Progr Colloid Polym Sci (1997) 106:52–56

T. Imae
M.-P. Krafft
F. Giulieri
T. Matsumoto
T. Tada

Fibril–vesicle transition and their structures – investigation by microscopy and small-angle scattering

Received: 13 October 1996
Accepted: 24 March 1997

Dr. T. Imae (✉)
Department of Chemistry
Faculty of Science
Nagoya University
Nagoya 464, Japan

M.-P. Krafft · F. Giulieri
Laboratoire de Chimie Moléculaire
Unité Associée au CNRS n° 426
Université de Nice-Sophia Antipolis
06108 Nice Cedex 2, France

T. Matsumoto · T. Tada
Division of Material Chemistry
Faculty of Engineering
Kyoto University
Kyoto 606, Japan

Abstract The formation of fibrous assemblies by fluorinated amphiphiles and the temperature-dependent fibril–vesicle transition were investigated by using microscopy and small-angle scattering. The results were compared with that of fibrous assemblies by nonfluorinated amphiphiles. Sodium (F-octylethyl) nonylmethylene *O*-6-phospho-glucoside (F-Glu) formed hollow tubules in water at room temperature (~25 °C). Tubules transformed into vesicles above 60 °C. Similar tubule–vesicle transition for hydrogenated-analog, sodium decylnonylmethylene *O*-6-phospho-glucoside (H-Glu), was observed below room temperature. The mixture of [2-(F-octyl)penthyl] dimorpholinophosphate (F8C5DMP) and [2-(F-decyl)ethyl] dimorpho-linophosphate (F10C2DMP) in water constructed U- or V-shape assemblies, which changed to vesicles at 60 °C.

Key words Vesicle – fibril – cryo-TEM – small-angle X-ray scattering – fluorinated amphiphile

Introduction

It has been known that various types of supramolecular assemblies are constructed in the medium by noncovalent self-organization of small molecules. Many workers reported assembly structures and solution properties [1]. Rod-like micelles which are one group of linearly extended supramolecular assemblies are formed by the hydrophobic interaction between long alkyl chains of amphiphiles. Rod-like micelles are transformed from spherical micelles [2]. In a few cases, rod-like micelles change to vesicles when cinnamic acid is added to a solution of hexadecyl-dimethylamine oxide [3]. The spontaneous transition from polymer-like micelles to vesicles was observed in lecithin–bile salt solutions [4].

Fibrous chains are another group of linear assemblies and were found in gel-like solutions of amphiphiles [5–7], steroids [8], oligobipiridine metal complexes [9], and cyclic peptide [10]. These compounds reveal specific intermolecular interaction such as hydrogen bonding, π–π stacking, and so on, besides hydrophobic interaction. Among supramolecular fibers, helical assemblies are characteristic for molecules with chiral hydrophilic head groups such as amino acids, nucleosides, and sugars [1]. It is also known that some of the fibrous assembly systems display fibril–vesicle transition depending on temperature [11–13].

The formation of supramolecular fibers were mainly confirmed by the transmission electron microscopic (TEM) and the dark-field optical microscopic observation. On the other hand, a few investigations were carried out using techniques of NMR [6], X-ray diffraction [9, 14, 15], small-angle neutron scattering [8, 16, 17], and small-angle X-ray scattering (SAXS) [16, 17].

In this paper, we examined the formation of different kinds of fibrous, linear assemblies from fluorinated amphiphiles by using microscopy and small-angle scattering. We discuss the structure of fibrous chains and the fibril–vesicle transition.

Experimental section

Sodium (F-octylethyl)nonylmethylene *O*-6-phosphoglucoside (F-Glu), sodium decylnonylmethylene *O*-6-phosphoglucoside (H-Glu), [2-(F-octyl)penthyl]dimorpholinophosphate (F8C5DMP), and [2-(F-decyl)ethyl] dimorpholinophosphate (F10C2DMP) were same samples as previously synthesized and used [18–20].

