Photophysics of 9-aminoacridinium hydrochloride

D D PANT, G C JOSHI and H B TRIPATHI

Photophysics Laboratory, D.S.B. College, Kumaun University, Nainital 263 002, India

Abstract. The steady state and time domain spectroscopy of 9-aminoacridinium hydrochloride have been studied. 9-aminoacridine (I), 9-aminoacridinium (II) and the double protonated ion (III) follow Waterman's principle with respect to their spectra and lifetimes. It is established that the excimer formation in (II) is from the ground state dimers which undergo either thermally-activated radiationless excimer conversion or a geometrical rearrangement in the excited state at room temperature. The quenching of monomer emission by dimers or foreign quenchers (KI) is found to be of transient nature as suggested by the continuum model.

1. Introduction

The photophysics and spectroscopy of 9-aminoacridinium are sufficiently interesting to warrant a detailed study. The spectra of amines were studied earlier (Acheson 1956; Zanker and Reichel 1959). There is some confusion whether the ring nitrogen or the amino group is protonated first. Recently, Gangola et al (1981a) observed from their steady state investigations that 9-aminoacridinium shows an intense hypochromism on dimerisation, with a small excitonic red shift. At low temperatures only the dimer emission is observed which converts into excimer emission at room temperature. Besides, the molecule has a high quantum yield and shows delayed fluorescence of the p-type (Gangola et al 1981b). Despite these characteristics 9-aminoacridinium has not occupied the prominent position which pyrene and perylene have in the domain of photophysics.

In the present investigation we have studied in detail the steady state and dynamical excited state to explain the nature of excimer formation and quenching of monomer emission as reflected in the lifetimes. It is shown that (i) the earlier suggestion regarding the excimer formation from the dimer is essentially correct and (ii) the monomer quenching at high concentrations is not simple Stern Volmer type but shows transient effects. We have also studied the effect of ionization on the spectra of 9-aminoacridine and have determined the excited state lifetime of the neutral, single and double ionized species.

2. Experimental

9-aminoacridinium hydrochloride monohydrate (Fluka AG) was purified by repeated crystallization from alcohol water mixture. Spectrapure grade solvents and triply-distilled water were used. Steady state absorption, emission and excitation spectra were taken using a Spex Fluorolog (model 1902). The spectra of neutral, single-protonated and double-protonated species were scanned at pH = 12, 6·0 and concentrated H_2SO_4 from a stock solution of 9-aminoacridinium hydrochloride.

The fluorescence lifetimes were measured using a subnanosecond spectrometer (Edinburgh 199 model) using single photon counting technique (Shah *et al* 1985; Pant *et al* 1986). For lifetime measurements at 80 K a transparent dewar was placed in the sample compartment and the samples were immersed in liquid air. The instrumental profile was collected in this case at the excitation wavelength under the same geometry. Temperature variations were recorded with an iron-constantan thermocouple.

3. Results and discussion

3.1 *Spectra, lifetimes and ionization*

The room temperature emission spectra are given in figure 1 for 9-aminoacridine (I), 9-aminoacridinium (II) and double protonated ion (III). The peak values are given in table 1. Corresponding to the shift and structure, the spectra obey the normal rules as given below.

(a) Although all the primary aromatic amines absorb at longer wavelength, with diffuse structure, the spectra of the cations are identical with their parent hydrocarbons. This is because when the nitrogen atom of the aromatic amine becomes quaternary, it can no longer supply an electron to engage in resonance with the π electrons of the ring system and therefore can no longer maintain the distinctive difference from the normal hydrocarbon spectrum. However, the spectrum of monocation of 9-aminoacridine
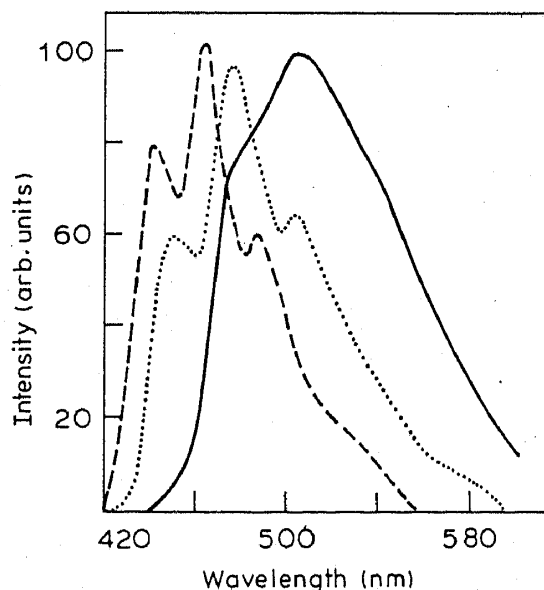

