Highly Swollen Lamellar Phases in the System Calcium Dodecyl Sulfate, Pentanol or Hexanol, and Water

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Received March 6, 1997. In Final Form: February 18, 1998

Calcium dodecyl sulfate (CDS) is insoluble both in water and in alcohols at room temperature. However, it can be dissolved up to high concentrations in mixtures of water and ethanol, propanol, or butanol. No liquid-crystalline phases are formed with ethanol and propanol at 25 °C but are observed with butanol at higher concentrations of CDS. With pentanol and hexanol, lamellar phases are observed, which can be swollen largely. Neutron scattering measurements of phases with a weight ratio CDS:hexanol = 1:1 show stiff lamellae in the concentration range of 1.5−25 wt % CDS. The repeat distance grows linearly with dilution. The effective thickness for the hydrocarbon part of the lamellae decreases to some extent at high CDS concentrations.

1. Introduction

Anionic surfactants with bivalent counterions have been investigated intensively. They are relevant with regard to the hardness of water in cleaning processes as well as in comparison to monovalent cations.[1−9] Many works describe the precipitation of surfactants with bivalent counterions. At room temperature, calcium dodecyl sulfate (CDS; Krafft point 50 °C[3]) is only soluble in water up to 2.5 mg/100 g (solubility product at 25 °C: $K_{SP} = 3.72 \times 10^{-10}$ mol^3 L^{-3} [10]). CDS is nearly insoluble in alcohols. There are various papers concerning physical properties and precipitation of CDS.[11−16] In the systems calcium octyl sulfate/decanol/water[17] and calcium benzenesulfonate/water[6] a condensed lamellar phase but no swelling behavior was found as expected from electrostatic reasons.[18] Similar results have been found with magnesium dodecyl sulfate/decanol/water.[1] At 50 °C, lamellar phases at high CDS concentrations have been described in the system CDS/decanol/water.[1] It is well-known that sodium dodecyl sulfate (SDS) forms swollen lamellar phases in water at room temperature when pentanol and hexanol are added. The system with pentanol has been studied most intensively.[19] In the following, the properties of CDS will be discussed together with short-chain alcohols from ethanol to hexanol in water.

2. Experiments

Calcium dodecyl sulfate (Ca(DS)$_2$, CDS) was obtained by reacting 100 g of SDS (Fa. Serva, 99.9%) with 34 g of CaCl$_2$ (Fa. Merck) in 1 L deionized water at 40 °C.[3] The product was washed with 3 L deionized water at 40 °C and dried with a HV pump. All alcohols used for preparation of the samples were purchased by Fluka. To determine the phase behavior, the samples were weighed into 10-mL sample tubes and homogenized at 50 °C by repeated shaking and heating. The accuracy of the phase boundaries is determined by the concentration intervals of the samples. The step widths are given in the figures. For the neutron scattering, ^2H_2O (Euriso-top, CEA group) of 99.9% isotopic purity was used. The sample tubes were observed over at least 3 weeks in order to ensure that no further phase chances take place and that equilibrium had been reached.

The identification of the phases was done by macroscopic observation of the samples between crossed polarizers, polarization microscopy (microscope of Zeiss), and measurement of electric conductivity (conductivity meter from WTW). The small-angle neutron scattering (SANS) measurements were performed with the instrument SANS in Risø, Denmark. Differential scanning calorimetry (DSC; Micro-DSC, Seteram) was used for further characterization.

3. Results

3.1. Characterization of Calcium Dodecyl Sulfate (CDS). A dispersion of 5 wt % CDS in water is completely dissolved at 52.0 °C. This value was determined by means of electric conductivity measurements. For this, a 5 wt

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S0743-7463(97)00247-3 CCC: $15.00

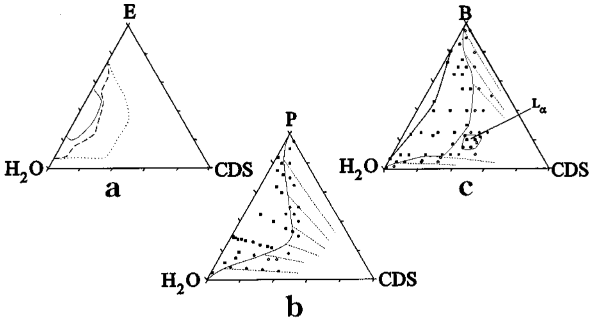

Figure 1. Ternary phase diagrams of CDS/short-chain alcohols/water. (1a) Ethanol (E). Increased solubility with temperature: 25 °C, straight line; 30 °C dashed line; 40 °C, dotted line. (1b) Propanol (P) at 25 °C. The isotropic and clear single-phase region extends from the binary systems up to two-phase regions isotropic/crystalline CDS. (1c) Butanol (B) at 25 °C with dotted data points. The miscibility gap butanol/water disappears with increasing CDS concentrations, and an isotropic clear single-phase region is formed up to two-phase regions isotropic/crystalline CDS (tie lines) and to narrow multiphase regions between the lamellar phase L_α and the isotropic phase.

