actions.[9] The solvent used in the earlier study contained acetonitrile as a solvent.

## Experimental Section

Cyclohexaamylose samples obtained from Aldrich Chemical Co. were allowed to aerate for several days before use. Prepared in this way, the amylose consisted of the hexahydrate form as determined by heating (~110 °C) to constant weight in a vacuum oven. All other materials were reagent grade. pH measurements employed conventional glass and either external calomel or Ag/AgCl reference electrodes and were standardized with 0.05 *m* KHP at the measurement temperature. Electrodes were always equilibrated at the temperature of measurement until no thermal drift (<0.001 pH) was detectable for a period of 20–30 min, a time period comparable to the duration of the subsequent experiment. Readings were obtained after equilibration periods of 2–3 min subsequent to addition of cyclohexaamylose or substrate samples. Mixed solvent solutions were prepared either as bulk stock solutions (2-methyl-2-propanol and cyclohexanol) or volumetrically just before use. Volume additivity was assumed in calculating concentration values.

NMR measurements employed a Bruker HX-270 spectrometer operating at 67.89 MHz for $^{13}C$ observation. Instrument settings of 30° tip angle, 1.3 s recycle time, and 1K–2K transients were used to scan solutions contained in 10-mm sample tubes which were maintained at 30 ± 1 °C.

Benzoic acid mixed solvent solubility measurements involved dissolution of excess benzoic acid in a suitable quantity of the organic solvent followed by addition of water. The stirred thermostatted mixtures containing large excess of benzoic acid solid were equilibrated for 30 min to 1 h at which time samples were withdrawn, filtered, and titrated with standardized NaOH to the phenolphthalein end point. Subsequent samples taken at intervals of 30 min always yielded the same results within the estimated ±1% precision of our titrations. Most solubility measurements were repeated with fresh solutions and these too gave results to within ±1%. Finally, the water solubility of benzoic acid was determined by withdrawing and titrating samples from a stirred bulk solution over a period of several days.

**Acknowledgment.** The Bruker HX-270 experiments were performed at the NMR facilities of the Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology. The NMR facility is supported by Grant 00995 from the Division of Research of the National Institutes of Health and by the National Science Foundation under Contract C-76D. We gratefully acknowledge the support of the National Institute of General Medical Sciences, U.S. Public Health Service (Grant no. GM 26004). We thank Mr. Lev Gelb and Mr. Aaron Gelb for their assistance with the benzoic acid solubility measurements.

**Registry No.** Cyclohexaamylose, 10016-20-3; acetonitrile, 75-05-8; phenol, 108-95-2; ethanol, 65-17-5; 2-propanol, 67-63-0; 2-methyl-2-propanol, 75-65-0; cyclohexanol, 108-93-0; dioxane, 123-91-1; dimethyl sulfoxide, 67-68-5.

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# Exciplex Formation in Dodecylammonium Propionate Reversed Micellar Systems

**E. Geladé, N. Boens, and F. C. De Schryver***

*Contribution from the Department of Chemistry, K. U. Leuven, Celestijnenlaan 200 F, B 3030 Heverlee, Belgium.* *Received March 5, 1982*

**Abstract:** On the basis of the study of some heteroexcimer systems in pure cyclohexane and in dodecylammonium propionate reversed micelles, information on the average localization site of the probes, solubilized in these micelles, is obtained. Probes used were 1-methylnaphthalene, other naphthalene derivatives, and sodium 1-pyrenesulfonate, and quenchers were triethylamine, *m*-dicyanobenzene, and dimethylaniline. For detergent-like probes, which are bound to the micelle, the quenching probability and fluorescence properties are strongly affected by the chain length of the probe, making the determination of the variation of the dielectric constant in the vicinity of the waterpool possible. The influence of water on the quenching process is also investigated, indicating a higher micelle density with increasing water amount.

## Introduction

Exciplexes have been studied for many years[1] and are characterized by a sufficiently large dipole moment, that their fluorescence properties are dependent on the polarity of the environment. The formation of radical ions is in strong polar media energetically more favorable than exciplex formation, and exciplex emission is usually not observed. Because of this dependence on the environment, the study of exciplexes in micelles offers an interesting possibility to obtain information on these supramolecular structures.

Although several exciplex studies have been carried out in aqueous micelles,[2] liposomes,[3] and W/O microemulsions,[4] no information on exciplex formation in reversed micelles is available. On the basis of the results obtained in these heterogeneous systems, it appears that this method can give information about the probe localization, an important feature in quenching studies.[5]

In this work, exciplex formation between several naphthalene derivatives and triethylamine (TEA) has been examined in the reversed micellar system dodecylammonium propionate ([DAP] = 0.12 M)/cyclohexane/water ($R = [H_2O]/[DAP] = 1.375$). From earlier measurements in our laboratory,[6] it is known that TEA is a good quencher for 2-methylnaphthalene. However, to make sure that the earlier obtained results can be generalized for

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[1] (a) P. Froehlich and E. L. Wehry, "Modern Fluorescence Spectroscopy", Vol. 2, Plenum Press, New York, 1976, p 319; (b) M. Gordon and W. R. Ware, Ed., "The Exciplex", Academic Press, New York, 1975; (c) M. Ottolenghi, *Acc. Chem. Res.*, **6**, 153 (1973); (d) K. B. Eisenthal, *ibid.*, **8**, 118 (1975); (e) H. Leonhardt and A. Weller, *Ber. Bunsenges. Phys. Chem.* **67**, 791 (1963).

