Association of Tris(dipicolinato)terbium(III) Anions with Cetyltrimethylammonium Micelles in Aqueous Solution

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Precise measurement of the decay constant of the $^5D_4 \rightarrow {}^7F_J$ emission of tris(dipicolinato)terbium(III) in aqueous solution containing cetyltrimethylammonium micelles differentiates complex ions bound to the micelle and those in the bulk solution and permits the study of interionic interactions on the surface of the micelle although there is little change in the luminescence spectra of the two species.

Lanthanide ions are widely used as probes of the structure of complex macromolecular and biological systems. In optical spectroscopic studies, changes in the luminescence spectrum of Tb^{III} and Eu^{III} species resulting from coordination of the substrate to the metal ion have frequently been exploited.[1] Microheterogeneous systems involving micellar or liposome assemblies play an important rôle in drug delivery systems and in toxicological studies.[2,3]

There is a need for a method of studying the interaction of ions with the surface(s) of these assemblies, especially when the interaction is weak. In this communication we show that the decay constants of the emission from lanthanide complex ions are very sensitive to weak interactions with the micellar surface and with each other. This enables the study of the layer of ions surrounding the micellar assembly, even when spectral changes are too small to be informative. We have used the much studied lanthanide ion tris(dipicolinato)terbium(III), $Tb(PDC)_3^{3-}$ in aqueous and D_2O solution (pH 7.0) at room temperature, preliminary experiments showed that, in the presence of a small excess of the ligand, no other complex ion was detectable in solution [limit of detection <1% relative to $Tb(PDC)_3^{3-}$] in agreement with previous work.[4] We also use the familiar surfactant cation, cetyltrimethylammonium (CTA), introduced as the bromide salt, for which the critical micelle concentration (CMC) is 0.8 mmol dm^{-3}.

In addition to the CTA and $Tb(PDC)_3^{3-}$ the solutions contained significant concentrations of Cl^-, Br^-, PDC^{2-} and Na^+. Trial experiments showed that none of the results were dependent on moderate changes in the concentrations of these species (see below).

All decay curves were measured using excitation at 487.60 nm into the terbium $^7F_6 \rightarrow {}^5D_4$ transition from a pulsed dye laser (10 mJ per pulse at 11 Hz), observing the emission at 545 nm in the $^5D_4 \rightarrow {}^7F_5$ transition and averaging the decay curves over 1000–5000 pulses. A simplex optimization was used to extract the decay constant from the average curves. In all cases the decay curves were exactly exponential over more than six half-lives. Each decay curve on a given solution was measured at least four times, the results quoted are the average of these measurements. The results of these four determinations of the decay constant for some hundreds of solutions invariably agreed within ±2% (10 s^{-1}). Replicate measurements on different solutions agreed within the same precision. The precision of the results permits the reliable differentiation of decay curves differing by 3% (15 s^{-1}) or more.

The decay constant of the $^5D_4 \rightarrow {}^7F_5$ transition of 0.065 mmol dm^{-3} $Tb(PDC)_3^{3-}$ in aqueous solution under the conditions specified above is 321 ± 3 s^{-1}, increasing to 330 ± 3 s^{-1} as the concentration of $Tb(PDC)_3^{3-}$ is increased to 1.50 mmol dm^{-3}. Introduction of CTA to a solution of 0.065 mmol dm^{-3} $Tb(PDC)_3^{3-}$ at concentration above the CMC (1.5 mmol dm^{-3}) causes the decay constant to increase to 360 s^{-1}. We attribute this increase in rate on association with the micelle to the small distortion of the complex ion from D_3 symmetry which thereby enhances the electric dipole $^5D_4 \rightarrow {}^7F_J$ (J = 0–6) transitions of the complex ion. The luminescence spectrum of the $Tb(PDC)_3^{3-}$ emission is unchanged at the linewidths limited by inhomogeneous broadening in room temperature solutions.

