Photoinduced Processes in Copper(II)–Crown Ether Surfactant Micelles

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Abstract: Photoinduced processes were studied with a functional macrocyclic surfactant containing complexed Cu^{2+} ions. Micellar aggregates of this compound, formed above 5×10^{-4} M concentration, are relatively large, the molecular weight being 5.7×10^6 M. These assemblies exhibit unusually high efficiency in quenching the excited state of fluorophores such as cyanine dyes and pyrene. In the case of the cyanines, the photochemical stability of the dye is drastically augmented by this effect. The complexed Cu^{2+} may be reduced to Cu^+ in a light-driven redox reaction by donors such as N-methylphenothiazine (MPTH). This process is so rapid that it cannot be resolved by nanosecond laser techniques. A significant fraction of the donor cations produced is subsequently expelled from the micelle into the aqueous phase leading to charge separation. Thermal reduction of Cu^{2+} by $NaBH_4$ or $TiCl_3$ is also possible. The reaction product is probably Cu^0, which through stabilization by the macrocyclic ligand is prevented from precipitation.

Introduction

Macrocyclic compounds of the "cryptate" type with a paraffinic tail have first been described by Cinquini et al.[2a] Micelle formation and fast cation transfer of these surfactants were subsequently investigated by Le Moigne et al.[2b] In a recent communication[3] we reported on the surface activity and micelle formation of Cu^{2+} and Ag^+ containing aza crown ether surfactants. Amphiphilicity was achieved through linkage of the crown ether group with a long aliphatic chain. These compounds are of considerable interest in a variety of domains; for example, they may be employed as phase-transfer catalysts[4] or ion transducers in membranes. In our present research activity we are pursuing the development of functional micellar assemblies which could act as mediators in photoinduced processes.[5-8] Of particular interest are light-driven electron transfer reactions:

$$A + D \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} A^- + D^+ \qquad (1)$$
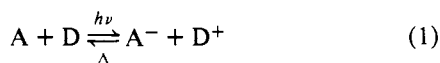
where A and D stand for the acceptor and donor, respectively, since they may be exploited to convert light into chemical energy.[9] In this type of reaction we speak of functional units when either A or D constitutes part of the detergent molecules that form the micelle. Crown ether surfactants are particularly suited to serve as electron acceptors or donors in redox reactions since different metal ions covering a wide range of standard potentials may be inserted into the macrocyclic ring.

In this paper we report on investigations carried out with the Cu^{2+} complex of 2-n-tetradecyl-1,4,7,10-tetraazacyclododecane (**I**) as the micelle-forming agent. Steady-state and

I
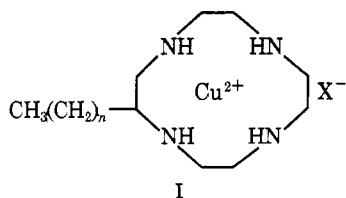
time-correlated light scattering techniques will be applied to determine the shape and size of the aggregates. The fluorescence behavior of solubilized probe molecules will be investigated and finally photochemical and thermal redox reactions explored leading to reduction of the complexed Cu^{2+} ion.

Experimental Section

Materials. Compound 1 was synthesized by a metal template synthesis described previously by Tundo et al.[10] The cyanine dye, 5,5'-diphenyl-3,3'-diethylbenzoxazolecarbocyanine iodide (**II**), was a

II

Ph = phenyl
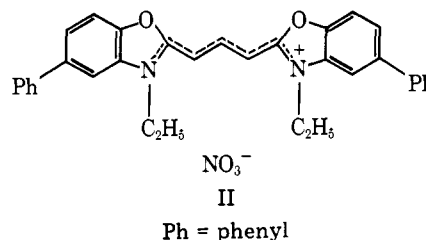
generous gift from Ciba-Geigy Ltd. N-Methylphenothiazine and sodium 12-(10-phenothiazinyl)dodecyl-1-sulfonate (**III**) were kindly

III
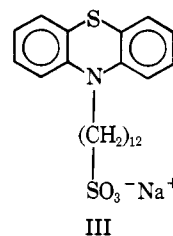
prepared by Dr. A. Braun. The products were characterized by NMR, IR, and mass spectral data and checked for purity by elemental analysis and chromatography. Pyrene (Eastman Kodak) was purified by chromatography. The micellar solutions were made up in deionized water that had been distilled from alkaline permanganate and subsequently twice from a quartz still. All other compounds employed were analytical grade and were used as supplied.

