per incident photon. Assuming an average energy corresponding to a wavelength of 320 nm, we estimate 1.4×10^{-7} and 1.0×10^{-8} molecules/incident photon for CH_3Br and CH_3I. Because the photon absorption cross section is unknown, we cannot estimate quantum yields.

Acknowledgment. This work was supported in part by the National Science Foundation Grant CHE 8505413.

Kinetic Studies of the Sphere-Rod Transition of Micelles

Shoji Harada,* Nobuya Fujita, and Takayuki Sano

Department of Materials Science, Faculty of Science, Hiroshima University
Naka-ku, Hiroshima 730, Japan

Received May 11, 1988

Some surfactants change their micellar shape from sphere to rodlike by an increase of concentration or by the addition of electrolytes.[1] The sphere-rod transition of micelles has been widely studied, but no kinetic experiment has been done, and the mechanism of the transition has not been clarified. In this work, we studied the sphere-rod transition of cetyltrimethylammonium bromide (CTAB) micelle both statically and kinetically and reached a conclusion that the rodlike micelle is formed by successive association of the monomers to the sphere micelles.

The aggregation behaviors of CTAB were studied by conductivity and ultrasonic velocity measurements. In the plots of these properties against the CTAB concentration, a break point was observed at 1.0 mM, which was ascribed to the CMC.[2] As seen in Figure 1, another break point was observed at around 250 mM, which is in accordance with the reported value for the sphere-rod transition concentration of CTAB micelle.[3] In contrast to these, the plots for the cetyltrimethylammonium chloride (CTAC) solution where the micellar shape remains unchanged were linear, and any break point was not observed.

Pressure-jump studies were performed on the CTAB solution in a wide concentration range. In a solution of concentration a little above the CMC, two relaxations were observed. Temperature dependencies of their reciprocal relaxation times are shown in Figure 2 where we can observe that they are similar to those for other surfactants.[4] Following preceding studies[5] the fast relaxation with a time constant of about 10 ms might be ascribed to the monomer exchange and the slow relaxation with a time constant of about 1 s to the overall formation and dissolution of the sphere micelles. The relaxation amplitudes and the relaxation times reduced with an increase of CTAB concentration, and the relaxations were not observed in a concentration range of about 20-230 mM. As the CTAB concentration approaches the sphere-rod transition concentration (250 mM), two new relaxations appeared. These relaxations could be induced even in 200 mM CTAB solution by the addition of 20 mM NaBr to decrease the sphere-rod transition concentration to 190 mM. On the other hand, no relaxation was observed in a CTAC solution. These results imply that the relaxations are related to the rodlike micelles of CTAB.

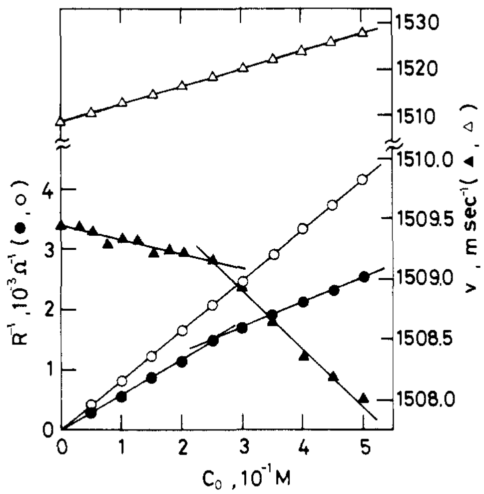


Figure 1. Concentration dependencies of the conductivity (●, ○) and the ultrasonic velocity (▲, △) for CTAB (filled signs) and CTAC (open signs) solutions at 30 °C. Experimental errors are about 4×10^{-5} Ω^{-1} and 0.15 m s^{-1}, respectively.

