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Phase behavior of methoxypolyoxyethylene dodecanoate as compared to polyoxyethylene dodecyl ether and polyoxyethylene methyl dodecyl ether

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Abstract: The phase behavior of binary systems composed of water and nonionic surfactants were investigated. The nonionic surfactants studied were the methoxypolyoxyethylene dodecanoates ($R_{11}COO(EO)_nCH_3$, $n = 4.9$, 6.1, 7.3, 9.3, and 12.8, where n is the average number of oxyethylene units).

The phase behaviors of $R_{11}COO(EO)_nCH_3$ were compared with those of the polyoxyethylene dodecyl ethers ($R_{12}O(EO)_pH$) and polyoxyethylene methyl dodecyl ethers ($R_{12}O(EO)_qCH_3$) which have been previously reported. It was found that the $R_{11}COO(EO)_nCH_3$s have lower cloud points and lower upper limit temperatures for the existence of the mesophase as compared to the other two types. A $R_{11}COO(EO)_{12.8}CH_3$/water system had favorable solution properties for practical use, such as a relatively narrow hexagonal liquid crystalline region and a lower melting point than the ordinary alcohol ethoxylate type nonionics.

Key words: Methoxypolyoxyethylene dodecanoate – phase diagram – upper limit temperature of mesophase – cloud point

Introduction

Methoxypolyoxyethylene alkanoates are conveniently obtainable from the reaction of fatty acid methyl esters with ethylene oxide utilizing a special metal oxide catalyst [1]. Some of their solution properties have been reported by Nakagawa et al. [2–6]. They examined critical micelle concentrations (CMC), aggregation numbers, and some other properties of the methoxypolyoxyethylene decanoates and dodecanoates having various polyoxyethylene chain lengths in order to verify their hypothesis relating to the micelle formation of nonionic surfactants. According to their results, the micellar properties of the surfactants were regarded to be analogous to those of conventional polyoxyethylene alkyl ethers. However, it is presumed that the difference in the molecular structure is reflected more pronouncedly in the phase behaviors rather than in the micellar properties. Conroy et al. [7] investigated the phase behaviors of the polyoxyethylene dodecyl ether derivatives in which the terminal hydroxyl group was capped by a methyl residue ($R_{12}O(EO)_qCH_3$), and compared them with the conventional polyoxyethylene dodecyl ethers ($R_{12}O(EO)_pH$). They concluded that the terminal methyl group significantly affects their phase behaviors. Namely, the cloud points and the upper limit temperatures of the mesophase for $R_{12}O(EO)_qCH_3$ are lowered by a decrease in hydrophilicity due to methyl capping. A similar influence can be expected with respect to the methoxypolyoxyethylene alkanoates, but their phase behaviors have not been reported.

In this work, the phase behaviors of the methoxypolyoxyethylene dodecanoates having various polyoxyethylene chain lengths ($R_{11}COO$-$(EO)_n$-CH_3) were investigated and compared with the conventional nonionic surfactants, such as the polyoxyethylene ether type and the methyl capped one, in order to clarify the effect of the molecular structure on the solution properties.

Experimental

Materials

A $R_{11}COO(EO)_{11.4}CH_3$ with widely distributed oxyethylene units (namely, crude product) was prepared from methyl dodecanoate and ethylene oxide in the presence of a solid metal oxide catalyst, according to the method of Hama et al. [1]. The crude product was then separated by vacuum distillation (0.12–0.20 torr, 220–340 °C) into five fractions (A–E) having the individual distributions of oxyethylene units.

A sample of $R_{12}O(EO)_{12.9}H$ was synthesized from dodecyl alcohol and ethylene oxide by an ordinary liquid phase condensation reaction in the presence of an alkaline catalyst.

Analysis for distribution of oxyethylene units

The distribution of oxyethylene units for both $R_{11}COO(EO)_nCH_3$ and $R_{12}O(EO)_{12.9}H$ were analyzed by HPLC equipped with tandem double-reversed phase columns joined in series (Du Pont Co. Ltd., Zorobax-C8, 4.6 mm ⌀ × 25 cm). The mobile phase was CH_3CN/H_2O (6/4 by vol./vol.).

