

Phase Behavior of Polyoxyethylene Phytosterol / Polyoxyethylene Dodecylether / Water Systems

Noboru NAITO^{1*}, Durga P. ACHARYA², Junichi TANIMURA² and Hironobu KUNIEDA²

¹ *Research & Development Division, Kosé Corporation
(48-18 Sakae-cho, Kita-ku, Tokyo 114-0005, JAPAN)*

² *Graduate School of Environment and Information Sciences, Yokohama National University
(Tokiwadai 79-7, Hodogaya-ku, Yokohama 240-8501, JAPAN)*

Edited by A. Noda, Shiseido Co. Ltd., and accepted August 23, 2004 (received for review July 5, 2004)

Abstract: The phase behavior of environment-friendly surfactants, polyoxyethylene phytosterylether (PhyEO_m) in water and water/polyoxyethylene dodecylether (C₁₂EO₄) systems was studied. In the PhyEO₁₀/water binary system, micellar solution (W_m), unidentified optically anisotropic liquid crystal (X) phase and lamellar (L_α) phases are formed successively with increasing surfactant concentration at room temperature. With hydrophilic PhyEO₂₀, the W_m, micellar cubic and hexagonal phases are formed in the binary system. With addition of C₁₂EO₄ to the dilute micellar solution of both PhyEO_m type surfactants, a highly viscoelastic solutions of worm-like micelles are formed. Addition of C₁₂EO₄ to the liquid crystalline phases formed in binary system results in the formation of the L_α phase, which extends over wide concentration range. In the PhyEO₁₀/C₁₂EO₄/water system, the X-L_α phase transformation occurs via rectangular ribbon phase. The phase behavior of 5% PhyEO_m with various EO-chain length, ranging from m = 5 to 20 was studied in a wide range of temperature (20° – 100°C). A phase separation occurs in the lipophilic PhyEO_m (m < 8) aqueous systems at all temperature. In the PhyEO_m with intermediate EO-chain length (11 < m < 16), small micelles undergo enormous one-dimensional growth upon increasing the temperature and form viscoelastic solution, followed by a phase separation; whereas in the long EO-chain PhyEO_m (m = 17–20), the W_m phase of small aggregates exists in the entire temperature range.

Key words: polyoxyethylene phytosteryl ether, sterol surfactant, phase behavior, liquid crystal, ribbon phase

1 Introduction

Surfactants are extensively used in various applications such as detergents and household cleanser, cosmetics as well as in industrial processes. Therefore, there is a growing concern over the impact of the surfactants on the environment as well as human body. Similarly, biocompatibility is another important factor in the selection of surfactants in various applications, especially in the formulation of cosmetics and personal

healthcare products.

Polyoxyethylene sterol surfactants consist of either cholesterol or phytosterol as lipophilic part and polyoxyethylene chain as the hydrophilic part. Due to the presence of sterols of natural origin, the surfactants are biocompatible, mild to skin and possess low toxicity (1). In fact, these surfactants are used as emulsifiers, and are available commercially. The bulky and nonflexible sterol groups are also expected to affect the self-aggregation and phase behavior of these surfactants in

*Correspondence to: Noboru NAITO, Research & Development Division, Kosé Corporation, 48-18 Sakae-cho, Kita-ku, Tokyo 114-0005, JAPAN

E-mail: n-naito@kose.co.jp

solvent. Phase behavior of polyoxyethylene cholesterylether (ChEO_m, m=10 and 15) in water and water/cosurfactant systems showed some interesting features such as the formation of a ribbon (R₁) phase over considerably wide range of composition (2,3). This liquid crystal phase is composed of very long rod-like aggregates with somewhat elliptical cross-section. Formation of the R₁ phase is attributed to the bulky and rigid lipophilic part due to which the circular cross-section on the rod-like aggregates gets deformed easily with increasing surfactant cosurfactant concentration. In fact, even at low surfactant concentrations, the presence of bulky sterol group induces sphere-rod transition in micellar shape of the aggregates (4). Upon addition of lipophilic nonionic surfactants such as polyoxyethylene dodecylether (C₁₂EO_n) or alkanoyl *N*-methylethanolamide (NMEA-*n*) to the dilute micellar solution of ethoxylated sterol surfactants, the packing constraints in the lipophilic core increases and small micellar aggregates undergo rapid one-dimensional micellar growth to form worm-like micelles (4,5). Above certain surfactant concentration, called overlap concentration, the worm-like micelles form transient network and dramatically increase the viscoelasticity of the solution. It has been found that additional branching in the terminal alkyl group of the sterol increases the micellar growth and modifies the rheological behavior remarkably.

