

representative of a cyclic compound. Ketene and butatriene are examples of molecules with adjacent double bonds and are taken here only for a comparison. The nonadditivity in these molecules has been demonstrated in the preceding sections. Significant differences of the estimated and calculated values are observed only in CH_2CCCH_2 , H_2CCO , and HCCCCCH . Little difference is found in butadiene and formic acid (both with conjugated double bonds) as well as in cyclic C_3H_4 . Since the bond lengths in these molecules exhibit significant changes in comparison with bonds in molecules from which the bond contributions were calculated, the conclusion about the additivity in these cases requires further study. For example, it may be the result of the mutual compensation of changes in individual bond energies in single and double bonds.

Concluding Remarks

The results presented in this paper show some interesting regularities in correlation effects in molecules. In our analysis the dependence of the correlation energy on the specific bonding character in the molecule is stressed. Systems with single C-C bonds have the lowest values of the correlation energy. The multiple bonds generally increase its value. This effect is reinforced when the adjacent double bonds are present. The conjugation leads to no substantial effect; the same also holds for the cyclic compounds. The higher (triple and quadruple) excitations are important especially in molecules with multiple bonds and with adjacent double bonds. The percentage participation of triple and quadruple excitations in alkanes exhibits an increase with the number of electrons. However, this increase is so small that it cannot be taken as significant, so that no definitive conclusions on the role of higher excitations in extended systems may be drawn (we recall the forecast of Davidson⁴⁰ on the important role of

higher excitations in very extended systems; of course, also higher than quadruple excitations come into consideration). The problem of the correlation energy in extended systems is very topical in the present-day quantum chemistry. Since presently it is not possible to obtain reliable ab initio data on such systems directly, some investigations may be inferred from results of calculations for model systems, see, e.g., ref 41-44.

Since we have used the canonical orbitals, we cannot analyze the contributions to the correlation effects from individual orbitals. This requires the use of localized orbitals (within the MB-RSPT and CCSD scheme, the use of localized orbitals has been pioneered by Laidig, Purvis, and Bartlett;⁴⁵ at the semiempirical level localized orbitals have been used by Kapuy et al.⁴⁶ through the fifth order of MB-RSPT). Nevertheless, our results are useful in energy predictions. The knowledge of regularities in correlation energies may be helpful in the prediction of enthalpies of chemical reactions, relative energies of various isomers, etc.

Acknowledgment. V.K. is grateful to the DAAD for providing a fellowship for a stay in Garching.

Registry No. CH_4 , 74-82-8; C_2H_2 , 74-86-2; C_2H_4 , 74-85-1; $\text{CH}_3-\text{C}-\text{H}_3$, 74-84-0; $\text{CH}_3-\text{CH}_2-\text{CH}_3$, 74-98-6; $\text{CH}_3-\text{CH}=\text{CH}_2$, 115-07-1; $\text{H}_2\text{C}=\text{C}=\text{CH}_2$, 463-49-0; $\text{H}_2\text{C}=\text{C}=\text{C}=\text{CH}_2$, 2873-50-9; $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, 106-99-0; $\text{CH}_3-\text{C}\equiv\text{CH}$, 74-99-7; $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$, 460-12-8; $\text{CH}=\text{CH}-\text{CH}_2$, 2781-85-3; H_2O , 7732-18-5; H_3O^+ , 13968-08-6; CO , 630-08-0; CO_2 , 124-38-9; CH_3OH , 67-56-1; H_2CO , 50-00-0; HCOOH , 64-18-6; $\text{H}_2\text{C}=\text{C}=\text{O}$, 463-51-4.

(41) Bartlett, R. J.; Purvis, G. D. *Ann. N.Y. Acad. Sci.* **1981**, 367, 62.
(42) Takahashi, M.; Paldus, J.; Čížek, J. *Int. J. Quantum Chem.* **1983**, 26, 707.

(43) Malrieu, J. P. *J. Chem. Phys.* **1979**, 70, 4405.
(44) Sasaki, F. *Int. J. Quantum Chem. Symp.* **1977**, 11, 125.
(45) Laidig, W. D.; Purvis, G. D., III; Bartlett, R. J. *Int. J. Quantum Chem.* **1982**, 16, 561.

(46) Kapuy, E.; Csépes, Z.; Kozmutza, C. *Int. J. Quantum Chem.* **1983**, 23, 981.

(40) Davidson, E. R. In "The World of Quantum Chemistry"; Daudel R., Pullman B., Eds.; D. Reidel: Dordrecht, Holland, 1974; pp 17-30.

Energy Transfer in Inverse Micelles

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Abstract: Energy transfer between several naphthalene derivatives and Tb^{3+} in inverse micelles of dodecylammonium propionate and water in cyclohexane was found to be very efficient. In the case of the micelle-bound probes, the efficiency is determined by the donor and acceptor concentrations, the distance between the chromophore and the water pool, the water concentration, and the rate of intermicellar collisions. From the results it could be deduced that the apolar tails of the probes are time-averaged nonfolded and that the probe location is dependent on the water concentration. A kinetic scheme allows the estimation of the rate of solubilization exchange between micelles by intermicellar collisions. Because of a very rapid exchange ($k_E \approx 10^9 \text{ M}^{-1} \text{ s}^{-1}$), the Poisson distribution of probe and quenchers has no influence on the kinetics.