[2] (a) M. Grätzel and J. K. Thomas, *J. Am. Chem. Soc.*, **95**, 6885 (1973); (b) H. Masuhara, K. Kaji, and N. Mataga, *Bull. Chem. Soc. Jpn.*, **50**, 2084 (1977); (c) B. Katusin-Razem, M. Wong, and J. K. Thomas, *J. Am. Chem. Soc.*, **100**, 1679 (1978); (d) S. S. Atik and J. K. Thomas, *J. Am. Chem. Soc.*, **103**, 3550 (1981); (e) Y. Waka, K. Hamamoto, and N. Mataga, *Chem. Phys. Lett.*, **53**, 242 (1978); **62**, 365 (1979); *Photochem. Photobiol.*, **32**, 27 (1980).

[3] (a) Y. Waka, N. Mataga, and F. Tanaka, *Photochem. Photobiol.* **32**, 335 (1980); (b) R. McNeil and J. K. Thomas, *J. Colloid Interface Sci.*, **73**, 522 (1980); (c) K. Kano, H. Kawazumi, T. Ogawa, and J. Sunamoto, *Chem. Phys. Lett.*, **74**, 511 (1980); *J. Phys. Chem.*, **85**, 2204 (1981); (d) J. Sunamoto, K. Iwamoto, H. Iwamoto, H. Kondo, K. Kano, and T. Ogawa, *Chem. Lett.*, **1**, 15 (1981); (e) K. Kano, H. Goto, and T. Ogawa, *Chem. Lett.*, **5**, 653 (1981).

[4] S. S. Atik and J. K. Thomas, *J. Am. Chem. Soc.*, **103**, 4367 (1981).

[5] E. Geladé and F. C. De Schryver, *J. Photochem.*, **18**, 223 (1982).

[6] (a) F. Meeus, M. Van der Auweraer, J. C. Dederen, and F. C. De Schryver, *J. R. Neth. Chem. Soc.*, **98**, 220 (1979); (b) F. Meeus, M. Van der Auweraer, and F. C. De Schryver, *J. Am. Chem. Soc.*, **102**, 4017 (1980).

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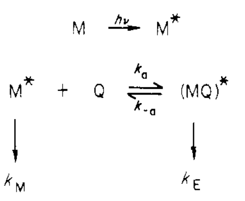
Scheme I



all the naphthalene derivatives used in this study, quenching experiments were first carried out in homogeneous cyclohexane, the apolar solvent used to obtain reversed DAP micelles.

## Experimental Section

The probes 1-methylnaphthalene (1MeN) (Aldrich) and 2-(1-naphthyl)acetic acid (NAA) (Aldrich) were purified as previously reported.[5] The other naphthalene derivatives, 4-(1-naphthyl)butyric acid (NBA), 6-(1-naphthyl)hexanoic acid (NHA), and 12-(1-naphthyl)dodecanoic acid (NDA) were synthesized and purified in our laboratory.[7] The purity of all these compounds was checked on HPLC (>99.9%). Sodium 1-pyrenesulfonate (synthesized in our laboratory) was purified several times by shaking a methanol solution with $Al_2O_3$, followed by filtration and evaporation of the methanol.

The quencher triethylamine (TEA) (Aldrich) was distilled from $LiAlH_4$ under argon atmosphere before use. The same procedure, without $LiAlH_4$, was used for the purification of *N,N*-dimethylaniline (DMA) (Aldrich). *m*-Dicyanobenzene (*m*-DCNB) (Aldrich) was recrystallized from ethanol, followed by vacuum sublimation.

Dodecylammonium propionate (DAP) was prepared by the method of Kitahara.[8] Cyclohexane (c-$C_6H_{12}$) (Riedel-de Haen AG spectranal) was distilled from sodium wires and stored over Lynde type 4Å molecular sieves. The water was bidistilled and added using Pipetman micropipets (2–20 and 20–200 μL). Solubilization of water and of the probes ((1–4) × $10^{-5}$ M) and quenchers in the micellar solutions was effected by sonication. All solutions were degassed by repeated freeze–pump–thaw cycles.

Corrected fluorescence spectra were measured on a "FICA spectrofluorimètre absolu et différentiel". Absorption spectra were taken on a Perkin-Elmer 124 spectrophotometer. Fluorescence lifetimes were measured on a single photon counting apparatus and the decay curves were analyzed with deconvolution using a PDP-11/computer.

## Results and Discussion

In homogeneous medium, exciplex formation is generally described by Scheme I, where $k_a$ is the rate constant for exciplex formation, $k_{-a}$ is the rate constant for back reaction to excited monomer (M*) and quencher (Q), $k_M = k_{FM} + \sum_i k_{iM} = 1/\tau^\circ_M$, $k_E = k_{FE} + \sum_j k_{jE}$, $k_{FM}$ and $k_{FE}$ are the rate constants for the radiative monomer (M) and exciplex (E) decay, respectively, and $\sum_1 k_{iM}$ and $\sum_i k_{jE}$ the sum of the rate constants for the monomer (M) and exciplex (E) nonradiative decay, respectively.

