

LETTERS

Classic L_α Phases as Opposed to Vesicle Phases in Cationic–Anionic Surfactant Mixtures

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It is now generally believed that stable vesicles form spontaneously in cationic–anionic surfactant mixtures. We show in this investigation that the vesicles that are observed in such mixtures may be the result of shearing forces that occur during mixing of the two components. When the two components are mixed but shear is avoided during the process the result is a classic L_α phase. The L_α phase can then be transformed into vesicles by the shearing forces that occur when samples with the L_α phase are turned upside down a few times. The stacked L_α phase is prepared by solubilization of methyl laurate in tetradecyltrimethylammonium laurate and the subsequent hydrolysis of the ester by the tetradecyltrimethylammonium hydroxide. When the sample is prepared in this way, the shear during the solubilization process can have no effect on the final structures because the hydrolysis occurs much slower than the mixing process (within a few hours). On the other hand, when the final products are produced by mixing tetradecyltrimethylammonium hydroxide and lauric acid or tetradecyltrimethylammonium bromide and sodium laurate, vesicle phases are obtained. The different structures in the mesophases can easily be distinguished on the basis of their different appearance between crossed polarizers. The vesicle phases are practically isotropic and show little birefringence while the stacked bilayer phases show the typical domainlike “Schlieren” texture. The different structures have also been demonstrated by FF-TEM micrographs. It is furthermore shown that the vesicle phases that are produced by the combination of the cationic and anionic surfactants have different macroscopic properties from the systems that were prepared from the acid and the cationic hydroxide. In the latter situation, the vesicle phases contain no excess salt and the ionic charges on the vesicles are not shielded. As a consequence, the vesicular solutions are strongly viscoelastic and have a yield stress.

Introduction

The main purpose of this investigation is to demonstrate that vesicles in aqueous cationic–anionic surfactant mixtures¹ do not form spontaneously, but may be produced by shear forces that are due to the mixing of the components.

Most of the work on vesicles has been carried out on phospholipid vesicles.² Vesicles from phospholipids do not form spontaneously, but have to be prepared by various techniques such as sonication or extrusion of phospholipid dispersions.^{3,4}

It is well known now that vesicles are also found in single-chain surfactant systems.⁵ Vesicles can be produced in mixtures of cationic and anionic surfactants, in mixtures of surfactant and cosurfactants, and very recently in mixtures of alkyldimethylaminoxid and calciumdodecyl sulfate.^{1,6,7} It is generally assumed that the vesicles in these systems do form spontaneously when the right mixing ratios are established and the vesicles are thermodynamically stable species. The experimental results for many systems have also been supported by theoretical models.^{8,9} However there are still recent publications where the existence of vesicles as thermodynamic stable species is doubted and where it is assumed that given enough time the vesicles

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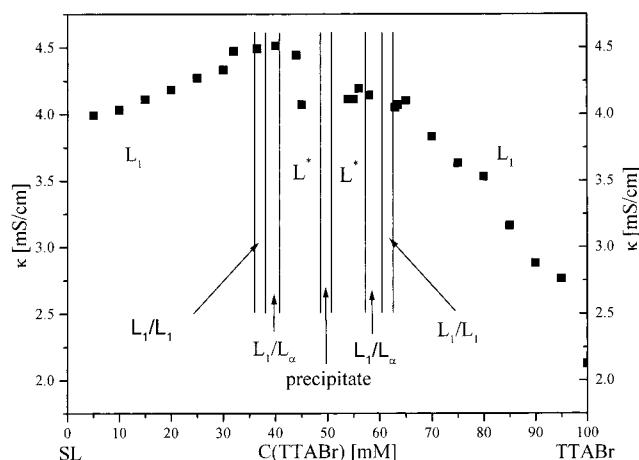


Figure 1. Phase behavior of mixtures of 100 mM TTABr and 100 mM SL at different mixing ratios.

will transform or condense into an L_α phase.¹⁰ In recent years there also has been a considerable amount of work on vesicle systems in shear flow. It is now well known that the size distribution of vesicles can be altered by the strength of the shear rate.^{11–13}

