

Short Communication

Aging of micellar solutions of ethylene oxide surfactants

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1. Introduction

Because of our interest in electron transfer quenching in micellar solutions we have studied the quenching of emitting molecules by quenchers which are so insoluble in water that they cannot be solubilized via the water phase [1, 2]. Consequently, redistribution via the water phase should be impossible. Quenching then would indicate exchange of solubilized guest molecules during collisions or merging of micelles, a process also of importance in the establishment of equilibrium in certain micellar solutions [3].

In many experiments with non-ionic surfactants we have had problems with reproducibility. Generally the results of quantum yield determinations, measurements of lifetimes or monomer-to-excimer emission ratios were reproducible to within an order of magnitude, but not as reproducible as in homogeneous solutions. We realized that these effects are due to aging of micellar solutions of the ethylene oxide detergents [4] and investigated the temporal changes.

A property that indicates temporal changes in the micellar solutions is the temperature of the cloud point, irrespective of the nature of the phenomenon [5]. As we are interested in the spectroscopy of probe molecules we have also recorded the decay of one of our probe complexes $\text{Ru}[(\text{C}_{11}\text{H}_{23})_2\text{bpy}]_3^{2+}$ (where bpy \equiv bipyridyl) as an indicator.

2. Materials

In order to obtain relevant results we used "uniform" surfactant material C_8E_5 (Bachem, Bubendorf, Switzerland), C_8E_6 and C_8E_9 (gifts of Dr. Schwuger, Henkel G.m.b.H., Düsseldorf, F.R.G.) and C_8E_{12} (Nikko Chemical, Tokyo, Japan). The purities were checked by thin-layer chromatography (TLC) and were found to be at least 90% for the new detergents. We generally used 50 mM solutions which were stored in screw-capped bottles; oxygen was removed for lifetime measurements only. From previous experiments we had 10-month-old samples of C_8E_6 and C_8E_9 left in the refrigerator. These samples were absolutely clear to the eye and obviously had not been attacked by micro-organisms.

3. Methods and apparatus

The temperature of the cloud point was determined by a simple set-up consisting of an He-Ne laser (Spectra Physics), a rectangular four-sided spectroscopic scattering cell in a thermostated holder, a double monochromator and a photomultiplier. Its output was fed to the y axis of an HP 4047A recorder. The voltage of a thermocouple lowered into the scattering cell through a hole in the stopper was fed to the x axis. Scattering was determined at right angles to the laser beam and in the transmission mode. The approach to the cloud point was degree by degree of the thermostat setting in order to avoid extensive convection in the scattering cell.

Lifetimes were measured by flash excitation using an XeCl-excimer-laser-pumped dye laser at 453 nm (both lasers from Lambda Physik, Göttingen, F.R.G.). The emission was monitored by means of a Tektronix 7834 storage oscilloscope and was photographed. Oxygen was removed by bubbling argon through the solutions in spectrophotometric sealable cells equipped with a bulb (about 100 ml in capacity) to break the foam. A fit-program with one or two exponential functions executed on a 4052 Tektronix computer was used for evaluation.

TLC was carried out on silica F 254 (Merck) with ethyl-methylketone:water (9.75:1, by volume) with development using Dragendorff's reagent (Merck 118) and subsequently a 5 wt.% NaNO_2 solution in water.

4. Results

The results of the cloud point measurements are shown in Fig. 1. They reveal an increase in the cloud points of about 5°C within 2 months. The aged samples indicate a still larger increase within about 1 year. We have 8-months-old cloud point determinations from an identical sample which show that clouding at that time occurred at 69°C .

Since we do not have the equipment to determine micellar structures directly, we are limited to the indirect methods of probing the system by using emitting molecules. We used the water-insoluble ruthenium complex $\text{Ru}[(\text{C}_{11}\text{H}_{23})_2\text{bpy}]_3^{2+}$ and determined its phosphorescence decay in new and aged micellar solutions. The result is shown in Fig. 2.

The decay in the aged micelles is strictly monoexponential whereas it is clearly non-monoexponential in the new micelles. We analysed the decay and fitted it rather well using a bi-exponential equation, but we are hesitant about stating two distinct decay times. The photographic method might not be sufficiently accurate to discriminate between two and a multitude of decay times. However, it is obvious that the lifetime of the ruthenium complex is reduced to about 400 ns compared with that in the homogeneous ethanol solution (710 ± 20 ns).

Oxygen is obviously retained in the polyoxyethylene micelles. Flushing with argon for 2, 3 and 4 h with newly prepared micellar solutions increased the lifetime of the substituted ruthenium complex (as taken from plots such as Fig. 2 at long times) from 390 to 415 and 430 ns. Admission of air only slowly effected a decrease in lifetime. Bubbling of oxygen over 2 h changed

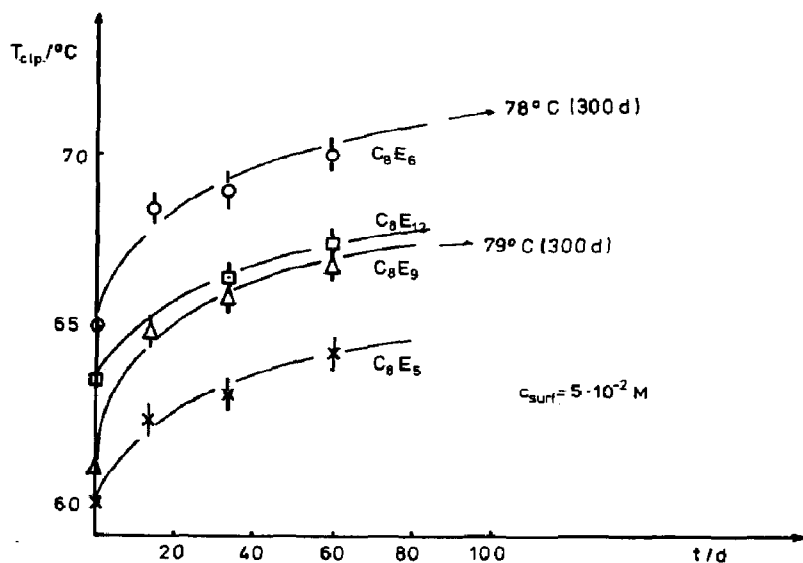


Fig. 1. Aging of polyoxyethylene surfactants with time (surfactant concentration, 5×10^{-2} M): \circ , C_8E_6 (78 °C; 300 days); \square , C_8E_{12} ; \triangle , C_8E_9 (79 °C; 300 days); $*$, C_8E_5 .

