data of free quinine dication in water/ethylene glycol solvent mixtures.

its vinyl group, and this clue was derived from the fluorescence intensity of the copolymer sample with respect to the optical density.

In a second procedure, a derivative quinine containing a styrene pendant group (QS-STY) was synthesized (see scheme 1). Dried QS (0.5 g) in dry dioxane was treated with NaH in inert N_2 atmosphere to form the respective alcoxide, followed by direct reaction with p-chloromethyl-styrene. The reaction course was accompanied by thin layer chromatography. The reaction mixture was cooled, and a small amount of saturated NaCl aqueous solution was added. The system was dried over anhydrous magnesium sulfate, and the liquid phase was separated. After evaporation of the solvent and the residual monomer under reduced pressure, the final product was recrystallized from methanol.
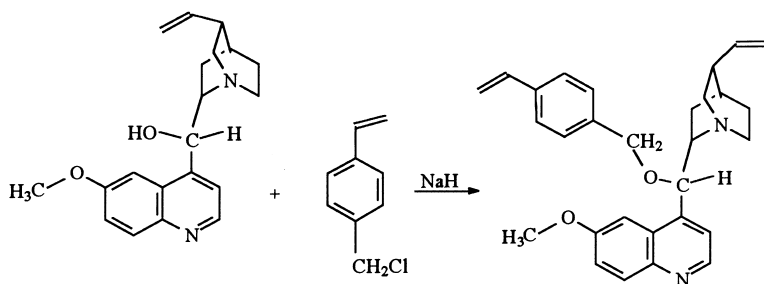
2. Experimental

Quinine sulfate (Fluka, 99%, D) was used without further purification. MAA was distilled prior to polymerization to remove the inhibitor. All other chemicals like solvents and sodium halides were of the analytical grade. QSH was prepared by catalytic hydrogenation of QS in methanol using 10% palladium on activated carbon powder (product 807104 from Merck-Schuchardt) under a hydrogen atmosphere at room temperature [16]. Later, the catalyst was removed by filtration through Celite and the solvent was evaporated under reduced pressure. The yield of the product was higher than 95%, and it was purified by recrystallization from methanol. The ^1H NMR analyze of the product in $CDCl_3$ confirmed the absence of vinyl protons when compared with the spectrum of starting material.

Quinine sulfate bound to polymethacrylic acid was obtained in two different forms. In the first one, direct copolymerization of QS dissolved in MAA using benzoyl peroxide as the thermal initiator was performed using deoxygenated sample heated at 60°C. The copolymer was recrystallized from methanol. A concentrated aqueous solution was prepared and later submitted to dialysis in the presence of aqueous sodium sulfate using a membrane for molar masses between 12 000 and 14 000 d. This procedure was repeated several times in order to remove the free QS and MAA which did not react. The copolymer formed had a small amount of bound QS due to the low reactivity rate of

The QS-STY was copolymerized with MAA in a molar ratio of 10^{-3} using the same procedure as described later for QS. The formed copolymer (QS-STY-MAA) was also submitted to recrystallization from methanol followed by dialysis.

Absorption measurements were performed on a Hitachi U-2000 spectrophotometer. Corrected steady-state fluorescence spectra were recorded on a CD-900 Edinburgh spectrofluorimeter. Fluorescence decay were measured by single-photon counting technique using a CD-900 spectrometer operating with a hydrogen filled ns flash lamp at 30 kHz pulse frequency. The FWHM of the instrument response obtained from pulse scattering was of the order of 1.5 ns. Multi-exponential decay analysis in single curve as well as in global method (surface decay analysis) were performed by a non-linear least-squares iterative reconvolution analysis routine based on Marquardt algorithm. The software for data analysis was supplied by Edinburgh Instruments. For measurements, samples in a 1×1 cm quartz cuvette were thermostatted by circulating fluid through a jacketed cuvette-holder at 298 K, in air equilibrated condition. In all aqueous samples, H_2SO_4 was added corresponding to a 0.5 molar final concentration which leads to complete formation of quinine dication in solution. In the quenching experiments by halides, fresh stock concentrated solution of the corresponding sodium salt was added in small amounts via a microsyringe to the cuvette containing 3 ml of quinine solution at a concentration of about 2×10^{-5} M. The viscosity of the water/ethylene glycol solvent mixtures at

