

Phase Behavior of Aqueous Solutions of a Dimeric Surfactant

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The effect of salt (KBr) additions on the behavior of the dimeric surfactant 12-2-12 (ethanediyl-1,2-bis(dodecyldimethylammonium bromide)) has been investigated using small angle neutron scattering (SANS) and dynamic light scattering (DLS). The effect of temperature and additions of DTAB (dodecyltrimethylammonium bromide, "monomer" of 12-2-12) has also been investigated. Upon increasing salt content, the partial phase diagram of the water/salt/12-2-12 system shows the sequence wormlike micelle phase, lamellar phase, and biphasic systems with a salt-rich, surfactant-poor lower phase and a salt-poor lamellar upper phase. This study is the first one reporting a salt-induced transition between a wormlike micelle phase and a lamellar phase. Additions of DTAB at low mole fraction (<5%) produced no significant changes of the phase diagram. The scattering curves for the lamellar phase show a maximum which becomes extremely sharp as the temperature is decreased and reveals the occurrence of L_α to L_β phase transition at around 30 °C. In addition, the SANS data reveal the presence of highly curved defects. The analysis of the SANS data suggests that above 30 °C the lamellar phase is constituted by perforated lamellae, with the water-filled holes (defects). The existence of this phase was predicted theoretically as an intermediate one, together with branched wormlike micelles, between lamellar and wormlike micelle phases. DLS was used to determine the viscoelastic relaxation time and amplitude of the wormlike micelle phase. The increase of amplitude at the approach of the isotropic-to-lamellar phase transition suggests increasing intermicellar interactions that may be responsible for the formation of branched micelles.

Introduction

The phase behavior of aqueous solutions of ionic surfactants is generally assumed to be mainly controlled by the surfactant packing parameter $p = V/la$, where V is the effective hydrophobic chain volume, a the area per polar head, and l the surfactant alkyl chain length. For single chain surface active molecules such as sodium dodecyl sulfate (SDS) or cetyltrimethylammonium bromide (CTAB), p is close to 0.4, favoring spherical or cylindrical micelles at high dilution. Lyotropic liquid crystals appear at high concentration. In particular the lamellar liquid crystals form at very high concentration and cannot be swollen with pure water, unless a cosurfactant is added. The role of the latter is either to reduce the area a^1 or to reduce the bending stiffness of each layer which enhances entropic repulsion between layers.²

For double chain ionic surfactants like the didodecyldimethylammonium bromide (DDAB), the packing parameter p is around 1, allowing for the formation of bilayers at high dilutions. The binary phase diagram of such systems has been extensively studied by Dubois and Zemb, and four microstructures have been identified by their scattering properties in the dilute range.³ At temperatures larger than the Krafft temperature the following sequence of phases was observed upon increasing surfactant concentration: an isotropic micellar phase, a metastable L_3 sponge phase, a dispersion of pure crystallites of lamellar phase in an isotropic phase, and eventually a pure lamellar phase L_α . Below the chain

melting temperature, the L_α phase transforms in a L_β phase characterized by bilayers whose interior is made of crystallized hydrocarbon chains. In the presence of salt the L_3 phase is replaced by a biphasic system whose bimodal tie lines correspond to equilibrium between very diluted isotropic dispersions and a spherulite structure.

Recently, there has been much interest in dimeric (gemini) surfactants in which two quaternary ammonium moieties ($C_mH_{2m+1}(CH_3)_2N^+Br^-$) are linked at the level of the head groups by a hydrocarbon spacer (C_sH_{2s}).^{4,5}

The properties of these systems cannot be described only in terms of surfactant packing parameter because the connection between polar heads can modify both the spontaneous curvature and the bending modulus. In fact, for a given hydrophobic chain, the structure in aqueous solutions depends strongly on the spacer. As an example, it was found for the series with $m = 12$ and $2 \leq s \leq 16$ (referred to as 12- s -12), that the surfactants aggregate into spherical micelles, cylindrical micelles, or vesicles, depending on the value of s . Measurements of the surface area a at the air/water interface show that this parameter varies in a non-monotonic manner. It increases rapidly for short spacers, reaches a maximum for medium spacers (containing 10 to 12 methylene groups), and decreases for even larger spacers. As for the two other parameters involved in the shape parameter, l is supposed to remain unchanged as the spacer carbon number is increased and v is expected to have a slow monotonic increase, except for very long spacers ($s \geq 14$). Therefore, it seems that changes in the aggregate morphology for dimeric surfactants are mainly related to the influence of the spacer on

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(1) Israelachvili, J.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1525.

(2) Di Meglio, J. M.; Dvolaitzky, M.; Taupin, C. *J. Phys. Chem.* **1985**, *89*, 871.

(3) Dubois, M.; Zemb, Th. *Langmuir* **1991**, *7*, 1352.

(4) (a) Zana, R.; Talmon, Y. *Nature* **1993**, *362*, 228. Danino, D.; Talmon, Y.; Zana, R. *Langmuir* **1995**, *11*, 1448. (b) Zana, R.; Benrraou, M.; Rueff, P. *Langmuir* **1991**, *7*, 1072. (c) Alami, E.; Beinert, G.; Marie, P.; Zana, R. *Langmuir* **1993**, *9*, 1465. (d) Alami, E.; Lévy, H.; Zana, R.; Skoulios, A. *Langmuir* **1993**, *9*, 940.

(5) Kern, F.; Lequeux, F.; Zana, R.; Candau, S. J. *Langmuir* **1994**, *10*, 1714.

the surface area. In particular small values of “ a ” imposed by short spacers lead to rather large shape parameters p , and this explains why cylindrical rather than spherical micelles form.