Some decades ago, mainly by the groups of Weissman¹ and Crosby², it was found that luminescence of rare-earth (RE) ions can be sensitized by excited aromatic ligands. They concluded that the transfer occurred from the triplet state of the sensitizer.

That the sensitizer need not to be chelated to the RE ion was indicated by Heller and Wasserman,³ studying the transfer facilities of several aromatic aldehydes and ketones to Tb^{3+} and Eu^{3+} .

Although it was originally assumed that this process was diffusion controlled, it follows from more recent work that the energy transfer is slower than for a diffusion-controlled process.⁴

Energy transfer from the triplet state of aromatic hydrocarbons to Tb^{3+} could be measured at 77 K. From these studies, Weller et al.⁵ concluded that the transfer process occurred at short dis-

(1) Weissman, S. I. *J. Chem. Phys.* **1942**, 10, 214. (b) Yuster, P.; Weissman, S. I. *Ibid.* **1949**, 17, 1182. (c) Weissman, S. I. *Ibid.* **1950**, 18, 1258.

(2) (a) Crosby, G. A.; Kasha, M. *Spectrochim. Acta* **1958**, 10, 377. (b) Crosby, G. A.; Whan, R. E.; Alire, R. M. *J. Chem. Phys.* **1961**, 34, 744. (c) Freeman, J. J.; Crosby, G. A. *J. Phys. Chem.* **1963**, 67, 2717.

(3) Heller, A.; Wasserman, E. *J. Chem. Phys.* **1965**, 42, 949.

(4) (a) Morina, V. F.; Ermolaev, V. L.; Khudenskii, Yu. K. *Opt. Spectrosc. (Engl. Transl.)* **1967**, 23, 349. (b) Ermolaev, V. L.; Tachin, V. S. *Ibid.* **1971**, 31, 316. (c) Wagner, P. J.; Schott, H. N. *J. Phys. Chem.* **1968**, 72, 3702. (d) Lamola, A. A.; Eisinger, J. In "Molecular Luminescence"; Lim, E. C., Ed.; W. A. Benjamin: New York, 1969. (e) Ermolaev, V. L.; Tachin, V. S. *Opt. Spectrosc. (Engl. Transl.)* **1969**, 27, 546. (f) Ermolaev, V. L.; Kazomskaya, N. A.; Moshinskaya, A. V.; Kheruze, Yu. I. *Ibid.* **1972**, 32, 41.

(5) Breuninger, V.; Weller, A. *Chem. Phys. Lett.* **1973**, 23, 40.

tances by an electron-exchange mechanism.

By compartmentalization of such chromophores and Tb^{3+} in aqueous⁶ or inverse⁷ micellar systems, efficient energy transfer could be observed at room temperature.

In this work we have studied this process between several naphthalene derivatives and Tb^{3+} , both solubilized in the inverse micellar system consisting of dodecylammonium propionate (DAP), cyclohexane, and small amounts of water. Besides an interpretation of the transfer kinetics, a way to control the efficiency of the process by changing the probe location is presented.

Experimental Section

The surfactant dodecylammonium propionate (DAP) was prepared from distilled dodecylamine (Aldrich) and distilled propionic acid (Aldrich), following the method of Kitahara,²¹ and kept in a desiccator over P_2O_5 under vacuum. The donors 1-methylnaphthalene (1-MeN), 2-(1-naphthyl)acetic acid (NAA), 4-(1-naphthyl)butanoic acid (NBA), 6-(1-naphthyl)hexanoic acid (NHA), and 12-(1-naphthyl)dodecanoic acid (NDA) were synthesized in our laboratory and/or purified by standard procedures.¹¹ The acceptor terbium chloride ($\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$, Alfa Ventron, 99.9%) was used without further purifications. Cyclohexane (C_6H_{12}) (Riedel-de Haen AG spectrometer) was passed over a column of Al_2O_3 (neutral)/carbon black (50/50) before distillation from sodium wires on Lynde-type 4-Å molecular sieves. The distilled and deionized water was added by using Pipetman micropipettes.

The sample solutions were made by adequately mixing three stock solutions: (1) DAP (0.1 M)/ C_6H_{12} /water ($R = [\text{H}_2\text{O}]/[\text{DAP}] = \text{variable}$); (2) a weighed amount of $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$, dissolved in a part of stock solution 1 to obtain an overall Tb^{3+} concentration of 5×10^{-3} M; (3) naphthalene derivative in methanol (5×10^{-3} M). From the pipetted volume of stock solution 3, the methanol was evaporated before stock solutions 1 and 2 were added. Mixing was effected by sonicating ("Sonomatic 150 Martin Walther" sonicator) for about 15 min. All samples were degassed by repeated freeze-pump-thaw cycles on a high-vacuum line (10^{-3} torr).

(6) (a) Escabi-Perez, J. R.; Nome, F.; Fendler, J. H. *J. Am. Chem. Soc.* **1977**, *99*, 7749. (b) Almgren, M.; Grieser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 2021.

