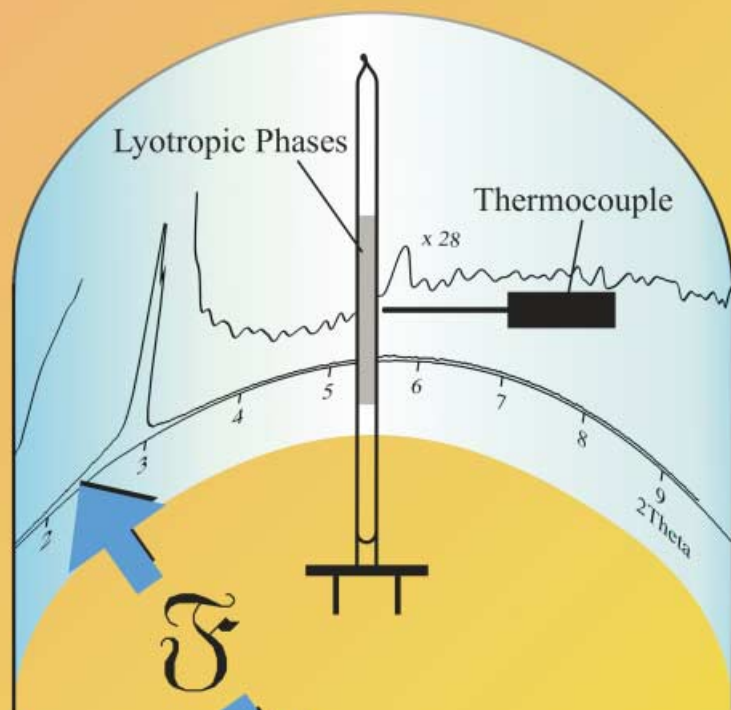
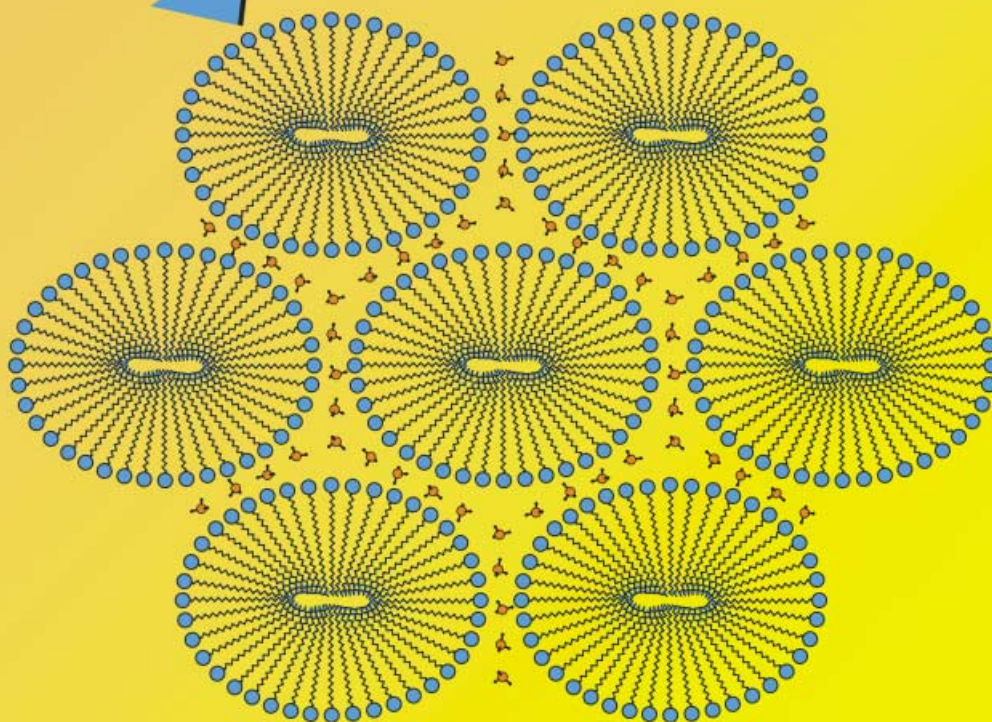


Lyotropic Phases in Liquid Ammonia



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X-ray Diffraction Studies on Mesophases of Cetyl- and Dodecyltrimethylammoniumbromide in Liquid Ammonia

Stefan Bzik and Martin Jansen*[a]

Abstract: We have studied solutions of the surfactants cetyltrimethylammoniumbromide (CTAB) and dodecyltrimethylammoniumbromide (DTAB) in liquid ammonia with respect to the formation of lyotropic phases. For this purpose, a set-up for performing X-ray scattering experiments at temperatures up to 120 °C on samples containing liquid ammonia has been developed. Both systems form hexagonal and mono-

clinic lyotropic phases above the dissolving temperature of the surfactant, thus representing the first examples for lyotropic phases in liquid ammonia, and for monoclinic phases in nonaqueous solvents. The phase diagrams of CTAB/liquid NH₃ and DTAB/liquid NH₃ show

similarities to their respective aqueous systems. However, the regions of existence of monoclinic phases are much larger in the ammonia system, while the cubic phases, as observed in the water based systems, do not seem to exist. The liquid-crystalline phases found provide potentiality for preparing mesoporous, nitride-based solids.

