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ORIGINAL CONTRIBUTION

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Mixtures of branched non-ionic oligo-oxyethylene surfactants in aqueous solutions – the effect of molecular geometry on LC phase behaviour 4

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Abstract The LC phase behavior of ternary mixtures of the two corresponding branched non-ionic surfactants 1,3-bis-(methoxy-tetra-oxyethylene)-2-propoxy-tetradecane (Y-surfactant) and 1,3-bis-(heptyloxy)-2-propoxy-octaoxyethylene mono-methyl ether (V-surfactant) and water were studied by polarizing microscopy. The two branched surfactants, which have different molecular geometries but nearly the same hydrophilic-lipophilic volume ratio, exhibit extremely different phase behavior in binary surfactant/water systems. For the ternary mixtures of Y- and V-surfactant and water we found–according to established packing models–a continuous stabilization of the cubic and hexagonal phases and a destabilization of the lamellar phase with increasing amount of Y-surfactant. On the other hand, we observed a thermal stabilization of the lamellar phase. The maximal transition temperatures of the lamellar phase pass a maximum with increasing amount of Y-surfactant.

Key words Non-ionic surfactants – oligo-oxyethylene surfactants – mixtures of surfactants – lyotropic liquid crystal – phase behavior

Introduction

Above a critical micelle concentration (CMC) surfactants form micelles in aqueous solutions which can aggregate to lyotropic liquid crystalline (LC) phases. The shape and size of the micelles depend mainly on the molecular structure of the surfactant, the concentration, and temperature. The simple packing model of Israelachvili et al. [1] relates the molecular structure of the surfactant to the shape of the micelles. Neglecting micellar interactions, the packing parameter F,

$$F = \frac{V_1}{l_c \cdot A}, \qquad (1)$$

where V_1 denotes the lipophilic chain volume, l_c the lipophilic chain length, and A the area of the hydrated hydrophilic headgroup at the micellar interface, predicts the preferred micellar geometry. Above the CMC it is predicted that for $0 < F \leq 1/3$ spherical micelles, for $1/3 < F \leq 1/2$ cylindrical micelles, for $1/2 < F \leq 1$ disc-like micelles, and for $F > 1$ inverse micelles will form. Modifications of the molecular structure and therefore of the packing parameter are directly reflected in the shape of the micelles and in the LC phase structure. In a mixture of two surfactants with different F and water the packing parameter of the mixture (F_{mix}) and the curvature of the mixed micelles (r_{mix}) depend on the mixing ratio, as shown by Marques et al. [2]. In the quasi binary two surfactants/water system F_{mix} and r_{mix} no longer refer to the molecular geometry of one **single** molecule, but rather to an **average** lipophilic chain volume ($\bar{V}_1$), an **average** lipophilic chain length ($\bar{l}_c$), and an **average** area of the headgroup ($\bar{A}$).

In previous papers [3, 4], the syntheses and LC phase behavior of a homologous series of branched non-ionic surfactants with the general formula $C_nG(E_mM)_2$ (Y-surfactants) and $(C_n)_2GE_mM$ (V-surfactants) were presented, where C_n denotes an alkyl chain, G a triglyceryl unit, and E_mM an oligo-oxyethylene mono-methyl ether. For example, a comparison of the two surfactants $C_{14}G(E_4M)_2$ and $(C_7)_2GE_8M$ shows that these surfactants have nearly the same hydrophilic-lipophilic volume ratio but different molecular geometry. In this special case, the molecular geometry of the Y-surfactant leads to a quantitatively smaller packing parameter **F** compared to the V-surfactant ($F_Y < F_V$). As a consequence, the interfacial curvature of the micelles (r) of the Y-surfactant is larger than that of the V-surfactant and a change in the dominant phase structure from cubic/hexagonal for the Y-surfactant to lamellar for the V-surfactant can be observed (see Fig. 1a) and 1c). The extremely different LC phase behavior of the binary surfactant (Y or V)/water systems leads to the following considerations: i) how is the phase behavior of the ternary surfactants (Y and V)/water system influenced by a systematic variation of the mol fraction of Y- and V-surfactant, and ii) what kind of phase behavior exhibits an equimolar mixture (1:1) of the Y- and V-surfactant with water.