Despite the attractive features of sterol-based surfactants in various applications, only few reports on the phase behavior of the sterol-based surfactants are available so far (2,3,6,7,8,9). In this context, we studied the phase behavior of polyoxyethylene phytosterol (PhyEO_m) in water and water/C₁₂EO₄ systems over wide range of temperature and concentrations. In this paper, we first discuss the phase behavior of PhyEO₁₀ systems, which is followed by the phase behavior of PhyEO₂₀ systems. Then, we will present the phase behavior of 5% PhyEO_m aqueous system.

2 Experimental

2.1 Materials

Polyoxyethylene phytosterol (PhyEO_m, m=5, 10 and 20) and polyoxyethylene dodecyl ether (C₁₂EO_n, n=1, 2, 3 and 4), products of Nikko Chemicals Co., were used as received. The PhyEO_m of other EO chain length was prepared by mixing PhyEO₅ and PhyEO₁₀, or PhyEO₁₀ and PhyEO₂₀ at appropriate ratio. Schematic

molecular structure of PhyEO_m is shown in **Scheme 1**.

2.2 Phase Diagram

For the study of phase behavior, sealed ampoules containing the required amount of the reagents were homogenized and left in water bath at 25°C for a few days (for the micellar phase) to several weeks (for liquid crystal phase) for equilibration. Phases were identified by visual observation. The liquid crystals were identified by observing the samples through polarizing microscopy (Nikon) and / or small angle X ray scattering (SAXS).

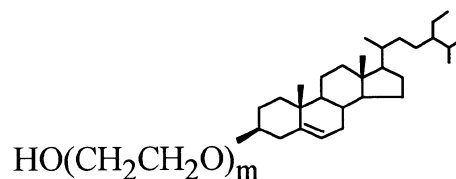
SAXS: SAXS measurements were performed on a 40kV-20mA rotating anode goniometer (Nanoviewer, Rigaku Denki Inc., Japan). The samples were covered with plastic films (Mylar seal method) for the measurement.

3 Results and Discussion

3.1 Phase Behavior of PhyEO₁₀/Water and PhyEO₁₀/C₁₂EO₄/Water Systems

The phase diagram of the PhyEO₁₀/water system at room temperature is shown in **Fig. 1**. It can be seen that the micellar (W_m) phase extends over relatively narrow concentration range, and transforms to an optically anisotropic liquid crystal phase denoted by X at room temperature. At higher surfactant concentration, a lamellar (L_α) liquid crystalline phase is formed. At higher temperatures, the phase boundary between the X and L_α domain could not be identified by visual observation. For the same system, Folmer et al reported the narrow domains of the W_m, nematic and hexagonal (H₁) phases, followed by a wide domain of a gel phase at room temperature with increasing PhyEO₁₀ concentration (7).

SAXS measurements were carried out to study the structural evolution within the X-domain as a function



Scheme 1 Molecular Structure of Polyoxoethylene Phytosterol (PhyEO_m).

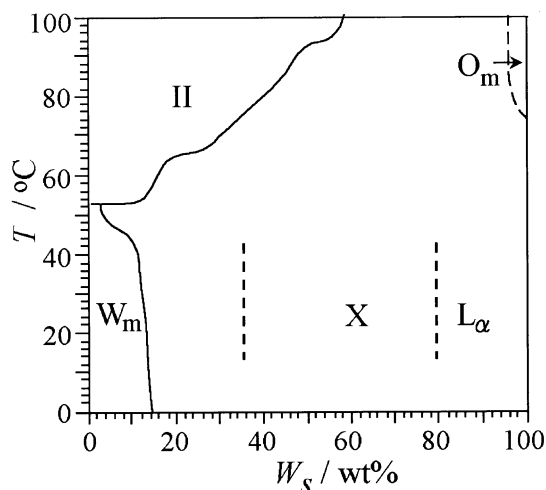


Fig. 1 Phase Diagrams of PhyEO₁₀/Water Binary Systems. W_m and O_m represent normal and reverse micellar phases respectively, L_α stands for the lamellar liquid crystal phase. X is the optically anisotropic liquid crystal phase of unknown structure and II is the two-phase region. W_s is the concentration of surfactant in the system.