SAXS was measured at 25 °C by a 6 m point focussing SAXS camera at the High-Intensity X-ray Laboratory in Kyoto University. TEM observation was carried out on a Hitachi H-800 electron microscope. A Hitachi H5001-C cold stage was used for the cryo method. Freeze–fracture replica film was prepared by using a balzers BAF 400 freeze–fracture device.

Results and discussion

Figure 1 shows cryo-TEM photographs for aqueous 3% solution of hydrogenated/fluorinated phosphoglucolipid, F-Glu, at various temperatures. F-Glu in water formed very long tubules with hollow inside at room temperature (~25 °C) (Fig. 1a). The diameters were almost uniform. SAXS data (Fig. 2a) fitted to the theoretical curve for a hollow tubule with parameters of external and internal diameters, 280 and 70 Å, respectively. There was a Bragg peak which can be assigned to the reflection from lamellar layers, suggesting the formation of concentric lamellar layers in the cross section of a hollow tubule.

When aqueous F-Glu solution was heated up to more than 60 °C, tubules changed to vesicles (Fig. 1c). The tubule–vesicle transition temperature must be 50–60 °C, because tubules and vesicles coexisted at that temperature (Fig. 1b). It should be noticed that tubules transferred to vesicles through plate (sheet) or tubule expansion. In accord with tubule–vesicle transition, the characteristic Bragg peak in SAXS diminished, as seen in Fig. 2b, indicating the disappearance of multilamellar (concentric lamellar) arrangement of bilayers in vesicles.