% CDS solution was used and started at 15 °C to heat up with a heating rate of 2 °C/h. The DSC measurement of the same sample yielded the same temperature. For this a heating/cooling rate of 0.2 °C/min was chosen, and here strong supercooling was observed (about 30 K). The solubility enthalpy was found to be 60 kJ/mol of CDS. The solution temperature of 5 wt % samples is somewhat higher than the "Krafft point" quoted before in the literature (50 °C).[10] This result indicates that the Krafft-boundary or solution temperature of CDS depends somewhat on the concentration of the dispersion. This is a characteristical behavior of surfactant systems in solution.[20]

3.2. Phase Behavior. The determination of thermodynamical phase diagrams with all significant tie lines was far beyond our scope. We only have measured a few characteristical tie lines which were given in our phase diagrams. Figure 1a shows that the addition of ethanol to a dispersion of CDS in water at 25 °C acts like an increase in the temperature of the binary system CDS/water. Above a distinct concentration of ethanol in water, CDS becomes strongly soluble. There is nearly no solubility at lower ethanol contents. The solution concentration decreases with increasing temperature. This means that the addition of ethanol lowers the Krafft boundary of CDS. It is of interest that the solubility of CDS in ethanol is increased by the addition of water in similar matter rather than the solubility of CDS in water by addition of ethanol.

The crystalline state of CDS seems not to be influenced by addition of ethanol. Crystal hydrates[20] were not detected due to lack of data. Crystalline CDS occurs together with the isotropic solution at CDS concentrations above the solubility.

Figure 1b shows that the solubility of CDS in water at 25 °C increases when propanol or butanol (Figure 1c) is added instead of ethanol (Figure 1b). It is of interest that there are no liquid-crystalline phases in the ethanol and propanol systems. Butanol forms a small liquid-crystalline phase with lamellar polarization microscopic texture in the mediate concentration region. The multiphase behavior around this lamellar phase was not investigated in detail. Tie lines are given for the two-phase-region crystalline CDS/isotropic solution. It is noted that such liquid-crystalline phases are also found for the lower chain alcohols at higher temperatures. The binary system butanol/water shows a miscibility gap. The extension of this gap was determined by titration of butanol/water mixtures with different solutions of CDS in butanol/water.

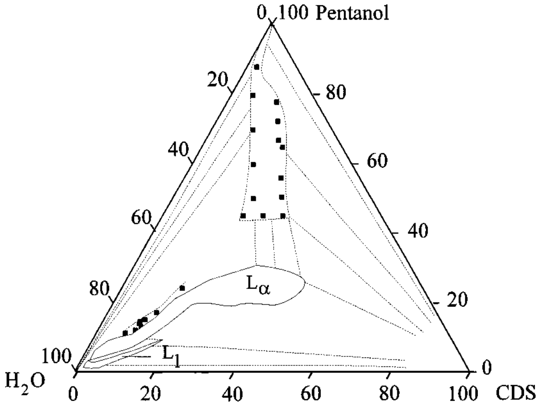

Figure 2. Incomplete phase diagram of CDS/pentanol/water in wt % at 25 °C; L_α is the lamellar phase and L_1 the isotropic, micellar phase. The filled squares show the data points of the isotropic, water-clear phase above the lamellar phase. The region above but close to the lamellar phase is denoted as L_{3h}. L_1 (L_{3l}) is an isotropic phase below the lamellar phase with nonspherical mixed micelles.

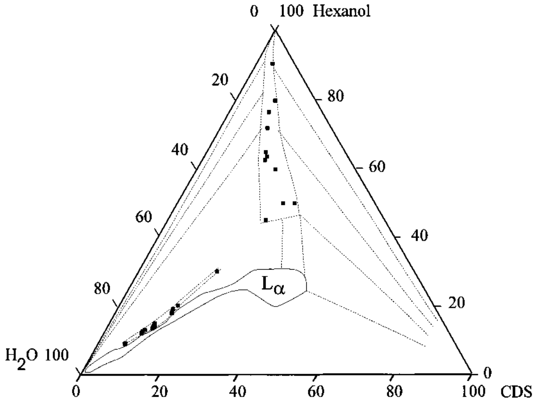

Figure 3. Lamellar region (L_α) and isotropic regions (the filled squares are data points) of CDS/hexanol/water in wt % at 25 °C.

The results indicate that CDS/water/short-chain alcohol mixtures show in essential parts the typical behavior of systems with water-soluble ionic surfactants which is extensively explained in textbooks on surfactant science.[20] Therefore, it is not surprising that this is also the case for the systems CDS/water with pentanol and hexanol (Figures 2−5). The primary difference to the shorter chain alcohols is that for pentanol and hexanol a lamellar phase is present which extends far into the water corner of the phase diagram. This lamellar phase is highly transparent up to high dilution.

Pentanol and hexanol systems follow the phase rule as well as simple multicompound mixtures. However, their phase behavior is extremely complex, especially in the region above the lamellar phase. Here we find at least two different three-phase regions which are very narrow but extended into the phase diagram. Another problem which makes the estimation of the phase diagrams more difficult is yield stresses in regions which contain lamellar dispersions which can prevent phase formation and phase separation. Large regions with dispersions of CDS and lamellar dispersions which do not separate start from the

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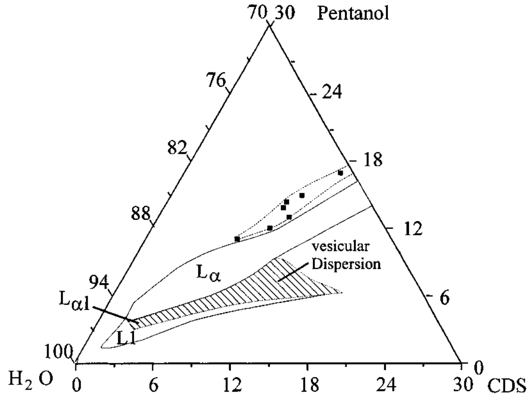

Figure 4. Dilute region of CDS/pentanol/water in wt % at 25 °C (0−30 wt % CDS). Vesicular dispersions are white coagulations of lamellar droplets at higher concentrations of CDS which look more and more like a $L_{\alpha l}$ phase at the lowest concentrations of CDS.

