Mixing Oil and Water by a DNA-Based Surfactant

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The self-assembly behavior of a cationic surfactant (dodecyltrimethylammonium) with DNA as counterion in mixtures of water and decanol was investigated. The phase diagram was established and the different regions of the phase diagram characterized with respect to microstructure by ^{2}H NMR (D_2O), small-angle X-ray scattering (SAXS), and other techniques. The DNA−cationic surfactant aggregate is virtually insoluble in water but shows a high solubility in decanol; in decanol, highly viscous solutions/rubberlike solid material is found. In the presence of both solvents, there is a formation of liquid crystalline phases. Both lamellar and reversed hexagonal phases are found, the former favored by higher water contents, the latter by higher concentrations of decanol. The liquid crystalline phases are in equilibrium, via two-phase and three-phase regions, with the essentially pure components.

Introduction

While the interaction between oppositely charged colloid pairs, in particular polyelectrolyte−surfactant systems, have a broad relevance and have received considerable attention in fundamental and applied research,[1−10] the case of DNA interacting with cationic polymers and surfactants or lipids have naturally been a particular focal point. Because of the biological relevance (interaction with histones in chromatin) as well as several potential biotechnological applications, including protection, purification and gene delivery, there are a very large number of studies of the interaction between DNA and different cationic surfactant systems, lipid vesicles, and liposomes as well as polycations.[11−18] The interaction between DNA and cationic cosolutes has a number of manifestations, i.e., association, phase separation, compaction, and adsorption.

Polyelectrolyte−surfactant interactions in aqueous solution have received considerable attention in recent years. In particular, if the polyelectrolyte owes its aqueous solubility to the presence of charges, reflecting the contribution to translational entropy of the counterions,[19] solubility is strongly influenced by addition of any ionic species. Phase separation of the associative type is particularly marked with polyvalent cosolutes, including polyelectrolytes and charged surfactant self-assemblies. The associative phase separation in polymer−surfactant systems leads to a dilute aqueous solution and a concentrated phase of polyelectrolyte and surfactant; this phase can be different in nature depending on the system: different liquid crystalline phases, solid crystalline phases, and a concentrated solution or gel.[8,20,21]

A system of polyelectrolyte, oppositely charged surfactant, and water, must, as any system containing solvent and two electrolytes without common ion, be treated as a four-component system in a thermodynamic analysis:[22] there are four ionic species and the water solvent, but the requirement of charge neutrality reduces the number of components by one. The large number of components leads both to extensive and demanding experimental characterization and to difficulties in visualization. A novel approach to these phase behavior studies that greatly facilitates progress in understanding was recently adopted by Lennart Piculell's group.[8] This approach concerns the preparation of the so-called complex salt, which is the combination of polyelectrolyte and surfactant with the small counterions removed. Mixing the complex salt with either the polyelectrolyte or the ionic surfactant in the solvent (water) then results in true ternary mixtures, the phase behavior of which can be more easily investigated and can be represented in two dimensions (at constant temperature and pressure).

The interactions between DNA and cationic surfactants were early on investigated with respect to binding isotherms,[16] DNA conformation and precipitation.[12,23−25] Ourselves, we have, for simple and mixed surfactant systems, investigated DNA compaction, phase diagrams and phase structures.[23,26−28] This has inter alia lead to a description of a double cooperativity in the binding of surfactant, the description of different ways of packing the surfactant, and reversibility in compaction and phase separation, as obtained in working on mixtures of cationic and anionic surfactant systems.[29] Macroscopic phase separation of DNA and cationic surfactant out from water can be described in terms of replacing the monovalent counterions with highly charged surfactant aggregates, which both renders the complex less polar and reduces the entropic driving force for dissolution. The fact that these complexes become nonpolar has been verified in observations of solubility in certain nonpolar solvents including octanol and decane;[30−32] a similar behavior has also been demonstrated for other mixtures of a polyelectrolyte and an oppositely charged surfactant.[33] In this study we have been interested in a detailed investigation of a DNA−cationic surfactant system in a mixture of water and a nonpolar solvent.

In investigating these systems, we have on the basis of the principles of Piculell et al.[8] developed a related approach. Thus, we have prepared the complex salt of DNA and cationic surfactant, removing the inorganic counterions, and mixed it with two solvents, water, and a nonpolar "oil". In this first study we have chosen as the "oil" decanol, which is only very slightly

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miscible with water. Here we present an investigation over all ranges of composition of the phase behavior and phase structures as well as some other pertinent observations. As will be seen, the "DNA-based surfactant" can mix oil in water in a somewhat analogous way as classical surfactants, a phenomenon widely investigated in the field of microemulsions.[34−37] For the present case, the homogeneous phases corresponding to the mixing of similar volumes of oil and water are liquid crystalline, since the surfactant films formed by the DNA-based surfactant are quite rigid.

