Colloid Polym Sci 278:899–904 (2000)
© Springer-Verlag 2000

SHORT COMMUNICATION

M. Ishitobi
H. Kunieda

Effect of chain length distribution on the phase behavior of polyglycerol fatty acid ester in water

Received: 11 January 2000
Accepted: 8 March 2000

M. Ishitobi (✉)
Yokohama Research Center
Mitsubishi Chemical Corporation
Kamoshida-cho 1000, Aoba-ku
Yokohama 227-8502, Japan
e-mail: 3200012@cc.m-kagaku.co.jp

H. Kunieda
Division of Artificial Environment Systems
Graduate School of Engineering
Yokohama National University
Tokiwadai 156, Hodogaya-ku
Yokohama 240-8501, Japan

Abstract The effect of the chain length distribution on the phase behavior, the structure of liquid crystals, and physicochemical properties was investigated in water/polyglycerol fatty acid ester. Polyglycerol fatty acid esters with sharply distributed polyglycerol (10G*0.7L) and with broadly distributed polyglycerol (10G0.7L) were used. Unreacted polyglycerol in both surfactants was removed. 10G*0.7L forms hexagonal liquid crystals at a higher concentration than 10G0.7L. The effective cross-sectional area of the lipophilic parts in the hexagonal phase of 10G0.7L is smaller than that of 10G*0.7L owing to the difference in the chain length distribution. Evidently, 10G0.7L molecules are tightly packed in aggregates; therefore, 10G0.7L decreased the surface tension more strongly and promoted emulsification.

Key words Polyglycerol fatty acid ester · Small-angle X-ray scattering · Liquid crystals

Introduction

Polyglycerol fatty acid esters are widely used as surfactants for food, cosmetics, and toiletries. Since a polycondensation reaction is used for the production of polyglycerols, especially for food, the polyglycerols have a broad distribution in their chain lengths. There is also a wide distribution in the degree of esterification because many fatty acids can bond to one hydrophilic chain. Moreover, a large amount of unreacted polyglycerol is, in general, contained in commercial products. Commercially available polyglycerol fatty acid esters are mixtures of different compounds. It is necessary to find out the effect of the mixed surfactants on the phase behavior and the properties of commercially available polyglycerol fatty acid esters.

Surfactant functions such as lowering surface and interfacial tensions, the solubilization of oil and water in microemulsions, and the stability of microemulsions are enhanced by mixing of surfactants [1–4]. The mixing of poly(oxyethylene)-type nonionic surfactants with different chain lengths remarkably improves the surfactant functions and the solubilization of oil and water in bicontinuous microemulsions is increased [5]. The surface tensions of the mixed surfactant solutions are considerably lower than those of single-surfactant solutions [6–8]. Some scientists showed that poly(oxyethylene)-type nonionic surfactants with broadly distributed hydrophilic chains have a greater ability for lowering surface tension, emulsification, and foam stabilization [9, 10].

The distribution of the chain length seems to affect the packing of surfactant molecules at the water–air interface or the water–oil interface. Various structures, such as micelles, vesicles, microemulsions, and liquid crystals, are formed in surfactant/water and/or surfactant/water/oil systems when the chain length is changed [11]. The shape of the self-organizing structure is determined by the packing parameter, $v_L/a_S l$, on the basis of the balance of repulsive and attractive forces at the hydrophobic interface of the aggregates, where v_L is the volume of the lipophilic chain, l is its length, and a_S is the effective cross-sectional area per surfactant molecule [12, 13]. However, this model does not consider the interaction between the hydrophilic parts, paying attention only to the lipophilic part of the surfactant. One must also consider the curvature of the self-organizing structures in order to apply this theory to actual systems. Kunieda et al. [14, 15] improved Israelachvili's theory and submitted a new theory to determine the types of the self-organizing structures in water-poly(oxyethylene alkyl ether) systems which takes into account the curvature effect and the changes in the repulsion forces between poly(oxyethylene) chains. Also, the effect of the mixing of surfactants with different poly(oxyethylene) on the effective cross-sectional area was considered.

Similarly to poly(oxyethylene)-type nonionic surfactants, the functions and physicochemical properties of polyglycerol fatty acid esters would be influenced by the distribution of the polyglycerol chain lengths. There is no study on the effect of polyglycerol distribution on the functions and physical properties of polyglycerol fatty acid esters at a molecular level.

In this study, the phase behavior and self-organizing structures of polyglycerol fatty acid esters with different chain length distributions were investigated.