(7) (a) Eicke, H.-F.; Shepherd, J. C. W.; Steinemann, A. *J. Colloid Interface Sci.* **1976**, *56*, 168. (b) Correll, G. D.; Cheser, R. N., III; Nome, F.; Fendler, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 1254.

(8) (a) Marchetti, A. P.; Kearns, D. R. *J. Am. Chem. Soc.* **1967**, *89*, 768. (b) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley: New York, 1970. (c) Görrler-Walrand, C.; Peeters, H.; Beyens, Y.; De Moitié-Neyt, N.; Behets, M. *Nouv. J. Chim.* **1980**, *4*, 715.

(9) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.

(10) (a) Geladé, E.; Boens, N.; De Schryver, F. C. *J. Am. Chem. Soc.* **1982**, *104*, 6288. (b) Van Bockstaele, M.; Gelan, J.; Martens, H.; Put, J.; Dederen, J. C.; Boens, N.; De Schryver, F. C. *Chem. Phys. Lett.* **1978**, *58*, 211.

(11) Geladé, E.; De Schryver, F. C.; *J. Photochem.* **1982**, *18*, 223.

(12) Geladé, E.; De Schryver, F. C. "Reverse Micelles: Biological and Technological Relevance of Amphiphilic Structures in Apolar Media"; Luisi, P., Ed.; Plenum Press: New York, 1984; pp 143-164.

(13) (a) Fletcher, P. D. I.; Robinson, B. H. *Ber. Bunsenges. Phys. Chem.* **1981**, *85*, 863. (b) Atik, S. S.; Thomas, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 3543, 4367, 7403.

(14) Eicke, H. F. *Top. Curr. Chem.* **1979**, *87*, 86-145.

(15) (a) Lemaire, B.; Bothorel, P.; Roux, D. *J. Phys. Chem.* **1983**, *87*, 1023-1028. (1983) (b) Brunetti, S.; Roux, D.; Bellocq, A. M.; Fourche, G.; Bothorel, P. *Ibid.* **1983**, *87*, 1028-1034.

(16) We are grateful to Dr. Helmut Görner of the Max-Planck Institute of Mülheim for the determination of the triplet lifetime, using a KrF-excimer laser ($\lambda_{\text{ex}} = 249$ nm) of which the pulse energy (E_L) was varied between 40 and 80 mJ. Since the lifetime decreases with E_L , indicating triplet-triplet annihilation, and since the Xe lamp of the SPEX-fluorolog has only a very low energy, the real τ_{NAA}^T value must be higher than 15 μs determined with $E_L = 40$ mJ. The T-T absorption spectrum of NAA in this system has a maximum at 425 nm and is comparable with the spectrum of 1-bromonaphthalene in CTAB micelles in water (*J. Phys. Chem.* **1981**, *85*, 1851).

(17) (a) Latt, S. A.; Cheung, H. T.; Blout, E. R. *J. Am. Chem. Soc.* **1965**, *87*, 995. (b) Stryer, L.; Hangland, R. P. *Proc. Natl. Acad. Sci. U.S.A.* **1967**, *58*, 720.

(18) Sunamoto, J.; Hamada, T.; Seto, T.; Yamamoto, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 583.

(19) (a) Kropp, J. L.; Windsor, M. W. *J. Chem. Phys.* **1965**, *42*, 1599. (b) Kropp, J. L.; Windsor, M. W. *J. Phys. Chem.* **1967**, *71*, 477.

(20) (a) Wong, M.; Thomas, J. K.; Nowak, T. *J. Am. Chem. Soc.* **1977**, *99*, 4730. (b) Eicke, H.-F.; Rehake, J. *Helv. Chim. Acta* **1976**, *59*, 2833.

(21) Kitahara, A. *Bull. Chem. Soc. Jpn.* **1955**, *28*, 234.

(22) The d values are equal to the length of the probe chains, calculated by using $d_{\text{naphthalene-C}} = 1.53$ Å, $d_{\text{C-C}} = 1.54$ Å, $d_{\text{C-COOH}} = 1.516$ Å, and $d_{\text{OH-C=O}} = 1.3$ Å.

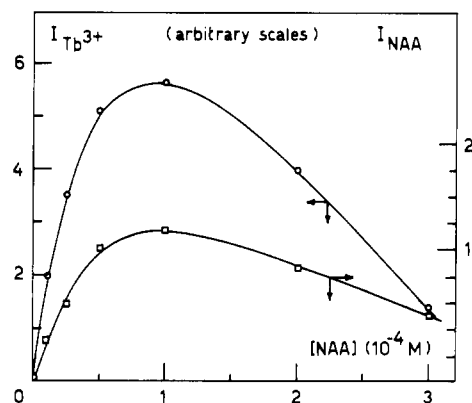


Figure 1. Influence of the NAA concentration on the luminescence intensity (I) of 1×10^{-3} M Tb^{3+} ($\lambda_{\text{em}} = 546$ nm) and NAA ($\lambda_{\text{em}} = 335$ nm), solubilized in the system DAP (0.1 M)/ C_6H_{12} / $R = 2.750$. The excitation wavelength is 283 nm.

