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Energy Transfer from Triplet Aromatic Hydrocarbons to Tb^{3+} and Eu^{3+} in Aqueous Micellar Solutions

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Abstract: The sensitization of Tb^{3+} and Eu^{3+} luminescence by energy transfer from aromatic triplet donors like naphthalene, bromonaphthalene, biphenyl, and phenanthrene in micellar sodium lauryl sulfate solution has been studied. Formal second-order rate constants for the energy transfer process in the micellar solutions were determined as 5×10^5 and 1.8×10^5 M^{-1} s^{-1} for transfer from 1-bromonaphthalene to Eu^{3+} and Tb^{3+}, respectively, and 4×10^5 M^{-1} s^{-1} for transfer from biphenyl to Tb^{3+}. The method of converting these rate constants to second-order constants pertaining to the micellar microenvironment is discussed; it is estimated that the transfer process at the micelles is characterized by rate constants about one order of magnitude smaller than the formal ones. The transfer process is thus extremely slow.

Introduction

The early work[1] on energy transfer from excited aromatic ketones and aldehydes, either chelated to rare-earth (RE) ions or as collision partners, clearly showed that the transfer occurred from the triplet state of the sensitizer. It was also shown that the triplet energy of the sensitizer had to be greater than or close to the energy of the acceptor level of the rare-earth ion. In these respects the energy transfer process appeared to be similar to what had been observed in other triplet-triplet transfer reactions.[2,3] Later,[4,5] when collisional sensitized transfer was studied on a time-resolved basis, it was found that the second-order rate constants for the energy transfer to the RE ion were in the region of 10^6–10^8 M^{-1} s^{-1}, far below the normal exothermic triplet-triplet transfer rate of 2-5 $\times 10^9$ M^{-1} s^{-1}.

Subsequent work[6-8] on rare earth/aromatic aldehyde (and ketone) systems postulated that a complex between the excited sensitizer and the RE ion was formed prior to energy transfer, and that the length of time this complex existed governed the rate of the transfer reaction.[8]

Energy transfer from aromatic hydrocarbon triplets to RE ions had not been observed in fluid solution until recently (Fendler et al.).[9] It was shown that triplet naphthalene solubilized in an anionic micelle (sodium lauryl sulfate) was capable of sensitizing Tb^{3+} "bound" to the micelle surface. It was proposed, with some reservations, that the rate-limiting step of the transfer process is the diffusion of the naphthalene in the micelle to an encounter with surface-bound Tb^{3+}. In solution without the presence of a surfactant no sensitization of Tb^{3+} was observed. This result was attributed to naphthalene triplet-triplet annihilation reactions competing with the energy-transfer process.

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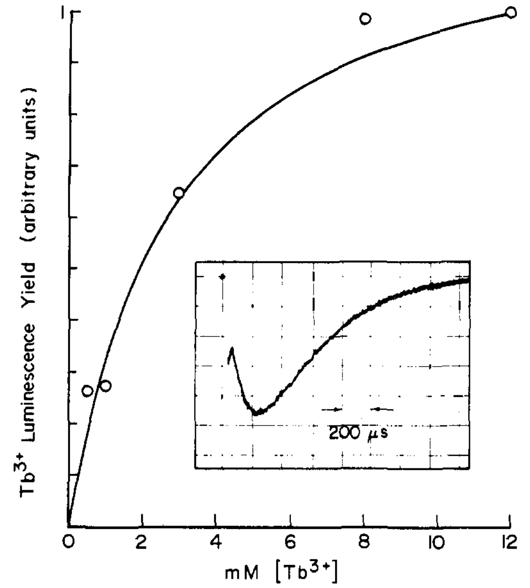

Figure 1. The relative yield of sensitized Tb^{3+} luminescence at 550 nm by triplet biphenyl. The biphenyl was excited at 280 nm. The full curve represents the calculated yield based on the parameters given in Figure 5 and eq 18 (also see text). The insert shows the growth and decay of the Tb^{3+} luminescence following flash excitation of a deoxygenated aqueous solution containing 12 mM $TbCl_3 \cdot 5H_2O$, ~10^{-4} M biphenyl, and 0.1 M NaLS.

In view of the results from the aldehyde and ketone sensitization of rare-earth ions, the diffusion-controlled mechanism for aromatic hydrocarbons seems unusual. In order to clarify the situation we have studied the triplet energy transfer process in micellar solutions using 1-bromonaphthalene and biphenyl as the sensitizers with Tb^{3+} and Eu^{3+} as acceptors. Our results indicate that the energy-transfer process is indeed slow, even in a micellar solution. Analysis of the kinetic processes which follow the initial excitation of the aromatic hydrocarbon shows that the excited arene can leave and reenter a micelle before triplet energy transfer to the RE ion occurs.

