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Solvent polarity and viscosity effect on the fluorescence spectrum and excited state lifetime of quinine dication

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Abstract

Steady state and time domain fluorescence studies were carried out on doubly charged quinine (QS^{2+}) in a series of alcohols. The effects of polarity, viscosity and temperature were studied.

Keywords: Solvent polarity; Viscosity; Fluorescence; Excited state; Quinine dication

1. Introduction

Pant et al. [1,2] have carried out an extensive study on the steady state and fluorescence decay characteristics of quinine sulphate dication (QS^{2+}) in aqueous solutions at different excitation and emission wavelengths. They found that, in aqueous solutions, QS^{2+} shows a biexponential decay with two decay times (τ_1 and τ_2) which are viscosity and temperature dependent. From the temperature dependence of the fluorescence characteristics, it was suggested that, at around 160 K, a rapid charge transfer (CT) relaxation from the methoxy group to the quinoline ring (causing a major geometric change) takes place. They have extended their study to other derivatives, namely 6-methoxyquinoline ($6MQ^+$) and quinidine (Qd^{2+}), and a comparison of the photophysical data of QS^{2+}, Qd^{2+} and $6MQ^+$ has been made. Although there are similarities in the major relaxation processes, i.e. an accelerated CT around 160 K and an unusually large solvent orientational relaxation time in fluid solution, there are some differences in these molecules which are suggested to be due to the differences in photochemistry and geometric structure of quinine, quinidine and 6-methoxyquinoline [3]. In the cinchonidine dication, which is similar to the quinine dication except that the methoxy group in the sixth position of the quinoline ring is absent in the former, no evidence of a CT process was observed [4].

In spite of the extensive steady state and time-resolved measurements on quinine and related compounds, the dynamics of the locally excited (LE) to CT conversion are not well established. Therefore, we have undertaken a study of the decay curves of the fluorescence emitted from QS^{2+} and CT bands at different polarities, viscosities and temperatures.

2. Experimental details

Quinine sulphate (obtained from Aldrich) was recrystallized several times from water. All the solvents were either of spectroscopic grade or were checked for their fluorescence purity. The absorption spectra were recorded using a Beckmann DK-2A spectrophotometer. The emission and excitation spectra were recorded using a Spex 1902 Fluorolog and a home-built spectrofluorometer, which consists of an HRS-2 monochromator for scanning the fluorescence emission. The decay times were measured with an EI 199 time domain spectrometer using the time-correlated, single-photon-counting technique [5,6]; data analysis was performed with a PDP 11/2 microcomputer by the reconvolution method using a least-squares fitting program. The goodness of fit was estimated by χ^2, distribution residuals, standard deviation, the correlation function and the Durbin–Watson parameter. The instrument is capable of measuring lifetimes up to about 200 ps. For lifetime measurements at low temperatures, a transparent Dewar flask was placed in the sample compartment and the samples were immersed in liquid air. The temperature variations were recorded with an iron–constantan thermocouple. The data presented here

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for temperatures below 0 °C are accurate to within 5 °C. Protonated solutions were prepared using 1 N H_2SO_4. The concentration of the solutions used was about 10^{-4} M.

3. Results and discussion

3.1. Absorption and Fluorescence Spectra

The absorption spectra of quinine dication (QS^{2+}) were recorded in a series of alcohols. The absorption spectra are identical in all the solvents studied and resemble that in aqueous medium [1]. The long-wavelength absorption bands have peaks at 315 and 350 nm corresponding to the ^1L_a and ^1L_b bands of quinoline [7].

The fluorescence emission spectra of QS^{2+} show a blue shift with increasing size of the alcohol (methanol to octanol). The steady state spectra parameters of QS^{2+} in different alcohols are given in Table 1 together with the viscosity (η), polarity ($E_T(30)$) and dielectric constant (ϵ) of the solvents. The normality of sulphuric acid (1 N) and the concentration of the solute (10^{-4} M) are constant for all the solvents studied. Although there will be a slight variation due to this in the physical parameters (η, $E_T(30)$ and ϵ), this has not been taken into account. Fig. 1 shows the absorption and emission spectra of QS^{2+} in methanol. A large Stokes shift in emission is evident.

