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New lyotropic nematics of double chain surfactants

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The phase behaviour of N,N-dialkyl-N,N-dimethyl ammonium bromide double chain surfactants was investigated by polarization microscopy, $^2\text{H-N.M.R.}$ spectroscopy, and surface and magnetic field alignment in order to find new lyotropic nematic systems. Decanol was utilized to cause a rod to disc transition in the nematic phase. The sign of the anisotropy of the diamagnetic susceptibility $\Delta\chi$ was inverted by substituting the bromide counter-ion with the benzenesulphonate ion. The phase behaviour was modified within a wide range by varying the length of the two alkyl chains. Using these tools we were able to prepare any of the four kinds of uniaxial nematic phases: rod-like and disc-like aggregates with both negative and positive anisotropy of the diamagnetic susceptibility. Several new binary, ternary and quaternary systems of these double chain surfactants and some experiments are described to classify the different nematic phases.

1. Introduction

Lyotropic nematic systems are very new compared with thermotropic ones [1]. Since the discovery of the first binary lyotropic nematic phase by Boden *et al.* in 1979 [2] not many nematic surfactant-water systems have been found and investigated [2-10]. A biaxial nematic phase was discovered and investigated in ternary surfactant-alcohol-water systems [11, 12]. The formation of lyotropic nematic phases always occurs in a narrow concentration and temperature range. There is still a lack of understanding about the dependence between molecular structure of a surfactant and its tendency to build up nematic phases. Therefore, most of the known nematic systems were found by chance when the phase behaviour of many systems was carefully investigated.

To obtain a better understanding between micellar structure and the potential to build up nematic phases we used a selection of cationic double chain dimethyl ammonium bromides. The hydrophobic and steric features of the surfactant can be controlled by changing the length of the two hydrocarbon chains. Decanol may be regarded as a non-ionic surfactant with a very small polar head-group. Adding small amounts of decanol to a surfactant-water system is a good instrument to modify the head-group area when there are mixed micelles consisting of decanol and surfactant. The head-group area of an ionic surfactant can be modified, too, by exchange of the counter-ion. If all of these possibilities to modify a system are used it should be possible to prepare nematic phases without having to invest much time in the detailed investigation of many systems.

Starting from N-alkyl-N,N-dimethylamines it is possible to introduce any second alkyl chain by reaction with alkylbromide. Using this reaction we were able to produce a large set of dialkyl dimethyl ammonium bromide surfactants.

2. Experimental

2.1. Preparation of double chain dimethyl ammonium bromides

Dodecyl-, tetradecyl-, hexadecyl- and octadecyl dimethyl amine were a gift from Hoechst Gendorf. The purity of these amines was checked by gas chromatography

and was always higher than 90 mol %. Products with different chain lengths (mainly ± 2) were the main impurities. All alkylbromide compounds were purchased from Fluka in p.a. quality and were not purified further. Acetonitrile (Merck Darmstadt, 95 per cent) was used as solvent for quaternization.

To 100 ml acetonitrile at room temperature 0.1 mol of alkyldimethylamine and 0.11 mol of alkylbromide were added in a 1000 ml round-bottomed flask equipped with a reflux condenser. The resultant two-phase system was stirred and refluxed until there was a one-phase, slightly yellow solution. The reaction time depends on the chain length of the alkylbromide compound and increases with chain length. When the reaction was finished the solvent was carefully removed *in vacuo*. The crude product was purified by recrystallization from ether-methanol. Short alkylbromides yield up to 90 per cent, longer compounds about 50 per cent of double chain surfactant.

The purity was checked by $^1\text{H}/^{13}\text{C}$ -N.M.R. (remaining alkyldimethyl amine), measuring and cmc by surface tension and conductivity and by titration of the bromide, counter-ion. No considerable amount of impurities was found. Before preparing any solution, moisture has to be removed *in vacuo* when the surfactant has been stored for longer than 1 day.

2.2. Preparation of double chain dimethyl ammonium benzene sulphonates

All compounds investigated were prepared via ion exchange from the corresponding dialkyl dimethyl ammonium bromide surfactants. Direct exchange of the counter-ion succeeds, but the product is not very pure. A much better access to benzene sulphonate surfactants is an exchange of the bromide counter-ion with hydroxide and titration of the aqueous solution with benzene sulphonic acid. Benzene sulphonic acid was prepared by ion exchange, too, from sodium benzene sulphonate, because the acid was not available in high purity.

Preparation of benzene sulphonic acid

Seventy grams of cation exchange material (Kationenaustauscher I Merck Art 4765) was activated with 1000 ml of 1 M HCl and was washed neutral afterwards. After this procedure the column was filled with 1000 ml of a 0.1 M aqueous solution of sodium benzene sulphonate and the first 50 ml passing the column were discarded. The acidity of the solution leaving the column has to be controlled during the whole exchange reaction. When the benzene sulphonate solution had passed the column the resultant aqueous solution containing the benzene sulphonic acid was freeze dried.

Preparation of dialkyl dimethyl ammonium hydroxide

Sixty grams of anion exchange material (Anionenaustauscher III Merck Art 4767) was activated with 500 ml of 1 M NaOH and washed neutral afterwards. Of a 0.05 M bromide surfactant solution, 1000 ml was sent through the column and the first 50 ml were discarded after passing the column. It is necessary to check whether bromide is present after the column during the whole reaction.

Preparation of double chain dimethyl ammonium benzene sulphonates

The aqueous solution of dialkyl dimethyl ammonium hydroxide was titrated with the benzene sulphonic acid. The resultant solution was freeze dried.

2.3. Recording of the phase diagrams

The sign of birefringence and the kind of liquid-crystalline texture was determined with a polarization microscope (Zeiss Standard Pol 16) equipped with a λ -plate and a hot stage (Mettler FP 80). All samples investigated by microscopy were prepared in microslides (Camlab) and quartz cells (Hellma) with path lengths of 0.1 and 0.2 mm.

A Jeol FX 90 Q F.T.-N.M.R. spectrometer with external lock was used for the ^2H -N.M.R. measurements. In order to obtain good spectra within a short accumulation time all solutions were prepared with a mixture of 5 per cent D_2O and 95 per cent H_2O as solvent. Larger amounts of D_2O provide better spectra but affect the phase diagram.