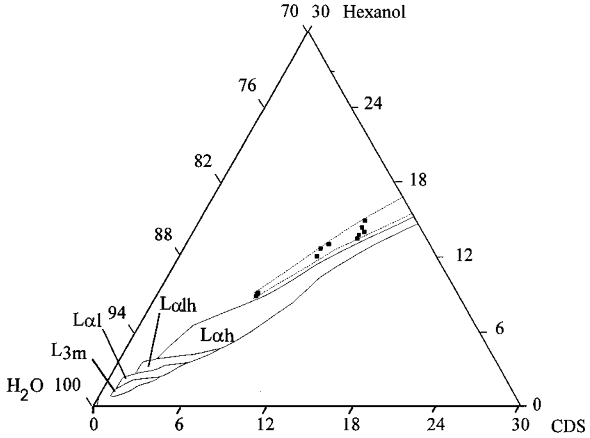

Figure 5. Dilute region of CDS/hexanol/water in wt % at 25 °C (0−30 wt % CDS). $L_{\alpha l}$ (schlieren), $L_{\alpha lh}$ (focal cones), and $L_{\alpha h}$ (pseudoisotropic orientation and oily streaks) are three different texture regions within the lamellar phase. L_{3m} is an optically isotropic, densely packed dispersion of multilamellar droplets.

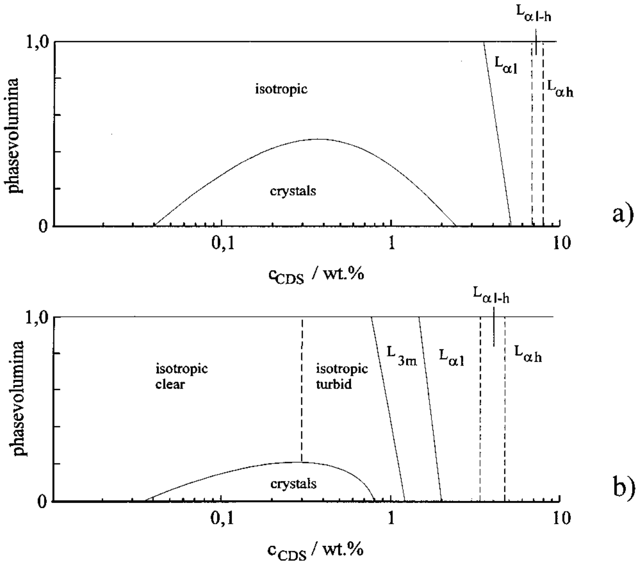

Figure 6. 25 °C phase volume intersection of an 1:1 per mass mixture of CDS with pentanol or hexanol showing the dilution path. Crystalline CDS means loosely packed crystals of CDS. L_{3m} is a densely packed dispersion of multilamellar vesicles: (a) pentanol; (b) hexanol.

CDS corner far into the phase diagram. Therefore, we worked out partial phase diagrams which show mainly the location of the lamellar phase which extends far into the water corner and only some important aspects of the other phases. The boundaries of the lamellar phase were estimated with increased accuracy especially in the highly dilute region and along the lines of hexanol addition. The concentration intervals at the lowest concentrations of the lamellar region are 0.1 wt % CDS and pentanol or hexanol. The accuracy of the boundaries of the other important regions is elucidated by drawing the datapoints of the samples which belonged to these phases.

The lamellar regions in the system of CDS/hexanol or pentanol/water were investigated in detail by means of polarization microscopy and their macroscopic behavior. Based on the observed textures, the phases were subdivided into the following regions:[21−23]

The region $L_{\alpha h}$ corresponds to a classical lamellar phase, where the texture exhibits pseudoisotropy. The region $L_{\alpha lh}$ is marked by focal conic texture; i.e., no pseudoisotropic orientation can be reached here. $L_{\alpha l}$ shows a schlieren texture, which is similar to the one observed for nematic phases of rods. The structure of $L_{\alpha l}$ is not fully established. We assume that $L_{\alpha l}$ corresponds to tubular mono- or multilamellar arrangements. $L_{\alpha lh}$ is structurally a mixture of both $L_{\alpha h}$ and $L_{\alpha l}$, which does not phase separate macroscopically.

The boundaries between these different regions depend on the chosen sample thickness and the observation time. For thinner samples and longer times they are displaced to lower concentrations. All these regions are of waterlike transparency. For still higher dilution one more region can be discerned which is optically isotropic but exhibits pronounced streaming birefringence already for very weak shear. Because of its location in the phase diagram and its macroscopic properties, this region is assigned to L_{3m}. It consists of densely packed multilamellar vesicles. Therefore, one can understand that the boundary L_{3m}/L_{α} may move at lower concentrations with time and move to higher concentrations during shear.

