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Light-Induced Charge Injection in Functional Crown Ether Vesicles

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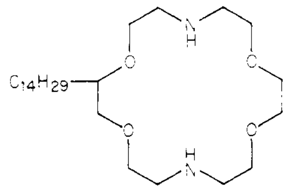
Abstract: A surfactant analogue aza crown ether when complexed with silver(I) ions aggregates spontaneously in aqueous solutions to form vesicles of approximately spherical shape. The values of the hydrodynamic radius and radius of gyration are 450 and 420 Å, respectively. Photoinduced electron transfer from two senstitizers, a cyanine dye and a surfactant ruthenium complex, leads to production of zerovalent silver which is stabilized by the microenvironment of the vesicles. The electron transfer is so rapid that it occurs in the nanosecond time domain. The advantages in using such functionalized redox relays to achieve light-induced charge separation are discussed.

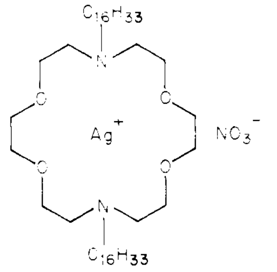
Introduction

Self-assembly of functional surfactants frequently leads to aggregates displaying cooperative effects. By means of suitable molecular engineering, systems may be designed that can achieve light-induced charge separation and efficient energy conversion.[2,3] Previously, crown ethers were developed which were substituted by long alkyl chains.[4-6] These are particularly suited to serve as electron relays in redox reactions since a variety of transition-metal ions covering a wide range of redox potentials can be inserted in the macrocyclic ring. Thus, when Ag^+ ions are incorporated into I, one observes photoinduced reduction of Ag^+ to silver atoms by a variety of donor molecules.[7] While monoalkyl-substituted macrocycles such as the Ag^+ derivative of I form micellar aggregates, it is expected that dialkyl-substituted complexes undergo vesicle formation. The latter have the advantage of being relatively rigid, compartmented aggregates that can be formed even at very low surfactant concentration.



I

We wish to report here on the silver derivative of a dialkyldiaza crown ether (II) which is capable of vesicle formation. These can interact with donor molecules which when excited by light will reduce Ag^+ to the zero valency state.



II

Experimental Section

Materials. The two chain diaza crown ether was a gift which had been made by the method described by Ginquini and Tundo.[8] The cyanine dye was obtained from Ciba-Geigy and the surfactant ruthenium complex was a gift from Professor Sasse. All the other chemicals used were reagent grade (Fluka).

Physical Measurements. Decay kinetics were studied by laser flash photolysis. The doubled frequency pulse (530 nm) of a JK neodymium Yag laser was used as the exciting frequency. The details of the optical system have been published elsewhere. The transient curves were recorded by using a Tektronix transient digitizer and a PDP 11/04 computer. The raw data were treated by using the HP9825A calculator and software written in this Institute.

Absorption spectra were recorded on a Cary 14 spectrometer and fluorescence spectra were measured by using a Perkin-Elmer MPF-44A which had a correction unit. Light-scattering data were obtained by using the setup in Milan belonging to Professors Corti and Degorgio. The details of the instrument have been published by them.[9] pH measurements were made by using an Orion 701 pH meter.

The vesicles were prepared by sonication using a Branson Sonifier-B-12. Sample solutions were then degassed by bubbling argon and all spectroscopic measurements were made using 1-cm cells.

Results and Discussion

(i) Characterization of Crown Vesicles. Dynamic light scattering was used to characterize these surfactant aggregates. This technique was used in preference to electron microscopy because complicated staining and sample preparation procedures could be avoided. The optical source used on the light-scattering aggregates is an argon ion laser operating at 5145 Å with an output power of about 50 mW. The average scattered intensity was measured at three angles, viz., θ = 30, 90, and 150°. The time-dependent correlation function of the scattered intensity was also determined at these angles. Intensity correlation data were derived by using a 108 channel digital correlator.

Figure 1 shows correlation functions obtained at different angles with 10^{-4} M solutions of II. The semilogarithmic plot is linear over approximately one lifetime. Thereafter, positive deviations occur indicating a medium degree of polydispersity of the samples. The slope $1/\tau$ of the linear portion increases with scattering angle. This is illustrated in Figure 2, where $1/\tau$ is plotted against the scattering parameter

$$K = \left[\frac{4\pi n}{\lambda}\sin\frac{\theta}{2}\right] \qquad (1)$$

where n is the refractive index and λ is the wavelength of the incident light beam. In the homodyne mode the relation $1/\tau = 2DK^2$ should hold as is indeed the case. The diffusion coefficient

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(1) (a) Ecole Polytechnique Fédérale; (b) Universita di Turino.