Solutions were typically prepared by putting a measured aliquot of the methanolic stock solution into a flask and then the methanol was evaporated off under reduced pressure. The soap solution was then added to give the desired analytical concentration.

The solution was degassed by freeze–pump–thaw cycles and by bubbling with high-grade argon for 20 min prior to laser and fluorescence studies.

Apparatus. Steady-state fluorescence experiments were carried out with a Perkin-Elmer MPF-44A spectrofluorimeter which is equipped with a corrected spectra unit. The instrument displays true fluorescence spectra, the measured quantity being photon flux per unit wavelength interval. The fluorescence quantum yields were obtained by comparison of optically dilute samples[11] (OD < 0.02) with a standard acidified quinine sulfate solution. All ground-state absorption
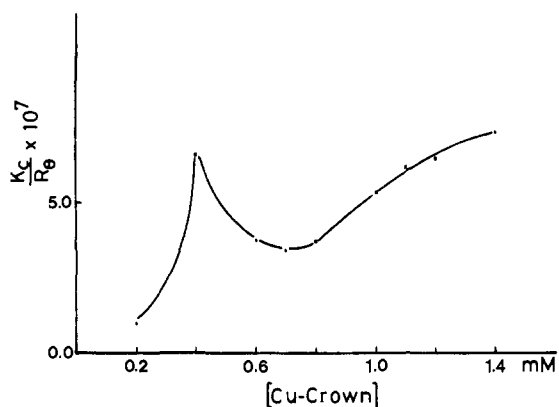
Figure 1. Zimm plot for the Cu macrocyclic surfactant in water at 25 °C. Intercept at zero concentration is equal to 1.57 × 10⁻⁷.

spectra were measured by a Varian-Cary 219 recording spectrophotometer.

Time correlated experiments were performed with either a neodynium or a ruby solid state laser supplied by J. K. Lasers. The laser systems (J. K. 2000 series) were frequency doubled or tripled in order to obtain a Q-switched pulse of suitable wavelength. The laser emission could be readily controlled up to 20 mJ/pulse, determined using a "black glass" calorimeter made by Laser Instrumentation. Single pulses of 15 ns (25 ns for the ruby) duration were monitored using a fast ITT biplanar photodiode F-4014 which sampled light at 90° to the laser axis using a quartz beam splitter. Results were normalized and made quantitative on a routine basis using this diode. The laser excitation pulse and the xenon analyzing light were arranged in a crossed beam manner, intersecting in a quartz optical cell of 10 × 10 mm cross section. The probed sample volume had dimensions of 5 mm by 3 mm diameter and was situated just inside the cell wall incident to the laser.

Kinetic absorption spectrophotometry of the generated transients was observed using a high-intensity Bausch & Lomb monochromator coupled with either a RCA 1P28 or EMI 9785B photomultiplier and associated circuitry[12] (overall rise time ≤ 1 ns). The electrical signal from the photomultiplier was either displayed on a Tektronix oscilloscope (7834-400 MHz) or directly processed by a Tektronix Transient digitizer (R7912-500 MHz) followed by spectral or kinetic analysis on a HP-9825A calculator.

Actinometry of the transients was based upon pyrene in cyclohexane. The T–T spectrum of pyrene was monitored at 412 nm (using narrow slits and low laser intensity), taking $\epsilon_{412} = 3.04 \times 10^4$ M⁻¹ cm⁻¹ [13] and $\phi_{isc} = 0.28$.[14]

Light-scattering measurements were made using a low-angle scattering photometer supplied by Chromatix (KMX-6). The molecular-weight determination of the scattering aggregates was obtained by measuring the excess Rayleigh factors of the micellar solution to that of water. The intensity fluctuations of the scattered light were used to determine the radii of the aggregates using a Ford designed autocorrelator (resolution 0.1 μs, 64 channels). For these measurements the photomultiplier voltage was set at ca. 1300 V.

