

Formation Kinetics of an Emulsion in the System Water, Didodecyldimethylammonium Bromide, and Sodium Xylenesulfonate

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The ternary phase diagram, the colloidal structures involved and the kinetics of an unusual emulsion formation in the system water, sodium xylenesulfonate (a hydrotrope) and didodecyldimethylammonium bromide (a surfactant) were determined using visual observation, optical microscopy, light scattering, electrical conductance and the stop-flow method.

The results showed as expected that addition of the hydrotrope to the surfactant-water lamellar liquid crystal caused a disordering of it to an isotropic liquid, a microemulsion, but, surprisingly, for lesser hydrotrope/surfactant ratios the result of the addition was more ordered structures; a cubic liquid crystal and a plastic crystal.

The results of stop-flow/light scattering analysis of the microemulsion-water mixing into an emulsion showed a marked reduction in scattering after mixing with decay times in the 2–3 seconds range but also the presence of anisotropic material which is found only outside the realm of mixing. This complex behavior after formation was explained by the difference in the kinetics of formation of different association structures.

This article is dedicated to Professor Egon Matijević on the occasion of his 75th birthday.

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INTRODUCTION

The interest in the phase behavior of cationic surfactants with water and hydrocarbons has been highlighted by their many practical applications, such as anti-statics in the detergent industry, as performance chemicals in the petroleum industry, as well as structure modifiers in the personal care sector. Additional stimulus has been provided by the discovery that cationics are potent immunoderpressants,¹ and by the fact that bichain cationic surfactants turned out to be stabilizers for W/O microemulsions,²⁻⁵ with an efficiency at a level significantly higher than the traditional ionic surfactant/nonionic cosurfactant combinations. A combination of electrical conductivity determinations and NMR diffusion measurements⁶ was used to clarify the structures in the W/O microemulsion. Interestingly, the didodecyldimethylammonium bromide has been shown to form a well defined cubic liquid crystalline region when combined with water and octane. The phase region showed a transition from a diamond structure (space group $Pn3m$) to a bodycentered cubic structure (space group $Im3m$) with increased amount of water⁷ and this structural change has later been related to the rheological properties.⁸

These results provide a fundamental knowledge of the behavior of these medium chain length bi-chain cationic surfactants, when combined with water and a hydrocarbon. However, in a large number of applications another property of these surfactants – the fact that their primary association does not lead to the formation of micelles but, instead, to a lamellar liquid crystal – is the most important factor. This lamellar liquid crystal is disordered⁹ forming an isotropic liquid¹⁰ upon the addition of a hydrotrope molecule.¹¹

Our group has recently used this fact to prepare liposomes by addition to water of a microemulsion formed by a liposome forming surfactant and a hydrotrope;¹² a stop-flow equipment combined with light scattering detection¹³ has been used to determine the growth rate for liposomes of nonionic surfactants¹⁴ prepared in this manner.

With this article we present the phase diagram and the kinetics of emulsion formation in a combination of water, didodecyldimethylammonium bromide and sodium xylenesulfonate. The results showed the influence of the hydrotrope to be dual; at sufficiently high hydrotrope/surfactant ratios the expected transition from a lamellar liquid crystal to a microemulsion took place, but for lower ratios, surprisingly, the addition of hydrotrope changed the lamellar liquid crystal to a more ordered gel phase. In addition, the stop-flow experiments showed intermittent existence of birefringent structures, when mixing two isotropic liquids to create an emulsion of two liquids.

EXPERIMENTAL

Materials

Sodium xylenesulfonate (SXS) (purity < 9% Na₂SO₄) obtained from Aldrich, Milwaukee, WI, was purified by washing three times each with hexane and acetone to remove organic substances, by water to remove the salt, and dried in a vacuum oven until no changes in weight were found. Didodecyldimethylammonium bromide (DDDMAB) (purity 98%) was obtained from Fluka, Ronkonkoma, NY, purified by recrystallization from an acetone-ether solution dried in a vacuum oven at temperature less than 35 °C.¹⁵ Distilled water was used without additional purification.

