

Phase equilibria and structures in ternary systems of a cationic surfactant ($C_{16}TABr$ or $(C_{16}TA)_2SO_4$), alcohol, and water

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Abstract: The dependence of alcohol chain length on the isothermal phase behavior of the ternary systems hexadecyltrimethylammonium bromide/alcohol/water has been investigated. A liquid crystalline phase (the normal hexagonal one) occurs in the phase diagrams along the surfactant/water axis and this phase extends in the interior of the diagrams.

When the alcohol is methanol, ethanol or butanol, there is in the ternary phase diagram a continuous solution region from the water to the alcoholic corner, and in the butanol case, in addition, a small region of lamellar liquid crystalline phase in the interior of the diagram. When the alcohol chain length is increased, the continuous solution region is divided into two subregions, an aqueous L_1 and an alcoholic L_2 . The lamellar phase occupies the center of the phase diagrams and has the capability to incorporate large amounts of water under one-dimensional swelling. On the alcoholic side of the lamellar phase occur a reversed hexagonal liquid crystalline phase and a cubic liquid crystalline phase in the octanolic system; in the decanolic system the cubic phase is missing, but instead another liquid crystalline phase, presumably with rod-structure, occurs in addition to the reversed hexagonal phase.

In a decanolic system where the monovalent bromide ion is replaced by the divalent sulphate ion there are the same solution regions L_1 and L_2 , and phase regions with liquid crystalline normal hexagonal and lamellar structures. The lamellar phase has lost much of its capability of incorporating water. That is in analogy with the conditions in anionic systems where the counterion charge has been increased. There is no reversed hexagonal phase, but on the alcoholic side of the lamellar phase, there is the same "foreign" liquid crystalline phase with a presumed rod-structure as in the monovalent system.

Key words: Phase equilibria; l.c. structures; alcoholic $C_{16}TABr$ systems; divalent counterion

Introduction

In order to understand surfactant self-association phenomena, knowledge of the phase behavior, isothermal and isoplethal, is of vital importance. The factors controlling the phase behavior are rather well-known for anionic surfactants in binary systems with water and in ternary

systems containing, in addition to water, an amphiphilic additive of varying polarity [1], but cationic surfactant systems have not been studied in this regard to the same extent.

The intention of the present paper is to present isothermal phase diagrams for ternary systems of a cationic surfactant/alcohol/water when the alcohol chain length is varied from methanol

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to decan-1-ol. The surfactant is the monovalent hexadecyltrimethylammonium bromide ($C_{16}H_{33}N(CH_3)_3Br$). A phase diagram for a decanolic system where the bromide ion has been replaced by the divalent sulphate ion is also presented.

Experimental

Materials

Hexadecyltrimethylammonium bromide ($C_{16}TABr$ for short) was purchased from different sources, Merck, Fluka, Suchardt, and BDH. It was recrystallized from pure water utilizing the different solubilities above and below the Krafft temperature, or alternatively from an ethanol-acetone mixture.

Hexadecyltrimethylammonium sulphate $\{(C_{16}TA)_2SO_4$ for short} was prepared by converting the $C_{16}TABr$ in aqueous solution to its hydroxide-form on a column filled with Dowex 21 K ion-exchange resin (BDH). The $C_{16}TAOH$ was immediately neutralized with sulphuric acid to pH 6 and a white crystalline product was obtained by freeze-drying. Chemical analysis showed that the product had a purity above 99%.

The alcohols used were ethanol (99%, spectrograde, Spritbolaget, Sweden), methanol, butan-1-ol and hexan-1-ol (Merck p.a.), and octan-1-ol and decan-1-ol (BDH, especially pure). The water was twice distilled. Heavy water (99.7 at.-% 2H) was obtained from Norsk Hydro, Norway.

Sample preparation

The samples (gross size ~ 1.5 g) were prepared by weighing appropriate amounts of the components into glass tubes which were flame-sealed. The samples were warmed and equilibrated by repeated centrifugation back and forth until equilibration was deemed complete. After that, the samples were stored at 25 °C for at least a week. The equilibrium was checked repeatedly, in some cases after months or years.

Methods of investigation

The isothermal phase diagrams were determined by optical inspection, polarizing microscopy, x-ray high- and low-angle diffraction, centrifugation, and analysis. 2H NMR methods were in addition used in the study of the decanolic $C_{16}TABr$ and $(C_{16}TA)_2SO_4$ systems.

The samples were first examined between crossed polaroids by the naked eye for homogeneity and birefringency. In multiphase samples, separation into the individual phases often occurred spontaneously, but this could be augmented by centrifugation in an ordinary desk centrifuge.

For the birefringent samples, characteristic textures of hexagonal and lamellar liquid crystalline structures were studied by polarizing microscopy [2]. The hexagonal phases typically

displayed a fan-like angular or a striated nongeometric texture, while the lamellar phases showed a mosaic planar texture. The isotropic cubic phases were black.

The phase assignments obtained were checked by low-angle x-ray diffraction and inspection of 2H NMR-spectra [3, 4].

The broad diffuse x-ray reflection at about 4.5 Å in the wide-angle region confirmed the liquid nature of the hydrocarbon chains. The low-angle pattern for the hexagonal phases showed sharp diffraction peaks in the ratio $1:\sqrt{3}:\sqrt{4}$, while the ratio for the lamellar phases was 1:2:3. Diffractograms from the cubic samples had a characteristic cubic "habitus" of irregular diffraction spots. However, it was difficult to determine the corresponding Bragg spacings and to index them.

The 2H NMR spectra were obtained at a resonance frequency of 39.14 MHz on a home-built Fourier transform spectrometer equipped with an Oxford Instrument 6T wide-bore superconducting magnet. The quadrupolar splittings, Δ , were measured as the peak-to-peak distance in the spectra. The identification of anisotropic liquid crystalline phases in surfactant/water systems by NMR is based upon the following [4–6]:

A homogeneous anisotropic liquid crystalline phase is characterized by a single splitting in the 2H NMR spectrum. Its magnitude, Δ , depends on the sample composition and phase structure. In ternary systems the values of Δ in a particular phase have been found to depend primarily on the water content and, to a lesser extent, on the surfactant/additive ratio. Normally, samples with high water content give small Δ values irrespective of the ratio of surfactant to amphiphilic additive, while those with low water contents give large splittings.

For hexagonal and lamellar phases, it has been shown theoretically that $\Delta_{lam} \approx 2\Delta_{hex}$ when account is taken of differences in water content.

Plots of Δ vs $(1 - X_w)/X_w$ (X_w = mole fraction water) should yield straight lines going through the origo and the values for the slopes give information about the probable phase structure, two-dimensional or one-dimensional (lamellar or nonlamellar).

In the estimation of the various parameters (the lipid bilayer thickness and the area per polar head group at the polar/nonpolar interfaces) derived from the x-ray diffraction findings, the composition by weight has in principle to be converted to volume fractions. As no density measurements were performed in this study, this conversion was based upon the partial specific volume 0.989 ml/g for $C_{16}TABr$ (obtained from [7]). For the different alcohols, the specific volumes for the pure compounds [8] were used and for the water the value 1.0 ml/g (heavy water 1.1 ml/g) was used. (This assumption is certainly not valid in the case of methanol and ethanol; however, in their systems, only the hexagonal liquid crystalline phase occurs and as the volume fraction enters as a square root in the equations, the error will be rather small.)

No x-ray diffraction studies were performed on the phases in the $(C_{16}TA)_2SO_4$ system.

The phase equilibria findings are presented as isothermal ternary phase diagrams (Fig. 1). The fiduciary points on the binary axes of the phase diagrams, i.e., the mutual solubilities of the compounds, are listed in Table 1.

