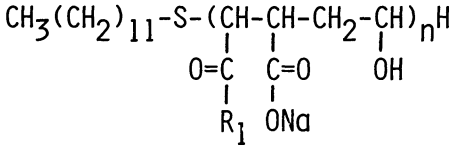
CHEMISTRY LETTERS, pp. 43-46, 1983.

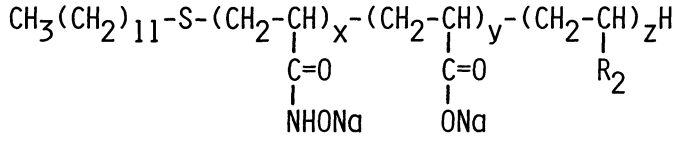
Cu^{2+}-INDUCED BILAYER FORMATION OF SINGLE-CHAIN TELOMER SURFACTANTS IN DILUTE AQUEOUS SOLUTION

Kimiho YAMADA*, Hideto SHOSENJI, Hirotaka IHARA, and Osamu HOTTA
Department of Synthetic Chemistry, Faculty of Engineering
Kumamoto University, Kumamoto 860

A large enhancement (35 to 480 fold) of the aggregate weight was observed in the presence of Cu^{2+} for single-chain telomer surfactants containing the hydroxamic acid group in water. Electron microscopy indicated a drastic morphological change from micelles to multi-lamellar vesicles was induced by Cu^{2+}.

Although many amphiphiles which could form the bilayer membrane similar to the liposome from phospholipids have been synthesized,[1-4] they were restricted to single-chain compounds containing rigid segments[3,4] and double-chain compounds.[1,2] On the other hand, we have reported the colloidal and catalytic properties[5,6] of multi-functional surfactants prepared by telomerization of hydrophilic monomers in long-chain alkyl mercaptan. In this paper we would like to describe that these surfactants form a bilayer structure by the complex formation between the hydrophilic part of the telomer and Cu^{2+}. The structures of telomers used in this study are given below. The





R_1= NHONa or ONa
1a: n=9.6, [NHONa]/[ONa]=3.1/1.7
1b: n=16.6, [NHONa]/[ONa]=4.5/3.8

2: R_2=OH, x=6.5, y=1.3, z=3.4
3: R_2=CH_2OH, x=6.9, y=1.6, z=2.6

degree of polymerization and the composition of 1, 2 and 3 were determined from elemental analyses, the molecular-weight measurement by vapor-pressure osmometry and estimation of the hydroxamic acid residue in the telomers.[6]

These telomer surfactants formed a water-soluble Cu^{2+} complex which showed an absorption maximum at 630 nm. The absorbance of the complex of 1a and Cu^{2+} increased with the increasing concentration of Cu^{2+}, reaching a maximum approximately at the concentration of the hydroxamic acid group as the 2:1 complex. Although in general the

Cu^{2+} complexes of polymeric hydroxamic acids are insoluble in water,[7] this telomer-complex (up to the equivalent concentration as to the hydroxamic and carboxylic acid groups) can maintain water-solubility by virture of the residual hydroxyl group. However the addition of a large excess of Cu^{2+} made the telomer-complex insoluble in water.

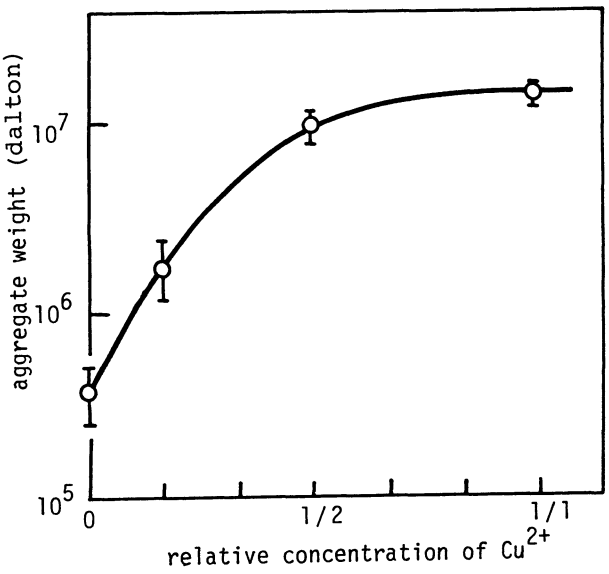


Fig 1. A relationship between the aggregate weight of 1a and the concentration of Cu^{2+} at room temperature (see Table 1)