In stationary conditions of light excitation, the following equations can be derived

$$\phi_M = \frac{k_{FM}}{k_M + \dfrac{k_a \cdot k_E}{k_{-a} + k_E}[Q]} \tag{1}$$

$$\phi_E = \frac{k_{FM} k_a [Q]}{(k_{-a} + k_E)\left\{k_M + \dfrac{k_a \cdot k_E}{k_{-a} + k_E}[Q]\right\}} \tag{2}$$

$$\frac{\phi_M{}^\circ}{\phi_M} = 1 + \frac{k_a \cdot k_E}{(k_{-a} + k_E) k_M}[Q] = 1 + K_{SV}[Q] \tag{3}$$

The ratio of the monomer fluorescence quantum yield in absence ($\phi_M{}^\circ$) and presence ($\phi_M$) of quenchers is described by the Stern–Volmer equation (3), where $K_{SV}$ is the Stern–Volmer constant. $\phi_E$ is the exciplex fluorescence quantum yield.

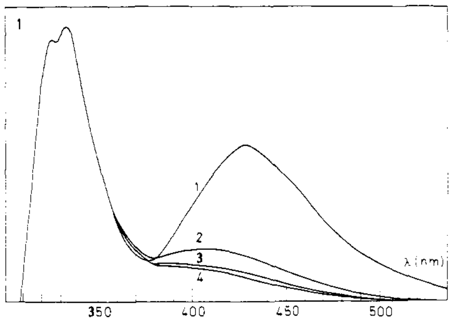


**Figure 1.** Fluorescence spectra of NAA (1), NBA (2), NHA (3) and NDA (4), normalized at 325 nm, when quenched by TEA (2.155 × $10^{-2}$ M) in the micellar system DAP (0.12 M)/c-$C_6H_{12}$/$H_2O$ ($R$ = 1.375).

Table I. Values of the Quantum Yield ($\phi$) of Monomer (M) and Exciplex (E) Fluorescence, the Wavelength of Maximum Exciplex Fluorescence ($\lambda_{max}$), the Quenching ($k_q$) and Stern–Volmer ($K_{SV}$) Constants, and the Lifetime ($\tau$) in Absence of Quencher (°) for the Quenching of the Naphthalene Derivatives by TEA in Homogeneous Cyclohexane[a]

| probe | NAA | NBA | NHA | NDA | 1MeN |
|---|---|---|---|---|---|
| | | Stationary Measurements | | | |
| $\phi_M{}^\circ \times 10^{-2}$ | 15.62 | 27.00 | 28.10 | 26.47 | 24.89 |
| $\phi_M \times 10^{-2}$ | 5.27 | 17.7 | 19.37 | 18.31 | 16.22 |
| $\phi_E \times 10^{-2}$ | 7.21 | 7.57 | 5.5 | 4.64 | 5.5 |
| $\phi_E/\phi_M \times 10^{-2}$ | 136.8 | 42.7 | 28.0 | 25.0 | 33.9 |
| $\lambda_{max}$, nm | 429 (±2) | 410 (±2) | 408 (±2) | 407 (±2) | 408 (±2) |
| $K_{SV}$, $M^{-1}$ | 91.13 | 24.38 | 20.9 | 20.71 | 24.8 |
| $k_q$, $10^8$ $M^{-1}$ $s^{-1}$ | 19.5 | 3.75 | 3.15 | 3.22 | 3.45 |
| | | Nonstationary Measurements | | | |
| $\tau_M{}^\circ$, ns | 46.6 | 64.97 | 66.32 | 64.26 | 71.89 |
| $K_{SV}$, $M^{-1}$ | 135.7 | 35 | 17.77 | 16.25 | 19 |
| $k_q$, $10^8$ $M^{-1}$ $s^{-1}$ | 29.1 | 5.38 | 2.68 | 2.53 | 2.64 |

[a] Stationary conditions of light excitation: [TEA] = 2.155 × $10^{-2}$ M. Nonstationary conditions: [TEA] = (0.539, 1.078, 1.617, and 2.155) × $10^{-2}$ M.

The decay parameters of the excited monomer and exciplex, obtained by time resolved measurements can be fitted to eq 4 and 5, respectively

$$I_M(t) = C_1 e^{-\lambda_1 t} + C_2 e^{-\lambda_2 t} = C_1(e^{-\lambda_1 t} + A e^{-\lambda_2 t}) \tag{4}$$

$$I_E(t) = C_3(e^{-\lambda_1 t} - e^{-\lambda_2 t}) \tag{5}$$

where

$$A = C_2/C_1 = (X - \lambda_1)/(\lambda_2 - Y) \tag{6}$$

$$\lambda_{1,2} = 0.5\{(X + Y) \mp [(Y - X)^2 + 4k_a \cdot k_{-a}[Q]]^{1/2}\} \tag{7}$$

$$X = k_M + k_a[Q] \tag{8}$$

$$Y = k_E + k_{-a}[Q] \tag{9}$$

The ratio of the lifetimes of the excited monomer in absence and presence of quenchers can also be described by the Stern–Volmer relationship (eq 3).