Figure 6 explains the very similar behavior of 1:1 per mass mixtures of CDS and pentanol or hexanol on increasing concentrations. Very loosely packed CDS crystals are found above 0.04 wt %. They become dissolved in the water phase as soon as aggregates of CDS and alcohol are built. Then the hexanol systems form turbid dispersions of probably small lamellar droplets which give no macroscopic birefringence. These vesiclelike droplets are swelling on increased concentrations of CDS/hexanol until they undergo a loose coagulation which finally forms the L_{3m} phase. The pentanol system shows a clear isotropic single phase when the crystalline CDS is dissolved. On increased concentrations, the $L_{\alpha l}$ phase is formed, passing a two-phase-region isotropic/$L_{\alpha l}$.

The L_{3m} phase of the hexanol system is optically rather clear. Shear waves are observed between crossed polarizers when the probe tubes are slightly pushed from the side. From the propagation speed c_s which is on the order of 1−2 cm/s an elastic shear modulus $E \approx 0.3$ Pa can be approximated according to the following equation:

$$c_s = \sqrt{E/P}$$

The amount of this clear phase increases. At 1.2 wt % of the mixture the whole volume is filled with this single

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phase of type L_{3m}. These single-phase samples behave much less elastically than the birefringent lower phases which occur at lower concentrations of the mixture. The L_{3m} phase changes smoothly on increasing concentrations to a $L_{\alpha l}$ phase which is characterized by its steady birefringence and its typical schlieren texture. The smooth transitions to the $L_{\alpha lh}$ region with focal cone texture and to $L_{\alpha h}$ take place at 3.5 and 4.5 wt %, respectively.

The phase diagram in Figure 4 shows that the isotropic region which is only found in the pentanol system is extended far along but below the dilute lamellar region. We measured diffusion coefficients by means of dynamical light scattering. Assuming water viscosity, hydrodynamic radii of 25−30 Å were found. However, the viscosity of this region increases exponentially with the concentration of CDS/pentanol and is up to 4 times higher than the viscosity of pure water. These results indicate that the pentanol phase should contain nonspherical mixed micelles which undergo structural transitions.[24,25] Although no visible flow birefringence can be observed, we assume that there is the same L_{3l} phase as was found in earlier investigations.[21] However there are indications that a narrow continuous connection to the water corner could exist.

Above the lamellar region, at higher contents of pentanol or hexanol, a two-phase region (I/L_{α}) is observed, which separates the lamellar phase from an isotropic phase which extends from the alcohol corner down to the lamellar region. This isotropic phase seems to follow the lamellar region down to the very dilute region. However, the phase is interrupted by two-phase regions lamellar/isotropic and isotropic/isotropic and extremely narrow three-phase region lamellar/isotropic/isotropic. It was not clear until now whether both regions of the isotropic phase above the lamellar phase are connected through a 25 °C single-phase channel. This isotropic phase is located in the region of the phase diagram, where typically a conventional sponge phase L_{3h} is to be expected. Therefore, we denote these regions of the CDS system as L_{3h} although it is remarkable that there is no visible birefringence on shear in any region. Highly diluted sponge phases of nonionic systems are known to exhibit strong streaming birefringence.

The phase diagram intersection in Figures 7 and 8 are given in order to elucidate the complex phase behavior in the regions with condensed lamellar phases and crystalline CDS. A 10 wt % CDS dispersion in water fills nearly half the volume of the probe tube because the crystallites of CDS are not densely packed (Figure 9a). Above 0.5 wt % hexanol swelling occurs, which indicates the formation of a third phase. Polarization microscopic pictures prove that the new phase is a condensed lamellar phase with large multilamellar vesicle-like structures which exist together with crystalline CDS (Figure 9b). The swelling increases, yield stress builds up, and crystalline CDS disappears on increased amounts of hexanol. Coagulation starts above 6 wt % hexanol, which leads to a sedimented, low-viscous emulsion of vesicle-like lamellar droplets without birefringence (Figure 9c). This apparently isotropic emulsion is swelling again and seems to change smoothly into a more and more birefingent state until a clear lamellar phase is formed (10.0 wt % hexanol). At 12.6 wt % hexanol a clear isotropic single phase is found. This transition goes over a two-phase state with a lower lamellar and an upper isotropic phase.

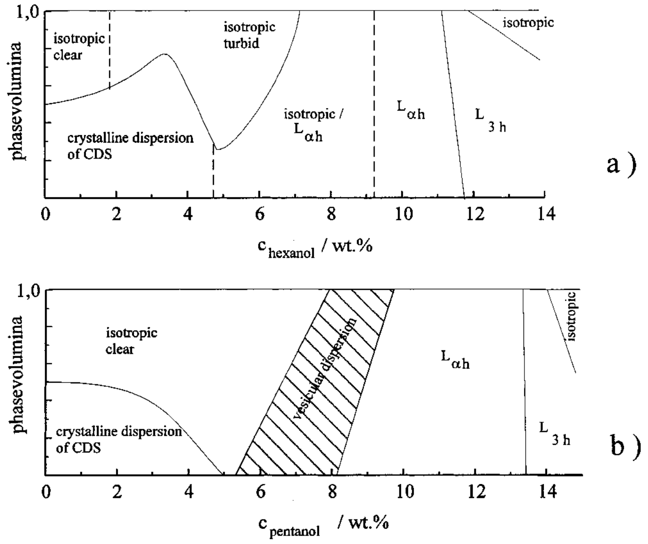

Figure 7. 25 °C phase volume intersection of a 10 wt % CDS system with increasing concentrations of pentanol (b) or hexanol (a).