Figure 1. Room temperature emission spectra of 9-aminoacridinium hydrochloride -- in water (pH = 6); .... (pH = 12) and —— concentrated H_2SO_4.

Table 1. Band positions in emission and lifetimes of 9-aminoacridine and its ionized species.

Solution	Band position (nm)	Lifetimes at room temperature (nsec)	Remarks
H_2O (pH = 12)	450, 476, 506, 546	14·6	Structured spectrum
H_2O (pH = 6)	440, 460, 490, 525	16·6 (water) 15·7 (Glycerol: water)	Structured spectrum
H_2SO_4 (Concentrated)	480, 510, 555	27·9	Diffused spectrum

does not differ greatly from that of neutral molecule except for small blue shift. As is known in the neutral species, the amino group is so situated that its lone pair of electrons is strongly delocalized by C-9 which is the most electron-deficient carbon atom. The dissimilarity in the monocation of 9-aminoacridine and primary aromatic amines is due to this reason.

(b) In the acridine spectra ^{1L}A is the longer wavelength peak and the effect of protonation at the ring nitrogen is to shift the spectra further to longer wavelengths with some loss of structure. 9-aminoacridine in strongly acidic solution shows a structure similar to that of acridinium ion. This fact, along with what has been said earlier, shows that the second proton goes to the ring nitrogen.

It is seen from table 1 that the above mentioned two rules can be used to decide which of the nitrogen receives the proton first. The successive added proton occupies position as shown below:

(I)   (II)   (III)
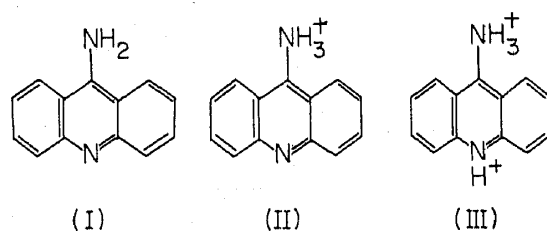
In table 1 we have also included the lifetimes measured at room temperature. The lifetimes of neutral and singly-protonated species are almost equal whereas the lifetime of the double protonated species is considerably higher. A comparison of these lifetimes with acridine (9·6 nsec) and acridinium ion (29 nsec) shows that only the second proton gets attached to the ring nitrogen as in acridinium.

3.2 *Excimer formation*

In what follows we describe the excimer emission and other photophysical characteristics of (II). As already mentioned extreme hypochromism and excimer emission are the characteristic properties of 9-aminoacridinium at higher concentrations ($\sim 10^{-2}$ M). In figure 2 we show the excimer emission of (II) with increasing concentration. It is seen that the monomer has a structured spectrum with λ_{max} at

460 nm. The broad excimer hand with a large stokes shift ($\lambda_{max} = 555$ nm) begins to appear at a concentration approximately 10^{-2} M and increases in intensity with increasing concentration. Only the excimer emission is observed on excitation at higher wavelengths corresponding to dimer absorption (450 nm). We have investigated thoroughly the mechanism of this excimer formation by measuring and analyzing the decays of monomer and dimer.

The kinetics of usual pyrene type excimer formation in the excited state is as follows (Birks 1970)

$$M + h\nu_1 \to M^*, \tag{1}$$

$$M^* + M \underset{k_{-ex}}{\overset{k_{ex}}{\rightleftharpoons}} E^*, \tag{2}$$

