

## STUDY OF ELECTRON TRANSFER REACTION IN RHODAMINE 6G – AMINE SYSTEMS

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## ABSTRACT

Electron transfer (ET) reactions between excited Rhodamine 6G (Rh6G) dye and different amines, n-butyl amine (BTA) and triethyl amine (TEA) donors, have been investigated in the solvents DMF and DMSO using steady - state (SS) and time-resolved (TR) fluorescence quenching measurements. No ground state complex has been indicated in these systems. SS and TR measurements give similar quenching constants for each of the Rh6G - amine pairs, suggesting dynamic nature of interaction in these systems. <sup>1</sup>H NMR spectra of Rh6G without and with BTA and TEA have also been recorded and analyzed.

**Keywords:** Rh6G, n-butylamine, Triethyl amine, Fluorescence, <sup>1</sup>H NMR.

## INTRODUCTION

Electron transfer (ET) is one of the interesting subjects that have experienced extensive experimental and theoretical research for last few decades <sup>1-13</sup>. Studies on ET reactions have immense importance from the viewpoint of both academic and applied implications, as these reactions are ubiquitous in chemistry and biology. Understanding various factors that control ET reactions is the main impetus in most of the research on ET processes. Photo induced ET reaction, where either the acceptor or the donor is photoexcited to trigger the reaction, is the most suitable experimental scheme, and has been used quite extensively to investigate various factors that control the ET mechanisms and dynamics in various ET systems <sup>1-13</sup>.

In some of the earlier studies on bimolecular ET reactions<sup>14-22</sup>, it has been observed that the quenching process is largely dependent on the aliphatic and aromatic nature of the quenchers involved. In the present study bimolecular ET reactions in DMF & DMSO solutions have been investigated following the fluorescence quenching for a series of Rh6G dyes by different amines BTA and TEA donors to understand how the nature of the amines affect the ET process.

## MATERIALS AND METHODS

Rhodamine 6G, was purchased from Sigma Aldrich, Bangalore. Amine samples, n-butyl amine and triethyl amine were obtained from S.D fine chemicals (India).

Steady-state (SS) fluorescence spectra were measured in a VARIAN CARY ECLIPSE fluorescence spectrophotometer. Time-resolved (TR) fluorescence measurements were carried out using a HORIBA JOBIN YNON-SPEX F<sub>13</sub>-111 spectrofluorimeter. <sup>1</sup>H NMR spectra were recorded using Bruker 300 MHz (Ultrashield) NMR spectrometer.

## RESULTS AND DISCUSSION

## Steady-state and time-resolved fluorescence quenching studies

Ground state absorption spectra and steady-state (SS) fluorescence spectra of the Rh6G were recorded in DMF and DMSO solutions.

Table 1 lists the absorption maxima ( $\lambda_{abs}^{max}$ ) and fluorescence maxima ( $\lambda_{flu}^{max}$ ) of the Rh6G dye in DMF and DMSO solutions.

Table 1:  $\lambda_{abs}^{max}$ ,  $\lambda_{flu}^{max}$ , molar extinction coefficient and stoke's shift values of Rh6G in DMF and DMSO

Solvents	Quencher	$\lambda_{abs}^{max}$ (nm)	$\lambda_{flu}^{max}$ (nm)	Molar extinction co-efficient	Stoke's shift
DMF	BTA	535	561	7.825	866
	TEA	535	560	7.825	834
DMSO	BTA	540	564	7.829	788
	TEA	540	565	7.829	819

SS fluorescence quenching measurements for the Rh6G dye by amine donors were carried out in DMF and DMSO solutions. In these measurements, the samples were excited at the absorption maxima of the concerned Rh6G dye. From these measurements it is indicated that the fluorescence of Rh6G is significantly quenched by the two amines used in this study. The fluorescence spectral shapes of the dye, however, do not undergo any observable change in the presence of the amine donors. Typical SS results for Rh6G - BTA and Rh6G - TEA systems are shown in Figs. 1 to 4.

## Concentrations of TEA in DMSO

From the absorption measurements, it is seen that the absorption spectra of the dyes do not undergo any observable change in the presence of the amines. From the visually observed results, it is indicated that the excited Rh6G dye are mainly

interacted with the ground state amine donors, without involving any ground - state complex or emissive exciplex formation in these systems.

Quenching of the SS fluorescence intensity of Rh6G by amine donors were analyzed using stern - volmer (SV) relationship as,

$$I_0 / I = 1 + K_q \tau_0 [Q]$$

Where  $I_0$  and  $I$  are the fluorescence intensities at the emission maxima of the dye in the absence and presence of the quenchers (Q; amines)  $\tau_0$  is the fluorescence lifetime of the dye in the absence of Q and  $k_q$  is the bimolecular quenching constant. As expected, the ( $I_0/I$ ) versus [Q] plots were linear for all the Rh6G - amine systems studied. Typical such plots are shown in Figs. 5& 6 (in DMF and DMSO respectively).