Keywords: liquid ammonia • liquid crystals • X-ray diffraction

Introduction

Mesoporous silica was discovered by scientists of the Mobil Research and Development Corporation in 1992.^[1] Since then approximately 2000 papers related to this topic have been published. The interest in such materials is nourished by their important potential applications, mainly in catalytic and separation technologies, and many groups have tried to vary the catalytic properties by substituting the cations silicon and aluminium by other metals, especially by transition metals.^[2–7] However, much less attention has been paid toward the replacement of the linking oxygen atoms by other anions in these structures so far. Only few examples for mesoporous metalsulfides are known.^[8, 9] Our long term aim is to develop a method for preparing mesoporous Si₃N₄ with defined pore diameters and arrangements.^[10–14] Such a material should have catalytic properties different from M41S materials, because of the higher basicity of nitrogen relative to oxygen. Moreover, it is to be expected that the thermal stability of a nitrogen-containing porous solid would be superior to that of mesoporous silica, in accordance with the melting or decomposition points of the reference materials SiO₂ (m.p.(quartz): 1550 °C; (cristobalite): 1705 °C) and Si₃N₄ (d.p.: 1900 °C), respectively.

To develop a route to mesoporous nitrides, analogous to the preparation of mesoporous silica, we have investigated systems that consist of the detergents CTAB or DTAB and liquid ammonia for their capability to form liquid crystalline phases.

In aqueous systems the liquid-crystal phases of CTAB have been examined by X-ray diffraction, thoroughly.^[15] Depending on the concentration of CTAB, several phases have been detected. With increasing concentration, first a hexagonal arrangement of surfactant tubes forms, then a monoclinic distorted arrangement of these tubes and, finally, at the highest concentrations, different cubic and lamellar phases.

Results

CTAB is completely soluble in liquid ammonia above 72 °C. The turbidity degree and viscosity of the initially clear samples increase with rising concentration. The first appearance of micelles in liquid ammonia was observed at a concentration of 69.5% (Figure 1a and point A in the phase diagram Figure 7 below). The broad Bragg reflection at about $2\theta = 2.74^\circ$ indicates the presence of lyotropic phases of relatively low order. On increasing the concentration to 81% and 88%, markedly narrower reflections develop, compare Figure 1b and c (points C and G in Figure 7 below). Dropping the temperature to 65 °C leads to a spontaneous precipitation of the surfactant, the diffraction pattern of which is given in Figure 1d. Note the strong spread of the 2θ scale which makes the reflections of the crystalline surfactant

[a] Prof. Dr. M. Jansen, Dr. S. Bzik
Max-Planck-Institut für Festkörperforschung
Heisenbergstr. 1, 70569 Stuttgart (Germany)
Fax: (+49) 711-689-1502
E-mail: m.jansen@fkf.mpg.de

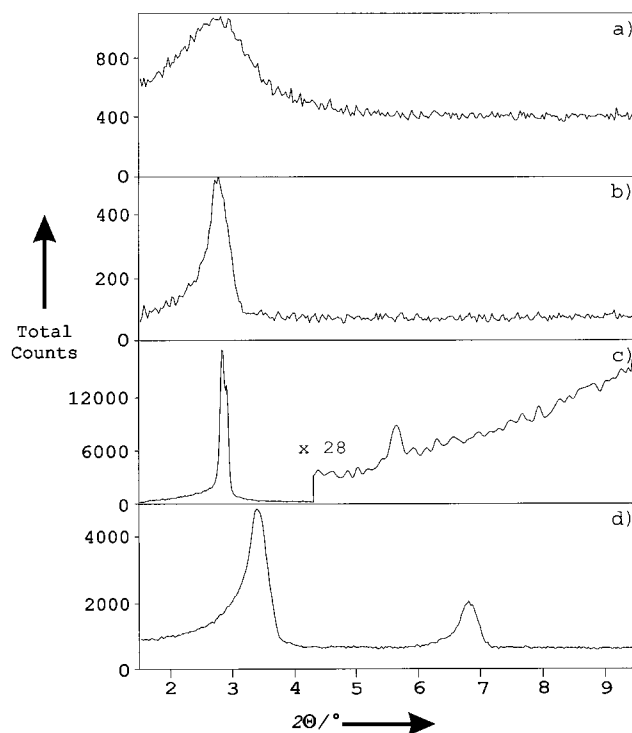


Figure 1. Diffraction patterns: a) 69.5 wt % solution of CTAB in NH_3 at 80°C (9.8 mg CTAB; 4.3 mg NH_3); b) 81 wt % solution of CTAB in NH_3 at 80°C (11.6 mg CTAB; 2.7 mg NH_3); c) 88 wt % solution of CTAB in NH_3 at 75°C (7.3 mg CTAB; 0.6 mg NH_3); d) CTAB at RT (as precipitated from liquid ammonia).

appear rather broad. At the same time, the extremely small half widths of the liquid crystalline phases, in particular in Figure 1c, become apparent.

An unequivocal determination of the crystal system was not possible, due to the reduced quality of the diffraction patterns. Moreover, the reflections broaden with increasing temperature, and the intensities of diffraction peaks with higher indices are strongly suppressed. Only in one instance, by applying an extremely long measuring time, was a Bragg intensity observed at double the diffraction angle to the main reflection (Figure 1c). Unfortunately, this additional Bragg peak does not provide further information concerning the crystal system.