In the isothermal phase diagrams, the required three-phase triangles and two-phase zones were identified. For reasons of

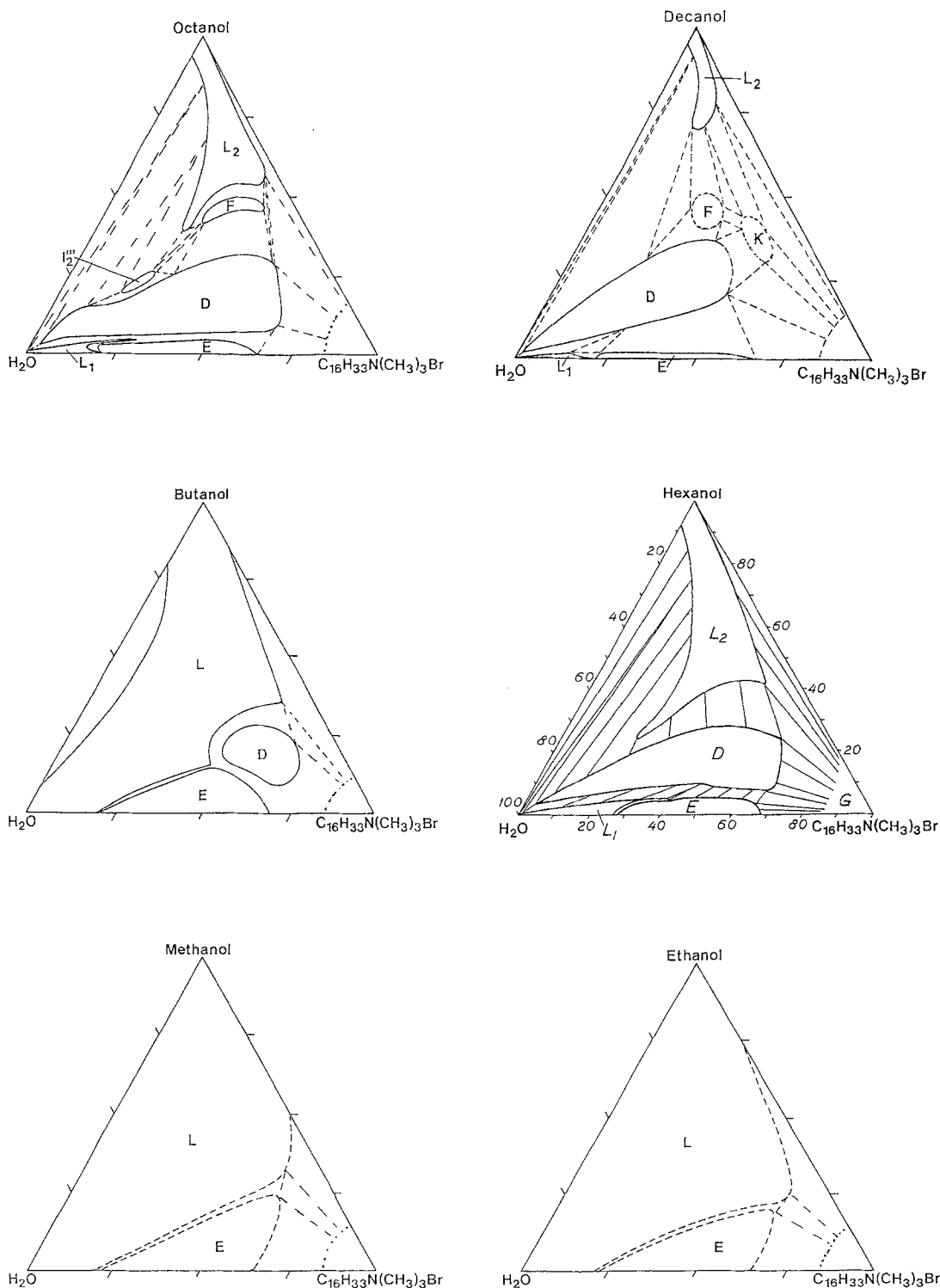


Fig. 1. Isothermal phase diagrams at 25 °C for ternary systems of hexadecyl-trimethyl ammonium bromide/alcohol/water (Fontell and Puang-Ngern). The hexanolic diagram is taken from [8]. The phase notations are according to [1], viz. L (L₁, L₂) isotropic solutions, D liquid crystalline lamellar phase, E liquid crystalline hexagonal phase, F liquid crystalline inverted hexagonal phase, I₂^m viscous isotropic cubic phase, and K liquid crystalline phase, presumably, with a non-hexagonal inverted rod-structure

Table 1. Mutual solubilities of the compounds, 25 °C

Alcohol/water (%)	Water/alcohol (%)	C ₁₆ TABr/alcohol (%)	(C ₁₆ TA) ₂ SO ₄ /alcohol (%)
Methanol	∞	∞	~ 50
Ethanol	∞	∞	~ 27
Butanol	~ 8.5	~ 20	~ 15
Hexanol	~ 0.3	~ 7–8	~ 7
Octanol	< 0.1	~ 6	~ 2–3
Decanol	~ 0.003	~ 3.8	~ 1
	C ₁₆ TABr/water (%) (molar ratio water/surfactant)		(C ₁₆ TA) ₂ SO ₄ (%) (molar ratio heavy water/surfactant)
Phase L ₁	20.5*)	> 78.5	Phase L ₁ 40.5 Phase I'' ₁ 41–46.4
Phase E	26–65	60.8–10.9	Phase E 51.8–67.4 31–16

*) This value is obtained for a product from Merck; present batches from BDH give the same value. Ekwall et al. [8] found the higher value 26% (mr 57.3) for a product from BDH.

readability, they are not always inserted. The accuracy in the determination of the phase borders varied from system to system. In the best studied systems they lay within 1% weight units of the individual components; in the other systems the determinations were less accurate.

Results

Binary systems with water

Hexadecyltrimethyl ammonium bromide: At 25 °C, the binary system of C₁₆TABr and water forms an aqueous L₁ solution phase up to about 20.5% of surfactant. After a narrow two-phase zone, there is a hexagonal liquid crystalline phase, E, which extends up to about 65% of surfactant and at still higher content, the hexagonal phase is in equilibrium with crystalline C₁₆TABr [7, 9, 10].

At elevated temperature, one encounters, in addition, cubic and lamellar liquid crystalline phases [7, 9].

This is the normal phase pattern for assembling in ionic surfactant systems, viz. above the Krafft temperature, when the water content is increased, there is first an aqueous solution, L₁, nonmicellar and micellar, which is followed by various liquid crystalline phases and the sequence ends up with the pure surfactant, crystalline or liquid, hydrated or nonhydrated. The phases are separated by the appropriate two-phase zones.

Numerous studies have shown that in the aqueous solution region, L₁, the micelles are small and globular between CMC and about 11%, but above that concentration they grow in size and assume an elongated rodlike shape [10–17]. The minimum

water requirement for the solution phase to be formed is about 79 moles per mole of surfactant.

The hexagonal phase E spans from about 11 moles of water per mole surfactant to about 60 moles per mole (Table 1). The hexagonal structure is established by microscopic observations, x-ray diffraction (Table 2) [7], and from the magnitude of the quadrupolar splittings in the NMR spectra (Table 3). The structure is built up of nonpolar amphiphilic rods arranged hexagonally in an aqueous polar surrounding [7]. The size of the two-dimensional hexagonal unit cell decreases from about 75 Å to about 54 Å when the surfactant content is increased. However, the diameter of the rod aggregates is about 45 Å throughout and the area per polar group at the polar/nonpolar interfaces remains constant at about 53 Å² (Fig. 2) (Table 2).

Hexadecyltrimethyl ammonium sulphate: The binary phase diagram of the divalent system (C₁₆TA)₂SO₄/heavy water has been determined by Maciejewska et al. [18]. At 25 °C, there is an aqueous solution phase, L₁, up to 40.5% surfactant; a cubic liquid crystalline phase, I''₁, between 41% and 46.4%; and between 51.8% and 67.4% a hexagonal liquid crystalline phase, E (Table 1). The hexagonal phase is, in turn, in equilibrium with the hydrated surfactant.