Corrected fluorescence and excitation spectra were recorded on a "Spex Fluorolog Photon Counting" fluorimeter. Fluorescence lifetimes were obtained by using a single-photon counting apparatus, connected to a DEC P.D.P.-11/23 computer. The measured decay curves were one exponential. All measurements were made at room temperature.

Results and Discussion

Energy transfer (ET) between two molecules requires an energy level of the donor (D) to be adequately situated in relation to the energy level of the acceptor (A). In the case of naphthalene (N) and Tb^{3+} , the absorption and emission spectra indicate that there is an overlap between the phosphorescence band of N (450–550 nm)^{8a} and the ${}^7\text{F}_6 \rightarrow {}^5\text{D}_4$ absorption band of Tb^{3+} in water ($\lambda_{\text{max}} = 486.4$ nm).^{8c} Since on one hand the quantum yield of naphthalene phosphorescence is very low at room temperature ($<10^{-4}$)^{8b} on the other hand the extinction coefficient of the Tb^{3+} absorption band is only $0.029 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 486.4 nm,^{8c} the transfer can only occur at short distances by an electron-exchange mechanism, the rate constant of which is given by eq 1:⁹

$$k_{\text{ET}} \propto e^{-2r/L} \int_0^\infty \langle \bar{\nu} \rangle \epsilon_A(\bar{\nu}) d\bar{\nu} \quad (1)$$

where σ is the distance between D and A, L is the mean effective orbital radius of the initial and final state of D and A, and $\int_0^\infty \langle \bar{\nu} \rangle \epsilon_A(\bar{\nu}) d\bar{\nu}$ is the overlap integral (on a wavenumber scale and normalized to one) between the emission spectrum of D and the absorption spectrum of A.

In homogeneous medium, energy transfer between naphthalene (derivatives) and Tb^{3+} cannot be observed at room temperature because of the low efficiency compared to the other deactivating processes.³

Increasing the local concentration (decreasing r in eq 1) by solubilizing them in micellar solutions resulted in efficient energy transfer.^{6,7}

1. Naphthaleneacetic acid (NAA) as Donor. Adding NAA (10^{-4} M) to 10^{-3} M TbCl_3 in the presence of DAP (0.1 M) and water ($R = [\text{H}_2\text{O}]/[\text{DAP}] = 2.750$) in cyclohexane resulted in a remarkable enhancement of the Tb^{3+} emission after excitation at 283 nm, the maximum of the NAA absorption band.

The excitation spectrum analyzed at 546 nm (maximum of the Tb^{3+} emission) consisted of about 1% of the Tb^{3+} transition due to direct excitation at that wavelength, mainly of the NAA- 1L_a transition.

The presence of Tb^{3+} had no influence on the intensity and shape of the NAA fluorescence spectrum.

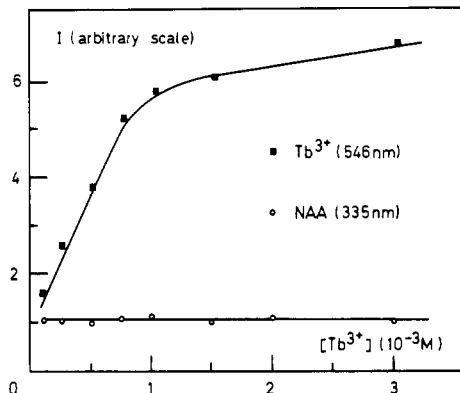
These results indicate a very efficient energy transfer between the triplet level of the naphthalene chromophore ($S_0 \rightarrow T_1$: 21.100 cm^{-1} in the case of 1-MeN) and Tb^{3+} (${}^7\text{F}_6 \rightarrow {}^5\text{D}_4$: 20.599 cm^{-1}) (eq 2).



The high-ET efficiency is in agreement with the results of Fendler et al.^{7b} for the system pyrenebutyric acid (PBA)/ Tb^{3+}

Table I. Fluorescence Lifetime of NAA as a Function of Total NAA and Tb^{3+} Concentrations, in the System DAP (0.1 M)/c- C_6H_{12} /R = 2.750

[NAA], 10^{-4} M	$[\text{Tb}^{3+}]$, 10^{-3} M	τ , ns
0.25	1.0	43.3
0.5	1.0	42.4
1.0	1.0	43.3
1.0	0.5	43.8
1.0	0.25	44.1

**Figure 2.** Influence of the Tb^{3+} concentration on the luminescence intensity (I) of Tb^{3+} (■) and 1×10^{-4} M NAA (○), solubilized in the system DAP (0.1 M)/c- C_6H_{12} /R = 2.750. The excitation wavelength is 283 nm.

in DAP/cyclohexane and is mainly due to the very high local concentrations in this specific medium. Indeed, Tb^{3+} , since it is ionic, is certainly solubilized in the water pool of the reversed micellar system (RMs), and NAA is located in the interphase, very close to the water pool.^{10a} At low water concentrations (below the concentration of maximal hydration of the polar head groups) the distance between the donor NAA and the acceptor Tb^{3+} is therefore always small (~ 5 Å).