Magnetic alignment experiments were carried out in the same sample cells which were used for the polarization microscopy experiments. Fields up to 2.1 T were available with a Bruker BE 20 magnet.

3. Binary surfactant-water systems

3.1. Nematics consisting of rod-like aggregates with positive $\Delta\chi$

In the following the dialkyl dimethyl ammonium bromide surfactants are abbreviated as $\text{C}_x\text{C}_y\text{DMABr}$, where x is the number of carbon atoms in the first hydrocarbon chain and y the number in the second chain. The benzene sulphonate surfactants are abbreviated in the same manner as $\text{C}_x\text{C}_y\text{DMA}\text{O}\text{SO}_3$. Table 1 shows the selection of double chain ammonium bromide surfactants and the phase behaviour of the binary surfactant-water systems.

The binary systems indexed with ⁽¹⁾ in table 1 form nematic phases consisting of rod-like micelles with positive sign of anisotropy of the diamagnetic susceptibility $\Delta\chi$ and negative birefringence Δn . All systems have the same phase sequence L_1 -nematic (N_c^+)- H_1 with increasing surfactant concentration. The region beyond the hexagonal phase was not investigated further because the high viscosity of the hexagonal phase

Table 1. Phase sequence of the investigated dialkyl dimethyl ammonium bromide surfactant systems as a function of the chain lengths of the two alkyl chains.

2nd chain	1st chain			
	12	14	16	18
1	L_1/H_1 ⁽²⁾	$L_1/\text{N}_c^+/\text{H}_1$ ⁽¹⁾	$L_1/\text{N}_c^+/\text{H}_1$ ⁽¹⁾	—
2	L_1/H_1 ⁽²⁾	L_1/H_1 ⁽²⁾	$L_1/\text{N}_c^+/\text{H}_1$ ⁽¹⁾	$L_1/\text{N}_c^+/\text{H}_1$
3	—	—	$L_1/\text{N}_c^+/\text{H}_1$ ⁽¹⁾	—
4	L_1/H_1 ⁽²⁾	L_1/H_1 ⁽²⁾	$L_1/\text{N}_c^+/\text{H}_1$ ⁽¹⁾	$L_1/\text{N}_c^+/\text{H}_1$
5	—	—	L_1/H_1 ⁽²⁾	—
6	L_1 up to 95 wt % ⁽³⁾	L_1 up to 95 wt % ⁽³⁾	L_1 up to 80 wt % ⁽³⁾	—
7	L_1 up to 95 wt % ⁽³⁾	$L_1/L_\alpha/\text{isotr.}/\text{LC}/\text{cryst.}$ ⁽⁴⁾	L_1 up to 75 wt % ⁽³⁾	—
8	$L_1/L_\alpha/\text{isotr.}/\text{LC}/\text{cryst.}$ ⁽⁴⁾	—	$L_1/L_\alpha/\text{isotr.}/\text{LC}/\text{cryst.}$ ⁽⁴⁾	—
10	$L_1/L_\alpha/\text{cryst.}$ ⁽⁵⁾	—	$L_1/L_\alpha/\text{cryst.}$ ⁽⁵⁾	—
12	—	—	$L_1/L_\alpha/\text{cryst.}$ ⁽⁵⁾	—
14	—	—	$L_1/L_\alpha/\text{cryst.}$ ⁽⁵⁾	—
16	—	—	$L_1/L_\alpha/\text{cryst.}$ ⁽⁵⁾	—

L_1 = micellar solution; H_1 = hexagonal phase; L_α = lamellar phase; *cryst.* = solid crystals; *isotr.* = isotropic phase with low viscosity; N_c^+ = nematic phase, consisting of rod-like micelles with positive anisotropy of the diamagnetic susceptibility; LC = liquid crystal phase; all sequences for ambient temperature of just above the Krafft temperature.

prevents the preparation of bulk solutions. The following experiments and features prove the existence of rod-like micelles in the nematic phase.

The nematic phase is a neighbour to a hexagonal phase consisting of rod-like aggregates, too. When the nematic phase is filled into a microslide and observed under the polarization microscope, flow alignment with the optical axis parallel to the direction of flow is visible. A nematic phase consisting of disc-like aggregates would align with the optical axis perpendicular to the direction of flow. With the help of a λ -plate and the interference colours the negative sign of birefringence can be determined in the flow-aligned phase. This procedure is described in detail in [13]. No pseudo-isotropic texture is obtained by decreasing the path length and storing the samples for some hours. Disc-like aggregates would give this pseudo-isotropic texture because of surface alignment with the optical axis perpendicular to the glass surface and parallel to the direction of view under the polarization microscope [4, 14, 15].

The positive sign of $\Delta\chi$ was proved by magnetic field alignment combined with polarization microscopy and $^2\text{H-N.M.R.}$ quadrupole splitting measurements. In a magnetic field of 2.1 T complete alignment with the optical axis parallel to the field can be obtained within several hours. This alignment is visible between crossed polarizers in an N.M.R. sample tube. When a magnetic field was applied to a sample in a microslide typical transient textures for nematic rods with $\Delta\chi > 0$ were visible: a striated pattern parallel to the direction of the magnetic field (see figure 1). Nematic phases of disc-like particles with positive $\Delta\chi$ would give a similar texture but with the dark stripes perpendicular to the magnetic field [14].

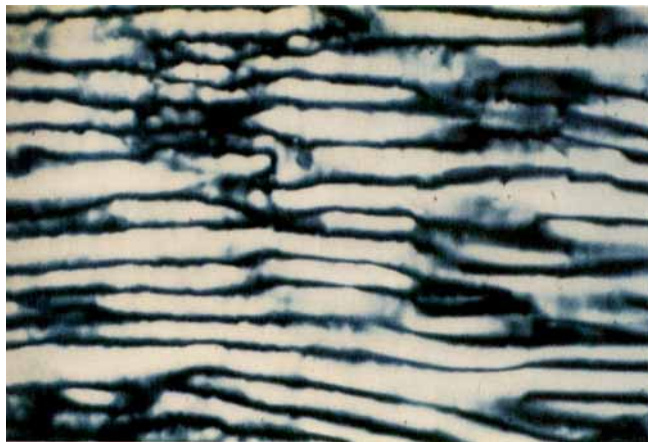


Figure 1. Transient texture of a nematic phase consisting of rod-like micelles (magnetic field applied parallel to the striated texture).