Materials and Methods

Materials. Deoxyribonucleic acid sodium salt from herring testes (Sigma) was used as received. Herring testes DNA is highly polydisperse with an average molar mass of 700 bp, as estimated by electrophoresis (0.8 wt % agarose gel in TBE). The concentration of DNA was determined by a spectroscopic method using the molar extinction coefficient $\epsilon_{260} = 6600$ L mol^{-1} cm^{-1} at 260 nm. The A_{260}/A_{280} ratio of DNA solutions was found to be 1.9 suggesting that DNA was free of proteins.[38]

Sodium bromide (Riedel-deHaen extra pure quality) was used as received. Dodecyltrimethylammonium bromide (DTAB) was obtained from Tokyo Kasei Kogyo Co., Ltd and used as received. Decan-1-ol especially pure, BDH Chemicals Ltd., was used as received. The water used was from a Milli-Q filtration system (Millipore).

D_2O was obtained from Dr. Glaser AG, Basel.

Preparation of the Complex Salt DNA—DTA. DNA solutions were prepared by weighing the desired amount and dissolving it in 10 mM NaBr. The pH of all solutions was 7 ± 0.2. DNA−surfactant stoichiometric aggregates were prepared my mixing equal amount of moles of negative charges of DNA and positive charges of DTAB (200 mL of 5 mM solutions) under stirring. Under these conditions, the counterion release should be maximal and nearly complete.[39] The precipitate was equilibrated in solution for 48 h. It was then separated from the aqueous phase by filtration (Duran, pore size 12 μm) at reduced pressure and washed extensively with Millipore water. The macromolecular complex salt (DNA−DTA) was dried for 3 days in a DW6−85 freeze-dryer.

Sample Preparation. Appropriate amounts of the DNA−DTA complex, decanol, and water (for the NMR experiments, heavy water was used) into 8 mm (i.d.) glass tubes, which were flame-sealed immediately. First the components were mixed with a Vortex vibrator; the mixing was continued in a centrifuge over a few days at 4000 rpm and 40 °C. The tubes were turned end over end every 15 min. The samples were left to equilibrate in a temperature-controlled room at 25 ± 0.5 °C for 2 months. After 6 months, five samples with different $\phi_{DNA-DTA}/\phi_{dec}$ ratios in region 4 in the phase diagram (Figure 1) were investigated and produced the same results.

Methods. The samples were investigated by visual inspection in normal light and between crossed polarizers to detect anisotropic (birefrigent) and isotropic (nonbirefrigent) phases, as well as to distinguish between one-phase (transparent) and two-phase (nontransparent) regions.

^2H NMR (D_2O). The NMR spectrum from the deuterated water is dominated by the interaction of the deuteron quadrupole moment with the electric field gradients at the nucleus. In anisotropic liquid crystalline (LC) samples, the quadrupole interaction generates a NMR spectrum with two peaks of equal intensity, while for an isotropic LC phase or a solution a single sharp peak is obtained because of the rapid and isotropic molecular motions which average the interactions to zero.[40,41]

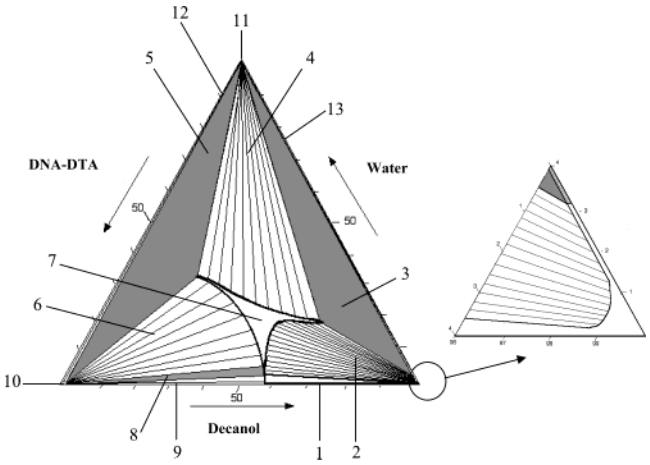

Figure 1. Phase diagram of the DNA−DTA (1:1) complex/decanol/water system at 25°C. The inset is an expansion of the decanol rich corner. Key: (1) one-phase region, isotropic decanolic solution; (2) two-phase region, isotropic solution + liquid crystal (LC) region; (3) three-phase region, aqueous solution + LC + isotropic solution; (4) two-phase region, aqueous solution + LC; (5) three-phase region, aqueous solution + LC + DNA−DTA; (6) two-phase region, LC + DNA−DTA; (7) LC region; (8) three-phase region, LC + isotropic solution + DNA−DTA; (9) two-phase region, isotropic solution + DNA−DTA; (10) one-phase region, DNA−DTA complex with a small amount of adsorbed water and decanol; (11) one-phase region, aqueous solution with a very small amount of dissolved decanol; (12) two-phase region, DNA−DTA + aqueous solution; (13) two-phase region, aqueous solution + isotropic decanolic solution.