A detailed rheological study has been recently reported for the dimeric surfactant with $m = 12$ and $s = 2$, usually denoted 12-2-12, and that can be considered as the dimer of DTAB.⁵ This study concluded that the energy associated with the surfactant packing at the end-cap is much larger than that found for single chain surfactant with the same counterion, like for instance CTAB. In the absence of salt, this end-cap energy is partly counterbalanced by the electrostatic energy, a situation which leads to the micellar growth process described by Mackintosh et al.⁶ The screening of the electrostatic interactions by addition of salt should promote a change of morphology of the aggregates, because of the unbalanced end-cap energy.

The above results led us to study the effect of salt on the properties of aqueous 12-2-12 solutions. A partial phase diagram surfactant concentration–salt concentration has been determined at a temperature $T = 30$ °C. Three main domains have been delimited: a pure lamellar phase L_{∞} , a biphasic domain made of a lamellar phase in equilibrium with an isotropic solution containing essentially water, and an isotropic phase of cylindrical micelles. The lamellar phase has been characterized through optical observations and small angle neutron scattering (SANS). The effect of the surfactant concentration and temperature on the scattering curves has been studied. The structural properties of the cylindrical micelles were investigated by means of SANS.

We have also studied the effect of salt on the structure of mixed 12-2-12/DTAB (dodecyltrimethylammonium bromide) micelles at low DTAB content (mole fraction 0–0.05) calculated using equivalent per liter for 12-2-12. The intermolecular structure is characterized by SANS experiments while dynamic light scattering (DLS) measurements provide information on the viscoelastic behavior which is mainly controlled by the mean micellar length. Recall that mixed micellar solutions of 12-2-12 and of DTAB have been recently studied by SANS using a contrast variation method, in order to obtain information on the localization of DTAB in the wormlike micelles.⁷ The two surfactants were found to mix intimately, with no evidence for a preferential localization of the spherical micelles-forming DTAB at the hemispherical end-caps of the threadlike micelles. Cryo transmission electron microscopy (cryo-TEM) experiments have revealed that the threadlike micelles are transformed into spherical ones in the range 0.14–0.30 DTAB mole fraction.^{4a} This indicates that the incorporation of DTAB produces a decrease of the mean length of the micelles which can result only from a decrease of the end-cap energy.

Also a recent SANS study of similar dimeric surfactants with $m = 10$ and $s = 2-6$ showed that the end-cap energy decreases as s increases.⁸

II. Materials and Methods

The surfactant preparation, purification, and characterization have been reported.⁴ Deuterated water was used as a solvent. The samples were prepared by weighing. The density of the surfactant is about 1. The surfactant volume fractions Φ (v/v) have been determined from the concentrations (w/w).

(6) (a) Safran, S.; Pincus, P.; Cates, M. E.; Mackintosh, F. *J. Phys. (Paris)* **1990**, *51*, 503. (b) Mackintosh, F.; Safran, S.; Pincus, P. *Europhys. Lett.* **1990**, *12*, 697.

(7) Schosseler, F.; Anthony, O.; Beinert, G.; Zana, R. *Langmuir* **1995**, *11*, 3347.

(8) Hirata, H.; Hattori, N.; Ishida, M.; Okabayashi, H.; Frusuka, M.; Zana, R. *J. Phys. Chem.* **1995**, *99*, 1778.

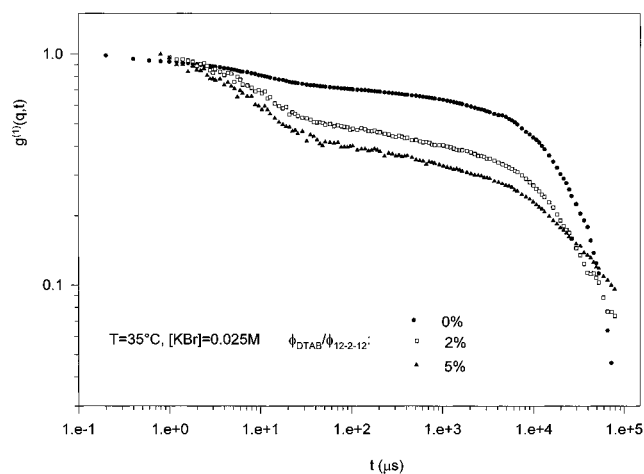


Figure 1. Normalized autocorrelation functions of the electric field for isotropic solutions at a surfactant volume fraction of 5.5% and for different ratios $C_{DTAB}/C_{12-2-12}$.

In the biphasic systems, the KBr content in the dilute phase was measured by conductometry by means of a calibration curve. The KBr concentration of the lamellar phase was deduced from the salt content of the dilute phase and the phase volumes.

The optical observations were carried out by using an analyzer–polarizer microscope, Jena Telaval 3.

Light Scattering. In DLS experiments, one measures the normalized time autocorrelation function $g^{(2)}(q, t)$ of the scattered intensity

$$g^{(2)}(q, t) = \frac{\langle I^*(q, 0) I(q, t) \rangle}{\langle I(q, 0) \rangle^2}$$

The latter can be expressed in terms of the field autocorrelation function or equivalently the autocorrelation function of concentration fluctuations $g^{(1)}(q, t)$ through

$$g^{(2)}(q, t) = 1 + \beta |g^{(1)}(q, t)|^2$$

β is a coherence factor which in our experiments is equal to 0.85–0.90. The experiments were performed by means of a spectrometer equipped with an argon ion laser ($\lambda_0 = 488$ nm) and an ALV 5000 correlator.

Figure 1 shows log–log plots of $g^{(1)}(q, t)$ for a solution of 12-2-12 with $\Phi = 5.5\%$ in 0.025 M aqueous KBr for different DTAB contents and at $T = 35$ °C. For the three systems, the autocorrelation function of scattered field can be described by a sum of two relaxations widely separated in time. The fast mode is a diffusive one, with a characteristic time varying as q^{-2} , whereas the slow mode is of viscoelastic nature and is independent of q .