The crystal systems of the phases in liquid ammonia have been assigned by comparisons with literature data for the CTAB/ H_2O system. The phase with 81% CTAB has hexagonal symmetry (Figure 1b and point C in Figure 7 below), corresponding to the liquid-crystalline phases with low surfactant concentration in all other solvents. Starting with a concentration of 83.5% CTAB, the (10) reflection splits (Figure 2a and point E in Figure 7 below); this indicates a transition to monoclinic symmetry, as in aqueous systems. This phase survives up to a concentration of 93% (point I in Figure 7 below), corresponding to the highest concentrated measurable sample in this system. At these concentrations the temperature was raised to 100°C ; this corresponds to an ammonia vapour pressure of more than 6 MPa.

In the system DTAB/ammonia, preliminary investigations yielded a dissolving point of 48°C . This is, as expected, clearly

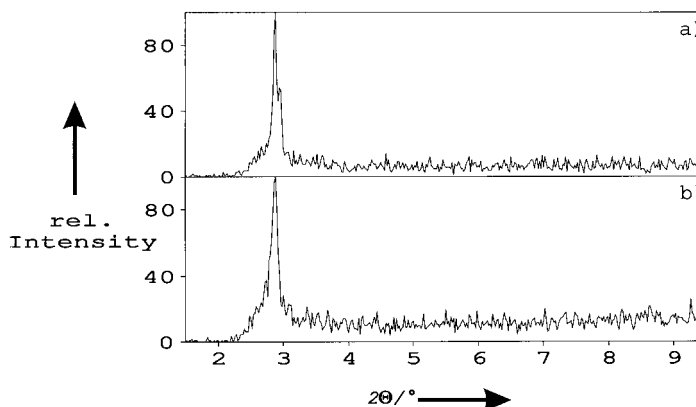


Figure 2. Diffraction pattern of a solution of CTAB (83.5 wt %) in ammonia: a) at 85°C ; b) at 90°C .

below the dissolving temperature of CTAB in ammonia (72°C). First signs for the existence of lyotropic phases emerge at a concentration of 81.7% (Figure 3a and point K in Figure 8 below). Increasing the concentration to 83.9% leads

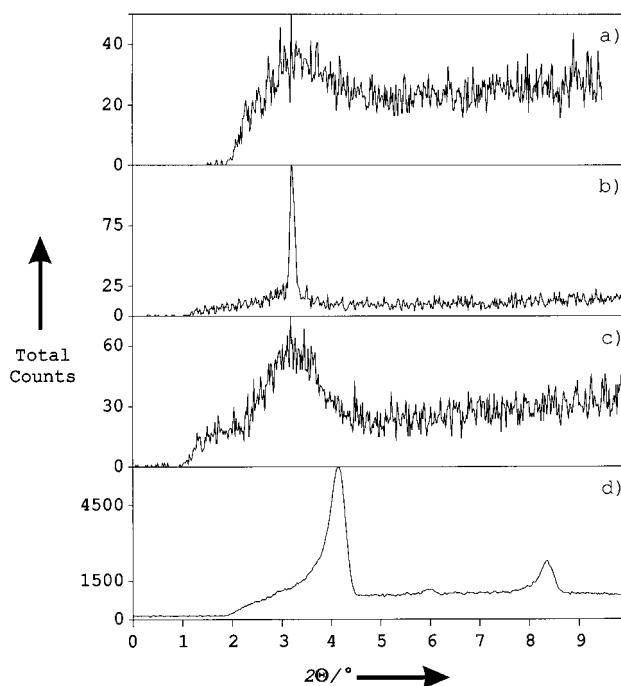


Figure 3. Diffraction patterns: a) 81.7 wt % solution of DTAB (6.7 mg) in ammonia (1.5 mg) at 50°C ; b) 83.9 wt % solution of DTAB at 50°C (2.0 mg NH_3 , 10.4 mg DTAB); c) 83.9 wt % solution of DTAB in ammonia at 60°C ; d) DTAB at RT (as precipitated from liquid ammonia).

to the formation of a lyotropic phase of rather high structural order; this is reflected by a narrow X-ray reflection, see Figure 3 and point A in Figure 8 (below). A temperature increase of 10°C disturbs this order (Figure 3c and (L) in Figure 8 below). Reducing the temperature below the dissolving point leads to a spontaneous precipitation of the surfactant, the diffraction pattern of which is shown in Figure 3d. At higher concentrations the main reflection splits into two components, indicating again reduction from hexagonal to monoclinic symmetry (Figure 4a and b; points A

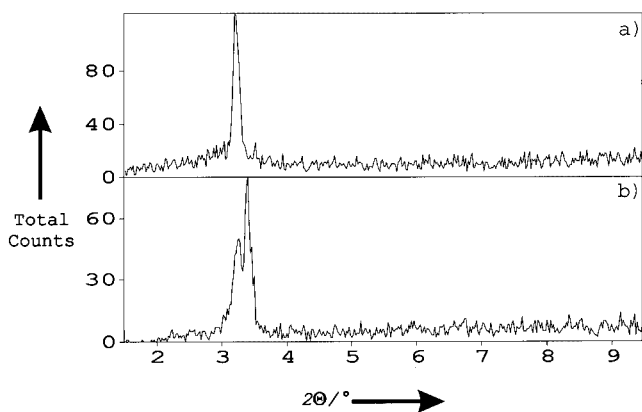


Figure 4. Diffraction patterns: a) 83.9 wt% solution of DTAB (10.4 mg) in ammonia (2.0 mg) at 50 °C; b) 85.7 wt% solution of DTAB at 70 °C (0.6 mg NH₃, 3.6 mg DTAB).

and B in Figure 8 below). When increasing the temperature, the hexagonal symmetry is also recovered in this system, and above 100 °C the liquid crystalline phases fully degrade.

