CHEMISTRY LETTERS, pp. 1089 - 1092, 1984.

BILAYER FORMATION FROM SINGLE-CHAIN AMMONIUM AMPHIPHILES DUE TO MULTIPLE HYDROGEN BONDING[1)]

Toyoki KUNITAKE,* Norihiro YAMADA, and Nobuto FUKUNAGA
Department of Organic Synthesis, Faculty of Engineering,
Kyushu University, Fukuoka 812

Stable bilayer assemblies were spontaneously formed in water from single-chain, alkylammonium surfactants which possess multiple hydrogen bonding capacities. The specific component interaction in the bilayer matrix was inferred from the DSC study.

Stable bilayer membranes have been formed from a variety of synthetic amphiphiles.[2)] The major driving force of bilayer assemblage in these cases is the hydrophobic interaction. The hydrophobic interaction is basically a non-directive force, however, and the molecular arrangement in the assembly is determined predominantly by close packing of the hydrophobic moiety. It is necessary to use more directive forces in order to produce highly specific orientations and distributions of component molecules. Hydrogen bonding is a highly directive force and plays a central role in the precise maintenance of and the specific interaction in biological molecular systems. It is expected, therefore, that incorporation of multiple hydrogen bonds facilitates sophisticated assemblage of bilayer components.

Acylurea and related moieties appear especially suited for this purpose, as is shown typically by Endo and coworkers in the designed reaction control.[3)] Thus, we prepared single-chain ammonium amphiphiles which possess amide, urea, or acylurea moieties(Chart 1).[4)] It is to be noted that the hydrogen bond unit (-CO- or -NH-) is replaced by CH_2 successively in the three types of amphiphiles.

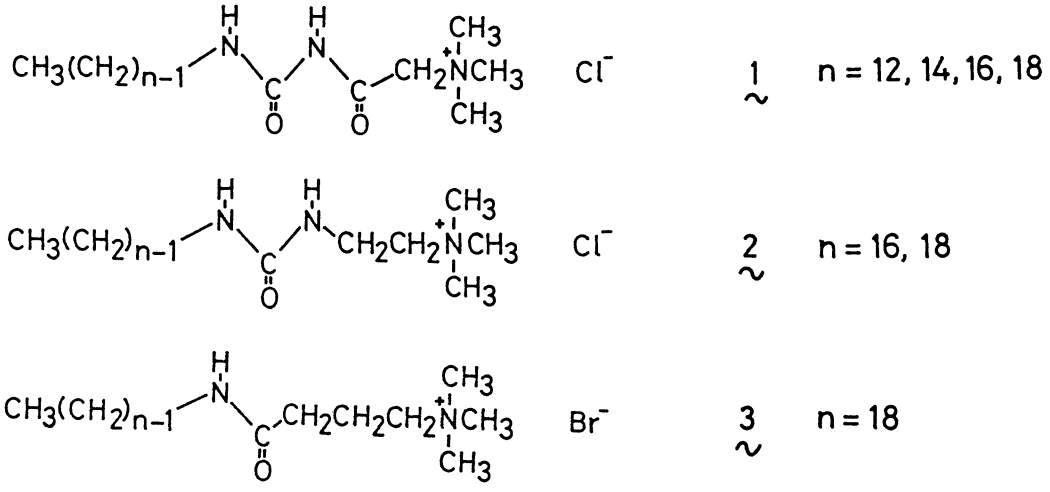

Chart 1.