Table 1
Lifetimes and normalized pre-exponential factors from bi-exponential global fitting with one linked components (τ_2) of QS and QSH in 1 N H_2SO_4 aqueous solution at 298 K

QS, $\tau_2=18.8\pm0.3$ ($\chi_g^2=1.12$)			QSH, $\tau_2=18.9\pm0.3$ ($\chi_g^2=1.24$)	
λ_{em} (nm)	τ_1	$\tilde{b}_1$	τ_1	$\tilde{b}_1$
400	4.1	0.32	3.3	0.36
410	4.6	0.25	4.2	0.28
420	4.8	0.19	4.3	0.22
430	4.8	0.15	4.7	0.16
440	5.2	0.11	4.7	0.11
450	5.1	0.07	5.3	0.07

Excitation wavelength of 340 nm. $\tilde{b}_1 + \tilde{b}_2=1$.

298 K were determined relative to the viscosity of pure water using a capillary viscometer (VB2 Lauda).

3. Results and discussion

3.1. Quinine and hydrogenated quinine dications in aqueous solution

The fluorescence decay surface of both QS and QSH allows a global bi-exponential analysis where the longer lifetime is linked over different curves while the short component is a local parameter which depends on the emission wavelength. Table 1 gives the lifetimes and their normalized amplitudes as a function of the observed emission wavelength. In general, shorter lifetime is observed in the lowest wavelength, and the weight of τ_1 decreases as the emission wavelength increases. On the other hand, the lifetimes of QS and QSH are practically the same if one

takes into account the standard deviations of the measurements. This means that the double bond attached to the quinuclidine group does not affect the deactivation photophysics of the methoxyquinoline chromophore in its singled excited state. The emission spectrum of QS and QSH are very similar, but the absorption spectrum has a small difference since the L_a band of the hydrogenated derivative has a lower extinction coefficient than standard QS in acidic aqueous solution (see Fig. 1).

3.2. Solvent viscosity effect

Decay surfaces of free quinine dication in water/ethylene glycol solvent mixtures were measured and analyzed. Table 2 gives the lifetimes and normalized amplitudes of the decay traces at 420 nm emission wavelength as a function of the solvent viscosity. The lifetime τ_2 remains practically constant but the short component τ_1 is highly dependent on viscosity. Similar behavior was reported by
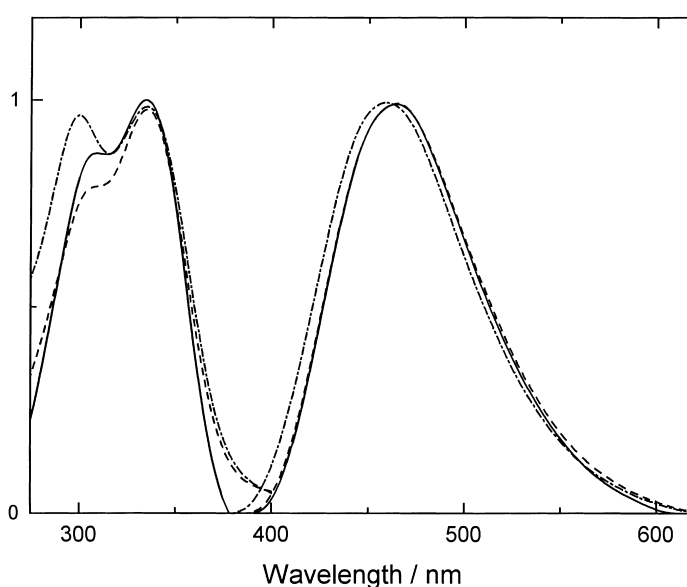

Fig. 1. Absorption and emission spectra of QS (———), QSH (—— ——), QS-MAA (– • –) in 1 N H_2SO_4 aqueous solution at 298 K. $\lambda_{ex}=340$ nm.