Actually, large multilamellar vesicles can be transformed to small unilamellar vesicles under high shear.¹⁴ It also has been shown that L_α phases can be transformed to vesicle phases and the thus produced vesicles do not relax to L_α phases when the shear is stopped. One simple method to produce vesicles is by mixing an L_3 phase with an ionic surfactant.¹⁵ In practically all systems where vesicles were observed, the systems were prepared by mixing two surfactant solutions. This means that shear was involved. It is therefore conceivable that the vesicles were not produced by the thermodynamic conditions in the system but by the shear that was due to the mixing. Recently it actually was shown that a normal L_α phase is obtained when the bilayers of the L_3 phase are ionically charged by a chemical reaction and not by mixing.¹⁵ For this reason we were looking for a way to produce cationic–anionic mixtures without shear. We hoped to be able to do this by producing one component for the cationic–anionic combination by a chemical reaction in a solution which is at rest and does not flow. The idea was to mix two low viscosity L_1 phases. The mixing time in such a situation can be kept very much shorter than the reaction time. For our goal we used the cationic surfactant tetradecyltrimethylammonium hydroxide and the methyl ester of lauric acid. As is shown in this investigation there are some problems with this strategy. The problems could however be solved, and it is finally shown that L_α phases are indeed obtained when the two components are mixed without shear.

Results and Discussion

We have prepared catanionic mesophases for the system tetradecyltrimethylammonium laurate by three different routes. In the first route we mixed tetradecyltrimethylammonium bromide (TTABr) and sodium laurate (SL).¹⁶ The total surfactant concentration was 100 mM, and the mole fraction varied from 0 to 1 for each component. On the second route we mixed tetradecyltrimethylammonium hydroxide with lauric acid.¹⁷

On the third route we prepared the vesicle phase with exactly the same composition as in the second route but in a different way. We solubilized methyl laurate in TTAL and hydrolyzed the ester by adding an equimolar amount of TTAOH. The hydrolysis takes several hours to reach completion. During this

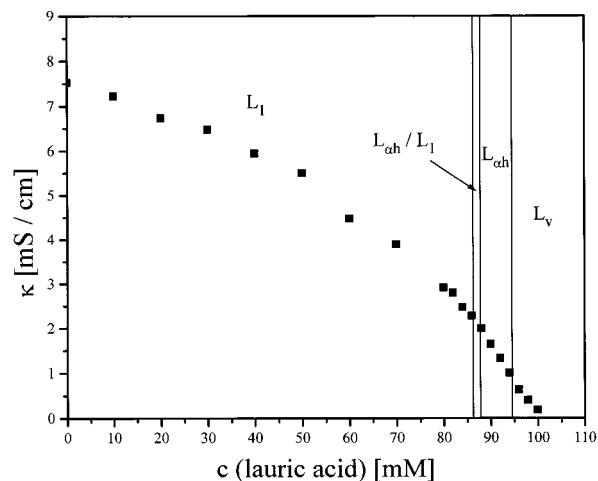


Figure 2. Phase behavior of 100 mM solution of TTAOH with increasing amounts of lauric acid.

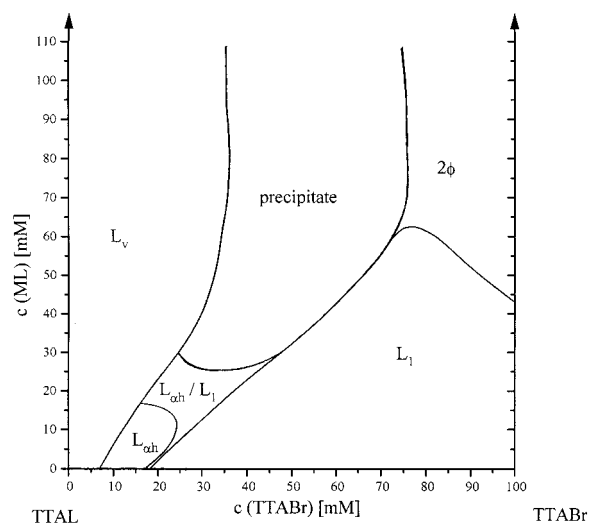


Figure 3. Cut through the quaternary phase diagram of TTAL/TTABr/ML at a total surfactant concentration $c(\text{TTAL}) + c(\text{TTABr}) = 100$ mM.