The behavior of a 10 wt % CDS dispersion on addition of pentanol is somewhat different (Figure 7b). Crystalline CDS disappears because it becomes incorporated into the mixed micelles of the clear isotropic (L_{3l}) phase. Above 5.5 wt % pentanol intransparent white coagulations of condensed lamellar droplets occur. The volume of the white coagulations increases continuously until the whole sample is filled with it. The white coagulations transform to a more and more schlieren-like and transparent state from which finally a clear $L_{\alpha h}$ phase is formed.

The best method to use in order to visualize the state of dilute vesicle-like dispersions is differential−interference−contrast microscopy (DIC). Figure 10 is a DIC picture of a 5 wt % CDS dispersion with 3.2 wt % hexanol. The lamellar phase is dispersed in the form of very small vesicle-like droplets. This means that the droplets are filled with the same isotropic volume phase in which they are dispersed. This type of structure seems also to be followed in the tubular arrangements which are alternative dispersion states of the system. Such tubular arrangements seem to be responsible for the yield stress values of the systems.

3.2.1. Neutron Scattering.

Small-angle neutron scattering (SANS) experiments were performed on samples containing equal amounts (by weight) of hexanol and CDS. To achieve good contrast conditions, for these samples D_2O (instead of H_2O) was used as the solvent. The samples contained 1.5, 3, 5, 10, and 25 wt % both of CDS and hexanol. All samples were located in the phase region where a lamellar phase is observed.

The SANS intensity curves are shown in Figure 11 as a function of the scattering vector $q = (4\pi/\lambda)\sin(\Theta/2)$). For all samples a pronounced correlation peak can be seen and the position of the peak moves to higher q-values with increasing concentration, thereby indicating a decrease of the mean repeat distance of the lamellar phase. A confirmation of the presence of a lamellar phase is given by the fact that apart from the primary peak one can discern a second peak at twice the q-value of the first peak; that in the scattering curves shows up as a shoulder (particularly pronounced for the 3 and 5 wt % samples). The mean repeat distance d of the lamellae can directly be computed from the position of the peak maximum, $q_{\max}$, via

$$d = 2\pi/q_{\max} \qquad (1)$$

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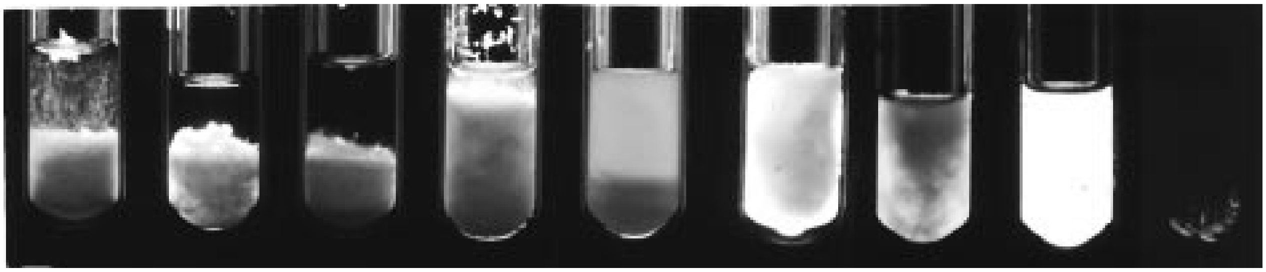

Figure 8. Photographic pictures between crossed polarizers belonging to Figure 7a which show the transition from the crystalline dispersion of CDS in water (left picture, 0.1 wt % hexanol) to the clear lamellar phase (10.8 wt % hexanol) and to the isotropic phase (right picture, 12.6 wt % hexanol). From left to right: 0.1, 0.5, 1 (Figure 9a), 3 (Figure 9b), 5 (Figure 9c), 8, 9, 10 ($L_{\alpha h}$), 12.6 (L_{3h}) wt % hexanol (8 and 9 look like $L_{\alpha l}$ but are a mixture of $L_{\alpha h}$ isotropic phase).