The entire L₁-solution region seems to contain only small micelles. This is evident from studies of the ¹H NMR line width and from NMR self-diffusion data [18].

The hexagonal nature of phase E is inferred from microscopical observations and the magnitude of

Table 2. X-ray diffraction parameters in systems of C₁₆TABr/alcohol/water for (A) the "normal" hexagonal phase E, and (B) the phases on the alcoholic side of the lamellar phase D (the phases F, K and I₂''). Φ_a and Φ_w , volume fraction amphiphilic matter and water, respectively; d , the Bragg spacing; d_p , the two-dimensional hexagonal unit cell parameter; d_c , the diameter of the rod-aggregates; S , the area per polar group at the polar/nonpolar interfaces of the rod-aggregates; a , the cubic unit cell parameter; $m = \sqrt{(h^2 + k^2 + l^2)}$

		Composition (%)		Φ_a	d_p (Å)	d_c (Å)	S (Å ²)	Ref.
(A)								
E-phase								
	33.1	—	66.9	0.327	74.8	44.9	53.2	[8]
	51.3	—	48.7	0.509	59.8	44.8	53.3	
	64.6	—	35.4	0.642	53.7	45.2	53.0	
Ethanol								
	55.0	9.9	35.1	0.656	54.7	46.5	61.9	This work
	54.6	17.5	27.9	0.732	44.5	39.9	81.3	
	54.9	20.1	25.0	0.761	41.8	38.3	87.7	
	54.9	23.0	22.1	0.781	40.1	37.9	92.6	
Hexanol								
	32.0	2.4	65.6	0.344	72.3	44.5	46	[8]
	49.2	3.7	47.1	0.529	58.9	45.0	45.6	
(B)								
F-phase								
				Φ_w				
Octanol								
	29.4	41.0	29.6	0.273	49.2	27.0	17.8	This work
	29.9	42.3	27.8	0.249	47.2	24.8	17.7	
	32.9	48.0	19.1	0.174	39.6	17.3	15.9	
	33.0	47.0	20.0	0.182	40.8	18.2	16.0	
	35.0	47.0	18.0	0.164	40.9	17.4	15.0	
	37.0	47.0	16.0	0.146	38.7	15.5	14.8	
	40.0	47.0	13.0	0.118	37.8	13.6	13.5	
	42.0	47.0	11.0	0.102	35.9	12.0	12.0	
Decanol								
	25.0	50.0	25.0	0.227	61	31.0	13.0	This work
(C)								
K-phase								
Decanol					d (Å)			
	50.0	35.0	15.0		45	This work		
					22.5			
					15.2			
					11.6			
(D)								
Cubic phase I ₂ ''								
Octanol				d (Å)	m	a (Å)		
	20.0	22.0	58.0	72	3	124.7	This work	
				39.3	10	124.3		

the quadrupolar splittings in the ²H NMR spectra (Table 3). The water content in the phase on molar basis spans from about 16 to 31 moles per mole of surfactant (Table 1).

Ternary C₁₆TABr systems with alcohols

The methanolic system: As methanol is completely miscible with water there is a continuous solution

region along the water/methanol axis and the region extends far into the interior of the phase diagram (Fig. 1).

In the absence of water, C₁₆TABr is soluble in methanol up to about 50% (Table 1). At higher contents of C₁₆TABr some water is needed in order for the solution phase to be formed.

The only other phase present is the normal hexagonal liquid crystalline phase E, extending from

Table 3. Water deuteron NMR quadrupolar splittings (Δ) given by one-phase and multiphase samples in systems of $C_{16}TABr$ and $(C_{16}TA)_2SO_4$, respectively, decanol and heavy water (26 °C) (20). k is obtained by dividing the splitting Δ with $(1 - X_w)/X_w$

	Surfactant	Composition (%)		Δ (Hz)	$(k/Hz) 10^{-3}$
		Decanol	Heavy water		
A. $C_{16}TABr$					
Phase E	31.0	—	69.0	30	1.2
	53.5	—	46.4	69	1.1
	30.3	1.0	68.7	35	1.3
Phase D	24.6	17.8	57.6	238	3.8
	38.4	28.0	33.6	532	3.2
	43.0	31.5	25.5	787	3.2
Phases D + F	27.1	46.1	26.8	710, 490	~ 1.8 for F
Phases D + F	24.7	46.0	29.3	660, 470	—
Phases $D + K$ $+ F$	42.3	37.9	19.8	1240, 650	—
				420	—
Phases D + K	47.0	35.0	18.0	930, 500	—
Phase K	43.2	37.5	19.1	628	1.8
B. $(C_{16}TA)_2SO_4$					
Phase E	52.3	—	47.7	133	2.0
	64.8	—	35.2	286	2.6
	50.3	3.4	46.3	151	2.0
Phase D	40.0	22.0	38.0	650	4.8
	48.2	28.0	23.8	1200	4.4
	52.5	28.3	19.2	1700	4.9
	58.1	25.0	16.9	1990	5.0
	48.6	38.1	13.2	2000, 1170	—
Phases D + K $+ L_2$	58.9	27.8	13.3	1880, 1150	—
Phase K	64.8	27.7	7.5	1350	1.4
Phase K	60.6	31.5	7.9	1440	1.5

the surfactant/water axis up to a maximal content of about 25% methanol. The water content at the maximum is about 20%.

No x-ray diffraction studies have been performed in the methanol-containing hexagonal phase.

The ethanolic system

The phase diagram for the ethanolic system is similar to that for the methanolic system (Fig. 1). In the absence of water $C_{16}TABr$ is soluble in ethanol up to about 27% (Table 1).

The maximum ethanol content of the hexagonal phase E is about 20% at a water content of about 20%. X-ray diffraction studies for a series with a constant amount of surfactant (55%) and increased amounts of ethanol show that the size of the two-dimensional unit cell decreases from about 59 Å to about 40 Å (Fig. 2) (Table 2). The diameter of the

rod-aggregates decreases from about 45 to about 38 Å and the area per trimethylammonium bromide group increases from about 53 Å² to about 90 Å². These nominal values suggest that the ethanol molecules (maximally, about three per mole surfactant) in some manner are located around the trimethyl groups and force them apart.

The butanolic system

Butanol and water are not miscible, but have a rather high mutual solubility (Table 1). In the ternary phase diagram, the region L extends from the water to the butanol corner and penetrates rather deep into the interior of the phase diagram (Fig. 1). The solubility of $C_{16}TABr$ in nonaqueous butanol is about 15%. At higher contents of the surfactant, the border of the solution region to the righthand side lies at about two moles of water per mole of surfactant.

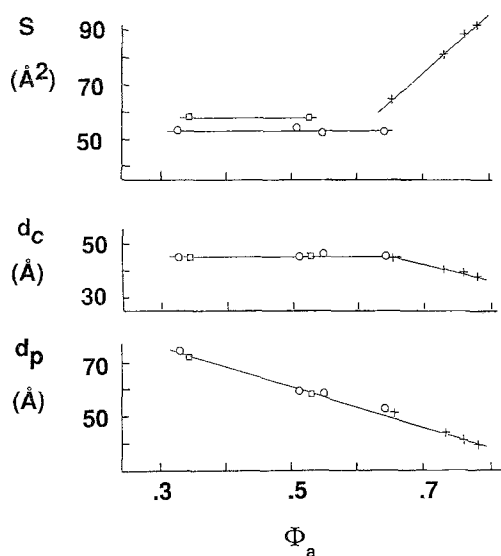


Fig. 2. X-ray diffraction parameters in systems of $C_{16}TABr$ /alcohol/water for the two-dimensional hexagonal phase E as a function of volume fraction amphiphilic matter, (Φ_a); d_p , the two-dimensional hexagonal unit cell parameter; d_c , the diameter of the amphiphilic rod-aggregates; and S , the area per polar group at the polar/nonpolar interfaces. \circ the binary system $C_{16}TABr$ /water [8]; $+$ the ethanolic system, constant content of $C_{16}TABr$, 55%, (the d_c - and the S -values refer to rod aggregates containing only $C_{16}TABr$); \square the hexanolic system [8], molar ratio hexanol/ $C_{16}TABr$ 0.27, (the d_c - and the S -values refer to rod aggregates containing $C_{16}TABr$ + hexanol)

The hexagonal phase E along the surfactant/water axis incorporates maximally about 14% butanol, which is about mole per mole.