## Quenching of Naphthalene Derivatives by TEA in Homogeneous Medium

**Stationary Measurements.** In the literature, only the quenching of naphthalene[9] and 2-methylnaphthalene[6] by TEA has been studied. Hence, before measuring the quenching in reversed micellar medium, it was necessary to check the fluorescence behavior in pure cyclohexane. Since there is no TEA absorption below 290 nm, independent excitation of the naphthalene chromophore at 305 nm was always possible. The absorption spectrum

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[7] M. Van Bockstaele, J. Gelan, H. Martens, J. Put, J. C. Dederen, and F. C. De Schryver, *Chem. Phys. Lett.*, **70**, 605 (1980).

[8] A. Kitahara, *Bull. Chem. Soc. Jpn.*, **28**, 234 (1955).

[9] (a) M. G. Kuzmin and L. N. Guseva, *Chem. Phys. Lett.*, **3**, 71 (1969); (b) S. P. Van and G. S. Hammond, *J. Am. Chem. Soc.*, **100**, 3895 (1978); (c) H. Knibbe, D. Rehm, and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 839 (1969); (d) E. A. Chandross and H. T. Thomas, *Chem. Phys. Lett.*, **9**, 393, 397 (1971).

of the naphthalene derivatives ($\lambda_{max}$ = 283 nm) did not change with the addition of TEA, indicating that interaction in the ground state can be excluded within experimental error.

Under stationary conditions of light excitation a new structureless band appeared which shifted to longer wavelengths than the monomer emission ($\lambda_{max}$ = 335 nm). The excitation spectra at wavelengths in both fluorescence bands are identical with the absorption spectrum, indicating that the new emission band is due to exciplex formation. The quantum yield ($\phi_E$) and the wavelength at maximum intensity ($\lambda_{max}$) of the exciplex fluorescence are dependent on the naphthalene derivative (Figure 1 and Table I). The fluorescence properties of 1MeN, NDA, and NHA are almost identical. However, if the chain length decreases further, as in the case of NBA and NAA, $\phi_E$ and $\lambda_{max}$ increase. Shortening the methylene chain has an analogous effect on the exciplex emission as has increasing polarity or decreasing temperature, namely stabilization of the exciplex. The quenching of the monomer fluorescence can be described by eq 3. The determined values of $K_{SV}$ are listed in Table I.

**Nonstationary Measurements.** The decay curves in both the monomer and exciplex region could be measured by the single-photon-counting method (S.P.C.). Again, the fluorescence behavior of NBA and NAA differs from that of 1MeN, NDA, and NHA (Table I). In the case of 1MeN, NDA, and NHA, the decay curves in both fluorescence regions are monoexponential. This is in agreement with the results of Meeus[6] for the system 2MeN/TEA/isooctane; it can be explained by a fast equilibrium between the local excited state and the exciplex (Scheme I). $K_{SV}$ can be described as

$$K_{SV} = \frac{k_a \cdot k_E}{k_{-a} + k_E}\tau_M{}^\circ = k_q \tau_M{}^\circ \qquad (10)$$

The values of $\tau_M{}^\circ$, $K_{SV}$, and $k_q$ are listed in Table I.

The decay curves of the quenching of NBA are no longer monoexponential. The decay curves in the monomer region consist of a fast [$\exp(-\lambda_2 t)$] and a slow [$\exp(-\lambda_1 t)$] decaying part. In the exciplex region, the rate of growing in or formation of the exciplex [$-\exp(-\lambda_2 t)$] agrees with the fast decay in the monomer region while the exciplex decay [$\exp(-\lambda_1 t)$] agrees with the slow monomer decay. Hence, it may be concluded that, probably by exciplex stabilization, $k_E$ is no longer negligible against $k_{-a}$.

The NAA/TEA exciplex is even more stabilized ($k_E \gg k_{-a}$). In the monomer region, the decay curves are again monoexponential and the calculated lifetimes are identical with the growing-in times of the exciplex. The exciplex decay is within the concentration range measured (($(0.5\text{–}2.155) \times 10^{-2}$ M) independent of the quencher concentration and hence equal to the exciplex lifetime. The quenching rate constant now equals the rate constant of exciplex formation.

From the results in homogeneous medium, it is clear that the difference of the fluorescence properties between especially NAA but also NBA, and the other naphthalene derivatives, will have to be taken into account when studying quenching experiments in heterogeneous medium.

## Quenching of Naphthalene Derivatives by TEA in Heterogeneous Medium: An Approach to Probe Localization

**Stationary Measurements.** In this part, the influence of adding detergent and water on the fluorescence properties of the different probes in cyclohexane is investigated. The reversed micellar system contains the probe (1MeN, NDA, NHA, NBA, or NAA), DAP (0.12 M), water ($R$ = [$H_2O$]/[DAP] = 1.375) and quencher (TEA). The absorption spectra indicate no experimental measurable ground-state interactions between the probes and the quencher.

The results from stationary fluorescence measurements are clearly different from those in pure cyclohexane (Table II). The quantum yield of exciplex is for all probes smaller in the micellar medium than in the homogeneous medium and in the case of NAA no exciplex emission at all is observed. The difference between the $\phi_E$ values in both media decreases with increasing chain length and is smallest for 1MeN.