Table 1. Aggregation Characteristics

Amphiphile	cmc	Aggregate weight	Aggregate	DSC
	10^5x mol·dm^{-3}	million	morphology	peak top, °C
1 n = 18	1.2	120	lamella	44.0
16	1.6	22	lamella	29.0
14	1.4	0.12	no structure	not detected
12	1.3	0.05	no structure	not detected
2 n = 18	1.0	72	lamella	37.0
16	1.1	0.9	no structure	21.3
3 n = 18	1.4	12	no structure	33.5

Stable aqueous dispersions(clear to translucent) were obtainable from these compounds with or without sonication. Table 1 summarizes their aggregation characteristics. The critical micelle concentrations determined by the conductivity method were close to 1 x 10^{-5} mol·dm^{-3} in all cases. The aggregate weight estimated by the small-angle light scattering method(instrument, Toyo Soda LS-8; He-Ne laser source)[5] differed extensively. The largest value(120 million) was obtained for 1(n = 18), and decreased with decreasing tail lengths(n = 18 → 16) and with decreasing sites of hydrogen bonding(1 → 2 → 3). The aggregate weight of bilayer membranes is usually greater than 1 million. Electron microscopy[6] indicated formation of lamellar aggregates for three compounds, as typically shown for 1(n = 18) in Fig. 1. The layer thickness in this case is ca. 40 Å, which is shorter than two times of the full molecular length(32 Å per molecule, as estimated by the CPK molecular model), as is found often for synthetic bilayer systems.[7]

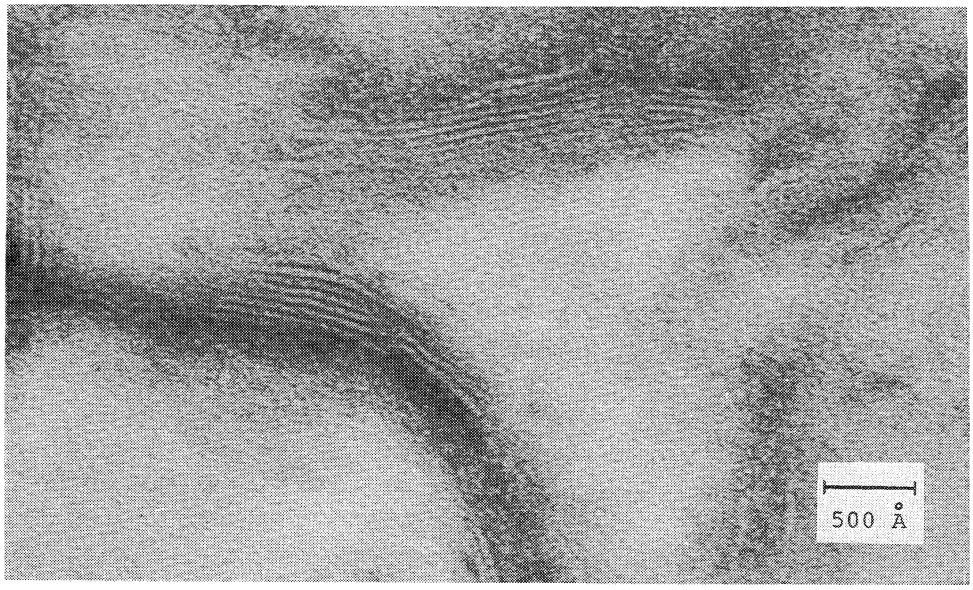

Fig. 1. Electron micrograph.
Sample, 0.01 mol·dm^{-3} aqueous dispersion of 1(n = 18); stained by uranyl acetate; original magnification, x 40000.

The huge aggregate weight and the lamellar morphology are indicative of bilayer formation for $\underset{\sim}{1}$(n = 18), $\underset{\sim}{1}$(n = 16), and $\underset{\sim}{2}$(n = 18). Endothermic peaks (phase transition) found for these aggregates in differential scanning calorimetry (DSC)[8] are consistent with this supposition. The other amphiphiles do not appear to form bilayer aggregates; in particular, the layer structure was not found for $\underset{\sim}{3}$(n = 18) in electron microscopy, though huge aggregates are formed and phase transition was detected.