Measuring the quadrupole splitting of D_2O associated on the surface of the micelles is a good way to determine the sign of $\Delta\chi$ in a nematic phase [13]. If a nematic sample with positive $\Delta\chi$ is put into the N.M.R. spectrometer first a powder pattern typical for a non-aligned liquid-crystalline phase is visible (see figure 2, trace 1). If the nematic phase orients parallel to the magnetic field of the N.M.R. spectrometer the shoulders of the powder pattern will increase and the middle peaks vanish with time as seen in figure 2.

In the binary systems labelled with a question mark ($\text{C}_{18}\text{C}_2\text{DMABr}$ and $\text{C}_{18}\text{C}_4\text{-DMABr}$) it is not quite clear whether there is a nematic phase in the concentration

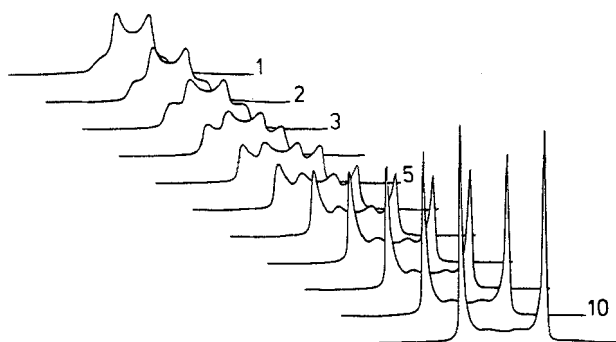


Figure 2. Alignment of rod-like nematics with positive $\Delta\chi$ studied by time-resolved ^2H -N.M.R. measurement (system $\text{C}_{16}\text{C}_4\text{DMABr-H}_2\text{O}$).

range below the hexagonal phase. Under the polarization microscope there is a texture typical for neither a hexagonal nor a nematic phase. Once we observed a weak orientation in the magnetic field when the quadrupole splitting was measured, but the temperature range was too small to reproduce the measurement. If there is a nematic phase in these two systems it should have the same features as the phases mentioned before, but a very narrow range of concentration and temperature. The main reason for this behaviour is the decreasing solubility in water with increasing chain length of the surfactant. Therefore the Krafft temperature of both systems is high (38 and 42°C, respectively). On the other hand, the clearing point of all nematic systems mentioned before is not much higher than 40°C. Table 2 summarizes the features of the binary nematic dialkyl dimethyl ammonium bromide surfactant systems investigated.

Table 2. Binary nematics of rod-like micelles with positive $\Delta\chi$.

Surfactant	Molecular weight/g mol ⁻¹	Concentration of a typical sample		References
		wt %	mol kg ⁻¹ of H ₂ O	
$\text{C}_{14}\text{C}_1\text{DMABr}$	336	36	1.67	[3, 14]
$\text{C}_{16}\text{C}_1\text{DMABr}$	364	25	0.92	[13]
$\text{C}_{16}\text{C}_2\text{DMABr}$	378	32	1.25	[13]
$\text{C}_{16}\text{C}_3\text{DMABr}$	392	35	1.37	This paper
$\text{C}_{16}\text{C}_4\text{DMABr}$	406	40	1.64	[13]

The binary systems indexed with ⁽²⁾ in table 1 do not form nematic phases. There is a transition between the L_1 and H_1 phases with a narrow two-phase region. With decreasing length of the first alkyl chain the concentration range of the isotropic phase is increasing and the temperature range of the H_1 phase is decreasing.

In the systems indexed with ⁽³⁾ in table 1 there is no liquid-crystalline phase up to high surfactant concentrations. The surfactants $\text{C}_{12}\text{C}_6\text{DMABr}$ and $\text{C}_{14}\text{C}_6\text{DMABr}$ do not form a liquid-crystalline phase in aqueous solution. $\text{C}_{16}\text{C}_6\text{DMABr}$ builds up a cubic phase at a surfactant concentration of 80 wt %. The elasticity of this phase is so high that it is possible to excite the phase to mechanical vibrations within the audio-frequency range.

In the three systems indexed with ⁽⁴⁾ in table 1 there is a quite different phase sequence: L_1 - L_α -isotropic-liquid crystalline-crystalline. The lamellar phase beginning

at low surfactant concentration with low viscosity is surrounded by broad two phase regions L_1 - L_α . The liquid-crystalline phase at high surfactant concentrations shows lamellar textures under the polarization microscope, too, but the sign of birefringence is the opposite of the lamellar phase at low concentrations. Further investigations are needed.

The systems labelled with ⁽⁵⁾ in table I build up a lamellar phase beginning at low surfactant concentrations over the whole concentration range up to the phase boundary of crystalline surfactant. The concentration range of this crystalline phase increases with the length of the second alkyl chain, as expected.

Investigating the physical properties of this set of surfactants, we discovered an interesting correlation between the melting points, phase behaviour and hygroscopic behaviour. If the first chain remains the same, the melting point of the surfactants decreases with the length of the second chain. The melting points of $C_{16}C_n$ DMABr for $n = 1-8$ are $> 230^\circ\text{C}$ dec., 190, 120, 85, 47, 61, 40 and 145°C . Most of the surfactants investigated also exhibit thermotropic liquid crystals and sometimes it is not easy to detect the phase boundary between solid and liquid crystals. In some cases the thermotropic liquid-crystalline region covers a temperature range up to 25°C as for $C_{16}C_2$ DMABr and $C_{16}C_3$ DMABr. When the second chain exceeds six carbon atoms the melting points increase again. This minimum corresponds with the incapability to build up liquid-crystalline phases in aqueous solutions and with hygroscopic behaviour. All surfactants of this set which have minimum melting points are extremely hygroscopic.

