Reversible Formation and Disruption of Micelles by Control of the Redox State of the Surfactant Tail Group

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Reversible disruption and re-formation of micelles is observed by following the redox reaction of the redox-active micelles formed by the bromide salt of (11-ferrocenyl)undecyltrimethylammonium having a ferrocene moiety instead of the terminal methyl proton.

Redox-active surfactant micelles with attached redox probes are of considerable interest since they are expected to play an important role in energy storing photoreactions.[1—4] However, no studies have so far dealt with the change in the aggregation behaviour of surfactants by control of the redox state of the surfactant molecules. This communication reports that micelles formed by the univalent surfactant $Fc\text{-}C_{11}H_{22}\text{-}N^+Me_3$, denoted as $(\mathbf{1})^+$, (Fc = ferrocene)† are reversibly disrupted into monomers and re-formed from the monomers, by oxidation to the divalent surfactant $Fc^+C_{11}H_{22}\text{-}N^+Me_3$, $(\mathbf{1})^{2+}$, and re-reduction, respectively.

Figure 1 shows the concentration dependence of the diffusion coefficient of $(\mathbf{1})^+$ and $(\mathbf{1})^{2+}$ in 0.2 M Li_2SO_4 aqueous solution at 25 °C. The values of the diffusion coefficient, D, were determined by potential-step chronoamperometry.[5] The $(\mathbf{1})^{2+}$ solution was prepared from a solution of $(\mathbf{1})^+$ by controlled-potential bulk electrolysis. A large difference in the value of D between $(\mathbf{1})^+$ and $(\mathbf{1})^{2+}$ suggests that most of the $(\mathbf{1})^+$ molecules exist in the form of micelles, whereas all of the $(\mathbf{1})^{2+}$ molecules are in the monomeric form.

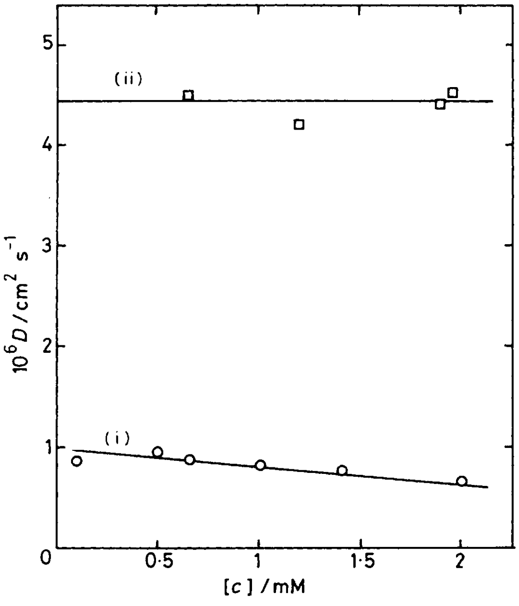

Figure 1. Concentration dependence [c] of the diffusion coefficient, D, of (i) $(\mathbf{1})^+$ and (ii) $(\mathbf{1})^{2+}$ in 0.2 M Li_2SO_4 aqueous solution at 25 °C.

The micellar weight of $(\mathbf{1})^+$ in 0.2 M Li_2SO_4 was determined to be 1.1×10^5. The aggregation number was determined as 230 at 25 °C by the quasielastic light scattering method.[6]

As the ferrocene moieties of $(\mathbf{1})^+$ are oxidized, the $(\mathbf{1})^+$ surfactants forming micelles may separate into the monomers owing to the enhancement in hydrophilicity of the surfactant tail groups.

The feasibility of control of micelle formation and disruption was also demonstrated by investigating the ability of solutions of $(\mathbf{1})^+$ and $(\mathbf{1})^{2+}$ to solubilize a water-insoluble substance, 1-(*o*-tolylazo)naphthalen-2-ol, TAN. Figure 2 shows u.v.–visible absorption spectra of the following test solutions: solutions A, $(\mathbf{1})^+$ (2.0 mM) + TAN (sat.) and A′, $(\mathbf{1})^+$ (2.0 mM); solutions B, $(\mathbf{1})^{2+}$ (2.0 mM) + TAN (sat.) and B′, $(\mathbf{1})^{2+}$ (2.0 mM); and solution C, re-reduced $(\mathbf{1})^+$ + TAN. Solution B was prepared by the oxidation of solution A with $Ce(SO_4)_2$, and solution C by the reduction of solution B with $Na_2S_2O_4$. The amount of TAN in the $(\mathbf{1})^{2+}$ solution, which can be estimated by subtracting the spectrum of solution B′ from that of solution B, is less than 15% relative to that of TAN solubilized in the $(\mathbf{1})^+$ micelles. The latter can be estimated by subtracting the spectrum of A′ from that of A. These findings suggest that TAN is solubilized in the $(\mathbf{1})^+$