The following procedure was used to analyze the data. We first plot in semilog coordinates the function $g^{(1)}(q, t)$. In the long time scale one observes an asymptotic linear behavior. From the slope and the intercept of the asymptote, one determines the slow (viscoelastic) relaxation time T_L and the corresponding relative amplitude A_L .

Alternately, T_L , A_L , and the short diffusive time were determined by using the Contin method based on the Laplace transform of $g^{(1)}(q, t)$. The two methods yielded the same values for the relaxation times.

SANS. For the biphasic systems, the two phases of the samples obtained after sedimentation were put into separate scattering cells, having a thickness of 1 mm. SANS experiments were carried out on a PAXE spectrometer in Laboratory Léon Brillouin at Saclay.

The incident wavelength was 10 or 12 Å depending on the set of experiments. For a given wavelength, the range of the amplitude of the transfer vector q was selected by changing the detector distance, in order to get the configuration allowing a good characterization of the scattering peaks. The range is typically $0.01 \leq q(\text{Å}^{-1}) \leq 0.1$ or $0.02 \leq q \leq 0.2$. The data are put on an absolute scale following the standard procedures.

Intensities relative to the incoherent scattering of H_2O in a cell with a path of 1 mm are obtained from the measured

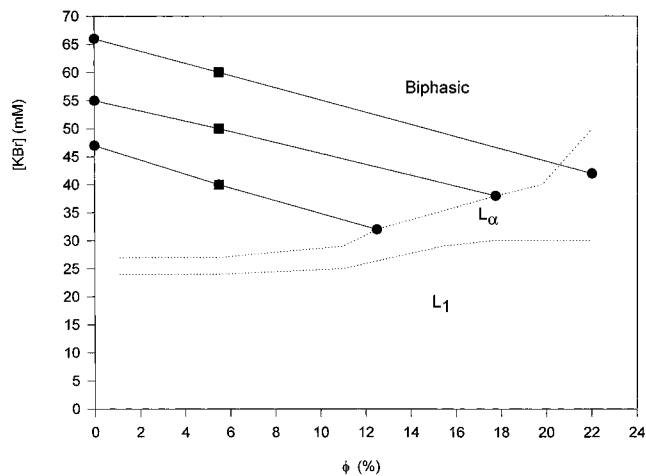


Figure 2. Partial phase diagram of the 12-2-12/KBr system at $T = 30\text{ }^\circ\text{C}$. The three tie lines represented connect points (●) representative of the compositions of the two phases obtained after demixing of systems with initial composition given by (■).

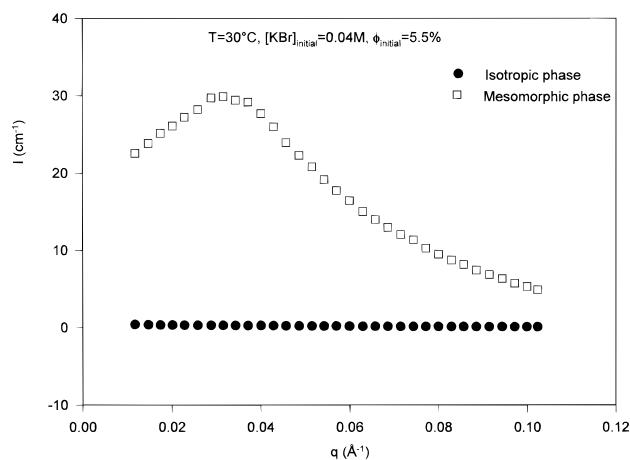


Figure 3. SANS spectra of the isotropic and of the mesomorphic phases obtained from the demixing of a system with initial volume fraction $\Phi = 5.5\%$ and initial salt content $[\text{KBr}] = 0.04\text{ M}$.

intensities after subtraction of the solvent and empty cell contributions.

III. Experimental Results

1. Partial Phase Diagram. The partial phase diagram of the KBr/12-2-12/ D_2O system obtained by visual inspection for surfactant volume fractions varying from 0.2 to 20% and salt content in the range 10–70 mM KBr is shown in Figure 2.

At low salt concentrations one observes an isotropic viscous phase that does not exhibit any birefringence under flow. Intermediate salt contents correspond to a monophasic birefringent domain: the higher the surfactant concentration, the larger the range of salt concentration over which this domain exists. At higher salt concentrations, the systems separate into an isotropic lower phase and a turbid birefringent upper phase. The phase separation is rather fast due to the significant difference of density between 12-2-12 and D_2O . SANS experiments performed on the isotropic phase show that the amount of surfactant solubilized in that phase is almost negligible and that this phase is essentially an aqueous KBr solution (see Figure 3). Binodal tie lines obtained by combining conductivity experiments and measurements of phase volumes correspond to an equilibrium between a very dilute isotropic dispersion and a birefringent phase. In Table 1 are reported the compositions of the birefringent

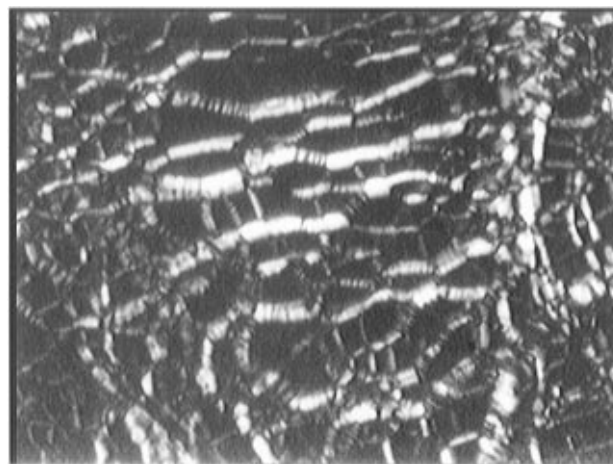


Figure 4. Photomicrograph between crossed polarizers of a mesomorphic sample with $\Phi = 12.5\%$, $T = 30\text{ }^\circ\text{C}$, and $[\text{KBr}] = 0.032\text{ M}$.

