Journal of Photochemistry and Photobiology A: Chemistry 122 (1999) 185–189

Edge excitation red shift and micro environmental effects on the photophysics of quinine bisulphate dication

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Received 15 August 1998; received in revised form 21 October 1998; accepted 20 January 1999

Abstract

Photophysical properties of quinine bisulphate dication (QSD) in polymer matrices viz. polymethyl methacarylate (PMMA), cellulose acetate (CA), Nafion®-117 and polyvinyl alcohol (PVA) along with a comparative study in fluid media (frozen glass) has been reported. Edge excitation red shift (EERS) is observed in all these media. The magnitude of EERS increases in the frozen glass as compared to liquid phase. The polymers also differ in the magnitude of EERS. The results suggest the presence of the molecule in different geometries in the polymeric media. The photophysical behavior has been found to be sensitive to the micro-environmental polarity and free volume of the matrix. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Quinine bisulphate dication; EERS; Polymer; Fluoresence

1. Introduction

The photophysics of quinine bisulphate dication (QSD) (Fig. 1) in 0.1 N H_2SO_4 solution has been the subject of extensive research in the past because of its medicinal applications as well as its use as a fluorescence standard [1–3]. It was much later that its applicability as lifetime standard was questioned as it does not exhibit a monoexponentail decay [4,5]. It has been found to exhibit a biexponential decay at the shorter wavelength edge and a rising part at the red edge of the emission band.

To explain the nonexponential nature, solvent reorientation relaxation was considered to be the responsible mechanism. Recently, the photophysics of quinine sulphate and related compounds in different solvents and at various temperatures [5–11] has been reported from this laboratory with a view to unraveling some hitherto obscure interactions which again question the unique position occupied by QSD as quantum yield and lifetime fluorescence standard. From the temperature dependence of the fluorescence characteristics, it was suggested that at around 160 K, a rapid charge transfer (CT) from the methoxy group to the quinoline ring takes place followed by solvent reorientation relaxation at ambient temperatures [6] in the polar fluid medium.

In the present work we report anomalies in spectral properties and lifetimes of QSD in fluid and frozen solutions and in different polymer matrices showing inhomogeneous interactions leading to edge excitation red shift (EERS). Since the emission of QSD has been shown to be a CT dependent upon solvent and possibly auxochrome motion, its characteristics in polymers will depend upon the polarity, free volume etc. It can act as a probe for the determination of free volume and micropolarity of the polymer.

2. Experimental

Quinine bisulphate from Aldrich was recrystallised from water. All the solvents were either of spectroscopic grade or were checked for their purity. Polymethyl methacrylate (PMMA) and cellulose acetate (CA) were from Aldrich. Polyvinyl alcohol (PVA) used, was from BDH. Purity was checked by fluorescence run test of the neat polymer film. Nafion® (Aldrich; average weight 1100) was cleaned by first boiling it in nitric acid and then in distilled water for about half an hour. QS in dicationic form was loaded in the Nafion® film from 0.1 N H_2SO_4 (aqueous) solution. Nafion® has a polar head group SO_3H^+ surrounded by the nonpolar or hydrophobic fluorocarbon backbone. The chemical structure is given in Fig. 2. The estimated concentration from absorption measurements was about 10^{-3} M. QSD doped CA films were prepared by dissolving

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PII: S1010-6030(99)00029-5

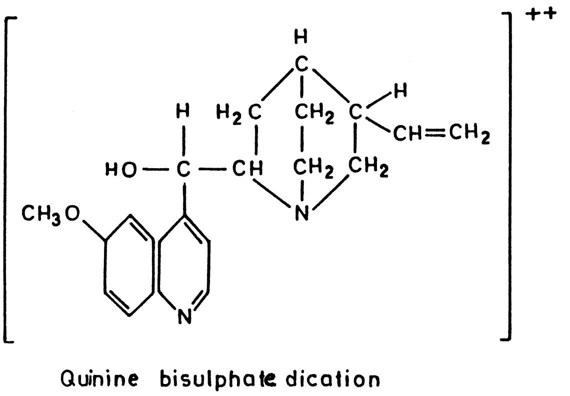

Fig. 1. Structural formula of QSD.