Results and Discussion

(i) Size and Shape of the Aggregates. The critical micelle concentration of I in aqueous solution has been derived from surface tension–concentration plots as 5×10^{-4} M.[3] From these measurements one also obtains the surface requirement per head group, which corresponds to an area of 155 Å²/molecule. The Chromatix laser low-angle scattering photometer was employed to determine the molecular weight of the aggregates. First, steady-state values of the scattering intensity were measured as a function of Cu–crown concentration. The familiar Zimm plot representation[15] of the data is given in Figure 1. Upon diluting a concentrated micellar solution one notices a decrease in the parameter K_c/R_θ. However, as the cmc is approached an increase is observed, the curve falling off sharply after passing through a maximum. Such a behavior of the scattering function in the neighborhood of the cmc is indicative of small amounts of solubilized im-

Table I

	ϕ_F		ϕ_F
Pyr/NaLS	0.28	MPTH/NaLS	0.005
Pyr/CuCrown	<10⁻⁶	MPTH/CuCrown	0.0002
Cyn/MeOH	0.09	PTHDS/NaLS	0.006
Cyn/NaLS	0.45	PTHDS/CuCrown	0.0005
Cyn/Cu(LS)₂	0.20		
Cyn/CuCrown	0.002		

purities—presumably uncomplexed ligand—which undergo reorganization to large aggregates as the host micelles start to disintegrate. Similar phenomena have been observed for sodium lauryl sulfate in the presence of lauryl alcohol.[16] The sensitivity of the intensity-correlation technique to the presence of small amounts of water-insoluble material was shown to be very high. In order to evaluate the molecular weight (M_w) of the aggregates, only the data obtained at higher micellar concentrations which are not perturbed by these effects were used. K_c and $R(\theta)$ values were corrected for contributions of monomer surfactant and plotted against the difference in concentrations, i.e., Cu-crown$_{total}$ − cmc. The extrapolated intercept of the ordinate has a value of $(1.7 \pm 0.4) \times 10^{-7}$, corresponding to $(5.7 \pm 1.4) \times 10^6$ in molecular weight. Such a molecular weight may seem surprisingly high for a micelle; however, in the case of macrocyclic surfactants charge repulsion between adjacent head groups is decreased allowing for the formation of large aggregates.

Further useful information regarding the structure of the crown-amine micelles was obtained from applying quasi-elastic light scattering technique. The autocorrelation function was measured at various concentrations of I above the cmc. The decay was fitted to a single exponential

$$I(t) = I(t_0) \exp(-K^2 Dt) \qquad (2)$$

where $K = (4\pi n/\lambda_0) \sin(\theta/2)$ (n = refractive index, $\lambda = 6328$ Å, and $\theta = 4.5°$). Deviating points at longer time arising from polydispersity were discarded. By applying the Stokes–Einstein equation $R_H = kT/6\pi\eta D$ the diffusion coefficient D of the particles can be converted into the hydrodynamic radius. One obtains $R_H = 543$ Å. If a spherical shape is assumed for the aggregates, one can also obtain R_H from the molecular weight. For a density of one and $M_w = 5.7 \times 10^6$ one derives $R_H = 130$ Å. Evidently, these two values are not compatible. Apart from this fact, packing requirements do not allow for the formation of spherical micelles with an aggregation number as high as that observed for I.[17,18] Hence, a nonspherical shape of the aggregates must be assumed. In order to render the molecular weight compatible with the hydrodynamic radius two alternative molecular dimension sets can be evaluated, an oblate form with the axes $a = 224$ Å, $b = 30$ Å, or a prolate structure having axes $a = 1685$ Å, $b = 30$ Å. The prolate model is in closer agreement to the experimental data.

(ii) Fluorescence Experiments. The purpose of these investigations was to explore the potential of complexed Cu²⁺ to quench the fluorescence of probes associated with or solubilized in the crown ether aggregates. An illustrative case is the behavior of the cyanine dye II. In homogeneous solution, i.e., methanol, this dye fluoresces with a quantum yield of 0.09 (Table I). When II is associated with sodium lauryl sulfate micelles (NaLS), the emission intensity is greatly increased ($\phi_F = 0.45$). This effect has been explained in terms of a rigidization of the cyanine in the micellar microenvironment preventing destructive pathways of excited-state deactivation.[19] If the Na⁺ counterion atmosphere is replaced by Cu²⁺ ions, i.e., if copper lauryl sulfate (Cu(LS)₂) micelles are employed, the quantum yield decreases by a factor of 2.5. However, a much more drastic quenching effect leading to almost complete annihilation of the fluorescence is displayed by mi-