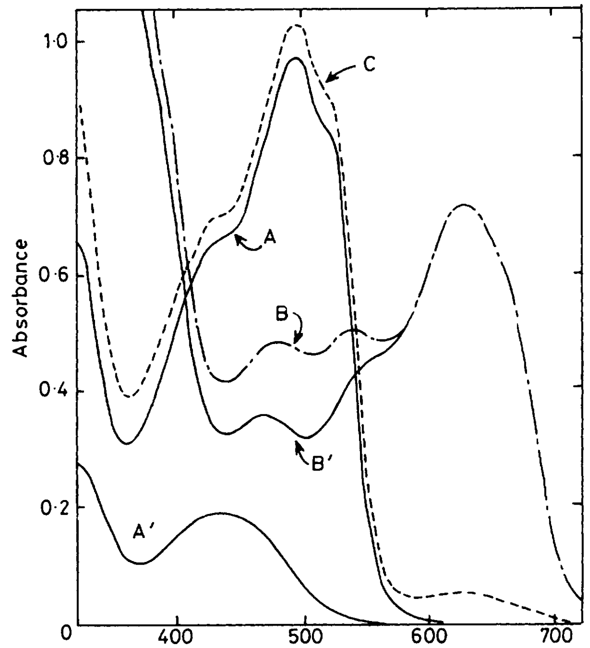

Figure 2. Electronic absorption spectra of TAN saturated in 0.2 M Li_2SO_4 containing solutions A, 2.0 mM $(\mathbf{1})^+$, and B, 2.0 mM $(\mathbf{1})^{2+}$. Solutions A′ and B′ are the spectra for 2.0 mM $(\mathbf{1})^+$ and $(\mathbf{1})^{2+}$ not containing TAN, respectively.

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† Preparation of $(\mathbf{1})^+$: 11-bromoundecanoic acid is converted into 11-bromoundecanoyl chloride with $SOCl_2$. Friedel–Crafts acylation of the ferrocene ring is accomplished with the acid chloride in the presence of $AlCl_3$. The Clemmensen reduction of the resultant ketone to a methylene group gives 11-bromoundecylferrocene. The quaternization of trimethylamine with 11-bromoundecylferrocene yields the $(\mathbf{1})^+$ surfactant. This sample was characterised by i.r. and u.v.–visible spectra and elemental analysis.

micelles, and, when **(1)**$^+$ is oxidized into **(1)**$^{2+}$, the micelles are broken up, and TAN is released and precipitated.

The reversibility of this process is demonstrated by the following experiment: addition of $Na_2S_2O_4$ to solution B under stirring yielded almost the same spectrum as that of A (solution C, Figure 2), which indicates the re-formation of **(1)**$^+$ and hence its micelles by re-reduction.

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References

1 N. J. Turro, M. Grätzel, and A. M. Braun, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 675.
2 R. Humphry-Baker, M. Grätzel, P. Tundo, and E. Pelizzeti, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 630.
3 K. Takuma, T. Sakamoto, T. Nagamura, and T. Matsuo, *J. Phys. Chem.*, 1981, **85**, 619.
4 P. A. Brugger, P. P. Infelta, A. M. Braun, and M. Grätzel, *J. Am. Chem. Soc.*, 1981, **103**, 320.
5 *E.g.* A. J. Bard and L. R. Faulkner, 'Electrochemical Methods,' Wiley, New York, 1980, p. 136.
6 *E.g.* K. Shinoda, T. Nagamura, B. Tamamushi, and T. Isemura, 'Colloidal Surfactants,' Academic Press, New York and London, 1963, p. 112.