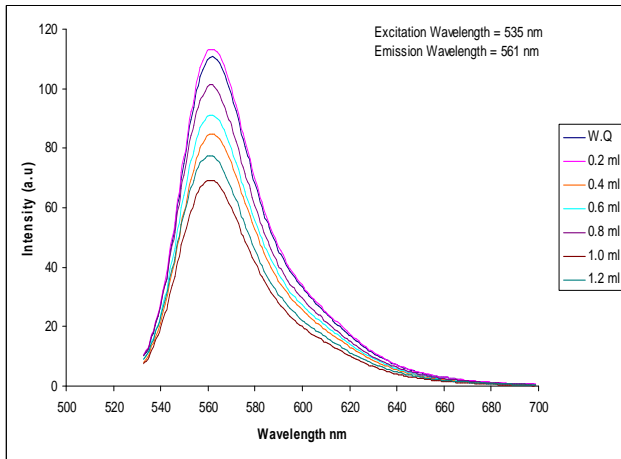


Fig. 1: Fluorescence Spectrum of Rh6G with different concentrations of TEA in DMF

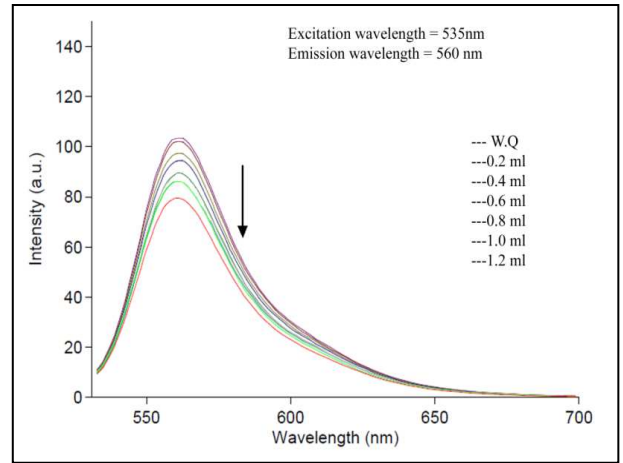


Fig. 2: Fluorescence Spectrum of Rh6G with different concentrations of BTA in DMF

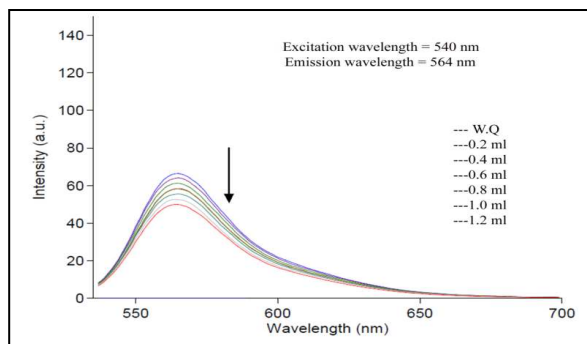


Fig. 3: Fluorescence Spectrum of Rh6G with different concentrations of BTA in DMSO

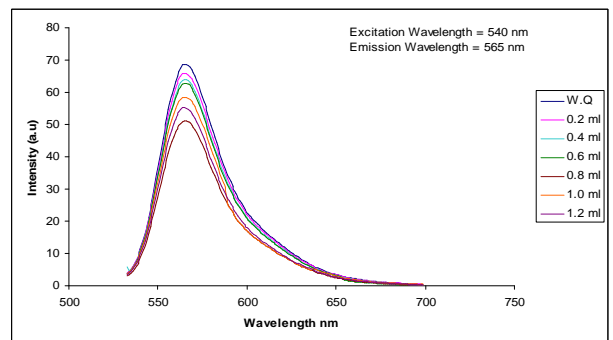


Fig. 4: Fluorescence Spectrum of Rh6G with different concentrations of TEA in DMSO