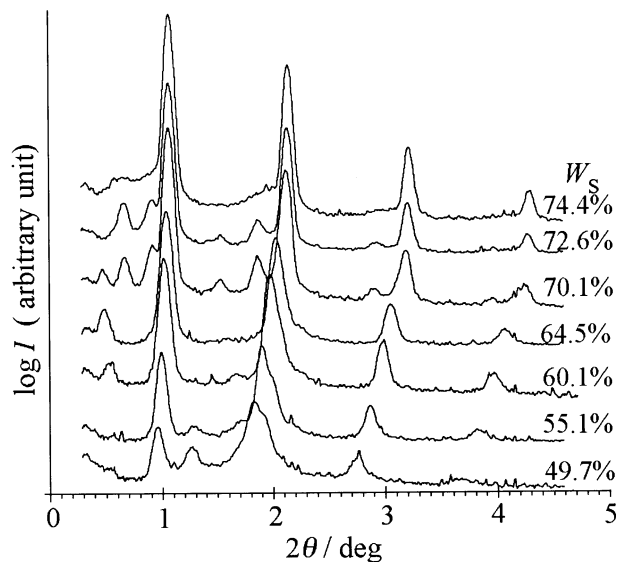


Fig. 2 SAXS Pattern of the X Phase Formed in the Water/PhyEO₁₀ System at Different Surfactant Concentrations, W_s (in wt%) at 25°C.

of surfactant concentration; W_s (in wt%), at 25°C and the results are summarized in **Fig. 2**. The SAXS pattern of the X phase, as is shown in **Fig. 2**, could not be fitted to any of the structures of liquid crystals, which are more commonly observed in this region, such as the H₁ or L_α phases. It can also be seen that the SAXS pattern changes with surfactant composition, indicating a continuous evolution of the structure with composition, ultimately leading to the lamellar structure. Although the exact structure of the mesophases present inside the X domain is not known at this moment, some indications about the structure may be obtained from the phase diagrams of the PhyEO₁₀/C₁₂EO₄/water shown in **Fig. 3**.

As can be observed in the phase diagram of the PhyEO₁₀/C₁₂EO₄/water system (**Fig. 3**), successive addition of the cosurfactant, C₁₂EO₄, to the micellar solution of the aqueous PhyEO₁₀ system in dilute region results in the sharp increase of the viscosity leading the formation of worm-like micelles. The high-viscosity region inside the W_m domain is shown as the shaded region. The rheological behavior of the worm-like micellar solution of this system has been presented elsewhere. With further addition of C₁₂EO₄, a phase separation

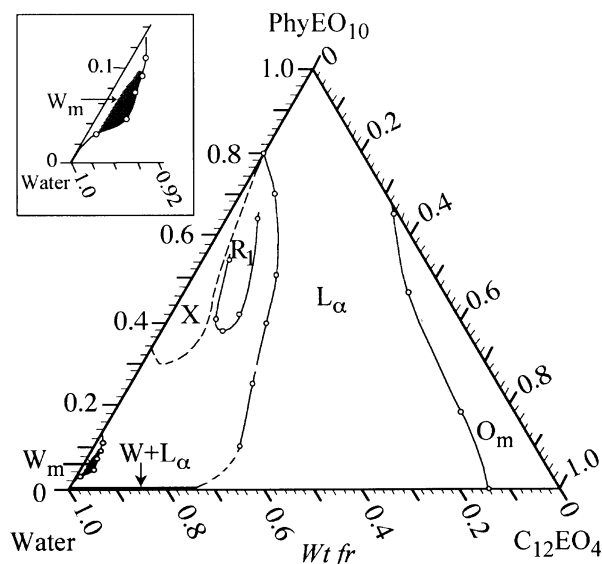


Fig. 3 Phase Diagrams of PhyEO₁₀/C₁₂EO₄/Water System at 25°C. R₁ is the rectangular ribbon phase and W is water. Other notations are same as in **Fig. 1**. A magnified view of the W_m domain and the viscoelastic region of wormlike micelles (shaded area) are shown in the inset.

occurs, with the formation of turbid solution of vesicular dispersion coexisting with the micellar phase.