The Phase Diagram

The experiments were carried out at room temperature, unless stated differently. The phase diagram was determined as follows. The samples were prepared at different weights and one-phase compositions were identified by visual observation. In cases, when needed, samples were left and observed for several weeks in order to estimate the long term stability of phases and, also, to obtain improved separation. Different liquid crystalline phases were identified using optical microscope with the sample between crossed polarizers. As a complementary method X-ray diffraction was applied to determine the boundaries of the liquid crystal phases.

Small Angle X-ray Diffractometry

A small amount of the sample was drawn into a glass capillary of 0.7 mm in diameter, and placed in a brass sample holder. The X-ray radiation is K α copper filtered by nickel foil to yield a wavelength of 0.1542 nm at 40 kV and 18 mA. The system is a Simens Crystalloflex 4 using a Kiessig low-angle camera, Richard Seifert, and an ORDELA detection system, which allows the angle 2θ to range between 0.7 and 5.7 degrees.

Dynamic Light Scattering Measurements

Dynamic light scattering (DLS) measurements were performed on a Brookhaven Instruments system. The light source is an Argon ion laser, Model 85, Loxel Laser, operating at a wavelength of 514.5 nm, and 90° scattering was collected by a BI-DS photomultiplier tube. Samples were maintained at a constant 25.0 ± 0.1 °C.

Stop-flow Measurements

The stop-flow device has been extensively described elsewhere^{13,16} and has been modified to detect both the total scattering and that of the anisotropic part. An He-Ne laser, Hughes Model 5040, operating at 632.8 nm, was used as the light source. The light scattered at 90°, was passed through two polarizers, with polarization directions perpendicular to each other, and its intensity and that of totally scattered light was determined by separate photomultiplier tubes. The measurements were made 15 times or more and an average of the results reported. The difference between the average curve and the individual results was less than 5% on the voltage

scale. In this apparatus, the initial microemulsion solution (W 63%, SXS 32%, and DDDMAB 5%) was mixed with equal volume of water in the stop-flow equipment.

Static Mixing

In the static experiments water was placed on top of equal amounts of L1 phase with 65% water, 30% SXS and 5% DDDMAB, and observed both visually and with the aid of a microscope, until phase separation was complete.

RESULTS

The phase diagram of water, didodecyldimethylammonium bromide (DDDMAB) and sodium xylenesulfonate is shown in Figure 1. The diagram shows two lamellar phases, LLC 1 and LLC 2, along the water-DDDMAB axis in accordance with the results by Fontell *et al.*⁶ Addition of SXS to the water/DDDMAB compositions resulted in the formation of a gel phase (α) at low water content and at enhanced water content a cubic liquid crystal,

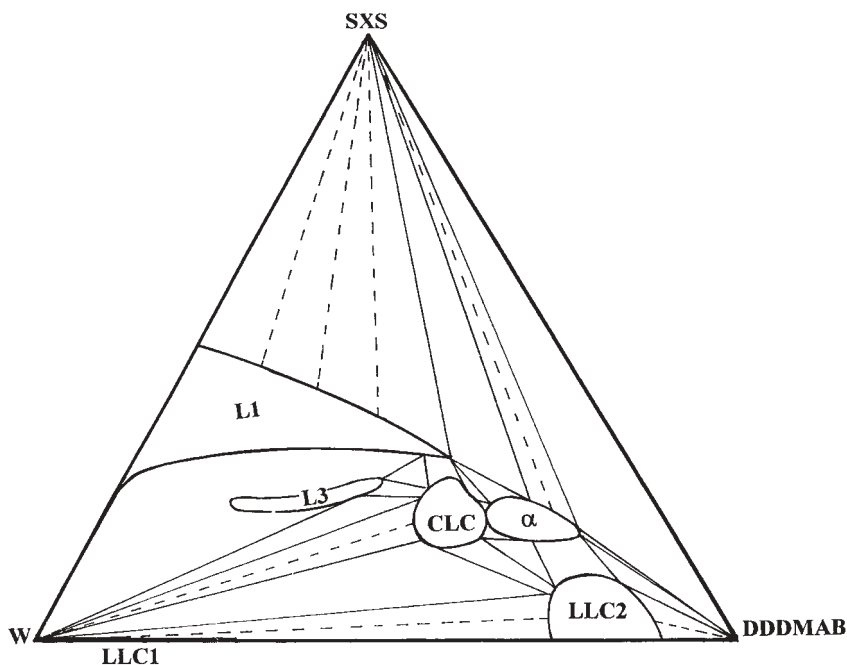


Figure 1. The phase diagram of water (w), didodecyldimethylammonium bromide (DDDMAB) and sodium xylenesulfonate (SXS); L1, L3 = micellar solutions, CLC = cubic liquid crystal, α = crystalline (gel) phase, LLC1, LLC2 = lamellar liquid crystals.