In order to achieve still higher concentrations, extremely long sample tubes (approx. 8 cm) were filled with a high ratio of surfactant/ammonia (see below). Each of the individual phases that formed within a sample tube was homogeneous and impressingly stable, and a mixing of the different phases did not take place during the measurement. An exact determination of the concentrations of the individual phases was not possible, but a crude estimate on the basis of the viscosity and the turbidity relative to the total concentration of the sample can be given nevertheless. The liquid-crystalline zones can be remelted and recrystallised repeatedly, producing phases of different concentrations. In Figure 5, three

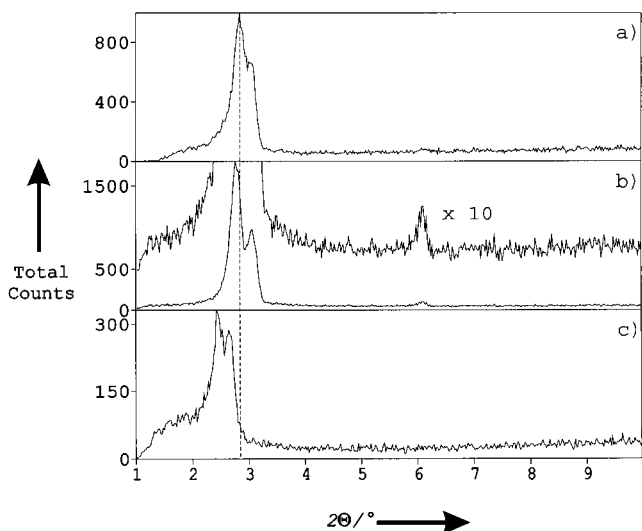


Figure 5. Diffraction patterns of a subarea of a solution of DTAB (14 mg) in NH₃ (1.6 mg): a) ≥ 89.7% at 80 °C; b) > 89.7% at 70 °C; c) ≫ 89.7% at 80 °C.

diffraction patterns of different heating cycles are shown that belong to the phases of highest concentrations. The turbidity, and thus the concentration, of the corresponding phases increases from samples a to c (Figure 5 and points G, E and H

in Figure 8 below). All three phases show monoclinic symmetry according to the split main reflection. The diffraction angles in these phases decrease with increasing concentrations of the samples, as has been observed for the system CTAB/ammonia. The diffraction pattern in Figure 5b clearly shows the (02) reflection, in addition to the (10) and (01) reflections. This reflection was observed whenever long exposure times were applied to well-diffracting samples at comparatively low temperatures. An increase of temperature restores hexagonal symmetry. In Figure 6a and b (points J and I in Figure 8 below) the diffraction patterns of samples a and b at a higher temperature are shown.

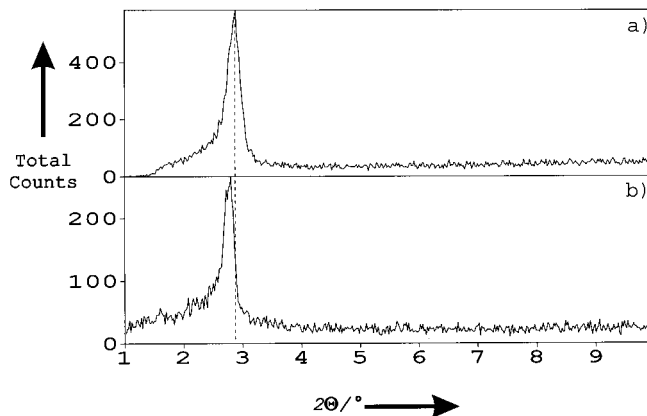


Figure 6. Diffraction patterns of a subarea of a solution of DTAB (14 mg) in NH₃ (1.6 mg): a) ≥ 89.7% at 90 °C; b) > 89.7% at 85 °C.

Phase diagram of CTAB in liquid ammonia: Based on the results discussed above, a phase diagram of the lyotropic phases of CTAB in ammonia can be sketched (Figure 7). Below a temperature of 72 °C and a concentration of approximately 70% CTAB, no lyotropic phases occur. The splitting of the (10) reflection, and thus the transition to the monoclinic phase, takes place at a concentration of 83% CTAB. An increase of the temperature from 85 °C to 90 °C, within this area of concentration, leads to a phase transformation back to the hexagonal phase (Figure 2, points E and F in Figure 7). The slight inclination of the phase boundary in the phase diagram between the hexagonal and monoclinic phase takes account of this observation. The monoclinic phase could be observed up to a concentration of 93% in this system (dotted line).