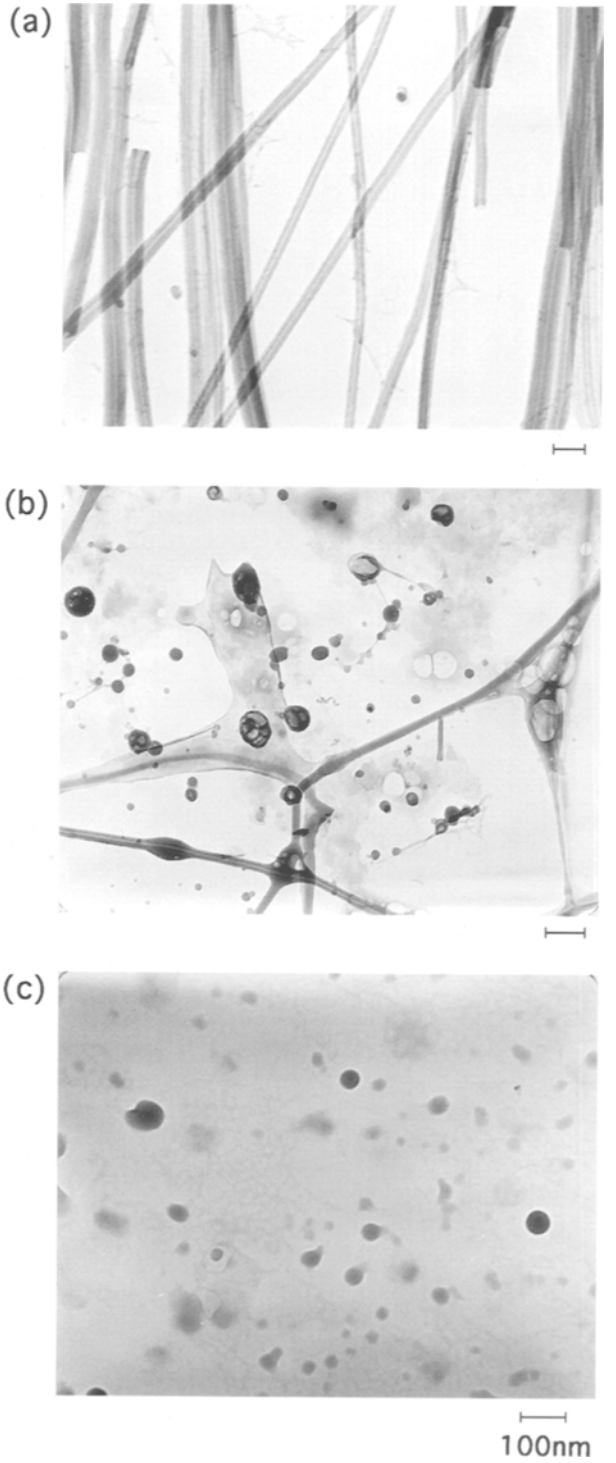

Fig. 1 Cryo-TEM photographs of an aqueous 3% F-Glu solution at various temperatures: (a) ~25 °C; (b) 50–60 °C; (c) 60–70 °C

Hydrogenated phosphoglucolipid, H-Glu, in water constructed unilamellar vesicles and tubules at room

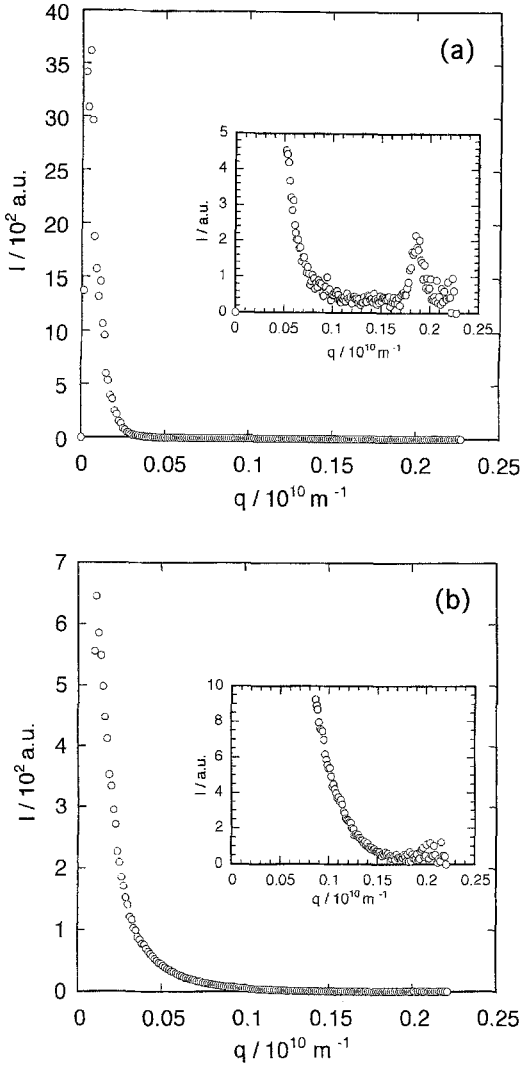

Fig. 2 SAXS data for an aqueous 3% F-Glu solution at different temperatures: (a) 25 °C; (b) 60 °C