CLC, in equilibrium with water. The gel phase gave an initial pattern that could be mistaken for that of a hexagonal liquid crystal, Figure 2A, but heating to an isotropic liquid followed by cooling displayed the pattern of a substance crystallizing in a thin film, Figure 2B. The crystallinity was confirmed by the wide angle X-ray diffraction pattern; showing a number of sharp diffractions at 3.8, 4.2, 4.4 and 4.6 Å indicating a crystalline packing of the hydrocarbon parts of the amphiphiles. At higher contents of hydro-

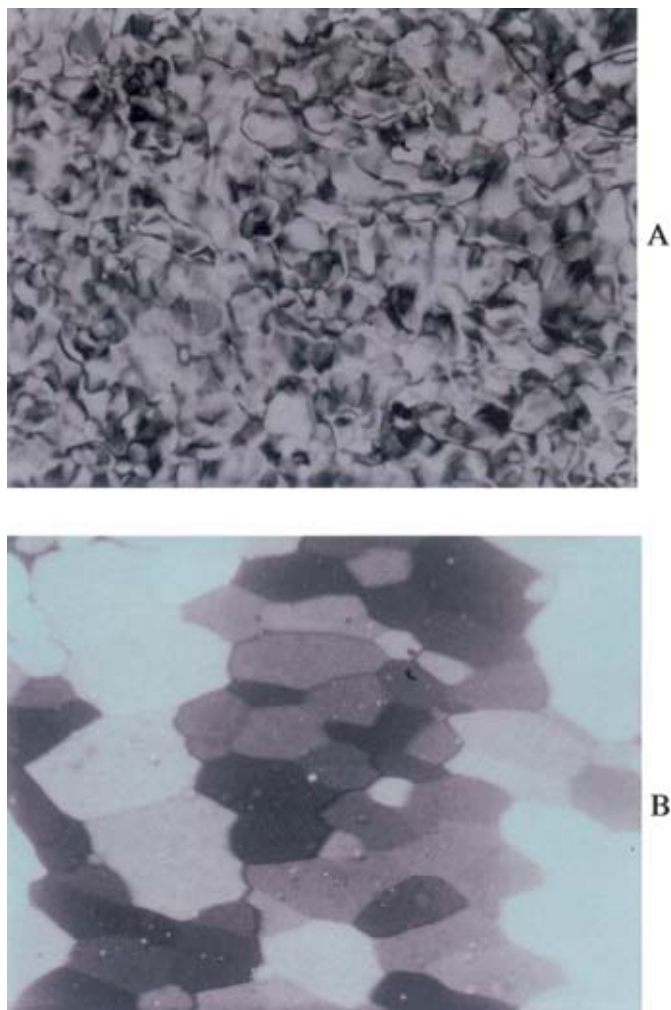


Figure 2. Optical microscopy photographs of phase α , Figure 1; (A) after mixing at room temperature, (B) after heating to isotropic liquid state and cooled to room temperature.

trope the expected micellar solution¹⁰ appeared; in fact two isotropic regions were found, L1 and L3. No phases were in equilibrium with LLC1 except the trivial one with LLC 2.

The aqueous solution of SXS, as expected¹² solubilized huge amounts of DDDMAB, 42% by mass (mass fraction, w), at SXS concentrations in excess of 28%. Practically the entire border of the L1 solution with minimal amount of SXS was in equilibrium with the isotropic solution L3. In the region between L1 and L3 with a water-DDDMAB ratio of 1.5 a small amount of an anisotropic substance were observed. Attempts to obtain a formulation consisting entirely of this structure failed and its presence must be referred to impurities present in spite of the rather extensive efforts to purify both SXS and DDDMAB.