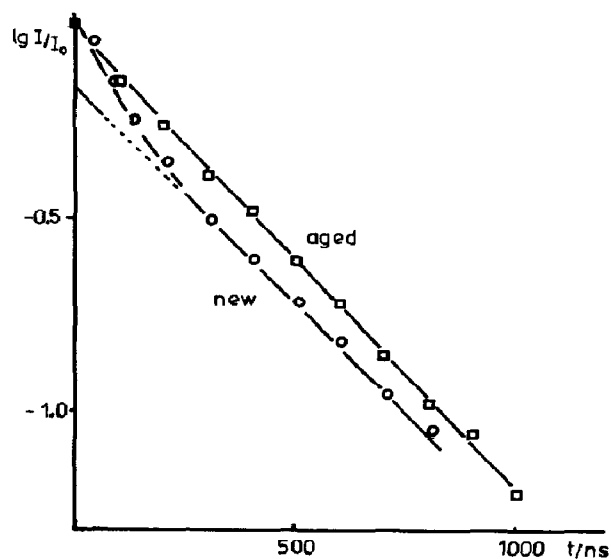


Fig. 2. Decay of emission of $Ru[(C_{11}H_{23})_2bpy]_3Cl_2$ in C_8E_6 .

it to 280 ns. Ionic electron transfer quenchers such as methylviologen or $AgClO_4$ did not reduce the emission decay time of the ruthenium complex in C_8E_6 micelles.

The thin layer chromatograms of the new surfactants showed a main fraction of the correct compound and only minor contamination with lower and higher ethylene oxide homologues. The chromatograms of fresh and

middle-aged solutions of older surfactants exhibited more of the faster and slower compounds, and the chromatograms of the 1-year-old solutions were rather simple again, showing the correct compound and one main impurity.

5. Discussion

The emission of ruthenium trisbipyridyl complexes is quite sensitive to environmental influences. Hydrocarbon-substituted complexes have emission lifetimes of 1100 ns in sodium dodecylsulphate micellar solution [2], 710 ns in ethanol and 400 ns in polyoxyethylene micelles.

The results of this study indicate that there is a profound change in micellar structure with time. The aging is substantial and it is surprising that in most publications there is no account on the stage of the aging process. Obviously the surfactants are subject to chemical degradation in the bottle and in aqueous solution. This may be due to contact with polyethylene screw caps, metals and oxygen [6].

Corti *et al.* [4] have reported aging effects of C_mE_n , but they have found a decrease in the critical temperature of demixing with time and a small effect at room temperature. They assume oxidative degradation of the surfactant molecules. The degradation reduces the concentration of the surfactant. This causes a displacement of the locus of the micellar system in the phase diagram. As the concentrations used in this work (50 mM or about 1.5%) are below the concentration where the critical temperature of demixing is at its minimum [7], the decrease in concentration takes the system to a region in the phase diagram where the temperature of clouding is increased.

It is surprising that the old solutions should be more uniform than the middle-aged solutions. A possible rationalization may be that the degradation of the original surfactant occurs via smaller surfactant molecules, which have a critical micelle concentration of their own, to the final products. If the absolute amount of surfactant material decreases sufficiently there are still micelles of the original surfactant, but the concentrations of the intermediate products of degradation fall below their critical micellar concentration. The final products disappear from the thin layer chromatogram, perhaps being adsorbed at the surfaces of the vessels or solubilized in the remaining micelles.

6. Conclusion

It has been shown that micellar solutions of polyoxyethylene surfactants exhibit pronounced aging. Aging is attributed to degradation of the surfactant molecules. Phenomena that are influenced by interaction with the environment, *e.g.* lifetimes of excited molecules, and bimolecular processes will be dependent on the history of the system. This has to be taken into account when polyoxyethylene micelles are used for purposes such as reaction compartments or in energy or electron transfer experiments. Aging may be, unfortunately, of relevance for comparison of data from different investigations.

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References

- 1 G. Schneider and H. Rau, unpublished work.
- 2 F. Steinmüller and H. Rau, *J. Photochem.*, **28** (1985) 297.
- 3 E. Lessner, M. Teubner and M. Kahlweit, *J. Phys. Chem.*, **85** (1981) 3167.
J. Lang, C. Tondre, R. Zana, R. Bauer, H. Hoffmann and W. Ulbricht, *J. Phys. Chem.*, **89** (1975) 276.
M. Kahlweit, *J. Colloid Interface Sci.*, **90** (1982) 92.
- 4 M. Corti, C. Minero, L. Cantu and R. Piazza, *Colloid Surf.*, **12** (1984) 341.
- 5 H. H. Paradies, *J. Phys. Chem.*, **84** (1980) 599.
M. Corti and V. Degiorgio, *J. Phys. Chem.*, **85** (1981) 1442.
- 6 M. Corti, personal communication, October 21, 1986.
- 7 M. Zulauf and J. P. Rosenbusch, *J. Phys. Chem.*, **87** (1983) 856.