In this paper, the LC phase behavior of the ternary mixtures of $C_{14}G(E_4M)_2$ $(C_7)_2GE_8M$, and water is presented. Since these surfactants differentiate only in their molecular structure, a dependence of the LC phase behavior on the surfactant mixing ratio can be expected. The LC phase behavior (as examined by contact preparation) of these ternary mixtures as a function of the surfactant mixing ratio will be described with respect to the LC phase behavior of the binary systems. Additionally, the quasi binary phase diagram of the equimolar surfactant mixture and water will be presented.

Experimental section

Materials

In previous papers [3, 4], the syntheses of $C_{14}G(E_4M)_2$ and $(C_7)_2GE_8M$ were described. The surfactants were purified by column chromatography and their purity (ca. 99%) was confirmed by high-pressure liquid chromatography.

Polarizing microscopy

All microscopic investigations were carried out with a Leitz-Ortholux II Pol-BK microscope equipped with a modified Mettler FP 80/82 hot stage which can be cooled with liquid nitrogen down to $-60\,^{\circ}C$. All points of the phase transitions were determined by heating the samples (heating rate: $1\,^{\circ}C/min$) and each solution was prepared using deionized water which had been fed through a Milli-Q ion-exchange system and were homogenized in isotropic solution.

For the contact preparations [5] surfactant mixtures of different molar fractions ($0 < \alpha < 1$, where α denotes the relative molar fraction of the Y-surfactant in the surfactant mixture) were prepared using an analytical balance. By penetration of water into the surfactant mixture, a concentration gradient is established from pure water to pure surfactant mixture (0–100 wt%). By heating the samples the phase transitions can be observed. Solid phases, hexagonal H_1, and lamellar L_α phases are birefringent and can be identified by their typical fan-shaped (H_1) and focal conic, mosaic, oily streak (L_α) textures between crossed polarizers. The cubic I_1' and I_1'' phases are optically isotropic. They can be determined by their high viscosity and the phase boundary lines to the isotropic L_1 phase and between the two different cubic I_1 phases without polarizers.

To determine the phase diagram of the surfactant mixture with $\alpha = 0.49$ and water, defined ternary mixtures were prepared using an analytical balance.

Results and discussion

LC phase behavior of the ternary system $C_{14}G(E_4M)_2/(C_7)_2GE_8M/$ water as a function of the mixing ratio

The ternary mixtures were examined by contact preparation from $\alpha = 0.1$ to 0.9, where α denotes the relative molar fraction of the Y-surfactant in the surfactant mixture. Basic for the discussion of the ternary systems are the phase diagrams of the binary systems which are presented in Fig. 1a and 1c. The LC phase behavior of the Y- and the V-surfactant in water correspond to the packing model of Israelachvili. According to Eq. (1), the large area of the branched headgroup (**A**) and the long lipophilic chain (l_c) of the Y-surfactant lead to a low packing parameter (F). A low F is equivalent to a large interfacial curvature of the micelles (**r**) so that the formation of spherical micelles and – at higher concentrations – of cubic I_1 respectively hexagonal H_1 phases is preferred, as one can see in Fig. 1a. Comparing the Y-surfactant with the V-surfactant, it becomes evident that the **A** of the V-surfactant is smaller and the l_c is shorter which results in a quantitatively higher **F** and therefore in a lower r. For V-surfactant, cylindrical or disc-like micelles are predicted which prefer to form at