The deuterium-NMR technique is thus applicable in phase behavior studies of amphiphile−water systems.[42] The experiments were performed at a frequency of 15.371 MHz on a Bruker DMX 100 spectrometer equipped with 100 MHz (2.3 T) wide-bore superconducting magnet. The temperature was controlled with an air flow through the sample holder.

Small-Angle X-ray Scattering (SAXS). The measurements were performed on a Kratky compact small-angle system equipped with a position sensitive detector (OED 50 M from M. Braun, Graz, Austria) containing 1024 channels with 53.0 μm width. Cu Kα radiation of wavelength 1.542 Å was provided by a Seifert ID300 X-ray generator operating at 50 kV and 40 mA. A 10 μm thick nickel filter was used to remove the Kβ radiation, and a 1.55 mm tungsten filter was used to protect the detector from the primary beam. The sample-to-detector distance was 277 mm. The volume between the sample and the detector was kept under vacuum during data collection in order to minimize the background scattering. The temperature was kept constant at 25 °C (±0.1 °C) with a Peltier element.

NMR Self-Diffusion. The diffusion experiment is performed by using two pulsed field gradients (PFGs) in the dephasing and refocusing periods of a spin echo (SE), $90°-\tau-180°-\tau-$echo, or a stimulated echo (STE), $90°-\tau_1-90°-\tau_2-90°-\tau_1-$echo, pulse sequence. A description of the method can be found elsewhere.[43,44]

The experiments were performed on a 200 MHz Bruker DMX spectrometer equipped with a Bruker DIFF-25 gradient probe driven by a Bruker BAFPA-40 unit. The temperature was 25 °C. The first set of diffusion experiments was performed with the STE technique; the gradient pulse length δ was 0.5−2 ms. The separation between gradient pulses is $\Delta = \tau_1 + \tau_2$, and the effective diffusion time is $t = \Delta - \delta/3$. In the experiments Δ varied between 20 and 200 ms. Hahn spin echos were used in the second set of experiments where δ was 0.5−1 ms and Δ was 70 ms.

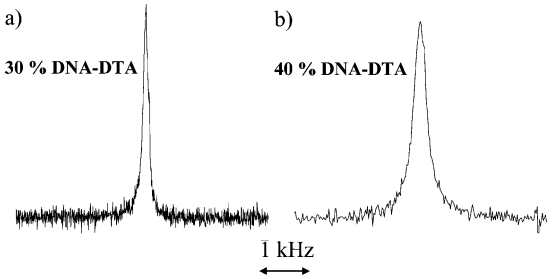

Figure 2. ^{2}H NMR spectra of binary mixtures of decanol and water: (a) 30 wt % DNA−DTA and (b) 40 wt % DNA−DTA.

Results

General Outline of Phase Diagram. The phase diagram of the ternary system DNA−DTA/decanol/water at 25 °C is presented in Figure 1. Sample compositions are given in weight percent of the components.

The phase diagram is based on the analyses of nearly 150 samples. First the samples were investigated visually in normal light and between cross polarizers to detect anisotropic phases. The samples were then studied by ^{2}H NMR, and it was established whether a certain sample consisted of a single homogeneous phase, of two phases, or of three phases. The structure of the various phases was investigated by SAXS and ^{2}H NMR. The isotropic solution of the DNA−DTA complex in decanol was studied by diffusion NMR.

There are 13 regions in this phase diagram: (1) one-phase region, isotropic decanolic solution; (2) two-phase region, isotropic solution + liquid crystalline (LC) region; (3) three-phase region, aqueous solution + LC + isotropic solution; (4) two-phase region, aqueous solution + LC; (5) three-phase region, aqueous solution + LC + DNA−DTA; (6) two-phase region, LC + DNA−DTA; (7) LC region; (8) three-phase region, LC + isotropic solution + DNA−DTA; (9) two-phase region, isotropic solution + DNA−DTA; (10) one-phase region, DNA−DTA complex with a small amount of adsorbed water and decanol; (11) one-phase region, water with a very small amount of dissolved decanol; (12) two-phase region, DNA−DTA + aqueous solution; (13) two-phase region, aqueous solution + isotropic decanolic solution.

Isotropic Phase Region (Area 1 in Figure 1). The solubility of the DNA−DTA 1:1 stoichiometric complex in decanol is about 42 wt %. The solutions are transparent, nonbirefrigent and strongly adhesive. The solutions are highly viscous for high contents of the DNA−DTA complex and show rubberlike mechanical behavior. In Figure 2 is presented the ^{2}H NMR line shape for samples in this region. A singlet is observed as expected for isotropic phases. The peak width increases with DNA−DTA content. This suggests that, for higher DNA−DTA content, a more restricted viscous environment is obtained which allows for rapid quadrupole relaxation.