At rather high $C_{16}TABr$ contents and between about 9% and 28% butanol, there is, in addition, a region with lamellar liquid crystalline phase D . The identification of this phase structure is based upon observations in the polarizing microscope; no x-ray diffraction studies have been performed. The water content for this phase is between 4.1 and 15.9 moles per mole of surfactant and the molar ratio between alcohol and surfactant is between 2.65 and 0.7.

The hexanolic system

The phase diagram contains two isotropic solution regions (L_1 and L_2), a hexagonal liquid crystalline phase (E), and a lamellar liquid crystalline phase (D) (Fig. 1) [7]. The two liquid crystalline regions are separated by a two-phase zone.

The L_1 -phase dissolves, at most, 5.2% of hexanol. The phase extends a narrow tongue between

the hexagonal and lamellar phases, and the composition at the end of the tongue is about 39.8/5.2/55, viz. the molar ratio is about 1:0.47:28 between surfactant, hexanol and water. The structure of the solution region has been studied by several groups [10–17]. The hexanol molecules enter the micelles on equal basis with the surfactant molecules and all polar groups are located at the polar/nonpolar interfaces. At high hexanol and surfactant contents the rod-like micelles presumably obtain an oblate shape.

The L_2 -phase extends a finger towards the water corner which ends at a composition of about 21.5/24/54.5, viz. about 51 moles water and 4 moles hexanol per mole of surfactant. The solubility of $C_{16}TABr$ in hexanol is about 7% and above that amount, a minimum amount of water, about 3–4 moles per mole of surfactant, is needed for the solution to be formed. The L_2 -structure has been studied by Ekwall et al. [19]. It is a reversed micellar one where the hydrophilic groups of $C_{16}TABr$ and some of the hexanol are anchored in the polar cores of water and form micelles in an hexanolic environment. The conditions in the reversed micellar L_2 -regions are not as clear-cut as in normal micellar L_1 -regions.

The hexagonal phase E dissolves, like the L_1 -phase, maximally about 5% of hexanol, viz. about 0.44 moles per mole surfactant. As soon as hexanol is added, the water content has to be increased in order for the phase to exist. X-ray diffraction studies have shown that the influence of the hexanol on the dimensional parameters is rather small (Fig. 2) (Table 3) [7].

The lamellar phase D needs a minimum water content (about 3–4 moles per mole surfactant) in order to be formed. This amount is about the same as in the solution phase L_2 . The span of the molar ratio between hexanol and surfactant is from 0.35 to 3.29. At molar ratios 2:1 and 1:1 between alcohol and surfactant the phase has an especially large capability to incorporate water, up to about 94%. This corresponds to about 540 moles per mole of surfactant.

The structure of this lamellar phase has been studied by Ekwall et al. [7]. In the series towards the water corner the structure is the "ideal" lamellar one. This is manifested by the slope of unity for the curve of $\log d$ vs ($-\log \Theta_a$) (Fig. 3), viz. the amphiphilic bilayers have a constant thickness and molecular packing, and the thickness of the water

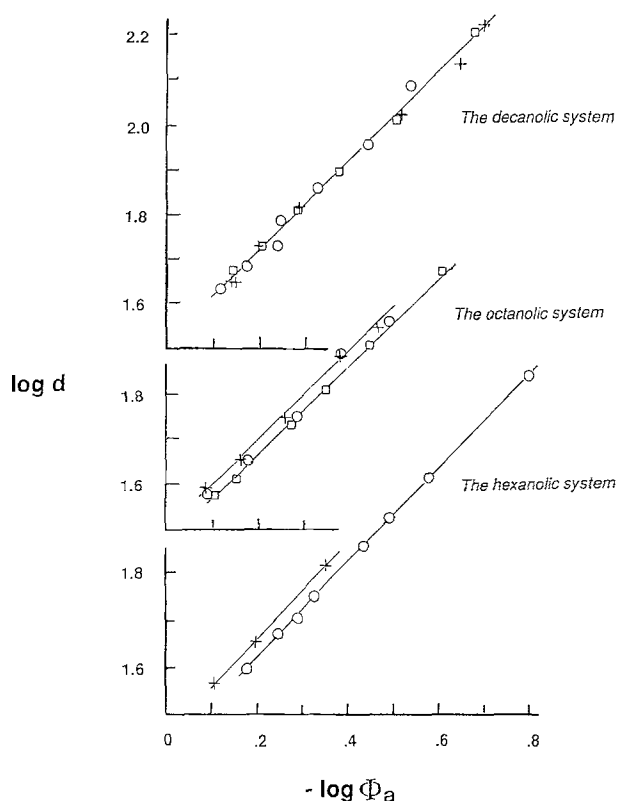


Fig. 3. Plots of $\log d$ vs. $(-\log \Phi_a)$ for the lamellar phases in the hexanolic, octanolic, and decanolic $C_{16}TABr$ systems. d , fundamental repeat; Φ_a , volume fraction amphiphilic matter. Molar ratios alcohol/surfactant: in the hexanolic system 1.08:1, +, and 2.38:1, \circ ; in the octanolic system 1:1, +, 1.68:1, \square , and 2:1, \circ ; in the decanolic system 1:1, +, 2:1, \circ , and 2.3:1 \square .

layers increases in a regular manner with the water content. In the series with the molar ratio of 1.08:1 between alcohol and surfactant, the amphiphilic bilayer thickness is about 29 Å and in the series 2.38:1 the corresponding value is about 27 Å (Table 4) (Fig. 4). The molecular packing increases with the hexanol content, the area per polar group is about 27 Å² in the series 1.08:1 and about 24 Å² in series 2.38:1 (Fig. 4).

In series with molar ratios below unity between hexanol and surfactant the water content is limited. The lamellar behavior is no longer ideal; the slope of the log-log curve is below unity inside the individual series. That means that the bilayer thickness decreases and the area per polar group increases with the water content in these series.

A rheological study has indicated that the structure in a series with constant molar ratio between

alcohol and surfactant through the lamellar phase is cooperative [20].

The octanolic system

The phase diagram is similar to the previous one with the same two isotropic solution phases (L_1 and L_2), and two liquid crystalline phases (the lamellar phase D , and the normal hexagonal phase E). New features are the occurrence of a reversed hexagonal phase (F) and a viscous isotropic cubic phase (I_2''').

The maximum octanol content in the L_1 -phase is about 4%. Similar to the hexanolic case, the phase extends a narrow finger between the normal hexagonal and the lamellar liquid crystalline phases. The composition at the end is about 30/4/66 (molar ratio 1:0.4:45).

The region of the L_2 -phase has shrunk somewhat in comparison with that of the hexanolic system. The solubility of $C_{16}TABr$ in octanol is about 2–3%. The molar ratio of water to surfactant at the border to the righthand side is about 5:1. The maximum water content at the end of the tongue towards the water corner is about 35% at a surfactant content of about 25% (molar ratio about 1:4.5:28.4).

The micellar structures in regions L_1 and L_2 have not been studied, but by analogy one may infer that the structures are similar to those in the hexanolic system, viz. in the L_1 -phase there is the normal micellar behavior in an aqueous solution, and in the L_2 -phase the reversed micellar behavior.

The normal hexagonal liquid crystalline phase E incorporates about 4% of octanol (molar ratio alcohol/surfactant is about 0.3:1). The structure in this phase has not been studied by x-ray. The maximum content of octanol is so low that one can hardly expect that the hexagonal structure will differ from that in the binary phase (or in the ternary phase with hexanol).