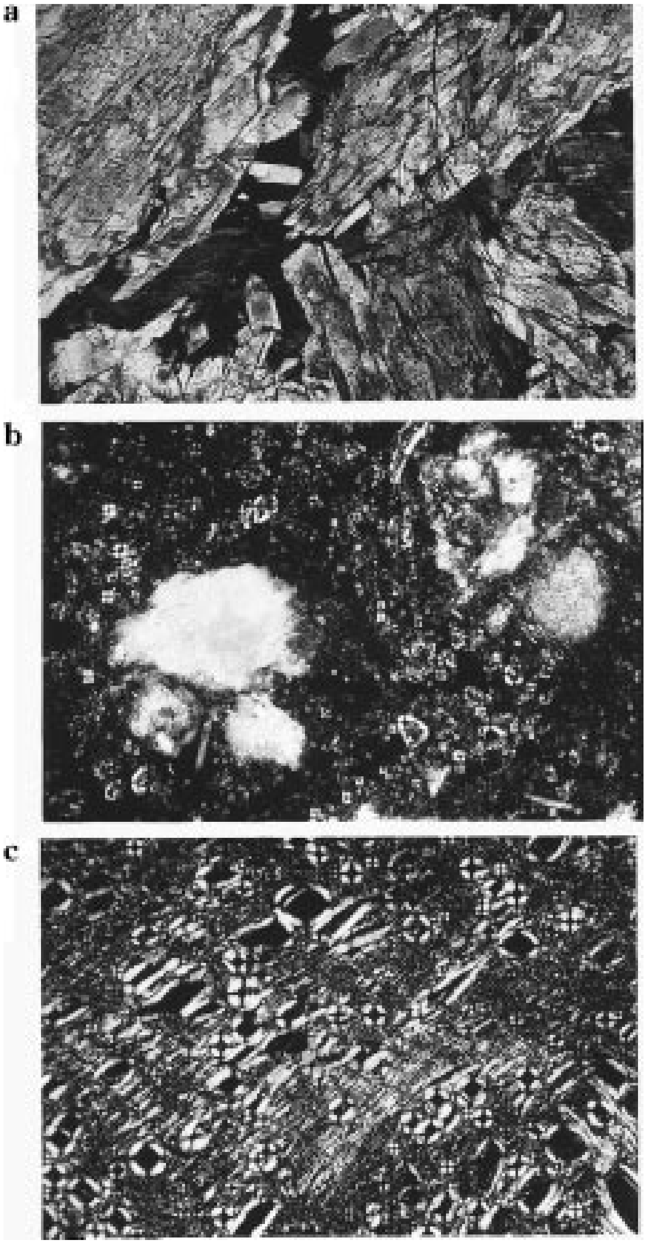

Figure 9. Polarization microscopic picture of 10 wt % CDS and different concentrations of hexanol: (a) crystalline dispersion of CDS, 1.0 wt % hexanol. Middle (b) crystalline dispersion of CDS together with some vesicle-like dispersions of a condensed lamellar phase, 3.0 wt % hexanol; (c) lamellar dispersion from the lower phase of the two-phase region lamellar/isotropic with 5.0 wt % hexanol. Scale: 10 mm ≈ 220 μm.

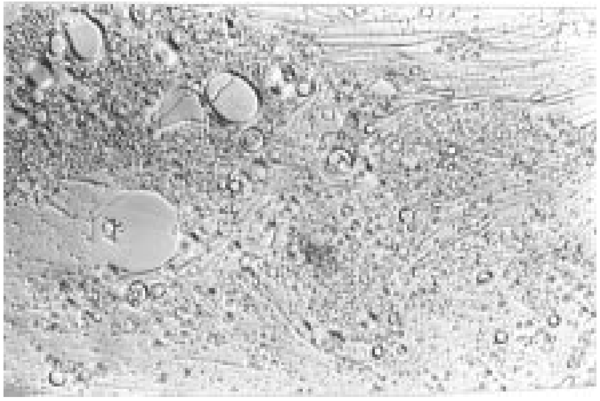

Figure 10. Differential interference contrast microscopic picture of the vesicle-like dispersion and tubular arrangements of a condensed lamellar phase with 5.0 wt % CDS/3.2 wt % hexanol at 25 °C. Scale: 10 mm ≈ 220 μm.

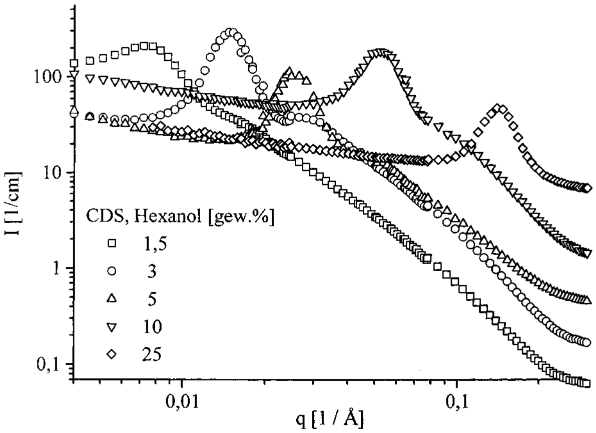

Figure 11. SANS intensity curves for lamellar phases in the system of CDS/hexanol/D_2O. c(CDS) = c(hexanol); concentration is given in wt % (subsequent curves are each multiplied by a factor 4 for better lucidity).

The obtained values for d are given in Table 1. For an ideal lamellar system a swelling behavior would be expected where d is inversely proportional to the volume fraction Φ of the lamellar system. For Φ we used the experimentally determined density of 1.0 g/mL (as measured for the system CDS/hexanol (1:1)) and subtracted the portion due to the Ca; i.e., only the DS part is taken into consideration.

d vs $1/\Phi$ is plotted in Figure 12, and a linear dependence over the whole concentration range is found. This linearity confirms the lamellar phase in this system with a lamellar structure that is simply swollen by the addition of water. From the slope of the straight line through the experimental data points, a thickness D of 24.1 Å can be calculated. This value corresponds well to the thickness observed for other lamellar phases of ionic surfactants with a high content of cosurfactant.[26−29]

Table 1. Composition, Volume Fraction Φ (DS), Lamellar Spacing *d*, Membrane Thickness *D* (=*d*Φ), Membrane Thickness D_l (fitted with Eq 2), Head Group Area a_s, and Relative Width σ/q_{max} for Samples in the Lamellar Phase with Equal Amounts of CDS and Hexanol

wt % CDS + hexanol (1:1)	3	6	10	20	50
Φ (DS)	0.0279	0.0558	0.0930	0.1860	0.465
d Å	857.2	422.5	245.6	120.1	44.75
σ/q_{max}	0.692	0.263	0.255	0.286	0.263
D, Å	31.3	30.7	30.5	28.	24.7
D_l, Å	21.2	20.6	18.7	18.9	14.3
a_s, Å^2	67.2	68.4	70.9	73.2	80.9