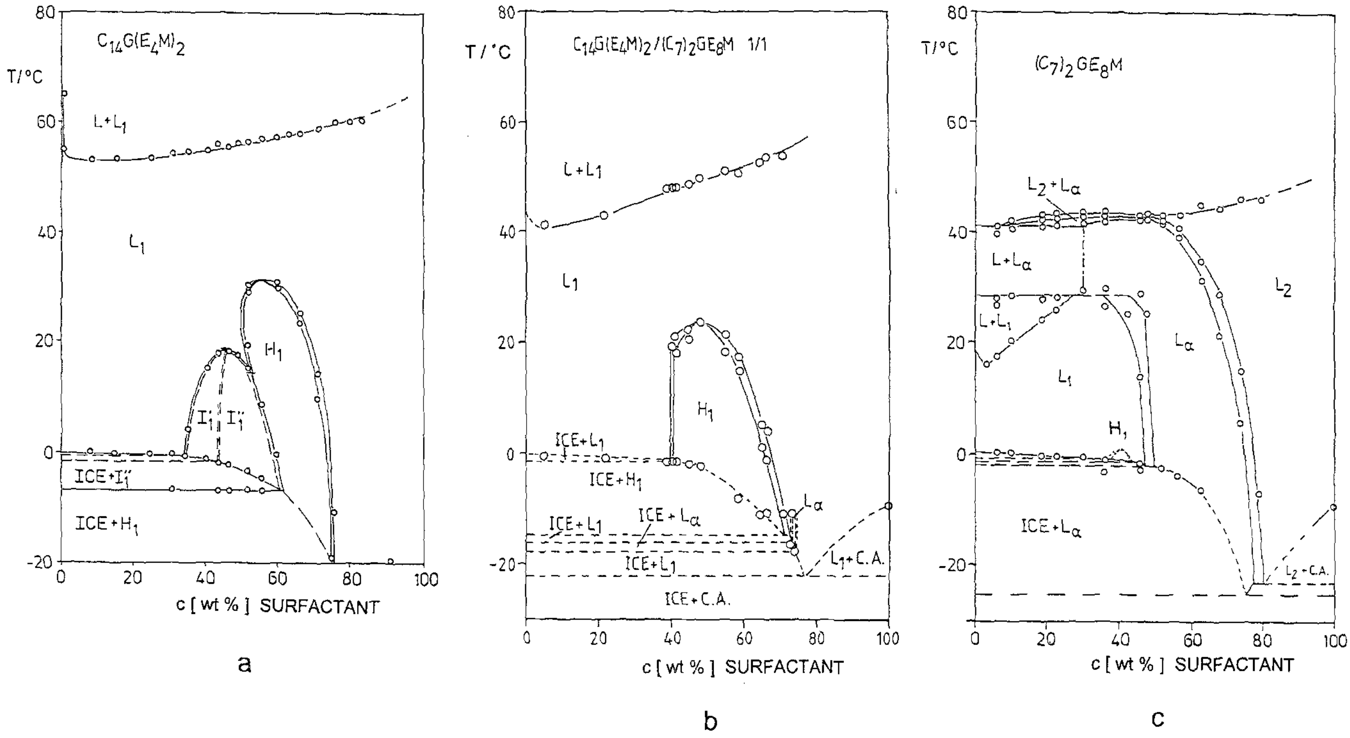


Fig. 1 Phase diagrams of a) Y-surfactant and water, b) surfactant mixture with $\alpha = 0.49$ and water, c) V-surfactant and water, L, L_1 and L_2 denote isotropic solutions, I_1, H_1 and L_α denote the LC phases and C.A. is the crystalline surfactant

higher surfactant concentrations a lamellar L_α phase, as presented in Fig. 1c.

In the following, we will discuss the LC-phase behavior of the ternary system $C_{14}G(E_4M)_2/(C_7)_2GE_8M$/water as a function of the mixing ratio. The observed maximal transition temperatures (T_{max}) of the LC phases I'_1, I''_1, H_1 and L_α and the lower critical consolute temperatures (T_c) are summarized in Table 1 and are shown in Fig. 2 as a function of α. The discussion of the LC phase behavior of this ternary system is also based on the packing model. In the present surfactant mixture, one has the interaction of a surfactant which tends to form spherical micelles – $C_{14}G(E_4M)_2$/water with a low F and a high r – with a surfactant which tends to form cylindrical or disc-like micelles – $(C_7)_2GE_8M$/water with a much higher **F** and a lower **r**. We expected a decrease of the F_{mix} value and an increase of the r_{mix} value by adding Y-surfactant to the V-surfactant/water system. In this case, one should observe a change in the dominant phase structure from lamellar for the V-surfactant-rich mixtures over hexagonal to cubic for the Y-surfactant-rich mixtures.