The lamellar liquid crystalline phase D has a large extension in this system. The minimum water content is somewhat higher than that in the L_2 -phase, about 5.4 moles of water per mole of surfactant. The phase extends far towards the water corner and the water content at the end point ($\sim 95\%$) corresponds to about 770 moles per mole of surfactant. The lamellar structure is "ideal" (Fig. 3), the bilayer thickness for series 1:1 is about 31 Å, and for series 2:1 about 29 Å (Fig. 4) (Table

Table 4. X-ray diffraction parameters in systems of C₁₆TABr/alcohol/water for the lamellar liquid crystalline phase D. Φ_a , volume fraction amphiphilic matter; d , fundamental repeat; d_a , bilayer thickness; S , area per polar group at the polar/nonpolar interface

Composition (%)	Φ_a	d (Å)	d_a (Å)	S (Å ²)	Ref.
Hexanol					
molar ratio hexanol/surfactant 0.68					
53.1 10.1 36.8	0.637	45.4	28.9	30.5	[8]
59.5 11.3 29.2	0.714	41.5	29.6	29.7	
65.8 12.6 21.6	0.788	38.4	30.3	29.0	
molar ratio hexanol/surfactant 1.08					
33.4 10.1 56.5	0.444	66.0	29.5	26.7	[8]
48.0 14.6 37.2	0.635	45.4	28.8	27.4	
59.2 17.9 22.8	0.778	37.0	28.8	27.5	
molar ratio hexanol/surfactant 2.38					
9.0 6.0 85.0	0.160	171.4	27.4	23.6	[8]
15.0 10.0 75.0	0.264	103.0	27.2	23.7	
18.4 12.2 69.4	0.322	84.0	27.3	23.8	
21.0 14.0 65.0	0.367	72.6	26.6	23.9	
27.0 18.0 55.0	0.469	58.7	27.5	23.5	
29.6 19.7 50.7	0.512	51.0	26.2	24.7	
33.0 22.0 45.0	0.568	47.1	26.8	24.1	
39.0 26.0 35.0	0.667	39.6	26.4	24.5	
39.7 26.5 33.8	0.678	38.1	25.8	25.1	
Octanol					
molar ratio octanol/surfactant 1					
25.0 8.8 66.2	0.349	88.4	30.8	28.0	This work
30.0 10.6 59.4	0.417	75.9	31.7	27.3	
40.0 14.2 45.8	0.554	55.8	30.9	27.9	
50.0 17.8 32.2	0.688	45.1	31.0	27.8	
60.0 21.4 18.6	0.821	39.1	32.1	26.8	
molar ratio octanol/surfactant 1.68					
20.0 12.0 70.0	0.329	89.5	29.4	26.3	This work
25.0 15.0 60.0	0.417	75.6	31.5	24.6	
30.0 20.0 50.0	0.519	56.0	29.1	26.1	
40.0 25.0 35.0	0.666	44.8	29.8	24.5	
50.0 30.0 20.0	0.811	37.0	30.0	25.9	
molar ratio octanol/surfactant 2					
14.0 9.9 76.1	0.253	116.3	29.5	25.5	This work
20.0 14.5 65.5	0.363	80.7	29.3	25.5	
25.0 18.0 57.0	0.450	64.1	28.8	25.9	
30.1 21.5 48.4	0.536	53.5	28.7	26.1	
40.0 28.5 31.5	0.701	40.9	28.7	26.2	
45.0 32.0 23.0	0.784	37.4	29.3	25.6	
Decanol					
molar ratio decanol/surfactant 1					
13.9 6.1 80.0	0.209	166.5	34.7	26.3	This work
15.5 6.7 77.8	0.231	137	31.7	28.9	
20.9 9.1 70.0	0.312	106	33.0	27.7	
27.9 12.1 60.0	0.413	65.8	27.2	33.7	
35.0 15.0 50.0	0.513	65.0	33.4	27.5	
41.5 18.2 40.3	0.632	53.6	33.9	27.9	
molar ratio decanol/surfactant 2					
15.0 13.0 72.0	0.281	116.5	34.8	23.6	This work
18.3 15.9 65.8	0.350	90.6	33.0	24.9	
24.1 20.9 55.0	0.542	61.2	34.6	23.8	
29.5 25.5 45.0	0.550	53.5	30.6	26.9	
34.9 30.3 34.8	0.652	48.2	32.3	25.4	
41.5 33.5 25.0	0.750	43.0	32.4	25.2	

Table 4. (Continued)

Composition (%)	Φ_a	d (Å)	d_a (Å)	S (Å ²)	Ref.
molar ratio decanol/surfactant 2.3					
10.0 10.0 80.0	0.215	162	34.9	23.1	This work
15.0 15.0 70.0	0.319	103	32.9	24.4	
20.0 20.0 60.0	0.422	79	33.8	23.8	
24.9 25.1 50.0	0.524	64.8	33.7	23.7	
29.9 30.1 40.0	0.623	53.5	33.3	24.2	
35.2 35.0 29.8	0.720	47.3	34.1	23.6	

4). There is an increased molecular packing with the alcohol content, which is shown by the small decrease in the values of the area per polar group with the octanol content, from about 27 to about 26 Å² (Fig. 4).

The viscous isotropic, cubic phase, I_2'' is located on the octanolic side of the lamellar liquid crystalline phase around the composition 21/22/57 (molar ratio about 1:3.2:55). The scanty x-ray data available suggest that the structure is primitive cubic with a unit cell of about 125 Å (Table 2).

The F -phase region is crescent shaped and its location is the "traditional" one just below the L_2 -phase. The minimum water content is about 10% and the maximum about 29%. The octanol content lies between about 42% and 48%. The parameters of the two-dimensional unit cell vary between about 36 and 50 Å, the diameters of the polar rod-aggregates of water between about 12 and 27 Å, and the areas per polar group at the polar/non-polar interfaces between about 12 and 18 Å² (Table 2). These values are estimated under the assumption that all polar groups lie at the interface; the low values indicate that part of the octanol acts as solvent.

The decanolic system

The phase diagram of this system displays, like the octanolic one, two isotropic liquid solution phases (L_1 and L_2), a lamellar liquid crystalline phase (D), and two hexagonal liquid crystalline phases (E and F). In contrast to the octanolic system, there is no cubic phase on the alcoholic side of the lamellar phase D , but instead one additional anisotropic phase (K) with rather low water content at high decanol and moderate surfactant contents.

The aqueous solution region L_1 dissolves rather little decanol, maximally about 1.8% at a sur-

factant content of about 15% (molar ratio 1:0.3:112). Above about 15% C_{16} TABr the decanol solubility decreases to very low values; there is no finger penetrating between the normal hexagonal phase E and the lamellar phase D .

The region of phase L_2 has also shrunk, the maximal values for water and surfactant are about 10% and 15%, respectively (the molar ratio surfactant/decanol/water is 1:11.5:13.5). The minimum water content of the phase at high surfactant content is about 3–4 moles per mole.

No studies of their structural behavior have been performed in the L_1 and the L_2 phases. On analogy, one may infer that their structures are similar to those in the hexanolic system. However, it is doubtful if the micelles in the L_1 -phase obtain an ellipsoidal shape upon addition of decanol.

The hexagonal phase E dissolves only about 2% decanol (about 0.12–0.25 moles per mole of surfactant). This content will hardly alter the structural parameters from those in the binary system and in the ternary system with hexanol. There are no x-ray diffraction studies performed in this phase. The ²H NMR spectra display a single splitting with a rather small value ($\Delta = 30$ –70 Hz); the parameter k , which is obtained by dividing the splitting value with the molar ratio surfactant/water, obtains values between 1.2 and 1.3 10³ Hz (Table 3).