In Figure 3i, are presented the SAXS spectra of the isotropic solution of complex and decanol with increasing DNA−DTA weight fraction. The SAXS spectra, containing only one diffraction peak, become clearer and sharper with increasing DNA−DTA content. The solution containing 40 wt % DNA−DTA is more ordered. For higher temperatures the solution becomes more fluid and less ordered. In Figure 3ii is shown that increasing temperature reduces the intensity of the Bragg peak.

The decanol self-diffusion coefficient within the isotropic DNA−DTA/decanol solution was obtained by diffusion NMR for different DNA−DTA content. In Figure 4 are presented the self-diffusion coefficients of decanol (D) as a function of the

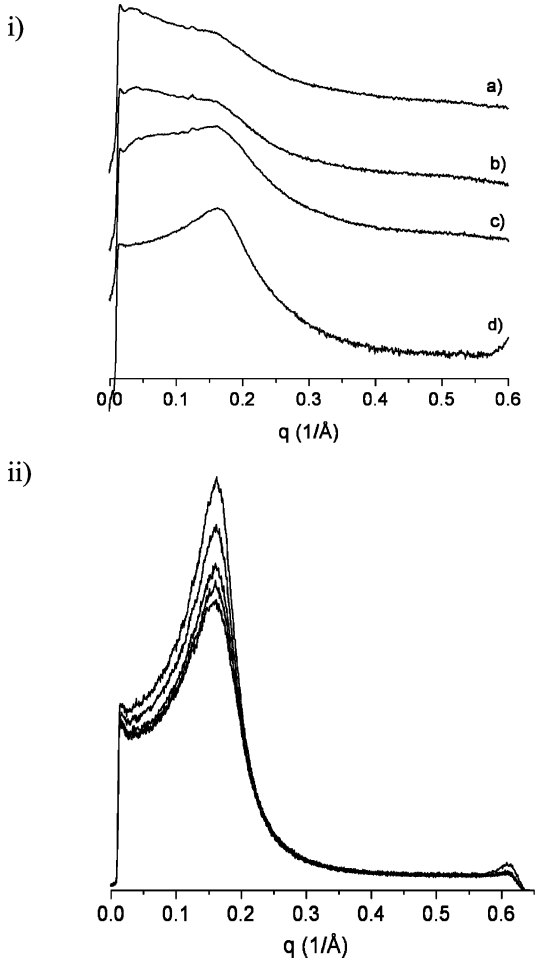

Figure 3. (i) SAXS spectra of the DNA−DTA/decanol solutions at 25 °C. DNA−DTA complex content: 15 (a), 20 (b), 30 (c), and 40 wt % (d). (ii) SAXS spectra of an isotropic solution of DNA−DTA/decanol/water (40:59.5:0.5 wt %) at different temperatures, from top to bottom, 25, 35, 45, 55, and 65 °C.

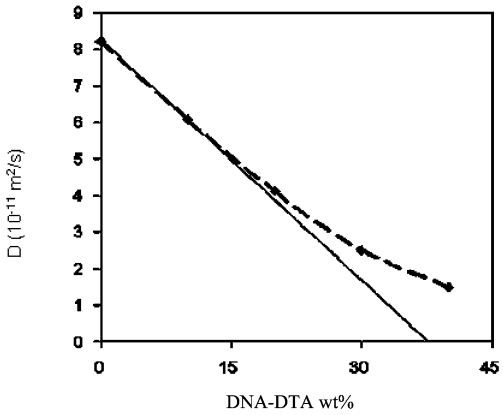

Figure 4. Decanol self-diffusion coefficient as of DNA−DTA (1:1) content in DNA−DTA/decanol isotropic solutions at 25 °C.

DNA−DTA content. The self-diffusion coefficient of the continuous phase decreases nonlinearly on increasing DNA−DTA content. The dependence of the decanol self-diffusion coefficient with increasing DNA−DTA content is consistent with an obstruction of the continuum medium due to the presence of spherical aggregates.[45,46]

Two-Phase Region: Upper Bulk "Oil"—Lower LC (Area 2 in Figure 1). In Figure 5, parts a and b, is presented the ^{2}H NMR spectra for two samples in the two-phase region indicated