Addition of cosurfactant to the X phase of the binary PhyEO₁₀-water system in the higher surfactant concentration region results in a phase transformation to the L_α phase via an intermediate liquid crystalline phase having a SAXS pattern as shown in **Fig. 4**, which is typical of the R₁ phase. The Bragg's reflections for the R₁ phase are given by the following equation (10).

$$d_{hk} = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} \right)^{-1/2} \quad (1)$$

where, d_{hk} is the spacing corresponding to the reflection by hk plane, and a and b are the parameters of the rectangular unit cell, as shown in the inset of **Fig. 4**. For the structure with rectangular cmm symmetry, as shown schematically in **Fig. 4**, $h + k = 2n$, where $n \geq 0$ whereas for the rectangular pgg symmetry, Miller indices h and k can have any positive integer n , with the restriction that for $h = 0$, $k = 2n$ and $k = 0$, $h = 2n$ (11). The pgg symmetry group differs from the cmm symmetry in that the cross section of the aggregates slightly tilted with respect to the sides of the unit cell. All the reflection peaks indexed in **Fig. 4** can be fitted to both cmm and pgg symmetries. However, absence of peaks corresponding to 12 and 21 planes indicates that the structure possibly has the cmm symmetry.

The domain of the R₁ phase is noticeably wide and it

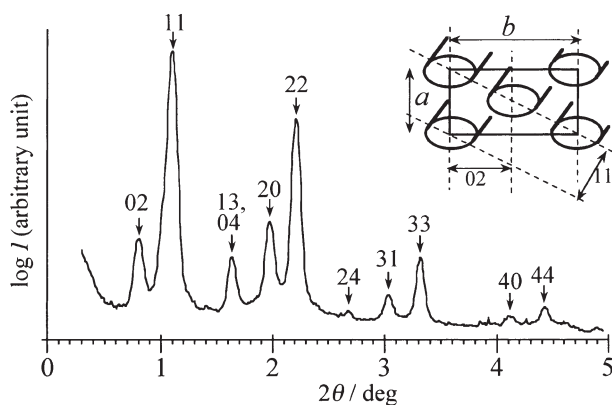


Fig. 4 SAXS Pattern of the Intermediate Phase Formed in the PhyEO₁₀/C₁₂EO₄/Water System at Total Surfactant Weight fraction, $W_s = 64.8$ wt% and PhyEO₁₀/C₁₂EO₄ = 90/10 by wt. The schematic diagram of the structure of the rectangular ribbon (R₁) phase with cmm symmetry is also shown.

extends toward the surfactant-water binary axis with increasing surfactant concentration. In fact, the SAXS pattern of the X phase at high surfactant concentration ($W_s = 70.1$ and 72.6wt%) in the PhyEO₁₀-water binary system (**Fig. 2**) is close to that of the R₁ phase, indicating a close structural relationship between the R₁ phase and the X phase in this region. The region between two conventional liquid crystalline phases, namely the H₁ and L_α, is the usual location of the R₁ phase in the phase diagrams of surfactant systems. However, in the present system, no clear evidence of the hexagonal packing is observed. Nevertheless, the X phase, which forms the R₁ phase upon addition of cosurfactant, is likely to be composed of the rod-like aggregates. It is possible that due to the bulky lipophilic (sterol) group, the cross-section of the rod-like aggregate in the X phase is not circular, but already distorted to an elliptical shape. The structure gradually evolves toward the R₁ phase with addition of the cosurfactants or surfactant. Similar pattern of phase diagram has been observed in the ChEO₁₀/cosurfactant/water system (2).