Phase diagram of DTAB in liquid ammonia: A phase diagram of the lyotropic phases of DTAB in ammonia is given in Figure 8. Below a concentration of 81% DTAB and a temperature of 48 °C no lyotropic phases were observed. At increasing the concentration up to 85.7% DTAB, and beyond, the stability field of the hexagonal phase is left, and monoclinic symmetry is observed, fully in line with the findings on the system CTAB/NH₃.

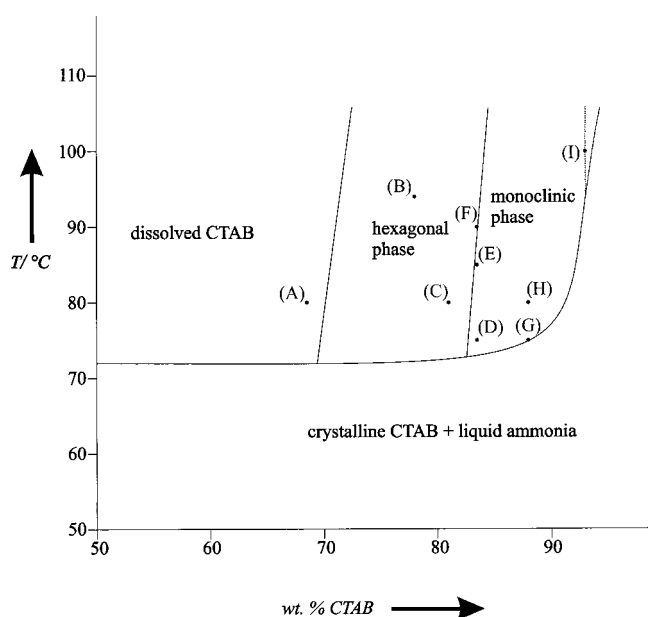


Figure 7. Phase diagram of CTAB in ammonia with all experimental points presented in this article.

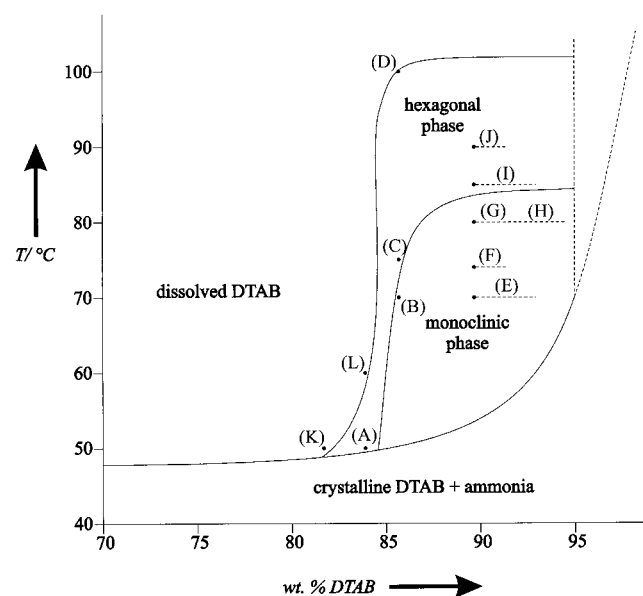


Figure 8. Phase diagram of DTAB in ammonia with selected experimental points; the concentrations at points E–J have not been determined exactly (see text); the full circles represent the overall concentration and the dotted lines the range of concentration of the measured samples; the lattice parameters [in Å] of these phases are: A 31.74; B 31.31, 30.02; C 30.32; D 30.50; E 36.93, 33.34; F 36.16, 33.60; G 35.91, 33.63; H 41.73, 38.31; I 36.46; J 35.44.

The results obtained here correspond well with the observations on monoclinic lyotropic phases of CTAB in water. A comparison of the phase diagrams of CTAB/NH₃ and DTAB/NH₃ shows that for the surfactant with the longer hydrocarbon chain, the formation of the lyotropic phases occurs at lower concentrations (ca. 70 wt % with CTAB, ca. 82

wt % with DTAB, i.e., 10.1 mol % CTAB, 20.1 mol % DTAB). This difference can be understood in terms of different solubilities of the individual surfactant molecules in polar solvents. The concentration of dissolved monomer molecules with shorter hydrocarbon chains is higher before the formation of micelles begins, and these micelles are less stable.

Discussion

The development of micelles in a given solvent depends on a characteristic concentration of the surfactant in the system, called the critical micelle concentration (CMC). Below this concentration the surfactant molecules are dissolved as monomers. At the CMC the surfactant molecules start to form micelles in the shape of spheres or tubes. With increasing concentration, these micelles start aligning and form liquid-crystalline phases.^[16] In the first stage, normally hexagonal arrangements of tubes occur. In aqueous systems the distances between the tubes are rather large at low concentrations, due to the thick solvent layers between them. The change of size and shape of the micelles, and of the unit cells, at varying concentrations is shown in Figure 9. Though the diameters of