Table 2
Variation of QS fluorescence lifetimes at 420 nm as a function of water/ethylene glycol solvent mixtures at 298 K

(%) Ethylene glycol	η (cP)	τ_1 (± 0.5) (ns)	τ_2 (± 0.2) (ns)[a]
20	1.35	5.6	19.5
40	2.25	7.2	19.2
60	3.85	8.7	19.0
80	7.00	9.4	18.8
90	9.61	11.1	19.1

[a] Linked parameter.

Pant and coworkers in a study of QS dication in a series of alcohols. Fig. 2 shows the plot of $1/\tau_1$ as a function of the inverse of viscosity. The linear behavior allows to analyze the result using the simple Stokes–Einstein equation

$$\tau^{-1} = \left(\frac{kT}{V}\right)\eta^{-1}, \tag{1}$$

where V is the hydrodynamic molecular volume. Using Eq. (1), $kT/V=0.13\pm0.01$ cP/ns is obtained. This value at 298 K corresponds to a $V=290$ Å^3. In the approach of a spherical shape, the molecular radius subject to a reorientation under a solvent friction is about 4 Å. The value calculated has the magnitude of the molecular dimension of the 6-methoxy-quinoline group. Thus it suggests that changes in fluorophore conformation and solvation shell is associated to a torsional relaxation of the quinoline group probably around the carbon of the chiral center. In polar protic solvent, specially in water, there is a possibility of a solvent bridge via hydrogen bonding between the oxygen of the 6-methoxy and that of the hydroxyl group of the chiral carbon.

3.3. Quinine bound to polymethacrylic acid

The decay kinetics of quinine bound to MAA has a behavior slightly more complex than that of free QS in aqueous acidic solution. In both QS bound MAA systems, good fitting in global multi-exponential analysis were obtained only considering the decay as a three-exponential function. Table 3 gives the lifetimes and respective normalized amplitudes in global analysis with two linked components. Two recovered lifetimes, one short- and the other long-lived, as in the case of free QS in aqueous homogeneous phase, are still present, but a new component with lifetime in between the extremes appears in a comparable percent. Fig. 3 gives a decay trace at 430 nm emission wavelength obtained in global three-exponential analysis.

If one considers the polymer environment as a micro-heterogeneous system, fluctuations in polarity and viscosity in the site of the quinine fluorophore will account for the behavior observed in the decay kinetics. Nevertheless, this change may be analyzed considering essentially a viscosity effect, and comparing it with the previous data of free quinine dication in water/ethylene glycol solvent mixtures. In the limit of a high viscous medium, from the data in Fig. 2, τ^{-1} converges to 0.082 ns^{-1} which corresponds to limiting lifetime of 12.2 ns. This result indicates that the recovered third lifetime of 9.4$\pm$1.6 ns in QS-STY-MAA and of 11.7$\pm$1.9 ns in the QS-MAA could be related to a fraction of the QS probe trapped in a site of high viscosity, bear in mind that polymethacrylic acid in water at low pH has a compact coil structure due to the low dissociation degree of the carboxylic acid groups. The presence of inhomogeneous lifetime when a fluorescent probe is confined into a compact
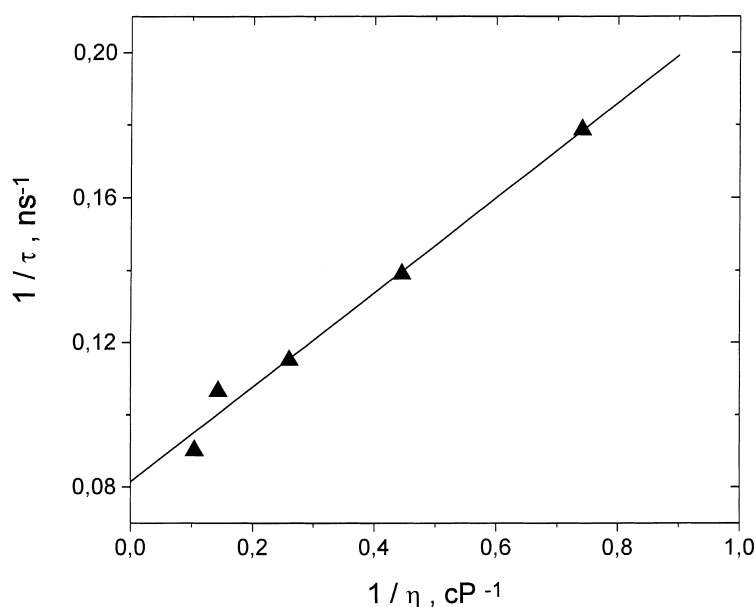

Fig. 2. Plot of the inverse of the lifetimes as a function of the inverse of the viscosity of water/ethylene glycol solvent mixtures at 298 K. Data from Table 2.