Table 1 Maximal transition temperatures of the LC-phases (T_{max}) and lower critical consolute temperatures (T_c) as a function of α; α is the relative molar function of the Y-surfactant in the surfactant mixture. Temperatures in °C ± 0.4 °C.

α	T_{max} I'_1	I''_1	H_1	L_α	T_c
0.00 V-surfactant			0.8	44.4	16.5
0.10			10.6	48.1	27.6
0.19			14.8	47.7	31.7
0.30			18.0	37.8	35.5
0.39			21.4	20.2	39.0
0.49			24.1	– 10.7	42.3
0.59	4.0		26.6		45.1
0.68	7.9	2.6	28.3		47.0
0.80	12.2	9.2	29.5		50.0
0.90	16.0	14.0	30.3		51.8
1.00 Y-surfactant	19.0	17.6	31.6		53.4

Cubic I'_1, I''_1 and hexagonal H_1 phases

From a relative molar Y-surfactant fraction of $\alpha \approx 0.6$ and $\alpha \approx 0.7$ up to $\alpha = 1$ the cubic LC phases I'_1 and I''_1 respectively are formed. In contrast to the I_1 phases, the H_1 phase is stable over the whole concentration range ($0 \leq \alpha \leq 1$). With increasing α, the T_{max} values of the I_1 and H_1 phases as well as the concentration ranges in which the

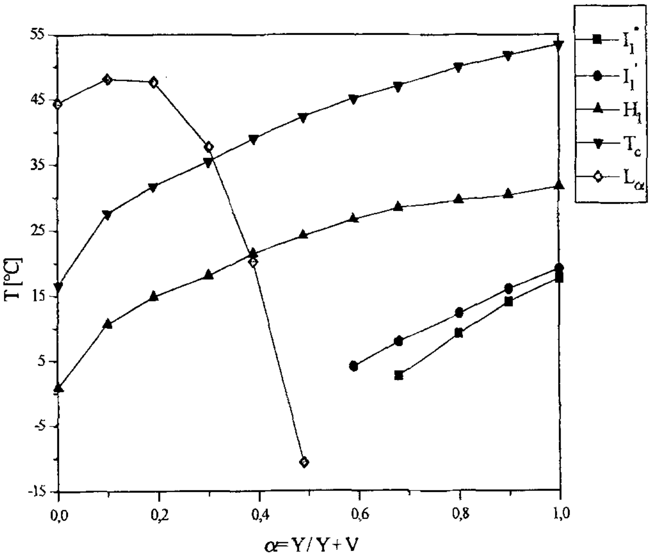


Fig. 2 Maximal transition temperatures of the LC-phases (T_{max}) and lower critical consolute temperatures (T_c) as a function of the relative molar fraction of the Y-surfactant in the surfactant mixture (α). The size of the symbols contains the error of ± 0.4 °C

LC phases are stable, increase. This means that the stability of these phases increases with increasing amount of Y-surfactant. It must be noted that the contact preparation gives only an initial insight into the establishment of LC phases–qualitative considerations of concentration ranges are not possible. As expected, the observed development of the LC phases indicates that the packing parameter of the mixture (F_{mix}) decreases and the curvature of the micelles (r_{mix}) increases with increasing α. These observations are understandable as an increase of the Y-surfactant concentration results in i) an increase of the **average** lipophilic chain length ($\bar{l}_c$) and ii) an increase of the **average** area of the headgroup ($\bar{A}$).