Quasi-elastic Light Scattering

The diameters of the colloid particles in a series of samples along minimum content of SXS calculated using the CONTIN method are given in Table I. The size of the micelles, a diameter of approximately 20 nm is of the same magnitude as those found in a similar system with a nonionic surfactant.¹⁴

TABLE I

Dynamic light scattering results on DDDMAB-SXS-H₂O system

DDDMAB ($w \times 100$)	SXS ($w \times 100$)	H ₂ O ($w \times 100$)	Diameter nm
2.0	27.1	70.9	13.2 ± 2.1
6.0	28.5	65.5	19.5 ± 2.9
10.0	30.5	59.5	19.2 ± 2.9
16.1	32.0	51.9	15.8 ± 2.5
23.0	32.0	45.0	18.4 ± 3.2
29.0	32.0	39.0	19.3 ± 3.8
34.9	31.5	33.6	26.5 ± 4.5
41.0	31.5	27.5	24.5 ± 2.4

Small Angle X-ray Diffraction

The interlayer spacings, Figure 3, showed only a small influence of the water content; however, a slightly negative slope appears statistically proven. Addition of SXS gave a small but significant reduction of the interlayer spacing extrapolated to zero water content.

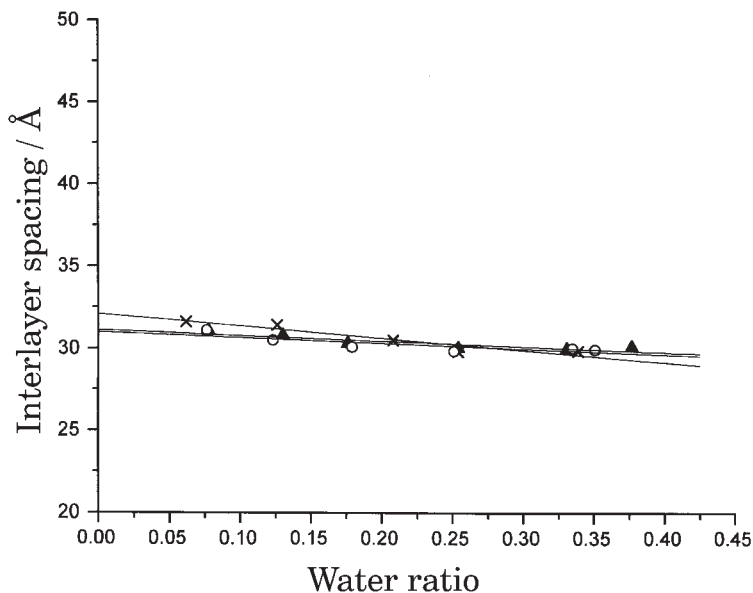


Figure 3. Interlayer spacing *versus* water volume ratio from small angle X-ray diffractometry of the lamellar liquid crystal LLC2, Figure 1. DDDMAB/SXS = 1/0 (X), 95/5 (O), 90/10 (▲).

Static Experiments

The results of the static experiments showed the formation of a lamellar and a cubic liquid crystal as indicated in the cartoon in Figure 4. The lamellar liquid crystal was identified from its microscope pattern when viewed between crossed polarizers, Figure 5.

Stop-flow Measurements

The results of stop-flow measurements showed strong reduction with time, Figure 6, and decay times of the order of 1 s. The scattering from birefringent particles was significant, Figure 7, but highly erratic.

DISCUSSION

The results complement earlier information about the behavior of didodecyltrimethylammonium bromide when combined with water and another

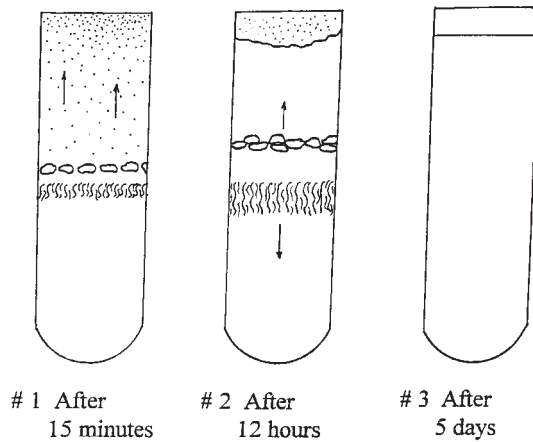
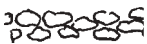


Figure 4. Features observed after water was carefully layered on top of a solution: water ($w = 65\%$), sodium xylenesulfonate ($w = 30\%$), and didodecyldimethylammonium bromide ($w = 5\%$).