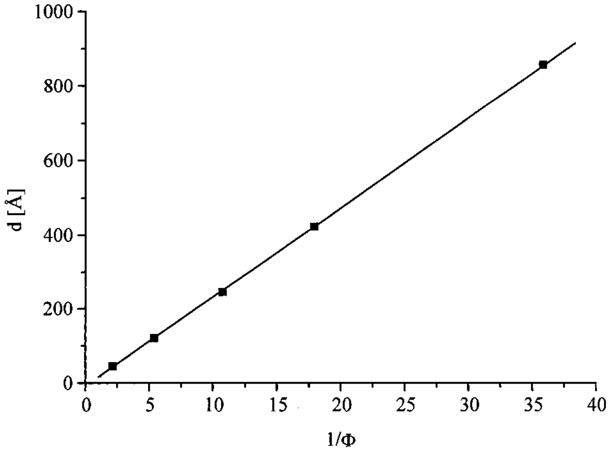

Figure 12. Plot of *d* (=$2\pi/q_{max}$) vs 1/Φ as obtained from the SANS curves.

Of course, one can calculate as well *D* for each individual sample via $D = \Phi d$. However, here it appears that the membrane thickness *D* decreases with increasing concentration (see Table 1), as a systematic deviation for the peak position is observed with increasing concentration. (In Figure 12 this corresponds to a systematic deviation at low values of 1/Φ which is not so evident due to the chosen presentation of the data).

Additional information on the lamellar structure can be obtained by using the high q-range of the scattering curves. For homogeneous lamellae the scattered intensity should be given by[30]

$$I(q) = \left[\frac{2\pi}{q^2}\Phi(\Delta\rho)^2\, D_l \sin\left(\frac{qD_l}{2}\right)\right] \Big/ \left(\frac{qD_l}{2}\right)^2 \qquad (2)$$

where Φ is the volume fraction of the lamellae and $\Delta\rho$ the difference of the scattering lengths of solvent and lamellae.

From fitting eq 2 to the experimental data in the high q-range, i.e., well beyond the Bragg peak, the thickness D_l has been determined and is given in Table 1. The values obtained for D_l are about 3−4 Å lower than those calculated from Φ*d*. The reason for this difference should be due to the fact that in applying eq 2 one observes the thickness corresponding to the scattering length density. However, the main contrast is due to the alkyl part of the surfactant (or cosurfactant) whereas the headgroups hardly contribute. In contrast, when calculating *D* via Φ*d*, the headgroups are fully counted in Φ and therefore the difference of 3−4 Å is to be explained by the thickness of two such headgroup layers at the surface of the lamellae; i.e., additional information is obtained on the headgroup layer thickness from the combination of the peak position and the slope in the high *q*-range.

For both values for *D*, i.e., D_l and Φ*d*, the same trend of decreasing thickness with increasing concentration is observed. This could be interpreted by a model where the surfactant molecules are pressured into the membrane (due to the increasing repulsive interaction with increasing concentration) and thereby the alkyl chains of the surfactant begin to interdigitate.

It is also possible to calculate the headgroup area from the lamellar spacing *d*. Simple geometry gives

$$a_s = \frac{2}{dcN_A} \qquad (3)$$

The calculated values for a_s are also summarized in Table 1, where a_s means the surface per DS molecule (i.e., here the hexanol is neglected). Of course, a_s is inversely proportional to *D* and therefore increases with increasing total concentration. For the lower concentrations it has a value of about 67−70 Å^2, which is not very much higher than the 53 Å^2 observed at the planar air−water interface for SDS.[31] This means that the presence of large amounts of hexanol in the system (about 2.8 hexanol molecules/DS molecule) does not influence the headgroup requirement of the DS molecules to a larger degree.

Another piece of information regarding the structure of the lamellar system is contained in the width of the Bragg peak. Therefore, the peak was fitted with a Gaussian function (of type $\exp(-(q - q_{max})^2/2\sigma^2)$) in order to obtain an estimate of its width. The corresponding values for the standard deviation σ of these Gaussians are also given in Table 1. Apart from the most diluted sample, σ/q_{max} has a constant value of about 0.25−0.28, already a value well above that of the experimental resolution (since the wavelength distribution had a width of 18% fwhm, i.e., that corresponds to a σ/q_{max} of less than 0.07). This means that the degree of long-range ordering remains constant along this dilution line. The fact that the pronouncedness of the peak remains constant over a large range of concentrations and that the peak is still well-visible even for the lowest concentration indicates that the lamellae should be quite stiff since for membranes of low rigidity one usually observes that the correlation peak of the lamellar phase disappears for high dilution due to the flexibility of these membranes.[32] A somewhat different situation is given for the most dilute sample, which is located in the L_{3m} region of the phase diagram. Here the peak is much broader, which indicates that the long-range order is much lower; i.e., the domain size of the lamellar structure is much smaller than that in the lamellar phase at higher concentration.

