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INVITED ARTICLE

Micelles forming biaxial lyotropic nematic phases

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The paper by Yu and Saupe on the first biaxial nematic phase created excitement for a number of reasons. Some theories of biaxial phases already existed, but experimental observation was still lacking. The phase was discovered in a lyotropic system with three components, which in theory is difficult. Lyotropic liquid crystals are composed of supramolecular assemblies of amphiphilic molecules, which may change shape and size as a function of concentration and temperature. The experimental phase diagram of the lyotropic biaxial phase was rather complex, with the biaxial region inserted between nematic cylindrical and nematic discotic phases via second-order transitions. In addition, re-entrant behaviour was evident. Saupe investigated further systems experimentally, observing that the biaxial phase might be absent in cases where a direct transition between the cylindrical and discotic phases occurred. He provided a range of theoretical and experimental contributions on the properties of these lyotropics, but was very cautious regarding the detailed amphiphilic assemblies involved. The present paper reviews this area, focusing on proposals for the structure of the micellar assemblies. Emphasis is placed on recent papers which indicate a transformation of the two uniaxial shapes, in mixing conditions, both from the theoretical and the experimental point of view, and to questions still requiring further study.

Keywords: biaxial phase; lyotropic systems; lyonematics; micelles; micellar shapes

1. Introduction

The discovery of the biaxial nematic phase in 1980 by Saupe, in collaboration with his student Yu [1], had been preceded by some years of work on lyotropic systems. The entrance of Saupe into the field of lyotropic liquid crystals can be defined by the paper on human bile by Saupe and Brown, together with Olszewski and Holzbach (from the School of Medicine of Cleveland), which described observations using optical microscopy, published in *Nature* in March 1973 [2]. The interest of Professor Glenn Brown in biological systems probably influenced Saupe also to start work on lyotropic liquid crystals following his move to Kent. In the same year Saupe published a review on liquid crystals, which focused more on thermotropics, but also included lyotropics [3]. In his important work on disclinations and properties of the director field in nematic and cholesteric liquid crystals in the same year [4], however, he made no mention yet of lyotropic nematics.

A significant contribution of Saupe to the field of lyotropic liquid crystals was his 1977 paper on textures, deformations and structural order of liquid crystals [5], focusing on middle soap, neat soap (in comparison with smectics), lyotropic nematics and also myelin figures and vesicles. He gave simple but insightful correlations between textures observed with polarised optical microscopy and lyotropic structural order, making use of elastic theory. He quotes lyotropic nematics, which were discovered only in 1967 [6] and published by Rosevear in 1968 [7]. By that time the basic theoretical papers predicting the biaxial nematic phase had already been published [8–12]. The initial proposal of a biaxial phase for particles of low symmetry [8] was followed by the idea that mixtures of plate-like and rod-like molecules [11] could also be responsible for biaxial phases. But no experimental results existed and nothing about biaxial phases was mentioned by Saupe in his review.

It seems clear that the interest of Saupe in lyotropics was enhanced by the discovery of lyotropic nematic phases, used as solvents in the NMR spectroscopy of molecules such as benzene [6]. But it was possibly the discovery of two types of lyotropic nematics, with their director orientation parallel and perpendicular to a magnetic field easily characterised by NMR [13], that led him to begin the search for a biaxial phase. In the so-called type I phase the director orients parallel to the magnetic field, while in type II it orients perpendicular to the magnetic field. The system studied was sodium decyl sulphate (SdS)/decanol/D_2O, in which transitions between the two types occurred by substitution of the cation or addition of an electrolyte [13]. Furthermore, a transition occurred with temperature in the ternary system with SdS, in type I above 17°C and in type II below, which does not occur among thermotropics [13].

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Radley, whose doctorate with Reeves in Canada defined the two types of lyonematics, became a post-doctoral student of Saupe at Kent. Saupe's research with Radley, although focused on lyonematics [14], did not, however, lead to the biaxial phase; the addition of a chiral molecule led instead to the first studies on lyocholesterics [15]. They obtained new nematic phases in the system decyl-ammonium chloride (DACl) and bromide/water/KCl, however, which allowed discrimination between magnetic orientation and the type of micellar structure [14]. Proton NMR was conducted using a specific solute that formed complexes with high symmetry and simple spectra. These complexes aligned parallel to the normal axis of the double layer in the micellar surface [14]. The degree of order of the symmetry axis of the complexes with respect to the nematic director was negative for nematics with cylindrical micelles and positive for those with lamellar micelles [14]. Optical microscopy showed reversible transitions between nematic and isotropic micellar solutions at ~45°C and between nematic and lamellar smectic phase at ~30°C, indicating what were called by Saupe *micelles of a bilayer structure*, meaning a discotic micelle [14]. This gave the correlation of type I with cylinders and of type II with discs, as already anticipated [13], but it was stressed that exceptions existed since molecular diamagnetic properties changed with molecular structure [14], and a type I phase with discotic micelles, obtained with addition of an aromatic ring, had already been reported [16].

The systems based on SdS studied by Radley in his work with Reeves were the first to be investigated by Yu and Saupe, but also did not lead to the elusive biaxial phase, being focused instead on nematic–nematic and cholesteric–cholesteric phase transitions [17]. In the meantime diffraction results indicated the existence of micelles of discotic and cylindrical shapes in the uniaxial nematic phases of the SdS system, both in our work in Brazil [18] and by the group of Charvolin in France [19]. Furthermore, Radley moved to England and a nematic phase was discovered in the binary system, caesium perfluoro-octanoate (CsDFO)/water mixture, whose partial phase diagram showed a tricritical point joining isotropic, lamellar and the nematic phase, proposed as being composed of discs [20]. This binary system, made of discs, had a positive diamagnetic anisotropy (type I) in view of the different properties of the fluorocarbon and hydrocarbon chains, and it was suggested that the capacity for fluorocarbons to engage more water molecules could explain why this binary system formed a discotic nematic phase without the necessity of additives.

Saupe then turned to the system based on potassium laurate (KL), in which a discotic nematic phase had been reported in 1973 [21], and succeeded in discovering the biaxial phase in the ternary system KL/decanol/D_2O between discotic and cylindrical phases [1].

The present paper reviews studies on biaxial lyotropic phases, with special emphasis on the contribution of Saupe to the field, but focusing specifically on the micellar structures. The paper is organised as follows. Firstly, the initial results obtained with biaxial phases is reviewed and the studies on other micellar phases are then discussed, stressing the information Saupe was able to obtain about the possible micellar structures, since this is pertinent to the controversy regarding the micellar aggregates that form the biaxial phase. Afterwards, phase diagrams of other lyotropic systems are considered, followed by the chemical aspects revealed in a more recent study of the KL system and its phases. The review is thus constructed from the perspective of what is now known about micellar systems. Our proposal for the change in the micellar shape is then set out, and finally we present recent work, both theoretical and experimental, which returns to the possibility of mixtures of cylindrical and discotic micelles, in exchange conditions to model the biaxial phase, including our own work [22].

