

THE DYNAMICS OF EXCITED CHARGE TRANSFER COMPLEXES IN NON IONIC MICELLES

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Exciplexes have been well characterized and their kinetics are now established^{(1) (2)} in simple solvents.

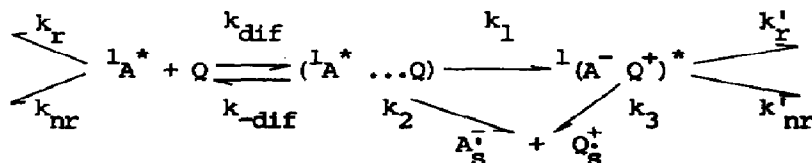
Recently Thomas⁽³⁾ has reported on the physical and chemical properties of charge-transfer complexes in micellar systems.

The present communication reports a study of the quenching of fluorescence of aromatic esters by triethylamine in non-ionic micelles, using transient and steady-state fluorescence techniques.

In the systems studied, the acceptor molecules are benzyl 9-anthroate (I) and benzyl 3-pyrenoate (II). These esters are insoluble in water and soluble in Triton X above the critical micelle concentration and their fluorescence increases linearly with the concentration of Triton X.

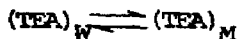
A comparison of the Stokes shift obtained for these esters in Triton X, with that obtained in several solvents, suggest that (II) is deeper located in the micelle than (I), the former having a surrounding media of polarity similar to diethyl ether, whereas (I) is probably nearer to the micelle surface.

Similarly to homogeneous solvents⁽⁴⁾, when triethylamine (TEA) is added to the system, the fluorescence of the esters is quenched due to the formation of a charge transfer complex, according to scheme I

SCHEME I

A - (I) or (II)
Q - (TEA)

The quencher (TEA) which acts as a donor is soluble in either water or Triton X and consequently is distributed among the two phases, an equilibrium being established.



This equilibrium is very fast compared with the diffusion in the micelle interior, making the last process the controlling step.

Whilst there is a concentration gradient in the micelle, the effective micelle concentration $[\text{TEA}]_M$ remains constant during the quenching process.

The quenching of fluorescence and fluorescence lifetimes studied in function of $[\text{TEA}]_M$, is represented in fig. 2.

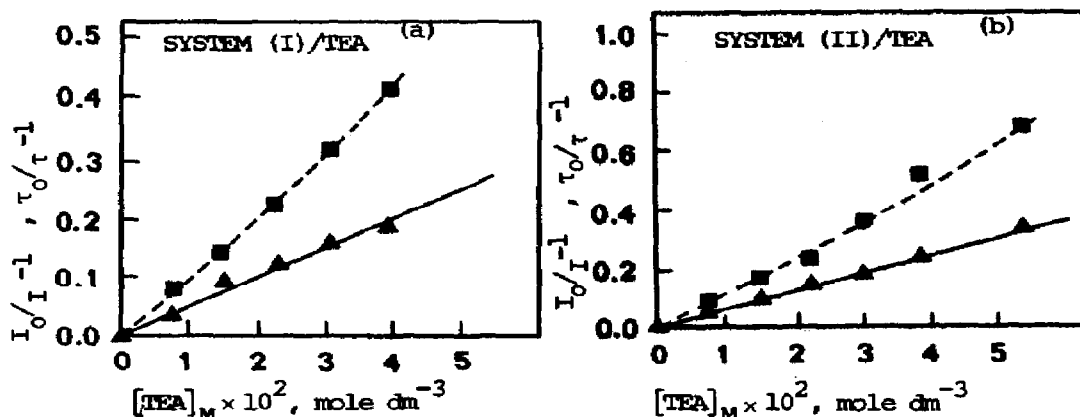


Fig. 2 - Quenching of fluorescence and fluorescence lifetimes by TEA

■ - $(I_0/I-1)_{\text{exptl}}$; ▲ - $(\tau_0/\tau-1)_{\text{exptl}}$; (---) Theoretical curve.

The derived rate constants are shown in table I.

TABLE - I

System	(a) $k_q \times 10^{-8}$ ($\text{dm}^3 \text{mole}^{-1} \text{s}^{-1}$)	(b) $k_q^{st} \times 10^{-8}$ ($\text{dm}^3 \text{mole}^{-1} \text{s}^{-1}$)	(c) $(k_q^{st})_{\text{cal.}} \times 10^{-8}$ ($\text{dm}^3 \text{mole}^{-1} \text{s}^{-1}$)	(d) $D \times 10^6$ ($\text{cm}^2 \text{s}^{-1}$)
(I)/TEA	4.8	8.6	8.2	0.9
(II)/TEA	8.1	15.2	14.5	1.6

a) from $\frac{\tau_0/\tau-1}{[\text{TEA}]_M} \approx k_q \tau_0$; b) from $\lim_{[\text{TEA}]_M \rightarrow 0} (I_0/I-1) / [\text{TEA}]_M = k_q^{st} \tau_0$;

c) $(k_q^{st})_{\text{cal.}} = k_q (1 + \frac{r}{\sqrt{\tau_0 D}})$ d) $D = k_q / 4\pi N^2 r$

The calculation of $[\text{TEA}]_M$ was made from an evaluation of the equilibrium constant which is established when the rate of entry in the micelle is equal to the rate of exit. The determination of the equilibrium constant was accomplished by two independent methods:

- a) Dependence of the quenching rate constant on the Triton-X concentration
- b) Dependence of the quenching rate on the pH

giving respectively the values of $k_e = 0.89$ and $k_e = 0.8$, which agree with each other.

The difference in the values of the constants obtained from steady state and transient measurements are attributed to transient effects on the diffusion controlled processes and indeed the results point out to the importance of the information gained from transient studies, whenever fluorescence lifetimes of the order of few nanoseconds are involved in systems of great viscosity such as micelles.

The diffusion coefficients are not constant inside the micelle and although D represents an average diffusion coefficient the experimental rate constants agree very well with the calculated ones.

The higher quenching efficiency obtained for (II) as regards to (I) is associated with a larger mobility of the former, reflected on the D values.

The rate constants k_q are also consistent with the value of $k_q = 3.4 \times 10^8 \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$ determined for the system pyrene-triethylamine in Triton-X⁽⁵⁾, since whereas pyrene is located in the inner micellar core, the esters being in the external core should suffer a stronger quenching.

References:

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