Experimental Section

1. Materials. 1-Bromonaphthalene and biphenyl obtained from Eastman Chemical Co. were used as supplied. Sodium lauryl sulfate (NaLS) specially pure was obtained from British Drug Houses Inc. and used as received. $EuCl_3 \cdot 6H_2O$ and $Tb(NO_3)_3 \cdot 5H_2O$, all ≥99.9% pure, were obtained from the Ventron Corp. Oxygen-free nitrogen (Airco) was used to deoxygenate the solutions. All micelle solutions were made with quadruply glass distilled water.

2. Procedure. A 0.1 M stock solution of the aromatic in benzene was prepared and aliquots were injected into a micelle solution to give ~10^{-4} M of arene in the system. To this micelle solution was added the required amount of Tb^{3+} or Eu^{3+} solution. These samples were than deoxygenated by bubbling with N_2 for about 0.75 h.

The sample was then excited by a 2.5-μs flash from a Xenon Corp. flash-lamp assembly; the emission produced at right angles to the excitation flash was monitored through a Bausch and Lomb monochromator, amplified by a 1P28 photomultiplier, and then displayed on a Tektronix 565 storage oscilloscope. This display was then photographed using 10 000 ASA Polaroid film for subsequent analysis.

Spectra and relative emission yields of excited Tb^{3+} and Eu^{3+} were measured on an Aminco-Bowman spectrophotofluorometer.

Results

The systems studied consisted of ~10^{-4} M aromatic probe, 0.1 M NaLS, and varying concentrations of either Tb^{3+} or Eu^{3+}. Addition of the RE solution to the micelle solution usually caused a precipitate to form which redissolved on stirring. The precipitate is presumably a RE lauryl sulfate compound which is redissolved by the excess NaLS present. At a particular surfactant concentration there is, however, a limit to the amount of RE that is solubilized. For 0.1 M NaLS, 15 mM of Tb^{3+} or Eu^{3+} is the upper limit for complete solubilization of the precipitate at room temperature.

The sensitizers which were observed to excite the terbium ion in deoxygenated micellar solution were biphenyl, phenanthrene, naphthalene, and 1-bromonaphthalene. The time scale over which this transfer was observed was between 200 μs and ~1 ms and similar for each of these four compounds. With the arenes pyrene and 1-bromopyrene no energy transfer was observed. The yield of the emission from excited Tb^{3+} and the decay rate of this emission were both dependent on the concentration of the ion. Figure 1 shows the variation of this dependence using biphenyl as the sensitizer. (The solid curve passing through the yield points is the result from computer simulation studies, and will be discussed in greater detail later.) The insert to Figure 1 shows the growth and decay of the Tb^{3+} emission at 550 nm. The initial portion of the trace is not shown, it is a sharp spike due to scattered light following the lamp discharge. The other sensitizers used also gave similar kinetic traces with comparable conditions to that shown for biphenyl. The intensity of the biphenyl fluorescence signal did not change as the [Tb^{3+}] was altered. This is a similar observation to that reported for naphthalene,[9] and supports the contention that the transfer to the Tb^{3+} ion is from the triplet state of the arene. This also explains why pyrene or 1-bromopyrene are not suitable sensitizers for Tb^{3+}, since their triplet states are energetically[10] too low to transfer to emitting levels of the Tb^{3+} atom. To study the behavior of the triplet level of an arene as well as the energy transfer kinetics to Tb^{3+}, 1-bromonaphthalene was used as a sensitizer. The bromine atom enhances the phosphorescence signal from the excited naphthalene so that it is easily monitored in deoxygenated micelle solutions.[11] This is not the case with the other sensitizers mentioned. Previous application[12] of solubilized 1-bromonaphthalene in NaLS solutions has given a detailed kinetic picture of the movement of this probe between the micelle and the bulk aqueous phase. Further, since the energy transfer under the conditions studied was relatively slow, such information is important in fully understanding the transfer mechanism.

1-Bromonaphthalene was also used in sensitizing Eu^{3+}; however, the luminescence signal from Eu^{3+} was considerably weaker than from the corresponding amount of Tb^{3+}. Also 1-bromonaphthalene was the only arene of the four mentioned which clearly showed sensitization of Eu^{3+}.[13]

The decay rate of phosphorescence from 1-bromonaphthalene as a function of Eu^{3+} and Tb^{3+} concentration is shown in Figure 2. As can be seen from this figure the quenching rate of Eu^{3+} is approximately three times greater than that for Tb^{3+}. Although the emission from directly excited Tb^{3+} and Eu^{3+} is much weaker than the sensitized emission, the luminescence signals can be monitored. From these signals the lifetimes of the Tb^{3+} ($^5D_4$) and Eu^{3+} ($^5D_0$) states in a micelle system without the presence of an arene were measured as 400 ± 20 and 100 ± 10 μs, respectively. Although the lifetimes are relatively long, the same values were obtained both in aerated and deoxygenated solutions. The low quenching rate of O_2 has been noted before and explained as due to the shielding effect exerted by the outer 4f electron orbitals.[1]

The many photophysical processes that can be involved in the excitation transfer reaction have been described by Fendler et al.,[9] and so will not be repeated here. We will consider only the reactions directly involved in the transfer sequence and those processes which pertain to the equilibria in a micelle/arene/RE system.