In aqueous micelles, efficient energy transfer between several aromatic donors and Tb^{3+} is only obtained for acceptor concentrations which are 1 order of magnitude higher than in the RMs.⁶ This has two main reasons. First, since arenes and ionic molecules are almost always solubilized in a 5-Å region near the polar head groups, the probability to find D and A close to each other is low compared to RMs. Second, during the lifetime of the donor, D and A are in equilibrium between the micellar and the aqueous phase increasing the mean distance between D and A. The latter has not been taken into account by Fendler et al.^{6a} in their study of ET between naphthalene (N) and Tb^{3+} solubilized in sodium dodecyl sulfate micelles. They assumed that N is solubilized in the micellar core, from where it diffuses to the surface to transfer its energy to Tb^{3+} . More recent results^{10b} proved that this probe is really partitioned over both phases.

Although aqueous and reversed micelles both organize D and A in a small volume, the RMs increases the local concentrations the most because D and A are in the micellar core while in aqueous micelles D and A are located in the outer surface of the micelles.

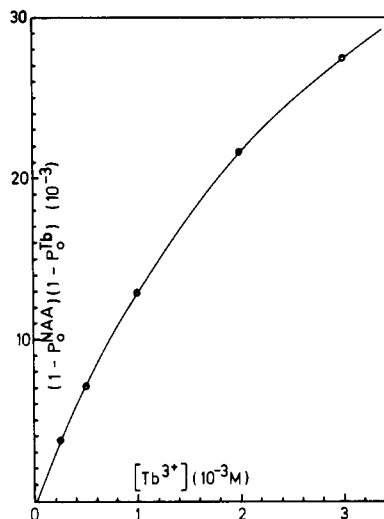
Influence of Changing the NAA Concentration at a Constant Tb^{3+} Concentration (1×10^{-3} M). The intensity of the Tb^{3+} emission as a function of the Tb^{3+} concentration goes, after an initial increase, over a maximum at a NAA concentration of 1×10^{-4} M (Figure 1).

This variation parallels that of the NAA-fluorescence intensity and indicates that the donor concentration determines the ET probability. The decrease of the NAA fluorescence above 1×10^{-4} M can only be explained by an inner filter effect. Two other possibilities, reabsorption and self-quenching, are excluded since there is not change in the fluorescence spectrum on one hand and since the fluorescence lifetime of NAA is unaffected by the NAA concentration on the other hand (Table I).

Optimal ET is obtained at a donor concentration of 1×10^{-4} M.

Table II. Mean Number (μ) of Tb^{3+} Ions per Micelle and Some Poisson Probabilities (Eq 3) as a Function of the Tb^{3+} Concentration, if [DAP] = 0.1 M, R = 2.750, and $N_{\text{agg}} = 40^{11}$

$[\text{Tb}^{3+}]$, 10^{-3} M	μ	P_0^{Tb}	P_1^{Tb}	$1 - P_0^{\text{Tb}}$
0.25	0.1	0.9048	0.0905	0.0951
0.5	0.2	0.8187	0.1637	0.1813
1.0	0.4	0.6703	0.2681	0.3297
2.0	0.8	0.4493	0.3594	0.5506
3.0	1.2	0.3012	0.3614	0.6988

**Figure 3.** Influence of the Tb^{3+} concentration on the probability to find donor (1×10^{-4} M) and acceptor in the same micelle (eq 4), if a Poisson distribution (eq 3) is assumed. The system in DAP (0.1 M)/c- C_6H_{12} /R = 2.750.

Influence of Changing the Tb^{3+} Concentration, at a Constant NAA Concentration (1×10^{-4} M). At a NAA concentration of 1×10^{-4} M, the Tb^{3+} emission shows a strong increase in the concentration region between 0.25 and 1×10^{-3} M to level off at higher concentrations (Figure 2).

In all cases, the NAA-fluorescence intensity remains constant, as does the fluorescence lifetime (Table I).

This proves the validity of eq 2. The variation of the Tb^{3+} luminescence cannot be explained by an inner filter effect. Two other possibilities should be discussed. First, assume that neither the donor nor Tb^{3+} can redistribute between micelles within the lifetime of the NAA triplet. In that case, the ET efficiency is determined by the Poisson distribution (eq 3) of the solubilizes, since transfer is only possible if donor and acceptor are both in the same micelle. In other quenching experiments,¹¹ it was found

$$P_n^S = \frac{\mu^n e^{-\mu}}{n!} \quad (3)$$

that the micellar aggregation number equals 40 if $R = [\text{H}_2\text{O}]/[\text{DAP}] = 2.750$. When eq 3 is used where P_n is the probability P that a micelle contains n solubilizes S if μ is the mean number of solubilizes per micelle, it can be calculated that less than 4% of the micelles contain a donor ($P_0^{\text{NAA}} = 0.9607$, $P_1^{\text{NAA}} = 0.0384$, and $P_2^{\text{NAA}} = 0.0007$). For the different Tb^{3+} concentrations, some P_n^{Tb} values are given in Table II.