CA (average molecular weight 30 000) powder in acetone and mixing it with the desired concentration of QS in 0.1 N H_2SO_4 solution in acetone. The resultant mass was spread in polypropylene dish to obtain the film. QSD doped PMMA films were prepared by dissolving PMMA (average molecular weight 200 000) grains in dichloromethane (DCM) and mixing it with desired concentration of QS in 0.1 N H_2SO_4 in DCM. The films were again obtained by drying the mass in polypropylene dish. QSD doped PVA films were prepared by mixing PVA (degree of polymerisation is 1700–1800) grains with desired amount of QSD in 0.1 N H_2SO_4 and dissolving it in water. The mass was spread in propylene dish and was dried in an incubator. The estimated concentration comes to about -10^{-3} M.

Absorption spectra were taken with the help of JASCO V-550 spectrophotometer and fluorescence and excitation spectra with the help of JASCO FP-777 spectrofluorometer and analysed by related software. Decay curves were recorded with the help of Edinburgh 199 spectrometer. The excitation source was a nanosecond flashlamp with hydrogen as a filler gas or a Nd : YAG mode locked synchronously pumped and cavity dumped dye (DCM in ethylene glycol and propylene carbonate) laser. The cavity dumped output is again redoubled using an angle tuned frequency converter to generate pico second pulses in the UV region (310–340 nm) The shape and duration of ps pulses is monitored from an autocorrelator trace in the oscilloscope. The pulse width monitored is ~10 ps. Using Time-Correlated Single Photon Counting (TCSPC) technique with laser as a excitation source and XP 2020 Q PMT as detector. The instrumental profile has a FWHM of about 600 ps. The Decay analysis is done by available FLA-900 software. The goodness of fit is judged by the residuals and χ^2 value.

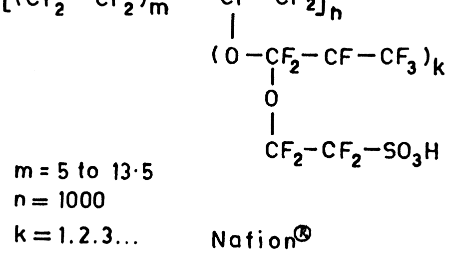

Fig. 2. Structural formula of Nafion®.

3. Results and discussion

3.1. QSD in fluid media and frozen glass

The emission spectra of QSD exhibit EERS in solution as well as in frozen glass [5]. However, the magnitude of EERS increases from 690 cm^{-1} at room temperature to 2080 cm^{-1} at 80 K. The decay behavior of QSD in solution and frozen glass are reported in ref. [11]. In fluid media, it exhibits a biexponential decay at shorter wavelength edge of emission profile, whereas at the longer wavelengths a rise time is observed. In frozen solutions, on the other hand, the decay is biexponential throughout the emission profile and no rise-time is detected even at the red side of the emission band.

As mentioned earlier, Pant et al. [6] have reported that QSD exhibits a charge transfer process between the auxochromes near the glass transition temperature followed by solvent reorientation relaxation process at room temperature with reorientation time comparable to the fluorescence decaytime. In fluid media the EERS can be rationalised by the fact that the excitation of the solute is accompanied by a large change in dipole moment and the solvent reorientation time is not fast enough to bring the molecule in the relaxed state during the decaytime. On the other hand EERS in the frozen glass at 80 K can be explained by the trapping of the molecule in different geometries which will be discussed in the latter section.

3.2. QSD in polymeric media

The emission spectra of QSD in Nafion® are given in Fig. 3. From the figure it is evident that the emission maximum shifts towards longer wavelengths (EERS) as the excitation wavelength is moved towards the longer wavelength side (REE). Similar behaviour is observed for other polymer films. The EERS increases in the order Nafion® > CA > PVA > PMMA. The difference in EERS can be attributed to change in free volume as well as the polarity of the matrix.

In QSD doped Nafion®, the excitation spectra are considerably red shifted with respect to the absorption and at the same time they exhibit a successive red shift for longer wavelengths of the emission profile (Fig. 4). However, in case of PMMA the excitation spectra show a small red shift.

The decaytime data of QSD in these four polymer films are given Tables 1 and 2. From Table 2, it can be seen that the decay fits with a monoexponential function at longer wavelengths (Fig. 5(a)) while at shorter wavelengths it fits with a biexponential function (Fig. 5(b)) for Nafion®, CA