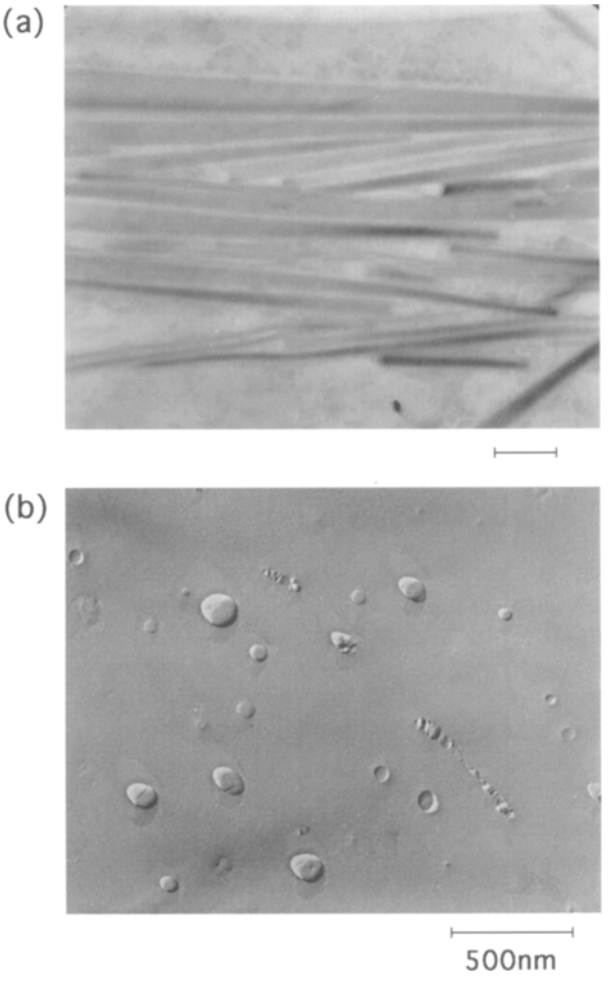

Fig. 3 TEM photographs of an aqueous 3% H-Glu solution at different temperatures: (a) ~4 °C; cryo-TEM; (b) ~25 °C; freeze-fracture TEM

temperature (~25 °C) and ~4 °C, respectively, as seen in Fig. 3. It may be noticed that tubule–vesicle transition temperature was low in comparison with that of F-Glu and that tubule diameter of 300–600 nm was thicker than that of F-Glu.

Although F8C5DMP molecules can form tubules, tubules transformed into a lamellar sheet structure within a short time. On the other hand, the mixture of F8C5DMP with F10C2DMP constructed more stable tubules with V- or U-shape at room temperature (~25 °C) (Fig. 4a). The structure was assumed to be cigar-like roll of a multilamellar sheet. Then a Bragg peak, which is seen in Fig. 5a, may correspond to the reflection from lamellar layers. The Bragg peak disappeared (Fig. 5b), when a solution was heated at 60 °C, suggesting the disappearance of multilamellar structure in molecular assembly. It was supported by TEM (Fig. 4b) that vesicles without multilamellar layers existed at 60 °C, and the tubule–vesicle transition had to be at 25–40 °C.

These results can be compared with the fibers of single-chain amphiphiles with amino acid head groups, *N*-dodecanoyl-*β*-alanine (C_{12}Ala) and *N*-acyl-L-aspartic acids (C_nAsp). C_{12}Ala molecules in water at pH below 6 were associated into nonhelical, cylindrical fibers without hole with circular cross section of 360–380 Å diameter at room temperature [7]. It was confirmed from the characteristic Bragg spacing in SAXS spectrum that cylindrical C_{12}Ala fibers consisted of concentric multilamellar layers [17]. The cylinder–vesicle transition was also observed for molecular assemblies of C_{12}Ala [13].

On the other hand, C_nAsp in water of medium pH at lower temperature formed fibrous molecular assemblies, which were the double strand of helical bilayer strands