Table II. Values of the Quantum Yield ($\phi$) of Monomer (M) and Exciplex (E) Fluorescence, the Wavelength of Maximum Exciplex Fluorescence ($\lambda_{max}$), the Quenching ($k_q$) and Stern-Volmer ($K_{SV}$) Constants, and the Lifetime ($\tau$) in Absence of Quencher (°) for the Quenching of the Naphthalene Derivatives by TEA in Heterogeneous Medium[b]

| probe | NAA | NBA | NHA | NDA | 1MeN |
|---|---|---|---|---|---|
| | | Stationary Measurements | | | |
| $\phi_M{}^\circ \times 10^{-2}$ | | 23.91 | 22.84 | 21.63 | 22.97 |
| $\phi_M \times 10^{-2}$ | | 10.39 | 8.86 | 8.94 | 9.45 |
| $\phi_E \times 10^{-2}$ | n.e.[a] | 0.412 | 0.867 | 1.427 | 3.140 |
| $\phi_E/\phi_M \times 10^{-2}$ | | 3.96 | 9.78 | 15.96 | 33.22 |
| $\lambda_{max}$, nm | | 427 (±3) | 423 (±3) | 413 (±3) | 408 (±2) |
| $\nu$, cm$^{-1}$ | | 23419 | 23640 | 24213 | 24510 |
| $K_{SV}$, M$^{-1}$ | 25 | 60.38 | 73.22 | 65.86 | 66.38 |
| | | Nonstationary Measurements | | | |
| $\tau^\circ$, ns | 42 | 64.6 | 64.7 | 63.6 | 74.9 |
| $K_{SV}$, M$^{-1}$ | 26.8 | 56.8 | 71.1 | 65 | 55 |
| $k_q$, $10^8$ M$^{-1}$ s$^{-1}$ | 6.38 | 8.79 | 10.99 | 10.2 | 7.34 |

[a] n.e. = no exciplex emission. [b] Stationary conditions of light excitation: [TEA] = $2.155 \times 10^{-2}$ M. Nonstationary conditions: [TEA] = $(0.539, 1.078, 1.618, \text{and } 2.155) \times 10^{-2}$ M.

The position of the exciplex band is also strongly influenced by the addition of detergent and water, except in the case of 1MeN, where $\lambda_{max}$ is identical in both media. The exciplex band of the other probes is shifted to longer wavelengths and the shorter the methylene chain, the stronger the bathochromic shift.

Although no exciplex emission can be detected, the NAA-monomer fluorescence is strongly quenched by TEA (Table II). The value of $K_{sv}$ is, however, 4 or 5 times smaller than in homogeneous medium. The quenching of the other probes is, in contrast, 2 or 3 times larger.

In heterogeneous medium, increasing the number of methylene units has a totally opposite effect on the fluorescence properties of these probes, when quenched by TEA. These results can be explained by the fact that all probes, except 1MeN, are coaggregated within the micelle[10] with the polar headgroup located near the water phase and the methylene chain with the naphthalene chromophore orientated in the direction of the apolar phase. Hence, possible effects of the carboxylic acid group on the fluorescence quenching by TEA, which are perhaps the reason for the different fluorescence behavior of NBA (compared with NHA, NDA, and 1MeN) in homogeneous medium, are negligible. Furthermore, since the $\tau^\circ$ values of NBA, NHA, and NDA are comparable, we may assume comparable properties of these naphthalene chromophores. Differences between the fluorescence properties of 1MeN, NDA, NHA, and NBA, quenched by TEA in micellar medium, are therefore mainly due to a difference in localization site in the reversed micellar system.

The bathochromic shift of the exciplex band, when decreasing the number of methylene units, indicates that the environment of the naphthalene chromophore becomes time-averaged more polar. The influence of the water pool on the chromophore decreases with increasing chain length. This is also reflected by the lifetime of the probes in the absence of quencher when compared with the values in pure cyclohexane.

On the basis of eq 11,[9b] reproducing the relation between the emission maximum of the exciplex in a certain solvent and the polarity of that solvent, it is possible to obtain information on the polarity increase in the direction of the water pool

$$\nu = \nu_{vac} - \frac{\mu^2}{4\pi\epsilon_0 h c \rho^3}\left[2\left(\frac{\epsilon - 1}{2\epsilon + 1}\right) - \frac{n^2 - 1}{2n^2 + 1}\right] \qquad (11)$$

$$= \nu_{vac} - S \cdot f(\epsilon, n) \qquad (12)$$

where $\nu$ and $\nu_{vac}$ are the emission maximum of the exciplex in

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(10) E. Geladé and F. C. De Schryver, "Proceedings of the ESR Workshop, Rigi-Kaltbad"; Luisi, P. L., Ed.; Plenum Publishing Corp.: New York, 1982.

Table III. Calculated $\epsilon$ Values (Eq 11) on the Basis of the Emission Maximum ($\lambda_{max}$ or $\nu$) of the Exciplex Band Using the Refractive Index of Diethyl Ether ($n_1$) and Cyclohexane ($n_2$)

| | | | $\epsilon$ | |
|---|---|---|---|---|
| probe | $\lambda_{max}$, nm | $\nu_\eta$ cm$^{-1}$ | $n_1$ = 1.35243 | $n_2$ = 1.42623 |
| 1MeN | 408 | 245 10 | | 2.0058 |
| NDA | 413 | 242 13 | 2.10 | 2.20 |
| NHA | 423 | 236 40 | 2.55 | 2.65 |
| NBA | 427 | 234 19 | 2.80 | 2.90 |
| NAA | n.e.[a] | n.e.[a] | n.e.[a] | n.e.[a] |

[a] n.e. = no exciplex emission.