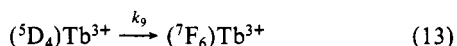
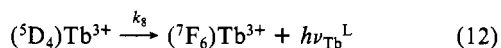
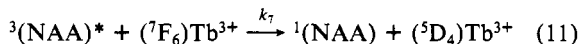
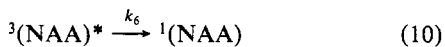
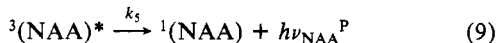
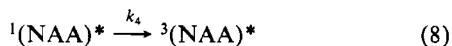
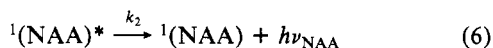
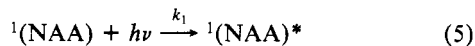
The probability that donor and acceptor are in the same micelle can be calculated by using eq 4 and is plotted against the Tb^{3+} concentration in Figure 3.

$$p^{\text{NAA}+\text{Tb}} = (1 - P_0^{\text{NAA}})(1 - P_0^{\text{Tb}}) \quad (4)$$

At the concentrations used, the calculated ET probability should according to this scheme always increase as presented in Figure 3 and in the concentration range studied not reach a plateau value, as is experimentally observed and reported in Figure 2. The assumption of an immobile donor and quencher seems not justified, in agreement with other quenching experiments in this¹¹ and

other¹³ RMs. Indeed, in the former, the decay curves of NAA quenched by anions in the system DAP/H₂O/cyclohexane could only be explained if a rapid exchange of probe and/or quencher by intermicellar collisions during the probe lifetime is taken into account. At $R = 2.750$, 10% of the collisions are efficient, resulting in an exchange rate constant of $1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for KI as quencher.¹¹ As we explained in detail in a previous article,¹² we think that both the probe in the interphase and Tb^{3+} in the water phase can exchange, as should be expected from the "coalesced dimer" mechanism proposed by Fletcher and Robinson.^{13a} The high exchange rate constant which is 2 orders of magnitude higher than in AOT¹³ is due to the DAP micellar structure and the NAA location in the interphase. Indeed, AOT micelles are more stable than DAP micelles since the sulfonate head groups of AOT interact stronger with the water pool than the ammonium head groups of DAP¹⁴ and since AOT has two branched isooctyl chains per head group while DAP has alternating one long dodecyl-ammonium chain and one short propionate chain. That the presence of the short chain enhances the intermicellar interactions is in agreement with recent theoretical and experimental results on water-in-oil microemulsions of SDS/decahe/ol/alcohol/water¹⁵ and with the influence of benzyl alcohol on earlier quenching studies in AOT/heptane/water.^{13b} The importance of the probe location on the intermicellar-exchange process was already explained in a previous article.¹²

It is thus reasonable to write down a kinetic scheme analogous to that in homogeneous medium¹⁶



where the excited singlet state of NAA (formed via process 5) deactivates by fluorescence (6), internal conversion, (7), and intersystem crossing, (8), the triplet state deactivates by phosphorescence, (9), nonradiative processes, (10), and energy transfer to Tb^{3+} , (11), and the excited Tb^{3+} deactivates by either radiative, (12), or nonradiative, (13), processes.

If we define $\tau_{\text{NAA}}^{\text{S}} = (k_2 + k_3 + k_4)^{-1}$, $\tau_{\text{NAA}}^{\text{T}} = (k_5 + k_6)^{-1}$, and $\tau_{\text{Tb}} = (k_8 + k_9)^{-1}$, it can be derived that

$$\frac{1}{I_{\text{Tb}}} = \frac{k_7 \tau_{\text{NAA}}^{\text{T}}}{A} + \frac{1}{A [\text{Tb}^{3+}]} \quad (14)$$

where I_{Tb} is the emission intensity of Tb^{3+} and $A = k_4 k_7 k_8 I_{\text{NAA}} \tau_{\text{Tb}} \tau_{\text{NAA}}^{\text{S}} \tau_{\text{NAA}}^{\text{T}}$. In the latter expression, I_{NAA} is the amount of light absorbed by NAA.

In this kinetic scheme the following assumptions are made. First, the amount of light absorbed by Tb^{3+} at 283 nm is negligible because of the very low extinction coefficient ($\epsilon < 0.20 \text{ L mol}^{-1} \text{ cm}^{-1}$) compared to the $7000 \text{ L mol}^{-1} \text{ cm}^{-1}$ value of NAA. Second, triplet-triplet annihilation between two NAA molecules is not taken into account since $P_{\text{NAA}} = 9 \times 10^{-4}$.