Taking all of this experimental data into account we obtain the following conclusion. A short second alkyl chain increases the head-group area and the tendency to build up globular aggregates (see figure 3). The beginning of the hexagonal phase is shifted to higher concentrations. If the first alkyl chain is shorter, the area of the

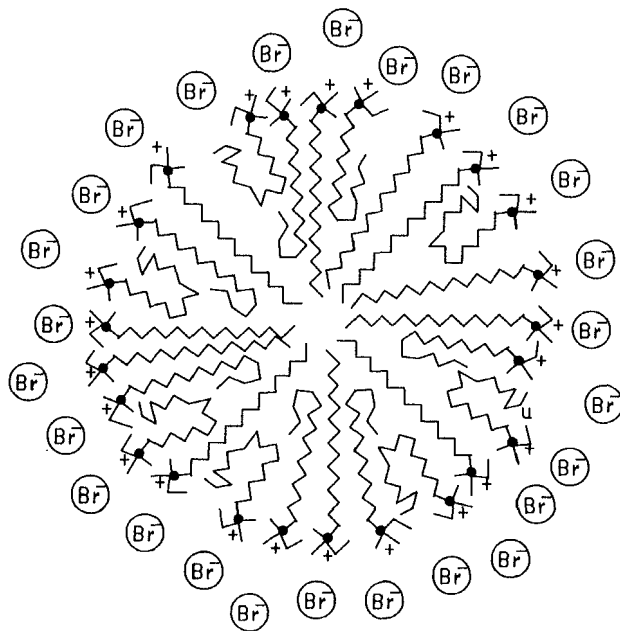


Figure 3. A short second alkyl chain contributes to the head-group area, globular micelles are preferred.

Table 3. Concentration of the first liquid-crystalline phase (in wt %) as a function of the lengths of the two alkyl chains.

2nd chain	12	14	16	18
1	47	36	25	—
2	55	46	32	25
3	—	—	38	—
4	57	48	40	35
5	—	—	60	—
6	95	95	80	—
7	95	10	75	—
8	5	—	7	—
10	5	—	5	—
12	—	—	5	—
14	—	—	5	—
16	—	—	5	—

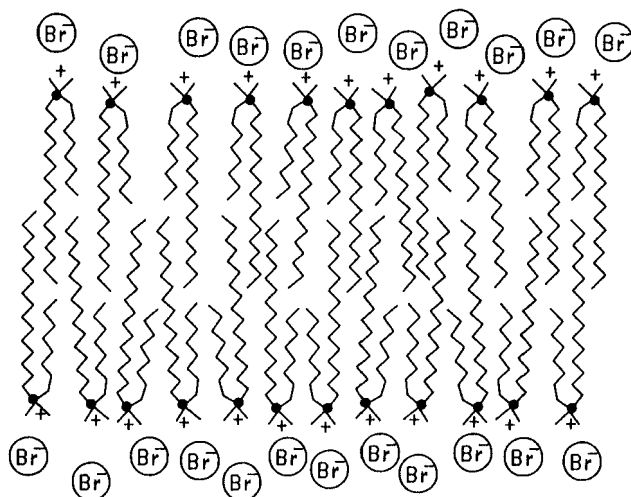


Figure 4. A long second alkyl chain contributes to the hydrophobic area, disc-like micelles or lamellar phases are preferred.

hydrophobic part is smaller than the polar head-group and the resultant phase behaviour is the same as before. This can be seen in table 3, where the concentration of the lowest liquid-crystalline phase is listed as a function of the chain length of both alkyl chains. When the second chain exceeds a certain length it contributes to the hydrophobic area. The hydrophobic area is now comparable in size with the head-group area and the formation of lamellar phases occurs at low surfactant concentrations (see figure 4). At the point where this transition of the phase behaviour takes place the formation of solid surfactant crystals seems to be disturbed most. This could explain the hygroscopic behaviour of these systems.

3.2. Nematics consisting of rod-like aggregates with negative $\Delta\chi$

The diamagnetic anisotropy of a nematic phase is caused by the molecular anisotropy of the single surfactant molecules [16]. The main contributions are the anisotropy of the C–C and C–H bonds in the hydrophobic part and the anisotropy

caused by the counter-ion. If the anisotropy of the hydrocarbon chain is dominant the nematic phases of hydrocarbon surfactants orient with the axis of the chain perpendicular to an external magnetic field. Therefore rod-like nematics align with the optical axis parallel to the disc-like aggregates with the optical axis perpendicular to a magnetic field. Perfluoro-surfactants usually behave in the opposite manner.

Aromatic groups in a surfactant molecule affect the sign of the diamagnetic susceptibility. It has been proved that the sign of $\Delta\chi$ can be inverted by substituting the bromide counterion by benzene sulphonate [3, 14].

We performed this exchange for all binary systems mentioned in the previous section. Table 4 summarizes the binary nematic systems we found and which consist of dialkyl dimethyl ammonium benzene sulphonate surfactants.

Table 4. Binary nematics of rod-like micelles with negative $\Delta\chi$.

Surfactant	Mol. weight	Concentration of a typical sample		References
		wt %	mol kg ⁻¹ of H ₂ O	
C ₁₄ C ₁ DMAØSO ₃	413	38	1.48	[3, 14]
C ₁₄ C ₂ DMAØSO ₃	427	44	1.91	This paper
C ₁₆ C ₁ DMAØSO ₃	441	32	1.07	This paper
C ₁₆ C ₂ DMAØSO ₃	455	38	1.35	This paper
C ₁₆ C ₃ DMAØSO ₃	469	45	1.74	This paper

The nematic phases in table 4 all occur in the concentration range below an H₁ phase. There is flow alignment with the optical axis parallel to the direction of flow. We found a typical nematic Schlieren texture under the polarization microscope and there was no pseudo-isotropic texture when we decreased the path length. These experimental data proves the existence of rod-like particles in all of these systems.