Following excitation of the aromatic probe the ensuing reactions in a deoxygenated solution can be formulated as follows.

$$_{\mathrm{M}}\mathrm{P}_{\mathrm{T}} \xrightarrow{k_1} {}_{\mathrm{M}}\mathrm{P} + h\nu \tag{1}$$

$$_{\mathrm{M}}\mathrm{P}_{\mathrm{T}} \xrightarrow{k_2} \mathrm{P}_{\mathrm{T}} + \mathrm{M} \tag{2}$$

$$\mathrm{P}_{\mathrm{T}} + \mathrm{M} \xrightarrow{k_3} {}_{\mathrm{M}}\mathrm{P}_{\mathrm{T}} \tag{3}$$

$$\mathrm{P}_{\mathrm{T}} \xrightarrow{k_4} \mathrm{P} + h\nu \tag{4}$$

$$_{\mathrm{M}}\mathrm{P}_{\mathrm{T}} + {}_{\mathrm{M}}\mathrm{RE} \xrightarrow{k_5'\bar{r}} {}_{\mathrm{M}}\mathrm{P} + {}_{\mathrm{M}}\mathrm{RE}^* \tag{5}$$

$$_{(\mathrm{M})}\mathrm{RE}^* \xrightarrow{k_6} {}_{(\mathrm{M})}\mathrm{RE} + h\nu \tag{6}$$

The subscript M indicates a micelle-bound species. The parentheses around M in reaction 6 indicate that the rate constant k_6 pertains to the rate of emission of the 5D level of the RE ion in a micellar solution—we do not know to what extent it actually stems from micelle-bound RE*. The energy transfer step (5) takes place between probe and RE ion bound to the same micelle. It is possible that other quenching processes are operating in parallel with energy transfer. The rate constant $k_5'\bar{r}$ includes these contributions as well. The rate constants k_1, k_4, and k_6 include radiationless deactivations and other inherent quenching modes in addition to spontaneous emission. The contribution from each individual pathway is not known. P_{T} and P refer to the triplet and ground states of the probe molecules. It is implicit in the above scheme that the micelle-bound RE ions are in rapid equilibrium with the aqueous phase, so that the probe in its triplet state experiences an average number of RE ions at the micelle surface. The rationale for this assumption is the following. The association rate constant in the equilibrium

$$\mathrm{RE} + \mathrm{M} \underset{k_-}{\overset{k_+}{\rightleftharpoons}} {}_{\mathrm{M}}\mathrm{RE}, \quad K = k_+/k_- \tag{7}$$

can be assumed diffusion controlled ($k_+ > 10^{10}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$) and, from Fendler's estimate of an equilibrium constant of 500 M^{-1} for Tb^{3+} on NaLS, k_- should then be about $2 \times 10^7\ \mathrm{s}^{-1}$. Therefore the characteristic time for establishing equilibrium is about 3×10^{-8} s, with a micelle concentration of 10^{-3} M ([NaLS] = 0.07 M). The equilibration time is more than two orders of magnitude shorter than the triplet lifetime of the probe.

The detailed interpretation of the pseudo-first-order rate constant $k_5'\bar{r}$ for the energy transfer at the micelle will be discussed below. We have assumed this rate constant to be proportional to the mean number $\bar{r}$ of RE ions at the micelle surface. At the low concentrations of RE ions employed (low in comparison to the total concentration of Na^+) $\bar{r}$ should be given by the equilibrium assumption (7)

$$\bar{r} = \frac{[{}_{\mathrm{M}}\mathrm{RE}]}{[\mathrm{M}]} = K[\mathrm{RE}]_{\mathrm{aq}} \tag{8}$$

or

$$\bar{r} = \frac{K}{K[\mathrm{M}] + 1}[\mathrm{RE}] \tag{9}$$

where $[\mathrm{RE}] = [{}_{\mathrm{M}}\mathrm{RE}] + [\mathrm{RE}]_{\mathrm{aq}}$. We can then introduce a formal second-order rate constant k_5 (at constant [M])

$$k_5 = k_5'\frac{K}{K[\mathrm{M}] + 1} \tag{10}$$

The rate equations associated with the mechanism above are then as follows:

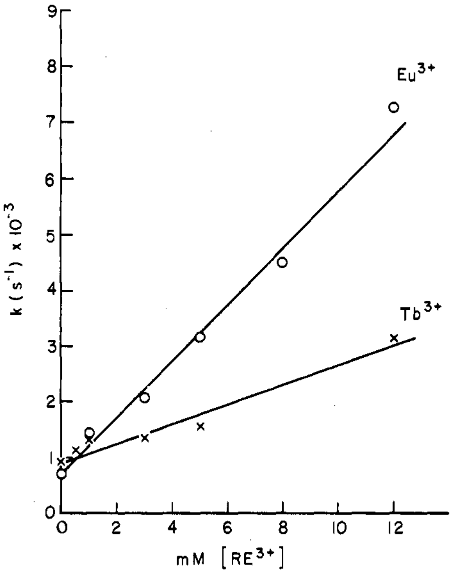

Figure 2. The pseudo-first-order decay rate of 1-bromonaphthalene phosphorescence as a function of the Eu^{3+} and Tb^{3+} concentrations in a 0.1 M NaLS micellar solution.