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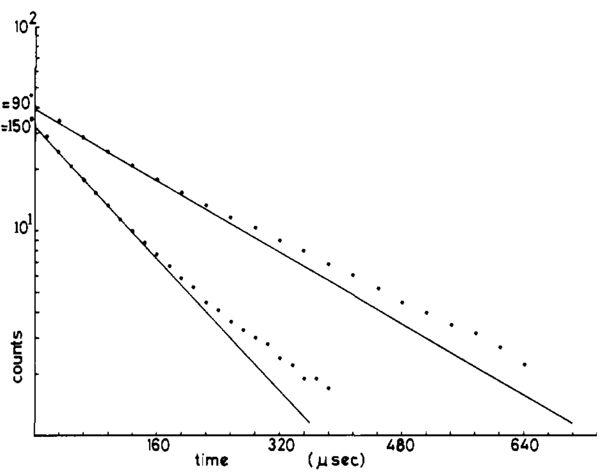


Figure 1. Plot of the autocorrelation functions (homodyne) of crown vesicle solutions of two different angles.

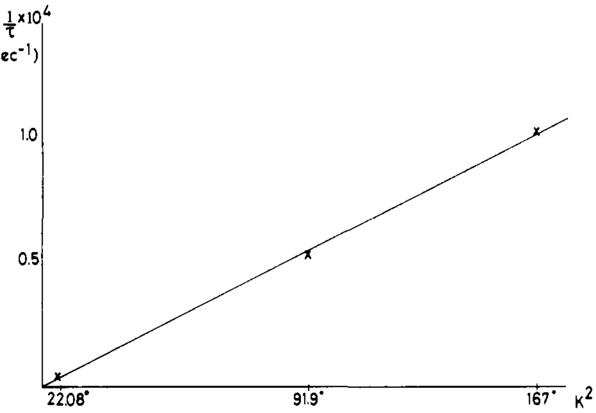


Figure 2. The reciprocal of the lifetimes obtained from correlation plots vs. the scattering parameter K^2. (The values of angles used were corrected for the internal angles of the cell.)

D is related to the hydrodynamic radius R_H via the Stokes–Einstein relation

$$D = kT/6\pi\eta R_H \quad (2)$$

where η is the microviscosity of the dispersion medium. From the data in Figure 2 one evaluates R_H = 450 Å. It should be noted that this parameter represents an effective radius of the aggregates from which no conclusions concerning the geometry of the aggregates can be derived. In fact, on the basis of the R_H determination alone, one cannot rule out the possibility that the crown ether surfactant is organized in the form of aggregates different from vesicles such as rod-shaped micelles. For this reason, the radius of gyration R_g was determined in addition to R_H.

The radius of gyration was obtained from the measurement of the time-averaged scatter intensity at the three angles. Solutions contained II in 10^{-4} M concentration. Let $\Delta/1,2$ be the difference in scatter intensity at two angles and K_1, K_2 the respective scatter parameters as defined by eq 1. Then

$$R_g^2 = 3\,\frac{1 - \Delta/1,2}{K_1^2 - (\Delta/1,2)K_2^2} \quad (3)$$

Inserting experimental data in eq 3 gives R_g = 420 Å. For spherical aggregates the relation $R_g = (3/5)^{1/2}R_H$ should hold,[10] which gives R_g = 350 Å. The agreement is satisfactory; in particular the existence of other structures such as rod-shaped micelles can be ruled out on the basis of projected $R_g \rightarrow R_H$ relations characteristic for these types of aggregates.[10] It is concluded that the crown ether assemblies are vesicles of approximately spherical geometry with a mean radius of 426 Å and a medium degree of polydispersity.