Particles of lamellar liquid crystal,



particles of cubic liquid crystal,



diffuse interface between the two liquid phases L1 (bottom) and water (top).

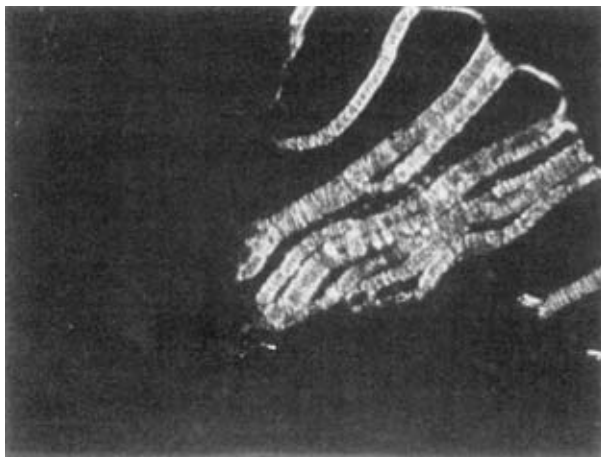


Figure 5. Optical pattern of the lamellar liquid crystal particles in Figure 4.

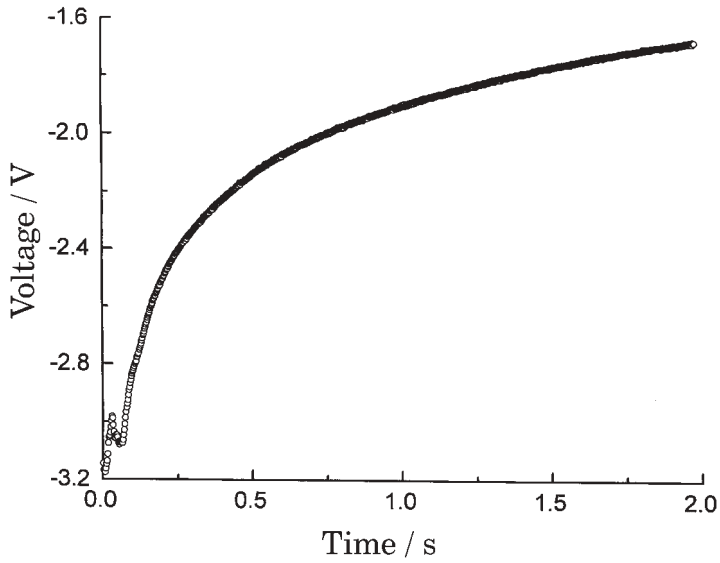


Figure 6. The voltage response to total scattered light after mixing in the stop-flow equipment. Lower voltage means less intensity. Decay time ≈ 1 s.

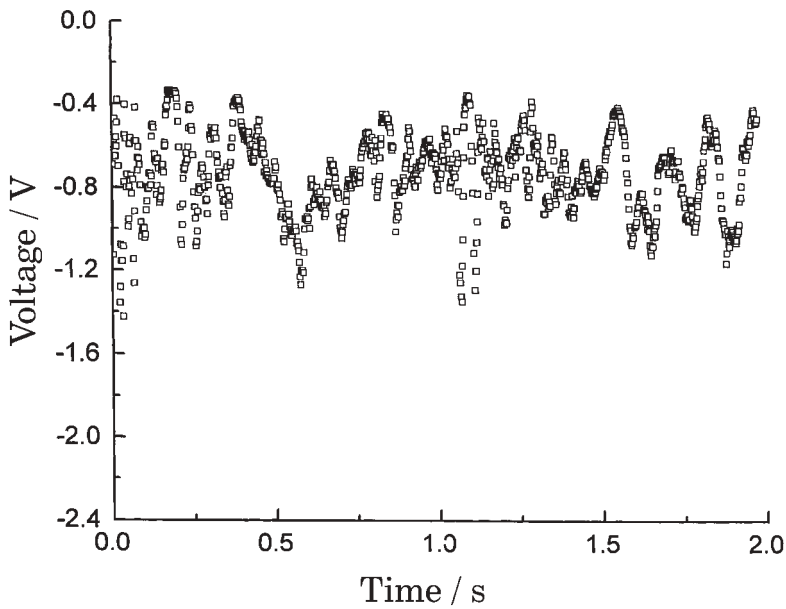


Figure 7. The voltage response of light scattered from birefringent particles after mixing in the stop-flow equipment.

substance. Both in Fontell's contribution⁶ and the ones by Radiman *et al.*^{7,8} a cubic liquid crystal was reported in addition to the lamellar ones and a cubic liquid crystal was found also in the present investigation.