3.2. Lifetime measurements

Table 2 shows the decay times at room temperature for various emission wavelengths in different alcoholic solvents. It can be seen from the table that, although in methanol the decay shows a single-exponential fit (Fig. 2) for all emission wavelengths, a biexponential fit is necessary to analyse the decay plots in the rest of the alcoholic solvents, as demonstrated by a larger χ^2 and higher standard deviations for the single fit (Fig. 3). As in aqueous medium [1], for QS^{2+} in alcoholic solvents, the contribution of the τ_1 component to the total intensity is marginal; however, this increases from 2.5% in ethanol to about 12.8% in octanol at the blue edge of the emission. The contribution of the τ_1 component is totally absent in methanol. At 390 nm, the τ_1 values show an increase from 725 ps in ethanol to about 1.44 ns in octanol and the τ_2 values show a decrease from about 22.02 ns in ethanol to about 20.35 ns in octanol. At the red edge of the emission, the τ_1 component of the emission decay shows a rise time in propanol, butanol and octanol. However, in methanol and ethanol, a monoexponential fit is sufficient to describe the decay, i.e. the rise time component, if any, is too fast to be resolved by the instrument. Furthermore, the τ_2 value shows an increase with an increase in emission wavelength in all solvents. This increase is at a maximum in octanol compared with the smaller alcohols. α_1 and τ_1 both increase from propanol to octanol.

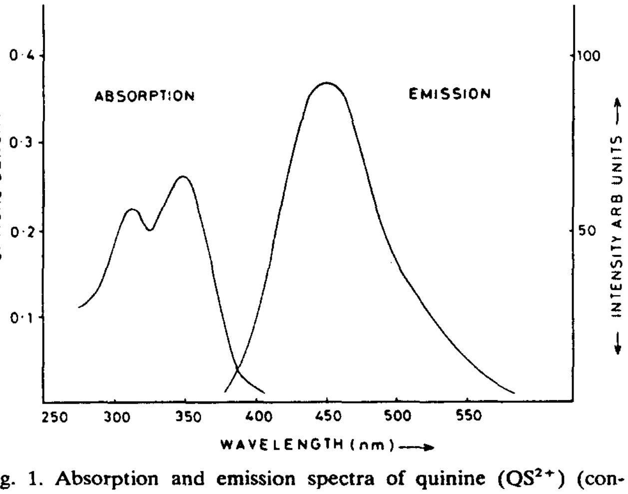

Fig. 1. Absorption and emission spectra of quinine (QS^{2+}) (concentration 10^{-4} M) in methanol (1 N H_2SO_4) at 290 K.

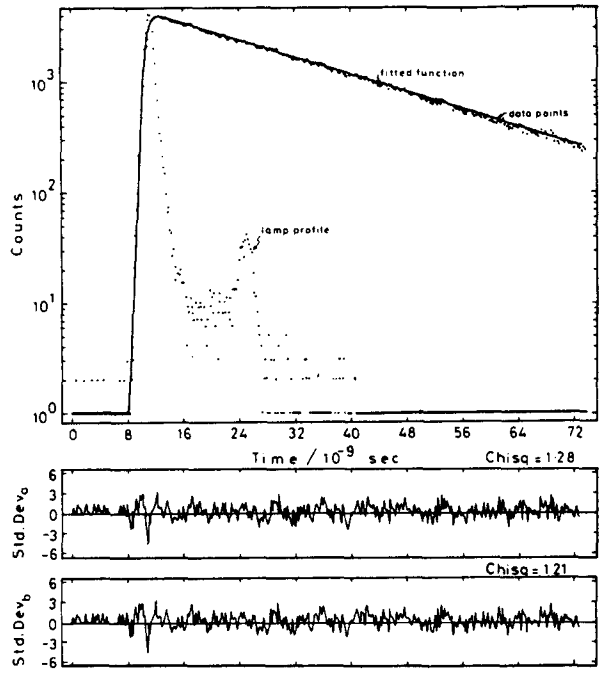

Fig. 2. Fluorescence decay curve of QS^{2+} in methanol (1 N H_2SO_4) at 290 K (λ_{ex}=360 nm, λ_{em}=390 nm). Std. Dev$_a$ and Std. Dev$_b$ correspond to the distribution of residuals for the single- and double-exponential function fits respectively for the same decay data points.