Experimental

Materials

Polyglycerols

A typical formula of polyglycerols is shown in Fig. 1. Two types of polyglycerols were used: one with a broad chain length distribution; the other with a sharp chain length distribution. The broadly distributed type had an average degree of polymerization of 10.90 and was purchased from Sakamoto Yakuhin Kougyo (polyglycerol #750) and was used without further purification, abbreviated as "10G" (Fig. 2A). The sharply distributed polyglycerol, with an average degree of polymerization of 10.65, abbreviated as "10G*", was prepared as follows. "Polyglycerol #500" with an average degree of polymerization of 5.90 (from Sakamoto Yakuhin Kougyou) was separated into two parts by pseudo-moving-bed chromatography [16] (four connected 650-mm × 65-mm columns packed with 230–240-μm UBK-530 Na^+ type ion-exchange resin, Mitsubishi Chemical Corporation; eluant: ion-exchanged water, 65 °C; flow rate: 60 ml/min; polyglycerol concentration: 45 wt%).

The portion of "polyglycerol #500" with a degree of polymerization of more than 4 is obtained as "10G*" (Fig. 2B). The average degree of polymerization, n, was calculated from the hydroxyl value (OHV), which is the number of KOH milliequivalent to the hydroxyl content (mole) of 1 g sample [17]. The degree of polymerization is related to OHV by

$$\mathrm{OHV} = 56110(n+2)/(74n+18) \ , \qquad (1)$$

where $74n + 18$ is the molecular weight of polyglycerol and $n + 2$ is the number of hydroxyl groups on one polyglycerol molecule.

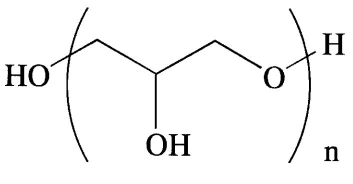

Fig. 1 Formula of polyglycerols

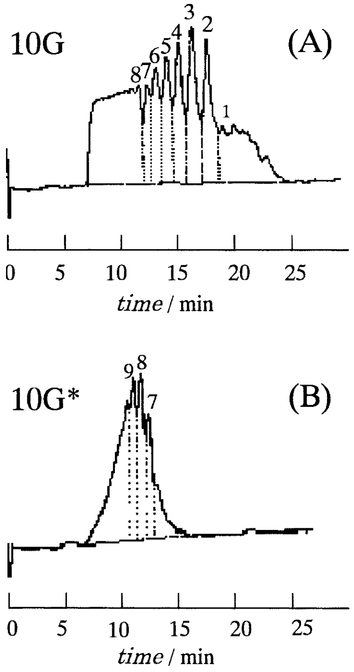

Fig. 2 High-performance liquid chromatography (HPLC) chromatogram of **A** 10G and **B** 10G*. HPLC conditions: column, MCI GEL CK06SH (300 mm × 8 mm); eluant 0.1 wt% phosphoric acid aqueous solution; temperature, 65 °C; flow rate, 0.5 ml/min; polyglycerol concentration, 1 wt%. The *numbers* on the chromatograms show the extent of polymerization of the polyglycerols

Polyglycerol fatty acid esters

The polyglycerol fatty acid esters were synthesized as follows. 10G or 10G* and lauric acid (Nihon Yushi, NAA-122, purity 99%) were mixed at a polyglycerol/fatty acid molar ratio of 1.0/0.7 and were reacted with 0.0025 wt% sodium hydroxide for 2.5 h at 240 °C and further reacted for 4 h at 260 °C under nitrogen flow at atmospheric pressure. The crude polyglycerol fatty acid esters obtained contained a large amount of unreacted polyglycerol (about 60%), which was removed by extraction. Isobutyl alcohol and an aqueous solution with 15 wt% sodium sulfate were mixed with the crude polyglycerol fatty acid esters and the mixture was agitated for 30 min at 70 °C. The unreacted polyglycerols were transferred into the aqueous phase and the polyglycerol fatty acid esters were enriched in the oil phase. The extraction process was performed twice. After evaporating the isobutyl alcohol, the polyglycerol fatty acid esters were dissolved in ethanol. A very small quantity of crystallized sodium sulfate was removed by decantation or filtration, then the ethanol was evaporated. The purified polyglycerol fatty acid esters contained less than 5 wt% free polyglycerol. Polyglycerol fatty acid ester of 10G is abbreviated as 10G0.7L and polyglycerol fatty acid ester with 10G* as 10G*0.7L. The average numbers of fatty acids bonding to one polyglycerol molecule are 2.64 for 10G0.7L and 2.23 for 10G*0.7L. They were calculated from the reaction ratio of polyglycerol/fatty acid, considering the amount of unreacted polyglycerol.