As plotted in Figure 4, the experimental results can very well be described by eq 14. Because of the rapid exchange of solubilizes by intermicellar collisions the detergent solution can, in the ms- μ s time region, be regarded as a homogeneous solution. The ratio of the intercept to the slope ($k_7 \tau_{\text{NAA}}^{\text{T}}$) is referred to as

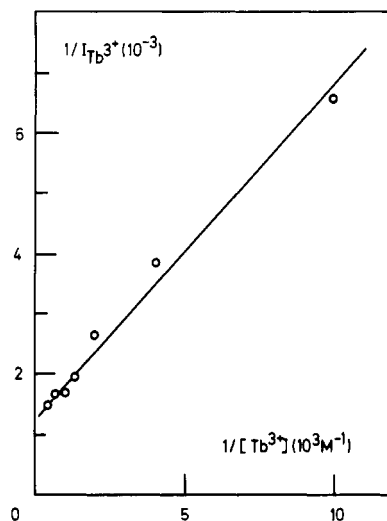


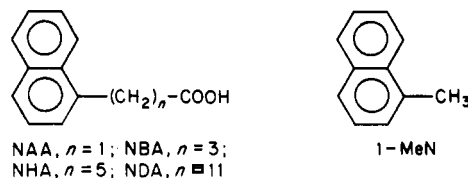
Figure 4. Plot of the Tb^{3+} luminescence vs. Tb^{3+} concentration according to eq 14, in the system DAP (0.1 M)/c-C₆H₁₂/R = 2.750/NAA (1×10^{-4} M).

the triplet sensitization constant (K_{ST}) and is equal to 2608 M^{-1} .

When the triplet lifetime of NAA, $\tau_{\text{NAA}}^{\text{T}} > 15 \times 10^{-6} \text{ s}$,¹⁶ is used, k_7 can be calculated to be smaller than $1.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. Compared to the rate constant of solubilize exchange ($1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), the k_7 value is about 1 order of magnitude lower. Therefore, not the solubilize exchange but the ET process is rate determining. The fact that the energy-transfer rate is slower than the diffusion-controlled rate is in agreement with other studies in homogeneous⁴ and micellar^{6b} solutions.

That rapid exchange really occurs is corroborated by the independence of the amount of sensitized Tb^{3+} emission on the detergent concentration ($0.04 \text{ M} \leq [\text{Det}] \leq 0.20 \text{ M}$) if the ratio $[\text{H}_2\text{O}]/[\text{DAP}]$ and the donor and the acceptor concentrations are kept constant at respectively 2.750, $1 \times 10^{-4} \text{ M}$, and $1 \times 10^{-3} \text{ M}$. If the solubilizes should not redistribute during the donor lifetime, the probability of ET (donor and acceptor in one micelle (eq 4)) should increase by a factor of 15 when decreasing the detergent concentration from 0.20 to 0.04 M. Since no measurable influence has been observed, the overall concentrations must be important, and this is only possible if rapid solubilize redistribution occurs.

2. Other Donors: Influence of the Number of Methylene Units between the HOOC Group and the Naphthalene Chromophore. The naphthalene derivatives used have the following structures:



The results are plotted in Figure 5.

The intensity of sensitized Tb^{3+} emission (I_{Tb}) strongly decreases with an increasing number of methylene units. I_{Tb} for NDA and 1-MeN equals the intensity in the absence of naphthalene chromophore.

Such variation can only be explained by the probe location. From our previous exciplex study in these systems¹⁰ we concluded that 1-MeN is in the apolar cyclohexane phase while the other probes are bound at the interphase.

In the latter case, the distance between the naphthalene chromophore and the water pool increases with n . Since the ET occurs via an electron-exchange mechanism at short distances, the exponential decrease of $I_{\text{Tb}^{3+}}$ with n (Figure 5 insert and Figure 6) is an indication of the fact that the methylene chains are almost not folded. Equation 1 indeed predicts an exponential decrease of I_{Tb} with the D-A distance. At distances larger than about 16 Å ($n = 11$) sensitization of Tb^{3+} is not efficient anymore. Like

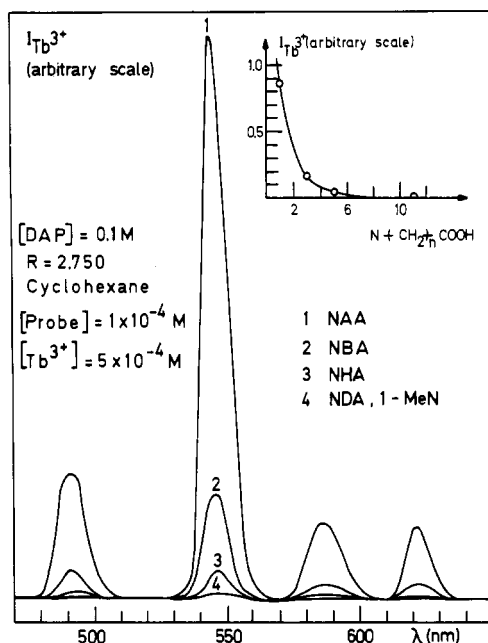


Figure 5. Influence of the number (n) of methylene units between the naphthalene chromophore and the acid group on the intensity (I) of the Tb^{3+} luminescence.