The steady state parameters and decay time data for QS^{2+} in n-alcohols indicate that excitation to the LE state produces emission from at least two emitting states (LE and CT). With increasing polarity and/or decreasing viscosity of the solvent, interconversion of the LE state to the CT state is accelerated. In a solvent of low polarity and/or high viscosity, the contribution of the LE state is about 12.8% (in octanol), whereas

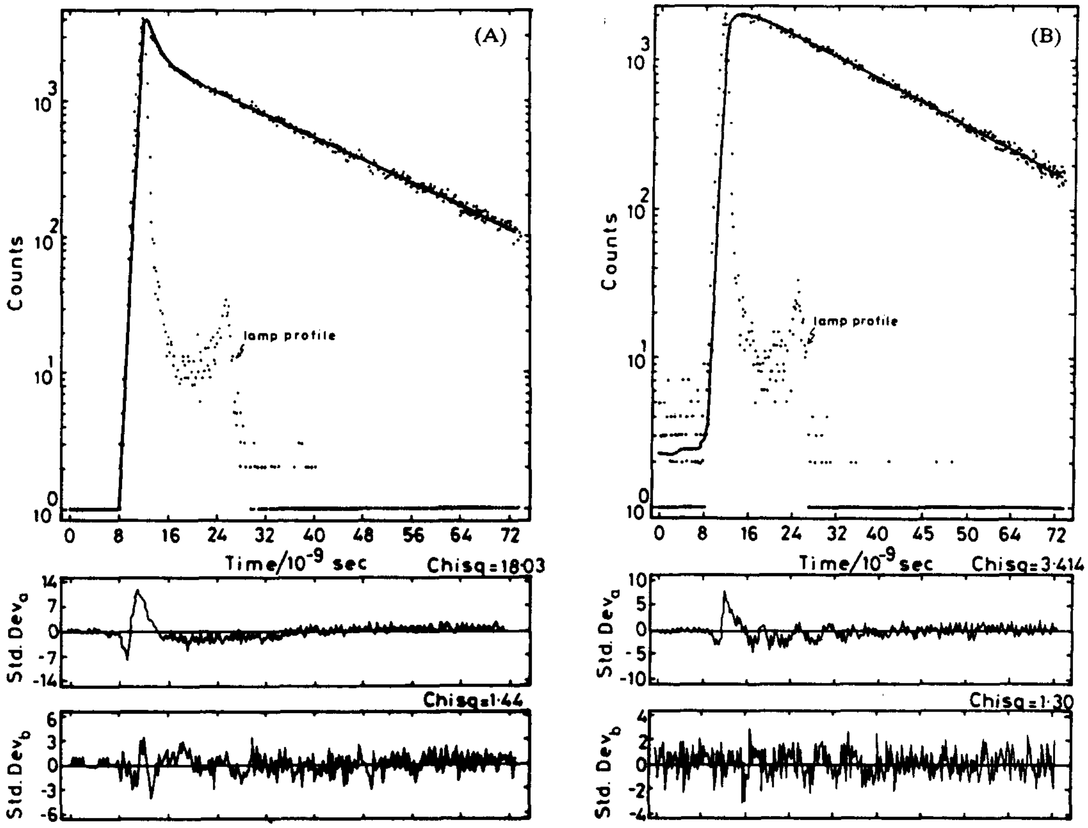

Fig. 3. (A) Fluorescence decay curve of QS^{2+} in octanol (1 N H_2SO_4) at 290 K fitted to a double-exponential function (λ_{ex} = 360 nm, λ_{em} = 390 nm). Std. Dev$_a$ and Std. Dev$_b$ correspond to the distribution of residuals for single- and double-exponential fits respectively. (B) Fluorescence decay curve of QS^{2+} in octanol (1 N H_2SO_4) at 290 K fitted to a double-exponential function (λ_{ex} = 360 nm, λ_{em} = 540 nm). Std. Dev$_a$ and Std. Dev$_b$ correspond to the distribution of residuals for single- and double-exponential fits respectively.