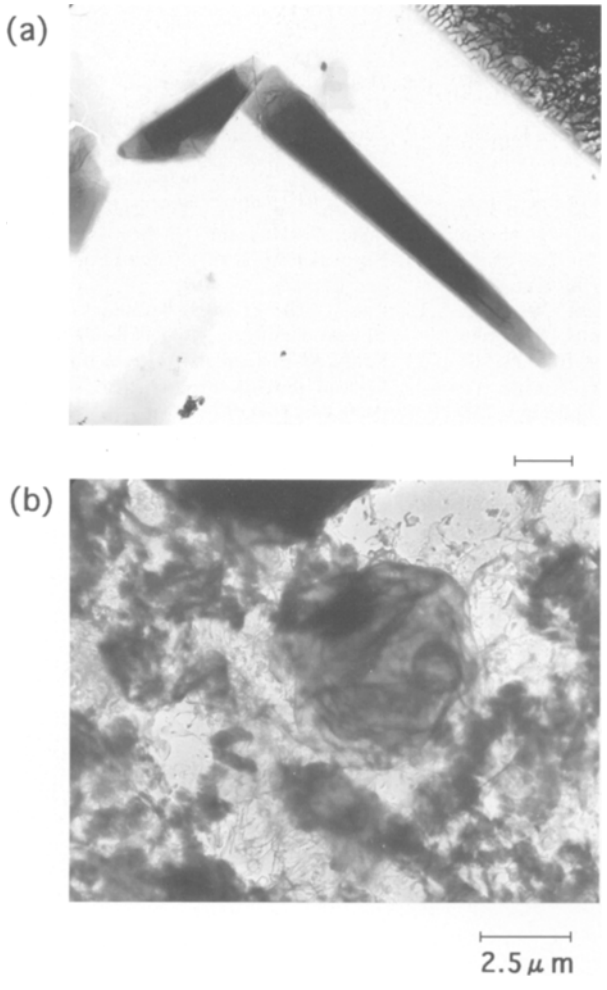

Fig. 4 Cryo-TEM photographs of an aqueous 3% solution of F8C5DMP and F10C2DMP mixture at different temperatures: (a) ~25 °C; (b) ~60 °C

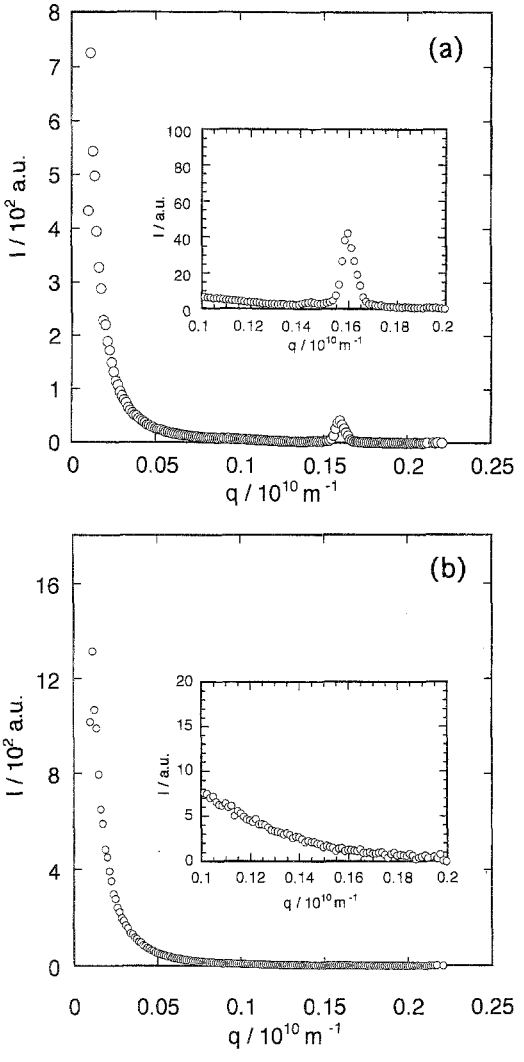

Fig. 5 SAXS data for an aqueous 3% solution of F8C5DMP and F10C2DMP mixture at different temperatures. (a) 25 °C; (b) 60 °C

with unit chain of a 50–60 Å diameter [7, 17]. Unit chains, where linear bilayers twist, formed a double strand with helical sense of ~650 Å pitch and with the distance between strands of ~230 Å. Vesicles were constructed, when fibrous solutions of C_nAsp were heated up above Krafft temperatures, which increased with alkyl chain length from 12 °C of C_{12}Asp to 52 °C of C_{18}Asp.