Table IV. Values of the Rate Constants $k_{FM}$, $k_E$, $k_q$, and $k_M$, Calculated on the basis of Eq 13–17 in Homogeneous (H) and Micellar (M) Medium for the Quenching of NHA, NDA, and 1 MeN by TEA

| | NHA | | NDA | | 1MeN | |
|---|---|---|---|---|---|---|
| | H | M | H | M | H | M |
| $\phi_M{}^\circ$ | 28.1 | 22.84 | 26.47 | 21.63 | 24.89 | 22.97 |
| $\tau_M{}^\circ$, $10^{-9}$ s | 66.3 | 64.7 | 64.26 | 63.6 | 71.89 | 74.9 |
| $k_M$, $10^7$ s$^{-1}$ | 1.50 | 1.54 | 1.55 | 1.57 | 1.39 | 1.335 |
| $k_{FM}$, $10^6$ s$^{-1}$ | 4.24 | 3.53 | 4.12 | 3.40 | 3.46 | 3.066 |
| $k_E$, $10^9$ s$^{-1}$ | 0.155 | 1.18 | 0.47 | 2.05 | 0.11 | 0.18 |
| $k_q$, $10^8$ M$^{-1}$ s$^{-1}$ | 3 | 10.9 | 2.5 | 10.2 | 3 | 7.34 |

solution and in vacuum, $\mu$ is the dipole moment of the exciplex in solution, $\rho$ is the radius of the spherical cavity occupied by the molecule, $h$ is Planck's constant, $\epsilon$ and $n$ are the dielectric constant and the refraction index of the solvent, $\epsilon_0$ is the permittivity of vacuum ($8.85 \times 10^{-12}$ C$^2$/Nm$^2$), and $c$ is the velocity of light in a vacuum. Hammond et al.[9b] determined $\nu$ in several solvents with known $\epsilon$ and $n$, for the system naphthalene/TEA. They found a linear relationship between $\nu$ and $f(\epsilon,n)$ (eq 12). From the slope ($S$ = 6800 cm$^{-1}$) and assuming that $\rho$ = 4.5 Å, they were able to calculate the dipole moment of the exciplex to be 11.1 D, in agreement with the value obtained by Kuzmin and Guseva.[9a] The intercept or $\nu_{vac}$ is equal to 25 880 cm$^{-1}$. For the solvents in which exciplex emission was observed, the most extreme values of $n$ are 1.35243 (diethyl ether) and 1.42623 (cyclohexane). No exciplex emission was detected in ethanol ($\epsilon$ = 24.58) and acetonitrile ($\epsilon$ = 37.5). If we want to correlate $\lambda_{max}$ in a micellar medium with a certain $\epsilon$ value, the following assumptions have to be made: (1) the dipole moment of the 1MeN/TEA exciplex is comparable with that of the naphthalene/TEA exciplex; (2) the micellar refraction index is between 1.35243 and 1.4263. The calculated $\epsilon$ values, using eq 11, are listed in Table III. Because $\lambda_{max}$ of 1MeN is identical in micellar and homogeneous media, only the value of $\epsilon$ was calculated, using the $n$ of cyclohexane. The agreement of the calculated $\epsilon$ value with the value in the literature[11] proves assumption 1 above. Concerning the other probes, it appears that the polarity of the environment increases from NDA to NBA. Since no exciplex emission is observed, using NAA, the polarity near the water phase must be high ($\epsilon > 10$).

Contrary to an increase of $K_{sv}$ with polarity (as pointed out by Meeus[6]) in homogeneous solvents, a decrease is found in the reversed micellar system. This is also contrary to an increase of $K_{sv}$ with decreasing chain length in a homogeneous medium and can be explained by a decrease in penetration probability of TEA in the direction of the water pool. The fact that $K_{SV}$, in all cases except NAA, is 2 or 3 times higher than in a homogeneous medium is probably due to a higher local TEA concentration in the reversed micelles.

In strong contrast with the values in a homogeneous medium, the fluorescence quantum yield of the exciplex decreases strongly with shortening of the methylene chain. This can be related on one hand to the lower penetration probability of TEA resulting in a decrease of the formation of the exciplex, and on the other hand to the increased polarity enhancing other nonradiative decay processes. This is further substantiated by the increase of $k_E$ (Table IV) in the micellar medium. Recently, Thomas and Atik,[4] studying the microemulsion system CTAB/hexanol/dodecane/water/pyrene derivative/DMA, found that the bound pyrene derivatives form anion radicals, while the nonbound pyrene does not.