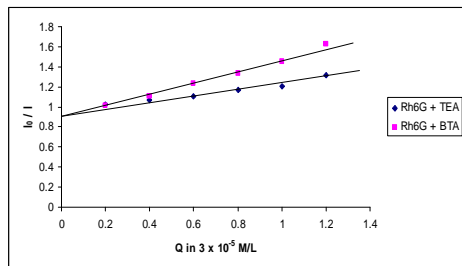


Fig. 5: Stern-volmer plot of Rh6G with BTA and TEA in DMF

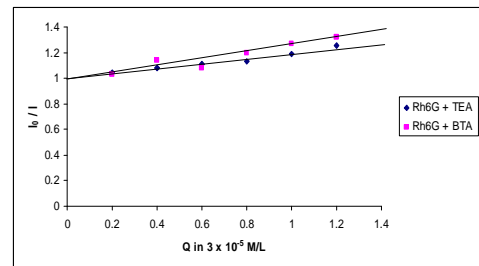


Fig. 6: Stern-volmer plot of Rh6G with BTA and TEA in DMSO

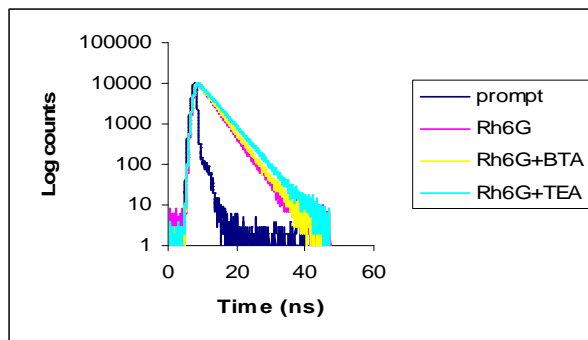


Fig. 7: Fluorescence decay curve of Rh6G without and with BTA and TEA

Time-resolved (TR) fluorescence quenching measurements for the Rh6G by amine donors were also carried out. The fluorescence decays, however, always follow a single exponential

function irrespective of the amine concentrations used. Typical of these results obtained for Rh6G-amine systems are shown in Fig.7.

Table 2:  $K_{sv}$ ,  $r$  and  $k_q$  values of Rh6G in DMF and DMSO

Solvents	Quenchers	$K_{sv}$		$r$	
		Calculated $10^5$	Graph $10^5$	Calculated	Graph
DMF	BTA	19.83	20.36	0.995	0.92
	TEA	9.30	10.3	0.984	0.94
DMSO	BTA	9.785	8.83	0.999	0.96
	TEA	6.652	5.6	0.9809	0.99

The values obtained from TR measurements for different Rh6G-amine systems are listed in Table 2.

### $^1\text{H}$ NMR spectral studies

The recorded  $^1\text{H}$  NMR spectra of Rhodamine 6G without and with n-butyl amine (BTA) and triethyl amine (TEA) are shown in figs. 8, 9 and 10 respectively.

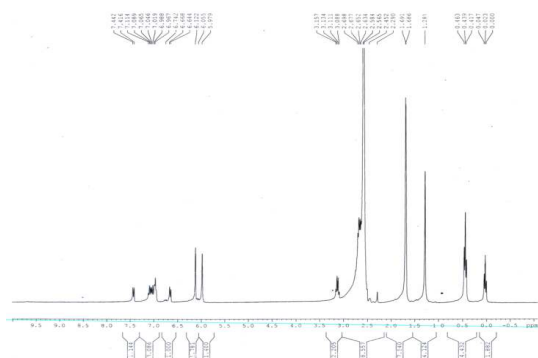


Fig. 8:  $^1\text{H}$  NMR spectrum of Rh6G BTA

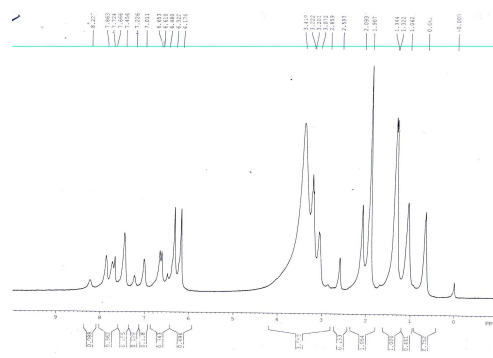


Fig. 9:  $^1\text{H}$  NMR spectrum of Rh6G +

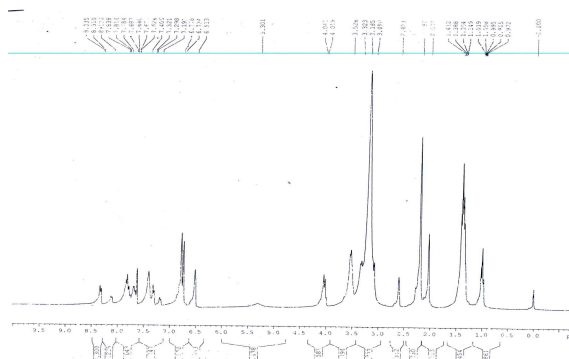


Fig. 10:  $^1\text{H}$  NMR spectrum of Rh6G + TEA

The spectral data and the change in chemical shift values are presented in Table 3.

Table 3:  $^1\text{H}$  NMR spectral data of Rh6G

Proton	Rh6G	Rh6g+BTA	Rh6g+TEA
H-1	7.5	2.0	7.7
H-2	6.8	-	1.3
H-3	7.0	3.3	-
H-4	2.6	-	3.1

### CONCLUSION

Kinetics of ET reaction in different Rh6G-amine systems has been investigated using fluorescence quenching studies in DMF and DMSO solutions. No ground-state complex formation has been indicated in these systems. The quenching constant values were calculated. The type of quenching is found to be dynamic in both DMF and DMSO solutions with BTA and with also TEA. Among the two quenchers n-

butyl amine is considered to be a best quencher in DMF and DMSO for Rh6G.

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