6P-14

THE 9-ANTHROATE CHROMOPHORE AS A FLUORESCENCE PROBE FOR WATER

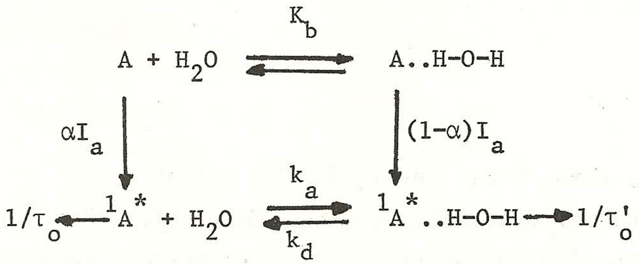
Fernando P. Costa, Sílvia M.B. Costa, Eurico C. Melo,
Manuel J. Prieto and António L. Maçanita
Centro de Química Estrutural, Complexo I
Instituto Superior Técnico
Av. Rovisco Pais, 1096 LISBOA CODEX - PORTUGAL

Photokinetics - The fluorescence quantum yield ϕ, and lifetime, τ, of methyl-9-anthroate strongly decrease in the presence of hydrogen bond donors, namely, in dioxane-water mixtures, ϕ and τ decrease 6 fold from pure dioxane to a mixture 24M in water.

From these data and from relative quantum yields of triplet formation it is concluded that i) the rate constant of intersystem crossing, k_{isc}, does not depend on water concentration, ii) the fluorescence rate constant, k_f, is almost constant, decreasing from 4.9×10^{7} s^{-1} in pure dioxane to 4.2×10^{7} s^{-1} in dioxane-water (24M), at 20°C and iii) the fluorescence quantum yields in the absence, ϕ_o, and presence, ϕ, of water, ϕ_o/ϕ, in dioxane, at 20°C are significantly larger than the correspondent fluorescence lifetimes ratios, τ_o/τ.

These results are interpreted on the basis of Scheme I, where a ground-state ester-water association is postulated.

Scheme I



In Scheme I, A represents, the methyl-9-anthroate ester, K_b is the ground-state equilibrium constant of ester-water association, k_a and k_d are the association and dissociation rate constants in the excited state, respectively and α is the molar fraction of free ester.

The fluorescence decays of 9-methylanthroate are independent of the emission wavelength and are single-exponential for all water concentrations, over the temperature range studied (20-80°C). These observations rule out the back-reaction (k_d) as a relevant process in the kinetics.

The ϕ and τ values and its temperature dependence were analysed in the context of this Scheme, yielding the following results: i) $k_a = 9\times10^6 M^{-1} s^{-1}$ at 20°C, two orders of magnitude lower than the diffusional limit and $E_a = 14.1$ kJ mol^{-1}($E_a = - R(d\ell n k_a/d(1/T))$. The value of the preexponential factor, $k_a^o = 3\times10^9$ $M^{-1}s^{-1}$,indicates severe enthropic restrictions, which are compatible with an hydrogen-bond formation. ii) $K_b = 0.5\times10^{-2} M^{-1}$ at 20°C.The van't Hoff plot of K_b is non linear, yielding a mean value of $\Delta H_b = -6$kJ mol^{-1} which is too low for an hydrogen bond. Both findings confirm that K_b is a pseudo equilibrium constant, containing the multiple equilibria between monomeric and self-associated water molecules.

An independent evidence for the postulated ground-state association was obtained, using FT-IR (Fourier Transform Infrared) spectroscopy, to monitor the stretching vibration of the anthroate carbonyl (1726 cm^{-1}). Upon addition of water, a new band at lower energies (1710 cm^{-1}), due to the hydrogen bound complex, is observed. From the integrated intensity of these two bands, the value of $K_b = 1.1\times10^{-2} M^{-1}$ is obtained which is of the same magnitude of the one given above.

Water Penetration in Micelles - The 9-anthroate chromophore attached to nth carbon atom of a stearic acid chain, n-(9-anthroyloxi) stearic acids(nAS), with n = 2, 6, 9 and 12, was included in Triton-X 100 (TX) and sodium docecylsulphate (SDS) micelles. Fluorescence lifetimes and quantum yields are presented in Table I.

TABLE I - Fluorescence quantum yields,ϕ,and lifetimes,τ,of 9-anthroate probes and calculated water concentrations,in Triton-X 100 and SDS, at 25°C.

		TX			SDS	
Probe	ϕ	τ,ns	$[H_2O]$, M	ϕ	τ, ^{a}ns	$[H_2O]$, M
A	0.21	9.2	5.3	0.05	1.6	52
2AS	0.14	9.1	6.2	0.07	1.9	43
6AS	0.31	9.9	4.0	0.08	3.8	20
9AS	0.41	12.4	1.9	0.12	4.6	15
12AS	0.55	14.3	0.3	0.12	5.4	12

(a) mean lifetimes from non exponential decays

The water concentration in the vicinity of each probe was calculated, from the fluorescence lifetimes, assuming the same value of k_a in dioxane and in the micellar media (the process is still reaction-controlled in micelles), Table I. In SDS,the water concentrations are much larger than those obtained in TX. Further, a gradual decrease in concentration with the increase of n is observed in both micelles.