Table V. Influence of the Number of Methylene Units of the Probe on the Quenching by KI in Micellar (m) ([DAP] = 0.08 M/$c$-$C_6H_{12}$/$R$ = 6.875)

| probe | $k_{qm}$, $10^7$ s$^{-1}$ | $k_{qa}$, $10^7$ M$^{-1}$ s$^{-1}$ |
|---|---|---|
| NAA | 18.0 | 250 |
| NBA | 10.0 | 390 |
| NHA | 8.8 | |
| NDA | 4.8 | |
| 1MeN | 0.04 | 490[a] |

[a] In 20% ethanol/water.[14]

Table VI. Results for the Quenching of $PySO_3{}^-$-$Na^+$ by DMA ((0.788, 1.577, 2.366 and 3.154) × $10^{-3}$ M) under Stationary and Nonstationary Conditions of Light Excitation

| | $K_{SV}$, M$^{-1}$ | $k_q$, $10^9$ M$^{-1}$ s$^{-1}$ | $\tau^\circ$, ns |
|---|---|---|---|
| stationary | 340 | 2.96 | - |
| nonstationary | 320 | 2.78 | 114.8 |

**Nonstationary Measurements.** The decay curves measured in the monomer and exciplex region are monoexponential, with an identical decay parameter in both regions, for all probes except for NBA where small deviations of monoexponentiality are observed. The lifetimes obtained by computer fitting are linearly dependent on the TEA concentration, and the $K_{sv}$ values are in good agreement with those obtained from stationary measurements (Table II).

The absence of NAA/TEA exciplex formation, although quenching occurs, is a further indication for an additional process. The close neighborhood of the water pool could make radical ion formation very efficient.[4]

The fast equilibrium between the local excited state and the exciplex, in the case of NHA, NDA, and 1 MeN, makes direct determination of the exciplex lifetime impossible. However, since $k_{-a} \gg k_E$, the decay parameter $\lambda_1$ may be simplified to

$$\lambda_1 = \frac{k_M + k_E K[Q]}{1 + K[Q]} = 1/\tau \qquad (13)$$

In that case, the following (rate) constants can be calculated

$$k_{FM} = \phi_M{}^\circ/\tau_M{}^\circ = k_M \phi_M{}^\circ \qquad (14)$$

$$K = \left(\frac{k_{FM}}{\phi_M \cdot \lambda_1} - 1\right)\frac{1}{[Q]} \qquad (15)$$

$$k_E = \frac{\lambda_1(1 + K[Q])}{K[Q]} - k_M \qquad (16)$$

$$k_q = \frac{k_a k_E}{k_{-a} + k_E} \qquad (17)$$

Indirect determination of $k_E$ thus becomes possible. The results in homogeneous (H) and micellar (M) media are represented in Table IV.

The most interesting feature is the difference of the $k_E$ values in both media. It is clear that this difference increases when the distance between the naphthalene chromophore and the waterpool decreases. This can be explained by an additional process, probably radical ion formation, the contribution of which increases with decreasing probe chain length.

## Corroboration of Probe Localization by Other Systems

From the results in previous sections, it may be concluded that the naphthalene probes having an HOOC group are bound to the

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[11] "Handbook of Chemistry and Physics", 56th ed, CRC Press, Cleveland, OH, 1975–1976, pp F50–55.

Table VII. Influence of Added Water ($R = [H_2O]/[DAP]$) on the Stern-Volmer Constant and Fluorescence Properties of NHA Quenched by TEA

| $R$ | $\phi_M^\circ \times 10^{-2}$ | $\phi_M^a \times 10^{-2}$ | $\phi_E^a \times 10^{-2}$ | $\phi_E/\phi_M^a \times 10^{-2}$ | $\lambda_{max}$, nm | $K_{SV}$, $M^{-1}$ | $\tau_M^\circ$, ns | $K_{SV}$, $M^{-1}$ | $k_q$, $10^8$ $M^{-1}$ $s^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1.375 | 22.84 | 8.86 | 0.867 | 9.78 | 423 (±3) | 73.2 | 64.7 | 71.1 | 10.99 |
| 2.750 | 22.84 | 10.23 | 0.376 | 3.68 | 423 (±3) | 57.2 | 64.6 | 56.0 | 8.67 |
| 4.125 | 22.84 | 10.90 | 0.256 | 2.50 | - | 50.8 | 65.7 | 44.8 | 6.81 |

[a] $[TEA] = 2.155 \times 10^{-2}$ M.

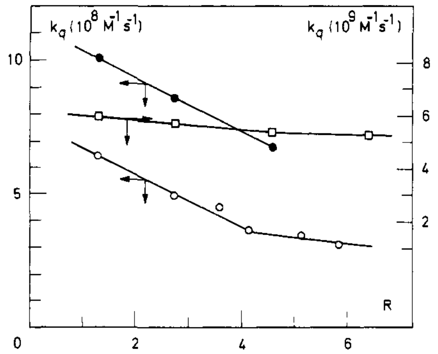

Figure 2. The variation of the quenching constant $k_q$ with the amount of water, solubilized in DAP-reversed micelles ($R = [H_2O]/[DAP]$), in the case of NAA quenched by TEA (○) or *m*-DCNB (□) and of NHA quenched by TEA (●).

micelle, with the HOOC group (like the polar surfactant headgroups) at the water pool and the methylene chains with the chromophore orientated to the apolar cyclohexane phase. The distance between the chromophore and the waterpool increases, and hence the possibility to form radical ions when quenched by TEA decreases with increasing number of methylene units.