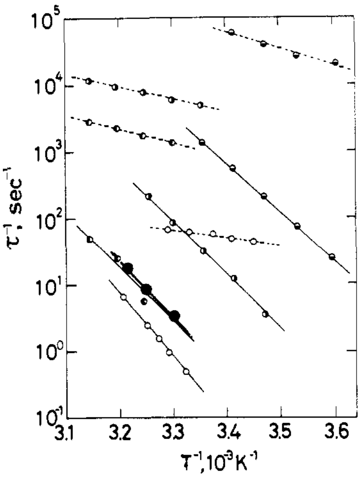


Figure 2. Temperature dependencies of the reciprocal relaxation times for the fast process (dotted line) and the slow process (full line) at a little above the CMC: (⊖), 10 mM sodium dodecylsulfate; (◑), 2.4 mM sodium tetradecylsulfate; (◐), 1 mM sodium hexadecylsulfate; (○), 1.1 mM CTAB. Data for the slow relaxation in a 400 mM CTAB solution is shown by (—●—).

Detailed kinetic experiments for the CTAB solutions in the concentration range above the sphere-rod transition concentration revealed the following facts. In the fast relaxation, the reciprocal relaxation time increases linearly with CTAB concentration. In the slow relaxation, the concentration dependency of the reciprocal relaxation time τ_s^{-1} is not monotonous but rather complicated as seen in Figure 3. Another feature of the slow relaxation is an unusually large temperature dependency of the relaxation time (Figures 2 and 3). Very interestingly, these concentration and temperature dependencies of the two relaxation times are very similar to those of the relaxations observed for the sphere micelles above the CMC.[4,5] With reference to the two relaxations for the sphere micelles, the data indicate that the fast relaxation is due to the monomer exchange, while the slow relaxation is due to the overall formation and dissolution of the rodlike micelles. Furthermore, the unusually large apparent activation energy of the slow process can be well understood by considering that a rodlike micelle might be produced by the monomer's successive association

---

(1) (a) Husson, F. R.; Luzzati, V. *J. Phys. Chem.* **1964**, *68*, 3504. (b) Hoffmann, H.; Platz, G.; Rahage, H.; Schorr, W.; Ulbricht, W. *Ber. Bunsenges. Phys. Chem.* **1981**, *85*, 255. (c) Missel, P. J.; Mazer, N. A.; Benedek, G. B.; Carey, M. C. *J. Phys. Chem.* **1983**, *87*, 1264. (d) Imae, T.; Kamiya, R.; Ikeda, S. *J. Colloid Interface Sci.* **1985**, *108*, 215.

(2) (a) Scott, A. B.; Tarter, H. V. *J. Am. Chem. Soc.* **1943**, *65*, 692. (b) Lawrence, A. S. C.; Stenson, R. *Proceedings of the International Congress Surface Activity*, 2nd ed.; London, 1957, Vol. II, p 368. (c) Mukerjee, P.; Mysels, K. J. Critical Micelle Concentrations of Aqueous Surfactant Systems. *Nat. Stand. Ref. Data Ser. Nat. Bur. Stand.* (*U.S.*) **1971**, 36.

(3) (a) Ekwall, P.; Mandell, L.; Solyom, P. *J. Colloid Interface Sci.* **1971**, *35*, 519. (b) Lindblom, G.; Lindman, B.; Mandell, L. *J. Colloid Interface Sci.* **1973**, *42*, 400. (c) Ulmius, J.; Lindman, B.; Lindblom, G.; Drankenberg, T. *J. Colloid Interface Sci.* **1978**, *65*, 88.

(4) (a) Folger, R.; Hoffmann, H.; Ulbricht, W. *Ber. Bunsenges. Phys. Chem.* **1974**, *78*, 986. (b) Aniansson, E. A. G.; Wall, S. N.; Almgren, M.; Hoffmann, H.; Kielmann, I.; Ulbricht, W.; Zana, R.; Lang, J.; Tondre, C. *J. Phys. Chem.* **1976**, *80*, 905. (c) Diekmann, S. *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 528.

(5) (a) Reference 4. (b) Aniansson, E. A. G.; Wall, S. N. *J. Phys. Chem.* **1974**, *78*, 1024. (c) Teubner, M.; Diekmann, S.; Kahlweit, M. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 1278.