Subsequently, the mixing behavior of these bilayers was studied by DSC. An equimolar mixture(0.01 mol·dm^{-3} each) of $\underset{\sim}{1}$(n = 18) and $\underset{\sim}{2}$(n = 18) gives a new endothermic peak at 41 °C in the 2nd scan(Fig. 2a). The peak shape does not change upon repeated scans or sonication. It is clear that these two bilayer components produce a homogeneous mixture very readily. When equimolar $2C_{16}N^{+}2C_1$[9] was added as a third component, two peaks at 29 °C and 41 °C resulted after repeated DSC scans (Fig. 2b). The $2C_{16}N^{+}2C_1$ bilayer possesses T_c at 28 °C. Therefore, the three-component mixture is made of single-component domains of $2C_{16}N^{+}2C_1$ and two-component domains of $\underset{\sim}{1}$(n = 18) and $\underset{\sim}{2}$(n = 18). These DSC data strongly suggest that $\underset{\sim}{1}$(n = 18) and $\underset{\sim}{2}$(n = 18) selectively form mixed clusters probably due to complementary hydrogen bonding(acylurea and urea).

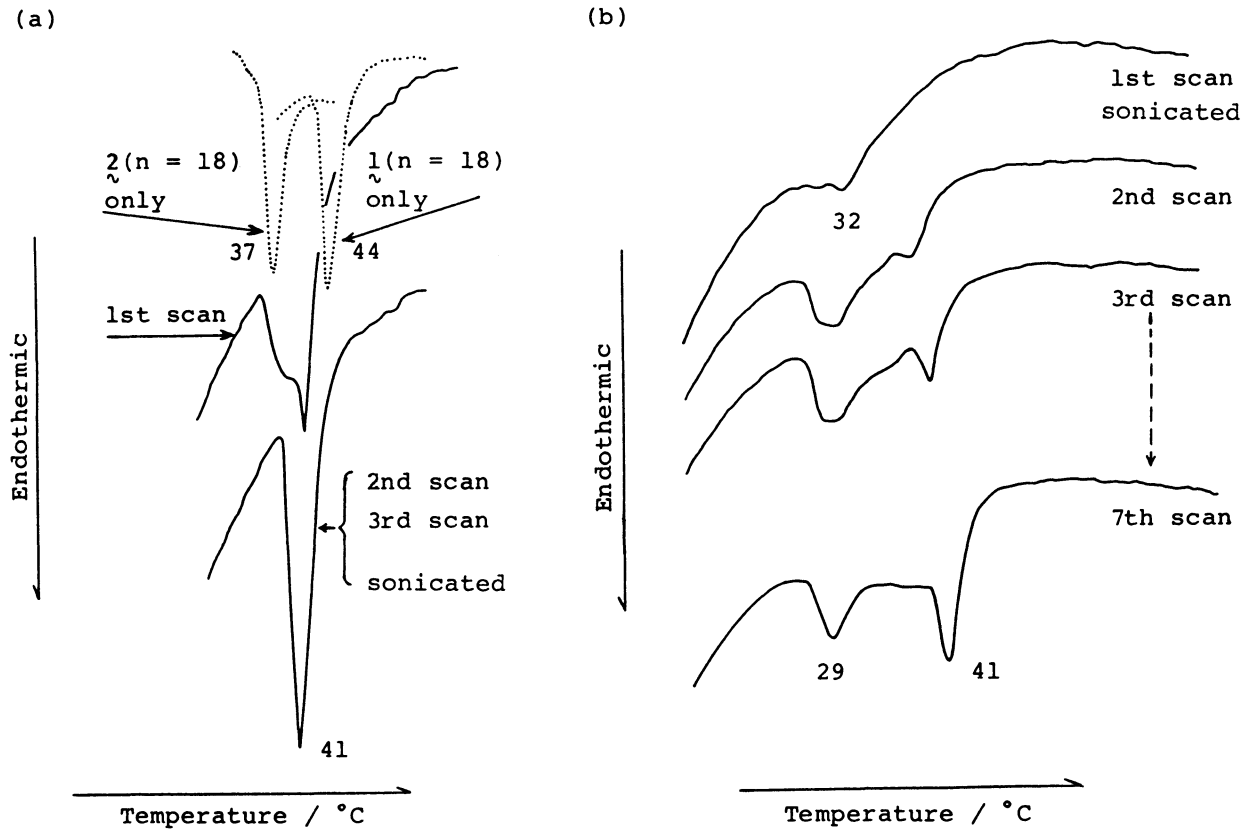

Fig. 2. DSC thermograms.
(a) Two component mixture; $\underset{\sim}{1}$(n = 18) and $\underset{\sim}{2}$(n = 18).
(b) Three component mixture; $\underset{\sim}{1}$(n = 18), $\underset{\sim}{2}$(n = 18) and $2C_{16}N^{+}2C_1$.