The systems described above formed linearly extended, fibrous self-assemblies, although the morphological structures depended on amphiphiles. The molecular arrangement in fibers were maintained by the formation of concentric multilamellar bilayer, besides hydrophobic interaction and hydrogen bonding, except C_nAsp fibers with chiral character. The assemblies underwent temperature-dependent fibril–vesicle transition. The fibril–vesicle transition resulted from the rearrangement of bilayers. Generally, multilamellar layers were diminished in vesicles. Transition temperature was higher for fluorinated amphiphile, F-Glu, than for hydrogenated amphiphile, H-Glu. The packing parameter defining the structure of self-assemblies [21] was lower for F-Glu than for H-Glu, supported by the larger surface curvature of F-Glu hollow tubules than of H-Glu vesicles, when compared at room temperature. The transition temperature was higher for F-Glu with double alkyl chains than for the mixture of F8C5DMP and F10C2DMP with a single alkyl chain, suggesting higher Krafft point of amphiphiles with double alkyl chains.

Acknowledgments This work was supported by the Cosmetology Research Foundation (No. JA-95-10). Authors are grateful to Mr. T. Iwamoto and Mr. K. Funayama of Nagoya University for their help in TEM measurement and SAXS analysis.

References

1. Fuhrhop JH, Koning J (1994) Membranes and Molecular Assemblies: The Synkinetic Approach. Roy Soc Chem, Cambridge, UK
2. Imae T, Ikeda S (1989) In: Mittal KL (ed) Surfactants in Solution. Vol. 7. Plenum Press, New York, pp 455–472
3. Imae T, Kakitani M, Kato M, Furusaka M (1996) J Phys Chem 100: 20051–20055
4. Egelhaaf SU, Schurtenberger P (1994) 98:8560–8573; Pederson JS, Egelhaaf SU, Schurtenberger P (1995) 99: 1299–1305
5. Tachibana T, Kambara H (1965) J Am Chem Soc 87:3015–3016
6. Fuhrhop JH, Schnieder P, Rosenberg J, Boekema E (1987) J Amer Chem Soc 109:3387–3390; Fuhrhop JH, Svenson S, Boettcher C, Rossler E, Vieth HM (1990) J Amer Chem Soc 112:4307–4312
7. Imae T, Takahashi Y, Muramatsu H (1992) J Amer Chem Soc 114:3414–3419
8. Terech P, Volino F, Ramasseul R (1985) J Phys 46:895–903
9. Lehn JM, Mascal M, DeCian A, Fischer J (1990) J Chem Soc, Chem Commun 479–481
10. Ghadiri MR, Granja JR, Milligan RA, Mcree DE, Khazanovich N (1993) Nature 366:324–327
11. Nakashima N, Asakuma S, Kim JM, Kunitake T (1984) Chem Lett 1709–1712; Nakashima N, Asakuma S, Kunitake T (1985) J Amer Chem Soc 107:509–510
12. Yanagawa H, Ogawa Y, Furuta H, Tsuno K (1988) Chem Lett 269–272; (1989) J Amer Chem Soc 111:4567–4570
13. Imae T, Kidoaki S (1995) J Jpn Oil Chem Soc 44:301–308
14. Hanabusa K, Miki T, Taguchi Y, Koyama T, Shirai H (1993) J Chem Soc, Chem Commun 1382–1384; Hanabusa K, Matsumoto Y, Miki T, Koyama T, Shirai H (1994) J Chem Soc, Chem Commun 1401–1402
15. Thomas BN, Safinya CR, Plano RJ, Clark HA (1995) Science 267:1635–1638
16. Terech P, Rodriguez V, Barnes JD, McKenna GB (1994) Langmuir 10: 3406–3418; Terech P, Furman I, Weiss RG (1995) J Phys Chem 99:9558–9566
17. Imae T, Hayashi N, Matsumoto T, Furusaka M (1997) Chem Eng Symp Ser, in press
18. Riess JG (1994) Colloids Surf A Physicochem Eng Aspects 84:33–48
19. Krafft M-P, Giulieri F, Riess JG (1994) Colloids Surf A Physicochem Eng Aspects 84:113–119
20. Krafft M-P, Giulieri F (1994) Colloids Surf A Physicochem Eng Aspects 84:121–127
21. Israelachvili JN (1985) Intermolecular and Surface Forces. Academic Press, London