2. Initial studies with nematic biaxial phases

Saupe's phase diagram with the KL system [1] is shown in Figure 1; the fitted lines in this refer to a recent paper [22] which will be commented upon later. The symbols for the nematic phases differ in the literature; N_D, N_B and N_C have here been adopted for discotic, biaxial and cylindrical lyomesophases, respectively. The decanol content was fixed at 6.24 wt%, and the wt% ratio of D_2O to KL varied between 2.67 and 2.56. Neither the decanol/KL nor the D_2O/KL molar ratios were therefore kept constant.

What seems striking about this phase diagram is the absence of any reference to the Krafft line, which in any lyotropic system separates the micellar dispersions above the Krafft temperature from the gel phases below it. It is well-known that micelles form not only above a critical micellar concentration (cmc), but also only above a certain temperature, known as the Krafft temperature; at higher concentrations the Krafft temperature coincides with the temperature for the order–disorder transition of the hydrocarbon chains [23, 24]. Below the Krafft temperature the chains have a straight conformation and form crystallites, either in a stable coagel phase (mixture of crystallites with water) or in a homogeneous gel phase, which is usually metastable [23]. The assignment of the lower temperature phase to a viscous isotropic phase in the KL system [1] was ambiguous. In the first work with the SdS system [17]

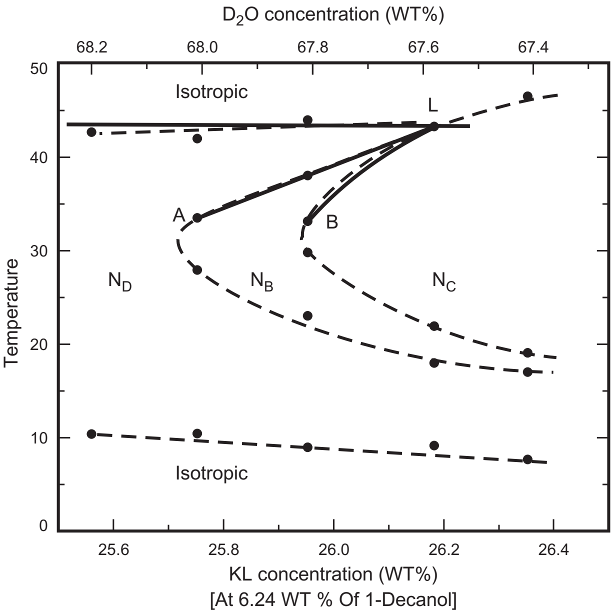

Figure 1. Experimental phase diagram obtained by Yu and Saupe [1] (dashed lines) compared with theory (solid lines) [22]. Here N_C and N_D are the nematic phases, L is the Landau point, N_B is the biaxial phase and A and B are the fitting points of adjustment. Figure reproduced from [22] with permission.

it was explicitly stated: *liquid crystalline states are only metastable at temperatures below about 20°C. Once the material has crystallised it has to be heated to above 20°C before it returns to a nematic state*. This raises the question as to whether the line at about 10°C which separates the viscous isotropic phase from the N_D phase in the KL phase diagram is in fact the Krafft line. This question will be considered later.

In the paper on the biaxial phase it is stated: *In view of the present findings we studied again the transitions between the uniaxial nematics of sodium decyl sulphate system and found that an intermediate biaxial phase is also formed for a certain concentration range while the observations in other range indicate a direct first-order N_C–N_L transition.*

The system SdS/decanol/water (not D_2O) was investigated by the French group of Charvolin [25], after their first paper [19], but still without reference to the paper on the biaxial phase, and following the methods used by Luzzati in his extensive study of amphiphile systems [23]. A detailed study was conducted at room temperature (22°C) using high-angle X-ray diffraction and always gave a broad diffraction at 4.6Å, the fingerprint of chains in a disordered state [23]. Samples were investigated along two lines: constant water content (45 wt%) with changing decanol concentration, and at a constant decanol/SdS ratio in wt% (3.35), varying the water content. This allowed disentanglement of the effect of each variable and gave information about the neighbouring phases. Increase in decanol promotes transitions from the hexagonal phase to the rectangular phase with ribbons, and to the lamellar phase. Water addition promotes the transition sequence: lamellar–ribbons–N_C (cylindrical and calamitic)–N_D (discotic and bilayer)–concentrated isotropic–diluted isotropic [25]. The estimated sizes corresponded to small micelles, in agreement with Saupe's conclusions from the observation of defects.

The biaxial phase in the SdS system (with H_2O) was afterwards confirmed in the work of Bartolino *et al.* in Italy [26] with microscopic observations, including measurement of the refractive indexes using an Abbe refractometer. The biaxial phase was observed between 36.0 and 36.2 wt% SdS, with the water concentration constant at 57 wt%, in the temperature range 20°C–65°C.

In the meantime Saupe published in 1981 a paper on the elastic and flow properties of biaxial nematics [27], before experimental results were available, stimulated by the observation of the biaxial phase and because there was need for a theory as a guideline for experiments and for the characterisation of elastic and viscous properties.

The next paper by Saupe *et al.* on biaxial nematic phases in amphiphilic systems, published in a French journal [28], was the most complete of this initial period. Emphasis is given to further experimental data confirming the biaxial phase in the two systems, based on KL and SdS. The introduction discusses the structural relationship of the micelles to the aggregates of neighbouring phases and that micelles of ribbon-like shape could be involved in the formation of N_B. But it was noted that micelles do not have a rigid structure and that their effective structure may change gradually through the phase transitions. The point that no thermotropic biaxial nematic phase had been found is stressed, and all the statistical and elastic theories previously proposed are mentioned. The paper then turns to the interest of having a Landau theory for phase transitional properties and biaxial order to be compared with experimental results. Leaving aside, therefore, any attempt to model the microscopic structures, it is shown that the nematic isotropic transition may become second-order at the point at which the uniaxial–biaxial and nematic–isotropic transition lines meet, and a schematic phase diagram of temperature versus concentration is presented. The difference between the two principal refractive indexes is obtained analytically at the transitions and can be used to test the experimental results [28]. Furthermore, the deuterium NMR splitting of the oriented molecules is also obtained. The temperature dependence of the splitting diverges in the biaxial phase at the N_D–N_B transition, while at the N_B–N_C transition it has only a discontinuous change in the derivative. In cases where the biaxial range is very small, so that the transition is quasi-direct from N_D–N_C, the deuterium NMR splitting will appear to increase discontinuously by a factor of two at the transition. The slope of the splitting as a function of temperature also changes discontinuously. It follows that the slope on the N_C side is larger by a factor of two than on the N_D side and of opposite sign [28].