$$\frac{\mathrm{d}[\mathrm{RE}^*]}{\mathrm{d}t} = k_5[\mathrm{RE}][{}_{\mathrm{M}}\mathrm{P}_{\mathrm{T}}] - k_6[\mathrm{RE}^*] \tag{11}$$

$$-\frac{\mathrm{d}[{}_{\mathrm{M}}\mathrm{P}_{\mathrm{T}}]}{\mathrm{d}t} = k_5[\mathrm{RE}][{}_{\mathrm{M}}\mathrm{P}_{\mathrm{T}}] + k_1[{}_{\mathrm{M}}\mathrm{P}_{\mathrm{T}}] + k_2[{}_{\mathrm{M}}\mathrm{P}_{\mathrm{T}}] - k_3[\mathrm{P}_{\mathrm{T}}][\mathrm{M}] \tag{12}$$

$$-\frac{\mathrm{d}[\mathrm{P}_{\mathrm{T}}]}{\mathrm{d}t} = k_4[\mathrm{P}_{\mathrm{T}}] + k_3[\mathrm{P}_{\mathrm{T}}][\mathrm{M}] - k_2[{}_{\mathrm{M}}\mathrm{P}_{\mathrm{T}}] \tag{13}$$

Since the concentration of P_{T} in the aqueous phases is very small, the steady-state assumption

$$-\frac{\mathrm{d}[\mathrm{P}_{\mathrm{T}}]}{\mathrm{d}t} \simeq 0$$

can be made; then

$$[\mathrm{P}_{\mathrm{T}}] = \frac{k_2[{}_{\mathrm{M}}\mathrm{P}_{\mathrm{T}}]}{k_4 + k_3[\mathrm{M}]} \tag{14}$$

Substituting (14) into (12) one obtains

$$[{}_{\mathrm{M}}\mathrm{P}_{\mathrm{T}}]_t = [{}_{\mathrm{M}}\mathrm{P}_{\mathrm{T}}]_0 e^{-t/\tau_{\mathrm{P}}} \tag{15}$$

where

$$\tau_{\mathrm{P}}^{-1} = k_5[\mathrm{RE}] + k_1 + k_2 - \frac{k_2 k_3[\mathrm{M}]}{k_4 + k_3[\mathrm{M}]} = [\tau_{\mathrm{P}}^0]^{-1} + k_5[\mathrm{RE}] \tag{16}$$

τ_{P} and τ_{P}^0 are the phosphorescence lifetimes in the presence and absence of RE ions, respectively; continuing gives

$$[\mathrm{RE}^*] = \frac{k_5[\mathrm{RE}][{}_{\mathrm{M}}\mathrm{P}_{\mathrm{T}}]_i}{k_6 - \tau_{\mathrm{P}}^{1}}[e^{-t/\tau_{\mathrm{P}}} - e^{-k_6 t}] \tag{17}$$

Under the experimental conditions used $k_3[\mathrm{M}] \gg k_4$ (for 1-bromonaphthalene $k_3 = 7 \pm 1 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ from ref 12 and $k_4 = 2.5 \times 10^3\ \mathrm{s}^{-1}$, measured in N_2-saturated water). Equation 16 then simplifies to $\tau_{\mathrm{P}}^{-1} = k_5[\mathrm{RE}] + k_1$. Thus in this approximation $k_1 \simeq (\tau_{\mathrm{P}}^0)^{-1}$, i.e., the observed phosphorescence decay rate in the absence of any RE ions is approximately equal to the inherent lifetime of the triplet in a micelle environment.

In the measurements with 1-bromonaphthalene the donor phosphorescence could be observed. It decayed exponentially. Figure 2 presents the variation of the reciprocal phosphorescence lifetime with the quencher concentration. The values of