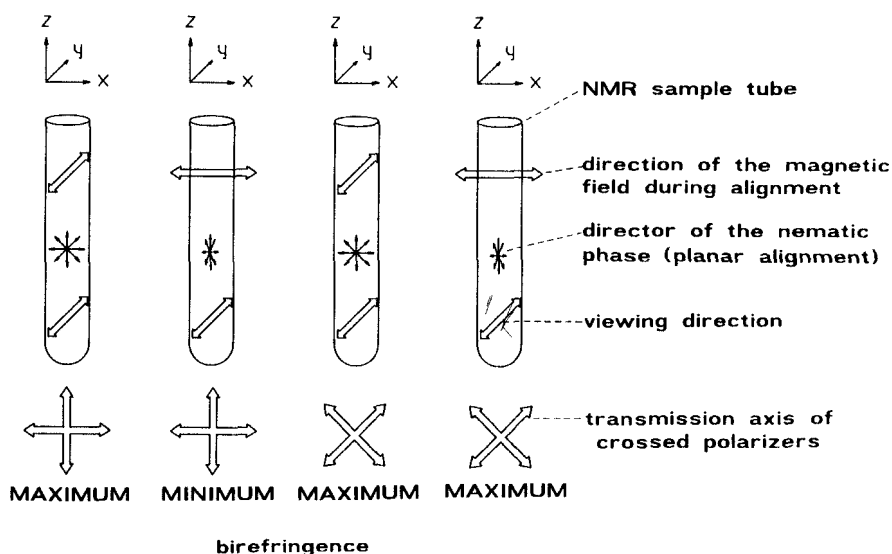


Figure 5. Features of a nematic phase of rod-like micelles with negative $\Delta\chi$ after several days in a magnetic field of 2.1 T.

Magnetic and $^2\text{H-N.M.R.}$ measurements were carried out to determine the sign of $\Delta\chi$. A 5 mm N.M.R. sample tube was filled with the nematic system and placed in a magnetic field of 2.1 T with the axis of the glass tube perpendicular to the magnetic field. After 48 h the sample was studied between crossed polarizers. Figure 5 summarizes the observations and shows the alignment of the nematic rods. We placed this aligned sample in an N.M.R. spectrometer with conventional electromagnet (magnetic field perpendicular to the axis of the sample tube) to prove this interpretation and we obtained the following set of $^2\text{H-N.M.R.}$ spectra. When the sample was put into the magnetic field of the N.M.R. spectrometer in the same position as in the previous experiment before we observed a sharp doublet (see figure 6 (a)). The director of the nematic phase is always perpendicular to the magnetic field of the spectrometer. In the next experiment the sample tube was turned 90° and the result was a two dimensional powder pattern, as expected (see figure 6 (b)).

Figure 7 shows a set of time dependent $^2\text{H-N.M.R.}$ spectra. A non-aligned sample was spinning during the whole measurement. The director orients parallel to the axis of the sample tube and perpendicular to the magnetic field. Thus, complete alignment can be achieved, but this takes several days. The quadrupole splitting is no longer a function of the turning angle when the spinning is finally stopped. All of our experiments prove the negative sign of $\Delta\chi$ in the nematic phases of table 4.

4. Ternary surfactant-decanol-water systems

Decanol may be regarded as a non-ionic surfactant with a small head-group. Small amounts of decanol added to a surfactant-water system increase the aggregation number, because the charge density on the surface of the aggregates is decreased by the non-ionic 'surfactant'. Simultaneously the curvature on the micellar surface is decreased, because the head-group area is decreased in the mixed micelles containing decanol and surfactant. This well known effect has been used in several systems [3, 10-14, 17-21] to increase the tendency of a system to build up disc-like aggregates or lamellar phases.

4.1. Nematics consisting of disc-like aggregates with negative $\Delta\chi$

When decanol is added to the nematic phase of rod-like micelles the result may be a nematic phase consisting of disc-like micelles with the opposite sign of $\Delta\chi$. This experiment has already been done for several surfactants [3, 10-14], but it does not succeed for all binary nematic systems of rod-like micelles. Table 5 lists some ternary systems resulting from those experiments.

All ternary systems above form nematic phases with low viscosity. Flow alignment with the optical axis parallel to the direction of flow is not possible. When the samples

Table 5. Ternary nematics of disc-like micelles with negative $\Delta\chi$.

Surfactant	Concentrations of a typical sample/ wt % (mol surfactant $\text{kg}^{-1} \text{H}_2\text{O}$)		References
	surfactant	decanol	
$\text{C}_{14}\text{C}_1\text{DMABr}$	30.2 (1.390)	4.9 (0.478)	This paper
$\text{C}_{16}\text{C}_1\text{DMABr}$	23.1 (0.866)	3.6 (0.312)	[13]
$\text{C}_{16}\text{C}_2\text{DMABr}$	28.3 (1.109)	4.3 (0.408)	[13]
$\text{C}_{16}\text{C}_3\text{DMABr}^*$	31.5 (1.252)	4.3 (0.420)	This paper

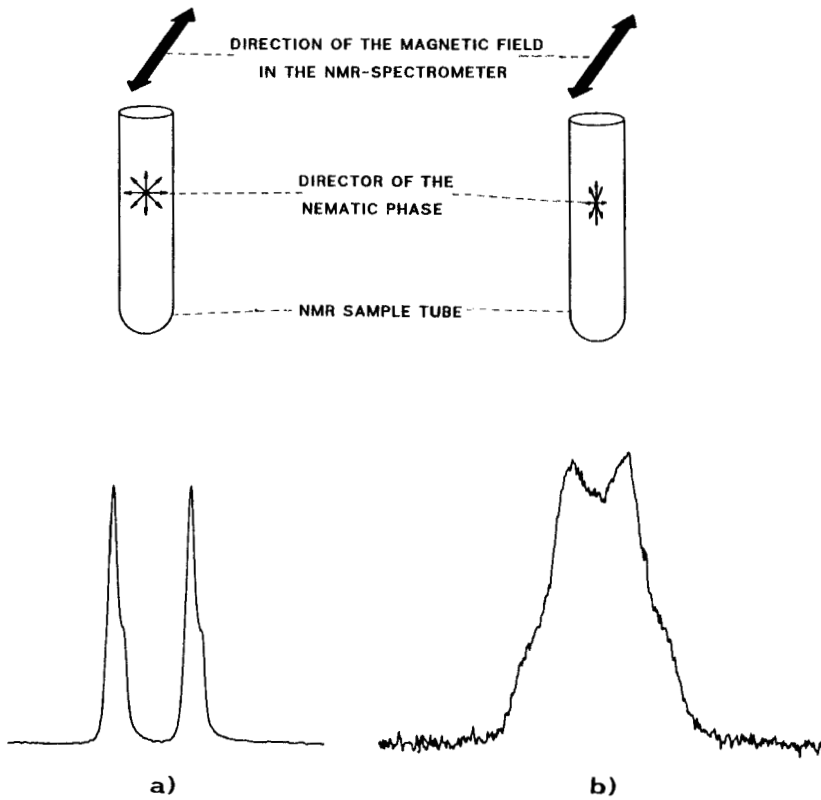


Figure 6. ^2H -N.M.R. spectrum of a nematic phase of rod-like micelles with negative $\Delta\chi$ after several days in a magnetic field of 2.1 T. (a) Measurement in the original position of prealignment and (b) measurement after turning the sample through 90° .