Fig. 1 shows the change in the $^5D_4$ lifetime of $Tb(PDC)_3^{3-}$ for a solution of CTA above the CMC of CTA as the concentration of the complex ion is increased. At low concentrations of $Tb(PDC)_3^{3-}$ ions the complex ions compete with the much smaller Br^- and Cl^- for positions on the surface of the micelle but are isolated from each other, owing to the distortion the decay constant is faster than for a $Tb(PDC)_3^{3-}$ ion in free solution. As the concentration of $Tb(PDC)_3^{3-}$ is increased, the decay constant of the ions on the surface of the micelle increases due to increased distortion of the complex ion when there are neighbouring $Tb(PDC)_3^{3-}$ ions and/or changes in the micellar structure. The curve has a flat maximum when the CTA : $Tb(PDC)_3^{3-}$ concentration ratio is 1 : 3 to 1 : 4 corresponding to the complete coverage of the micelle by the complex ion thereby excluding the more weakly bound singly and doubly changed anions. At higher concentrations the decay constant decreases, since there is an equilibrium between micellar bound and bulk solution $Tb(PDC)_3^{3-}$ ions and their decay constant is a weighted average of the decay constant for the micellar $Tb(PDC)_3^{3-}$ ($k = 487 \pm 5\ s^{-1}$) and the free solution $Tb(PDC)_3^{3-}$ ($k = 330 \pm 3\ s^{-1}$). The exact exponential decay curve demonstrates that the exchange between the 'micellar associated' and 'free' complex ions is fast on a millisecond timescale.

Fig. 2 shows the variation in decay constant for fixed concentration of $Tb(PDC)_3^{3-}$ as the concentration of CTA is increased. The increase in k for [CTA] = 0–0.5 mmol dm^{-3} (*i.e.* below the CMC) is due to the association of $Tb(PDC)_3^{3-}$ with small aggregates of CTA molecules. The maximum at [CTA] = 0.5–1.0 is close to the CMC (0.8 mmol dm^{-3}). At higher values of [CTA] the decay constant decreases as the occupancy of the micellar surface sites decreases (*c.f.* Fig. 1).

The above analysis assumes that non-radiative relaxation of the $Tb(PDC)_3^{3-}$ $^5D_4$ excited state is slow. To confirm this, the experimental observations were repeated in D_2O solution where non-radiative processes might be expected to be much reduced. In the absence of CTA the decay constant of the $^5D_4$ state is only slightly reduced from 321 to 305 s^{-1} in D_2O, radiationless relaxation is therefore unimportant. As the CTA concentration is increased the decay constant increases initially slightly more rapidly than for the H_2O solutions (Fig. 2). However, the maximum difference between the rate

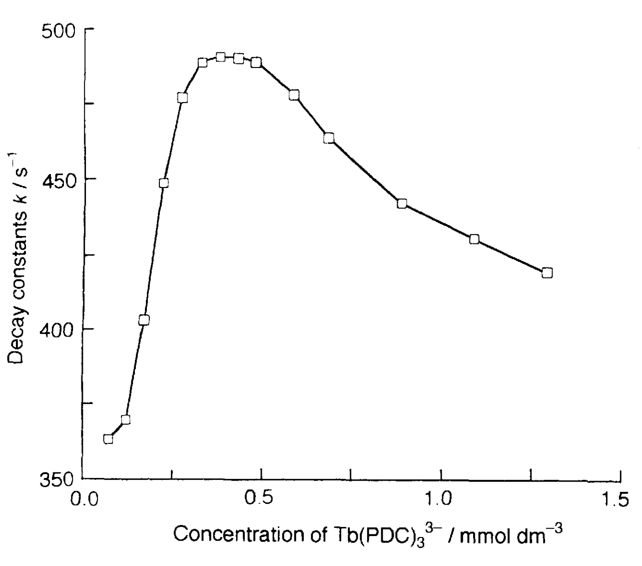

Fig. 1 The luminescence decay constant k/s^{-1}, of the $^5D_4 \rightarrow {}^7F_J$ transition of $Tb(PDC)_3^{3-}$ anion as a function of the concentration of $Tb(PDC)_3^{3-}$ for an aqueous solution containing 1.5 mmol dm^{-3} CTA at pH 7.0