0002-7863/88/1510-8710$01.50/0 © 1988 American Chemical Society

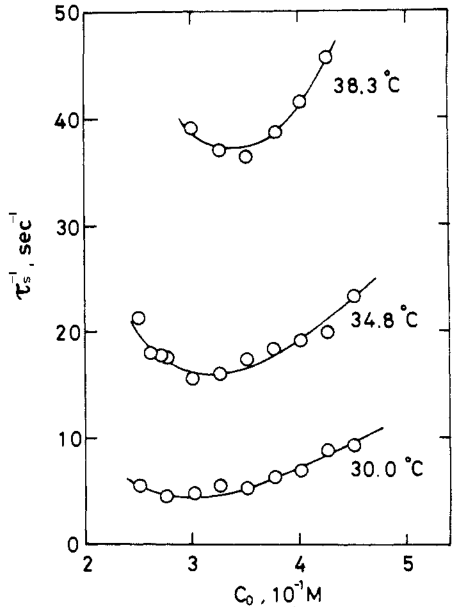
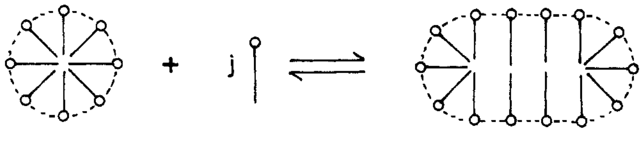


Figure 3. Concentration dependencies of the reciprocal relaxation time for the slow process in the CTAB solutions above the sphere–rod transition concentration at various temperatures.

to a sphere micelle in a similar manner as a sphere micelle is formed, i.e.



(1)

The breaks in the concentration dependencies of conductivity and ultrasonic velocity at the sphere–rod transition concentration were very similar to those at the CMC[6] and support our interpretation. A similar model has been discussed by Mukerjee.[7] Porte et al.[8] also claimed that successive association of the monomers to the sphere micelle leads to a rodlike micelle, energy barrier exists at the first step of elongation, and the elongated micelles with moderate association numbers are energetically disfavored.

For the mechanism of the sphere–rod transition of micelles another conflicting model has been proposed,[9] where a rodlike micelle (S_{mn}) is assumed to be formed by the agglutination of several (n) sphere micelles (S_m), i.e.

$$nS_m \underset{k_b}{\overset{k_f}{\rightleftharpoons}} S_{mn} \tag{2}$$

For reaction 2, the overall concentration of surfactant ($\sum[S]$) and the equilibrium constant (K) is given by

$$\sum[S] = m[S_m] + mn[S_{mn}] \tag{3}$$

$$K = \frac{[S_{mn}]}{[S_m]^n} \tag{4}$$

and the relaxation equation is given by

$$\tau_s^{-1} = n^2 k_f [S_m]^{n-1} + k_b \tag{5}$$

where the brackets indicate the concentration. Since n is estimated to be smaller than five under the present experimental conditions, eq 3 and 4 predict that the increase of $[S_m]$ is convex upward while that of $[S_{mn}]$ is concave upward at around the sphere–rod transition concentration. These facts predict that the solution properties, e.g., conductivity and ultrasonic velocity, vary gradually with surfactant concentration in relatively wide range around the sphere–rod transition concentration. Furthermore, by using the values of n and $[S_m]$ estimated above, eq 5 predicts that τ_s^{-1} increases very steeply with surfactant concentration. However, all these expectations were contradicted to the experimental results as shown in Figures 1 and 3. Then a mechanism of direct agglutination of sphere micelles to form a rodlike micelle was discarded.

Even though further studies are needed to provide quantitative interpretations, we may conclude that the rodlike micelle formation of CTAB occurs via successive association of monomers to the sphere micelle in the time region of several hundred milliseconds, while the monomer exchange on the rodlike micelle occurs in the time range of several milliseconds at 30 °C.

Acknowledgment. We thank Professor Z. A. Schelly of the University of Texas at Arlington for his helpful discussions.

---

(6) (a) Shinoda, K.; Nakagawa, T.; Tamamuchi, B.; Isemura, T. *Colloidal Surfactants*; Academic Press: 1963. (b) Yasunaga, T.; Oguri, H.; Miura, M. *J. Colloid Interface Sci.* **1967**, *23*, 352.

(7) (a) Mukerjee, P. *J. Phys. Chem.* **1972**, *76*, 565. (b) Mukerjee, P. In *Micellization, Solubilization, and Microemulsions*; Mittal, K. L., Ed.; Plenum Press: 1977; Vol. 1.