$$M^* \xrightarrow[k_M = k_{fM} + k_{dM}]{} M + h\nu_2, \tag{3}$$

$$E^* \xrightarrow[k_E + k_{fE} + k_{dE}]{} E + h\nu_3, \tag{4}$$

where M refers to the ground state monomer and M^* the lowest excited electronic state achieved after vibrational relaxation. k_{ex} and k_{-ex} are the rates of excimer formation and dissociation respectively. k_M is the fluorescence decay rate which comprises k_{fM}, the radiative and k_{dM} the radiationless decay. Similarly k_E is the excimer emission decay rate. The rate equations for monomer and excimer decays can be written as:
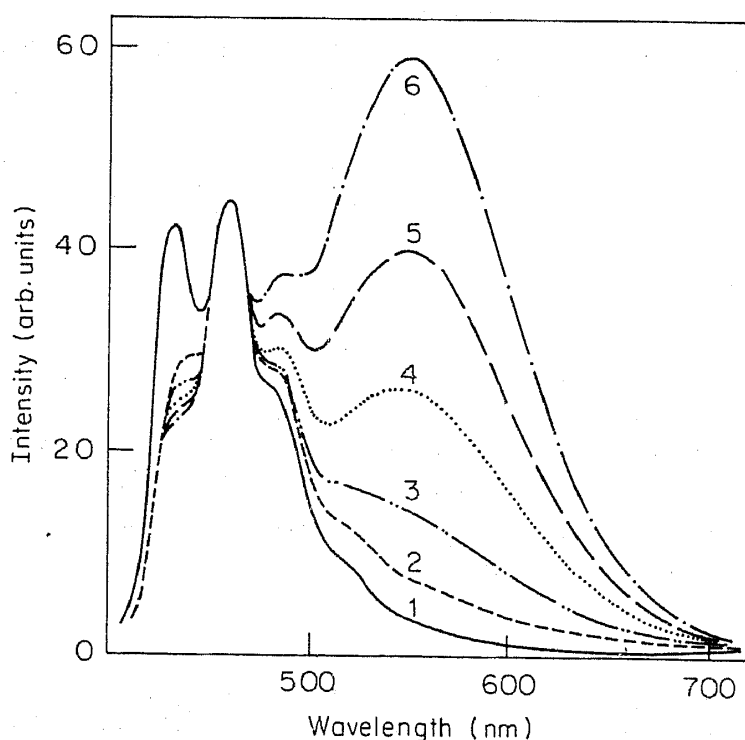

Figure 2. Concentration dependence of emission spectra of (II). 1. 10^{-5} M; 2. 10^{-2} M; 3. 2×10^{-2} M; 4. 3×10^{-2} M; 5. 4×10^{-2} M and 6. 5×10^{-2} M.

$$-\frac{d[M^*]}{dt} = k_M[M^*] + k_{ex}[M^*] - k_{-ex}[E^*], \tag{5}$$

$$-\frac{d[E^*]}{dt} = k_E[E^*] + k_{-ex}[E^*] - k_{ex}[M^*]. \tag{6}$$

As the excimer formation is in the excited state only $[E^*] = 0$ at $t = 0$ and (5) and (6) can be solved to give

$$I_{M^*}(t) = \alpha_1 \exp(-\gamma_1 t) + \alpha_2 \exp(-\gamma_2 t), \tag{7}$$

$$I_{E^*}(t) = \beta[\exp(-\gamma_2 t) - \exp(-\gamma_1 t)], \tag{8}$$

where $\gamma_1, \gamma_2 = 1/\tau_1, 1/\tau_2$

$$= 1/2\{(k_M + k_{ex} + k_E + k_{-ex})$$
$$\pm[(k_E + k_{-ex} - k_M - k_{ex})^2 + 4k_{ex}k_{-ex}]^{1/2}\},$$

$$\alpha_1 = k_{fM}[M^*(0)]\{\gamma_1 - (k_M + k_{ex})\}/(\gamma_1 - \gamma_2),$$

$$\alpha_2 = k_{fM}[M^*(0)]\{(k_M + k_{ex}) - \gamma_2\}/(\gamma_1 - \gamma_2),$$

and $\beta = k_{fE}[M^*(0)]k_{ex}/(\gamma_1 - \gamma_2).$

The decay curves for monomer and excimer will show the following properties.

(a) In the case where k_M, k_E, k_{ex} and k_{-ex} are of the same order, the monomer decay will be double exponential and the excimer decay will show a rise-time. The τ_1 and τ_2 obtained for both monomer and excimer decays will have the same values.