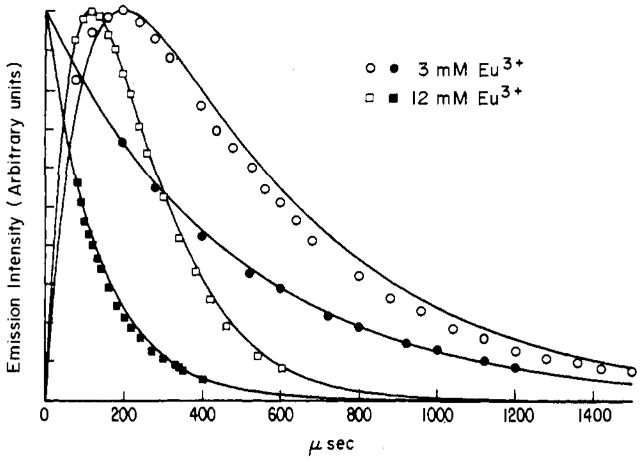

Figure 3. Experimental points and simulation curves from Eu^{3+} luminescence (at 590 nm) and phosphorescence (520 nm) decay of excited 1-bromonaphthalene at corresponding concentrations of Eu^{3+}. The parameters used in the simulations were $k_1 = 6.5 \times 10^2\ s^{-1}$, $k_2 = 2.5 \times 10^4\ s^{-1}$, $k_3 = 7 \times 10^9\ M^{-1}\ s^{-1}$, $k_4 = 2.5 \times 10^3\ s^{-1}$, $k_6 = 1.0 \times 10^4\ s^{-1}$, and $1/\tau_P = 2.0 \times 10^3$ and $7.3 \times 10^3\ s^{-1}$ for 3 and 12 mM Eu^{3+}, respectively. The micelle concentration used was 1.53×10^{-3} M. The maxima of the experimental and simulation curves of Eu^{3+} emission have been standardized to allow comparison of the kinetic forms (similarly for the phosphorescence decays).

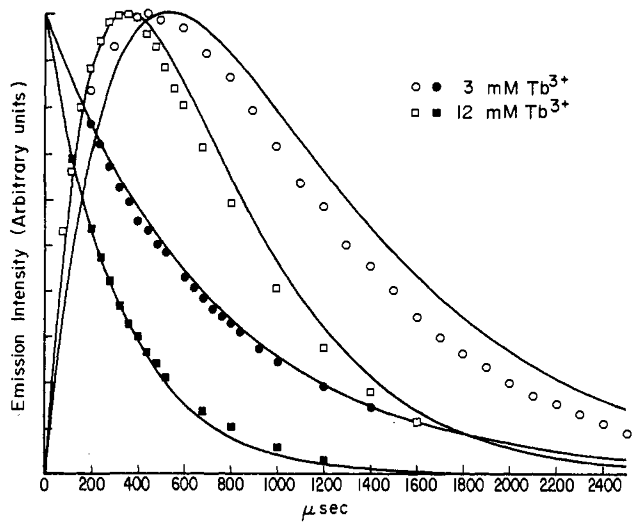

Figure 4. Experimental points and simulation curves from Tb^{3+} luminescence (λ 550 nm) and phosphorescence decay of excited 1-bromonaphthalene (at 520 nm) at corresponding concentrations of Tb^{3+}. At the lower concentration of Tb^{3+}, there is a significant contribution of the phosphorescence emission at 550 nm; this causes the poor match between the experimental and simulated curves. The parameters used to obtain the simulated curves were $k_1 = 9.4 \times 10^2\ s^{-1}$, $k_2 = 2.5 \times 10^4\ s^{-1}$, $k_3 = 7 \times 10^9\ M^{-1}\ s^{-1}$, $k_4 = 2.5 \times 10^3\ s^{-1}$, $k_6 = 2.5 \times 10^3\ s^{-1}$, and $1/\tau_P = 1.4 \times 10^3$ and $3.2 \times 10^3\ s^{-1}$ For 3 and 12 mM Tb^{3+}, respectively. [M] = 1.53×10^{-3} M.

the rate constant k_5 are obtained from the slopes of the linear plots of 5×10^5 and $1.8 \times 10^5\ M^{-1}\ s^{-1}$ for Eu^{3+} and Tb^{3+}, respectively. The significance of these values will be discussed in the following section.

The growth and decay of the RE luminescence were simulated using eq 17. For 1-bromonaphthalene as donor τ_P was taken from the measured phosphorescence decay; k_6 was independently determined in micellar solutions of the RE ions without arenes as described earlier. For the 1-bromonaphthalene-Eu^{3+} system reasonable fits were obtained over most of the RE concentration range (Figure 3). In the case of Tb^{3+} (Figure 4), the experimental data at low Tb^{3+} concentrations ($\leq$3 mM) deviate significantly from the simulated curve. This is due to substantial contributions of 1-bromonaphthalene phosphorescence at the wavelengths used for monitoring the Tb^{3+} emission. The emission lines from sensitized Eu^{3+} at 590 and 615 nm still overlap with the phosphorescence emission band, but not quite to the extent of the 550-nm emission of the Tb^{3+} ion. At concentrations below ~3 nM of Eu^{3+} deviations of the simulated curve from the experimental trace become increasingly more severe. In this concentration region contributions to the emission monitored at 590 and 615 nm from phosphorescence and sensitized luminescence become comparable.