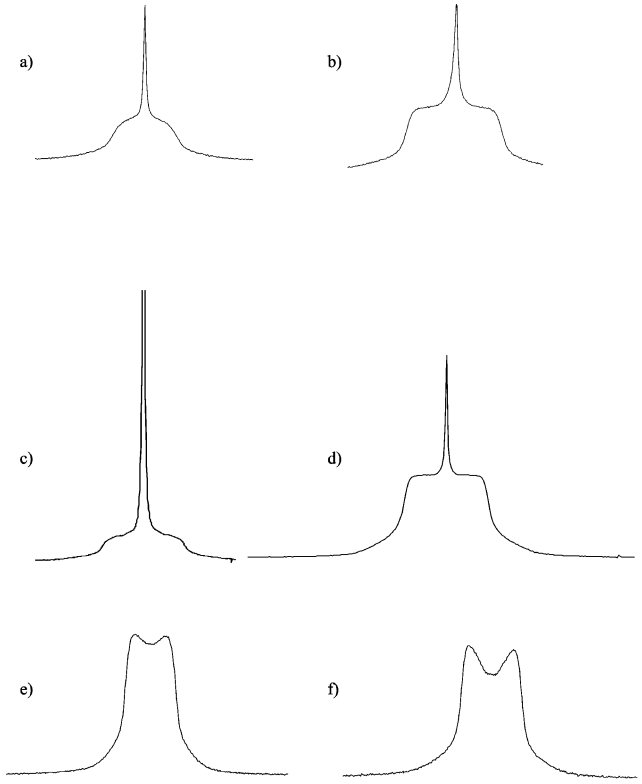

Figure 5. ^{2}H NMR spectra for samples in the two-phase upper oil−lower LC area 2 in Figure 1 at DNA−DTA/decanol/water weight compositions of: 30:60:10 (a) and 12:76:12 (b). (c) ^{2}H NMR spectrum for a sample in the three-phase upper oil−middle LC−lower water area 3 in Figure 1 at DNA−DTA/decanol/water weight composition of: 10:45:45. (d) ^{2}H NMR spectrum for a sample in the two-phase upper LC−lower water area 4 in Figure 1 at DNA−DTA/decanol/water weight composition of 23:54:23. ^{2}H NMR spectra for samples in the LC region, area 7 in Figure 1 at DNA−DTA/decanol/water weight compositions of (e) 31:50:19 and (f) 35:50:15.

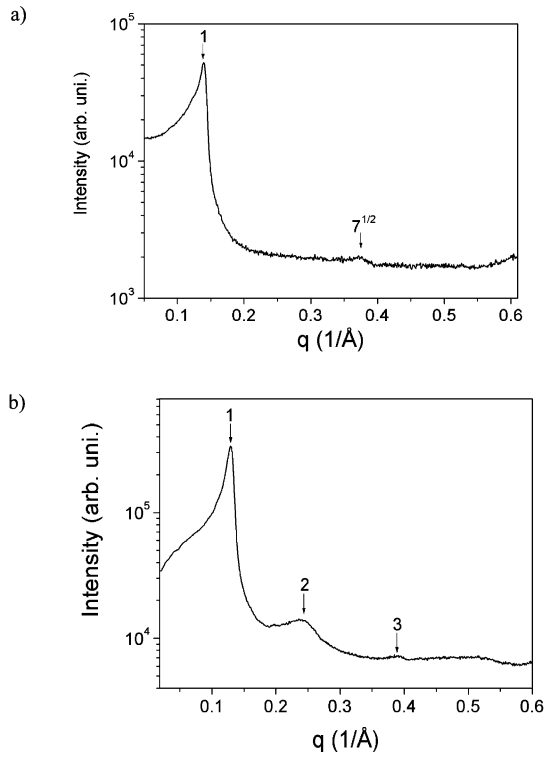

Figure 6. (a) SAXS diffraction pattern of the middle LC region in the three-phase upper oil−middle LC−lower water area 3 in Figure 1 at DNA−DTA/decanol/water weight composition of: 10:45:45. (b) SAXS diffraction pattern of the middle LC region in the three-phase upper LC−middle water−lower DNA−DTA area 5 in Figure 1 at DNA−DTA/decanol/water weight composition of: 40:17:43.

as area 2 in the phase diagram. The spectra consist of a singlet and a broad splitting that are typical for two-phase systems where an isotropic phase coexists with a liquid crystalline anisotropic phase. The SAXS spectra of the LC region are inconclusive. Only one strong diffraction peak was observed for all the samples tested in this area.

Three-Phase Region: Upper "Oil"—Middle LC—Lower Water (Area 3 in Figure 1). One of the ^{2}H NMR spectra of the samples in this region is presented in Figure 5c). The spectrum indicates, as in the previous region, a coexistence of isotropic and anisotropic phases. The SAXS spectrum obtained for the middle LC region is presented in Figure 6a; it is similar to the one obtained for the LC region described in area 2 of the phase diagram. However, in addition to one sharp Bragg peak, a second weak peak can be detected. The relative position for these peaks is $1:\sqrt{7}$ suggesting that the middle liquid crystalline phase is a hexagonal phase.

Three-Phase Region: Upper LC—Middle Water—Lower DNA—DTA (Area 5 in Figure 1). The liquid crystalline phase in this region is clearly a lamellar phase. As shown in Figure 6b), three diffraction peaks can be resolved with relative positions of 1:2:3.