Table 3
Lifetimes and normalized pre-exponential factors from three-exponential global fitting with two linked components (τ_2 and τ_3) of QS-MAA and QS-STY-MAA in 1 N H_2SO_4 aqueous solution at 298 K

λ_{em} (nm)	QS-MAA, τ_2=10.4 ns, τ_3=19.8 ns, (χ_g^2=1.13)			QS-STY-MAA, τ_2=9.4 ns, τ_3=21.9 ns, (χ_g^2=1.02)		
	τ_1	$\tilde{b}_1$	$\tilde{b}_2$	τ_1	$\tilde{b}_1$	$\tilde{b}_2$
400	1.1	0.46	0.32	2.1	0.37	0.52
410	1.2	0.36	0.32	2.3	0.28	0.54
420	1.0	0.33	0.28	2.2	0.23	0.53
430	1.1	0.25	0.27	2.4	0.19	0.50
440	1.1	0.20	0.24	2.4	0.17	0.46
450	0.8	0.20	0.22	2.4	0.16	0.42
460	1.0	0.10	0.20	3.4	0.18	0.35
470	0.6	0.12	0.17	3.3	0.18	0.35

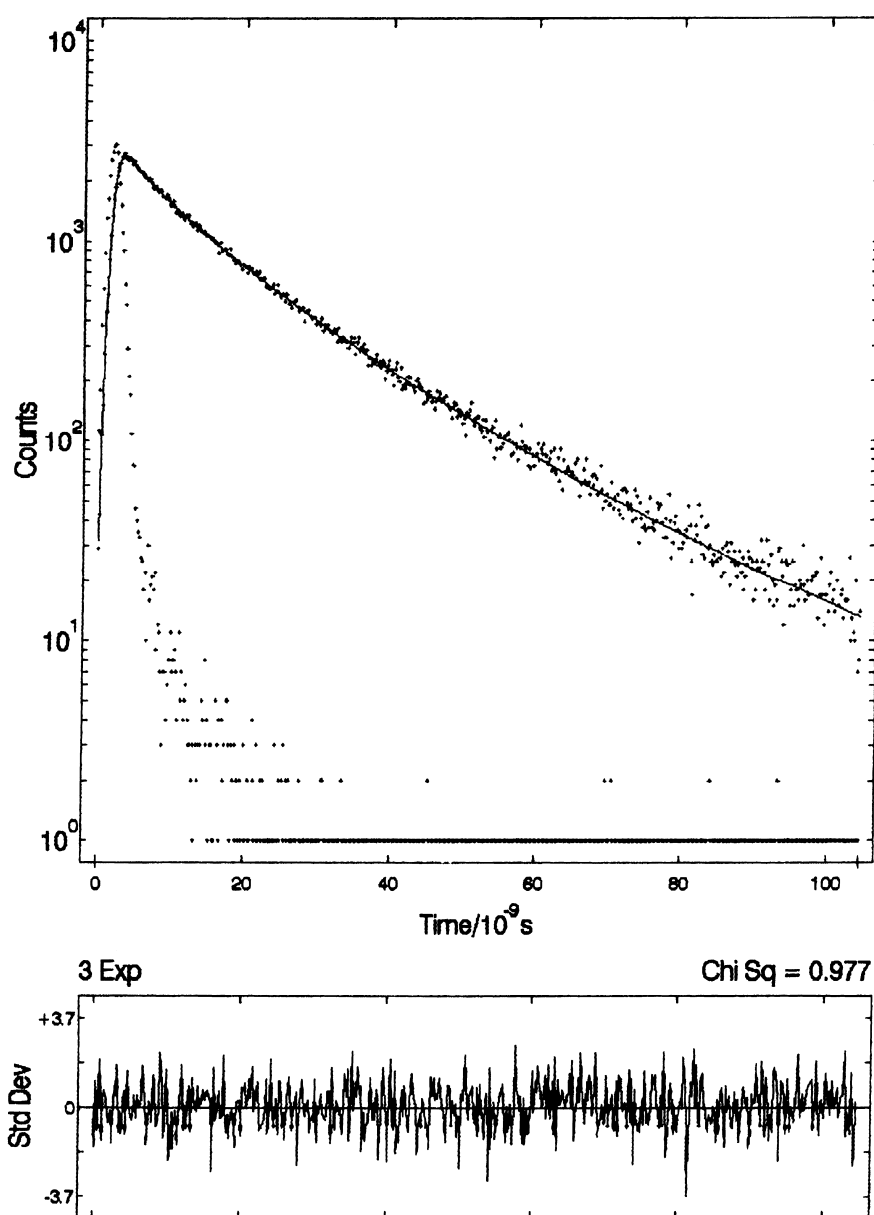Excitation wavelength of 340 nm. $\tilde{b}_1 + \tilde{b}_2 + \tilde{b}_3 = 1$.