Measurement of the aggregate weight of telomers in water was made using the low-angle light-scattering technique.[8] Fig 1 shows the dependence of the aggregate weight of 1a on the concentration of Cu^{2+}. The aggregate weight of 1a increased remarkably as the concentration of Cu^{2+} increased, reaching a constant value at the concentration theoretically required for formation of the complex with all the hydroxamic and carboxylic acid groups in 1a. Similar effects were observed for other telomers (Table 1). A large enhancement of the aggregate weight was observed in all telomers, especially in 1b (480 times in comparison with the solution without Cu^{2+}).[9] This fact cannot be accounted for by the formation of conventional micelles. Presumably a morphological change of the aggregate was produced by the formation of

Table 1. The aggregate weight of telomers in water

telomer	aggregate weight ($\times 10^{-6}$ dalton) relative concentration of Cu^{2+}				enhancement
	0	1/6	1/2	1/1	
1a	0.4 ± 0.1	1.6 ± 0.5	9.2 ± 2.0	13 ± 2	35
1b	0.4 ± 0.03	—	—	187 ± 30	480
2	0.4 ± 0.2	10.0 ± 3.0	—	62 ± 3	164
3	0.8 ± 0.03	—	—	33 ± 10	41

pH 8 - 9, [telomer]=2 - 6×10^{-5}mol/l
The value 1/1 corresponds to the theoretical amount to form Cu^{2+} complexes with all the hydroxamic and carboxylic acid functions in telomer, with 2:1 and 4:1 complexes for the former and latter, respectively.

of the complex of Cu^{2+} and the hydroxamic and carboxylic acid groups, especially the former residue, in telomer.

Electron microscopy of this solution provided significant information. Fig 2 shows a electron micrograph[10] of telomer $\underset{\sim}{1a}$ in the presence of Cu^{2+}. Multi-lamellar vesicles with diameters of 250 to 4000 Å are clearly seen. The width between the dark striation is ca. 33 Å which roughly corresponds to two times the length of the hydrophobic moiety of telomer $\underset{\sim}{1a}$. The morphological change of aggregate suggested by the light-scattering measurement appears to correspond to a change from micelles to bilayer membranes. However such highly ordered structures were not observed in the other telomers (only fragmentary lamella).

In conclusion, single-chain telomer surfactants, which form micelles by themselves,[11] proved to form larger aggregates (10^7-10^8 dalton) in the presence of Cu^{2+}. The complexation with Cu^{2+} at the hydrophilic moiety (i.e. at the hydroxamic and carboxylic acid groups) seems to increase the degree of the orientation of the long-alkyl chain resulting in the formation of the bilayer structure. That is to say, even micellar surfactants can form the bilayer structure by incorporation of the additional force such as the complex formation.