Methods

Density measurement

The densities of the 10G, 10G*, 10G0.7L, and 10G*0.7L solutions were measured using a DAM40 digital density meter (Anton Paar) at 25 ± 0.1 °C. Ethanol was used as the solvent for 10G and 10G*, redistilled water for 10G0.7L, and methanol for 10G*0.7L. The reciprocal of the weight fractions of the surfactant solutions were plotted against the density of the solutions and the density of polyglycerol or polyglycerol fatty acid ester was obtained by extrapolating to 100% surfactant. The following densities were measured: 10G, 1.33 g/cm^3; 10G*, 1.34 g/cm^3; 10G0.7L, 1.15 g/cm^3; 10G*0.7L, 1.20 g/cm^3.

Constructing phase diagrams

Samples of different compositions were sealed in glass ampoules with a narrow constriction. The homogeneity of the viscous samples was attained by passing them through the narrow constriction by repeated centrifugation. After the homogenization the ampoules were set in a thermostat and phase separation was observed visually. The existence of liquid crystals was detected with a crossed Nicol polarizer, and the types of liquid crystals were determined by small-angle X-ray scattering (SAXS).

Small-angle X-ray scattering

A small-angle scattering goniometer equipped with an 18-kW Rigaku Denki rotating anode generator (RINT 2500) was used. The samples were sealed in a steel holder covered with a thin plastic film (Mylar seal method). The measurements were made at 25 °C. The type of liquid crystal was determined by the SAXS peak ratios: 1:1/2:1/3 for lamellar and $1:1/\sqrt{3}:1/2$ for hexagonal phases, respectively [18].

Cloud point measurement

The cloud points of aqueous solutions containing 1 wt% polyglycerol fatty acid and different concentrations of sodium sulfate were measured as follows. The test tubes were set in a thermostat for 30 min at a given temperature to observe whether the solution turns turbid or not.

Surface tension measurement

The Wilhelmy vertical plate technique with an automatic surface tension meter (Kyouwa Kaimenkagaku, CBVP-A3) was employed. The measurements were carried out at 25 °C.

Emulsification

Polyglycerol fatty acid ester (5 wt%), oil (42.5 wt%), and water (42.5 wt%) were mixed in test tubes and shaken for 2 h. *n*-Decane and glycerol tri-2-ethylhexanoate were used as oil. Three hours after emulsification, the volume of the separated aqueous phase was measured and the emulsion stability was calculated from

$$\text{Emulsion stability}(\%) = [(\text{total volume} - \text{separated aqueous phase volume})/\text{total volume})] \times 100.$$

Results and Discussion

Phase behavior of 10G0.7L and 10G*0.7L in aqueous solutions

The phase diagrams of 10G0.7L/water and 10G*0.7L/water are shown in Fig. 3 as a function of temperature. Both 10G0.7L and 10G*0.7L form aqueous micellar solutions at low concentrations and liquid crystals at high concentrations. 10G*0.7L forms liquid crystals at higher concentrations than 10G0.7L. The intensity ratio $1:1/\sqrt{3}$ indicates the hexagonal form H_1. Compared with poly(oxyethylene alkyl ether) systems, the isotropic liquid crystal phase region is wider and a discontinuous cubic phase does not appear at compositions between the micellar solutions and hexagonal liquid crystal phases. Probably, spherical micelles are difficult to form because the polyglycerol fatty acid esters are mixtures and show a chain length distribution.

Hexagonal liquid crystals

The relationship between the interlayer spacing and the hexagonal structure of the liquid crystals is shown schematically in Fig. 4. If it is assumed that all polyglycerol fatty acid ester molecules form infinitely

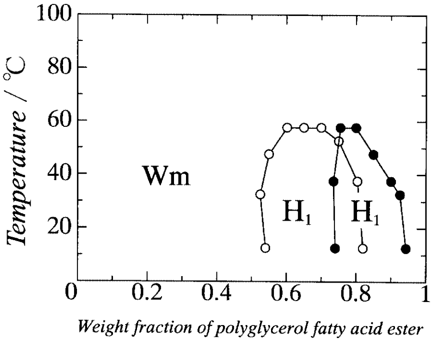

Fig. 3 Phase diagram of water/10G0.7L (○) and water/10G*0.7L (●). W_m: micellar solution; H_1: hexagonal liquid crystals