Table 1
Steady state spectral data of QS^{2+} in different alcohols together with the physical parameters of the solvents

Solvent	Viscosity η[a] (cP)	Polarity $E_T(30)$[a] (kcal mol^{-1})	Absorption		Emission maximum (λ_{ex} = 360 nm) (nm)	Dielectric constant ϵ[b]
			L_a (nm)	L_b (nm)		
Methanol	0.6	55.5	315	350	452.5	32.6
Ethanol	1.2	51.9	315	350	450.0	24.3
n-Propanol	2.1	50.7	315	350	447.5	20.1
n-Butanol	2.9	50.2	315	350	447.5	17.1
n-Octanol	8.2	48.3	315	350	445.0	–

[a] Values at 20 °C.
[b] Values at 25 °C.

it is almost absent in methanol where emission originates from the CT state alone indicating a fast LE to CT conversion. The presence of a rise time in the larger alcohols at the tail of the emission further confirms this excited state reaction.

In order to understand the mechanism of the LE → CT conversion in the excited state, we have performed experiments with isoviscous neat solvents (keeping $\eta \approx 2.1$ cP) at different temperatures. For these studies, the solvents methanol (223 K), ethanol (262 K), propanol (290 K) and butanol (306 K) were selected. The lifetimes for QS^{2+} in these solvents are given in Table 3. A biexponential fit is necessary to analyse the decay at the blue ($\lambda_{em} \approx 390$ nm) and red ($\lambda_{em} \approx 540$ nm) edge of the emission in all solvents at the mentioned temperatures, with a rise time at the tail of the emission spectrum. From these observations, the LE → CT rate (K_{LC}) was calculated for these isoviscous solvents and found to be of the same order ($((1\text{–}1.5) \times 10^9\ s^{-1})$, suggesting that K_{LC} is dependent on the viscosity of the solvent. These rates were calculated from the values of τ_{10} at 77 K where K_{LC} is small compared with the

Table 2
Emission wavelength dependence of the decay time of QS^{2+} in various alcohols at 290 K (λ_{ex} = 360 nm)

λ_{em} (nm)	Solvent	Single exponential		Double exponential					
		τ (ns)	χ^2	τ_1 (ns)	τ_2 (ns)	χ^2	α_1	α_2	$\alpha_1\tau_1/(\alpha_1\tau_1+\alpha_2\tau_2)$
390	Methanol	21.623 (0.051)	1.253						
	Ethanol	21.575 (0.084)	2.812	0.725 (0.101)	22.017 (0.061)	1.170	0.0878	0.111	0.0254
	n-Propanol	20.672 (0.116)	5.199	0.741 (0.052)	21.404 (0.059)	1.052	0.127	0.1002	0.042
	n-Butanol	19.923 (0.137)	7.107	1.299 (0.087)	21.145 (0.071)	1.293	0.093	0.093	0.0579
	n-Octanol	17.826 (0.24)	18.03	1.474 (0.051)	20.355 (0.087)	1.444	0.1258	0.0621	0.1279
420	Methanol	21.784 (0.051)	1.105						
	Ethanol	21.847 (0.053)	1.271	1.226 (0.261)	22.096 (0.056)	1.026	0.0222	0.1246	0.0010
	n-Propanol	21.426 (0.057)	1.494	2.209 (0.617)	21.715 (0.065)	1.27	0.0143	0.1269	0.0113
	n-Butanol	21.154 (0.058)	1.538	0.967 (0.162)	21.436 (0.051)	0.965	0.043	0.132	0.0145
	n-Octanol	20.352 (0.107)	3.55	1.642 (0.128)	21.179 (0.075)	1.229	0.0513	0.1036	0.0370
450	Methanol	21.977 (0.05)	1.158						
	Ethanol	21.794 (0.051)	1.213						
	n-Propanol	21.661 (0.048)	1.118						
	n-Butanol	21.505 (0.042)	0.909						
	n-Octanol	21.326 (0.048)	1.138						
500	Methanol	22.19 (0.051)	1.151						
	Ethanol	22.437 (0.055)	1.162						
	n-Propanol	22.239 (0.061)	1.435	0.395 (0.029)	22.093 (0.053)	1.177	−0.163	0.1422	−0.021
	n-Butanol	22.040 (0.057)	1.573	1.051 (0.183)	21.77 (0.052)	1.141	−0.038	0.1469	−0.013
	n-Octanol	22.288 (0.075)	2.626	2.583 (0.274)	21.509 (0.062)	1.318	−0.030	0.1319	−0.028
540	Methanol	22.633 (0.052)	1.213						
	Ethanol	22.127 (0.054)	1.195						
	n-Propanol	22.15 (0.056)	1.445	0.570 (0.137)	22.019 (0.057)	1.305	−0.046	0.1385	−0.009
	n-Butanol	22.408 (0.068)	1.854	0.790 (0.096)	22.098 (0.049)	1.031	−0.072	0.1377	−0.019
	n-Octanol	22.761 (0.102)	3.414	1.855 (0.157)	21.854 (0.064)	1.303	−0.052	0.1377	−0.033