Figure 5 shows the typical SAXS pattern of the system in the region between the W_m and the L_α at low PhyEO₁₀ concentrations. It shows the sharp peaks with 1: 1/2: 1/3... spacing ratio, along with a wide diffused band, which is probably due to the presence of lamellar-like structure perforated with large and uncorrelated micellar domains. With increasing surfactant and/or cosurfactant concentrations, the diffused band gradually shrinks and a clear lamellar-like SAXS pattern is devel-

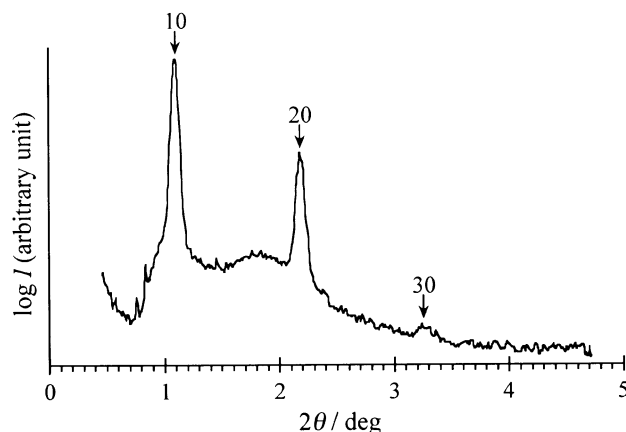


Fig. 5 SAXS Pattern of a Sample in the PhyEO₁₀/C₁₂EO₄/Water System at $W_s = 45$ wt% and PhyEO₁₀/C₁₂EO₄ = 65/35 by wt.

oped. The L_α -domain extends over wide range of concentration from water- $C_{12}EO_4$ binary axis to the surfactant-rich region. Even in the pure state, the $PhyEO_{10}$ shows a SAXS pattern typical of the L_α phase (data not shown), which is attributed to the micro segregation of the hydrophilic and bulky lipophilic parts to form a lamellar-like microstructure (9).

3.2 Phase Behavior in $PhyEO_{20}$ /Water and $PhyEO_{20}/C_{12}EO_4$ /Water Ternary Systems

Figure 6 shows the phase diagram of the $PhyEO_{20}$ /water binary system. With successive increase in surfactant concentration in the binary system, the W_m phase transforms to the micellar cubic (I_1) phase, followed by the H_1 phase persisting over wide range of concentration, which may be attributed to the big head group of the amphiphile that maintains the positive curvature aggregate over wide range of surfactant concentration. At very high concentrations of $PhyEO_{20}$, the solid phase is observed at low temperature and the reverse micellar phase (O_m) phase at high temperature. The domains of the I_1 and S phase in **Fig. 6** is noticeably wider than those shown in the schematic phase diagram of the same system reported by Folmer *et al.* (7).

The phase diagram of the $PhyEO_{20}/C_{12}EO_4$ /water system is shown in **Fig. 7**. In comparison to the W_m region of the $PhyEO_{10}/C_{12}EO_4$ /water system, the W_m region in

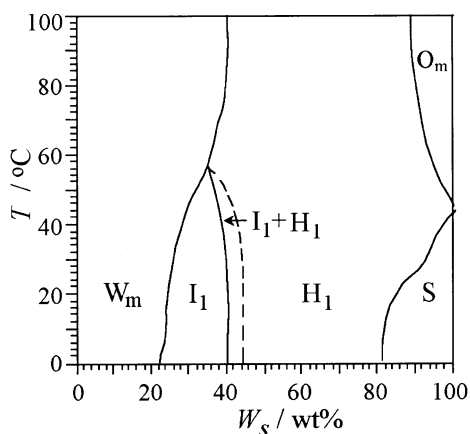


Fig. 6 Phase Diagrams of Water/ $PhyEO_{20}$ Binary Systems. I_1 and H_1 are the isotropic discontinuous (micellar) cubic and hexagonal liquid crystal phases. S is the solid-present region. Other notations are same as in **Fig. 1**.

this system is significantly wide, and relatively higher concentration of $C_{12}EO_4$ is required to form viscoelastic micellar solution. This is attributed to the higher interfacial curvature of the aggregates because of a longer EO chain length. It is interesting to note that despite the large head group of the $PhyEO_{20}$, which tends to maintain a curved interface, the one-dimensional micellar growth occurs. It is probably due to the branching of the alkyl group as well as the rigid skeleton of the lipophilic part, which create a hindrance in the packing of the surfactant in the spherical aggregate. With further addition of $C_{12}EO_4$, a phase separation occurs, with the formation of turbid solution of vesicular dispersion coexisting with the micellar phase. Upon adding $C_{12}EO_4$ to the liquid crystalline phases formed in the binary system, the interfacial curvature decreases and the domains of the liquid crystals extend to the water-rich region. The H_1 -domain extends over wide range of composition, which arises as a result of a mutually compensating contribution of the rigid and branched lipophilic chain and the considerably big head group toward the interfacial curvature. It is interesting to note that the H_1 domain approaches the high-viscosity region of the W_m phase composed of the worm-like aggregates, where the formation of cylindrical aggregate is highly favorable. Successive addition of $C_{12}EO_4$ to the