The lamellar phase D has a similar extension towards the water corner as do the corresponding phases in the hexanolic and octanolic systems. The maximal water content is about 96%, which means about 1000 moles per mole surfactant. The alcohol content lies between 0.8 and 3.3 moles per mole surfactant. Series with the molar ratios 1:1, 2:1, and 2.3:1 between decanol and surfactant show the "ideal" swelling behavior (Fig. 3); the amphiphilic bilayer thickness is about 33–34 Å, and the area per polar group decreases from about 28 to

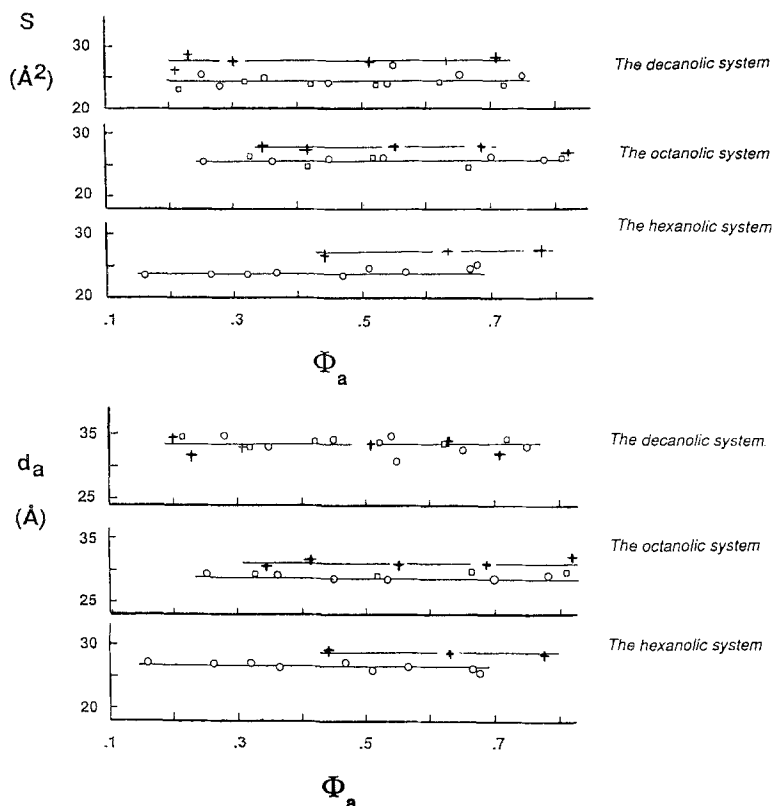


Fig. 4. The thickness of the amphiphilic layers, d_a , and the area per polar group, S , for the lamellar phases in the hexanolic, octanolic, and decanolic C_{16} TABr systems as a function of the volume fraction of amphiphilic matter, Φ_a . The same series as in Fig. 4 with constant molar ratios between alcohol and surfactant

about 24\AA^2 from the series 1:1 to series 2.3:1 (Fig. 4). The splittings in the ^2H NMR spectra have larger values than in the hexagonal phase ($\Delta = 238\text{--}787 \text{ Hz}$), and the values for the parameter k lie between 3.2 and $3.8 \cdot 10^3 \text{ Hz}$ (Table 3). These findings are in concordance with the lamellar structure.

The characterization and location of the two anisotropic phases F and K in this system presented some problems.

i) The region of phase F is centered around the composition 27/48/25 (molar ratio 1:4:19). The consistency of the phase is rather soft and at 25°C the phase is sensitive to composition and temperature. The phase identification and extension were based upon microscopical observations ($KF + SP$) and inspection of ^2H NMR spectra ($BL + DM + AK$, Fig. 5).

The hexagonal structural interpretation is confirmed by x-ray diffraction (for a sample with the composition 25/50/25 the Bragg spacings are 53.5, 31.0, and 26.5 \AA , viz. reflections in the sequence $1:\sqrt{3}:\sqrt{4}$, and $d_p \cong 61 \text{\AA}$ (Table 2)). Under the assumption that the structure is reversed and all

alcohol molecules are located at the polar/nonpolar interface, the diameter of the rod-aggregates is about 31 \AA and the value for the area per polar group 13\AA^2 (Table 2). This area value is so low that all the decanol cannot be located at the polar/nonpolar interfaces; part of it obviously acts as solvent.

ii) The phase K is centered around the composition 45/40/15 (molar ratio 1:2:6.75). The consistency is stiffer than for phase F , for which reason the extension of the phase is more definite. The texture in the polarizing microscope differs from the mosaic one displayed by the adjacent lamellar phase D and cannot be adapted to the classification of Rosevear [2]. The x-ray diffraction pattern for a sample with the composition 50.40/34.95/15.01 displays four sharp equidistant peaks in the ratio 1:2:3:4 (the fundamental repeat is 45 \AA , Table 2).

The ^2H NMR spectra for samples from regions F and K show a single splitting. The values for the parameter k is about half of the value in the lamellar phase D and, furthermore, is of the same magnitude as in spectra from the hexagonal phase E (Table 3).

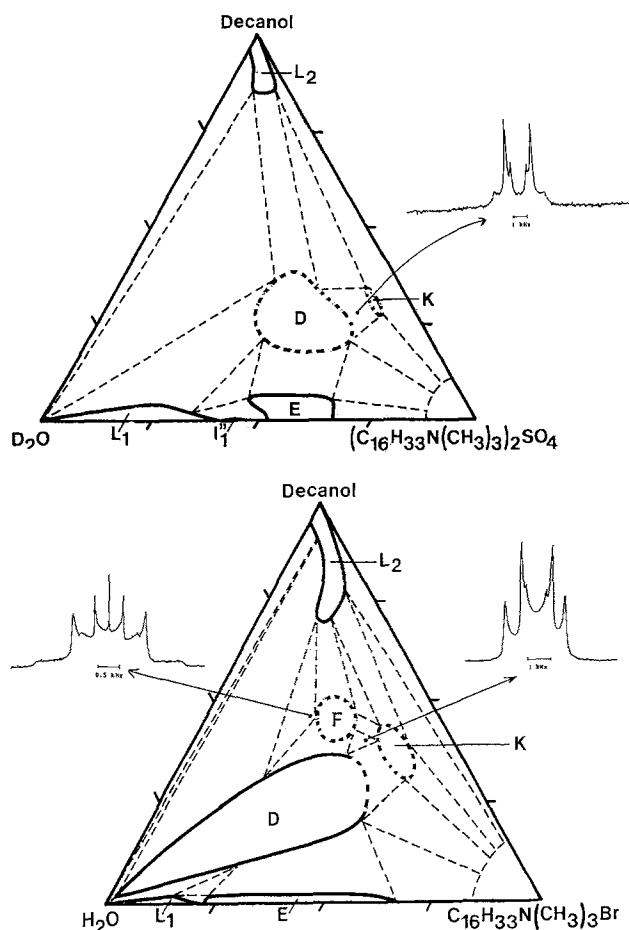


Fig. 5. The isothermal ternary phase diagrams at 25 °C for the decanolic systems of hexadecyl trimethyl ammonium bromide and sulphate, respectively, and (heavy) water. Notations as in Fig. 1. Sample composition for the inserted ^2H NMR spectra (at 35 °C), in the C_{16}TABr system 42.0/38.0/20.0 (phases $D + K + F$) and 24.5/46.0/29.5 (phases $D + F + L_2$), and in the $(\text{C}_{16}\text{TA})_2\text{SO}_4$ -system 59.0/27.8/13.2 (Phases D and K)

These findings indicate for the phase K a non-hexagonal structure of polar rod-aggregates in a nonpolar hydrocarbon environment.

The system $(\text{C}_{16}\text{TA})_2\text{SO}_4$ -decanol-heavy water

The phase equilibria in this ternary system have been determined by optical macroscopical and microscopical observations with and without crossed polaroids, and inspection of ^2H NMR spectra. The system (Fig. 5) displays two isotropic liquid solution regions (L_1 and L_2), three regions with anisotropic liquid crystalline matter (D , E , and K), and one region with viscous isotropic cubic phase (I_1').