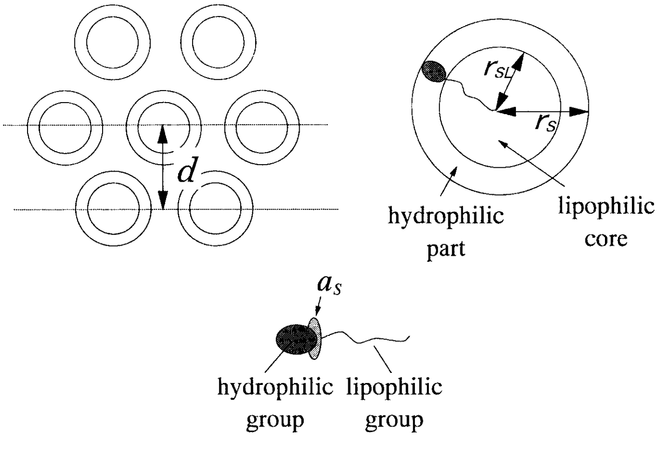

Fig. 4 Model of the hexagonal structure of liquid crystals. *d*: interlayer spacing; r_S: radius of cylindrical micelle; r_{SL}: radius of lipophilic part of cylindrical micelle; a_S: effective cross-sectional area per hydrophobic chain

long cylindrical micelles packed in a hexagonal array and that water does not intrude into the hydrophobic core, the following equation is derived from geometrical considerations.

$$d^2 = (\sqrt{3}\pi/2) r_S^2 (\rho_S/\rho_W)(1/W_S) + (\sqrt{3}\pi/2) r_S^2 (\rho_W - \rho_S)/\rho_W \ , \tag{2}$$

where d is the measured interlayer spacing, r_S is the radius of the cylindrical micelle, ρ_S and ρ_W are the densities of the polyglycerol fatty acid ester and water, respectively, and W_S is the weight fraction of the polyglycerol fatty acid esters.

Equation (2) indicates a linear relationship between d^2 and $1/W_S$, which is confirmed by Fig. 5. Hence, we can assume that the radius of the cylindrical micelles is constant and that only the distance between the micelles increases with decreasing surfactant concentration.

The radii of the micelles, r_S, derived from the slopes of the lines are 2.10 nm (10G*0.7L) and 2.33 nm (10G0.7L.) These r_S values include the hydrophilic and lipophilic parts of the surfactant molecules. Since the hydrophilic part is expanded by the hydrating water molecules, r_S is not coincident with the hydrodynamic radius of the micelles. We calculate the radius of the lipophilic part of the micelle in the following way. The molar volume of surfactant is

$$V_S = M_S/\rho_S \ , \tag{3}$$

where V_S, M_S, and ρ_S are the molar volume, the molecular weight, and the density of the polyglycerol fatty acid ester, respectively. The molar volume of the hydrophilic part is

$$V_H = M_H/\rho_H \ , \tag{4}$$

where V_H, M_H, and ρ_H are the molar volume, the molecular weight, and the density of the hydrophilic part of polyglycerol, respectively. Since the molar volumes of the functional groups of the surfactant molecule are approximately additive [11]

$$V_L = V_S - V_H \ , \tag{5}$$

where V_L is the molar volume of the lipophilic part of the polyglycerol fatty acid ester.

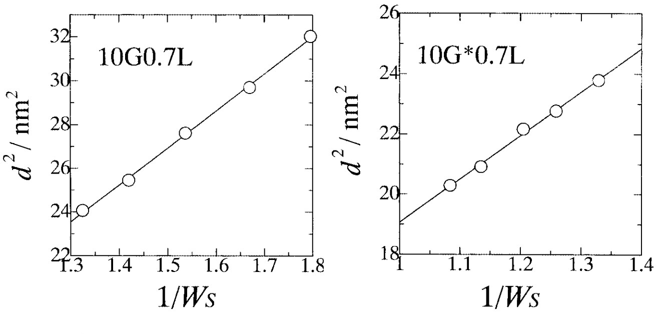

Fig. 5 d^2 as a function of $1/W_S$

The geometrical relation between volume and cross-sectional area of a cylindrical micelle gives

$$r_{SL} = r_S\sqrt{V_L/V_S} \ , \tag{6}$$

where r_{SL} is the radius of the lipophilic part of the cylindrical micelle.