Table 1. Compositions of the Surfactant Rich Phase as a Function of the Initial Volume Fraction ϕ_{initial} and the Initial KBr Content $[\text{KBr}]_{\text{initial}}$. $T = 30\text{ }^\circ\text{C}$

ϕ_{initial} (%)	$[\text{KBr}]_{\text{initial}}$ (M)	ϕ (%)	$[\text{KBr}]$ (M)
0.22	0.04	2.53	
	0.03	1.76	
0.55	0.04	5.28	0.031
	0.03	3.16	
1.1	0.04	8.09	0.033
	0.03	5.29	
2.2	0.04	10.58	
	0.03	6.6	
5.5	0.06	22	0.042
	0.05	17.74	0.0378
	0.04	12.5	0.0317
	0.03	8.8	
8.8	0.04	15.4	
	0.07	22	
11	0.06	18.87	
	0.05	15.72	
15.4	0.04	19.49	
	0.03	15.4	0.03
17.6	0.04	18.92	
	0.03	17.6	0.03
18.7	0.04	19.09	
	0.03	18.7	0.03
19.8	0.04	19.8	0.04
	0.04	22	0.04

systems obtained for different initial surfactant concentrations.

Qualitatively, the shape of this phase diagram is quite similar to that reported by Dubois and Zemb for aqueous solutions of DDAB in the presence of KBr at $T = 25\text{ }^\circ\text{C}$.³ However, the domain of existence of the phase of cylindrical micelles is much more extended for the gemini surfactant investigated here.

Both the pure birefringent phase and the upper phase of the demixing systems show under the polarizing microscope the same characteristic features of a lamellar phase. Figure 4 shows typical textures of the birefringent phase obtained after demixing of a system with 5.5% 12-2-12 and 0.04 M KBr at $30\text{ }^\circ\text{C}$. The composition of the mesomorphic phase is 12.5% 12-2-12 and 0.032 M KBr. Contrary to the DDAB systems, one does not observe here any $[\text{L}_\alpha]$ phase, which is a dispersion of pure L_α crystallites in an isotropic phase. This phase is generally gel-like whereas the lamellar systems studied here are very fluid.

The phase diagram is sensitive to temperature. The boundary between the isotropic phase and the lamellar

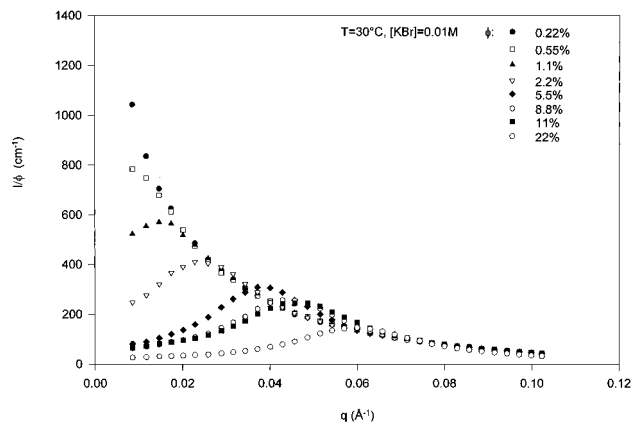


Figure 5. Scattering curves for isotropic micellar solutions with different surfactant volume fractions.

one is shifted toward higher salt concentrations upon increasing temperature. Also, the textures observed under the polarizing microscope become much more birefringent at temperatures below $\sim 30^\circ\text{C}$. As discussed below we ascribe this effect to a $L_\alpha \rightarrow L_\beta$ phase transition.

Additions of small amounts of DTAB (mole fraction $\leq 5\%$) with respect to 12-2-12 produce no significant change in the phase diagram. These systems, in the presence of increasing KBr content, exhibit the same phase sequence, that is, isotropic, lamellar, biphasic. However, higher salt contents are required to produce the transition isotropic-lamellar. In fact, adding DTAB has the same effect as increasing the temperature.

2. SANS Experiments. (a) Effect of Surfactant Concentration. A first series of experiments were performed on 12-2-12 micellar solutions in 0.01 M KBr as a function of surfactant concentration. The results are shown in Figure 5. The scattering curves exhibit a peak whose position characterized by q^* is shifted toward higher q values upon increasing concentration. The peak amplitude is a decreasing function of concentration. The variations of q^* and $I(q^*)$ are reported in log-log scales on Figure 6. The observed behavior is similar to that reported for the same system in the absence of salt:⁹ q^* is seen to scale with the surfactant volume fraction as $\phi^{1/2}$.

A second series of experiments were carried out on the lamellar systems. Figure 7 shows the scattering curves obtained from a system with an initial 12-2-12 concentration of 5.5% in the presence of 0.04 M KBr. The more concentrated system ($\Phi = 19.8\%$) does not phase separate, the totality of the sample being lamellar. The actual volume fractions of the samples and their salt contents are reported in Table 1. The scattering curves in Figure 7 exhibit a broad peak that becomes narrower for the most concentrated sample. The variations of the peak amplitude, $I(q^*)$, and of the periodicity of the lamellar phase, $d = 2\pi/q^*$, as a function of the inverse of the actual surfactant volume fraction are reported in Figure 8. The constancy of d in the low range of surfactant volume fraction is noteworthy.

(b) Effect of Temperature. The effect of temperature on the scattering behavior of the lamellar systems is illustrated in Figure 9, which shows the scattering curves obtained at temperatures varying from 24 to 45°C for lamellar samples with two different compositions (obtained respectively from an initial dispersion at $\Phi = 5.5\%$ and $[\text{KBr}] = 0.04\text{ M}$ and by forming directly a pure lamellar phase at $\Phi = 19.8\%$ and $[\text{KBr}] = 0.04\text{ M}$).