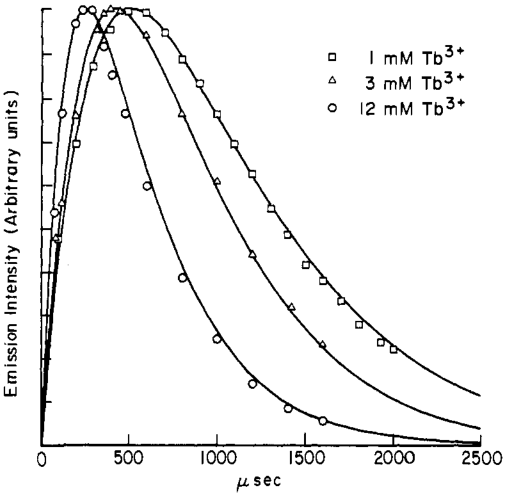

Figure 5. Experimental points and simulation curves for the sensitized luminescence of Tb^{3+} by biphenyl at various concentrations of Tb^{3+}. The parameters used in the simulation were $k_1 = 1.1 \times 10^3\ s^{-1}$, $k_2 = 1 \times 10^5\ s^{-1}$, $k_3 = 7 \times 10^9\ M^{-1}\ s^{-1}$, $k_4 = 2.5 \times 10^3\ s^{-1}$, $k_5 = 4 \times 10^5\ M^{-1}\ s^{-1}$, $k_6 = 2.5 \times 10^3\ s^{-1}$, and [M] = 1.53×10^{-3} M.

The parameters used in the simulation curves for the 1-bromonaphthalene-Tb^{3+} and -Eu^{3+} systems could be determined independently and no "fitting" of calculations to experimental data was justified. However, with the energy transfer of ^{3}biphenyl to Tb^{3+} the triplet lifetime of biphenyl could not be measured and, in the simulations presented in Figure 5, the transfer rate and the triplet lifetime were varied to obtain the fits shown. The exit rate of biphenyl has been measured as $1 \times 10^5\ s^{-1}$ in a previous study[12] and has been used in the simulation. The lifetime of τ_{P0} = 910 μs obtained with the simulation fits is of the order obtained in other studies[14] and can be considered a reasonable value. At RE concentrations less than ~3 mM the simulated decay of the sensitized emission was mostly dependent on the value of biphenyl triplet lifetime, whereas at higher RE concentrations (>3 mM) the simulated decay was predominantly affected by the transfer rate, k_5. The values used for the triplet lifetime ($\tau_P{}^0$) and quenching rate were the best set in obtaining a good fit to the experimental curves, and can be considered as unique to this system.

It is perhaps also worthwhile to comment briefly on the probe-micelle exit and reentry values used in the simulation. Since the reentry rate is considerably faster (k_3[M] = $1.1 \times 10^7\ s^{-1}$) than the lifetime of the excited probe in the bulk water phase ($1/\tau = 2.5 \times 10^3\ s^{-1}$), the value used for the exit rate is not a very sensitive parameter in the simulation. This is of course shown in the simplified form of eq 16. For completeness the measured values of (1) have been incorporated in the simulation.

Steady-state measurements of the RE ion luminescence intensity gave results given in Figures 1 and 6. An expression

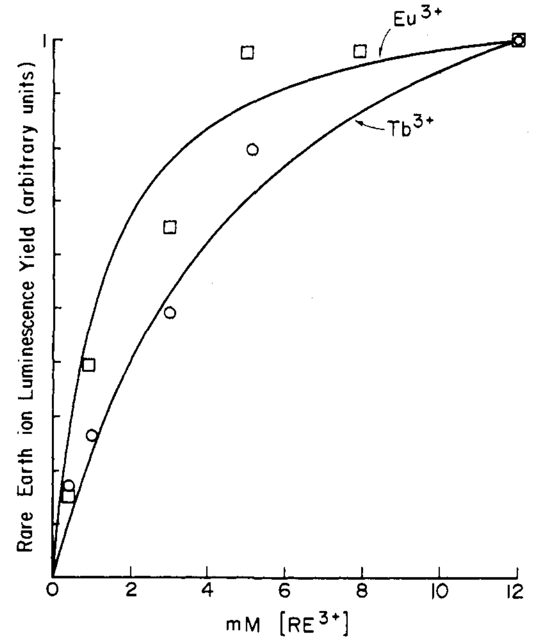

Figure 6. The steady-state yields of 1-bromonaphthalene sensitized emission of Tb^{3+} and Eu^{3+} as a function of the RE concentration. The full curves are calculated yields using the values in Figures 3 and 4 and eq 18. The experimental points have been corrected for the phosphorescence contribution at the wavelengths measured, 550 and 590 nm for Tb^{3+} and Eu^{3+}, respectively.

for the variation of the RE luminescence intensity, I_{RE}, with the RE concentration is simply obtained by integration of eq 17:

$$I_{RE} \propto \frac{k_5[RE]}{k_5[RE] + (\tau_P{}^0)^{-1}} \tag{18}$$

Using the values for k_5 and $\tau_P{}^0$ obtained in the time-resolved studies, and standardizing the expression with the maximum intensity observed experimentally, we obtain the solid curve shown in Figure 1 for the transfer of ^{3}biphenyl to Tb^{3+}. Figure 6 shows the results with the Eu^{3+} and Tb^{3+} and 1-bromonaphthalene as the sensitizer. Although the experimental scatter is quite high in the latter figure, a reasonable correlation is still seen.