With such well-defined theoretical results, a detailed analysis was made of the experimental results obtained using microscopy (textures and conoscopy), NMR and birefringence, in both SdS and KL systems. The textures have defined differences in the N_D (homeotropic pseudo-isotropic) and N_C (parallel schlieren) phases, as already described in the first paper on SdS [16]. In this a physical explanation was given in terms of microscopic properties: polar groups on the surface, and changes at the polar–apolar micellar interface. The N_D–N_B transition is characterised by the appearance of bright irregular spots, while the N_B–N_C transition cannot be readily recognised. But biaxial properties can be found by conoscopic observation of aligned samples and detailed NMR experiments [28]. The birefringence was measured using a laser, on surface and magnetic field aligned films. The difference $(n_1 - n_2)$ is zero in the N_D phase and changes rapidly with temperature in the biaxial phase. In a KL sample, with two biaxial ranges, the sequence N_D–N_B–N_C–N_B–N_D gave clear results for the changes in $(n_1 - n_2)$ [28]. There was also a clear indication that the width of the biaxial range reduced to zero when its limits approached the nematic-to-isotropic phase transition line.

The paper ends by mentioning [28] that the biaxial macroscopic properties may become of practical interest when thermotropic biaxial phases can be found, but anticipates that this will be difficult, since in amphiphilic systems the micellar structure is temperature-dependent, which aids the discovery of a biaxial phase, but the biaxial range exists only over a small temperature range.

In parallel with this a paper was published by a French group [29], also focusing on the two systems, SdS and KL, and also using D_2O. The mesophases were first identified by observing their textures in polarised light. NMR was used only to obtain the sign of the anistropy of the magnetic susceptibility, with no reference to the details that had been reported in the paper by Saupe *et al.* [28]. Therefore, no sign of the phase biaxiality could be detected in any system. The phase diagrams showed the two uniaxial lyomesophases, with a transition N_D–N_C with increasing temperature. But the boundaries were shifted in relation to the original results from Saupe, and no re-entrant behaviour was detected. The focus of the paper was to disentangle the effects of the form factor and interference functions in the scattering curves with X-ray and neutron scattering methods, obtained only at room temperature. As expected, the scattering was dominated by interference, and the sizes of the aggregates were not obtained directly. Two facts remained unexplained: the width of the diffraction band, indicating more correlation than in thermotropic nematics, and the high order parameter obtained from the angular aperture with $S \sim 0.7$.

This paper also revealed the problem of reproducibility in the phase diagrams with biaxial phases, related both to the physicochemical complexity of the lyotropic systems and the technical difficulties in detection of the phase biaxiality. In the French paper [29] the boundary of the N_D phase was shifted towards lower KL concentrations, and neither the re-entrant N_C behaviour nor the biaxial phase were found. But the biaxial phase was detected in the same year (1983) by Galerne *et al.* in the KL system, using conoscopic observations and measurement of the differences between the principal refractive indexes [30]. This allowed the determination of the tensor order parameter in all three phases, and the symmetric invariants of the order parameter were found to have a linear dependence on temperature [30], in good agreement with the predictions of the molecular field theory developed by Saupe. The sample had a small amount of ferrofluid ($<10^{-4}$ in weight%) added to help alignment in the magnetic field, giving the sequence I (10.5°C)–N_D (18°C)–N_B (20°C)–N_C [30]. Thus, although the transitions to the biaxial phase were fully confirmed, some differences in relation to the original phase diagram were also clear, and the re-entrant behaviour of the N_C phase was not observed.

The literature afterwards follows a number of different directions, with other researchers entering the field, and a complete review is outside the scope of the present paper. We shall pursue instead some defined lines in the direction of more recent proposals.

3. Further information on micellar structures

In parallel with the biaxial phases, Saupe focused on a number of micellar systems and it seems clear that he was very conscious of the non-trivial problem of the structure of the micellar aggregates in nematic lyomesophases. In the course of a decade he published a large number of papers with several collaborators. Only a few of these will be mentioned here, focusing on the information obtained on the structure of the micellar aggregates. Pertinent information obtained by other researchers regarding such structures, also in biaxial phases, is included.

Saupe presented a review of the structure and physical properties of micellar nematics at the meeting on lyotropics and related fields in Rende, Cosenza (where Bartolino worked) in 1982, and this was later published in an Italian journal [31]. The introduction emphasises that the lyonematic states occur only in exceptional cases, with new phenomena not observed in thermotropics, specifically the occurrence of several nematic phases in the same system, including the biaxial phase. The properties of uniaxial micellar nematics are given, from the point of view of the conventional physico-chemical approach to the self-aggregation process. The first reference in this paper is to the work of Tanford on the thermodynamics of the hydrophobic effect [32]. The structures formed with increasing concentration are discussed, as well as the effect of the addition of electrolytes and decanol, both decreasing the cmc and increasing the size of the micelles. Using specific examples it is shown that salt affects the packing of the headgroups, and may promote the nematic phase in the DACl system, whereas in the ternary SdS and KL systems decanol promotes the phase transitions between the different nematics. Reference to all known nematogenic systems is made [33], stressing that all are ionic but that the net electric charge of the micelles is not important [34]. The paper then turns to cholesteric phases and elastic properties, as well as to density and electrical conductivity results, stressing the surprising results for DACl, which gave no difference at the N_D–lamellar transition, indicating that instead of continuous bilayers the aggregates in the smectic state could be finite discoid micelles arranged in layers.

In other words, Saupe focuses on the physical properties of the bulk and the physico-chemical aspects of the microscopic molecular interactions, searching for hints as to the micellar structures. No attempt is made to develop a microscopic theory of lyonematics. Clearly, his approach is no longer related to the physics but to the physical chemistry of the complex aggregation involved in micelle formation.

A further paper on the critical behaviour of uniaxial–biaxial nematic phase transitions in amphiphilic systems [35] includes a comment on the previous theories for the formation of biaxial phases [8–12]: *The model systems imply particles that deviate significantly from rotational symmetry or mixtures of rod-shaped and disc-shaped particles. They are not directly applicable to biaxial amphiphilic nematics where the deviation from rotational symmetry of the structure on the amphiphilic compound does not seem to be a significant factor*. It is stated that in the KL and SdS systems the shape of the aggregates changes from rod-like to disc-like as a function of concentration and temperature, leading to the N_C and N_D phases, but the shape of the aggregates in the biaxial phase is not known. It may be ellipsoidal and deviate significantly from rotational symmetry, or there may be mixtures of rod- and disc-shaped micelles [35].