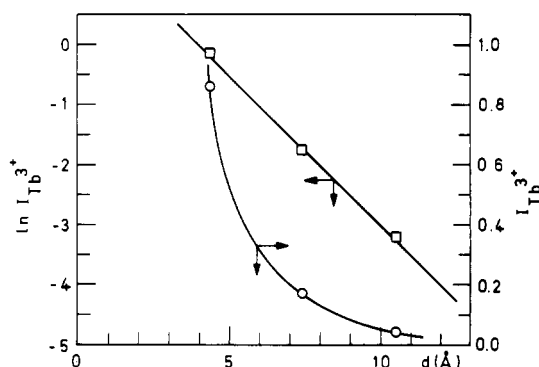


Figure 6. Plot of the intensity (I) of the Tb^{3+} luminescence (sensitized by, from left to right, NAA, NBA, and NHA) and of $\ln I_{\text{Tb}^{3+}}$ as a function of the estimated distance (d) between the micellar core (with Tb^{3+}) and the naphthalene chromophore, if a straight probe chain is assumed.²

certain steroid and oligomer structures,¹⁷ inverse micelles can control the distance between donor and acceptor by using appropriate probes.

3. Influence of the Water Concentration. To investigate this, we chose our "best" system, NAA/ Tb^{3+} . A constant DAP, Tb^{3+} , and NAA concentrations, the water amount was changed.

I_{Tb} increases with increasing R value to reach a constant value at $R = 3$ (Figure 7). Only the first amounts of water have an influence on I_{Tb} . By studying ET between hydroxyphenylacetic acid and Tb^{3+} in AOT micelles, Eicke et al.^{7a} found a decrease of $I_{\text{Tb}^{3+}}$ (or ϕ_n) instead of an increase if R was enhanced (Figure 7). As measured by Sunamoto et al.¹⁸ the intensity of Tb^{3+} emission in the absence of sensitizer shows in DAP micelles in hexane also a decrease until $R = 1$.

Since the Tb^{3+} emission is quenched by the high frequency OH vibrations of the surrounding water molecules¹⁹ a decrease rather than an increase should be expected. A constant I_{Tb} is probably obtained if the Tb^{3+} ion is completely hydrated. This process

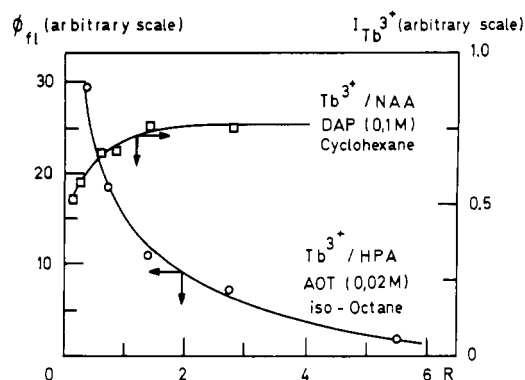


Figure 7. Variation of the quantum yield (ϕ_n) or the intensity (I) of the Tb^{3+} luminescence as a function of $R = [\text{H}_2\text{O}]/[\text{detergent}]$ for two detergent systems.

occurs in competition with the hydration of the polar head groups of which the hydration numbers are 4 and 10 in the case of DAP^{7b} and AOT,²⁰ respectively. This explains why I_{Tb} reaches already at $R \approx 1$ a constant value in DAP and only reaches a constant value at higher R values in AOT (Figure 7). In addition, the sulfonate head group of AOT interacts more strongly with water than the head groups of DAP do.^{20b}

The increase of sensitized Tb^{3+} emission in DAP micelles as a function of R could from that point of view be explained by a change in the donor-acceptor distance, compensating the decrease due to the hydration of Tb^{3+} . At low water concentrations, the Tb^{3+} ion may organize the negative propionate ions around itself, increasing the donor-acceptor distance. Adding more water induces changes in the positions of Tb^{3+} and NAA in the interphase which seem to favor ET.

Conclusions

Compartmentalization of donor and acceptor molecules in inverse micelles increases the local concentrations, making energy transfer very efficient even at room temperature.

The efficiency, however, is in our systems (DAP/ $c\text{-C}_6\text{H}_{12}/\text{H}_2\text{O}/\text{Tb}^{3+}$ /naphthalene derivatives) determined by two points: the location of the probe and the size of the water pool. Concerning the former point, we found that in the case of micelle-bound naphthalene derivatives the energy-transfer probability decreases exponentially with the number of methylene units between the chromophore and the polar head group, bound to the water pool, solubilizing the ionic acceptor. Since energy transfer between naphthalene derivatives and Tb^{3+} occurs by an exchange mechanism, this indicates that the methylene chain and probably all the detergent molecules are most of the time in a nonfolded conformation. Increasing the amount of solubilized water, on the other hand, changes the location site of the donor and the acceptor with respect to each other. Instead of the expected lower intensity of sensitized Tb^{3+} emission with increasing R (water is a quencher), we obtained a slight increase which levels off at $R = 3$.

The variation of the intensity is also determined by the maximal hydration number of the polar head groups of the surfactants.

Because of rapid exchange of solubilizates by intermicellar collisions, compared to the lifetime of the donor and acceptor, the Poisson distribution has no influence on the transfer kinetics. A kinetic scheme, analogous to that in homogeneous medium, where the total concentrations are used, explains the results very well.

Registry No. 1-MeN, 90-12-0; NAA, 86-87-3; NBA, 781-74-8; NHA, 22504-86-5; NDA, 73711-26-9; DAP, 17448-65-6; Tb, 7440-27-9; cyclohexane, 110-82-7.