(b) In the case k_{ex} and $k_{-ex} \gg k_M$, k_E the decay curves for both monomer and excimer will be mono-exponential. Both emissions will give the same lifetime.

Figures 3(a) and 3(b) show the decays for monomer and excimer emissions of 9-aminoacridinium hydrochloride respectively. No rise-time in the excimer emission is observed and the monomer and excimer decays have two different lifetimes. This proves that pyrene-type excimer kinetics does not hold good in the present case. The excimer decay has all the characteristics of a unimolecular reaction and this fact supports the earlier suggestion that excimer is formed at room temperature from the dimer. The lifetimes of monomer and dimer at 80 K and monomer and excimer at room temperature are given in table 2. If, at 80 K, glycerol water solutions containing higher concentrations of (II) are excited at longer wavelengths only dimer emission is observed with $\lambda_{em} = 480$ nm. The temperature variation of the dimer spectrum is shown in figure 4. It is seen that around 220 K a new band begins to develop ($\lambda_{em} \sim 550$ nm) and finally at room temperature the dimer band at 460 nm vanishes and only the excimer band remains.

The 80 K dimer emission has a monoexponential decay. However, as the temperature approaches room temperature, the dimer converts into an excimer emission. At 260 K, therefore, due to both emissions a biexponential decay is observed (figure 5). Again at higher temperatures (room temperature) the excimer decay is single exponential. Both the intensity and lifetime variations conclusively prove that excimer is formed out of dimer.
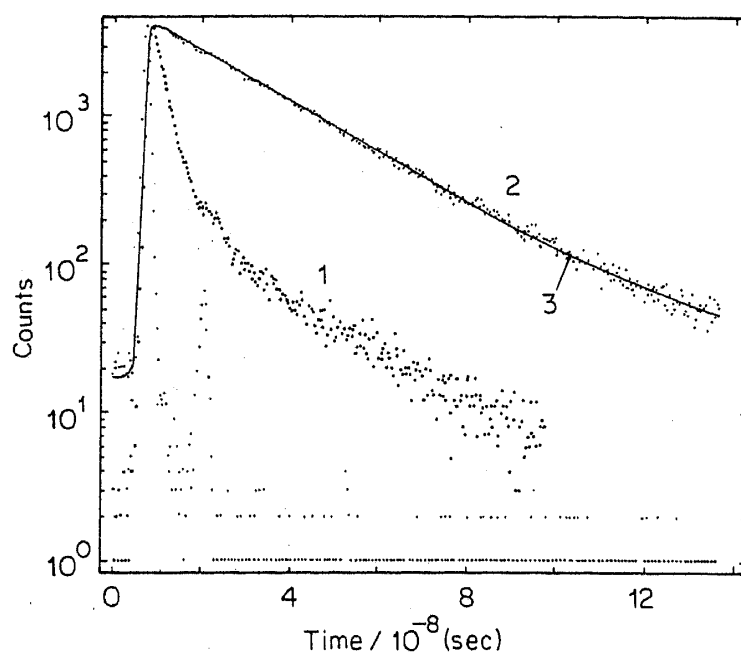
Figure 3. Decay curves for 5×10^{-2} M solution of (II). 1. Monomer emission (440 nm); 2. Excimer emission (560 nm); 3. Fitted function for single exponential fit.

The excimer formation from dimers is not an unusual phenomenon. Mainly, two types of mechanisms for such excimer formations have been suggested (Mataga 1970; Saigusa and Itoh 1985). The excited state of the dimer has a low barrier ($\Delta E \simeq 700\ \mathrm{cm}^{-1}$ in the present case) and the radiationless process to the excimer state occurs around room temperature. The excimer formation is schematically shown in figure 6. The other process may involve a displacement of the configuration of the dimer at room temperature.

3.3 *Quenching of the monomer emission*

At low concentrations ($10^{-5} - 10^{-3}$ M) the room temperature lifetimes of (II) remain almost constant. At higher concentrations (10^{-3} M to 10^{-2} M) lifetime decreases; yet the decay curve remains single exponential and the quenching is Stern-Volmer type. The quenching is obviously produced by diffusional processes in which the dimer participates as a quencher. The quenching is not due to Forster's type intermolecular energy transfer processes as the lifetime of the monomer in concentrated solution

Table 2. Lifetimes of monomer, dimer and excimer of (II) at 80 K and room temperature.