Table II

		NaLS	CuCrown
MPTH	ϕ^+	0.0	0.65
	ϕ_T	1.0	<0.1
PTHDS	ϕ^+	0.0	0.55
	ϕ_T	1.0	<0.1

celles of I where the Cu^{2+} ions are present in form of a complex with the tetraaza crown ether ligands forming the head groups of the aggregate.
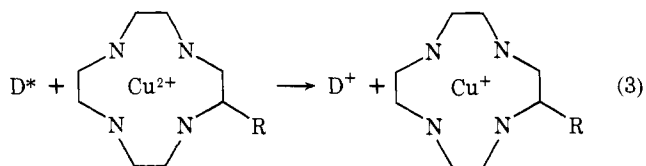
The high quenching activity of micellar Cu^{2+} crown ethers is not restricted to the cyanine fluorescence. For example, if pyrene is incorporated into the aggregates no fluorescence at all could be detected. By contrast, in sodium lauryl sulfate (NaLS) micelles pyrene fluoresces with a quantum yield of 0.28. In both cases the quenching does not lead to any chemical change in the system. On the contrary, the photostability of the cyanine dye, which is poor in homogeneous solution, is drastically increased in the presence of these aggregates.

To account for the above observations, one can evoke three different quenching mechanisms, i.e., energy transfer, paramagnetic effects, and electron transfer. Cu^{2+} ions bound to the aza crown ether show a band in the visible (λ_{max} 620 nm, ϵ 120 M^{-1} cm^{-1}) which is likely to represent a metal-centered transition. Energy transfer to this low-lying excited state could in principle occur even though the weak intensity of the band precludes any significant contributions from long-range resonance processes. However, as the Cu^{2+} aquo complex when present as a counterion of lauryl sulfate micelles exhibits an almost identical absorption as in I, it is difficult to explain with such a mechanism why the quenching efficiency of the two aggregates is so much different.

The concept of paramagnetic quenching is based on enhanced spin-orbit coupling induced by the perturber which usually promotes spin-forbidden transitions, i.e., intersystem crossing. Indeed, from this viewpoint the quenching efficiency of Cu^{2+} when bound in the aza complex is predicted to be higher than in the aquo complex since the ion is less shielded in the former environment. However, this effect should also lead to increased triplet production, which we failed to observe for the chromophores investigated.

These arguments favor electron transfer as the dominant quenching mechanism, the excited chromophore acting as donor and the aza crown ether complex as electron acceptor. The tetraaza ligand plays a key role inasmuch as it provides a bridging element for the transfer process.[20] In fact, a configuration where the electron is associated with the ligand sphere is identical with an ML excited state of the Cu^+ complex. This state could be the intermediate from which very rapid back-transfer to the donor cation takes place.

(iii) Light-Induced Electron Transfer. In these investigations the ability of the aza crown ether micelles was tested to participate in photoredox processes. A hydrophobic donor, i.e., N-methylphenothiazine (MPTH), was incorporated into the aggregates. The excited state of MPTH has strong reducing properties[5] and hence is expected to react with complexed Cu^{2+} according to (3) where R stands for $C_{14}H_{29}$.

$$D^* + \left[\begin{array}{c} N \quad N \\ Cu^{2+} \\ N \quad N \end{array} \right]_R \longrightarrow D^+ + \left[\begin{array}{c} N \quad N \\ Cu^+ \\ N \quad N \end{array} \right]_R \qquad (3)$$

where R stands for $C_{14}H_{29}$.

Indeed, laser photolysis experiments showed that reaction 3 occurs very rapidly, the end of pulse spectrum being identical
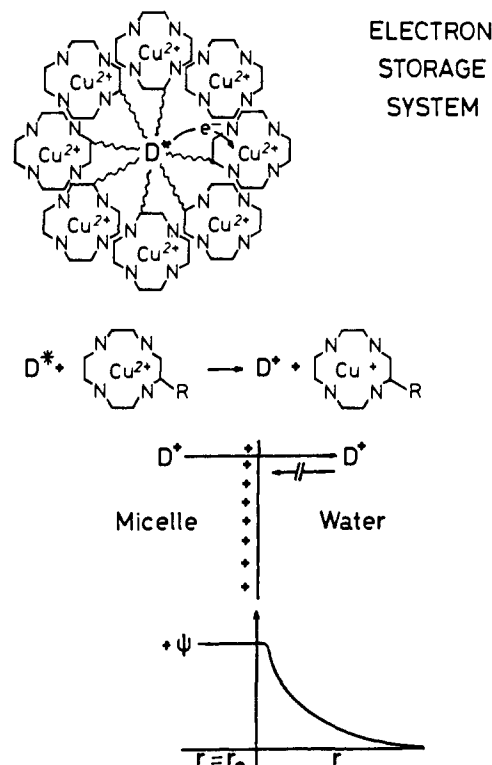

