

LETTERS

A Novel L₃-Phase from a Ca-Salt of an Anionic Surfactant and a Cosurfactant

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An L₃-phase is observed for the first time in a ternary phase diagram of a Ca-salt of an α -sulfonated alkyl fatty acid methyl ester, the cosurfactant (2-ethylhexyl)monoglyceride and water. As for other ternary surfactant/cosurfactant systems, the L₃-phase occurs with increasing cosurfactant/surfactant ratios after the L _{α} -phase. Some properties of the newly observed L₃-phases are the same as for other known L₃-phases. It is a low viscosity, optically isotropic fluid with a low flow birefringence. The time constants τ of the electric birefringence results scale with $\tau \sim \Phi^{-3}$. Its conductivity is very much higher than that of the neighboring L _{α} -phase, but there are some marked differences from known L₃-phases. This novel L₃-phase is thermodynamically stable despite ionic structure of the surfactant. We found no two phase region between the L _{α} and the L₃-phase, and the L₃-phase is stable over a wide cosurfactant/surfactant ratio between one and two. In SANS measurements it shows a broad correlation peak that occurs at about the same position as the sharper peak in the L _{α} -phase. The structure of the L₃-phase is demonstrated by FF-TEM micrographs.

The L₃-phase or so-called sponge phase is, based on its unusual properties, the most fascinating lyotropic mesophase. Compared with the long history of research in surfactant science, the L₃-phase has only recently been discovered to be a distinct phase.¹ This is due to the fact that, without detailed investigation, it can easily be mistaken for an L₁-phase. Since its discovery in 1980 by J. Lang and R. Morgan in the system C₁₀E₄/water,²⁴ it has been found in many other systems. It is general knowledge now that L₃-phases are encountered when dilute L _{α} -phases are made more lipophilic by changing a physicochemical parameter of the surfactant system. This is most easily done by increasing the cosurfactant/surfactant ratio in nonionic surfactant systems, by increasing the temperature in alkylpolyglycol systems or by increasing the salt concentration in mixed surfactant systems where one compound is an ionic surfactant.²⁻⁴

These common procedures for the preparation of L₃-phases do not always work. There are many known situations whereon

the L₃-phase is not observed when a dilute L _{α} -phase is made more lipophilic.⁵ While L₃-phases are generally observed in phase diagrams with zwitterionic surfactant and intermediate chain alcohols, the L₃-phase does not occur when the hydrocarbon cosurfactants are replaced by perfluorocosurfactants.⁶ L₃-phases are also not observed in zwitterionic surfactants, with longer chain cosurfactants, even though the L _{α} -phases are observed in these mixtures. These unexpected differences in the behavior of surfactants with cosurfactants are explained by the size of the normal bending and Gaussian bending constant of the bilayers.

L₃-phases can also be formed from block copolymers such as the Poloxamers.⁷ L₃-phases are low viscosity, slightly turbid, isotropic phases that usually show some flow birefringence at low concentrations of surfactant.

Even though at the beginning of its discovery there has been a controversy about the structure of the L₃-phase, its structure is now well-known. It has been determined by indirect methods such as small angle neutron scattering, and also by direct

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observation with FF-TEM micrographs. In early publications it had been suggested that the phase consisted of freely rotating disklike micelles in random orientation at the overlap concentration. While this model is certainly wrong, it still can be of use to estimate macroscopic properties such as the translational and rotational diffusion constants of the surfactant aggregate and the viscosity.⁸

Now it is well-known that the surfactant and cosurfactant in an L_3 -phase are present as a continuous network.⁹ The first experimental study proposing such a structure was done in Montpellier by Port et al.,²⁵ independently of a theoretical proposition by Cates et al.²⁶ The phase can therefore be considered as a molten L_α -phase, in which the aqueous part and the surfactant part are continuous in nature, and is therefore a bicontinuous phase. Despite this bicontinuous character, it has a low viscosity with a value in the range of several times the value of the water viscosity. What is even more surprising is the fact that the viscosity of the L_3 -phase has an extremely low concentration dependence.