Discussion

We have found that the results from both the time-resolved and the static measurements are in reasonable agreement with the proposed reaction scheme, eq 1-7. The resulting quantity, k_5, the experimentally obtained second-order rate constant for energy transfer in micellar NaLS solutions, has been determined for 1-bromonaphthalene with Tb^{3+} and Eu^{3+} as acceptors, and for biphenyl with Tb^{3+} as the acceptor, in all cases with a surfactant concentration of 0.1 M.

The rate constant k_5 is related to a pseudo-first-order constant k_5' through eq 10. The constant k_5' gives the probability per unit time for energy transfer in micelles containing one donor and one acceptor. Unfortunately the ion binding constants seem to be too small for a sensitive test of eq 10 by variation of the surfactant concentration. Fendler et al. have[9] estimated K for Tb^{3+} with NaLS micelles as 500 ± 100 M^{-1} by an NMR method. The product $K[M]$ is then about 1 at a NaLS concentration of 0.1 M. k_5 may thus be increased at most by a factor of 2 by decreasing the surfactant concentration, and we have found previously[12] that complications arise at NaLS concentration appreciably higher than 0.1 M.

Although it is far from certain that the fraction of ions that is deemed as bound in NMR measurements is the same as that which is reactive in the energy transfer process—or in micellar catalysis in general—we use the NMR value $K = 500\ M^{-1}$ for Tb^{3+}, NaLS, and obtain $k_5' = 6.2 \times 10^2\ s^{-1}$ for transfer from 1-bromonaphthalene and $k_5' = 1.4 \times 10^3\ s^{-1}$ for transfer from biphenyl.

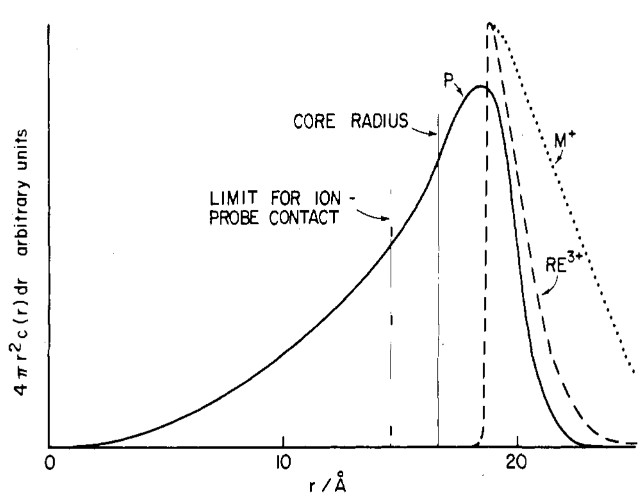

Figure 7. A schematic representation of possible distributions in and at a NaLS micelle of a probe with slight preference for the surface (full drawn curve), and ions with a charge of +3 (dashed curve) and +1 (dotted curve). It has been assumed that the probe radius is 2 Å and the ion radii are 2.3 Å. For further discussion see text.

No corresponding binding constant is available for Eu^{3+} in NaLS. However, it is clear that stronger binding of Eu^{3+} ions than Tb^{3+} ions to NaLS cannot be the only reason for the increase in the energy transfer rate by a factor of 3 in the former case. Even with $K[M] \gg 1$ for Eu^{3+} this would still only give an increase by a factor of 2. It seems reasonable to assume that Eu^{3+} and Tb^{3+} are bound about equally strong, which then yields a value of $k_5' = 1.8 \times 10^3\ s^{-1}$ for triplet 1-bromonaphthalene sensitization of Eu^{3+}.

To compare the effectiveness of the triplet energy transfer between the arenes and the RE ions with that between other species we have to convert the pseudo-first-order rate constant k_5' into a second-order rate constant. There is no unambiguous way of doing this. Since it is a problem of general importance in micellar catalysis we will discuss in some detail our semiquantitative approach.

Figure 7 shows schematically how we consider the arene and the RE ions to be distributed in and around the micelle. In constructing this figure we have been guided by our earlier treatment of solubilization[12] and by some recent calculations by Aniansson[15] on how the dynamic protrusion of the micelle monomers into the aqueous phase affects the size of the hydrocarbon core, the average distribution of the head groups, and the potential outside the micelle surface.

The solid curve in Figure 7 represents the distribution of the arene in the micelle as the probability of finding the probe in a spherical shell of thickness dr at a distance, r, from the center of the micelle. We have assumed that the concentration of probe in the core is constant everywhere, which means that the distribution grows as r^2. We assume a slight preference for the surface region—evidence for a preferential solubilization at the surface in the case of aromatic molecules has been discussed recently.[12,16] We have arbitrarily assumed a radius of 2 Å for the arene; however, we assume that the arene may protrude appreciably out into a region where it is not in contact with the core surface. This is to allow for the possibility that the arene to some extent follows the monomers in their protrusion. Aniansson has shown that the *average* protrusion of a monomer is 1.6 CH_2 groups—or close to 2 Å—and that as much as ⅓ of the monomers protrude beyond 2 Å.

The distribution curves for the ions have been calculated using the potential calculated by Aniansson. This potential curve is a crude one, calculated within the Gouy formalism, but taking the varying protrusions of the head groups into account. This makes the distribution of the ions much broader than what is usually anticipated. The dotted curve, representing a monovalent ion, has a half-maximum width of about 4 Å. The curve for the RE^{3+} ion is of course considerably narrower.