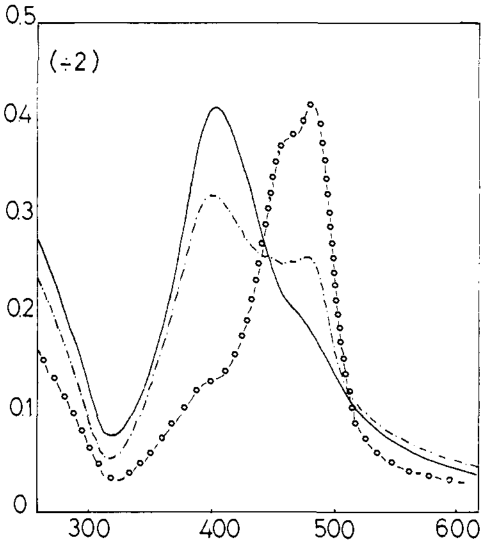


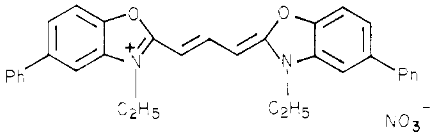
Figure 3. The absorption spectrum illustrating the changes observed in the continuous photolysis (λ 475 nm) of the cyanine dye (III) and the Ag^1 crown vesicle II.

(ii) Photoredox Processes Involving Crown Ether Vesicles. The following section will be concerned with the light-induced electron injection into crown ether vesicles of compound II. In these experiments, a photoactive donor is added to the solution which associates with the surfactant aggregates. The excited state (D*) is capable of reducing the complexed silver ion to the atomic state:

$$LAg^+ + D^* \rightarrow D^+ + LAg^0 \quad (4)$$

where LAg^+ stands for II.

The first donor employed in this study is the cyanine dye III.



III

Figure 3 shows spectral data obtained from the steady-state photolysis of III (5.85 × 10^{-6} M) in aqueous solution of AgL^+ (1 × 10^{-4} M). The absorption spectrum of III taken prior to illumination indicates that the dye is present mainly in its monomeric form.[11] Irradiation by visible light leads to bleaching of the cyanine absorption which is accompanied by the growth of a prominent peak centered around 400 nm. The latter can be attributed to zerovalent silver LAg^0, which is prevented from precipitation by the macrocycles surfactant.[11] The cation radical of the cyanine dye which is also formed during reaction 4 undergoes rapid dissociation into two fragments which do not absorb in the visible. Surprising in Figure 3 is the strong intensity of the LAg^0 transition. At most, one molecule of LAg^0 can be formed from one cyanine dye; then the extinction coefficient of the LAg^0 reduction product must be at least 1.4 × 10^5 M^{-1} cm^{-1}. Whether this extremely strong absorption arises from cooperative interaction of adjacent LAg^0 or aggregation of several Ag^0 atoms to extremely small units stabilized by the macrocyclic surfactant remains to be shown. Colloidal clusters of Ag^0 absorb at a similar wavelength but with a much smaller extinction coefficient.[11]

In order to obtain information on the rate of the electron-transfer process induced by light, laser photolysis experiments were carried out using the 15-ns pulse of a frequency doubled Nd laser for excitation of the cyanine. The solution composition was the

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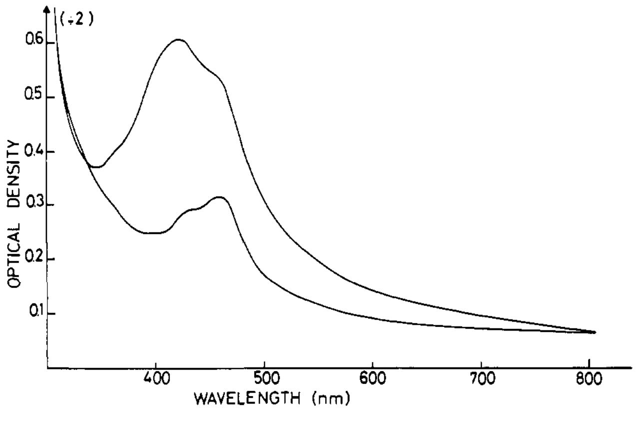
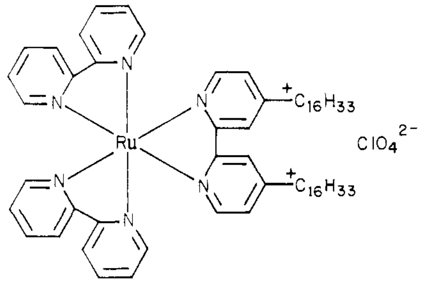


Figure 4. The absorption spectrum illustrating the changes observed in the continuous photolysis of the Ru^{2+} complex IV and Ag′ crown vesicle.

same as that used above for the continuous photolysis experiments. Measurements carried out at 405 and 478 nm with nanosecond time resolution showed that the bleaching of the cyanine and formation of the absorption at 405 nm are both extremely fast processes occurring simultaneously and within the laser pulse. The rapid nature of these redox events may be rationalized in terms of the high local concentration of LAg^+ in the vesicles which provides enough empty electronic states to allow for a rapid tunneling transition of the electron from the excited cyanine to the LAg^+ acceptor. Thus, this process can compete efficiently with the other pathways of S_1 deactivation which in micellar systems take place within a time span of only 1 ns.