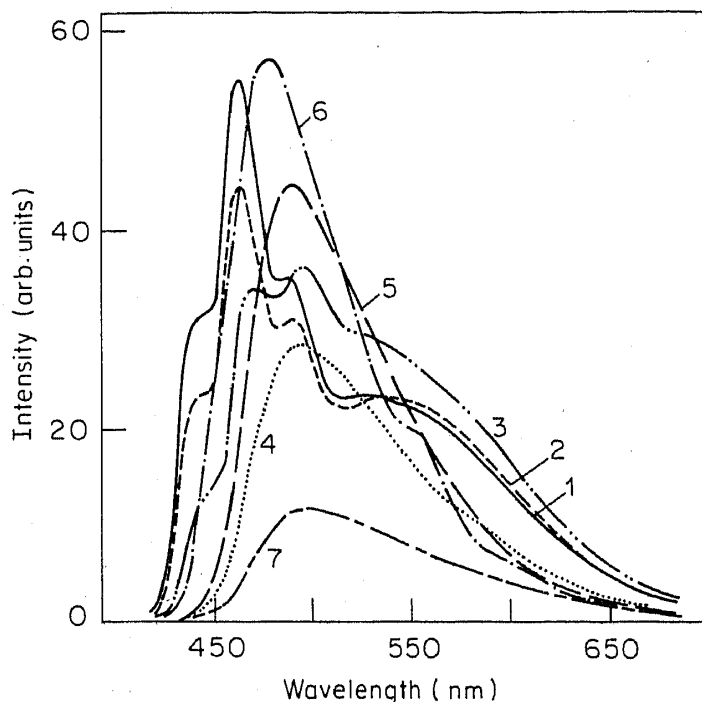|	$\tau_{80\ K}$ (nsec)	$\tau_{290\ K}$ (nsec)
Monomer (Gly: water)	16·6	15·5
Monomer (water)	17·9	16·6
Dimer	42·0	—
Excimer	—	24·5

Figure 4. Temperature variation of emission spectra of (II). 1. 290 K; 2. 275 K; 3. 263 K; 4. 206 K; 5. 176 K; 6. 80 K; 7. 247 K.
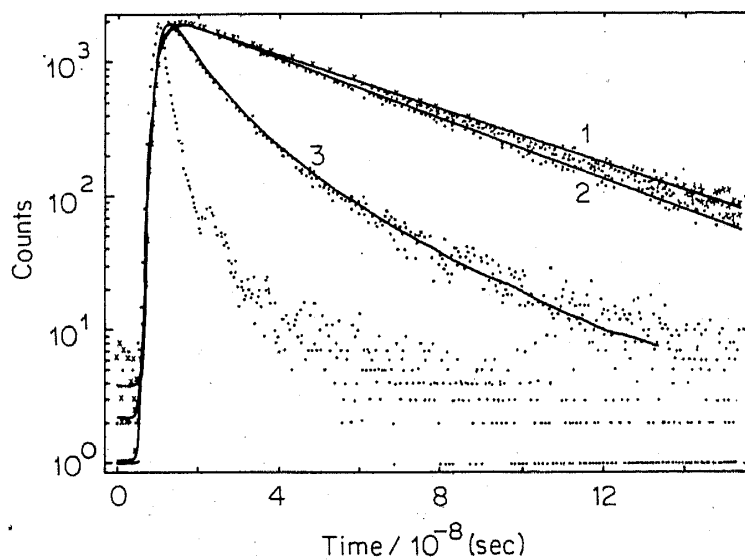

Figure 5. Decay curves for 5×10^{-2} M solution of (II): 1. 80 K; 2. 220 K; 3. 270 K.