The distributions of oxyethylene units for the crude product and for the fractionated samples, A–E, are shown in Fig. 1. The crude product has a broad distribution ranging from 0 to 40 units with an average oxyethylene unit of 11.4. On the other hand, the distributions of A–E are narrow. The average oxyethylene units of A–E were 4.9, 6.1, 7.3, 9.3 and 12.8, respectively. Hereafter, the fractions of A–E are abbreviated as $R_{11}COO(EO)_{4.9}CH_3$, $R_{11}COO(EO)_{6.1}CH_3$, $R_{11}COO(EO)_{7.3}CH_3$, $R_{11}COO(EO)_{9.3}CH_3$ and $R_{11}COO(EO)_{12.8}CH_3$, respectively.

Determination of phase diagram

Various compositions of surfactant and water in sealed glass tubes were kept above 80 °C for 30 min. in a thermostated water bath. After cooling, the sealed tubes were slowly heated to the prescribed temperature and then allowed to attain equilibrium within ±0.1 °C. A phase transition was detected by the change in both viscosity and birefringence. Each phase was confirmed using an optical microscope with crossed polarizers (Olympus Co. Ltd., Type 13H). Lamellar and hexagonal phases were identified by their specific textures with reference to literature data [8]. Since micellar solutions and cubic phases are both optically isotropic, they were separately identified by comparing their viscosities. One phase diagram was established by the preparation and observation of 50–70 binary mixture samples in order to keep the accuracy of the phase boundary composition better than 2% (by wt.).

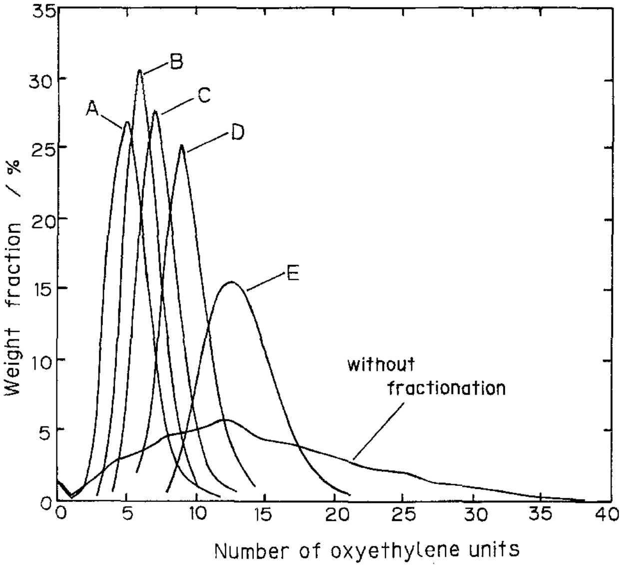

Fig. 1. Distributions of oxyethylene units for $R_{11}COO(EO)_nCH_3$

CMC measurement

The CMC of $R_{11}COO(EO)_nCH_3$ was determined by the TCNQ method according to Meguro et al. [9].

Results and discussion

CMC and cloud points

The CMC values and the cloud points (1 wt% solutions) of $R_{11}COO(EO)_{7.3}CH_3$, $R_{11}COO(EO)_{9.3}CH_3$ and $R_{11}COO(EO)_{12.8}CH_3$ are listed in Table 1 together with the results formerly reported by Nakagawa et al. [3]. The cloud points increased significantly with an increase in the

Table 1. CMC values and cloud points of $R_{11}COO(EO)_nCH_3$

Surfactant	CMC (m Moles/L)	Cloud point (°C)	ref.
$R_{11}COO(EO)_{6.0}CH_3$	0.15–0.20	31	[3])
$R_{11}COO(EO)_{7.3}CH_3$	0.12	46	[a])
$R_{11}COO(EO)_{8.4}CH_3$	0.20–0.27	53	[3])
$R_{11}COO(EO)_{9.3}CH_3$	0.19	58	[a])
$R_{11}COO(EO)_{11.2}CH_3$	0.25–0.32	74	[3])
$R_{11}COO(EO)_{12.5}CH_3$	0.28–0.35	79	[3])
$R_{11}COO(EO)_{12.8}CH_3$	0.29	76	[a])

[a]) This work

average oxyethylene units, whereas the increase in the CMC values was rather slight. Although the distributions of oxyethylene units in the study by Nakagawa et al. have not been quantitatively revealed, the CMC values and cloud points of nonionics having similar average oxyethylene units almost agree with each other.