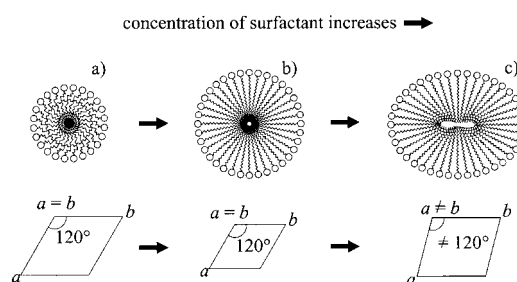


Figure 9. Change of the shape and the size of the micelles (upper sequence) and the unit cells (lower sequence) with rising concentration.

the micelles grow with rising surfactant concentration, the size of the unit cell decreases, since the number of solvent layers separating the tubes diminishes. The cross sections of the micelles are still circular, thus allowing for a perfectly hexagonal stacking of the tubes. If the maximum tube diameter is reached (twice the surfactant length in the case of water),^[15, 17] a further increase of concentration leads to an elliptical distortion of the micelles' cross sections.^[18] This is reflected in a decrease of symmetry from hexagonal to monoclinic and entails the splitting of the (10) reflection in the diffraction pattern. At the same time the minimum tube distance is achieved, and no further solvent layers can be removed. Consequently, a further increase of the surfactant concentration must lead to an enlargement of the unit cell. This behaviour, well-known for aqueous systems,^[15] has also been found in the system CTAB/ammonia, though much less pronounced. Figure 10 shows the (10) reflections of lyotropic phases of ammonia with different concentrations of CTAB. The concentration increases from a) to e) (in this order points B, C, D, H and I in Figure 7). First an increase of the diffraction angle (or a reduction of the lattice parameters or the *d* values) can be observed (Figure 10a–c), which is related

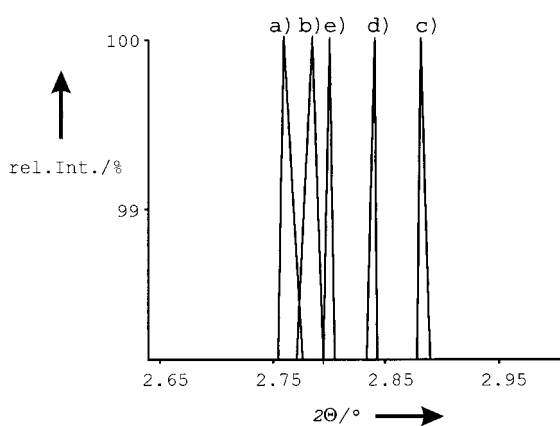


Figure 10. Positions of the (10) reflection of the hexagonal (h) and monoclinic (m) phases with rising concentration in the system CTAB/ammonia: a) 78 wt % (h) ($T=94^{\circ}\text{C}$); b) 81 wt % (h) ($T=80^{\circ}\text{C}$); c) 83.5 wt % (m) ($T=75^{\circ}\text{C}$); d) 88 wt % (m) ($T=80^{\circ}\text{C}$); e) 93 wt % (m) ($T=100^{\circ}\text{C}$).

to the loss of ammonia layers separating the tubes. At point c) the minimum tube distance is achieved, and a further increase of concentration causes an increase of the lattice parameters, as observed for samples d) and e). The splitting of the (1 0) reflection, that is, the transition to monoclinic symmetry starts at concentration c). At this concentration, the maximum diameter of the circular tubes and their minimum separations are reached.

The experimental conditions and lattice parameters for all the samples included in Figure 10 are given in Table 1. Also, the alternative *C*-centred orthorhombic indexing for the

monoclinic phases is shown there. Our data do not allow us to distinguish between these two assignments. In this context, it should be mentioned, however, that Auvray et al. disproved the existence of an orthorhombic lattice in the aqueous systems.^[15]

For DTAB/ NH_3 , lattice parameters and the concentrations are similarly correlated as in the system CTAB/ NH_3 . Starting with a small concentration of DTAB in ammonia, the lattice parameters decrease with rising concentrations, due to reducing the solvent layers between the micelles (Figure 8 A \rightarrow B). As soon as the monoclinic phase appears, the minimum distance between the tubes is reached, so that now the unit cell is growing with increasing concentration (see Figure 8 B \rightarrow F or F \rightarrow E). For this reason, apart from the turbidity, the lattice parameters can also be used to estimate the concentration of highly concentrated samples. To summarise, an indexing of all shown phases and the respective experimental conditions are given in Table 2.

In all diffraction patterns only the reflections with the indices (10), and more rarely (20) for the hexagonal phases, and (10), (01), in few cases (02) for the monoclinic phases, have been observed in the ammonia-based systems. Following the work by Oster and Husson an explanation seems to exist for the absence of the (11) reflections.^[19, 20] They have discovered a correlation between the concentration of the surfactants at constant temperature and the appearance of the (11) reflection in the hexagonal crystal system. We have applied the model for the DTAB/ NH_3 system by arranging DTAB molecules derived from the crystal structure in a circle with a diameter of 38.8 Å (Br–Br distance).^[21] Figure 11a shows the structure assuming a hexagonal packing of tubes

Table 1. Lattice parameters of the phases of CTAB and ammonia as addressed in Figure 10, and respective experimental conditions.