The aqueous solution phase L_1 and the normal liquid crystalline hexagonal phase E dissolve decanol, 4% and 6%, respectively (~ 0.6 moles per mole). The intermediate viscous isotropic cubic phase, I_1' , however, lacks this capability. Thus, as soon as decanol is added to the system, the tie-lines in the ternary system go from the L_1 -phase directly to the hexagonal phase E (Fig. 5) [18].

The micellar conditions in the decanol-containing part of the L_1 -region and in the decanolic L_2 -region have not been studied. The extent of the latter phase is small. The decanol dissolves about 5% of $(\text{C}_{16}\text{TA})_2\text{SO}_4$, the solubility of water in decanol is about 3.8% (Table 1) and the maximum content of water and surfactant in the L_2 -phase amounts to about 8% for both components.

The hexagonal structure of the E phase region is evident from the microscopical texture and the values for the splittings in the ^2H NMR spectra. The splitting values increase somewhat with the decrease in water content (Table 3).

The samples in the lamellar phase D have a rather soft consistency and have macroscopically a grayish colour. They have a mosaic texture in the polarizing microscope [2] and the values for the splittings in the ^2H NMR spectra are about twice of them in the E phase (Table 3). The amphiphilic composition (decanol/surfactant) varies between the molar ratios 4.2 and 1.4. The phase requires a minimum of about 16% water and its extension towards the water corner stops at 39%; that means that the water content spans from about 8.8 to about 36 moles per mole of surfactant (Table 5). The lamellar phase thus lacks the capability to incorporate large amounts of water under one-dimensional swelling that was observed in the corresponding C_{16}TABr system. This is a feature which is common with binary and ternary anionic systems where the counterions are divalent [21–26].

The location of phase K on the surfactant- and alcohol-rich side of the lamellar phase D indicates a reversed structure. The phase is clearly separated from the neighboring lamellar phase. The nature and extension of the phase have been determined by inspection of the ^2H NMR spectra (Fig. 5) (Table 3). The location is centered around the composition 61/31/8 (molar ratios 1:2.25:4.4). The splitting values are smaller than those in the neighboring lamellar phase and the k -values of about the same magnitude as in the normal hexagonal phase E (Table 3). That would suggest a

Table 5. Stability ranges of the lamellar liquid crystalline phases D and K in the systems C_{16} TABr or $(C_{16}TA)_2SO_4$, respectively/alcohol/water

A. C_{16} TABr Phase D	Water		Alcohol	
	n_{\max}	n_{\min}	n_{\max}	n_{\min}
Butanol	15.9	4.1	2.65	0.7
Hexanol	540	4.4	3.3	0.35
Octanol	770	5.4	2.3	0.4
Decanol	1000	10.9	3.3	0.8
Phase K Decanol	$n \sim 6.75$		$n \sim 2$	
B. $(C_{16}TA)_2SO_4$				
Phase D Decanol	36	8.8	4.2	1.4
Phase K Decanol	$n \sim 4.4$		2.6	1.8

n_{\max} and n_{\min} are the maximum and minimum numbers of moles of heavy water and alcohol, respectively, per mole of surfactant

reversed hexagonal structure. However, as the microscopical appearance is ambiguous (at least there is no clear hexagonal texture), we infer that this K-phase similar to the K-phase in the C_{16} TABr-system has a structure composed of polar rod-aggregates in some non-hexagonal conformation in a hydrocarbon environment.

Other ternary cationic systems

The third component is a polar one: Lawrence and coworkers have studied a number of systems of short-chain alkyltrimethylammonium bromides and water with alcohols of the chain-lengths C_4 , C_6 , C_8 , C_{12} as third compound [27, 28]. Systems of C_4 TABr just form an isotropic liquid solution phase extending from the water corner to the alcohol corner without any mesomorphic phases. The same is the case with the ternary system C_7 TABr/hexanol/water, but liquid crystalline phases occur in the hexanolic systems when the chain-length of the surfactant is increased.

With hexanoic acid as the third component, Lawrence et al. report a large liquid crystalline region in the middle of the phase diagrams for the C_8 , C_{10} , C_{12} , C_{14} , C_{16} , and C_{18} trimethyl ammonium bromide systems [27–30]. Figure 6 shows their phase diagram for the system C_{16} TABr/hexanoic acid/water. As the corresponding region in the C_{16} TABr/hexanol/water

system is divided in a lamellar and a hexagonal subregion which are separated from each other by a two-phase zone [7]; we infer that in the hexanoic acid system there is the same division in a normal hexagonal and a lamellar phase region. A strong indication to that is the tongue of the L_1 -phase which in the C_{16} TABr/hexanoic acid/water system (Fig. 6) makes an indentation in the liquid crystalline phase region in the same manner as in the hexanolic and octanolic C_{16} TABr systems (cf with Figs. 1 and 6).

The phase diagram for the C_{14} TABr/pentanol/water system determined by Friberg et al. is very similar to our diagram for the C_{16} compound and hexanol [31]. There are two isotropic solution phases (L_1 and L_2), and two liquid crystalline phases, one with hexagonal structure (E) and one with lamellar structure (D).

As regards the C_{14} compound, when the water in the binary system is replaced by other polar solvents (short chain alcohols, ethylene glycol, glycerol, formamide, *N*-methylformamide, and mixtures of them with water) the occurrence pattern of isotropic liquid solutions and liquid crystalline phases is the same as for the aqueous system of the C_{16} compound (Wärnheim et al. [32, 33]).

Kaler et al. have studied the lamellar phase in the quaternary system C_{16} TABr/decanol/butanol/water and the influence of small additions of ethyl-

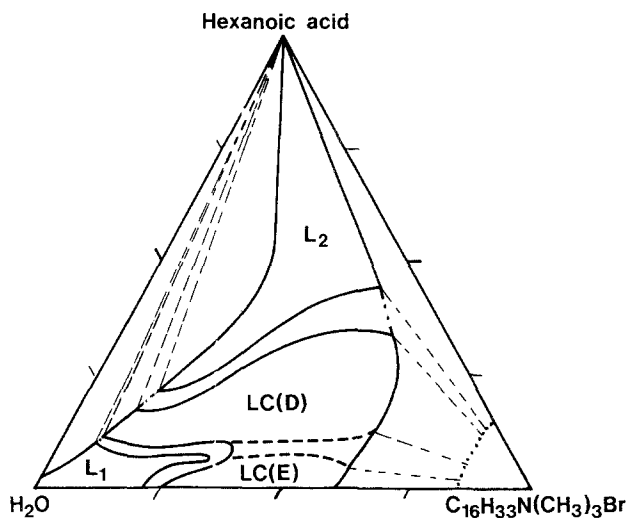


Fig. 6. The isothermal phase diagram at 27.5 °C for the ternary system C_{16} TABr/hexanoic acid/water. Modified after Lawrence et al. [21]. Phase notations as in Fig. 1. The suggested division of the liquid crystalline phase in two sub-regions (E and D) separated by a two-phase region is indicated

ene glycol, propylene glycol or dimethylformamide [34].

The third component is a hydrocarbon: Some exploratory investigations have shown that in ternary systems of $C_{16}TABr/p$ -xylene, benzene or octane/water, there occurs at $25^\circ C$ a large lamellar phase in the center of the phase diagram (Fig. 7). This is in contrast to the conditions in ternary systems containing an anionic surfactant, a hydrocarbon and water, which lack such a liquid crystalline phase [1]. There are indications of other phases in the hydrocarbon systems as well; however, the conditions for these phases have not been investigated further.

Ternary systems of double chain cationic compounds $\{(C_{12}H_{25})_2N(CH_3)_2Br\}$, hydrocarbon, and water have been shown to display in addition to a small L_1 -solution region and a large L_2 -region various liquid crystalline phases, among them a rather large cubic phase region [35–37].