Two-Phase Region: Upper LC—Lower Water (Area 4 in Figure 1). In this two-phase region the ^{2}H NMR spectral line shape shows the singlet expected for the isotropic aqueous phase and the splitting expected for a LC region (Figure 5d). The SAXS spectra of the upper LC region vary depending on the ratio between the DNA−DTA and decanol contents, $\phi_{DNA-DTA}/\phi_{dec}$, but are independent of water content. At $\phi_{DNA-DTA}/\phi_{dec} < 1$ the SAXS spectrum shows one sharp and one weak diffraction peak in the relative positions $1:\sqrt{7}$ (Figure 7a) suggesting the presence of a hexagonal phase. At $\phi_{DNA-DTA}/\phi_{dec} > 1$ all different compositions show four diffraction peaks in relative positions 1:2:3:4 (Figure 7c) suggesting the presence of a lamellar phase. Increasing decanol content induces a lamellar-to-hexagonal phase transition. In area 4 of the phase diagram, the LC phases are in equilibrium with the aqueous phase. When one goes from the lamellar to the hexagonal phase there is a region where both LC phases must coexist. At $\phi_{DNA-DTA}/\phi_{dec} = 1$ are observed four diffraction peaks in the relative positions $1:\sqrt{3}$:2:3 (Figure 7b). Although perturbations in diffraction patterns can indicate various things, the presence of a peak in the relative position of $\sqrt{3}$ (characteristic for hexagonal phases) for two different samples along the same tieline most likely reflects the coexistence region between the lamellar and the hexagonal phase.

Discussion

The primary objective of this work is to investigate and understand the self-assembly behavior of a cationic surfactant−DNA complex in mixtures of oil and water. In the study of phase behavior, the components should be totally mixed and equilibrium achieved. The phase behavior study of the ternary mixture DNA−DTA/decanol/water can be difficult because DNA is a high molecular weight polymer and therefore has low solubility. The mixture of the DNA−DTA complex in oil and

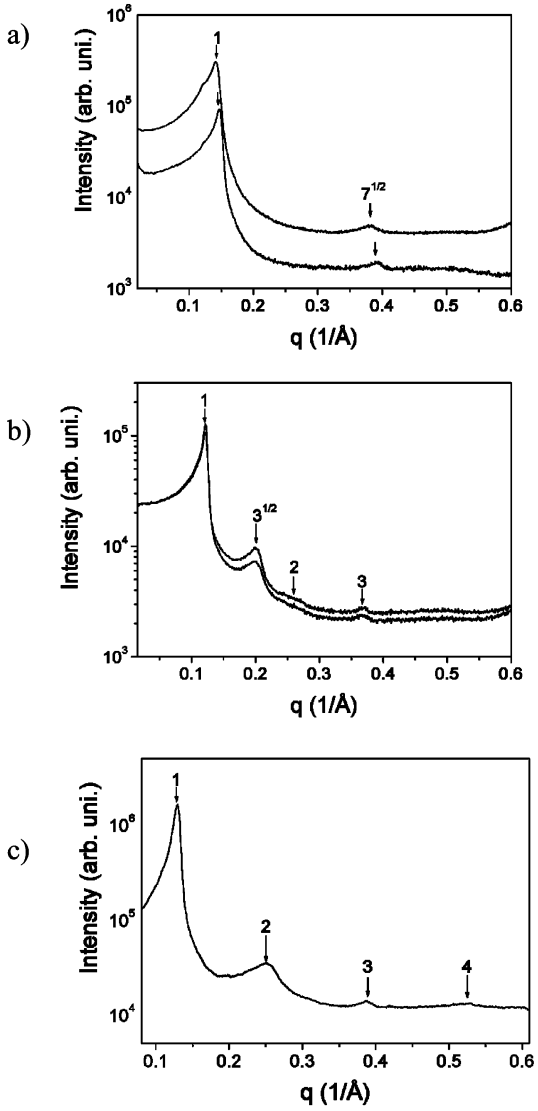

Figure 7. SAXS diffraction patterns for samples in the two-phase upper LC−lower water area 4 in Figure 1 at DNA−DTA/decanol/water weight composition of (a) upper line 29:43:28, lower line 23:54:23; (b) upper line 25:25:50, lower line 10:10:80; and (c) 40:20:40.

water yields viscous solutions and equilibrium takes a long time to be established. When the solvent contents are higher, there is a faster growth of the microcrystallites and the equilibrium is easier to achieve.