Phase	Conc. [wt %]	T [$^{\circ}\text{C}$]	Crystal system	2θ [$^{\circ}$]	d [Å]	lattice parameters ^[a] [Å]	lattice parameters orthorhombic I [Å]	lattice parameters orthorhombic II [Å]
a	78	94	hexagonal	2.760	31.98	$a = 36.93$		
b	81	80	hexagonal	2.785	31.70	$a = 36.60$		
c	83.5	75	monoclinic	2.883	30.62	$a = 35.36$ $b = 34.37$	$a = 61.24$ $b = 34.05$	$a = 59.52$ $b = 35.70$
d	88	80	monoclinic	2.843	31.05	$a = 35.85$ $b = 35.12$	$a = 62.10$ $b = 34.89$	$a = 60.84$ $b = 36.11$
e	93	100	monoclinic	2.801 ^[b]	31.51 ^[b]	$a = 36.34$ ^[b]		

[a] Assuming $\gamma = 120^{\circ}$. [b] The positions of the (10) and (01) reflections are not resolved; the 2θ corresponding to the highest intensity are given.

Table 2. Lattice parameters of all lyotropic phases of DTAB and ammonia presented in this article, and respective experimental conditions.

Figure	Conc. [wt %]	T [$^{\circ}\text{C}$]	Crystal system	2θ [$^{\circ}$]	d [Å]	lattice parameters ^[a] [Å]	lattice parameters orthorhombic I [Å]	lattice parameters orthorhombic II [Å]
3b + 4a	83.9	50	hexagonal	3.211	27.490	$a = 31.74$		
4b	85.7	70	monoclinic	3.256	27.112	$a = 31.31$ $b = 30.02$	$a = 54.23$ $b = 29.63$	$a = 52.01$ $b = 31.77$
5a	≥ 89.7	80	monoclinic	2.838	31.102	$a = 35.91$ $b = 33.63$	$a = 62.21$ $b = 32.96$	$a = 58.25$ $b = 36.79$
5b	> 89.7	70	monoclinic	2.760	31.982	$a = 36.93$ $b = 33.34$	$a = 63.97$ $b = 32.35$	$a = 57.74$ $b = 37.74$
5c	$\gg 89.7$	80	monoclinic	2.443	36.137	$a = 41.73$ $b = 38.31$	$a = 72.27$ $b = 37.34$	$a = 66.35$ $b = 43.08$
6a	≥ 89.7	90	hexagonal	2.876	30.694	$a = 35.44$		
6b	> 89.7	85	hexagonal	2.796	31.577	$a = 36.46$		

[a] Assuming $\gamma = 120^{\circ}$.

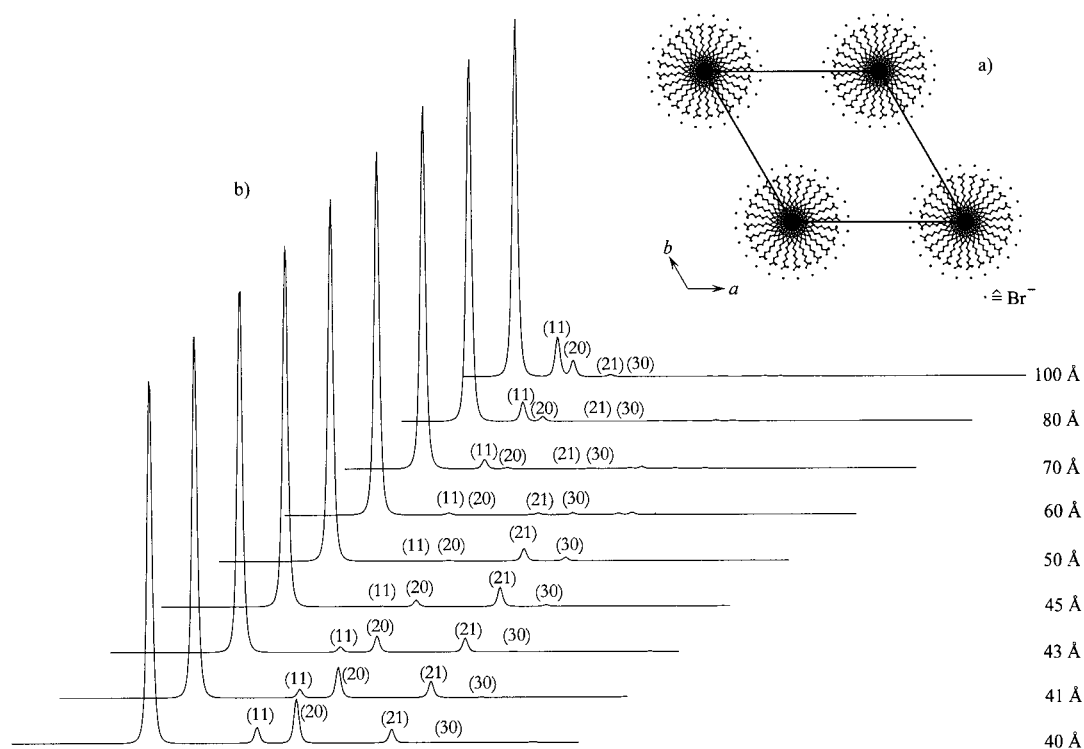


Figure 11. a) Structure model of a hexagonal lyotropic crystal based on DTAB. b) Calculated diffraction patterns in dependence on the lattice parameters.

that contain 24 DTAB-molecules. In Figure 11b the calculated diffraction patterns of this arrangement are shown in dependence on the lattice parameters. The diameter of the tubes was kept fixed. In particular, at low tube separations the reflection (20) shows a much stronger calculated intensity relative to the (11) and (21) reflections. According to our observation of only a small dependence of the lattice parameters on the concentration at low concentrations, only thin solvent layers are separating the tubes. This is in contrast to the aqueous systems, but similar to other solvents like formamide or glycerol.^[15] As a consequence, the relatively small lattice parameters lead to low calculated intensities for (11), explaining that this reflection was not observed at the conditions considered in this work.