Discussion

The $C_{16}TABr$ -systems

In the alcoholic ternary systems at $25^\circ C$, the solution structure (simplified) changes, when the chain length of the alcohol is short, (methanol to butanol) from a "normal" micellar structure at the water/surfactant axis over some intermediary stage which occupies a large part of the center of the diagram to a "reversed" micellar one at the alcohol corner. At high $C_{16}TABr$ content, a minimal amount of water (about 2 moles per mole surfactant) is needed for the solution phase to be formed.

When the chain length of the alcohol is increased, the continuous solution region splits into two subregions, an aqueous one, L_1 , and an alcoholic one, L_2 . The righthand border of region L_2 lies at about the molar ratio 5 between water and surfactant. The phases send out a tongue towards the water corner. The position of its tip retracts from hexanol to decanol.

In the binary system $C_{16}TABr$ /water there is the liquid crystalline normal hexagonal phase E , which is composed of nonpolar rod-aggregates of constant diameter (45 \AA) in an aqueous surrounding. The area per polar group at the polar/nonpolar interfaces is constant at 53 \AA^2 .

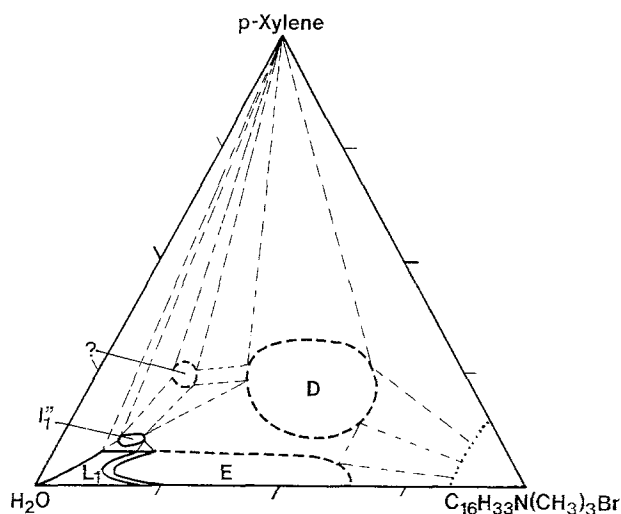


Fig. 7. The isothermal phase diagram at $25^\circ C$ for the ternary system $C_{16}TABr/p$ -xylene/water. A tentative sketch. Phase notations after [1]. (Fontell and Puang-Ngern)

The hexagonal phase has the capability of incorporating short-chain alcohol. The molar ratios for methanol, ethanol, and butanol are 5, 3, and 1 moles, respectively, per mole surfactant. In the methanolic and ethanolic systems, the extension in the phase diagram is about the same on a weight basis. If the nonpolar rod-aggregates in the ethanolic system are assumed to contain only the surfactant, their diameter decreases with increased ethanol content from 45 to about 38 \AA , while the area per trimethylammonium bromide group increases from about 53 to about 90 \AA^2 .

The capability of the hexagonal phase of incorporating the long-chain alcohols hexanol, octanol, and decanol is rather low. The influence on the structural parameters cannot be large.

In the methanolic and ethanolic $C_{16}TABr$ systems, there are no other liquid crystalline phases than the normal hexagonal one. In this respect they differ from alcoholic ternary anionic systems. The system of sodium octanoate and water has in the ethanolic case in addition a lamellar and a cubic phase [1].

All the other alcoholic $C_{16}TABr$ systems display a lamellar liquid crystalline phase D . The minimum water content is about 5 moles per mole surfactant, with the exception of the decanolic system where it is about 11 moles. Instead, there is in that system another liquid crystalline phase K (with a reversed non-hexagonal rod-structure) with a water content between 6 and 11 moles per mole.

The capability of the lamellar phase *D* to incorporate water in the butanolic system is restricted to about 17 moles per mole. When the chain length of the alcohol is increased, the water content of the phase increases (Table 5). When the ratio alcohol/surfactant is "right", the incorporation will occur under "ideal" one-dimensional swelling, viz. the lipid bilayer thickness is constant and all the water, in excess of the minimum amount that is needed for the phase to be formed, will form the intercalated polar layer.

The thickness of the lipid bilayers, consisting of the surfactant and the alcohol, is somewhat dependent on the alcohol content. Increased amounts of alcohol result in a more tight packing in the amphiphilic layers (Fig. 4).

In the octanolic system, there is on the alcoholic side of the lamellar phase a cubic phase (I_2'') at a rather high water content. A cubic phase with a similar location in the phase diagram has been observed in some other ternary cationic systems [1]. There is no firm information about the structure of this group of cubic phases.

There is further in the octanolic system on the alcoholic side of the lamellar phase a "reversed" hexagonal phase *F* having an "inverted" structure of polar aggregates of water and polar groups in a hexagonal array in an octanolic environment.

In the decanolic system there is no cubic phase on the decanolic side of the lamellar phase, but there occur instead two phases with reversed structures (phases *K* and *F*).

While the structure of phase *F* is the "reversed" hexagonal liquid crystalline one, the structure of phase *K* is presumably some non-hexagonal rod-structure.

The $(C_{16}TA)_2SO_4$ system

In the $(C_{16}TA)_2SO_4$ /decanol/water system there are the same types of phases (two isotropic liquid solution phases L_1 and L_2 , and various liquid crystalline phases) as in the monovalent $C_{16}TABr$ system. The influence of the divalent counterion is manifested in that

i) the normal micellar solution region L_1 in the binary system contains predominantly small spherical aggregates. The degree of counterion binding β is 0.83 [38] vs 0.7 for the monovalent bromide system [39]. On molar basis, the extension of the

phase is roughly the same as in the monovalent system (Table 1).

ii) the span of the water content of the normal hexagonal phase in the binary system along the surfactant/water axis is narrower in the divalent system, about 18–35 vs about 11–61 moles of water per mole of surfactant in the monovalent system (Table 1).

iii) the existence region towards the water corner of the lamellar phase has shrunk in the ternary system from about 1000 moles of water per mole of surfactant for the Br^- system to about 17 for the SO_4^{2-} system (Table 5). The minimum water contents are about 5 and 10, respectively; the Br^- ion has no water of hydration; the SO_4^{2-} ion is hydrated.

iv) The 2H NMR splittings in the spectra from the liquid crystalline phases are larger than those displayed by the corresponding phases in the monovalent decanolic system.

v) the liquid crystalline phase *K* on the water-poor side of the lamellar phase is of the same type as the phase *K* in the system $C_{16}TABr$ /decanol/water, and has presumably a non-hexagonal inverted rod-structure.

Conclusions

The phase behavior in the isothermal ternary systems $C_{16}TABr$ /alcohol/water follows a regular pattern when the alcohol chain length is varied.

The phase behavior is similar to that in corresponding systems with an anionic surfactant, but differences are noticeable.

When the alcohol chain length is short, there is in the isothermal phase diagram a continuous solution region from the water corner to the alcohol corner but when the chain length is increased, the solution region is divided into two subregions, an aqueous and an alcoholic one; in addition to the liquid crystalline hexagonal phase along the surfactant/water axis liquid-crystalline phases begin to appear in the middle of the diagram.

When the third component is a hydrocarbon, there occurs contrary to the conditions in the anionic surfactant systems, a lamellar phase with a large extension in the center of the phase diagram.

When the monovalent bromide ion is exchanged for the divalent sulphate ion, the lamellar liquid crystalline phase loses much of its capability to incorporate water. This feature is similar to that in anionic surfactant systems with divalent counterions.

The aqueous solution phase L_1 in the divalent system contains only small micelles.

In the decanolic systems occur on the water-poor side of the lamellar liquid crystalline phase in the $C_{16}TABr$ system two and in the $(C_{16}TA)_2SO_4$ system one liquid crystalline phase with reversed rod-structure. While one of the phases in the $C_{16}TABr$ system has the two-dimensional reversed hexagonal structure, so is the structure of the two other phases presumably a reversed non-hexagonal rod-structure. A liquid-crystalline phase with the same location has previously been found in the system potassium decanoate/octanol/water [40–41].

Acknowledgements

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