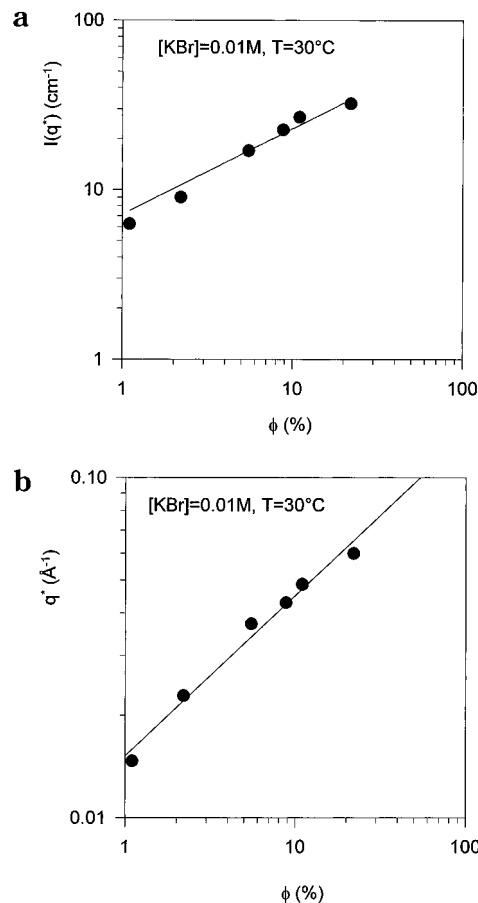


Figure 6. Effect of the surfactant volume fraction on (a) the intensity at the peak and (b) the position of the peak for micellar solutions. The straight lines represent the best fits to the data and have slopes equal respectively to (a) 0.51 and (b) 0.5.

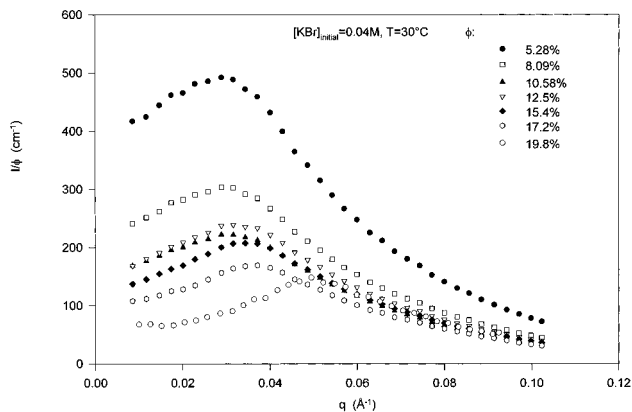


Figure 7. Scattering curves for lamellar systems with different surfactant volume fractions.

One observes a drastic change in the scattering profile from a broad peak at high temperature to a much narrower one at low temperature which suggests a reinforcement of the smectic order. For the less concentrated sample the position of the peak is shifted somewhat to lower q (Figure 9a) upon increasing T whereas q^* is independent of temperature for the sample at $\Phi = 19.8\%$ (Figure 9b). The transition occurs at about 30°C and as mentioned in the preceding paragraph is accompanied by a very large increase of birefringence. Furthermore a second order in the scattering pattern appears for the most concentrated sample at low temperature (see Figure 9b).

(c) Mixed 12-2-12/DTAB Systems. Figure 10 shows scattering curves for a system with overall initial volume fraction of 5.5% containing 2% (w/w) of DTAB. In Figure

(9) Schmitt, V.; Schosseler, F.; Lequeux, F. *Europhys. Lett.* **1995**, *30*, 31.

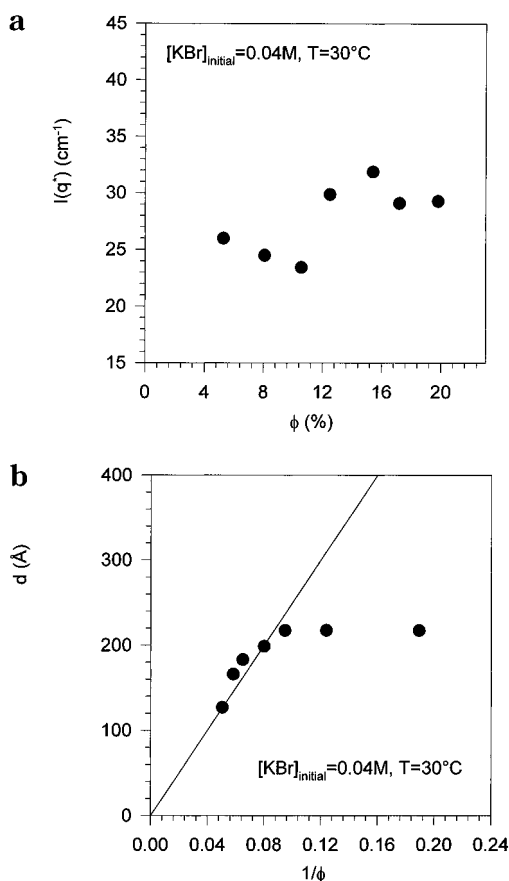


Figure 8. (a) Effect of the surfactant volume fraction on the intensity at the peak for lamellar phases. (b) Variation of the interlamellar distance with the inverse of the surfactant volume fraction. The straight line has been calculated assuming a linear swelling of defect free bilayers with thickness $\delta = 25 \text{ \AA}$.

10a are reported the curves obtained in the absence of salt and in presence of 0.01 M KBr. Under these conditions, the solution is isotropic and one observes again a peak with the same shape as for pure 12-2-12. Figure 10b shows the intensity pattern for the upper phase of the biphasic system obtained by adding 0.04 M KBr. The actual surfactant volume fraction is 12.5%. The broad peak is still quite similar to that obtained for lamellar phases of pure 12-2-12.

In fact, the addition of small amounts of DTAB does not produce any significant change of the structure factor. Figure 11 shows the comparison between scattering curves obtained at different 12-2-12/DTAB compositions in the isotropic phase. The curves are superimposed within the experimental accuracy. These results confirm the conclusions of Schosseler et al.⁷ that DTAB distributes evenly along the micelles without significant change of the intermicellar structure.