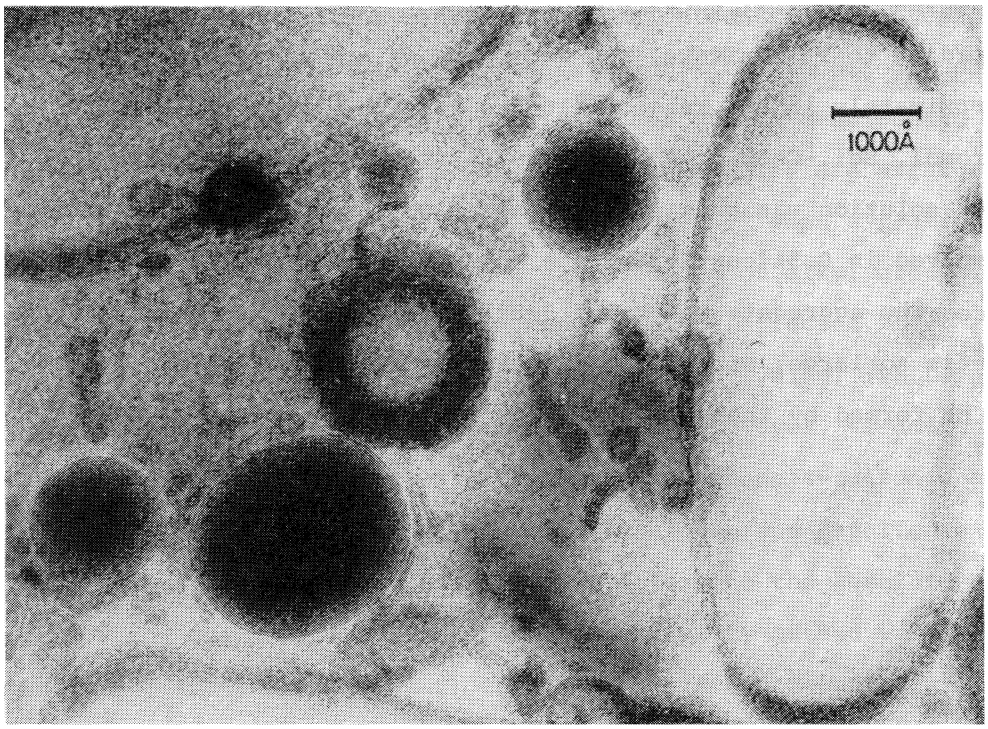


Fig 2. Electron micrograph of $\underset{\sim}{1a}$ (stained by cupric acetate)
magnification x150,000

The authors wish to thank Prof. Kunitake (Kyushu University) for the use of a light-scattering instrument.

References

1) T. Kunitake and Y. Okahata, J. Am. Chem. Soc., 99, 3860 (1977); T. Kunitake and Y. Okahata, Bull. Chem. Soc. Jpn., 51, 1877 (1978); T. Kunitake, N. Nakashima, and S. Hayashida, Chem. Lett., 1979, 1413.

2) Y. Murakami, A. Nakano, and K. Fukuya, J. Am. Chem. Soc., 102, 4253 (1980)

3) Y. Okahata and T. Kunitake, Ber. Bunsenges. Phys. Chem., 84, 550 (1980); T. Kunitake, Y. Okahata, M. Shimomura, Y. Yasunami, and K. Takarabe, J. Am. Chem. Soc., 103, 5401 (1981)

4) Y. Murakami, A. Nakano, K. Iwamoto, and A. Yoshimatsu, Chem. Lett., 1979, 951.

5) K. Yamada, T. Kihara, Y. Yamaguchi, and C. D. Tran, Yukagaku, 25, 347 (1976)

6) R. Ueoka, H. Mori, K. Yonezawa, M. Kato, Y. Ohtsuka, and K. Yamada, Nippon Kagaku Kaishi, 522 (1979); K. Yamada, H. Gota, K. Inaba, H. Tashiro, and H. Shosenji, Nippon Kagaku Kaishi, to be published.

7) M. Hatano and T. Nozawa, Nippon Kagaku Kaishi, 185 (1971)

8) Stock solution was prepared by sonication (Branson Sonifier 185) of telomers dissolved in distilled water for 3 min.

9) According to T. Kunitake, the aggregate weight of synthetic bilayer membranes is approximately in the range of 10^6 to 10^8, but rarely 10^5; T. Kunitake, J. Macromol. Sci.-Chem., A13, 587 (1979); T. Kunitake, Yukagaku, 31, 345 (1982)

10) Stock solution was prepared by sonication (Branson Sonifier B12) of telomers dissolved in 0.5% cupric acetate solution for 30 min.

11) Since the aggregate weight of $3\text{-}8\times10^5$ dalton of the telomer in the absence of Cu^{2+} is so large, stratified micelles or aggregates of micelles, for instance, may be formed by themselves.

(Received October 9, 1982)