Table 3
Decay times (τ_1 and τ_2) for QS^{2+} in various isoviscous solvents ($\eta = 2.1$ cP) ($\lambda_{ex} = 360$ nm)

Solvent	Temperature K	λ_{em} (nm)	τ_1 (ns)	τ_2 (ns)	χ^2	α_1	α_2	$\alpha_1\tau_1/(\alpha_1\tau_1+\alpha_2\tau_2)$
Methanol	223	390	0.176 (0.023)	26.541 (0.092)	1.129	1.165	0.0790	0.0891
		420	–	26.681 (0.079)	1.476			
		520	0.582 (0.196)	26.799 (0.079)	1.454	−0.033	0.1515	−0.0047
Ethanol	262	390	1.063 (0.096)	23.986 (0.077)	1.348	0.0767	0.1198	0.0276
		420	–	23.872 (0.064)	1.398			
		520	0.890 (0.156)	24.264 (0.067)	1.313	−0.033	0.1595	−0.0076
Propanol	290	390	0.741 (0.052)	21.404 (0.059)	1.052	0.127	0.1002	0.0420
		420	2.209 (0.617)	21.715 (0.065)	1.270	0.0143	0.1269	0.0113
		520	0.570 (0.137)	22.019 (0.057)	1.305	−0.046	0.1385	0.0087
Butanol	306	390	0.992 (0.092)	20.445 (0.059)	1.202	0.0943	0.1158	0.0380
		420	1.311 (0.370)	20.830 (0.055)	1.195	0.0233	0.1394	0.0104
		520	0.863 (0.147)	21.279 (0.055)	1.319	−0.035	0.1517	0.0095

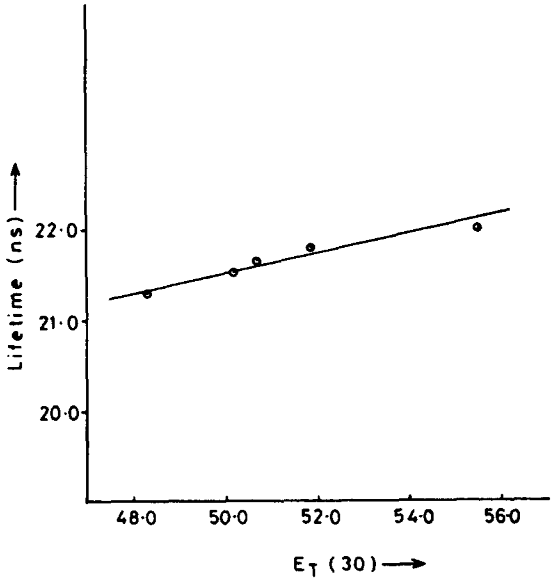

Fig. 4. Fluorescence decay time (τ) of QS^{2+} as a function of polarity $E_T(30)$ at 290 K ($\lambda_{ex} = 360$ nm, $\lambda_{em} = 450$ nm).