3. Viscoelasticity Measurements. The viscoelastic behavior of 12-2-12 solutions of wormlike micelles, in the absence and in the presence of small amounts of KBr, has been described in recent publications.^{5,10} Here we focus on mixed 12-2-12/DTAB micelles. Recall that the viscoelastic properties of wormlike systems are strongly dependent on the mean micellar length, that is controlled mainly by the end-cap energy. One of our aims is to investigate a possible effect of the DTAB on the latter parameter keeping in mind that generally it is drastically affected by the addition of a very small amount of cosurfactant. The viscoelastic behavior can be approached

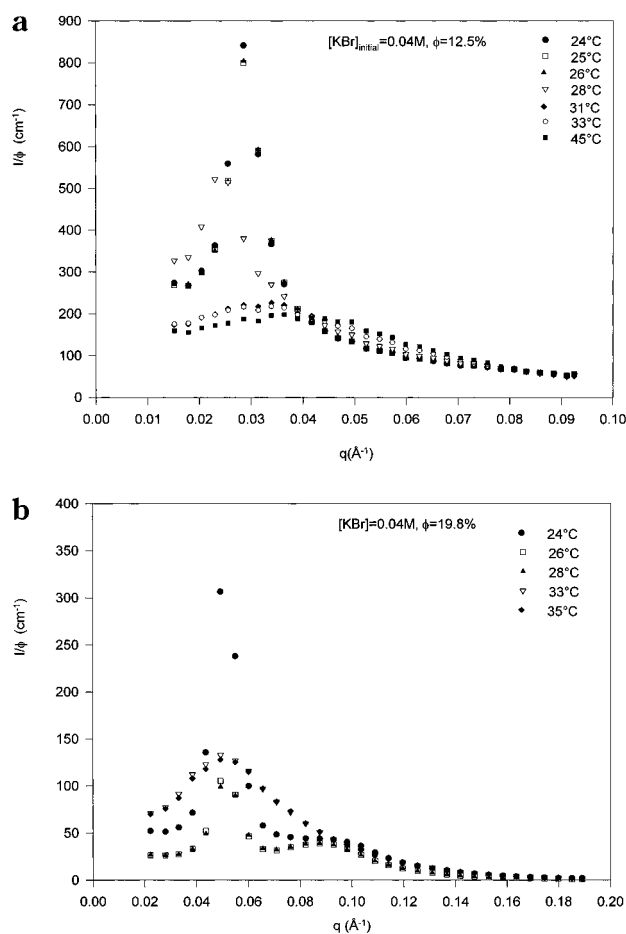


Figure 9. Effect of temperature on the scattering curves of lamellar samples: (a) Lamellar phase obtained after demixing of a system with $\Phi_{\text{initial}} = 5.5\%$ and $[\text{KBr}]_{\text{initial}} = 0.04 \text{ M}$. The actual values of Φ and $[\text{KBr}]$ are respectively 12.5% and 0.032 M. (b) Lamellar phase with $\Phi = 19.8\%$ and $[\text{KBr}] = 0.04 \text{ M}$.

by two complementary methods: DLS and classical rheology.¹¹ The former involves the analysis of the long-time behavior of the correlation function of the concentration fluctuations as explained in the subsection Materials and Methods.

Here we have used the DLS method because the characteristic relaxation time of the samples investigated is relatively short ($\sim 40 \text{ ms}$), at least at the temperature of 35°C where most studies have been realized. In this range, the accuracy of the conventional rheometer is limited. However, few measurements performed by both rheology and DLS led to values of the relaxation time close to each other.

Table 2 illustrates the effect of the DTAB content and of the temperature on the slow relaxation time measured by DLS and on the amplitude of this mode. It can be seen that DTAB addition modifies only slightly the relaxation time whereas the amplitude of the slow mode is drastically decreased. One observes the same effect on the amplitude as the temperature is increased. In fact, as mentioned earlier, both DTAB additions and increase of temperature amount to taking the system far from the isotropic/lamellar transition.

Discussion

1. Phase Diagram. The systems investigated here exhibit some similarities in their behavior with the DDAB/water mixtures³ but also some significant differences. The

(10) Candau, S. J.; Hebraud, P.; Schmitt, V.; Lequeux, F.; Kern, F.; Zana, R. *Nuovo Cimento* **1994**, *16D*, 1401.

(11) Buhler, E.; Munch, J. P.; Candau, S. J. *J. Phys. II* **1995**, *5*, 765.

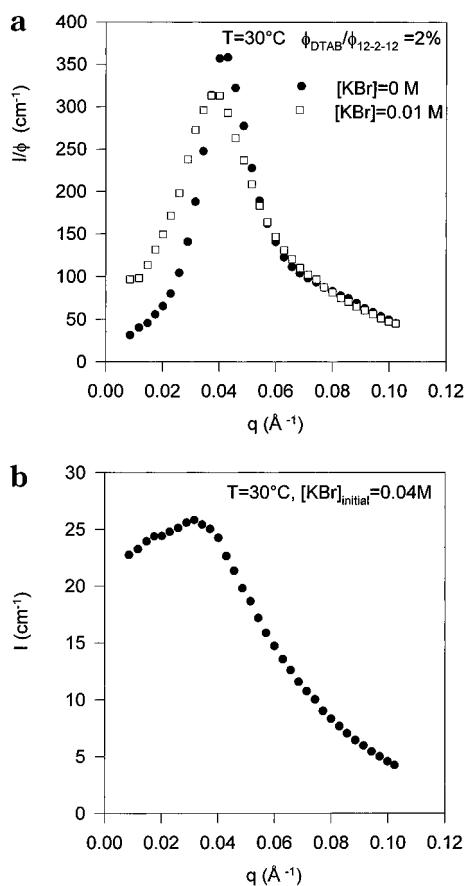


Figure 10. Scattering curves for mixed DTAB/12-2-12 systems: (a) micellar phase in the absence of salt and in presence of 0.01 M KBr; $\Phi = 5.5\%$; (b) lamellar phase obtained after demixing of a system with $\Phi_{\text{initial}} = 5.5\%$ and $[\text{KBr}]_{\text{initial}} = 0.04\text{ M}$; $\Phi = 12.5\%$ and $[\text{KBr}] = 0.032\text{ M}$.