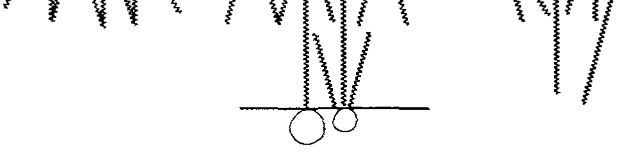
Lamellar L_α phase

In the concentration range $0 \leq \alpha < 0.5$ the lamellar L_α phase is stable. In accordance with the geometrical packing model we observed a destabilization of the L_α phase with increasing α, i.e., the L_α phase range decreases as α increases. At this point, it is interesting to note that the maximal transition temperatures (T_{max}) of the L_α phase show a remarkable course which is not comparable with the observed courses of the I_1 and H_1 phases. Taking the V-surfactant ($\alpha = 0$) as the starting point, at first the T_{max} values increase gradually before falling off steeply. In the range $0 \leq \alpha < 0.2$, the increasing concentration of Y-surfactant causes a thermal stabilization of the L_α phase; the T_{max} values reach a maximum. Further increase of the relative molar fraction of the Y-surfactant ($\alpha > 0.2$) leads to a decrease of the T_{max} values of the L_α-phase. Finally, for $\alpha > 0.5$ the L_α phase is no longer formed. In the following, the thermal stabilization of the L_α phase with increasing Y-surfactant concentration up to $\alpha \approx 0.2$ will be discussed on the basis of two different arguments (see Figs. 3 and 4).

Considering packing effects, the thermal stabilization of the L_α phase with increasing amount of Y-surfactant up to $\alpha \approx 0.2$ can be understood as a formation of ideal plane interfaces of the L_α bilayers. For the formation of bilayers with a zero interfacial curvature, the cross-sections of the lipophilic and hydrophilic surfactant moieties have to be similar. As the headgroup is dehydrated and therefore reduced with increasing temperature the cross-section ratio of the lipophilic and hydrophilic moieties changes. The bilayer interface assumes a slightly concave curvature resulting in the melt of the L_α phase. By adding a small amount of Y-surfactant to the V-surfactant/water system ($\alpha \leq 0.2$) we observed a thermal stabilization of the L_α phase. The difference in the size of the hydrophilic headgroup is one possible explanation for this phenomena. As the headgroup area of the Y-surfactant is larger than that of the V-surfactant, the plane interface of the bilayers can be maintained in spite of an increase in temperature. With further increase of the Y-surfactant amount ($\alpha > 0.2$) the L_α bilayers finally assume a convex interfacial curvature and the formation of cylindrical respectively spherical micelles becomes possible. As a consequence, the stability of the lamellar phase decreases and ultimately for $\alpha = 0.5$, the L_α phase disappears. One possible organisation of the surfactant molecules is presented in Fig. 3.

Another possible reason, however, for the thermal stability of the L_α phase with increasing $\alpha (0 \leq \alpha < 0.2)$ could be the structure of the bilayers. Due to the different lengths of the lipophilic and hydrophilic parts of the two surfactant molecules, one could assume that the molecules interlock, as presented in Fig. 4. Due to the bilayer structure, the movement of **mono**layers in relation to one another (induced by the increase in temperature) is delayed.

Fig. 3 Hypothetical organization of the surfactant molecules to disk-like micelles in the range from $\alpha = 0$ to $\alpha \approx 0.2$; the concentration of the Y-surfactant increases from left to right



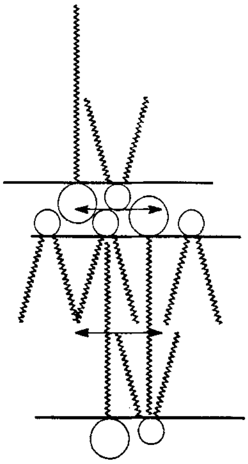


Fig. 4 Hypothetical organization of the surfactant molecules to a L_α-bilayer in the range from $\alpha \approx 0.1$–0.2. The arrows symbolize the directions in which the **mono**layers could move against one another

Therefore, the thermal stability of the L_α phase increases in this concentration range.

This offered account is given as a basis for further discussion and should not be considered as a definitive explanation of the thermal stabilization of the L_α phase.