These results conform well with the work of Auvray et al., who showed that the thickness of the solvent layer between the micelles strongly depends on the kind of solvent,^[15] and, particularly with water, also on the concentration (Table 3). The diameters of the micelles are, independent of the solvent, virtually the same for the same surfactants. One might see a further cause for the smaller d values of the liquid-crystalline phases in ammonia at the elevated pressures applied (4 MPa at 79 °C, and more than 6 MPa at 100 °C). These pressures

might suppress the unfolding of the surfactants to their full lengths, as it is observed under standard conditions. Respective overlaps of the hydrocarbon chains inside the micelles have been found in other solvents at increased temperature or at a low concentration of the surfactant (as long as no inflexible double bonds or phenyl groups are included in the hydrophobic part of the surfactant).^[17] In water, for example, the size of the micelles decreases at a given concentration with rising temperature, because the mobility and, therefore, the average degree of overlap of the hydrocarbon chains inside the micelles increases. In the liquid-crystalline phases in ammonia reported here, we have not observed such temperature dependencies.

Conclusion

It has been demonstrated that lyotropic phases can be realised in liquid ammonia. We regard this as a first important step towards the preparation of mesoporous nitrides through ammonolysis of suitable halides and amides. In this context we have developed a method for preparing and measuring lyotropic systems in liquid ammonia up to vapour pressures of about 6 MPa. Investigating the prototypic systems CTAB/NH₃ and DTAB/NH₃ we have proved, for the first time, the existence of lyotropic phases in ammonia. The stability ranges of the monoclinic phases here are comparatively large, because of the larger overlap in-

Table 3. The d values of different lyotropic phases in comparison.

System	d value [Å]	T [°C]	Concentration [wt %]	Reference
CTAB/water	80–42	25–38.5	20–77 (conc. of saturation)	[10]
CTAB/formamide	40–37	52–72	45–74 (conc. of saturation)	[10]
CTAB/glycerol	37–36	56–76.5	41–79 (conc. of saturation)	[10]
CTAB/water	40.5	75	64	[22]
CTAB/ammonia	32	80	81	this work

side the micelles; this is most probably due to the prevailing elevated pressures. Phase diagrams have been derived for both systems. Future work will be focused on attempts to obtain mesoporous oxygen-free solids by cross-linking suitable precursors in the pre-organised systems presented.

Experimental Section

CTAB or DTAB (both Fluka, $\geq 98\%$) were dried in vacuum for several hours at 100°C , and filled under argon into borosilicate glass capillaries with one end sealed (Hilgenberg, length: 100 mm, diameter: inside 0.84 mm, outside 1.2 mm). The capillary was then cooled to -78°C , and ammonia, dried over sodium, was condensed into it. The liquid was then frozen at -196°C and the capillary was sealed under vacuum. As the capillaries have to be as short as possible (1.5 to 2 cm) in order to keep the temperature gradient along the sample low, the sealing position was as close to the surface of the solid as possible. The compositions of the starting mixtures were determined with an accuracy of ± 0.1 mg by difference weighing.

The samples were measured on a powder diffractometer (STADI-P, STOE, Darmstadt (Germany), germanium monochromator) with $\text{Cu}_{\text{K}\alpha 1}$ radiation and heated by a tuneable hot-air dryer. The temperature was measured by using a thermocouple placed close to the lyotropic phases. The exposure time varied between 10 minutes and up to 10 hours. In the system CTAB/ NH_3 , the region of highest CTAB concentrations could not be examined because, on the one hand, the dissolving temperature rapidly approaches very high temperatures ($> 130^\circ\text{C}$) at which the capillaries burst. On the other hand, small sample sizes are a necessary prerequisite in order to achieve homogeneous liquid crystalline phases. This, however, leads in combination with the required high surfactant concentration to extremely small ammonia quantities of < 0.5 mg, which we were not able to charge with sufficient accuracy. In order to circumvent these difficulties, respective investigations with DTAB as surfactant were made, since the dissolving temperature proved to be lower than that of CTAB. To realise the high concentrations with sufficient accuracy, long sample tubes (approx. 8 cm) with a high amount of surfactant and a low amount of ammonia were filled. In such capillaries, several liquid-crystalline areas with different concentrations developed at the same time, due to the temperature gradients of the heating source. A special sample fixation was used for these extremely high concentrated samples of DTAB and ammonia; this also allowed for a vertical sample adjustment. Thus, the respective liquid phase under observation could be shifted into the X-ray beam, and X-ray analyses of all lyotropic phases within one capillary were possible.

Acknowledgement

We thank the Fonds der Chemischen Industrie and the Deutschen Forschungsgemeinschaft for their financial support.

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Received: September 4, 2002 [F4390]