In the meantime further work on mixtures of rods and plates appeared. After a paper on mixtures of rods and discs in thermotropics [36], Gelbart and collaborators made extensive studies focused on micellar systems, within an approach based on excluded-volume interactions. Of particular interest is the effect of micellar growth at the I–N_C transition and with the addition of decanol [37]. Parallel to this series of papers on micellar systems, theoretical papers on the instability of mixtures of discs and rods against demixing were published [38, 39], which, in fact, did not refer to the actual situation in micellar systems. It became clear that the stability of mixtures of rods and discs must take into account the short-range interactions between objects, which are very important in micellar systems. The Maier–Saupe theory, however, is based on long-range contributions to the intermolecular potential and is very successful for thermotropics, even neglecting the important short-range forces, a point discussed by Luckhurst and Zannoni [40]. As a result, controversies concerning the micellar structures in the biaxial phase were inevitable.

The first X-ray diffraction study on the sequence of nematic phases appearing on varying the temperature [41] showed similar diffraction patterns along the N_D–N_B–N_C transitions in the KL system, and this was interpreted as coming from aggregates of statistically biaxial shapes, which seems correct. But this result was extrapolated to the statement: *The only change at the uniaxial–biaxial nematic transitions is the long-range order* [41], which is not, in fact, correct. The detailed diffraction results over the sequence of second-order transitions provide evidence only that changes in the diffraction volume are smooth; the X-ray correlation length over several intermicellar distances says nothing about the short-range interactions at the molecular level, which may act to change the detailed and unknown form of the micellar object. The evidence from diffraction, which indicates only the distance between objects, was further extrapolated to give the idea that the micellar object itself was always biaxial in all nematic phases, with uniaxial phases corresponding to fluctuations about different axes of the same object [41]. But in the conclusion to the article, Figuereido Neto *et al*. state [41]: *The statistics which governs the biaxial shape and the size of the micelles is actually unknown (a mixture of disc-like and cylinder-like micelles may not be excluded)*. The hypothesis of a unique micellar object in all nematic phases is in clear contradiction to the change in the micellar surface in the two uniaxial phases, evidenced by the different surface or director orientations. Bartolino *et al*. stressed in their work on the biaxial phase of the SdS system that the surface orientation did not change, and this was the basis for their proposal that the N_C phase was made by the packing of discs in columns [26]. But a constant homeotropic surface orientation was not reported by Saupe *et al.* for the same system [28]. The problem has not been resolved at the molecular level, and these controversies still continue in the literature today.

In the next phase diagram for the KL system [42], with the same decanol content taken from Saupe's diagram (6.24 wt%), the re-entrance of the N_C phase did not occur, and a rather sharp separation existed between the N_D and N_C phases at a defined KL concentration, above which the biaxial phase was observed over a very small temperature range. The phase diagram at a fixed ratio of KL and decanol wt% ($R = 4$) showed larger temperature ranges for the N_B phase, but the point at which all nematic phases joined the isotropic phase did not exist [42].

After our initial work on SdS [18] we continued work on lyotropic phases with this amphiphile. However, in view of the controversies on micellar form in lyonematics we decided to turn to micellar systems in the isotropic phase, in order to understand better the physicochemical aspects of concentrated micellar systems. We chose sodium dodecyl (lauryl) sulphate (abbreviation SLS, in order to avoid confusion with sodium decyl sulphate, SdS), the amphiphile most used in studies of micelle formation, commercially available in high purity at reasonable prices and present in many cleaning products on the market. While working on the isotropic phase, we wondered why no work in lyonematics existed with SLS. The original paper on the first lyonematics [6] reported that C10 and C8 alkyl sulphates led to the nematic phase and *the C12 homolog produces a crystalline phase at room temperature*, and in fact this was the reason why Reeves focused on SdS [13]. We therefore began an attempt to find the nematic domain in SLS. By trial and error we succeeded in reaching a nematic phase, N_C, at room temperature [43], but with more water than in the SdS and KL systems. We then varied the molar ratios (instead of the wt% or ratios of wt% used previously with KL and SdS), in other words M_d = [decanol]/[SLS] for several values of the water molar ratio M_w = [water]/[SLS], and the nematic domain was localised [44].

Figure 2 shows the ternary phase diagram at room temperature for the system SLS/decanol/water with the nematic domain localised in [44] and the other phases (isotropic, I, hexagonal, H, and lamellar, L) previously reported [45]. The phase diagram as a function of temperature varying the molar ratio [decanol]/[SLS] = M_d is shown in Figure 3, for a fixed molar ratio [water]/[SLS] of 45.2. The N_C–N_D transition occurs sharply at $M_d = 0.38$ [44], with no sign of an intermediate biaxial phase. The two coagel phases below the nematic phases are lamellar, with extended chains as determined from X-ray diffraction [44].

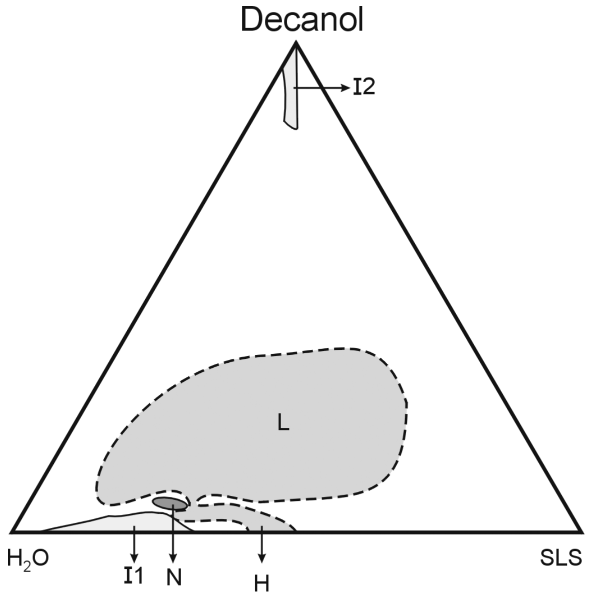

Figure 2. Localisation of the nematic domain (N) at room temperature, in the phase diagram of SLS (dodecyl, lauryl sulphate)/decanol/water [44], together with other phases reported in [45]. Figure reproduced from [44] with permission.