In addition, the lower critical consolute temperatures (T_c) should be briefly discussed (see Fig. 2). The T_c values continuously increase with increasing amount of Y-surfactant. At the same time the stability of the isotropic micellar solution (L_1) also increases. The increase of the micellar interfacial curvature with increasing α which efficiently screens the lipophilic micellar core from the interactions with water is offered as a possible explanation.

LC-phase behavior of the ternary system $C_{14}G(E_4M)_2$ $(C_7)_2GE_8M$/water for $\alpha = 0.49$

In the following, we will present the quasi binary phase diagram of the surfactant mixture of $\alpha = 0.49$ and water. The phase diagram was determined by polarizing microscopy-additional information was obtained by DSC-measurements (eutectic point). The phase diagram is shown in Fig. 1b. It should be noted that the quasi binary phase diagram presented here is a cut through a ternary phase diagram. To simplify matters, we will discuss it as a binary one.

Above the liquidus line the surfactant mixture is soluble in water over the whole concentration range, forming the isotropic micellar solution L_1. In the concentration range from approximately 40 to 70 wt% a H_1 phase with the typical fan-shaped texture is formed-the maximal transition temperature (T_{max}) of this phase is 24 °C. At higher concentrations, a L_α phase appears in a very small concentration range with an approximate T_{max} value of -11 °C. The isotropic solution L_1 is stable over the whole concentration range between the liquidus line, the mesophases, and the miscibility gap ($L + L_1$). The T_c of the miscibility gap appears at 42.3 °C. Below the liquidus line, at concentrations below the eutectic point, ice coexists with the isotropic solution (L_1) or the mesophases (H_1 and L_α). At higher concentrations, the two-phase region consists of L_1 and crystallized surfactant (C.A.). Finally, ice and C.A. coexist at temperatures below the eutectic temperature.

The discussion of the quasi binary phase diagram corresponds to the discussion of Fig. 2. This phase diagram demonstrates quite obviously the dependence of the packing parameter of the mixture (F_{mix}) on the mixing ratio. As a consequence of Fig. 2, for the equimolar mixture of the Y- and V-surfactant, a dominant H_1 phase was expected and indeed observed. Compared to the Y-surfactant, no cubic phase is present and in contrast to the V-surfactant the concentration range of the L_α phase is very small. This indicates that the F_{mix} value of this mixture lies between the packing parameters of the pure surfactants so that the mixture tends to form cylindrical mixed micelles. The dominance of the H_1 phase points out that the organization of the two differently structured molecules is nearly optimized in view of cylindrical micelles. One could even assume that there exists a mixture between $0.49 < \alpha < 0.59$ which forms **only** a H_1 phase. In summary, it may be said that one can construct certain phase diagrams with surfactant mixtures.

Conclusion

In the present paper we discussed the influence of the molecular geometry of surfactants on the self-organization to micelles and LC phases in water when two differently structured surfactants are mixed. The packing model of Israelachvili was transferred to mixed micelles and a packing parameter of the mixture (F_{mix}), which depends on the mixing ratio, was defined. Due to the observed I_1 and H_1 phase development in dependence on α, we concluded that the F_{mix} value decreases with increasing amount of Y-surfactant. On the other hand, the development of the L_α phase could still not be explained. In view of further measurements and discussions we suggested two possibilities which could perhaps explain these observations.

In summary, one may say that the molecular geometry, which essentially determines the LC-phase behavior, can be continuously varied by mixing two differently structured surfactants. One could assume that the "average" molecular geometry of the mixture lies between the pure surfactants and is therefore not symmetrical. First measurements of asymmetrical V-surfactants with two different alkyl chains indicate that their LC phase behavior in water is comparable to the LC phase behavior of the mixtures. This would underline the assumption of an "average asymmetrical" molecular geometry of the mixtures.

In a forthcoming paper we will present the investigations of asymmetrical V-surfactants in water, which will be helpful in reaching a better understanding of the influence of the molecular geometry on the shape of the micelles and the structure of the LC phases.

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