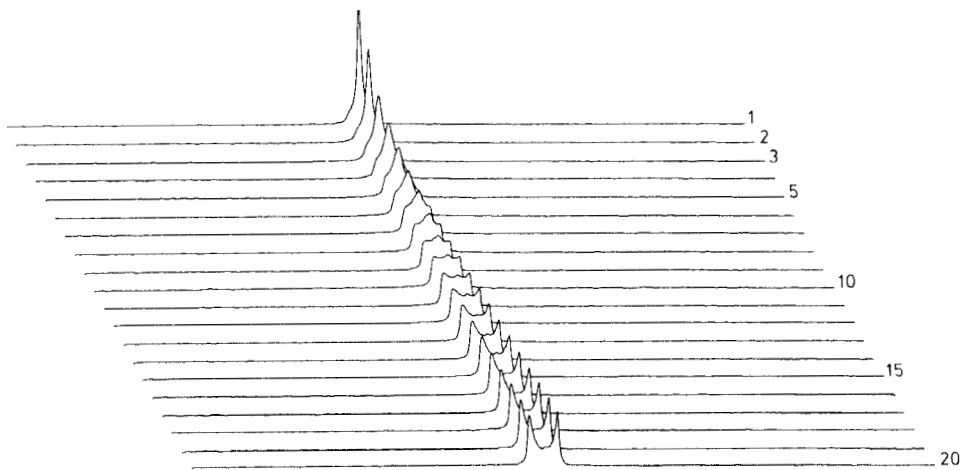


Figure 7. Alignment of rod-like nematics with negative $\Delta\chi$ studied by time-resolved ^2H -N.M.R. measurement. The sample was spinning round its axis during measurement.

were filled into microslides there was a nematic Schlieren texture which changed to a pseudo-isotropic texture within minutes. Birefringence remained only at the edges of the capillary when the sample was studied under the polarization microscope (see figure 8). This pseudo-isotropic texture could be disturbed by applying a magnetic field parallel to the optical axis of the pseudo-isotropic sample. The result was a transient Schlieren texture with strong birefringence (see figure 9) and finally a completely oriented sample when the field was applied for several hours (see figure 10). Complete orientation only happens because of wall effects and therefore is not observed in N.M.R. sample tubes where the path length is 50 times larger. The negative sign of $\Delta\chi$ was also proved by $^2\text{H-N.M.R.}$ measurements. The transition from rod-like to disc-like nematics and even a region of coexisting nematic phases could be observed with various amounts of decanol and surfactant. Extensive $^2\text{H-N.M.R.}$ measurements were published in [13]. The nematic system $\text{C}_{14}\text{C}_1\text{DMABr-decanol-NH}_4\text{Br-H}_2\text{O}$ has already been published by Boden and co-workers [3, 14], but NH_4Br seems not to be essential to prepare nematics from those surfactants and decanol. In the system $\text{C}_{16}\text{C}_3\text{DMABr-decanol-H}_2\text{O}$ the nematic range is very small. Excess decanol or surfactant at once causes the formation of a lamellar phase. When decanol was added stepwise to the binary nematic phase of $\text{C}_{16}\text{C}_4\text{DMABr}$ (see table 2) we observed the phase sequence nematic (rods)- $\text{L}_1\text{-L}_\alpha$.

5. Quaternary two-surfactant-decanol-water systems

5.1. Nematics consisting of disc-like aggregates with positive $\Delta\chi$

If it is possible to cause a transition from rod-like nematics with positive $\Delta\chi$ to disc-like nematics with negative $\Delta\chi$ by adding decanol, it should be possible to prepare disc-like nematics with positive $\Delta\chi$ when decanol is added to the binary nematic systems of the dialkyl dimethyl ammonium benzene sulphonate surfactants with negative $\Delta\chi$. We tried this for all the systems described before, but we did not succeed. Stepwise addition of decanol caused first a transition to an isotropic solution and further addition of decanol always caused the formation of a lamellar phase. Increasing the surfactant concentration yielded a lamellar phase, too, without passing a nematic phase. The phase behaviour was the same as of the ternary system $\text{C}_{16}\text{C}_4\text{DMABr-decanol-water}$ in §4.

The next idea to prepare nematics of disc-like aggregates with positive $\Delta\chi$ was to start from disc-like nematics with negative $\Delta\chi$. We tried to replace various amounts of dialkyl dimethyl ammonium bromide surfactant with dialkyl dimethyl ammonium benzene sulphonate. If the amount of dialkyl dimethyl ammonium benzene sulphonate is sufficiently large and the nematic phase of disc-like micelles can be maintained, then there should result a nematic phase of disc-like micelles with positive sign of $\Delta\chi$. Thus, we found the two quaternary systems listed in table 6.

Table 6. Quaternary nematics consisting of disc-like aggregates with positive $\Delta\chi$.