The use of molar ratios allows comparison of conditions for the N_C–(N_B)–N_D transitions in the related systems KL, SdS and SLS. Analyzing the various phase diagrams in the literature we were able to show

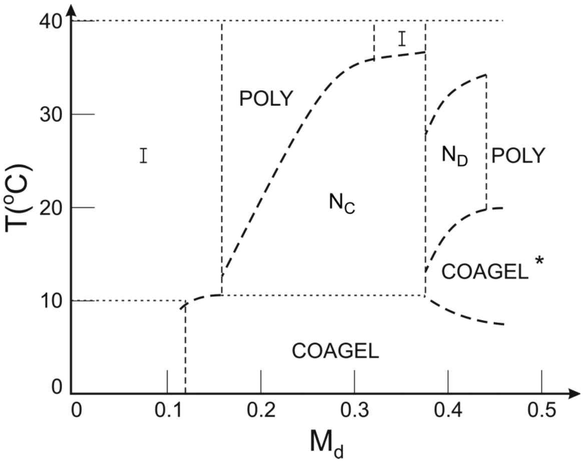

Figure 3. Phase diagram with varying temperature and molar ratio, M_d = [decanol]/[SLS] for a fixed molar ratio [water]/[SLS] = M_w = 45.2, taken from [44], with permission.

that the transition occurred for very similar values of the [decanol]/[amphiphile] molar ratio, 0.30 for SdS and 0.38 for both KL and SLS [44]. This molar ratio, however, changes markedly with the amphiphile (~20 for SdS, ~30 for KL and ~40 for SLS [44]). Decanol, with its tendency to stay in less curved micellar interfaces [37], promotes the change in micelle shape from cylindrical to discotic. The amount of water between the micelles increases with the micellar size, which is related to the amphiphile length. We have also reported evidence for the existence of a first-order transition between the uniaxial nematic phases in the SLS system [46].

A paper by Saupe *et al.* [47] from 1991 can be considered as his final view on micellar structures in lyotropic liquid crystals and phase transitions. The Introduction refers to basic concepts of the curvature determinant for the stability of the aggregates and that the intrinsic curvature can easily be influenced by the addition of co-surfactants such as decanol, or of electrolytes. It is emphasised: *The bilayers are composed of two plane monolayers while the cylinders are formed by strongly curved monolayers*. The item on formation of micelles and the theory of micellisation starts with the statement that micelles interact predominantly by repulsive forces, similar to rigid or semi-rigid particles, and the formation of nematic states via Onsager and Flory approaches are quoted. The effect of electrolytes is discussed, focusing on the addition of NH_4Cl to the DACl/water system which promotes the change from H to L phase. The effect of decanol is illustrated for the system MTAB/1-decanol/D_2O, with different results for changes in the weight % with a constant molar ratio [MTBA + decanol]/[water] and for changes in the [decanol]/[MTBA] molar ratio. This last procedure induces the phase transitions H–N_C–N_D–L, similar to our results with SLS [44]. It is explicitly mentioned [47] that: *The shape of the aggregates will predominantly be determined by the mole ratio of MTAB/decanol*, and it is stressed that the transitions between the two uniaxial nematic phases in the MTAB/1-decanol/D_2O system are first-order, separated by a small two-phase range. The biaxial phase in the SdS system is studied with electrical conductivity and birefringence measurements, with the same features obtained previously for the KL system. It is considered that the structural changes of the micelles have not been fully established, since X-ray scattering and conductivity measurements indicate only minor changes in micellar structure across the biaxial range. The case of aggregates formed by small discoid micelles which grow to infinite bilayers is discussed again in detail, as well as the effect of excluded volume on the aggregation process at phase transitions [47].

In the Conclusions, the second-order transition between N_D and lamellar phases is discussed both in relation to a lamellar structure made of small discs, and other alternatives such as the possibility of a defect-mediated transition, and ribbon structures. It is considered that transitions between different nematic states may result from relatively small changes in the micelle cross-section due to the changes in elastic properties. The paper ends with the statement: *Further research is required to test and elaborate various models in order to explain the transitions on a molecular basis* [47]. Apparently Saupe did not change his position regarding the problem of micellar structures.

4. Other phase diagrams with biaxial lyotropic phases

An interesting study has been conducted in Brazil on changes in the phase diagram of the KL system when decanol is replaced by DACl, leading to improved chemical stability [48]. The system was studied by X-ray and optical microscopy, varying the molar ratio R = [DACl/KL] at a constant [amphiphile]/[water] molar ratio (D_2O is not mentioned), with the addition of a ferrofluid dopant for better magnetic orientation. A biaxial phase was observed, but the topology of the phase diagram had changed [48]; the sequence of nematic phase transitions was inverted with temperature in relation to KL, with N_D (instead of N_C) phases at higher temperatures. Both DACl and decanol remain inside the micelles. However, the study did not stress the importance of the phases that surround the nematic domain: when DACl replaces decanol a hexagonal phase, H, is reported at lower temperatures, and, therefore, the full sequence is H–N_C–N_B–N_D, and even a triple point, H/N_C/N_B, appears [48]. No comparison with the DACl system (without KL) is made.

The system KL/DACl/D_2O was later studied in Italy [49], using a new characterisation technique involving NMR. In addition to the usual static measurements, followed by measurement after a $\pi/2$ rotation of the sample about an axis normal to the external magnetic field, a measurement with the sample spinning about that axis gave complete and independent characterisation of the biaxial phase. The phase diagram obtained had a topology similar to Saupe's original phase diagram, but without the inversion of the uniaxial nematics position with temperature. N_D phases in the two phase diagrams reported [48, 49] appear to have higher values of the molar ratio, R. The differences between phase diagrams with H_2O and D_2O are mentioned, but without further discussion.

The contradictions are emphasised here regarding the lower temperature phase, below 10°C, attributed to a viscous isotropic phase by Saupe, to a hexagonal H_α in the system with water [48] and to an ordered phase in the system with D_2O [49].

After we had localised the nematic domain with SLS [44], the Swedish group, with a long tradition in classical lyotropic liquid crystals [45], also began to investigate the nematic phases in the SLS system [50], with a number of papers in the following years.

At the same time theoretical papers also began to appear, following the theme of Gelbart's treatment of micellar systems, with excluded volume interactions. The role of flexibility in diminishing the micellar growth, coupled to alignment at the I–N_C transition, was treated within a second virial approximation [51]. Later, other papers by Herzfeld *et al.* for the first time gave a statistical mechanics treatment for the problem of micellar aggregation at the transitions I–N–hexagonal columnar and smectic phases with long-range positional correlations [52–55]. These theoretical phase diagrams did not have a biaxial phase, since the symmetry of the micellar object was a defined input, but they gave insight into micellar growth and flexibility. A further paper on the role of flexibility in the phase diagrams appeared later [56].