These conclusions are further corroborated by the quenching of the different probes by the water-solubilized potassium iodide (KI). Earlier quenching experiments[5] indicated that the decay curves of the excited naphthalene derivatives are monoexponential at low quencher concentrations ($<10^{-4}$ M) and that the calculated lifetimes are then linearly dependent on the quencher concentration. The rate constants in micellar ($k_{qm}$) and aqueous ($k_{qw}$) medium are listed in Table V.[12] The probe 1MeN, residing in the cyclohexane phase, is almost not quenched by KI, solubilized in the water pool, while the quenching by TEA, in the apolar phase, is analogous with that in homogeneous medium.

Using DMA as a quencher, we also tried to localize $PSA^-$-$Na^+$ in DAP-reversed micelles. In apolar homogeneous solvents DMA forms exciplexes with several pyrene derivatives.[13] Based on the low solubility of this probe in cyclohexane and on other quenching experiments in micellar systems,[2-5] this probe is supposed to be localized near the water pool. This assumption is confirmed by our experiments, since only quenching without exciplex formation is observed (Table VI).

## Influence of Water Content

It must be pointed out that the results of the quenching of the naphthalene probes by TEA are dependent on the amount of water solubilized in the reversed micelles. In Table VII, the influence of varying $R$ on the quenching of NHA is listed. If $R$ increases, $K_{sv}$ decreases. This is in analogy with the influence of water on the quenching of 1MeN by KI and can be explained by the micelle structure becoming more dense when $R$ and hence the aggregation number ($N_{agg}$) increases.[5] The possibility of the quencher to reach the probe within its fluorescence lifetime decreases, resulting also in lower $\phi_E$ and $\phi_E/\phi_M$ values. However, variations of, for instance, $k_E$ in the expression of $K_{sv}$ could be responsible for smaller $K_{sv}$ values as well. Because of the low quantum yields of exciplex formation, along with the fact that the exciplex band is very broad, accurate determination of $\lambda_{max}$ of this band is no longer justified.

Measurements of the effect of increasing the water concentration ($R = [H_2O]/[DAP]$) on the quenching of NAA/TEA and NAA/*m*-DCNB are in accordance with an increase of the density and $N_{agg}$ of the micelle (Figure 2). Concerning the NAA/TEA system, quenching without exciplex formation is observed at all $R$ values. The variation of $k_q$ with $R$ is identical with that of the quenching of NHA, but now $k_q$ is equal to $k_a$. Hence, possible influence of a changing $k_E$ value is excluded. Increasing the water amount decreases the surface area per surfactant headgroup and hence the space between the apolar tails,[5] resulting in a lower collision frequency between NAA and TEA. At the moment of maximal hydratation ($R = 4$),[14] the surface area per headgroup becomes almost constant, as does the $k_q$ value.

When *m*-DCNB is used as a quencher of the NAA fluorescence in DAP micelles, again quenching without exciplex formation is observed. Almost no influence of adding water could be detected. In contrast with TEA, *m*-DCNB has a rather low solubility in cyclohexane and is therefore probably statistically mainly located between the apolar tails of the micelles near the waterpool. A change of the micelle density will have almost no measurable influence on $k_q$, as was experimentally observed.

## Conclusions

Exciplex formation is a good method to obtain information on the average localization site of probes in reversed micelles. Apolar probes (e.g., 1MeN) are mainly residing in the bulk apolar phase, while probes having a polar headgroup are bound to the micelle. In the case of detergent-like probes, with a methylene chain between the polar group and the chromophore, the number of methylene units ($n$) determines the average distance between the chromophore and the water pool. This is indicated by a decrease of $K_{sv}$ and $\phi_E$ and an increase of $\lambda_{max}$ when $n$ decreases. From the variation of $\lambda_{max}$ with $n$, it was possible to calculate the dielectric constant, which slightly increases in the direction of the water pool and becomes very high in the close neighborhood of the water pool. In analogy with measurements in microemulsions,[4] radical-ion formation is proposed to explain the $\phi_E$ values in micellar medium. Increasing the amount of water increases the aggregation number and the density of the micelle. The ability of a quencher in the apolar phase to reach the chromophore therefore decreases. This is not the case when the quencher already resides between the apolar tails of the micelle.

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**Registry No.** 1MeN, 90-12-0; NAA, 86-87-3; NBA, 781-74-8; NHA, 22504-86-8; NDA, 73711-26-9; TEA, 121-44-8; DMA, 121-69-7; *m*-DCNB, 626-17-5; $H_2O$, 7732-18-5; KI, 7681-11-0; dodecylammonium propionate, 17448-65-6; sodium 1-pyrenesulfonate, 59323-54-5.

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(12) H. Shizuka, T. Saito, and T. Morita, *Chem. Phys. Lett.*, **56**, 519 (1978).

(13) (a) Reference 1c; (b) M. H. Hui and W. R. Ware, *J. Am. Chem. Soc.*, **98**, 4718 (1976); (c) K. Yoshihara, T. Kasuya, A. Inoue, and S. Nagakura, *Chem. Phys. Lett.*, **9**, 469 (1971); (d) H. Nakashima, N. Mataga, and C. Yamanaka, *Int. J. Chem. Kinet.*, **5**, 833 (1973); (e) E. J. Land, J. T. Richards, and J. K. Thomas, *J. Phys. Chem.*, **76**, 3805 (1972).

(14) G. D. Correll, R. N. Cheser, F. Nome, and J. H. Fendler, *J. Am. Chem. Soc.*, **100**, 1254 (1978).