In ternary phase diagrams, the L_3 -phase can usually be observed over a large concentration range or volume fraction, but only over an extremely narrow cosurfactant/surfactant ratio.^{10,11} On one side of the existence region is a narrow two-phase L_α/L_3 -phase region, while on the other side is a two-phase L_1/L_3 region. The existence of the phase is extremely sensitive to ionic charges. Usually it becomes unstable when in neutral cosurfactant/surfactant systems a few percent of the nonionic surfactant is replaced by an ionic surfactant. The phase also is shear sensitive, and high shear can transform the L_3 -phase into a metastable L_α -phase that relaxes back into the L_3 -phase when the shear is stopped.^{12–14} Many properties of the L_3 -phase can be described by power laws with specific exponents. These exponents can now be well described by a theoretical model.¹⁵ On the theoretical side it is now well-known that the sign and the size of the Gaussian bending constant plays a crucial role for the understanding of the L_3 -phase. It is a phase of bilayer membranes with a mean curvature of zero and a positive Gaussian module.¹⁶ According to Porte the transition from lamellar to L_3 occurs when the Gaussian bending modulus changes from negative to positive.²⁷ While these features are generally accepted, there are still some controversial details about some theoretical models.^{17,18,28}

Now we will describe a novel L_3 -phase for which some of properties agree with those of the well-known L_3 -phases, while others disagree completely. We have observed this novel phase while studying the ternary phase diagram of the Ca-salt of alkyl fatty acid methyl ester sulfonates plus the cosurfactant (2-ethylhexyl)monoglyceride. In this Letter we present the phases and the properties of some of the phases that are observed when a 50 mM solution of the Ca-salt is mixed with increasing amounts of the cosurfactant.

Results

In Figure 1 we show the section of the phase diagrams of the ternary system when for a 50 mM solution of the Ca-salt the cosurfactant concentration is increased. We also report the conductivities of the various phases when they were stirred. For this reason, only one conductivity value is given for two phase regions. The system shows the normal and expected behavior up to the $L_{\alpha h}$ -phase, which is a birefringent phase of low viscosity with the typical birefringence pattern of random domains.

With increasing cosurfactant concentration we observe the sequence L_1 , L_1/L_α , $L_{\alpha l}$, and $L_{\alpha h}$. At the end of the L_α -phase

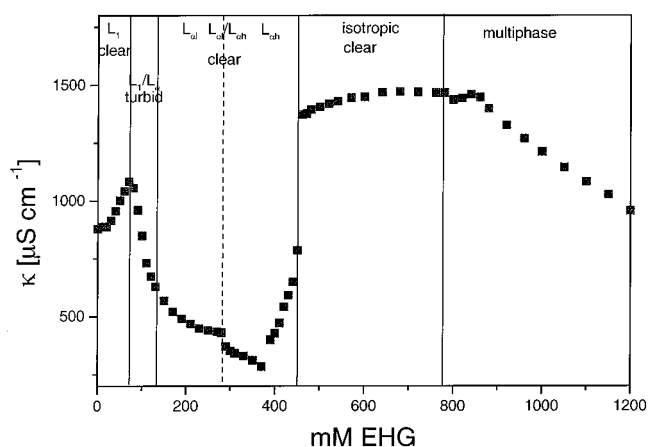


Figure 1. Plots of the electric conductivity κ against the EHG concentration for a constant surfactant concentration of 50 mM $\text{Ca}(\text{C}_{14}\text{-}\alpha\text{MES})_2$ at 25 °C. The sequence of different mesophases is shown schematically in the diagram.

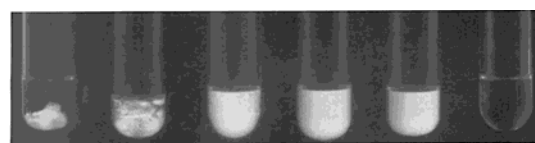


Figure 2. Samples of a solution of 50 mM $\text{Ca}(\text{C}_{14}\text{-}\alpha\text{MES})_2$ and EHG in water between crossed polarizers.

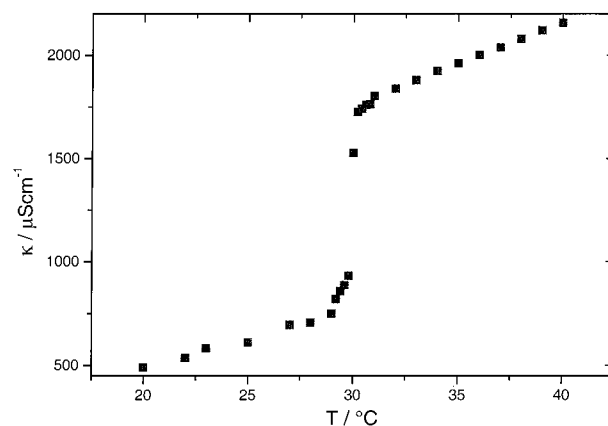


Figure 3. Plots of the conductivity κ versus the temperature for a 50 mM $\text{Ca}(\text{C}_{14}\text{-}\alpha\text{MES})_2$ solution and 440 mM EHG.

the conductivity increases and the birefringent L_α -phase is replaced by an isotropic, highly conductive phase that exists over a wide cosurfactant/surfactant region. We could not observe a two-phase region between the L_α and the isotropic phase, when we prepared samples with small variation in their composition around this transition and left the samples for long times under temperature controlled condition and without stirring.