Using Eq. (6), r_{SL} is calculated to be 1.57 nm for 10G0.7L and 1.34 nm for 10G*0.7L. Since the length of the hydrocarbon chain with 11 carbon atoms is 1.54 nm (in fully extended form) [19], the hydrocarbon chain in the hexagonal liquid crystals of 10G0.7L is almost fully expanded and that of 10G*0.7L is somewhat contracted.

The average effective cross-sectional area per hydrophobic chain, a_S, is calculated from

$$a_S = 2V_L/r_{SL}Lm \ , \tag{7}$$

where L is the Avogadro constant and m is the average number of fatty acid molecules bonding to one polyglycerol molecule.

For 10G0.7L and 10G*0.7L, a_S = 0.41 and 0.46 nm^2, respectively. a_S of 10G*0.7L is larger than a_S of 10G0.7L, which shows a wider distribution of hydrophilic chain lengths. For 10G*0.7L, the average number of fatty acids bonding to one polyglycerol molecule is 2.23 and the number of polyglycerol units per fatty acid chain is 10.65/2.23 = 4.78. For 10G0.7L, it is 10.90/2.64 = 4.13. Hence, the a_S of 10G*0.7L is expected to be larger than that of 10G0.7L owing to the difference in the average number of polyglycerol units. However, it is also known that the influence of the hydrophilic chain length on the a_S is not very large in a single-surfactant system when the surfactant molecular curvature is positive like in this H_1 phase [15]. The difference in a_S between 10G*0.7L and 10G0.7L cannot be attributed to the small difference in the hydrophilic chain length only. In the poly(oxyethylene alkyl ether) system with different chain lengths, a_S of mixed surfactants is smaller than that of the pure surfactants due to the reduction in repulsion between the hydrophilic moieties [15]. The sharper chain length distribution of 10G*0.7L (Fig. 2B) may be the main reason for the difference in a_S.

When a hexagonal liquid crystal is formed, the hydrophilic chains overlap. In other words, the distance between the cylindrical micelles is much shorter than the hydrophilic chain length in its extended form. As described before, the diameters of cylindrical micelles do not change with surfactant concentration in either 10G0.7L or 10G*0.7L; however, 10G0.7L contains longer polyglycerol chains compared with 10G*0.7L (Fig. 2A). This is the reason why 10G0.7L forms the H_1 phase at lower surfactant concentration.

Properties of 10G0.7L and 10G*0.7L

Cloud points

Since a_S for 10G0.7L is small, the molecules tend to be packed at the interface more densely than 10G*0.7L. The effect of Na_2SO_4 on the cloud point is shown in Fig. 6. 10G*0.7L has considerably higher cloud points than 10G0.7L. The difference is much larger than expected from the difference in the number of polyglycerol units per fatty acid. Sagitani et al. [20] reported that the difference in the cloud point between triglycerol dodecyl ether and tetraglycerol dodecyl ether is 68 °C. In other words, the cloud point increases by 68 °C for one polyglycerol unit. Since the difference in the number of polyglycerol units per fatty acid between 10G*0.7L and 10G0.7L is $4.78 - 4.13 = 0.65$, the difference in cloud point temperature should be $68 \times 0.65 = 44.2$ °C. The actual difference in the cloud points is about 80 °C at 15 wt% Na_2SO_4. Again, it is assumed that not only the difference in the chain length but also the different distribution causes the different cloud points.

Surface tension and emulsification

The surface tension of 10G0.7L is lower than that of 10G*0.7L (Fig. 7). As discussed before, 10G0.7L can be more tightly packed at the air–water interface and this causes the difference in surface tensions. The emulsifying ability of 10G*0.7L and 10G0.7L is shown in Fig. 8. The drainage rate of the water phase in the 10G*0.7L system is much higher. Since the surface tension is low for 10G0.7L, the oil–water interfacial tensions should also be low and 10G0.7L forms fine emulsion droplets. As a_S of 10G0.7L is smaller, the denser packing of the surfactant makes the interface film more rigid; therefore, the interfacial tension decreases and the emulsifying ability of 10G0.7L is higher than that of 10G*0.7L.