Phase diagrams

The phase diagrams of the $R_{11}COO(EO)_nCH_3$/water binary systems are shown in Fig. 2. The nomenclature of each phase mainly follows Mitchell et al. [10]; namely, L_1: micellar solution, L_2: surfactant liquid, I_1: cubic phase of close-packed spherical micelles, H_1: normal hexagonal phase, $L\alpha$: lamellar phase, and S: hydrated solid. For example, W + $L\alpha$ is the coexistence of the $L\alpha$ phase and the dilute surfactant solution phase. W + L_1 is the coexistence of the large aggregate of surfactant separated from the micellar solution and the dilute surfactant solution. W + L_2 is the coexistence of the surfactant liquid and the dilute surfactant solution. $L\alpha$ + L_2 is the coexistence of the surfactant liquid and the $L\alpha$ phase. The dotted lines in the phase diagrams represent schematic CMC lines.

Around room temperature, the W + $L\alpha$, $L\alpha$, $L\alpha$ + L_2, and L_2 phases were successively observed in the $R_{11}COO(EO)_{4.9}CH_3$/water system with an increase in the concentration. In the temperature range above 35 °C, the W + L_2 and L_2 phases were observed.

In the $R_{11}COO(EO)_{6.1}CH_3$/water system, the L_1, $L\alpha$, and L_2 phases were successively observed with an increase in the concentration in the range below 25 °C. The so-called double cloud phenomenon was observed in this system, since the successive phase transition of $L_1 \rightarrow W + L_1 \rightarrow W + L\alpha \rightarrow W + L_2$ was observed with an increase in temperature in the concentration range below 25 wt%.

In $R_{11}COO(EO)_{7.3}CH_3$/water system, the L_1, H_1, and S phases were observed in the temperature range lower than 20 °C.

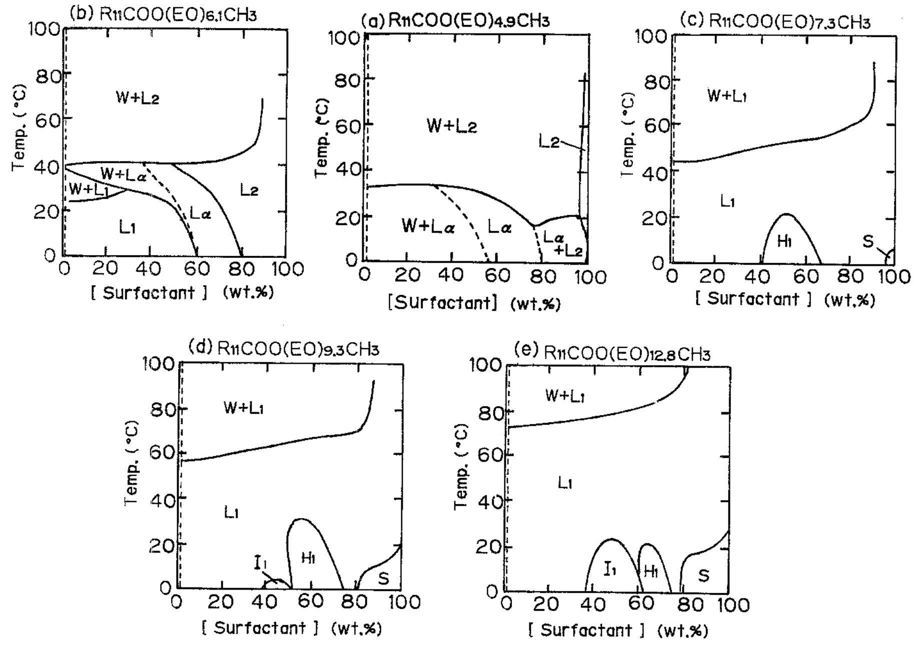

Fig. 2. Phase diagrams of surfactant/water systems
a) $R_{11}COO(EO)_{4.9}CH_3$/water;
b) $R_{11}COO(EO)_{6.1}CH_3$/water;
c) $R_{11}COO(EO)_{7.3}CH_3$/water;
d) $R_{11}COO(EO)_{9.3}CH_3$/water;
e) $R_{11}COO(EO)_{12.8}CH_3$/water
Symbols: L_1 = micellar solution; L_2 = surfactant liquid; I_1 = cubic phase of closed-packed spherical micelles; H_1 = normal hexagonal phase; $L\alpha$ = lamellar phase; S = hydrated solid; W = dilute surfactant solution