The results also confirmed the early report¹⁰ on the influence by a hydrotrope molecule transferring a lamellar liquid crystal structure to an isotropic liquid micellar solution. The size of the co-micelles formed by the bichain cationic surfactant and the hydrotrope in solution L1 are similar to those found in systems of sodium xylenesulfonate with a nonionic surfactant.¹²

However, the present system gave a distinct difference from earlier ones.^{10,12} At first the multi-phase region at high water content and at sodium xylenesulfonate contents less than that to form solution L1 did not, as in earlier cases^{10,12} include the lamellar liquid crystal, Figure 1. Instead, the entire aqueous hydrotrope solution was in equilibrium with the isotropic liquid solution L3. The consequence of this modification of equilibria is that the formation of vesicles by dispersing the L1 solution in water¹² is not possible and the dispersions formed in the stop-flow experiment were emulsions of two liquid phases; L3-in-aqueous solution of hydrotrope.

However, the formation of these emulsions was not the simple process expected from the equilibrium conditions in Figure 8. According to these, the encounter between water and a liquid composition in L1 (Start, Figure 8) should lead to a transport of hydrotrope molecules into the added water giving an aqueous, hydrotrope solution, $w = 13.5\%$, with negligible amounts of the surfactant. The accompanying reduction in hydrotrope content in the L1 solution would lead to a direct structural change of it into the solution L3 and both L1 and L3 solutions in addition to the aqueous hydrotrope solution should be found after contacting L1 solution with water, Figure 9. For an intermediate time before final equilibrium the conditions in Figure 9 would exist provided the transfer of hydrotrope to the water layer would proceed under close to equilibrium conditions in the L1 and L3 phases. The aqueous solution marked ① in Figure 9 would be temporarily close to equilibrium with L1 solution marked ② and this one with an L3 solution marked ③.

However, static experiments in which the water was carefully layered on the L1 solution revealed such a direct structural change not to be the process. Instead the static experiments revealed the formation of the LLC2 and CLC liquid crystalline phases after the L1 solution, Figures 4 and 5, was brought in contact with water.

Taking this information into account, the following interpretation of the events leading to the L3 structure is reasonable, albeit not completely proven. The first stage is a release of the hydrotrope molecules from the micelles in the L1 solution transferring them to the aqueous phase. This is a reasonable assumption considering the small size of the hydrotrope mole-

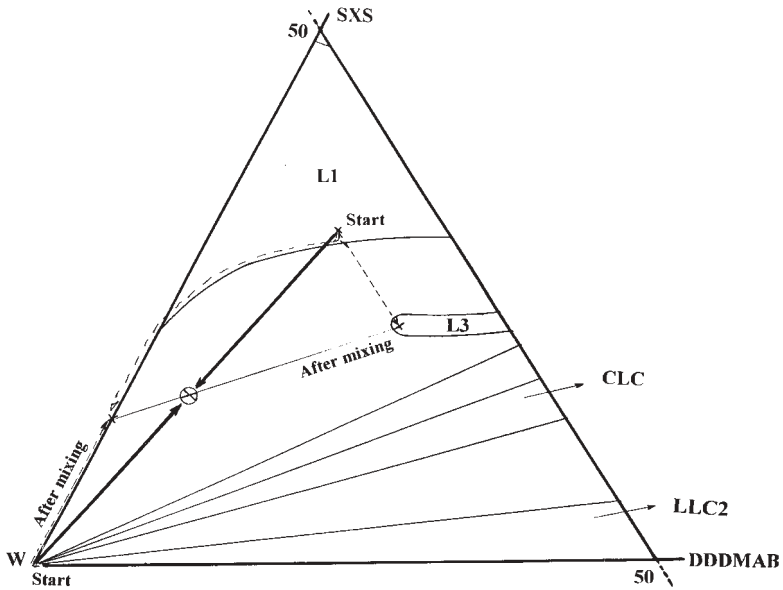


Figure 8. The two compositions »start«, when contacted, form the two liquid compositions »after mixing« at equilibrium.