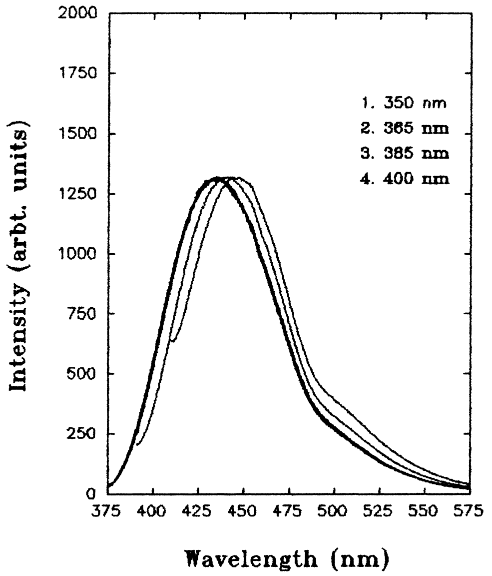

Fig. 3. Emission spectra of QSD for different excitation wavelengths in Nafion® at 290 K.

and PVA. Incase of PMMA throughout the entire emission the decay is biexponential. However, unlike the case of fluid media, [5], no such risetime is observed at longer wavelength in case of polymeric media.

The observed biexponential decay at the shorter wavelengths can be an approximated to a multiexponential decay of different geometries of the solute. While the monoexponential decay at longer emission wavelengths can be attributed to the contribution of only relaxed species.

Moreover, the recovered major decay component increases in the order Nafion® > CA > PVA > PMMA. For simplicity the amplitude averaged decay time (τ_{av}) has also been calculated (Table 2) from the relation.

$$\tau_{av} = \frac{\alpha_1\tau_1 + \alpha_2\tau_2}{\alpha_1 + \alpha_2} \qquad (1)$$

Table 1
Steady state parameters of QSD in various polymer films at 290 K

Polymer	λ_{exc} (nm)	λ_{em} (nm)	EERS(cm^{-1})
PMMA	350	428.8	343
	385	435.2	
PVA	350	433.8	417
	385	441.8	
CA	350	433.2	485
	385	442.5	
Nafion®	350	433.6	500
	385	443.2	

Where α_1 and α_2 are the amplitudes corresponding to decay time τ_1 and τ_2, respectively. It can be seen that τ_{av} changes across the emission profile. The change in τ_{av} is quite small for PMMA, whereas in the case of other polymers it is quite large. As the solvent motion is almost frozen in the polymer, the observed decay behavior can be rationalised by assuming the trapping of the solute molecules in different geometries. Moreover, the difference in the decay behavior of QSD in different polymers can be attributed to the change in the solvent polarity as well as free volume. The relatively large change in τ_{av} across the emission profile in case of Nafion®, CA and PVA can be attributed to more free volume available for the intramolecular motion of the solute whereas in PMMA because of less free volume the internal motion is restricted resulting in a very small change.

Another effect on the decay behavior appears to be of the micropolarity of the matrix. In non-polar matrix PMMA, τ_{av} is small whereas it increases with the matrix polarity. It is interesting to note that in water swollen Nafion®, the recovered decay time at 520 nm is 21.1 ns which is less

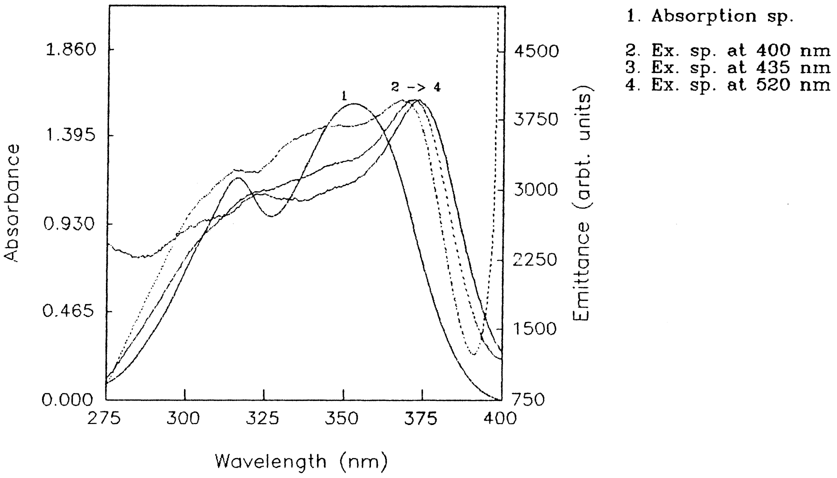

Fig. 4. Absorption spectrum (1) and excitation spectra (2–4) of QSD in Nafion® for different emission wavelengths.