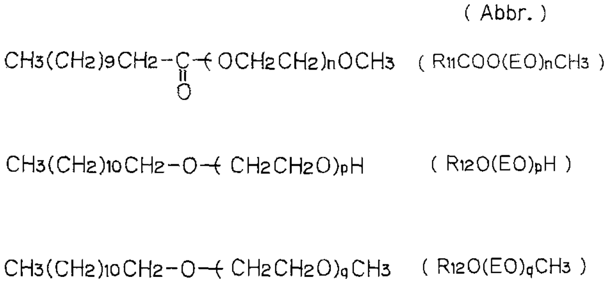

Fig. 3. Molecular structures of each nonionic surfactants

In $R_{11}COO(EO)_{9.3}CH_3$/water and $R_{11}COO(EO)_{12.8}CH_3$/water systems, the L_1, H_1, I_1, and S phases were observed in the temperature range lower than 30 °C. The $W + L_1$ phase was observed for these three systems in the temperature range higher than 46°, 58°, and 76 °C, respectively (Fig. 2(c), (d), (e)).

The specificity of the phase behavior of $R_{11}COO(EO)_nCH_3$ can be revealed by comparing with those of $R_{12}O(EO)_pH$ [10] and $R_{12}O(EO)_qCH_3$ [7]. The molecular structures of each nonionic surfactant are shown in Fig. 3. The phase behavior of $R_{11}COO(EO)_{4.9}CH_3$ was analogous to those of $R_{12}O(EO)_2H$ [7] and $R_{12}O(EO)_3H$ [10] with respect to the absence of the L_1 phase in the region of low temperature range and low concentration. However, the range of L_2 phase in the $R_{11}COO(EO)_{4.9}CH_3$/water system was much narrower than those in other nonionic surfactant/water systems, such as $R_{12}O(EO)_2H$ [7], $R_{12}O(EO)_3H$ [10], $R_{12}O(EO)_4H$ [10] and $R_{12}O(EO)_4CH_3$ [7]. The phase behavior of $R_{11}COO(EO)_{6.1}CH_3$, which showed the double cloud phenomenon, was analogous to that of $R_{12}O(EO)_4H$ [10] and $R_{12}O(EO)_4CH_3$ [7]. The phase behavior of $R_{11}COO(EO)_{7.3}CH_3$ was similar to that of $R_{12}O(EO)_6H$ [10] and $R_{12}O(EO)_6CH_3$ [7] with respect to the appearance of the H_1 phase, but it did not show the V_1 and $L\alpha$ phases. The phase behaviors of $R_{11}COO(EO)_{9.3}CH_3$ and $R_{11}COO(EO)_{12.8}CH_3$, which showed the coexistence of the I_1 phase and the H_1 phase, were similar to those of $R_{12}O(EO)_{12}H$ [10] and $R_{12}O(EO)_8CH_3$ [7], but the temperature ranges for the existence of the H_1 phases of $R_{11}COO(EO)_{9.3}CH_3$ and $R_{11}COO(EO)_{12.8}CH_3$ were very narrow.

The upper limit temperatures for each mesophase and the cloud points are summarized in Table 2. As shown in Table 2, the upper limit temperatures and cloud points of $R_{11}COO(EO)_nCH_3$ were markedly lower than those of $R_{12}O(EO)_pH$ and $R_{12}O(EO)_qCH_3$ having similar average oxyethylene units. This may be attributed to the following two effects resulting from their molecular structures. The first effect originates from the presence of a methyl group located at the end of the polyoxyethylene chain.