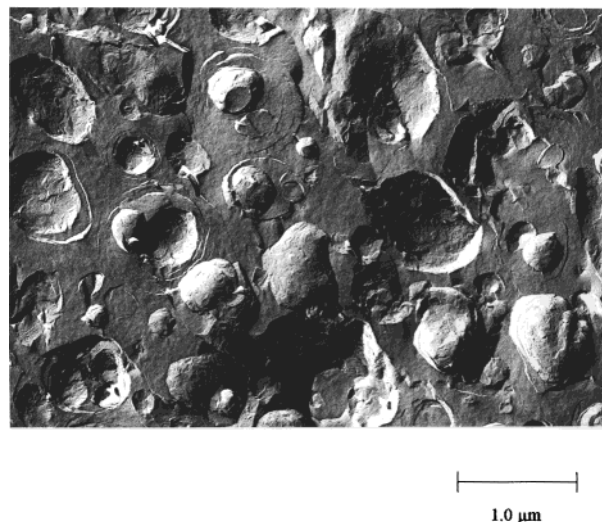


Figure 4. FF-TEM micrograph of the L^* phase at a concentration of 55 mM TTAB and 45 mM SL in 20% glycerol.

time the sample was not stirred and therefore the various micellar structures were not exposed to shear. On mixing, the sample becomes turbid, then transparent isotropic and finally after 2 h birefringent, with a typical texture of an L_α phase.

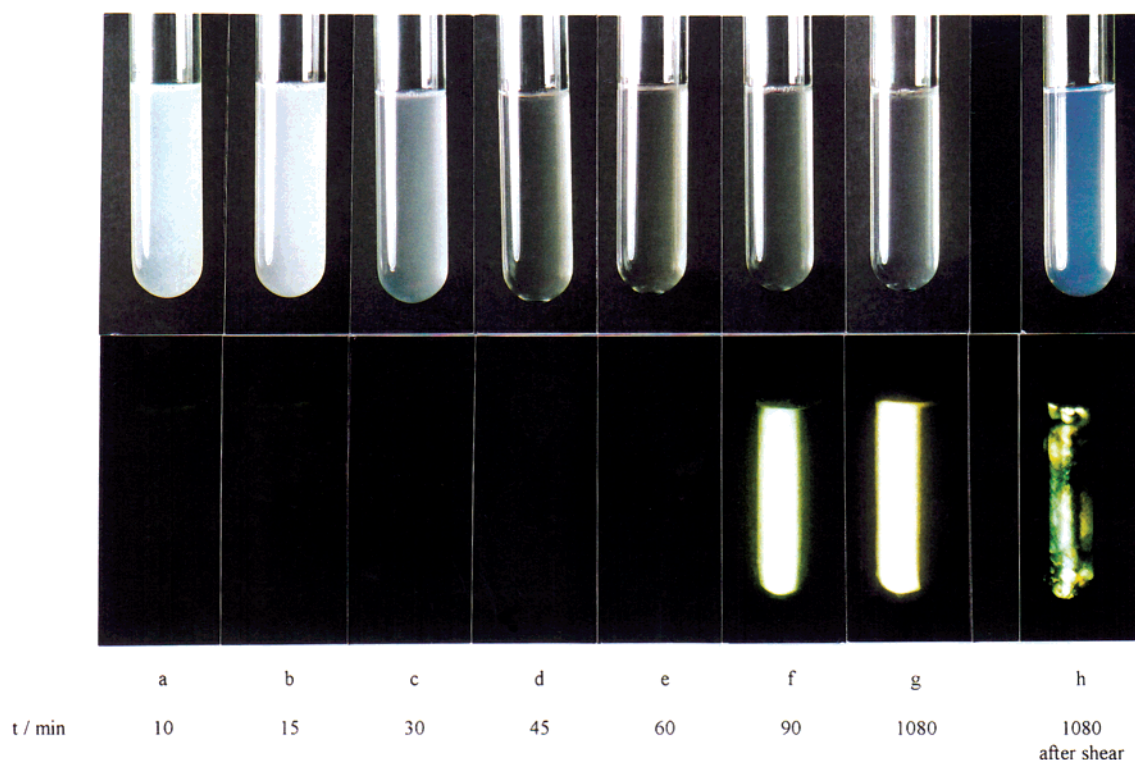


Figure 5. Phase transitions in a solution of 25 mM TTAL, 75 mM TTAOH, and 73 mM ML with time. Observation with (bottom row) and without (top row) crossed polarizers.

This low viscosity L_α phase can instantaneously be transformed into a highly viscoelastic phase with multilamellar vesicles. Our results thus demonstrate that the vesicles in this catanionic surfactant system do not form spontaneously but are a result of shear.