During the 1990s we investigated the SLS system, mainly using X-ray techniques, in order to gain insight into the phase transitions in concentrated binary and ternary systems [57, 58], comparing our results with these theories. We also focused on the H phase along different phase transition sequences in other systems and found a scaling behaviour for the exponent defining the variation of the hexagonal parameter with the amphiphile volume concentration, *cv* [59–62].

In parallel with our studies of the SLS system, in Sweden the doctorate of Quist produced a number of papers on lyonematics, and a more complete phase diagram for the system SLS/decanol/D_2O revealed the existence of two biaxial islands, with a topology different to that obtained with the KL and SdS systems [63]. Figure 4 illustrates the region of the SLS ternary phase diagram where the biaxial islands were found by Quist at 25°C with D_2O [63]; also shown are the A and B lines which we were investigating by focusing the different phase sequences I–N_C [64] and I–H–N_C [65] compared with the inverted theoretical prediction I–(N_C)–H [54–56].

The biaxial islands, surrounded by coexistence regions, disappear at 30°C, and the extension of the biaxial region increases with decreasing temperature, but the SLS precipitates out below 18°C [63]. The coexistence region around the biaxial islands is a fingerprint of first-order transitions, and the biaxial islands contain N_B^+ and N_B^- regions [63]. The shape of the surfactant aggregates in the nematic phases certainly varies with composition and temperature in the SLS system. Another system, also with biaxial islands and a different topology, has later been reported by another group in Brazil [66].

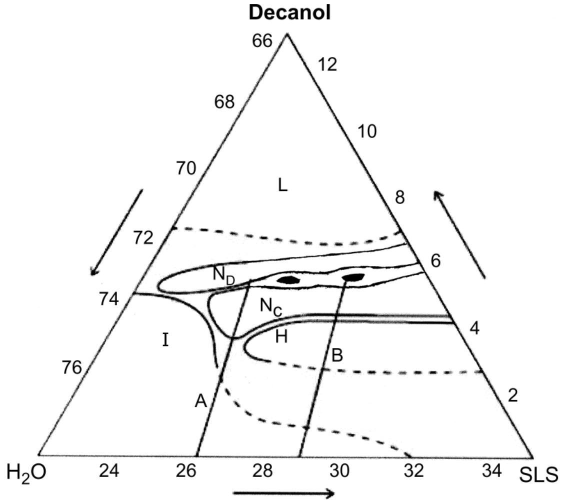

Figure 4. Ternary phase diagram of the system SLS/water/decanol as a function of weight composition, focusing on the nematic domain localised by us [43, 44] and the limits of the hexagonal phase given previously by Ekwall [45]. The limits of the nematic phases were later defined by the Swedish group with D_2O [50] and Quist found the biaxial islands [63]. Also shown are the lines investigated by us, A [64] and B [65].

5. Chemical aspects of the KL system

Some years later a detailed study of the KL phase diagrams was made, but using H_2O in place of D_2O, and focusing on the problem of reproducibility and possible standardisation of the nematic domain [67, 68], but the biaxial phase was not found. The first paper focused on the synthetic procedures and reproducibility, aiming at the use of the system as a carrier for ferrofluids [67]. KL has been synthesised in each research laboratory, starting from lauric acid. The purity of the precipitated KL, particularly the absence of residual lauric acid, can be verified using infrared spectroscopy [67]. It is concluded that reproducibility requires 99 wt% purity of KL, meaning no more than 1 wt% of residual lauric acid. Furthermore, it is found that the pH of the product when dissolved in H_2O at 20°C must be within the range 10.3–10.7, and it was stressed [67] that the pH value had not received attention in previous studies. The ternary phase diagram shows a biphasic domain located between the isotropic and nematic regions, characterised by a high dependency of its apparent viscosity on temperature and on the amount of alcohol. The second paper [68] focuses on the fluctuation zone along the boundary of the I–N transition as a function of temperature and the biphasic region, which corresponds to two gel phases: G–1 is a stable non-homogeneous suspension of optically anisotropic droplets within the isotropic medium, whereas G–2 is rheologically similar to the H phase. The N–I transition may be either clearly first-order at lower temperatures, via a gel phase, or may approach a second-order transition with strong fluctuations. The character of the transition changes at the point of intersection of the boundaries of I, G and N domains, and signs of transient biaxiality are observed in the N phase at temperatures above the intersection [68].

Although not mentioned in their papers, it seems clear that the two reported gel phases coincide with the coagel and gel phases reported by Luzzati for other systems [23]. In addition, these papers on the KL system with H_2O [67, 68] make no mention of the fact that the biaxial literature refers mainly to systems based on D_2O. On the other hand they stress the importance of the pH of KL in water (within ~4%), but the pH of D_2O is known to be ~6% higher than that of H_2O.

In conclusion, the biaxial nematic domain in a lyotropic system is a very subtle effect, involving variations of less than 1% in weight concentration, and its emergence depends on factors that are still not completely understood. These complex lyomesophases require focus on the chemical aspects, not found in the literature, in order to reach a better understanding of structures and behaviour at the molecular level.

6. Modelling the micellar shape transformation

There are a number of experimental facts leading to the concept of different micellar shapes in the two uniaxial lyonematics, N_C and N_D, but no theory for a change in micellar shape has existed. Partitioning of co-surfactant in mixed micelles has been analyzed theoretically [37], showing that the co-surfactant goes preferentially into the body rather than the caps of sphero-cylinder (SC) aggregates. Preferential partitioning of decanol in the lower curvature zones of the micelles has also been observed experimentally [69].

It is well-known that the membranes of amphiphilic aggregates in colloidal systems can be elastically deformed. The phenomenological theory of Helfrich [70] gives the bending energy as a function of the principal and spontaneous curvatures of the membrane interfaces via the elastic constants (bending rigidity and elastic modulus of Gaussian curvature), an approach widely used for membranes. Hyde has developed a semi-empirical model [71, 72] in which the same bending energy is expressed in terms of the surfactant parameter, connected with the curvature of the interface [73]. It has been discussed explicitly [74] how Helfrich's formulation is suitable for spontaneously planar surfaces, while Hyde's model accounts for spontaneously curved interfaces. In the case of micelles it is not possible to use the conditions of equal surface and volume to deduce the shape that minimises the energy, as can be done for vesicles [75]. The constant paraffin volume criterion instead implies a necessary change in the surface. Hyde's model is a convenient single parameter model to test the relative stabilities of different micellar forms, using the molecular quantity $p_0 = v/al$ (where v, l, and a are, respectively, the volume and length of the hydrophobic chain and the area per polar head at the apolar–polar interface).

The first application of Hyde's model to micelles was made when we analyzed the shape transformation from prolate ellipsoid to SC [76], favoured for anisometries >1.8. Such a shape transition in the concentrated isotropic phase of the SLS/water system may be a prerequisite for the occurrence of the I–H phase transition, since SC allows polydisperse growth.