remains 16·5 nsec at 80 K and does not change upto approximately 220 K. With further increase in concentration the decays deviate from single exponential and efforts to fit the new type of quenching with the formation of an intermediate complex which should give rise to a biexponential decay (equation (7)) proved unsuccessful. The lifetime data and deviations are indicated by increase in χ^2 (table 3). χ^2 is a measure of the accuracy of the fit and has to be approximately equal to 1 for a good fit.
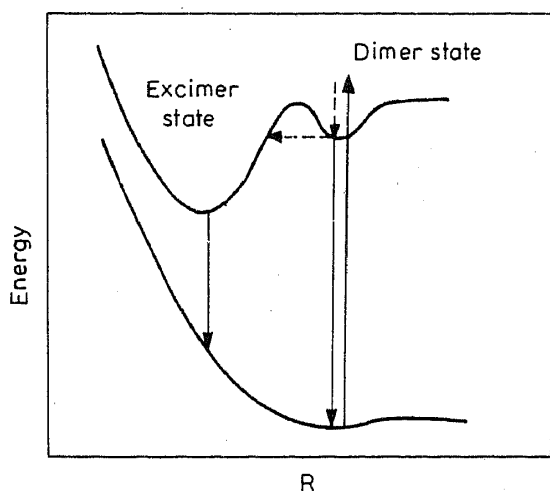
Figure 6. Schematic diagram for excimer emission of 9-aminoacridinium hydrochloride.

The theory of diffusion-controlled reactions based upon the application of Fick's law to a continuum model has received considerable attention during the past several decades after an early pioneering work by Smoluchowskii (1917). The experimental validity of the model was examined by Noyes (1964) and Ware and Novros (1966) in the steady state and by Ware and Nemzek (1975) in the time dependence of decay curves. Their approach is to study the transient phenomenon arising due to the time dependence of concentration gradient which has a considerable effect at short times, particularly at higher concentrations. On the basis of the above the following quenching scheme has been invoked.

$$M + h\nu_1 \rightarrow M^*, \tag{9}$$

$$M^* \xrightarrow{\quad} M + h\nu_2, \tag{10}$$
$$\overline{k_{fM} + k_{dM}}$$

$$M^* + Q \xrightarrow{k_{q(t)}} \text{products.} \tag{11}$$

The intensity of fluorescence as a function of time leads to the following equation:

$$M^*(t) = M_0^* \exp(-at - 2b\sqrt{t}), \tag{12}$$

where
$$a = 1/\tau_0 + 4\pi R' D_{AQ} N'[Q],$$

$$b = 4(R')^2 (\pi D_{AQ})^{1/2} N'[Q],$$

where $D_{AQ} = D_A + D_Q$, R' is related to the encounter distance and $N'[Q]$ is the number of molecules in a millimole. At lower concentrations when the coefficient b is small the decay curves obey the Stern Volmer law but deviations from single exponentials appear at higher concentrations. It is seen from figure 7 that attempts to fit the decay curve for $2 \cdot 5 \times 10^{-2}$ M solution in the above equation give a value of $\chi^2 = 1 \cdot 2$ which is a good fit. The values of $R'(AQ)$ and D_{AQ} calculated from different fits are also given in table 3(a). However, another possibility of a weak dimer emission at room temperature undetectable through steady state measurements could not be avoided.

We have done separate experiments to verify the existence of the transient phenomenon in which KI has been used as a quencher in a 10^{-4} M solution of (II) in
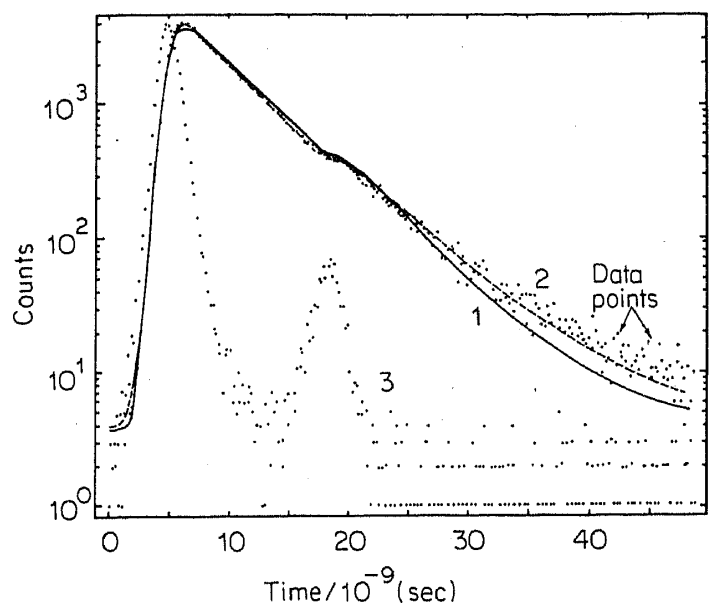
Figure 7. Decay curve for 2.5×10^{-2} M solution of (II) at 440 nm. Data points are fitted in 1. Single exponential fit; 2. Fit using equation (12); 3. Lamp profile.