The exact forms of the distribution curves are not important for the present approximate arguments. We regard the RE ion as residing in a spherical shell with a width of 2 Å, centered around $r = 19.5$ Å. RE ions in this shell may come into contact with probe molecules located from 2 Å inside the core radius and further out, which means about half the probe molecules as the distribution has been sketched. For many aromatic molecules the fraction is probably closer to unity. Even in a case where the probe molecule is confined to the core and the distribution goes rather abruptly to zero at the core radius, it would still have an appreciable probability of coming in contact with a water-bound ion.

However, compared to the situation in free solution there are severe restrictions in the possibilities for contact between the reaction partners. The arene molecules inside the hydrocarbon core are all more or less buried, but also those further out are envisaged as being partly covered by hydrocarbon chains. To take this into account we introduce a steric factor, roughly taken as $\frac{1}{3}$.[17]

We may now calculate a second-order rate constant as follows:

$$k_{\mathrm{ET}} = k_5'/(\text{fraction of probe at surface} \times \text{steric factors} \times \overline{V}_{\mathrm{SL}}^{-1})$$

where $1/\overline{V}_{\mathrm{SL}}$ is the concentration corresponding to one RE ion in the volume of the shell mentioned above.

With the fraction of probe molecules at the surface taken as $\frac{1}{2}$, the steric factor as $\frac{1}{3}$, and 0.17 M as the concentration of RE ions we obtain

$$k_{\mathrm{ET}} = 2 \times 10^4\ \mathrm{M^{-1}\ s^{-1}} \text{ for 1-bromonaphthalene, } \mathrm{Tb^{3+}}$$

$$k_{\mathrm{ET}} = 6 \times 10^4\ \mathrm{M^{-1}\ s^{-1}} \text{ for 1-bromonaphthalene, } \mathrm{Eu^{3+}}$$

$$k_{\mathrm{ET}} = 5 \times 10^4\ \mathrm{M^{-1}\ s^{-1}} \text{ for biphenyl, } \mathrm{Tb^{3+}}$$

These strikingly low energy transfer rate constants are in agreement with the fact that no quenching of 1-bromonaphthalene phosphorescence could be detected in aqueous solutions with Eu^{3+} or Tb^{3+} as quenchers. Considering the concentrations of RE ions used, this indicates an energy transfer rate constant lower than $5 \times 10^5\ M^{-1}\ s^{-1}$. In comparison with energy transfer rate constants of the aromatic aldehyde and ketones, these aromatic hydrocarbon values are two to three orders of magnitude lower. The results are also in agreement with the quenching rate constants of $10^5\ M^{-1}\ s^{-1}$ and less, reported by Porter and Wright[18] for the quenching of naphthalene triplet by RE ions.[19] Porter and Wright[18] pointed out the fact that the unpaired electrons of the RE ions are deeply buried in the f shells. The interaction between the unpaired electrons of the triplet and the RE ions is then very weak and, if the transfer occurred via a resonance-exchange[20] pathway, this would explain the low energy transfer rate. It is not clear from our data whether or not the actual mechanism involves an exchange of a water molecule in the hydration sphere of the RE ion for the triplet arenes. Such a ligand exchange mechanism and other types of complex formation have been proposed for energy transfer from aromatic ketones and aldehydes to RE ions.[4b,6-8]

One other explanation of the slowness of the transfer rate which was considered was the case of a reversed energy transfer[3] from the excited ion back to the deactivated aromatic hydrocarbon. In particular, the pair 1-bromonaphthalene and Tb^{3+} have excited states which are close in energy. We studied the lifetime of the Tb^{3+} emission in micellar solutions with increasing concentrations of the arenes. The solutions were aerated so that the arene triplet lifetime was short. No change in the Tb^{3+} emission rate could be detected. This shows that reverse transfer was not a complication in our study of the arene–Tb^{3+} transfer.

Another aspect of the low transfer rate is that the excited probes 1-bromonaphthalene and biphenyl, which have micelle exit rates of 2.5×10^4 and $1 \times 10^5\ s^{-1}$, respectively, actually migrate from micelle to micelle before transfer takes place. They nevertheless spend most of their time with the micelles. The micelle, by organizing the acceptor and donor molecules in a discrete volume region, has facilitated the energy transfer reaction above inherent quenching processes of the donor in homogeneous solution. This feature illustrates the importance of aggregated systems such as those of biological membranes which to some extent are mimicked by the micelle.

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(14) Many of the arenes which do not give a measurable phosphorescence signal in micellar solution can have their phosphorescence yield enhanced by the addition of Tl^+ (see ref 11). Though the yield of phosphorescence increases with the addition of Tl^+, the lifetime of the phosphorescence signal remains constant (at least up to 12 mM Tl^+ in 0.1 M NaLS). For biphenyl in NaLS the lifetime measured in this study was ~1 ms.
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