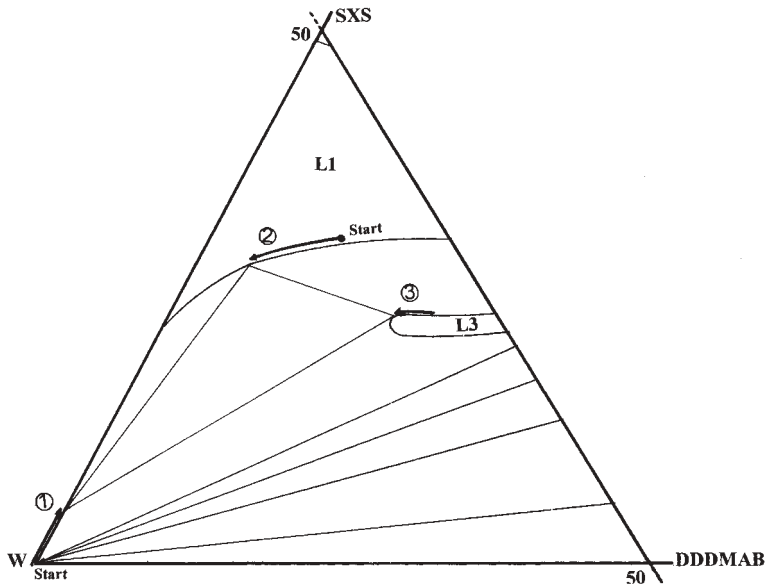


Figure 9. If local equilibrium existed, three isotropic liquid layers ①, ② and ③ would be formed after contacting the two liquids marked »start«.

cules in comparison with that of the micelles in the L1 solution. Such a change would leave the multilayered cores of these micelles without »hydro-trope protection« and, according to the phase diagram, they may now

- a) associate to form the lamellar liquid crystal, LLC2,
- b) associate with the hydrotrope molecules to form the cubic liquid crystal, CLC,

or

- c) associate with hydrotrope molecules to form the isotropic solution L3 depending on the local hydrotrope/surfactant ratio.

The static experimental results show reaction c) to be slower than the ones under a) and b) and the following assumption of the mechanism appears reasonable in lieu of additional experimental evidence.

The transport of the amphiphiles take place at the interface between the two solutions »start« in L1 and water start Figure 8. The micelles in the L1 solution encounter water at the interface, Figure 4, leading to the formation of a hydrotrope solution and a dispersion of the lamellar liquid crystal in the aqueous phase, the top layer in Figure 4. With time and increasing concentration of the hydrotrope, the cubic liquid crystal is formed and it as well as the lamellar liquid crystal rise to the top of the top layer, Figure 4 #2.

During that process the interface between the two liquids is becoming more diffuse and disappears. Instead, interface(s) are formed towards the liquid crystals at the top and these are transformed to the isotropic solution L3 observed at the end, Figure 4. Figure 10 shows the process explaining the disappearance of the interface between L1 and W; a key factor in the process. Phase separation due to transport is well known from the pioneering contribution by Ruschak and Miller¹⁷ and by later publications.¹⁸

Another essential change from the case of nonionic surfactants^{10,12} is the fact that addition of SXS to the DDDMAB in molar ratios less than 0.94 does not lead to the formation of an isotropic liquid. Instead, a crystalline compound is found; *e.g.* a more ordered structure. The fundamental reason for this behavior is obvious; the combination of electrostatic attraction between opposite charges and the hydrophobic forces will lead to a stronger and more ordered association than for the nonionic surfactant.^{10,12}

The results also provide an interesting comparison with those of Ninham *et al.*³⁻⁶ concerning the importance of curvature for microemulsion structures,¹⁹ and especially the influence by the penetration of oil molecules into the hydrocarbon part of the interfacial layer changing the packing ratio.²⁰ In the microemulsion case²¹ the size of the oil molecules is decisive for changed curvature; in the present case the interaction and penetration