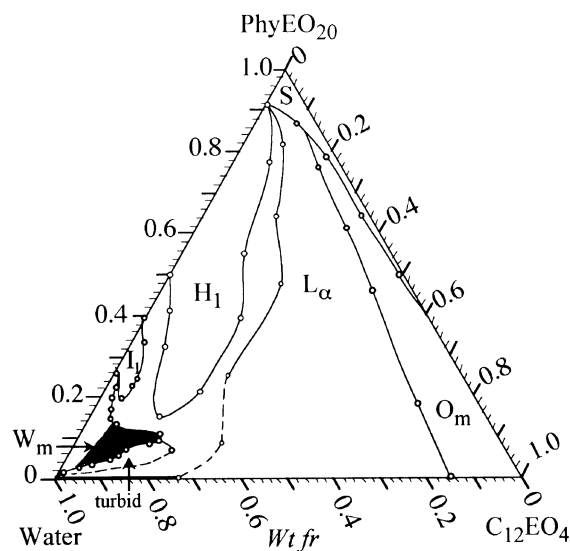


Fig. 7 Phase Diagram of $PhyEO_{20}/C_{12}EO_4$ /Water Systems at 25°C . The phase notations have usual meaning, as mentioned in **Fig. 1** and **6**. The shaded area inside the W_m domain corresponds to the high-viscosity region of wormlike micelles.

H_1 phase induces a H_1 - L_α phase transformation. At a very high $C_{12}EO_4$ concentration, a reverse micellar (O_m) solution is formed over a wide range of $PhyEO_{20}$ concentrations. A solid-present (S) phase is observed in the vicinity of the $PhyEO_{20}$ -rich region.

3.3 Phase Behavior of 5% $PhyEO_m$ Aqueous Solution

The effect of the variation of the hydrophilicity or EO-chain length of the $PhyEO_m$ on the phase behavior is shown in the phase diagram of 5% $PhyEO_m$ aqueous solution (Fig. 8). The surfactants with average EO number ≤ 8 are too lipophilic to form a single-phase system in the aqueous system. Hence a phase separation occurs at all temperatures. With higher EO-number, surfactant forms normal micellar aggregates. The two-phase and single-micellar phase region is separated by a narrow region consisting of liquid crystals. The $PhyEO_m$ surfactants with intermediate EO number ($11 < m < 16$) form a viscoelastic micellar solution of worm-like micelles at high temperatures. Progressive dehydration of the EO-chain with increasing temperature reduces the interfacial curvature of the aggregate, and consequently, induce sphere-rod transition in micellar shape, or, induce one-dimensional micellar growth if the aggregates are rod-like. It is interesting to note that the formation of worm-like micelles is a result of an intrinsic

balance between the hydrophilicity and lipophilicity of the surfactant. When the surfactant is lipophilic, the interfacial curvature decreases too rapidly, and a growth of the aggregate occurs in two-dimension, i.e., a lamellar-like aggregate is formed. With the strongly hydrophilic surfactant, on the other hand, the interfacial curvature decreases slightly and the micellar growth cannot be induced.

4 Conclusion

Due to presence of rigid and bulky lipophilic sterol group, Ethoxylated phytosterol surfactants ($PhyEO_m$) show unique phase behavior in presence of water and water/cosurfactant. Due to the packing constrain induced by sterol, sphere-rod transition and one-dimensional micellar growth in dilute micellar solution can be induced by adding cosurfactant or simply by increasing the temperature. In the aqueous system of hydrophilic surfactant $PhyEO_{20}$, W_m , micellar cubic and hexagonal phases are formed which is attributed to the large head group. In aqueous $PhyEO_{10}$ system, however, the W_m , an optically anisotropic liquid crystal (X) phase consisting of rodlike aggregates of non-spherical cross section and lamellar (L_α) phase are formed successively with increasing surfactant concentration. Upon addition of $C_{12}EO_4$ to the liquid crystalline phases formed in the binary systems, the L_α phase is formed. In the lipophilic $PhyEO_{10}$ surfactant $C_{12}EO_4$ /water system, the X - L_α phase transformation occurs via rectangular ribbon phase composed of rodlike aggregate.