Fig. 3. Decay and fitting of QS bond to polymethacrylic acid (QS-STY-MAA) obtained from global three-exponential analysis, in 1 N H_2SO_4 aqueous solution at 298 K. The lamp pulse profile is also shown. $\lambda_{ex} = 340$ nm; $\lambda_{em} = 430$ nm. Lifetimes: $\tau_1 = 2.4$, $\tau_2 = 9.4$, $\tau_3 = 21.9$ ns. See Table 3 for more details.
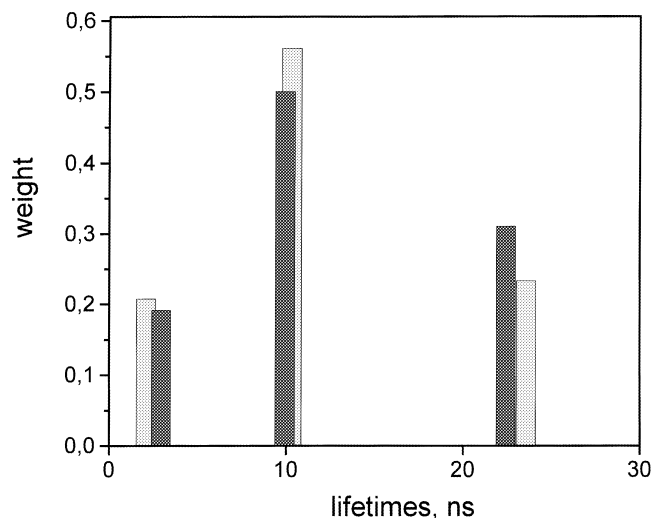
Fig. 4. Lifetimes and amplitudes of the fluorescence decay of QS bond to polymethahcrylic acid (QS-STY-MAA) from global three-exponential (▓) and distribution analysis (▒).

Table 4
Absorption and emission maxima of quinine derivatives in 1 N H$_2$SO$_4$ aqueous solution at 298 K

Compound	λ_{abs} (L_a band) (nm)	λ_{abs} (L_b band) (nm)	λ_{em} (nm)
QS	309	334	464
QSH	309	335	464
QS-MAA	300	335	459
QS-STY	312	339	445
QS-STY-MAA	310	335	431

polymer chain structure is a common effect very often observed in many systems.

On the other hand, the data obtained allows a distribution analysis in order to investigate whether there is a discrete or a continuous lifetime distribution, where the later could be ascribed to the presence of a large number of conformers in the polymer environment. The decay in Fig. 3 was analyzed considering a lifetime distribution with 20 components spread over the range 0.3–50 ns. The result obtained in this single curve analysis method is practically the same as that from global analysis with three-exponential decay function. The lifetimes and respective normalized amplitudes recovered using the two methods are plotted in Fig. 4.