(8) (a) Porte, G.; Appel, J. *J. Phys. Chem.* **1981**, *85*, 2511. (b) Porte, G. *J. Phys. Chem.* **1983**, *87*, 3541. (c) Porte, G.; Poggi, Y.; Appell, J.; Maret, G. *J. Phys. Chem.* **1984**, *88*, 5713.

(9) (a) Hayashi, S.; Ikeda, S. *J. Phys. Chem.* **1980**, *84*, 744. (b) Ozeki, S.; Ikeda, S. *J. Colloid Interface Sci.* **1982**, *87*, 424. (c) Ozeki, S.; Ikeda, S. *Colloid Polymer Sci.* **1984**, *262*, 409. (d) Ikeda, S. In *Surfactants in Solution*; Mittal, K. L., Lindman, B., Ed.; Plenum Press: 1984; Vol. 2.

Solution Study and Molecular Structure of a [3]-Catenand: Intramolecular Interaction between the Two Peripheral Rings

Jean Guilhem,[†] Claudine Pascard,*,[†] Jean-Pierre Sauvage,*,[‡] and Jean Weiss[‡]

Laboratoire de Cristallochimie, Institut de Chimie des
Substances Naturelles, CNRS, 91190 Gif-sur-Yvette, France
Laboratoire de Chimie Organo-Minérale, UA 422 au CNRS
Institut de Chimie, 67000 Strasbourg, France

Received June 20, 1988

For many years, topologically novel molecules such as catenanes (interlocked rings) have been the target of synthetic efforts in several laboratories.[1-4] With regard to synthetic efficiency, the copper(I) templated synthesis of catenates (complexes) and catenands (free ligands) appears to be among the most efficient methods.[5] Schill et al. have demonstrated syntheses of [3]-catenanes, consisting of three interlocked rings, by using carbon-based control units.[6] Recently, coordinating systems containing three interlocked macrocyclic subunits have been synthesized.[7,8] The X-ray structure of a dicopper(I) [3]-catenate has also been reported.[9]

In the course of our work,[7] we have prepared the dicopper(I) [3]-catenate $[1(Cu^I)_2]^{2+}\cdot[BF_4^-]_2$, and we have isolated the copper(I) [2]-catenate $[2(Cu^I)]^+\cdot BF_4^-$ as a byproduct.

The corresponding catenands **1** and **2** (see Figure 1) were readily obtained from their respective copper(I) catenates by demetalation with KCN. Both compounds **1** and **2** have been studied by ^{1}H NMR, and their conformational properties have been compared in the light of the crystal structure of **1**, determined by X-ray

---

[†] Laboratoire de Cristallochimie.

[‡] Laboratoire de Chimie Organo-Minérale.

(1) Frisch, H. L.; Wasserman, E. *J. Am. Chem. Soc.* **1961**, *83*, 3789.

(2) Schill, G. In *Catenanes, Rotaxanes and Knots*; Academic Press: New York, 1971.

(3) Walba, D. M. *Tetrahedron* **1985**, *41*, 3161.

(4) Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Chem. Rev.* **1987**, *87*, 795.

(5) Dietrich-Buchecker, C. O.; Sauvage, J.-P.; Kintzinger, J.-P. *Tetrahedron Lett.* **1983**, *24*, 5095. Dietrich-Buchecker, C. O.; Sauvage, J.-P.; Kern, J.-M. *J. Am. Chem. Soc.* **1984**, *106*, 3043.

(6) Schill, G.; Rissler, K.; Fritz, H.; Vetter, W. *Angew. Chem.* **1981**, *93*, 197.

(7) Sauvage, J. P.; Weiss, J. *J. Am. Chem. Soc.* **1985**, *107*, 6108. Weiss, J. Thesis, University of Strasbourg, 1986.

(8) Dietrich-Buchecker, C. O.; Khemiss, A. K.; Sauvage, J.-P. *Chem. Commun.* **1986**, 1376.

(9) Dietrich-Buchecker, C. O.; Guilhem, J.; Khemiss, A. K.; Kintzinger, J.-P.; Pascard, C.; Sauvage, J.-P. *Angew. Chem.* **1987**, *99*, 711.