In conclusion, stable bilayers are formed from monoalkylammonium surfactants when they have sufficient tail lengths and are capable of multiple hydrogen bonding. The present finding provides a new method of assembling amphiphiles and opens a way to highly specified(complementary as well as competitive) bilayer functions.

References

1) Contribution No. 726 from Department of Organic Synthesis.
2) For a recent summary, see T. Kunitake, N. Kimizuka, N. Higashi, and N. Nakashima, J. Am. Chem. Soc., 106, 1978(1984).
3) T. Mukaiyama, T. Endo, and S. Noguchi, Tetrahedron Lett., 1971, 2291: T. Endo, A. Kuwahara, H. Tasai, M. Hashimoto, and T. Ishigami, Nature, 268, 74(1977) and their subsequent papers.
4) Amphiphiles 1 and 2 were obtained by reaction of alkylamines with chloroacetyl isocyanate and 2-chloethyl isocyanate, respectively, and the subsequent quaternization with trimethylamine. Amphiphile 3 was similarly prepared by reaction of octadecylamine with 4-bromobutanoyl chloride followed by quaternization with trimethylamine. The final products were identified by IR and NMR spectroscopies, and by elemental analysis. 1(n = 18): Found: C, 64.19; H, 11.24; N, 9.36%. Calcd for $C_{24}H_{50}N_3O_2Cl$: C, 64.33; H, 11.25; N, 9.38%. 1(n = 16): Found: C, 61.82; H, 10.87; N, 9.83%. Calcd for $C_{22}H_{46}N_3O_2Cl\cdot 0.5H_2O$: C, 61.58; H, 11.04; N, 9.79%. 1(n = 14): Found: C, 60.30; H, 10.69; N, 10.30%. Calcd for $C_{20}H_{42}N_3O_2Cl\cdot 0.5H_2O$: C, 59.90; H, 10.81; N, 10.48%. 1(n = 12): Found: C, 58.48; H, 10.38; N, 11.38%. Calcd for $C_{18}H_{38}N_3O_2Cl\cdot 0.5H_2O$: C, 57.97; H, 10.54; N, 11.27%. 2(n = 18): Found: C, 61.26; H, 11.91; N, 9.01%. Calcd for $C_{24}H_{52}N_3OCl\cdot 2H_2O$: C, 61.31; H, 12.00; N, 8.94%. 2(n = 16): Found: C, 59.43; H, 11.74; N, 9.46%. Calcd for $C_{22}H_{48}N_3OCl\cdot 2H_2O$: C, 59.77; H, 11.85; N, 9.50%. 3(n = 18): Found: C, 59.44; H, 10.94; N, 5.88%. Calcd for $C_{25}H_{53}N_2OBr\cdot 2H_2O$: C, 58.46; H, 11.18; N, 5.45%.
5) T. Kunitake, and Y. Okahata, J. Am. Chem. Soc., 102, 549(1980).
6) T. Kunitake, Y. Okahata, M. Shimomura, S. Yasunami, and K. Takarabe, J. Am. Chem. Soc., 103, 5401(1981).
7) T. Kajiyama, A. Kumano, M. Takayanagi, Y. Okahata, and T. Kunitake, Chem. Lett., 1979, 645.
8) The experimental procedure is given in Y. Okahata, R. Ando, and T. Kunitake, Ber. Bunsenges. Phys. Chem., 85, 789(1981).
9) $2C_{16}N^+2C_1$; Dihexadecyldimethylammonium bromide, see Ref. 8.

(Received April 11, 1984)