In the QS bound to MAA systems in 1 N sulfuric acid aqueous solution, the three-exponential decay cannot be related to the presence of a monoprotonated form of QS. The absorption and emission spectra of QS monocation has a strong hypsochromic shift compared to the dication species (the deviation of the band maximum is of the order of 25 nm in absorption and 60 nm in emission) following the data from Pant et al. In our case, QS bound to MAA in 1 N H$_2$SO$_4$ aqueous solution has emission and absorption spectra similar to that of free precursor QS dication, as can be seen in Fig. 1. The values of the absorption and emission maximum are reported in Table 4, and Fig. 1 illustrates some of the

absorption and emission spectra of the compounds. The blue shift of the emission band of QS bound to polymethacrylic acid is in agreement with the percent of the short life components, and also reflects the location of a fraction of the probe in a high viscous medium.

In a further experiment, the free QS probe was incorporated into a nafion membrane in its acid form. The nafion membrane is an amphiphile membrane capable of adsorbing cationic dyes [17]. The decay surface was analyzed as before, and the three components recovered were 3.4, 11.2 and 22.4 ns. Again we see in a high viscous medium an intermediary lifetime component as in the case of QS bound to MAA.

3.4. The quenching by halides

The fluorescence quenching of quinine dication by halides have been reported early [9–13]. Quenching rate constants reveals that efficiency follows the series Cl$^-$<Br$^-$<I$^-$. For iodide quencher, the process may involve not only heavy atom effect over the singlet excited state leading to S$_1$–T$_1$ intersystem crossing, but also there is a possibility of a charge-transfer mechanism. Also for iodide the Stern–Volmer plot of the relative intensity is non-linear with an upper curvature which may indicate the presence of a "static quenching" coupled with a diffusion transient effect [18]. Table 5 gives the quenching rate constant k_q of QS, QSH, and of QS bound to polymer at 298 K 1 N sulfuric acid aqueous solution, obtained from time-resolved measurements. In order to calculate the average quenching rate constant from the slope of ratio of lifetimes or relative intensity as a function of halide concentration, we have assumed an average lifetime, which was calculated from the lifetimes τ_i and normalized amplitudes b_i recovered from the

Table 5
Stern–Volmer constants and average quenching rate constant of quinine derivatives by halides obtained from time-resolved quenching data at 450 nm emission wavelength and 298 K

Halide	QS $\langle\tau_0\rangle$=18.5 ns		QSH $\langle\tau_0\rangle$=18.6 ns		QS-MAA $\langle\tau_0\rangle$=18.0 ns	
Cl$^-$	191.2	1.0×10^{10}	98.4	5.3×10^{9}	84.6	4.7×10^{9}
Br$^-$	222.6	1.2×10^{10}	136.7	7.3×10^{9}	146.0	8.1×10^{9}
I$^-$	289.7	1.6×10^{10}	194.7	1.0×10^{10}	185.9	1.0×10^{10}