1st surfactant	2nd surfactant	Concentration wt % (mol surfactant kg^{-1} of H_2O)			References
		1st surfactant	2nd surfactant	Decanol	
$\text{C}_{16}\text{C}_1\text{DMABr}$	$\text{C}_{16}\text{C}_1\text{DMA}\text{O}\text{SO}_3$	10.1 (0.360)	10.5 (0.310)	2.5 (0.210)	This paper
$\text{C}_{16}\text{C}_2\text{DMABr}$	$\text{C}_{16}\text{C}_2\text{DMA}\text{O}\text{SO}_3$	15.7 (0.662)	17.0 (0.596)	4.6 (0.464)	This paper

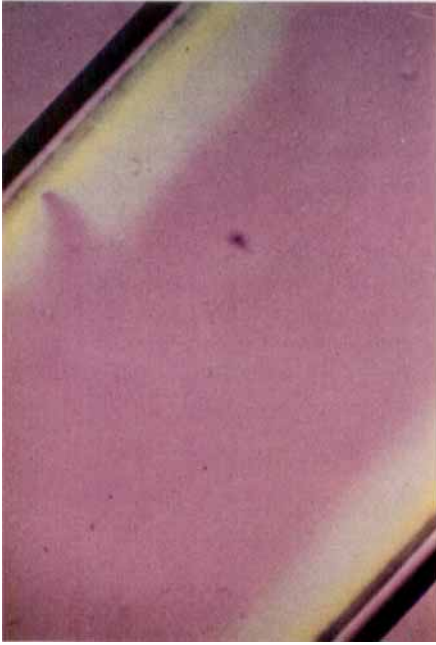
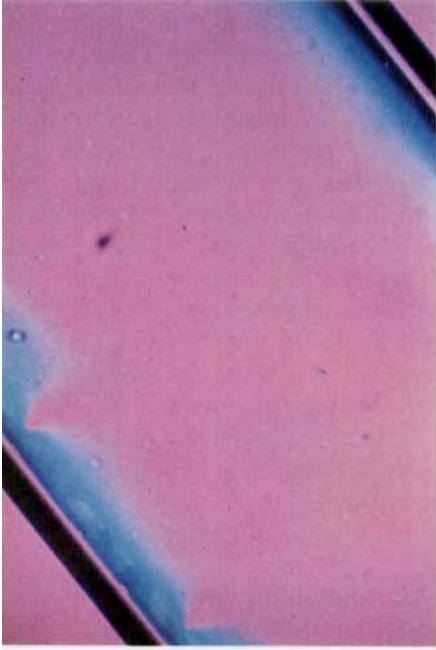


Figure 8.

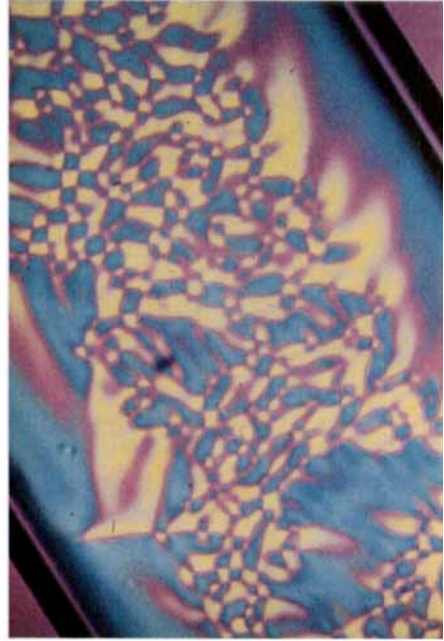


Figure 9.

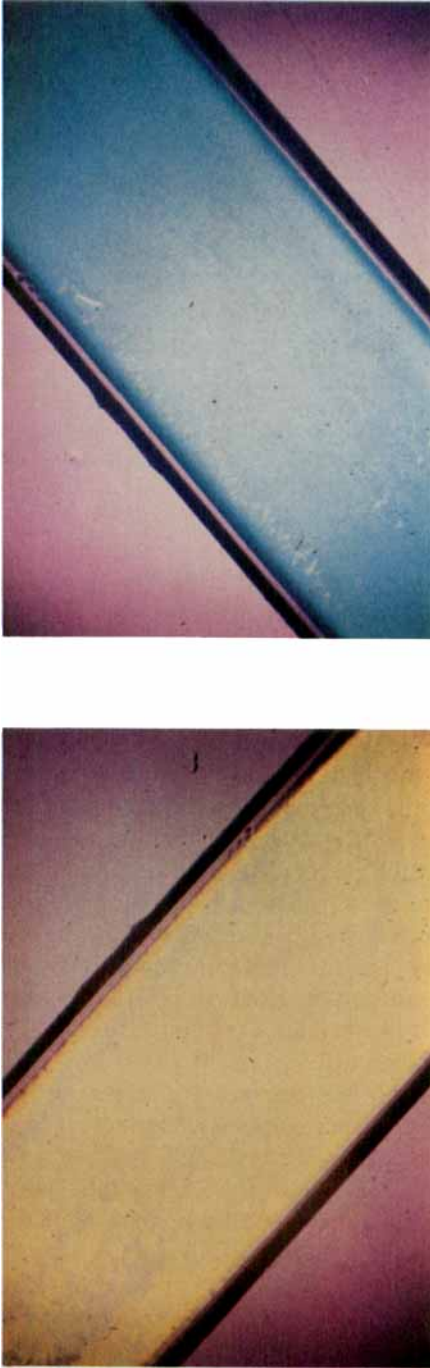


Figure 10.

- Figure 8. Pseudo-isotropic texture of a disc-like nematics. Photomicrograph of the system $C_{16}C_2$ DMABr-decanol- H_2O in a microslide with 0.1 mm path length with λ -plate. (Left) Subtraction and (right) addition of the birefringence of λ -plate and wall-aligned phase.
- Figure 9. Disturbed pseudo-isotropic texture of a nematic phase of disc-like micelles with negative $\Delta\chi$ when a magnetic field was applied normal to the glass surface. Transient Schlieren texture, photomicrograph with λ -plate.
- Figure 10. Completely aligned nematic phase under the polarization microscope with λ -plate. (Left) subtraction and (right) addition of the birefringence of λ -plate and aligned phase.