At first we would like to show some cuts through ternary phase diagrams that are relevant for our purpose. In Figure 1 we show the sequence of phases that occur when 100 mM solution of TTABr was mixed with 100 mM solution of sodium laurate. With increasing SL we observe an L_1 phase, a two-phase region L_1/L_α where the birefringent L_α phase is on the top of the sample. After the two-phase region we find a low viscosity, somewhat turbid phase (L^*), and finally at $X_2 \sim 0.5$ a precipitate is formed. On further increasing the SL concentration the sequence of the phases is reversed. The sequence in our system is the same as already observed for many cationic–anionic combinations of surfactants.^{17,18} The L^* phase contains vesicles as is demonstrated in Figure 4 in an FF-TEM micrograph. The formation of vesicles in such catanionic phase diagrams is usually taken as evidence that vesicles form spontaneously and that they are thermodynamically stable structures. We have to keep in mind, however, that the two components were mixed together and therefore the micellar structures were exposed to shear. Usually the history of the preparation of the vesicle phases has not been paid much attention.

In Figure 2 the different phases are shown when 100 mM solution of TTAOH is titrated with lauric acid up to the point of neutrality. The phase diagram is simple. We find an L_1 phase, a two-phase region L_1/L_α in which the birefringent L_α phase is on the top of a highly viscous L_1 phase, and finally a more or less transparent viscoelastic phase with the typical feature of a multilamellar vesicle phase. In comparison to the situation where we had mixed TTABr and SL, the phase diagram is simpler. There is no precipitation at the equimolar concentration and the phase boundaries of the two-phase region is shifted further

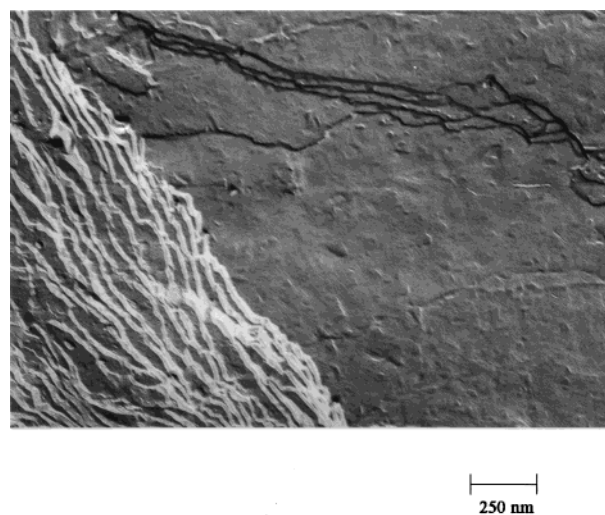


Figure 6. FF-TEM micrograph of the L_α phase of stacked bilayers prepared from a solution of 25 mM TTAL, 75 mM TTAOH, and 73 mM ML by hydrolysis of the ML.

to the side of the single component TTAOH. These two effects are a result of the different ionic strength in the two systems. The salt shields the charges of the mixed surfactants and makes the system more lipophilic. In the salt-free system there are some remaining charges on the bilayer of the vesicles that are due to dissociation of one of the components from the bilayer. In the presence of salt the charge is shielded, the repulsive interaction disappears and the bilayers collapse to a dense precipitate that has a lower density than water and shows up creaming.

In Figure 3 a cut is shown through a quaternary phase diagram. We added methyl laurate (ML) to a 100 mM mixture of TTAL and TTABr. We actually had hoped that the ester in the solubilization experiments would behave like a normal hydrocarbon. Under such conditions vesicles and entangled rodlike micelles can be transformed to microemulsion droplets

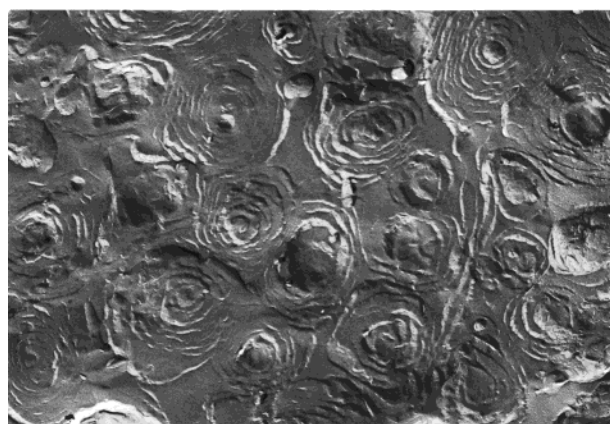


Figure 7. FF-TEM micrograph of the phase of multilamellar vesicles obtained from the L_α phase in Figure 6 by shearing.