Table 2
Decay parameters of QSD in various polymer films at 290 K (excitation wavelength = 320 nm)

Medium	λ_{em} (nm)	τ_1(ns)	τ_2 (ns)	α_1	α_2	τ_{av} (ns)	χ^2
PMMA	390	2.0	8.4	0.60	0.40	4.5	1.21
	430	1.8	9.6	0.55	0.45	5.3	1.12
	520	2.7	11.1	0.64	0.36	5.7	1.25
PVA	390	3.6	11.0	0.37	0.63	8.3	1.21
	430	6.9	16.7	0.27	0.73	14.0	0.93
	520[a]	–	18.0	–	–	–	1.26
CA	390	6.0	14.9	0.49	0.51	10.5	1.28
	430	7.3	17.8	0.33	0.67	14.2	1.25
	520		19.8	–	–	–	1.28
Nafion®	390	4.4	14.4	0.33	0.67	11.1	1.199
	430	7.1	21.2	0.19	0.81	18.4	1.151
	520[b]	–	23.0	–	–	–	1.118

[a] The decaytime is 19.6 ns when soaked with water.
[b] In water swollen Nafion® the decaytime is 21.2 ns.

than in case of dry Nafion® (Table 2). This can be explained by increase in the micropolarity in dried Nafion® as the QSD molecule may come closer to the more polar SO_3H^+ head group of Nafion®. Similarly, when the PVA film is soaked with water, the decay time at the edge of the emission profile increases from 18.0 ns to 19.6 ns which approaches the major decay component in water [5]. This again can be attributed to the increase in polarity of the

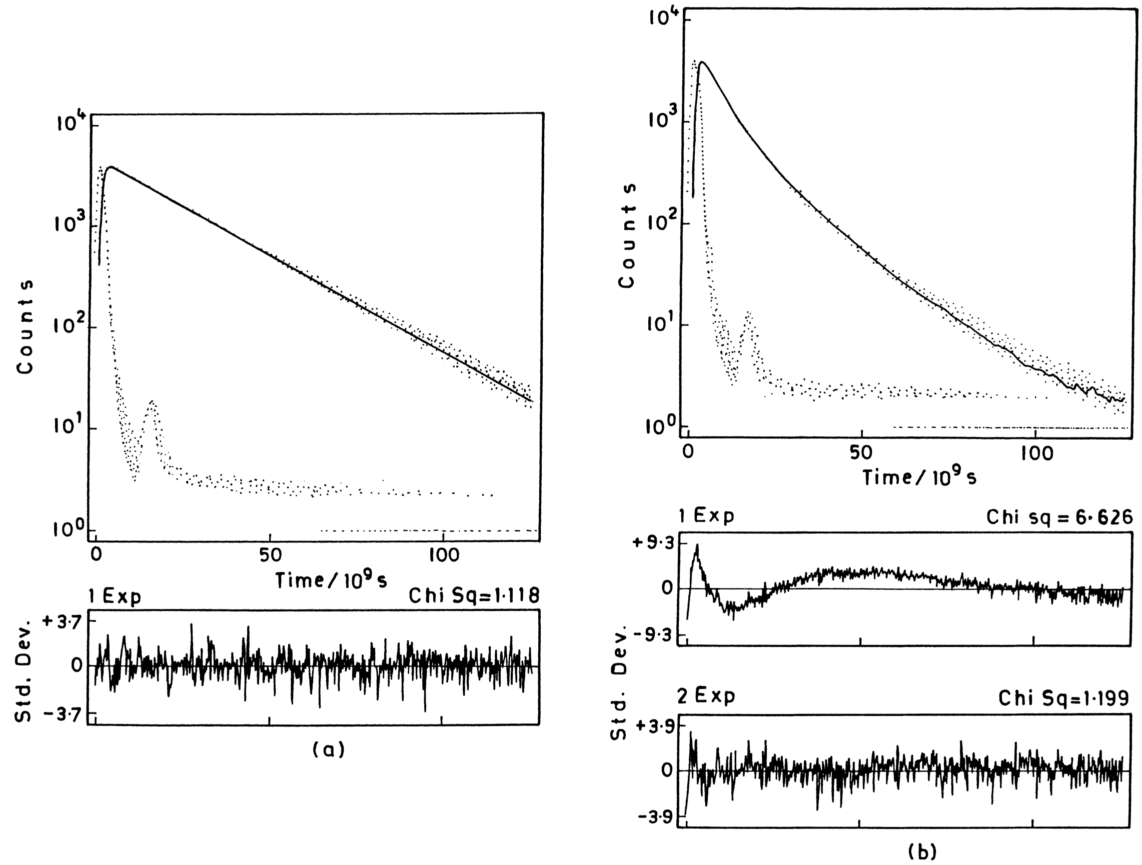

Fig. 5. Decay curves of QSD in Nafion®. (a) Monoexponential function fitted at longer wavelength and (b) biexponential function fitted at shorter wavelength.

matrix in the presence of water. Of course, In case of CA, the observed longer value of decay time as compared to PVA and PMMA can be explained by the fact that QSD is trapped in the polar site although cellulose moiety is itself hydrophobic.