Average lifetime in the absence of added quencher, $\langle\tau_0\rangle$, is calculated from Eq. (2). Quenching rate constants are in M^{-1} s^{-1}.
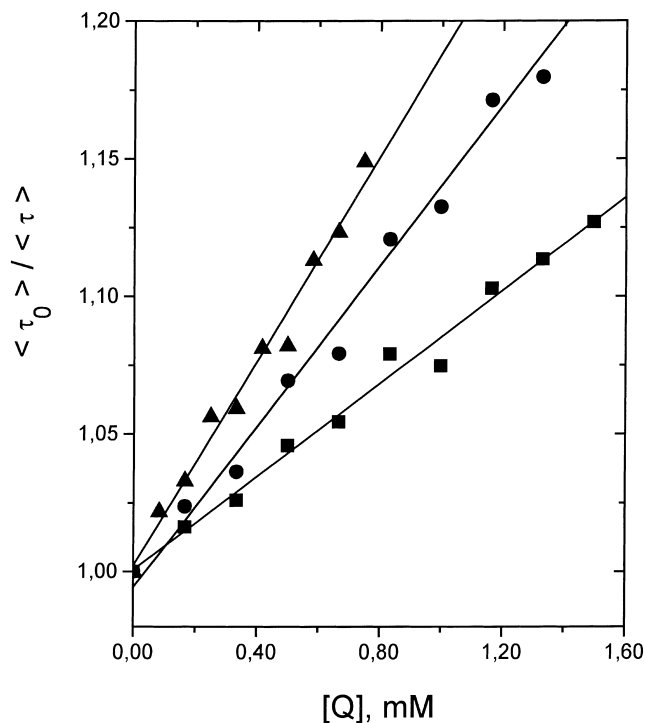
Fig. 5. Stern–Volmer plot of the ratio of the average lifetime in the absence and presence of halides for the system QS-MAA in 1 N H$_2$SO$_4$ aqueous solution at 298 K. (■) Chloride; (●) bromide; (▲) iodide.
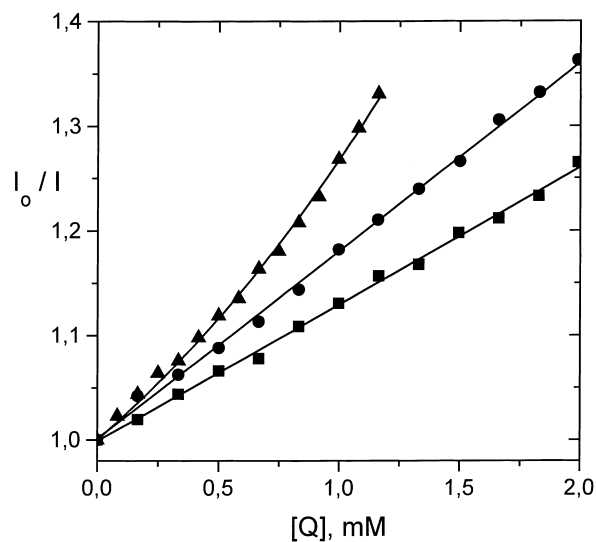

Fig. 6. Relative fluorescence intensity of QS-MAA quenched by halides in 1 N H$_2$SO$_4$ aqueous solution at 298 K. (■) Chloride; (●) bromide; (▲) iodide.

multi-exponential decay analysis, i.e.,

$$\langle \tau \rangle = \frac{\sum_i b_i \tau_i^2}{\sum_i b_i \tau_i}. \tag{2}$$

This approximation to an average quenching rate constant allows a more simple comparison between the quenching efficiency in different systems. Fig. 5 illustrates the Stern–Volmer plot of the ratio of average lifetimes for QS-MAA system quenched by halides. For the free probe in solution, it can be seen that the quenching rate constants in the case of QSH are smaller (about 50% less) than those calculated for QS. This result shows that despite no changes in lifetimes, the two compounds behave slightly different with respect to quenching process by halides.

The Stern–Volmer plots of the relative intensity are linear for Cl$^-$ and Br$^-$ for both QS bound to polymer systems in the lifetime plot and in relative intensity plot as well. A non-linear behavior occurs only in the relative intensity plot of QS-MAA quenched by I$^-$. Fig. 6 shows the plot of the relative fluorescence intensity of QS-MAA system quenched by halides. Table 6 reports the Stern–Volmer constants for all systems investigated.

The quenching rate constants are in general smaller in QS bound to polymer system than those values observed for free QS dication. The larger difference occurs in the quenching of QS-STY-MAA by chloride where K_{SV} is 1 order of magnitude lower than those found for Br$^-$ and I$^-$. This may reflect the less affinity of the Cl$^-$ ion to the polymer/

water environment which could reduce its local concentration around the polymer bound fluorophore.

The non-linear Stern–Volmer plots were analyzed considering a static quenching contribution, i.e., the relative intensity is considered as a product of the dynamic $(1+K_{sv}[Q])$ and static $(1+K_c[Q])$ contributions, where K_c is the association constant between the fluorophore and iodide. K_{sv} values are taken from the time-resolved data. The K_c values are given in Table 7. For QS we have a larger K_c value, while for QSH and QS-MAA it is three and four times less, respectively. The free energy corresponds to something of -3.2 kcal/mol for QS/I$^-$ association while

Table 6
Stern–Volmer constants from steady-state fluorescence quenching measurement of quinine derivatives by halides in 1 N H$_2$SO$_4$ aqueous solution at 298 K

Halide	K_{sv} (M^{-1})			
	QS	QSH	QS-MAA	QS-STY-MAA
Cl-	169.8	104.0	103.0	10.0
Br-	326.4	159.5	179.6	96.0
I-	a	a	a	157.0

Excitation wavelength of 340 nm.
[a] Non-linear plot, see Table 7 for association constants.