with increasing hydrocarbon concentration. This should have resulted in low viscosity microemulsion phases. As our results show, the transformation to small droplets does not occur. The ester in the solubilization experiments behaves more like a cosurfactant than a hydrocarbon. For a molefraction between 0.2 and 0.35 of TTA Br we reach, for instance, a two-phase L_1/L_α region from the L_1 phase by solubilization of the ester. The cut in Figure 3 was established in order to find out which two low viscosity solutions could be mixed in order to reach the final phase that contains only TTAL. For this purpose we actually should have used TTA OH as the component on the right side of the phase diagram. Solubilization experiments with ML, however, cannot be made quickly enough in the presence of TTA OH because the ester would hydrolyze. We assume, however, that apart for the hydrolysis TTA Br would behave similarly as TTA OH.

According to the diagram, it should be possible to mix a vesicle phase consisting of 100 mM TTAL and 80 mM ML with an L_1 phase of 80 mM TTA OH. Later experiments showed that we can actually start from two-phase solutions as long as the phases do not demix macroscopically. We also did not want originally to start with a vesicle phase for the experiment because we know that vesicle phases are shear sensitive. The results showed however that a low viscosity solution is reached after the mixing before the hydrolysis has started. The formation of the final structure starts therefore from an isotropic low viscosity solution which is at rest.

In Figure 5 several states of a sample are shown which are reached after the mixing process. Shortly after the mixing of the vesicle phase and the clear TTA OH solution we obtain a turbid mixture. It is likely that this state is a two-phase situation of an L_1/L_α phase in which ML is not yet hydrolyzed. It is likely that the first process is the incorporation of the excess TTA^+ surfactant ions into the bilayer of the vesicles. This is a fast process on the time scale less than 1 ms.¹⁹ As a consequence of the mixed bilayer formation, the bilayers break and the system is transformed into a transparent metastable L_1 phase which is then slowly transformed to the L_α phase. At no stage did we observe a macroscopic demixing of the samples. The final phase is a birefringent phase with a domain like "Schlieren" texture. It consists of stacked bilayers as is demonstrated by the FF-TEM micrograph in Figure 6. When the sample is slowly tilted it is evident that it has a low viscosity.

When the sample is, however, exposed to a shear gradient for some time, the stacked bilayers are transformed to densely

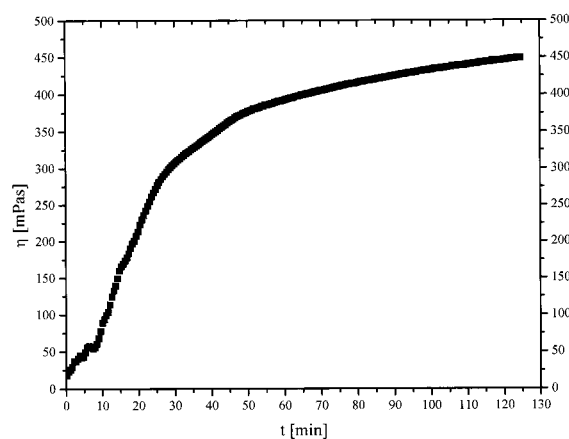


Figure 8. Transformation of the L_α phase in Figure 6 to a phase of multilamellar vesicles by shearing at a shear rate of 20 s^{-1} .

packed multilamellar vesicles (Figure 7). The viscosity rises abruptly and the sample remains in a highly viscoelastic state (Figure 8).

Conclusion

It is shown in this article that the vesicles which have been observed in many cationic–anionic surfactant systems do not form spontaneously but may be the result of shear during the mixing process of the components. If shear is avoided and one component in the system is produced by a chemical reaction, vesicles do not form but a classic L_α phase forms. This L_α phase can instantaneously be transformed into vesicles simply by shaking the L_α phase.

The L_α phase is prepared via a hydrolysis reaction of the methyl ester of lauric acid and tetradecyltrimethylammonium hydroxide. It is also shown that the ester in the solubilization experiments behaves like cosurfactants and not like hydrocarbons.

References and Notes

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