Different liquid crystalline phases are observed when water is added to a DNA−DTA/decanol solution. In the three-phase triangle with high decanol content (area 3 in the phase diagram in Figure 1) the liquid crystalline phase appears to be of the hexagonal type. Hexagonal phases are viscous phases. In this system where the solutions are already viscous, the study of the hexagonal phase can be problematic. In the SAXS spectrum, the second diffraction peak typical of a hexagonal arrangement ($\sqrt{3}$) cannot be seen. Nevertheless, the fact that two diffraction peaks with a relative position of 1:$\sqrt{7}$ can be detected is an indication of a hexagonal structure. The same kind of structure is obtained in the two-phase area 4 in the phase diagram for high decanol content. Given that this hexagonal arrangement is observed when the oil content is increased, it is reasonable to assume that the hexagonal phase observed for high oil content is of the reverse type.[47,48] This arrangement would consist of infinitely long surfactant cylinders decorating the DNA rods

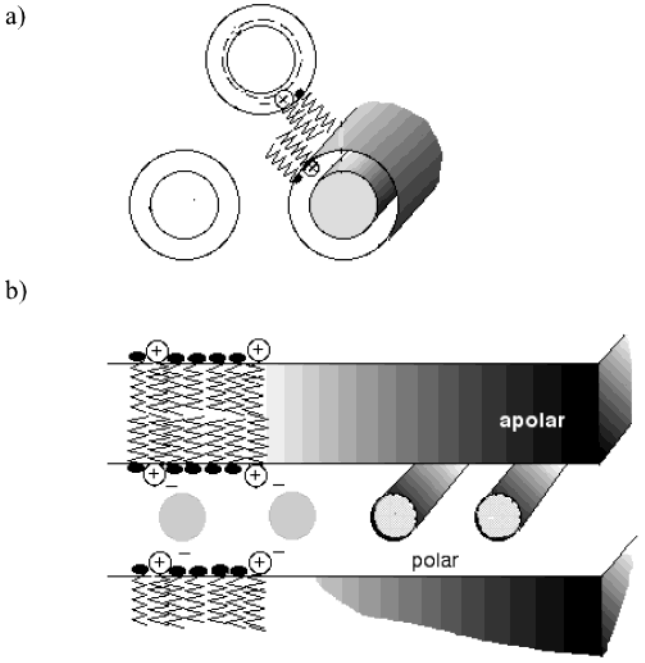

Figure 8. DNA−DTA/decanol/water structural model: (a) reversed hexagonal and (b) lamellar phases.

with the hydrophobic tails pointing toward the oil (Figure 8a). The repeat distance between the rods can be obtained from the first diffraction peak in the SAXS spectra, and it is calculated to be around 52 Å. Considering the length of an extended DTA molecule to be around 16 Å[47] and the radius of a DNA molecule to be 10 Å, a hexagonal lattice with a 52 Å distance between rods could accommodate the DNA and DTA components. When water is added to the hexagonal phase, a shift to smaller q values on the SAXS spectra is observed. Water is placed between the DNA charged groups and the surfactant headgroups and the spacing between rods is increasing with water content.

For the corner with low decanol content, lamellar phases are encountered both in the three-phase area 5 in the phase diagram and in the two-phase area 4 in the phase diagram. Lamellar phases in aqueous systems of DNA and amphiphiles have been found for different kinds of lipids and surfactants,[13,49] and they consist of surfactant bilayers intercalated with DNA rods as represented in Figure 8b. The bilayer thickness of a surfactant can be estimated as $\sim 1.6 l_{max}$,[47] where l_{max} is the length of an extended surfactant molecule. Considering a DTA molecule to be 16 Å long and DNA having a diameter of 20 Å, a bilayer of surfactant with incorporated DNA should have a thickness of around 46 Å. From the SAXS data, the bilayer thickness is measured to be 49 Å, which agrees well with the calculated value.

The liquid crystalline region (LC) is located in the center of the phase diagram (area 7 in Figure 1). The samples in this area have a solidlike morphology and show strong optical birefringence. In parts e and f of Figure 5, two ^{2}H NMR spectra in this region are shown. The splitting observed clearly indicates the presence of only liquid crystalline phases. The qualitative result obtained from SAXS data is that the LC region consists of two phases: hexagonal phase (at $\phi_{DNA-DTA}/\phi_{dec} < 1$) and lamellar phase (at $\phi_{DNA-DTA}/\phi_{dec} > 1$). In Figure 9 is presented an expansion of this central region of the phase diagram.

Reversed hexagonal phases,[14] lamellar phases,[13] and normal hexagonal phases[27] have been found for DNA−amphiphile aggregates in aqueous systems. DNA is highly negatively

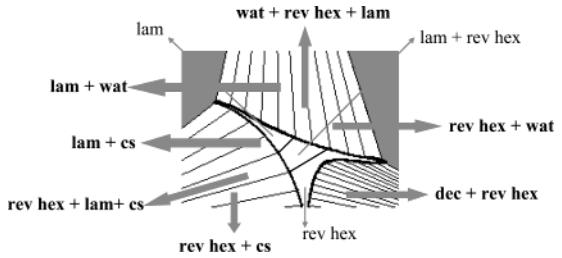

Figure 9. Expansion of the central area of the DNA−DTA/decanol/water phase diagram at 25 °C (Figure 1): lam, lamellar phase; wat, water; rev hex, reversed hexagonal phase; cs, complex salt DNA−DTA; dec, decanol. For the decanol-rich corner, reversed hexagonal phases (rev hex) are found in equilibrium with water or decanol. For lower oil contents a lamellar phase (lam) is present instead.