fluorescence rate. A slight disagreement in the K_{LC} values of the isoviscous solvents may occur due to the change in non-radiative deactivation at different temperatures. Had this conversion been due to polarity alone, we would have observed the nature of the decay in methanol at 223 K to be purely exponential, since the polarity of the liquid increases as the temperature is decreased [8]. To test whether the change in K_{LC} is due to the change in the viscosity of the solvent alone, a plot of log τ_1 vs. log η was analysed. Normally, for a system undergoing viscosity-dependent, radiationless transition rates, the fluorescence decay follows the relation $\tau_f = C\eta^{\alpha}$ where the viscosity power dependence $\alpha = \frac{2}{3}$ [9]. A lower value of α (0.42) in the present case indicates that, in addition to the bulk viscosity, some other microenvironmental process contributes to the above rate. Furthermore, in this isoviscosity region, we observed an increase in the value of τ_2 ($\lambda_{em} \approx 390$ nm) from 20.4 ns (in butanol at 306 K) to 26.5 ns (in methanol at 223 K). The increase in the value of τ_2 may be due to the increased polarity of the solvent. A plot of τ_2 vs. $E_T(30)$ (Fig. 4) shows a linear dependence. Such a dependence is in agreement with the increase in τ_2 in methanol at 223 K and ethanol at 262 K, compared with their room temperature values, where the polarity is larger than at 290 K. This increase in τ_2 is not simply a temperature effect (where, by decreasing the temperature, the temperature-dependent,

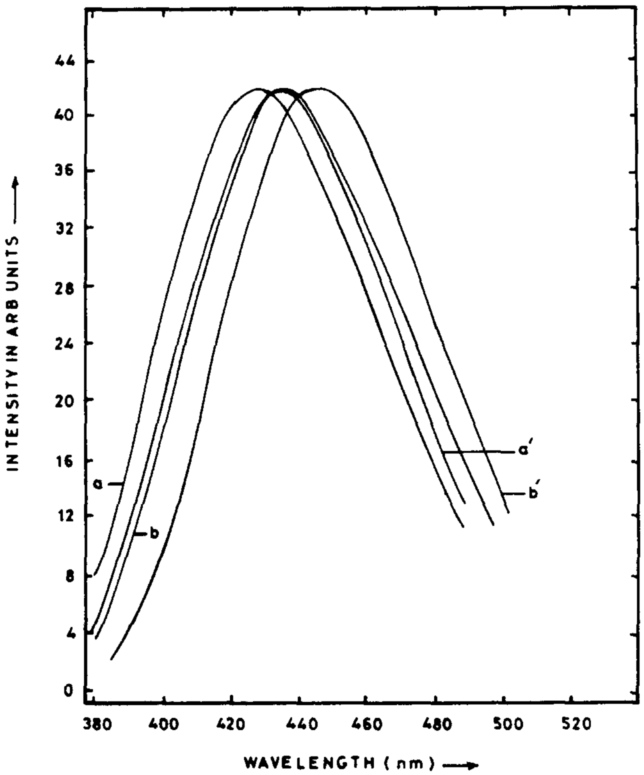

Fig. 5. Time-resolved emission spectra for QS^{2+} in isoviscous ($\eta = 2.1$ cP) butanol (at 33 °C) and methanol (at −50 °C) for short time delays (0–0.5 ns) (a, b) and long time delays (5.0–10.0 ns) (a′, b′).

non-radiative processes decrease) as no such unusual increase in τ_2 is observed in octanol at 223 K. Furthermore, the change in the value of τ_2 is not related to the change in the viscosity of the solvent since the variation of τ_2 with η shows a decrease in τ_2 with increasing η measured in different solvents.

The normalized, time-resolved emission spectra (TRES) for QS^{2+} in isoviscous solvents ($\eta = 2.1$ cP) for short time delays (0–0.5 ns) and long time delays (5.0–10.0 ns) are shown in Fig. 5. It is evident from the figure that the shift in the TRES is larger for higher polarity solvents (methanol at −50 °C), suggesting emission from a more stable state. Evidence of a lowering of the potential energy curve with increasing polarity of the medium has been invoked [8,10]. Thus the main factor responsible for the increase in τ_2 is the increase in polarity. It appears that, with increasing polarity of the solvent, selective solvent aggregation around the solute takes place, which may cause a decrease in the radiative rate [11,12] and may be responsible for the increase in τ_2 of QS^{2+}. The kinetics of CT state formation do not seem to obey a simple two-state model as τ_1 has different values at the blue and red sides of the emission peak. Similarly, for an excited state reaction measured at the red side of the emission peak, the amplitude (α_1) associated with the shorter lifetime component must be equal and opposite to that (α_2) associated with the longer lifetime component. However, $|\alpha_1| \neq |\alpha_2|$. Further work is in progress.

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