Using the same approach we later proceeded to model a change of micellar shape from SC to square tablet (ST), which occurs geometrically in a continuous manner, with an intermediate biaxial object [77]. The choice of the ST form was based on its favourable geometrical properties, since the geometrical transformation SC–rectangular tablet–ST does not introduce any cusp in the micellar surfaces.

In a ternary system the regions of different curvature can be occupied preferentially by distinct molecules, so that the whole micelle is stabilised. The partitioning of surfactant/co-surfactant in the SC form, due to minimisation of electrostatic strain [37], was accepted as a starting point for the SC–ST transformation, with the surfactant and co-surfactant randomly distributed in the mixed region (body of SC), leaving only surfactant in the spherical caps.

In order to evaluate the Hyde bending energy, two hypotheses have been considered: the independent-molecules model, with surfaces added according to the number of molecules of each type, and the effective-unity model, in which surfactant/co-surfactant in the average proportion is considered to be a new molecular unity. These two hypotheses each lead to an equation defining the SC–ST transformation, as a function of the fraction of the interface with the surfactant in the body of SC.

The [decanol]/[amphiphile] molecular ratio (M_d) at which the nematic cylindrical (N_C)–nematic discotic (N_D) phase transitions occurs for the three amphiphiles (KL, SdS, SLS) yields the fraction, x, in the body of SC, using the experimentally determined anisometries, μ, for the SC at the transition. The results are given in Table 1, showing a constant x value for the three systems. The

Table 1. Experimental M_d values (decanol/amphiphile molecular ratio), estimated anisometries, μ, of the SC and related x values (decanol/amphiphile ratios in the body of the SC), at the N_C–N_D transition, taken from [77], with permission. SdS, KL and SLS are, respectively, the amphiphiles sodium decyl sulphate, potassium laurate and sodium dodecyl sulphate.

	SdS	KL	SLS
M_d	0.30 ± 0.03	0.38 ± 0.02	0.38 ± 0.01
μ	2.3 ± 0.3	3.0 ± 0.3	3.0 ± 0.3
x	0.65 ± 0.03	0.64 ± 0.03	0.64 ± 0.03

elastic bending theory, for a single mixed micelle, correctly predicts a transformation at this x value for the expected p_0 values for amphiphile and co-surfactant, without entering into the details of the intermediate forms between SC and ST, neither in the intra- nor intermicellar interactions.

Assuming $p_{02} = 1$ for decanol, the prediction from the model gives $p_{01} = 0.47$ for independent molecules and $p_{01} = 0.6$ for an effective unity. The exact value of p_{01} in these nematic phases is not known, but a value of the order of 0.5, or slightly above, can be expected from the amount of available water and from the fact that the nematic domain occurs between hexagonal and lamellar phases. The indication is that some degree of coupling between surfactant and co-surfactant may be occurring.

This shape transformation, in addition to coinciding with N_C–N_D transitions, occurs also in the I phase, with increase of decanol, as studied by detailed analysis [78] of curves of small-angle X-ray scattering in the SLS/water/decanol system. A review of several papers we have published focusing on changes in aggregate form, size and flexibility along phase sequences in lyotropic liquid crystals, can be seen in more detail in [79].

7. Modelling the biaxial phase with mixture of uniaxial micelles

Our concept of shape transformation at the N_C–(N_B)–N_D phase sequence inspired a proposal for the statistical mechanics of polydisperse uniaxial forms, which was developed by Henriques and Henriques [80]. A discretised Maier–Saupe model for a polydisperse solution of micelles of axial symmetry was developed making use of a form parameter, which depends on the micelle anisometry, related to the quadrupole moment. An exact molecular field solution with a Gaussian distribution of anisometries gave a typical phase diagram, with temperature as a function of the average anisometry, symmetric around the Landau point joining the three phases (I, N_C and N_D) at null average anisometry [80]. The biaxial phase is a result of the mixture in the Gaussian distribution with small mean anisometry. This model did not, however, achieve a real fit of the experimental phase diagram.

An important result giving support to the idea of a mixture of uniaxial micelles in the biaxial phase came from optical parameters determined along the phase transitions re-entrant isotropic–N_D–N_B–N_C–isotropic in the KL/decanol/D_2O system [81]. For a particular temperature, approximately in the middle of the N_B phase, the result is as expected for a biaxial phase comprising a mixture of the two uniaxial forms [81].

Recently the statistical mechanics model [80] has been revised, together with the concept of a change in the micellar form induced by decanol partitioning [77], and the first truly statistical microscopic approach able to model the lyotropic biaxial nematic phases experimentally observed has been reported by us [22]. In order to prevent demixing of the two forms it is considered that form transformation of micelles takes place over much shorter times than micelle diffusion, thus yielding a homogeneous mixture. The model proposes that changes in uniaxial micellar form may occur either smoothly or abruptly; a smooth transformation of form in a polydisperse solution from rod-like into disc-like shapes requires a continuous distribution of Maier–Saupe interaction constants, while an abrupt change of monodisperse form is described by a discontinuous distribution of interaction constants.

As in the original Maier–Saupe model, particles interact via their quadrupoles, λ_i, satisfying the basic requirements of symmetry for the nematic phase, and assumed to be due to an expansion in multipoles of undefined interactions. The molecular field approach corresponds to considering only long-range interactions. For complex micellar systems it is quite clear that the micellar aggregates are defined by the short-range interactions, including the excluded volume. But if the changes in the aggregates can be taken into account through a shape parameter, then the molecular field approach might also be applicable to lyonematics. In our case, the quadrupoles, λ_i may be >0 (SC) or <0 (discs), with *ad hoc* distribution functions.

To model a smooth transition of micelle form, we have assumed a broad dispersion of quadrupoles in dynamic equilibrium in the cylinder–disc transition region. In this region, the average quadrupole should remain small. Figure 5 (from Henriques *et al.* [22]) shows the phase diagram obtained with a single Gaussian distribution (as in Henriques and Henriques [80]) together with a double-delta distribution, which mimics double-Gaussian in a simplified form, and also the results of Monte Carlo simulations.