The photophysics of QSD in frozen glass and polymeric media can be understood with the help of broad distribution-function model similar to DMABN [12] representing various species which are not interconvertible during the lifetime of the solute. On the other hand this explains the absence of the any rising portion in the decay. Therefore the multicomponent decay can be understood due to various trapped geometries of the molecule. In the broad distribution model the multicomponent decay curve can be well fitted in two or three components.

In fluid media the configurations are interconvertible within the decay time of the QSD molecule. The, solvent relaxation reorientation results in the EERS and biexponential decay at ambient temperatures is observed [7].

3.3. Correlation between EERS and lifetime

Fig. 6 depicts the observed EERS and lifetime in four different polymer matrices at 290 K. It is evident that a linear relation exists for EERS and lifetime values. The EERS is related to microenviromental changes both in the ground and excited state of the emitter. The observed changes in the lifetime are primarily due to the excited state effect. We have attributed these changes resulting from the free volume available in the polymer in the solid matrices. The free volume is known to affect the local relaxation in polymer matrices. Additionally, local relaxation of individual fluorophor affect the fluorescence behavior. Thus, the EERS and lifetime correlation corroborates our earlier conclusions regarding the multicomponent decay due to various trapped geometries of the molecule.

4. Conclusions

The present study shows that QSD exhibits various geometrical configurations in polymeric media as well as in frozen glass. Moreover, its fluorescent characteristics are sensitive to the micro-environmental polarity and free volume of the matrix.

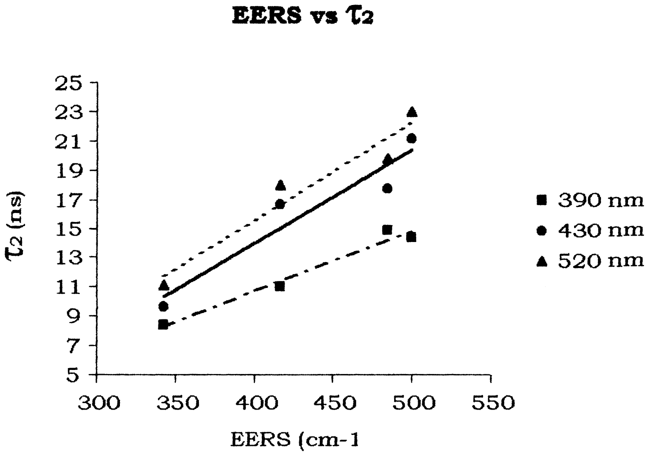

Fig. 6. Plot between EERS and lifetime of QSD in different polymeric media.

Acknowledgements

Referees of the manuscript are acknowledged for their valuable comments. The authors thank Prof. H.D. Bist for critical reading of the manuscript and helpful discussions. The authors are thankful to DST (under National Laser Programme) and UGC (DSA) for financial assistance. One of the author HM thanks to CSIR (India) for SRF.

References

[1] W.H. Melhuish, J. Phys. Chem. 62 (1960) 762.
[2] D.W. Moss, Clin. Chim. Acta 5 (1960) 283.
[3] S. R Meech, D. Phillips, J. Photochem. 23 (1983) 193.
[4] D.A. Barrow, B.R. Lentz, Chem. Phys. Lett. 104 (1984) 161.
[5] P. Gangola, N.B. Joshi, D.D. Pant, Chem. Phys. Lett. 51 (1977) 144.
[6] D. Pant, U.C. Tripathi, G.C. Joshi, H.B. Tripathi, D.D. Pant, J. Photochem. Photobiol., A: Chem. 51 (1990) 313.
[7] D. Pant, H.B. Tripathi, D.D. Pant, J. Photochem. Photobiol., A: Chem. 54 (1990) 239.
[8] S. Pant, H.B. Tripathi, D.D. Pant, J. Photochem. Photobiol., A: Chem. 85 (1995) 33.
[9] S. Pant, D. Pant, H.B. Tripathi, J. Photochem. Photobiol., A: Chem. 75 (1993) 137.
[10] D. Pant, H.B. Tripathi, D.D. Pant, J. Lumin. 50 (1991) 249.
[11] Pant, D., Ph.D. Thesis Kumaon University, Nainital, 1990.
[12] K.A. Al-Hassan, T. Azumi, Chem. Phys. Lett. 163, 1989, 129.