References

1. B.M. FOLMER, Sterol Surfactants: From Synthesis To Applications, *Adv. Colloid Interface Sci.*, Vol. **103**, 99-119 (2003).
2. Md. K. HOSSAIN, D.P. ACHARYA, T. SAKAI and H. KUNIEDA, Phase Behavior of Poly(oxyethylene) Cholesteryl Ether/Novel Alkanolamide/Water Systems, *J. Colloid Interface Sci.*, accepted for publication.
3. T. SATO, Md. K. HOSSAIN, D.P. ACHARYA, O. GLATTER, A. CHIBA and H. KUNIEDA, Phase Behavior and Self-Organized Structures in Water/Poly(oxyethylene) Cholesteryl Ether Systems, *J. Phys. Chem. B*, in press.
4. D.P. ACHARYA and H. KUNIEDA, Formation of Viscoelastic Wormlike Micellar Solutions in Mixed Nonionic Surfactant Systems, *J. Phys. Chem. B*, Vol. **107**, 10168-10175 (2003).
5. D.P. ACHARYA, Md. K. HOSSAIN, JIN FENG, T. SAKAI and H. KUNIEDA, Phase and Rheological Behavior of Viscoelastic Wormlike Micellar Solutions Formed in Mixed Nonionic Surfac-

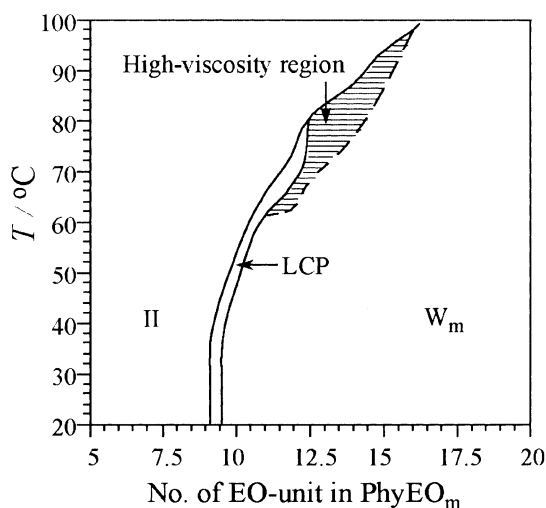


Fig. 8 Phase Diagram of 5% $PhyEO_m$ Aqueous Solution as a Function of the Number of EO-unit in $PhyEO_m$. LCP is the liquid-crystal-present region.

- tant Systems, *Phys. Chem. Chem. Phys.*, Vol. **6**, 1627-1631 (2004).
6. H. SODERLUND, J. SJOBLUM and T.J. WARNHEIM, Phase Diagrams and Solution Properties of Ethoxylated Cholesterols, *Dispersion Sci. Technol.*, Vol. **10**, 131 (1989).
 7. B.M. FOLMER, M. SVENSSON, K. HOLMBERG and W. BROWN, The Physicochemical Behavior of Phytosterol Ethoxylates, *J. Colloid Interface Sci.*, Vol. **213**, 112-120 (1999).
 8. C. RODRIGUEZ, N. NAITO and H. KUNIEDA, Structure of Vesicles in Homogeneous Short-Chain Polyoxyethylene Cholesterol Ether Systems, *Colloids Surf. A.*, Vol. **181**, 237-246 (2001).
 9. M.A. LOPEZ-QUINTELA, A. AKAHANE, C. RODRIGUEZ and H. KUNIEDA, Thermotropic Behavior of Poly(oxyethylene) Cholesterol Ethers, *J. Colloid Interface Sci.*, Vol. **247**, 186-192 (2002).
 10. S. GUSTAFSSON and P-O. QUIST, Nuclear Magnetic Resonance and X-Ray Study of a Rectangular Phase, *J. Colloid Interface Sci.*, Vol. **180**, 564-573 (1996).
 11. H. HAGSLATT, O. SODERMAN and B. JONSSON, The Structure of Intermediate Ribbon Phases in Surfactant Systems, *Liq. Crystals*, Vol. **12**, 667-688 (1992).
-