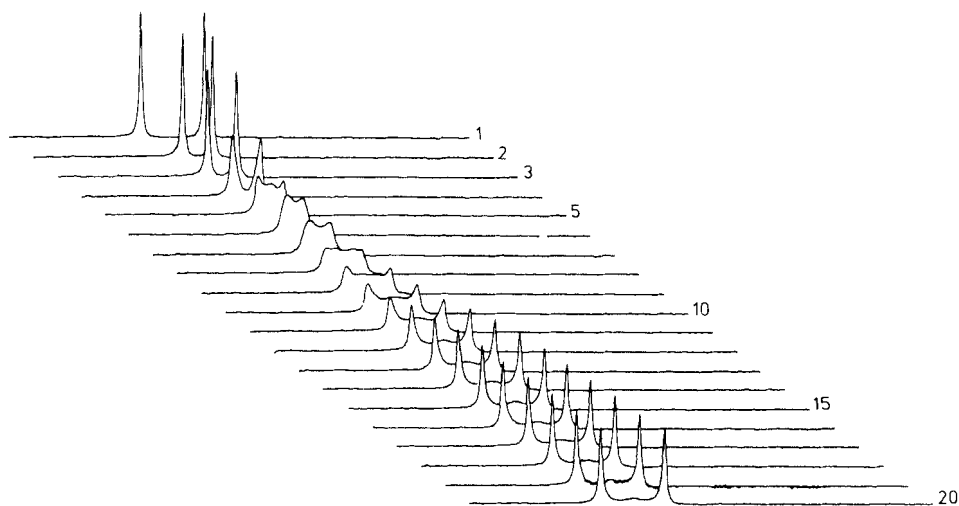


Figure 11. Realignment of disc-like nematics with positive $\Delta\chi$ studied by time-resolved ^2H -N.M.R. measurement (system $\text{C}_{16}\text{C}_2\text{DMABr}-\text{C}_{16}\text{C}_2\text{DMA}\text{O}\text{SO}_3$ -decanol- H_2O).

Under the polarization microscope these nematic systems with low viscosity showed typical textures for disc-like systems, as described in §4. The sign of $\Delta\chi$ was checked by magnetic field alignment and ^2H -N.M.R. experiments. The samples (table 6) were filled into 5 mm N.M.R. sample tubes and stored in a magnetic field of 2.1 T with the direction of the field perpendicular to the axis of the glass tube. After 5 h complete alignment with the optical axis parallel to the direction of the field could be observed between crossed polarizers. We made a realignment experiment in the N.M.R. spectrometer to prove the positive sign of $\Delta\chi$. For this experiment the complete aligned sample was placed into the spectrometer with the director parallel to the field (see figure 11, trace 1). A maximum quadrupole splitting was observed. The sample was then turned with the director perpendicular to the field and a set of spectra were recorded as a function of time. The realignment can be followed by the magnitude of the quadrupole splitting, which is changing continuously from $-0.5\delta_{\text{max}}$ to δ_{max} . In trace 5 of figure 11 the zero transition of the quadrupole splitting, corresponding to the magic angle of the director to the magnetic field, can be observed. Compared with the realignment of the rod-like nematics with positive sign of $\Delta\chi$ the realignment of these disc-like systems is much faster.

In the system $\text{C}_{16}\text{C}_3\text{DMABr}-\text{C}_{16}\text{C}_3\text{DMA}\text{O}\text{SO}_3$ -decanol- H_2O it was not possible to replace sufficient bromide surfactant by benzene sulphonate surfactant to change the sign of $\Delta\chi$. the resultant nematic phase of disc-like aggregates still had a negative $\Delta\chi$. Boden reported a similar system of $\text{C}_{14}\text{C}_1\text{DMABr}-\text{C}_{14}\text{C}_1\text{DMA}\text{O}\text{SO}_3$ -decanol- $\text{NH}_4\text{Br}-\text{H}_2\text{O}$ [3, 14], but we think NH_4Br is not essential to prepare these disc-like systems.

6. Conclusions

The tendency to build up a certain phase can be controlled by steric and polar features of the surfactant molecule and its counter-ion. The determining value for the phase behaviour is the ratio of head-group to chain area. Neither systems with a

strong tendency to build up lamellar phases nor systems with a dominating hexagonal phase are able to build up nematic phases.

The introduction to a second alkyl chain is a powerful instrument to modify the surface curvature of the aggregates and therefore the phase behaviour of a surfactant-water system. A short second chain contributes to the head-group area, increases the surface curvature and the beginning of an existing hexagonal or nematic phase consisting of rod-like aggregates is shifted to higher surfactant concentrations. A long second chain increases the hydrophobic area of the surfactant and decreases the surface curvature of the aggregates. The formation of lamellar phases beginning at low surfactant concentrations is preferred. The variation of chain lengths is limited, however, by the water solubility of the surfactant. Long chains increase the Krafft temperature. Short alkyl chains increase the solubility and shift the formation of liquid-crystalline phases to higher concentrations.

A co-surfactant with a different head-group to chain area ratio can be used to modify the surface curvature, too, when there are mixed micelles of surfactant and co-surfactant. The greater the discrepancy in head-group to chain area ratio of surfactant and co-surfactant is, the greater the influence on the phase behaviour when a co-surfactant is added to a binary system. This effect can be seen in the ternary systems of $C_{16}C_x$ DMABr-decanol-water when x was increased from 1 to 4. For $x = 1$ and 2 it is possible to obtain nematic discs by adding decanol to the binary nematic phase of rod-like micelles. When x was 3 the nematic range of disc-like micelles was very narrow in the ternary system and for $x = 4$ no nematic phase of disc-like micelles was found. The reason for this phase behaviour is the increasing head-group to chain area ratio when x was increased. For the same reason we did not succeed in preparing nematic phases of disc-like aggregates when decanol was added to the rod-like nematics of dialkyl dimethyl ammonium benzene sulphonate surfactants. The head-group area of these surfactants seems to be larger than that of the corresponding bromide surfactants.

From all of these data the phase sequence cubic \rightarrow hexagonal \rightarrow nematic (rod-like micelles) \rightarrow nematic (disc-like micelles) \rightarrow lamellar \rightarrow reversed phases can be deduced when the head-group to chain area ratio is decreased. Nematic phases only occur at certain ratios. This is obviously the reason for the narrow concentration and temperature ranges of nematic phases. If all of these parameters are taken into account it should be possible to prepare many nematic systems with plenty of surfactants. In the same way it should be possible to avoid hexagonal phases with high viscosities in technical systems by changing the head-group to chain area ratio in the surfactant system.

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