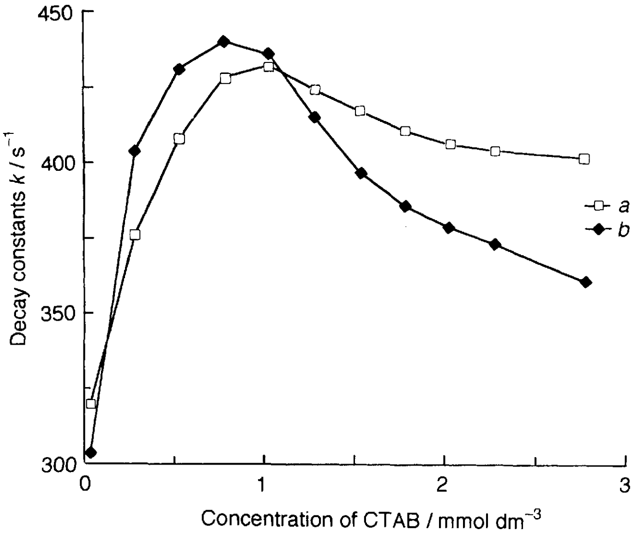

Fig. 2 (*a*) The decay constants, k/s^{-1}, as a function of the concentrations of CTAB (cetyltrimethylammonium bromide) in aqueous solutions containing [$Tb(PDC)_3^{3-}$] at 0.25 mmol dm^{-3} and pH 7.0; (*b*) as (*a*) except that all measurements were carried out in D_2O

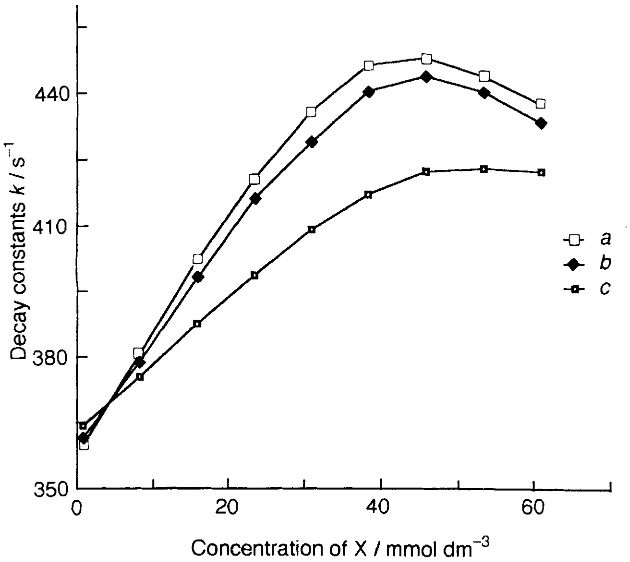

Fig. 3 Decay constants, k/s^{-1}, as a function of the added concentrations of NH_4Br (*a*), NH_4NO_3 (*b*) and NaCl (*c*) in a solution containing [$Tb(PDC)_3^{3-}$] = 0.1, [CTAB] = 2 mmol dm^{-3} and pH 7.0

constants is less than 15%, we attribute these differences in the maxima to a change in the CMC and/or ion–micelle interaction in H_2O and D_2O solutions.

Addition of Cl^-, Br^- or NO_3^- anions to a micellar solution when the micelle is only partially covered with the $Tb(PDC)_3^{3-}$ anion, causes an increase in the decay constant due to the distortion of the $Tb(PDC)_3^{3-}$ anion (Fig. 3) on the surface of the micelle by the incoming ion. The association of the mononegatively charged anions with the micellar surface is much weaker than for the trinegatively charged complex ions, however, at added anion concentrations above 40 mmol dm^{-3} they compete effectively for the available surface sites. There is then an equilibrium between the micellar bound complex ions and the complex ions present in bulk solution leading to a decrease in the decay constant. The effect of added anion on the decay constant for the micellar $Tb(PDC)_3^{3-}$ follows the sequence $Br^- \sim NO_3^- > Cl^-$, which is consistent with the reported sequence of binding affinity on the surface of micelles for Br^-, NO_3^- and Cl^-.[5]

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