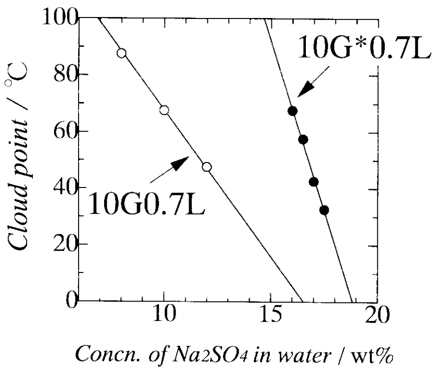

Fig. 6 Cloud point profiles of 10G0.7L and 10G*0.7L. Surfactant concentration: 1 wt%

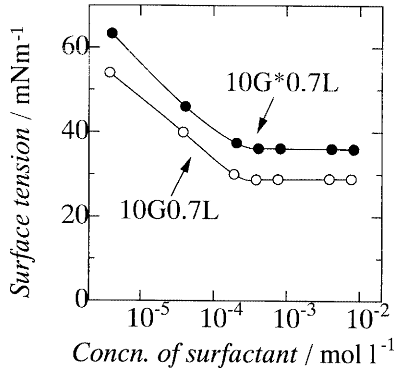

Fig. 7 Surface tension versus concentration for 10G0.7L and 10G*0.7L at 25 °C

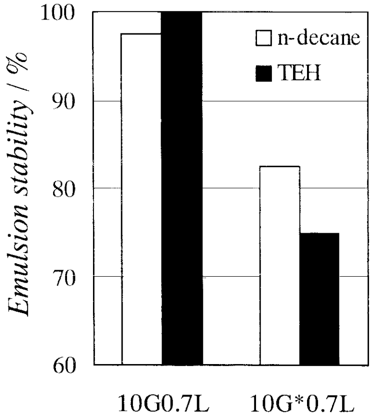

Fig. 8 Emulsion stability for 10G0.7L and 10G*0.7L. Polyglycerol fatty acid ester = 5%, oil = 47.5%, water = 47.5%. *TEH* = glycerol tri 2-ethylhexanoate

Conclusion

We investigated the phase behavior and properties of polyglycerol fatty acid esters which have about the same degree of polymerization but different chain lengths distributions.

1. The sample with broadly distributed polyglycerol chains has a smaller a_S than the sharply distributed sample.
2. The cloud point depends on a_S. The larger a_S, the higher the cloud point.
3. The polyglycerol fatty acid ester with broadly distributed polyglycerol shows higher ability in surface tension lowering and emulsification. These surfactant molecules are more tightly packed at the interface than the surfactant with the narrow distribution.

References

1. Sherman P (1968) Emulsion science. Academic, London, p 94
2. Attwood D, Flovence AT (1983) Surfactant systems. Chapman and Hall, New York, pp 469–566
3. Rosen MJ (1989) Surfactants and interfacial phenomena, 2nd edn. Wiley, New York, pp 304–336
4. Falbe J (1987) Surfactant in consumer products. Springer, Berlin Heidelberg, New York, p 142
5. Kunieda H, Nakano A, Akimaru M (1995) J Colloid Interface Sci 78:170
6. Schick MJ (1962) J Colloid Sci 17:801
7. Lange H (1962) Kolloid-Z 182:123
8. Lange H (1987) In: Schick MJ (ed) Nonionic surfactants, physical chemistry. Dekker, New York, pp 1–44
9. Crook EH, Fordyce DB, Trebbi GF (1963) J Phys Chem 67:1987
10. Shinoda K, Saito H, Arai H (1971) J Colloid Interface Sci 35:624
11. Kunieda H, Shigeta K, Ozawa K, Suzuki M (1997) J Phys Chem 101:7952
12. Israelachvili JN, Mitchell DJ, Ninham BW (1976) J Chem Soc Faraday Trans 2 72:1525
13. Hyde S, Andersson S, Larsson K, Blum Z, Landh T, Lidin S, Ninham BW (1997) The language of shape. Elsevier, New York
14. Kunieda H, Umizu G, Yamaguchi Y (1998) Yukagaku 47:879
15. Kunieda H, Umizu G, Yamaguchi Y (1999) J Colloid Interface Sci 218:88
16. Broughton DB (1961) US Patent 2,985,589
17. William H (ed) (1970) Official methods of analysis of the association of official analytical chemists, 11th edn. Association of Official Analytical Chemists, Washington, DC, p 444
18. Fontell K (1974) In: Gray GW, Winsor PA (eds) Liquid crystals and plastic crystals. Vol 2 Wiley, New York, pp 80–109
19. Tanford C (1972) J Phys Chem 76:3020
20. Sagitani H, Hayashi Y, Ochiai M (1989) J Am Oil Chem Soc 66:146