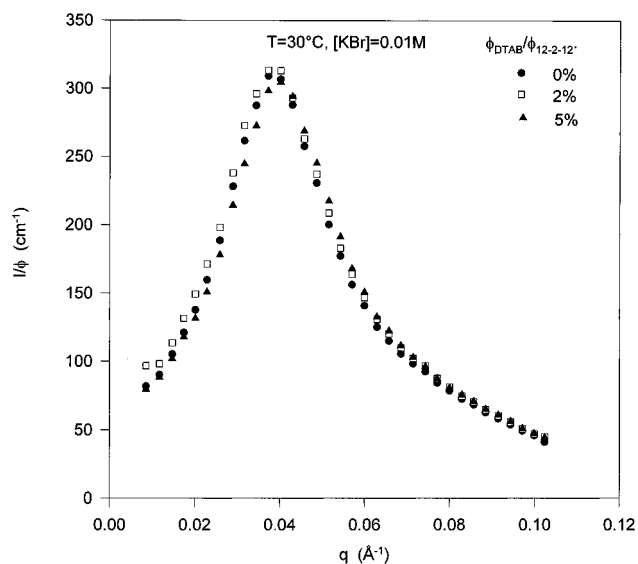


Figure 11. Effect of the 12-2-12/DTAB composition on the scattering curves of isotropic micellar solutions; $\Phi = 5.5\%$.

most striking similarity is the existence in the phase diagram of a diphasic domain where a highly dilute surfactant solution coexists with a swollen lamellar phase. In both systems, this lamellar phase is characterized by an interlamellar distance much larger than the screening Debye–Hückel length κ^{-1} . Also one observes for the two surfactants, DDAB and 12-2-12, a freezing of the 12 carbon atom chains at a temperature close to 30°C .

However, this study is the first report to our knowledge

Table 2. Effect of the DTAB Content and of the Temperature on the Relaxation Time and the Amplitude of the Slow Mode Obtained in the Field Autocorrelation Function for Mixed 12-2-12/DTAB Micellar Solutions ($[\text{KBr}] = 0.025\text{ M}$, $\phi = 5.5\%$, $T = 35^\circ\text{C}$)

$\phi_{\text{DTAB}}/\phi_{12-2-12}$ (%)	T_L (ms)	A_L (%)
0	51	31.5
2	42	12.6
5	42	11.4

T ($^\circ\text{C}$)	T_L (ms)	A_L (%)
45	21	6.65
40	31	11.7
35	42	12.6
30	78	22.5
25	193	30.4

of a salt-induced transition from cylindrical micelles to a lamellar phase. In the absence of salt, the 12-2-12 surfactant is characterized by a value of the packing parameter p that favors the formation of cylindrical micelles. It was shown that the end-cap energy of these micelles, that is function of both spontaneous curvature and Gaussian curvature coefficients,¹² is very large in the absence of salt. This is likely to be due to the constraint imposed by the linkage of the two polar heads of the surfactant, combined to the bulkiness of the hydrocarbon part. The addition of salt produces an increase of p through a reduction of the area per polar head. At the same time, the screening of the electrostatic interactions increases strongly the scission energy so that the formation of hemispherical end-cap becomes highly unfavorable.

The mechanism of phase separation of DDAB solutions in the presence of salt is likely to prevail here also.^{13,14} It was shown that the surfactant and salt concentrations in the lamellar phase are set by the equilibrium of osmotic pressure of solvent in the two coexisting phases. The equilibrium condition is the equality of the solvent chemical potential in both phases. This is the well-known Donnan equilibrium that leads to a deficit of salt in the lamellar phase. As an example one finds for the 5.5% 12-2-12, 0.04 M KBr system, a deficit of salt of about 25% in the lamellar phase. Theoretical expressions for the salt partition between the two phases as a function of the interlamellar distances have been derived.¹⁴ However this treatment cannot be applied to the systems considered here because of the anomalous behavior of the swelling distance between bilayers that is discussed next.

2. Lamellar Phases. At temperatures higher than $\sim 28\text{--}30^\circ\text{C}$ one observes a broad peak in the SANS spectra with a maximum at a wave vector q_{max} whose variation with surfactant concentration is much less than that expected from linear swelling of the lamellar phase with constant value of the bilayer thickness. A thinning of the bilayer upon dilution of the lamellar sample is unlikely in the presence of a large amount of water which warrants the full hydration of the polar heads,¹⁵ and therefore, the observed behavior must be attributed to the presence of defects or to the coexistence of two nonseparated phases. The DDAB lamellar systems, referred to as $[L_w]$ phases,

(12) Safran, S.; Turkevitch, L.; Pincus, P. *J. Phys. Lett.* **1984**, *42*, 1135.

(13) Dubois, M.; Zemb, T.; Belloni, L.; Delville, A.; Levitz, P.; Setton, R. *J. Chem. Phys.* **1992**, *96*, 2278.

(14) Zemb, T.; Belloni, L.; Dubois, M.; Marcelja, S. *Prog. Colloid Polym. Sci.* **1992**, *89*, 33.