Table 3. Quenching and concentration quenching of monomer lifetime.

Conc. (mol/lit)	$\tau^{\dagger}$ (nsec)	χ^2	$\tau(= 1/a)^{**}$ (n sec)	γ^*	χ^2	R' (Å)	$D_{AQ} \times 10^6$ (cm²/sec)
(a) Concentration quenching of monomer lifetime of II							
10^{-5}	16.7	0.98					
10^{-4}	16.5	1.09					
10^{-3}	16.4	1.12					
2×10^{-3}	15	1.00					
4×10^{-3}	12.8	1.20					
6×10^{-3}	11.0	1.18					
10^{-2}	8.50	1.46	9.9	0.15	1.03	13.2	3.64
1.66×10^{-2}	6.60	2.30	8.10	0.34	1.26	17.6	2.76
25×10^{-2}	5.0	2.69	7.3	0.44	1.25	17.7	2.23
5×10^{-2}	4.2	3.19	6.0	0.78	1.7		
(b) Quenching of monomer lifetime (Conc. 10^{-4} M) by KI in Gly: water							
0	15.4	1.14					
10^{-2}	11.7	1.2					
2×10^{-2}	9.5	1.8					
3×10^{-2}	7.69	1.5					
5×10^{-2}	5.4	2.5	6.6	0.263	1.36	9.92	2.11
10^{-1}	3.1	2.67	4.5	0.438	1.13	10.28	1.95
2×10^{-1}	1.77	3.29	3.42	0.77	1.26	11.4	1.6
3×10^{-1}	1.27	2.47	2.1	0.8	1.31	—	—

$*\gamma = b\sqrt{1/a}$; †Single exponential fit; **fit using equation (12).

glycerol water, thus avoiding dimer emission if any. These data are also given in table 3(b). There is a close correspondence between the dimer and KI as quenchers. It is seen that in the case of KI in 0.05 M concentration there is a better fit with equation (12).
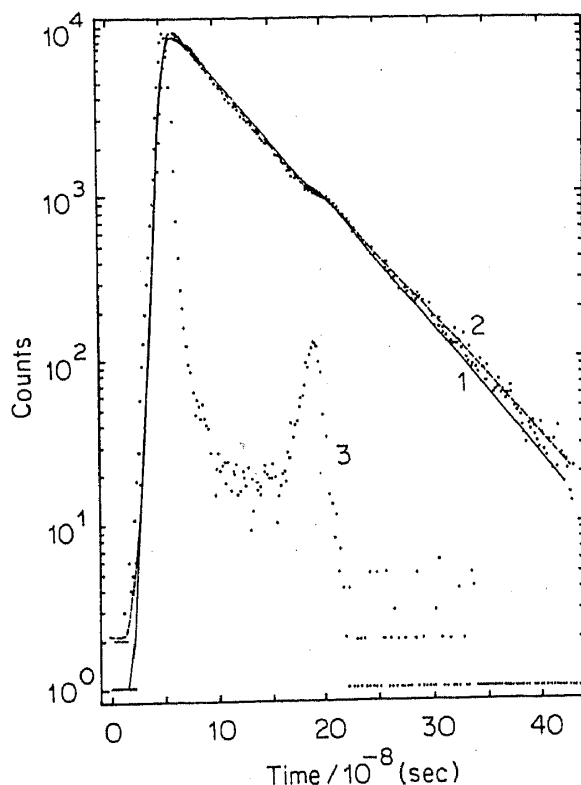
Figure 8. Decay curves for 10^{-4} M solution of (II) with 0·05 M *KI*. The data points are fitted in 1. Single exponential, 2. Fit using equation (12) and 3. Lamp profile.

Figure 8 shows the fit for monoexponential decays and transient equation for a typical 0·05 M quencher concentration for a glycerol-water solution of (II). The parameters calculated for this are also given in table 3b. Thus, 9-aminoacridinium hydrochloride is also suitable for testing the validity of the continuum model.

Acknowledgement

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