In Figure 2 we show samples in 10 mm test tubes between crossed pols. All samples around the phase boundary were either completely birefringent or completely isotropic. The transition can also be observed at constant composition but varying temperature. We changed the temperature for one sample by small steps of 0.2 deg and waited to reach equilibrium. Again we only observed a birefringent phase or an isotropic phase and the conductivities varied continuously from the low value of the L_α -phase to the high value of the isotropic phase. The results are shown in Figure 3.

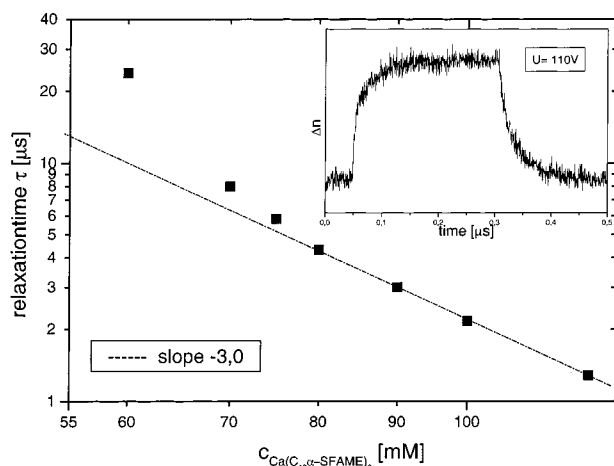


Figure 4. Relaxation time τ_R versus the concentration of $\text{Ca}(\text{C}_{18}\text{-}\alpha\text{MES})_2$ for the L_3 -phase; double logarithmic plot.

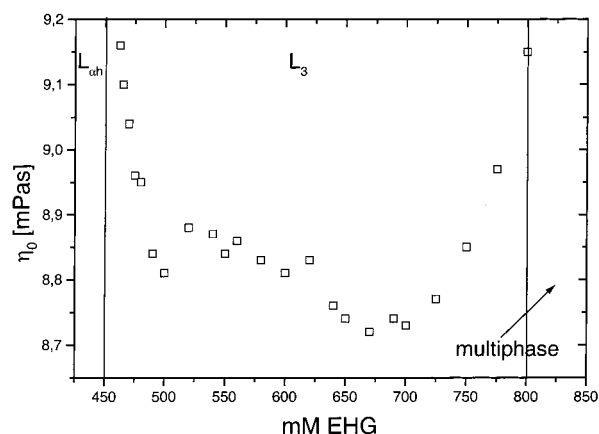


Figure 5. Zero-shear viscosity η_0 against EHG concentration in the L_3 -phase. The $\text{Ca}(\text{C}_{14}\text{-}\alpha\text{MES})_2$ concentration was 50 mM.

These results suggest that the observed transition in the studied systems is a second-order phase transition. This is in sharp contrast to previously studied L_α/L_3 phase transitions, which were always found to be first order and consequently had a two-phase region between the separate single phase region L_α and L_3 . From the results shown so far it is not clear that the newly found phase is indeed an L_3 -phase. Furthermore it is surprising that the new phase has such a wide cosurfactant/surfactant region over which it is stable. In view of results on previously studied systems, it is furthermore surprising that an L_3 -phase exists in this phase diagram at all, because the present micellar structure must be charged and there is no excess salt to shield the charge density. The absolute conductivities in the L_1 -phase indicate that the dissociation degree of the Ca^{2+} ions from the surfactants in the L_1 -phase is about 5% and that the charge density increases in the novel phase to about 10%. This increase is probably due to the decrease of the charge density of the surfactant aggregates by the incorporation of the cosurfactant into the surfactant assemblies.

In this context, it is noteworthy to mention that we tried to find the novel phase with other cosurfactants. We established the same cut as shown in Figure 1 with the cosurfactant hexanol. Surprisingly, the phase diagram up to the L_α -phase was very much the same as in Figure 1 but the single phase after the L_α -phase was not observed. Instead, we observed multiphase regions, the nature of which we have not determined so far.