(15) One referee pointed out to us that for lipids the addition of water can result in an increase of the head group area and a thinning of each bilayer but that such thinning must be very weak in the presence of an excess of water.

were biphasic with lamellar spherulites dispersed in an isotropic L_3 phase and were very viscous.³ The systems investigated here are very fluid and phase separate easily, and the birefringent phases do not show under the microscope the presence of an isotropic phase under the form of a continuous medium or of droplets. Therefore the defects of the lamellar organization must have a characteristic length much smaller than the scale of optical observations. In fact, it is likely that we deal here with lamellar phases containing highly curved defects such as those detected in nonionic lamellar phases using spin labels (a technique sensitive to very local effects). The existence of such a phase was predicted by Porte et al.¹⁶ who suggested that the transition between cylinders and lamellae would involve intermediate structures of branched cylinders and perforated lamellae. Evidence of lamellae pierced by water-filled defects was reported by Holmes et al.¹⁷ for systems in which a nematic phase forms between the isotropic and the lamellar phases. This however occurs at higher surfactant volume fraction ($\Phi \geq 30\%$). It was shown that the water-filled defects in the lamellae show no correlation between adjacent lamellae. In the 12-2-12 systems, the formation of defects can be favored by the fact that the surfactant packing parameter in the absence of salt is that of a cylindrical structure. One can thus envision as in the case considered by Holmes et al.¹⁷ that the lamellae consist of ribbonlike aggregates possibly interconnected, the hole edge being the curved cylinders. The number density and/or the size of the water-filled defects would increase upon decreasing the surfactant concentration.

The broad shape of the scattering curve is generally typical of lamellar phases stabilized by fluctuations forces.¹⁸ It was previously shown that, in that case, the neutron diffraction profiles exhibit a small-angle diffuse scattering pattern. There is no evidence of such behavior for the systems discussed here. Furthermore, when passing from L_α to L_β phases one does not expect a large change in scattering profile, like that observed in Figure 9, because the rigidification of the bilayers would be accompanied by a decrease of the contribution of the fluctuations and therefore there would not be any reinforcement of the smectic order. Here the broadening of the peak may come essentially from the presence of defects in the bilayers. It is significant in this respect that the most concentrated sample which is likely to have the least defects exhibits a narrower peak in its scattering profile.

Turning to the swelling behavior, Figure 8 shows that there is a significant change in the periodicity of lamellae, only at high surfactant concentration. The straight line in Figure 8 represents the swelling law for an infinite defect-free lamellar phase with a bilayer thickness of 25 Å. This straight line fits the values of d in the high concentration range. Conversely, at low surfactant concentration, one observes a nearly constant periodicity of about 200 Å (maximum swelling), i.e., 10 times the Debye–Hückel screening length. This is quite similar to the findings in the DDAB systems.

In our case, however when the lamellae are pierced with holes with curved hemicylindrical edges, the equilibrium structure should be set by a delicate balance involving the Donnan equilibrium and surface curvature effects linked to the special nature of the surfactant.

3. Wormlike Micellar Phases. The behavior of the wormlike micellar phase conforms quite well to that obtained previously for salt free solutions of 12-2-12

surfactant.⁵ In particular the scaling $q^* \sim \Phi^{1/2}$ confirms the picture of semidilute solutions of semirigid cylindrical objects.⁹ The scaling of $I(q^*)$ with Φ , according to $I(q^*) \sim \Phi^{1/2}$ was observed in salt free solutions but with a smaller exponent (0.2).

More interesting is the viscoelastic behavior of these systems upon approaching the isotropic/lamellar transition by varying the amount of DTAB and/or temperature. According to the Porte conjecture,¹⁶ one would expect that due to an increase of the packing parameter, branched micelles form in the vicinity of the transition. These branched objects would be the precursors of the perforated lamellae.

The DLS results are reported in Table 2 showing the effect of DTAB addition and of the temperature on the viscoelastic relaxation time T_L and the amplitude A_L of the slow mode. The behavior of the viscoelastic relaxation time is rather complex. The relaxation time and its activation energy are functions of the mean micellar length and of the rate constant of breaking, and both of these two parameters vary with temperature and cosurfactant content. Furthermore, the micellar branching modifies the reptation process.

On the other hand, the behavior of the relative amplitude A_L of the slow mode is simpler to interpret. Theory of semidilute solutions of polymers predicts that this relative amplitude is related to the gel modulus M_g and the osmotic modulus K of the solution through the relationship^{19,20}

$$A_L \approx M_g/K$$

For semidilute solutions of "classical polymers" M_g/K is of the order of 5×10^{-2} in good solvent and of 0.5 for theta solvent. In Table 2 and Figure 1, one sees that A_L increases upon decreasing DTAB content or temperature, i.e., upon approaching the isotropic/lamellar transition. This can be attributed to an improvement of the quality of solvent. The vicinity of the transition is then characterized by the enhancement of attractive forces, that can be at the origin of the micelle branching shown in previous studies.

Conclusion

The study presented here is the first report to our knowledge of a salt-induced transition between cylindrical micelles and lamellar phase in the high dilution range.

SANS experiments reveal that in lamellar systems the variation of the interlamellar distance is much less than that expected from linear swelling of a defect free lamellar phase. This strongly suggests the existence of perforated lamellae predicted some time ago¹⁶ and recently observed in more concentrated systems above a nematic phase of disks.¹⁷ In the temperature range above the crystallization temperature of the paraffinic chains, the scattering curve is rather broad without higher order peaks which is likely due to the presence of defects within the lamellae. Further scattering experiments in oriented samples would allow a better characterization of these phases.

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(16) Porte, G.; Gomati, R.; El Haitamy, O.; Appell, J.; Marignan, J. *J. Phys. Chem.* **1986**, *90*, 5746.

(17) Holmes, M.; Leaver, M.; Smith, A. *Langmuir* **1995**, *11*, 356.

(18) Helfrich, W. *Z. Naturforsch.* **1978**, *33a*, 305.

(19) Brochard, F. *J. Phys. (Paris)* **1983**, *44*, 39.

(20) Semenov, A. N. *Physica A* **1990**, *166*, 263.