Figure 2. Schematic illustration of the photoinduced reduction of Cu^{2+} by a donor D incorporated into the macrocyclic micelles and subsequent charge ejection.

with that of the $MPTH^+$ cation.[5] The yield of $MPTH^+$ calculated from the transient absorbance at 760 nm immediately after the laser flash is indicated in Table II. While in simple NaLS cation production is negligible, it occurs with an efficacy of 65% in the Cu^{2+}-crown aggregates. Interestingly, cations are produced at the expense of triplet states. From this it may be inferred that electron transfer occurs from a triplet precursor, i.e., the excited singlet state. Such a mechanism is corroborated by the fact that the fluorescence quantum yield is significantly decreased in the Cu^{2+} crown as compared to the NaLS aggregates.

It is instructive to examine the further fate of the $MPTH^+$ cation in such a system. The transient signal at 515 nm, which is characteristic of the $MPTH^+$,[5,6] decreases rapidly in time until a plateau is attained. A second decay follows thereafter on a much slower time scale of several milliseconds. The first component can be assigned to intramicellar back electron transfer from Cu^+ to $MPTH^+$. Similar reactions have been studied in detail earlier[6,21] and the observed rate constant $k = 8 \times 10^6$ s^{-1} is typical for such redox events. The second components accounts for ca. 50% of the total signal and is attributed to those $MPTH^+$ ions that are ejected from the micelle before back-reaction can occur. Such a process is favored by the repulsive electrostatic interaction between the cation and the local micellar environment.[22-24] Once in the water the reapproach of $MPTH^+$ to the micelle is prevented by the positive surface charge. The slow disappearance of $MPTH^+$ must therefore arise from dismutation or hydrolysis. These processes are illustrated schematically in Figure 2.

It should be noted that at least half of the electrons transferred to Cu^{2+} initially remain as stored charge in the form of Cu^+ available for further reduction processes. This electron storage effect, which is unique to macrocyclic micelles, has importance for a possible application to light energy conversion system. Any molecular organization which enhances and maintains light-induced charge separation is of great significance in this domain.

In order to check the above interpretations it appeared attractive to examine the same photoredox events with the functional phenothiazine derivative III. We reasoned that the sulfonated alkyl chains would tend to retain the phenothiazine cation at the site of Cu^{2+}-crown aggregates making its escape into the aqueous bulk less probable. The results are included in Tables I and II. The yield of cations approaches that for $MPTH^+$. Also, $PTHDS^+$ decays in two steps, the first component constituting about 55% of the total signal. The kinetics obey a first-order law with time constants of 1.3×10^7 and 4×10^4 s^{-1} for the fast and slow part, respectively. The main difference between the behavior of $MPTH^+$ and $PTHDS^+$ is that the latter decays much faster than the former in the second part of the reaction. This would in fact be expected if the slower component arose from those cations that leave the micellar core to exit into the aqueous phase. In contrast to $MPTH^+$ the detachment will not be complete as the cation remains anchored to the surface of its micelle or origin through the anionic sulfonate groups. Eventually, charge recombination with Cu^+ will occur, giving rise to the relatively fast decay process.

Finally, we wish to point out that, apart from the photoinduced electron transfer, the Cu^{2+}-crown can also be thermally or electrochemically reduced. For example, addition of $NaBH_4$ at neutral pH or $TiCl_3$ at pH 1 produces a hydrophobic species that can be readily extracted into chloroform. The product has a brownish color corresponding to a broad, featureless absorption which extends in the UV region. The NMR spectrum reveals considerable broadening of the $-CH_2-$ and $-NH$ peaks of the macrocyclic ring indicating the presence of a paramagnetic species within the macrocycle. This rules out Cu^+ as the reduction product. By inference from recent results obtained with silver aza crown ethers[25] it may be considered that Cu(0), i.e., monatomic copper in the zero valency state, is the probable reduction product. This is prevented from aggregation by the macrocyclic ligand. Such an interpretation is also supported by the fact that electron acceptors such as $Fe(CN)_6^{3-}$ reoxidize quantitatively the reduced complex back to the original blue form. This indicates that the Cu^{2+} macrocyclic surfactant can indeed act as an electron relay.

References and Notes

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