The second donor employed in these studies was the surfactant derivative of the ruthenium(II) 4,4′ trisbipyridine complex (IV).



IV

IV in deaerated methanolic solutions has an emission lifetime of $\tau = 700$ ns, which is distinctively longer than that for the unsubstituted complex. Incorporation of IV (1.8×10^{-5} M) in Ag^+–crown vesicles (1.4×10^{-4} M) produces quenching of the emission, $\tau = 500$ ns, as measured by laser photolysis technique. The spectrum of the species produced in the quenching event is shown in Figure 4. Apparently the absorption is significantly red shifted from that of simple LAg^0. Instead of a sharp peak at 405 nm a broad band is observed extending over several hundred nanometers. Under continuous illumination the solution assumes a dark red color which deepens with irradiation time attaining very high optical densities.

These phenomena may be rationalized in terms of electron transfer quenching of IV by the LAg^+ complex

$$Ru(bpy)_3{}^{2+*} + LAg^+ \rightarrow LAg^0 + Ru(bpy)_3{}^{3+} \qquad (5)$$

where for reasons of simplicity we have designated the surfactant ruthenium complex with $Ru(bpy)_3{}^{2+}$. An energy-transfer mechanism can be excluded since LAg^+ does not dispose of the appropriate low-lying excited states. However, reaction 5 alone cannot explain the strong photochromic effects found with this system. In particular the intense absorption above 450 nm cannot be accounted for by LAg^0 or $Ru(bpy)_3{}^{3+}$ since their extinction coefficient is small in this wavelength region. As the effect is specific for $Ru(bpy)_3{}^{2+}$ and does not occur with a number of other sensitizers it is likely to arise from a ligand transfer from $Ru(bpy)_3{}^{3+}$ to the reduced silver crown:

$$LAg^0 + Ru(bpy)_3{}^{3+} \rightarrow LAg^0 - (bpy) + Ru(bpy)_2{}^{3+} \qquad (6)$$

In fact, when LAg^0 is produced in the absence of $Ru(bpy)_3{}^{2+}$, for example, by cyanine-sensitized reduction of LAg^+, addition of 4,4′-bipyridyl (2×10^{-5} M) to the solution causes a distinct broadening of the LAg^0 spectrum. In particular, the absorption in the wavelength region above 450 nm is intensified, indicating the formation of a charge-transfer complex between zerovalent silver and the bipyridyl.

Further transformations of the ruthenium complex become apparent from fluorescence studies on solutions which prior to analysis were exposed to light. Laser photolysis experiments show that the red emission of the sensitizer decays here in two steps corresponding to lifetimes of 430 and 500 ns, respectively. Superimposed on the characteristic $Ru(bpy)_3{}^{2+}$ emission at 620 nm appears a red-shifted peak with a maximum around 675 nm. This, as well as the short-lived component in the luminescence decay, is likely to arise[12] from the aquated Ru complex $Ru(bpy)_2(H_2O)^{2+}$ formed from the trivalent state via reduction by water or the tertiary amine group of the crown ether. Such a reaction sequence could also explain the experimental fact that the photoprocess appears to be cyclic with respect to the sensitizer. If $Ru(bpy)_2(H_2O)^{2+}$ is photoactive with respect to LAg^+ reduction, the formation of LAg^0 under illumination will continue until all Ag^+ ions have been consumed.

Conclusion

The crown ether type surfactant employed in the present study aggregates spontaneously in aqueous solution to give stable vesicles of spherical shape. Light-induced electron ejection from sensitizers associated with the aggregate leads to irreversible formation of zerovalent silver. This process is so rapid that it can compete efficiently with other deactivation pathways of excited singlet states. In this context, it is interesting to note that simple Ag^+ ions in aqueous solution are not reduced by $Ru(bpy)_3$.[13] One notices here the advantage of using functionalized chromophores and redox relays to bring about photoinduced electron transfer.[14]

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