Table 2. Cloud points and upper limit temperature of mesophase for various surfactants (temperature in °C)

Surfactant	C.P.	I_1	H_1	V_1	$L\alpha$	ref.
$R_{12}O(EO)_4H$	4	–	– 2	< 0	68	[10])
$R_{12}O(EO)_4CH_3$	0.2	–	–	–	27	[7])
$R_{11}COO(EO)_{4.9}CH_3$	< 0	–	–	–	34	[a])
$R_{12}O(EO)_6H$	46	–	37	38	73	[10])
$R_{12}O(EO)_6CH_3$	35	–	24	18	43	[7])
$R_{11}COO(EO)_{6.1}CH_3$	25	–	–	–	42	[a])
$R_{11}COO(EO)_{7.3}CH_3$	46	–	19	–	–	[a])
$R_{12}O(EO)_8H$	77	16	59	43	22	[10])
$R_{12}O(EO)_8CH_3$	52	15	41	–	–	[7])
$R_{11}COO(EO)_{9.3}CH_3$	58	5	30	–	–	[a])
$R_{12}O(EO)_{12}H$	98	48	76	–	–	[10])
$R_{11}COO(EO)_{12.8}CH_3$	76	23	19	–	–	[a])

[a]) This work

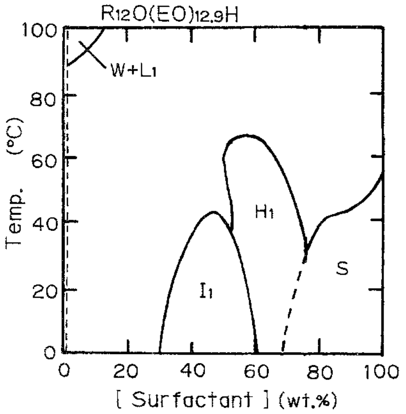

Fig. 4. Phase diagram of $R_{12}O(EO)_{12.9}H$/water system

Conroy et al. [7] reported that methyl capping of $R_{12}O(EO)_pH$ causes the lowering of the upper limit temperature of the mesophase and the cloud point by 20 ~ 30 °C. According to these temperature-lowering phenomena, they considered that the degree of hydrophilicity of the terminal hydroxy group corresponds to the hydrophilicity of three oxyethylene groups. The second effect is generated from the difference in inserted groups between the hydrophilic part and the hydrophobic one (ether group and ester group) in the molecules. For example, the upper limit temperatures of the I_1 and H_1 phases for $R_{11}COO(EO)_{9.3}CH_3$/water system were lower than those for the $R_{12}O(EO)_8CH_3$/water system [7].

In Fig. 4, the phase diagram of the $R_{12}O(EO)_{12.9}H$/water system was shown. The average number and the distribution of oxyethylene units of $R_{12}O(EO)_{12.9}H$ are very similar to those of $R_{11}COO(EO)_{12.8}CH_3$. The upper limit temperature of the H_1 phase for the $R_{11}COO(EO)_{12.8}CH_3$/water system was lower than room temperature, while that for the $R_{12}O(EO)_{12.9}H$/water system is 67 °C. The lower upper limit temperature of the H_1 phase of the $R_{11}COO(EO)_{12.8}CH_3$/water system seems to be attributed to the effects of both the inserted groups and methyl capping.

The useful advantages of $R_{11}COO(EO)_{12.8}CH_3$ as a raw material in detergent industry are deduced by comparing the phase behavior of the $R_{11}COO(EO)_{12.8}CH_3$/water system with that of $R_{12}O(EO)_{12.9}H$/water system. For example, the general industrial production of liquid-detergent composition is performed by diluting an anhydrous nonionic surfactant with water to 10 ~ 50 wt% aqueous solution. For smoothly accomplishing this process on a large industrial scale, the following conditions are necessary: 1) An anhydrous nonionic surfactant in a storage tank must be fluidic (liquid state) in order to transport it into a mixing tank by pumping, and 2) an anhydrous nonionic surfactant must be rapidly dissolved in water by simple stirring. For these requirements, the $R_{11}COO(EO)_{12.8}CH_3$ has the following superiorities compared with the $R_{12}O(EO)_{12.9}H$. 1) The $R_{11}COO(EO)_{12.8}CH_3$ can be a liquid above 27 °C, while the $R_{12}O(EO)_{12.9}H$ needs a constant temperature above 55 °C in order to remain as a liquid. 2) The $R_{11}COO(EO)_{12.8}CH_3$ dissolves rapidly in water at room temperature since it does not form a viscous H_1 or I_1 phase, whereas, the dissolution rate of $R_{12}O(EO)_{12.9}H$ is very slow even at temperatures of 50 ~ 60 °C since a viscous H_1 phase is formed around its surface as soon as it contacts with water.

As previously described, the $R_{11}COO(EO)_{12.8}CH_3$ is considered to have such advantages as convenience of handling and saving of energy on an industrial scale.

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