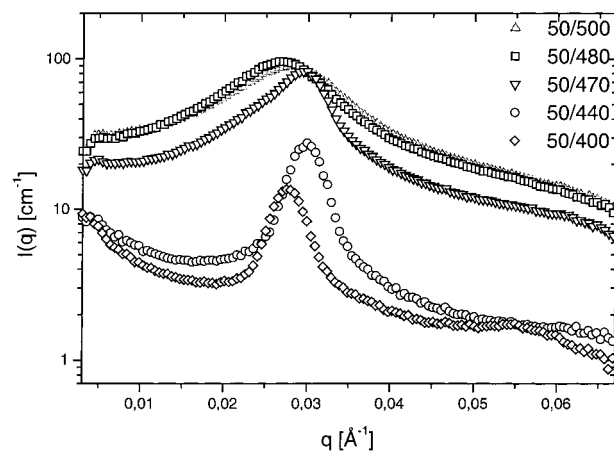


Figure 6. Radially averaged SANS scattering intensity I as a function of the scattering vector q . The composition of the samples is given in the inset, where the first number is the concentration of $\text{Ca}(\text{C}_{14}\text{-}\alpha\text{MES})_2$ in mM and the second the concentration of EHG in mM.

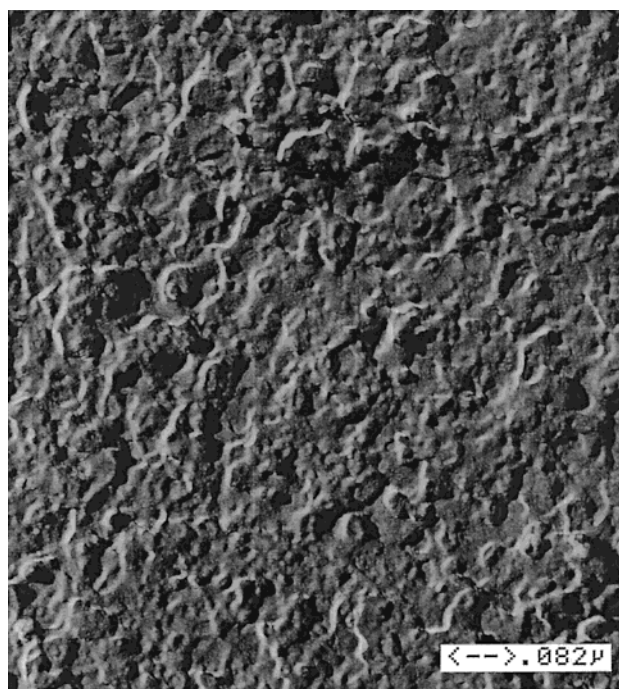


Figure 7. FF-TEM micrograph of the systems 50 mM $\text{Ca}(\text{C}_{14}\text{-}\alpha\text{MES})_2$ and 600 mM.

Properties of the Novel Phase

One of the characteristic features of the L_3 -phases is the unique power dependence of some of their properties. In Figure 4 we show the electric birefringence signal of a phase and the concentration dependence of the rotation time that was determined from these signals. Both the absolute values of the time constant and their concentration dependences are the same as for previously studied L_3 -phases. In particular we find the $\tau \sim \phi^{-3}$ dependence, which can be explained on the basis of a theoretical model.¹⁹

In Figure 5 the viscosities of the L_3 -phases are shown as a function of the composition of the phases. The viscosities are remarkably constant over the whole composition region, but exact measurements show subtle but characteristic variations. This result is again very surprising. It means that while the novel observed phase is indeed an L_3 -phase, its dynamic behavior remains about constant even when the cosurfactant/surfactant

ratio is varied by a factor of 2. Normally, one would expect the flexibility and bending constant of the phase to decrease with increasing cosurfactant/surfactant ratio. It is conceivable that this effect is counterbalanced by the increased degree of dissociation of the phase, which should lead to a stiffening of the bilayers.

In Figure 6 some SANS data are shown for some L_α and novel phases. For the L_α -phase we see the typical correlation peak that represents the interlamellar distance and an indication of a shoulder at double the scattering vector of the main correlation peak. The novel phase shows a much broader peak, which occurs, in contrast to results on normal L_3 -phases, at the same position as for the L_α -phase. Normally, the L_3 -peak is expected to shift by about $1/3$ to a lower q -value.

Finally, in Figure 7 we show a FF-TEM micrograph of the novel phase. The micrograph is more fuzzy than the micrographs that have been obtained on other L_3 -phases.^{20–22} However, it still shows the typical features of L_3 -phases. In particular, the spacings that can be evaluated from the micrograph are in the same range as the spacings expected for L_3 -phases of this concentration.²³ The dimensions for the spacing are also consistent with the dimensions that can be extracted from the SANS data. We are thus confident that the newly found phase is indeed an L_3 -phase, even though some of its properties are somewhat different from the L_3 -phases that have been found earlier.

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