4. Discussion

The SANS experiments show clearly that in our investigated system a conventional lamellar structure is present that can be diluted largely. The sharpness of the Bragg peak of the neutron scattering measurements indicates the presence of relatively stiff membranes. This much more pronounced stability of a lamellar phase for the case of pentanol and hexanol has to be due to higher

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rigidity of the amphiphilic film. This corresponds to other experiments that have shown that the bending elasticity in systems with cosurfactants present is the higher, the longer the alkyl chain of the corresponding alkanol.[33] The relative width of this Bragg peak is constant, thereby indicating that the long-range ordering remains constant as a function of the concentration.

The neutron scattering measurements also show that the lamellar distance of the system CDS/hexanol (1:1) decreases linearly and monotonically on dilution from the phases with stationary birefringence down to the phase without stationary birefringence (L_{3m}). So, it is proved that L_{3m} also consists of small lamellar fragments with high mutual disorder. The reason for the disordered state of the diluted region is the weak repulsion forces in systems with high interlamellar distances. The water-like transparency of the lamellar phases above L_{3m} with hexanol and pentanol indicates an extremely strong interlamellar order, and the preparation of liquid lamellar single crystals should be possible with these samples.

The neutron scattering measurements indicate that the thickness of the lamellae becomes smaller at high concentrations. One leading force for this hydrocarbon chain penetration can be understood when we assume that counterion condensation occurs at high concentrations, which may lead to an additional ion−ion correlation attraction between the lamellae.[17,18] The penetration enlarges the headgroup areas by some extent and reduces the ion−ion repulsion in the direction of the lamellar plains. On the other side, counterion condensation at low concentrations could be the reason for the unexpected stability of highly swollen lamellar phases with CDS/water and pentanol or hexanol. The charge density of the lamellae becomes very low, and the typical swelling behavior of the nonionic surfactant system could be found.

CDS is nearly insoluble in water and alkanols because there is a very high free electric lattice energy of the crystal state of CDS. Swelling is expected not to occur due to electrostatic consideration.[1,17] The discussed additional ion−ion correlation−attraction should prevent swelling even more. It is an important observation that mixtures of SDS with CDS are able to form swelling phases in decanol and water.[9] It is assumed that the bivalent calcium ions are bound to the lamellar layer. The sodium ions build the diffuse double layer. Such a system is able to undergo swelling because of the reduction of the electrostatic energy. It is also of interest that addition of sodium chloride to the system SDS/pentanol/water enlarges the extension of the swollen lamellar phase to lower surfactant concentrations.[19]

Experimental data[34,35] and general thermodynamic considerations[36,37] on the effects of a third compound on the dissolution temperature of surfactants are not very numerous. However, it is shown that the dissolution temperature of the crystalline nonionic surfactant *N*-dodecanoyl-*N*-methylglucamine decreases by adding short-chain alcohols because the cmc of the mixed micelles becomes lower than the solubility of the surfactant in water.[38] The enthalpy of dissolution was found to be independent of the alcohol concentration. This means that there is an entropic interaction with the alcohols. Our experimental results are in some accordance with these observations. CDS remains unchanged on addition of alcohols until a new third phase is formed. This means that the solubility product of CDS is not changed by addition of alcohol. Increased solubility can be achieved when free dodecyl ions are removed from the volume phase. This may occur by forming mixed micelles. However, one should take into account that alcohol molecules could associate even with a single dodecyl sulfate ion. This complexation would be advantageous because the entropy of the system increases in this case. The contact area between hydrocarbon chains and the water core becomes smaller and water molecules become unbound. The entropy of free water molecules is considerably higher than the entropy of bound water molecules.

The formation of very small aggregations should be important for alcohols with the shortest hydrocarbon chains which are known to destroy dodecyl sulfate micelles. From sterical reasons short-chain alcohols form spherical mixed micelles. With lower amounts of pentanol we find an isotropic phase which contains mixed micelles. In this case it can be assumed that the cmc of the mixed micelles is lower than the solubility of CDS in water. Increased incorporation of medium-chain alcohols reduces the packing parameter continuously. Therefore, lamellar phases are formed with a higher amount of pentanol as soon as the packing parameters are too large for spherical or rodlike aggregates. Condensed and vesicular phases are the stable forms at lower alcohol concentrations. Highly swollen lamellar phases are obtained when the ratio of alcohol and surfactant molecules is optimal for the plain lamellar structure. The micellar solution−lamellar phase transition is known to be favored by higher concentrations. Therefore, the micellar phase is not found with higher concentrations of CDS. Hexanol has a stronger influence on the packing parameter than pentanol, and no isotropic micellar phase is found below the lamellar phase.

It is apparently in contrast to our observations that the system CDS/decanol/water does not form highly swollen lyotropic phases.[1] However, it is known that continuous swelling from concentrated lamellar regions to highly diluted lamellar phases can be frequently obtained with systems containing C_{12} or C_{14} surfactants together with pentanol or hexanol but not together with butanol or decanol. Fluctuations are essential forces which stabilize diluted lamellar phases.[39] However, the neutron scattering data indicate that the lamellae of the CDS system should be rather stiff. Therefore, we assume that short-range fluctuations of the incorporated alcohol molecules prevent coagulation when the stiff membranes come into close contact. Butanol destroys the lamellar structures for sterical reasons and because the molecule would carry out nearly free rotations in a lamellar structure. Pentanol and hexanol are optimal stabilizers. The magnitude of the fluctuations decreases with longer hydrocarbon chains. The fluctuations of the longer alcohols like decanol should be too weak to prevent coagulation, and continuous swelling to highly diluted lamellar phases cannot occur.

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