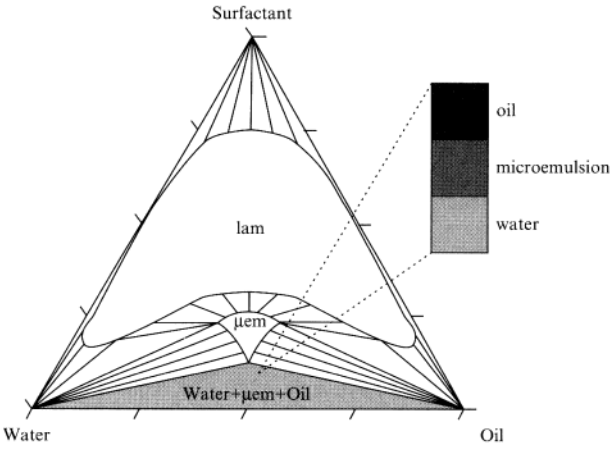

Figure 10. Phase behavior under balanced conditions of a surfactant−water−oil system. μem denotes the microemulsion region and lam the lamellar phase region. Figure modified from ref 50.

charged, so one expects a strong electrostatic interaction with cationic species such as alkyltrimethylammonium surfactants. The final supramolecular structure of the DNA−surfactant aggregate formed is strongly determined by the structure adopted by the surfactant itself which is a reflection of the balance between its hydrophobicity and hydrophilicity. A common measure of this balance is the surfactant parameter that is the ratio between the volume of the hydrophobic surfactant tails and volume of the surfactant headgroup in terms of electrostatic repulsions.[48] When the ratio between the hydrophobic tails and the hydrophilic headgroups is around 1, lamellar phases are preferred by the surfactant. When the hydrophobic part is bigger, structures of the reversed type are favored like reversed hexagonal and reversed micellar phases.

In this study, an apolar solvent is added to the system of DNA−DTA with water, making the ternary mixture a homogeneous liquid crystalline phase of the reversed hexagonal type for higher oil contents or lamellar type for lower contents of oil.

There are interesting analogies and differences between the DNA-based surfactant system and other types of ternary surfactant systems, in particular surfactant−oil−water systems in general and ionic surfactant−long-chain alcohol−water systems. In microemulsions, a surfactant achieves a mixing of oil and water into a thermodynamically stable isotropic solution. An illustration for a so-called balanced surfactant is given in Figure 10.[50] At similar amounts of oil and water there is, depending on surfactant concentration, a formation of a microemulsion or a lamellar liquid crystalline phase. Microemulsions are favored for more flexible surfactant films where rigid films favor the lamellar phase (or other liquid crystalline phases);[34] in the latter case, the microemulsion may not appear. The general similarity between the phase diagram of our DNA-based surfactant (Figure 1) and that of a classical microemulsion system is evident. In our system, the surfactant films are expected to be rigid; therefore, liquid crystalline phases are favored.

Several studies have been reported on simple ionic surfactant−long-chain alcohol−water systems.[51−53] They show in the middle of the phase diagram a large region of lamellar phase. On increasing the decanol content there is, as in our system and in agreement with packing considerations, a transition to a reversed hexagonal phase.

Summary

The cationic surfactant with DNA as counterion, the "complex salt", can mix one polar and one nonpolar solvent, which are otherwise immiscible, into a homogeneous phase. In the present case of dodecyltrimethylammonium and a relatively short DNA (700 bp), we have found evidence for two homogeneous phases, both liquid crystalline in nature, one of the reversed hexagonal type and one lamellar phase. The liquid crystalline (LC) region is located in the center of the phase diagram. Moving up in the diagram by increasing water content does not induce any additional phase change, but a two-phase region is obtained with a lower water phase and an upper LC region. Going to the right in the diagram toward increasing oil content a three phase region is encountered with upper oil, middle LC reversed hexagonal phase, and lower water phase. As the oil content is decreased in the mixtures, the reversed hexagonal phase evolves into a lamellar phase. The study of the different phases was facilitated in the two-phase region with upper LC and lower water phase (area 4 in Figure 1) due to the higher content of solvents. In this area, four diffraction peaks were detected for the lamellar phase when the ratio between the DNA−DTA complex and decanol contents was higher than 1. When the ratio of complex and decanol contents equals 1, it appears that the coexistence region between the hexagonal and the lamellar phases is observed. For decanol contents higher than the complex content, a reversed hexagonal phase is observed.

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