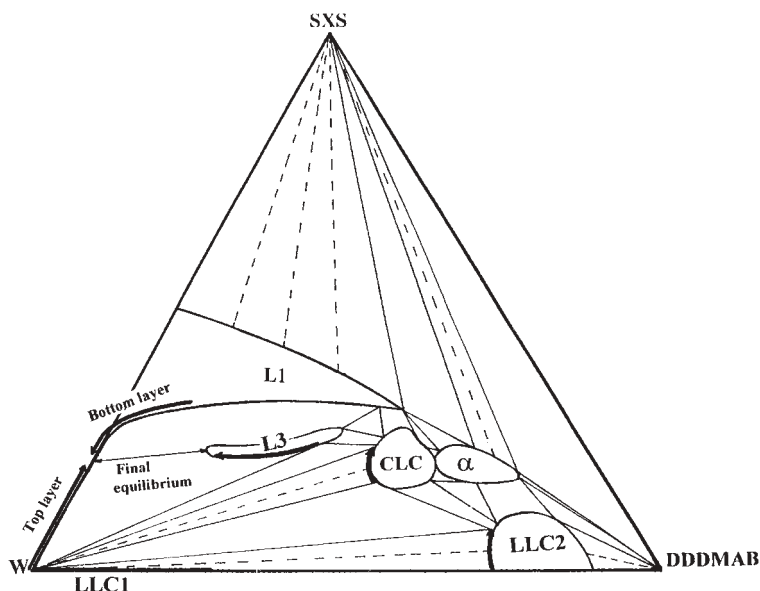


Figure 10. Kinetic factors make the intermediate state contain the liquid crystals (LLC2, CLC) from the surfactant particles after the hydrotrope is dissolved into the water layer (top layer) increasing its content in the aqueous phase. At the same time, the composition in L1 is following the limit for water solubility (bottom layer).

takes part close to the polar groups. With this fact in mind, the change in structure agrees with the following reasoning.

Primary addition of the hydrotrope to the lamellar liquid crystal causes a lateral contraction due to opposite charges giving a more ordered structure (α). Addition of water to this phase gives as expected²²⁻²⁴ a cubic phase with a bicontinuous layer structure^{25,26} and subsequent increase of the water/surfactant ratio would give L3, an isotropic liquid with a bicontinuous structure. Additional hydrotrope with its location close to the polar group, as indicated by the small angle X-ray results, Figure 3, is located close to the hydrophobic parts of the micellar core with the polar parts oriented towards the aqueous phase. The structural resemblance of these micelles to those of nonionic surfactant/sodium xylenesulfonate²⁷ and of bile salts/lecithin^{28,29} provides support for this reasoning.

Summary

A case is presented in which kinetic factors lead to the formation of non-equilibrium structures during mixing of amphiphilic association colloids.

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SAŽETAK

Kinetika nastajanja emulzije u sustavu voda, dodecildimetilamonijev bromid i natrijev ksilensulfonat

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Ternarni fazni dijagram, pripadajuća koloidna struktura i kinetika nastajanja neuobičajene emulzije u sustavu natrijev ksilensulfonat (hidrotrop) i dodecildimetilamonijev bromid (površinski aktivna tvar) određeni su metodom vizualnog opažanja, optičke mikroskopije, raspršenja svjetla, električne vodljivosti kao i metodom zaustavljenog protoka. Kao što je bilo očekivano, dodatak hidrotropa u laminarne tekuće kristale (površinski aktivna tvar – voda) uzrokuje smanjivanje uređenosti i transformaciju tekućih kristala u izotropnu tekućinu, tj. mikroemulziju. Međutim, iznenađujuće je da pri manjim omjerima hidrotrop/površinski aktivna tvar nastaju sređenije strukture; kubični tekući kristali i plastični kristali. Rezultati kinetičke analize metodom zaustavljenog protoka i mjerenja raspršenja svjetla smjesa mikroemulzija – voda u mikroemulziji pokazuju znatno smanjenje raspršenja svjetla nakon miješanja, s vremenom raspada unutar 2–3 s, ali također i prisutnost anizotropnog materijala koji je pronađen samo izvan područja miješanja. Takvo složeno ponašanje nakon nastajanja je objašnjeno razlikom u kinetici nastajanja različitih asocijacijskih struktura.