Table 7
Association constant K_c of quinine derivatives with iodide in 1 N H$_2$SO$_4$ aqueous solution at 298 K

Compound	K_c (M^{-1})	ΔG^0 (kcal/mol)
QS	228	3.2
QSH	64	2.5
QS-MAA	49	2.3

for the two other compounds, there is an increase of about 1 kcal/mol. This difference may be ascribed to the contribution of a more favored electronic and steric interaction between the ion I$^-$ and the quinine dication containing the edged double bond in the quinuclidine group (see scheme 1). A partial charge transfer influenced by the vinyl group would explain the higher k_q and K_c values found in the case of QS quenching by iodide.

4. Conclusions

The photophysics of quinine dication (QS) and derivatives in hydrogenated form (QSH) and bound to polymethacrylic acid (QS-MAA and QS-STY-MAA) in aqueous solution at low pH has been investigated by time-resolved and steady-state fluorescence measurements. The decay constants of QS and QSH dications obtained from bi-exponential fitting are very similar, showing the peripherical double bond of the quinuclidine group play no role in the excited state deactivation. The fluorescence decay process of the QS probe depends strongly on the solvent viscosity. Solvent friction and polarization seem to drive the interconversion rate between different conformers in excited state. In a compact polymer coil as in the situation of polymethacrylic acid at low pH, a fraction of the probe bound to the chain is placed on a high local viscous media, and the decay observed becomes three-exponential with an additional lifetime component of about 10 ns.

The quenching process by halides follows the efficiency series I$^-$>Br$^-$>Cl$^-$ in all cases investigated. The quenching rate constants are higher for QS than for the hydrogenated form or QS bound to polymer. In the case of iodide, there is a static quenching contribution which may be ascribed to a weak association between probe and quencher. The results obtained here are meaningful for future applications of quinine derivatives or other related fluorophores bond to polymers to halide fluorescence sensor research.

References

[1] D.V. O'Connor, S.R. Meech, D. Phillips, Chem. Phys. Lett. 88 (1982) 22.
[2] S.R. Meech, D. Phillips, J. Photochem. 23 (1983) 193.
[3] D.A. Barrow, B.R. Lentz, J. Biochem. Biophys. Meth. 7 (1983) 217.
[4] D. Pant, U.C. Tripathi, G.C. Joshi, H.B. Tripathi, D.D. Pant, J. Photochem. Photobiol. A 51 (1990) 313.
[5] D. Pant, H.B. Tripathi, D.D. Pant, J. Photochem. Photobiol. A 56 (1991) 207.
[6] D. Pant, H.B. Tripathi, D.D. Pant, J. Lumin. 50 (1991) 249.
[7] D. Pant, H.B. Tripathi, D.D. Pant, J. Lumin. 51 (1992) 223.
[8] D. Pant, H.B. Tripathi, D.D. Pant, J. Photochem. Photobiol. A 75 (1993) 137.
[9] D. Pant, H.B. Tripathi, D.D. Pand, J. Photochem. Photobiol. A 85 (1995) 33.
[10] R.F. Chen, Anal. Biochem. 57 (1974) 593.
[11] J.E. O'Reilly, J. Chem. Educ. 53 (1976) 191.
[12] D.A. Barrow, B.R. Lentz, Chem. Phys. Lett. 104 (1984) 163.
[13] B. Verity, S.W. Bigger, Int. J. Chem. Kinet. 28 (1996) 919.
[14] A. Martin, R. Narayanaswamy, Sensors & Actuators B 39 (1997) 330.
[15] F.M. Shiu, M.H. Chen, R.F. Tang, J. Non-Cryst. Solids 209 (1997) 61.
[16] M. Hudlický, Reduction in Organic Chemistry, Ellis-Horwood, Chichester, 1984.
[17] S.E. Mazzetto, I.M.M. Carvalho, M.H. Gehlen, J. Lumin. 79 (1998) 47.
[18] J. Keizer, J. Am. Chem. Soc. 105 (1983) 1494.