The phase diagrams for the Gaussian and bimodal distributions are entirely analogous, each displaying a stable biaxial phase and a Landau point with null

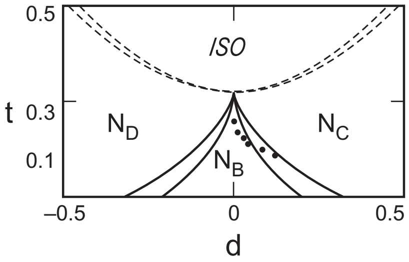

Figure 5. Molecular field theoretical phase diagrams for Gaussian and delta–function bimodal distribution of quadrupoles, taken, with permission, from [22]. The parameters, *t* and *d*, are the dimensionless temperature and the quadrupole. A biaxial phase, N_B, separates a cylindrical N_C from a discotic N_D phase. Solid lines represent critical transitions, with lower transition temperatures for the delta–function bimodal distribution, and dashed lines stand for the nematic–isotropic lines, with lower transition temperatures for the Gaussian distribution. Dots represent Monte Carlo simulation results for the critical N_B–N_C line.

anisometry at the same temperature. The fact that the single and bimodal distributions yield the same phases is an important result, because the delta-function bimodal model is much simpler to handle than the Gaussian distribution and serves very well as a first approximation.

Results for this model [22] show that the dispersive distributions give a biaxial phase, whereas an abrupt change of shape leads to coexistence of uniaxial phases. A comparison with the experimental phase diagram of Yu and Saupe [1] of the theoretical predictions of the model can be made near the Landau point through a transformation of variables. The strong asymmetry with respect to the N_C and N_D phases of the experimental phase diagram can be dealt with through an expansion, up to first-order in λ_o/σ_o, (the average quadrupole divided by the dispersion of the Gaussian distribution) into powers of the KL weight concentration and temperature.

Figure 1 shows the theory fitted to the experimental phase diagram [22]. The Gaussian and bimodal descriptions are indistinguishable near the Landau point and the phase transition lines coincide on the scale of Figure 1. The two distributions differ only in shape population variations. The implications are that positive quadrupoles, associated with cylinders, increase with KL concentration and decrease with temperature as we move from the Landau point. Absolute values for negative quadrupoles, associated with disc-like objects, decrease with KL concentration and increase with temperature.

In order to give a microscopic interpretation for the micellar change of shape, quadrupoles are explicitly expressed as functions of micellar geometrical parameters [22]. This was done considering that the intermicelle potential may be as suggested previously by a DLVO-model study [82]. The quadrupoles resulting from a multipole expansion of this potential will be integrals, depending on some internal micellar density and on the geometry of the micelles. Rounded discs have height H and sphero-cylinders have diameter D given by the bilayer length $2l$, with anisometries $\mu = H/D$ (>1 for cylinders, <1 for discs, and 1 for spheres), and explicit relations between the quadrupoles and the anisometries of the two shapes have been found [22]. We have considered the detailed micellar geometries, with preferential partitioning of KL and decanol, as well as the basic question of changes in chain length and volume with temperature [83].

Hydrocarbon chains are characterised by a chain length contraction with increasing temperature, and this effect has been invoked previously to explain the re-entrant nematic phase [84]. It should, however, be stressed that such a contraction, expressed by a negative temperature coefficient, holds only in the chain direction. The paraffin volume as a whole has a small positive temperature coefficient [83], and this is the essential point needed to achieve the phase diagram with a microscopic model of a mixture of cylinders and discs.

Specific assumptions for micellar volume and relative density are made at the Landau point, with equal micellar volumes and surfactant/co-surfactant densities. The anisometries at the Landau point were calculated with a partition model of surfactant and co-surfactant in each form, as in [77]. Assuming the paraffinic volumes and the number of decanol or laurate molecules of different shapes to be equal at the Landau point, as expected from a single micelle changing its shape, we obtain $\mu_c \sim 3.57$ and $\mu_d \sim 2.00$, in reasonable agreement with known values at the phase transition. The aggregate volume at the Landau point corresponds to micelles containing about 200 molecules [22].

The upper part of the phase diagram, near the Landau point, indicates micellar aggregation number variation following volume changes, as a consequence of fixed chain volumes. Micelles of either shape have increasing volumes as the temperature is lowered, with cylinders increasing much more rapidly than discs. The effect of the KL concentration is opposite in the case of cylinders and discs, as expected.

Finally, we suggest an interpretation for the lower temperature part of the phase diagram (below 30°C). The sequence of phases can be understood from a qualitative point of view from the variations in the micellar object with temperature and concentration [22]. While the direction of the chain is contracting with increasing temperature, its other dimensions are expanding, conserving the whole paraffin volume at a practically constant level over the temperature range of interest, since the number of molecules in the micelles does not change. This would imply that cylinders and discs become more anisotropic with increasing temperature. In a cylinder two dimensions are contracting with temperature, while in discs only one dimension contracts. Given the same chain contraction, cylinders therefore grow more quickly with increasing temperature, and the population of forms and the corresponding average quadrupoles therefore suffer distortions as a function of temperature. The N_D–N_B–N_C transitions observed with increasing temperature in the lower part of the phase diagram are in fact to be expected if the volumes and aggregation numbers of the micelles remain constant with temperature. So the full sequence observed with increasing temperature at KL 26 wt%, N_D–N_B–N_C–N_B–N_D, can be rationalised by an initially constant aggregation number, with increasing anisometries, followed by a combination of still increasing anisometries but decreasing aggregation numbers, by thermal agitation and excluded volume effects. This accounts for the re-entrant behaviour of the N_C and N_B domain in the N_D phase.

Complete modelling of the entire phase diagram, with an explicit definition of variations in the population of forms, would require better knowledge of the lower temperature phase, described by Saupe as the *viscous isotropic phase*. His phase diagram shows a clear Landau point in the higher temperature region, but in the lower temperature region the curves do not join together at a defined point. Specifically, the intersection of the boundaries of I, G and N domains mentioned in the study with H_2O [68] have not been found, nor have they even been searched for, in the KL system with D_2O. With the experimental definition of such an intersection point it would be possible, for instance, to follow the approach of reconstruction of the phase diagram using a non-critical order parameter, expressing the change in the micellar shape with temperature [85], with a defined choice of the micellar forms and number densities. Without such an intersection point, a qualitative agreement in the reconstruction can be obtained with the two uniaxial shapes (cylinder and disc) or with other hypothetical forms.

8. Conclusions

The studies of nematic phases of micellar systems by Saupe and collaborators over more than a decade have defined the field and the subsequent work of other researchers attracted to the subject. It now seems clear that possible biaxial thermotropic phases will be quite different at the molecular level than in their biaxial lyonematic counterparts. Recent theoretical work analyzing the Landau free energy has shown the possibility of new topologies in the phase diagrams involving biaxial nematic liquid crystals, with a direct isotropic–biaxial nematic phase transition and three different biaxial nematic phases [86].

Lyotropic liquid crystals have now found use as templates for a variety of nanostructures. For instance, the nematic phases discovered by us in the system SLS/H_2O/decanol [44] are now in use as templates for carbon nanotubes [87, 88]. Some questions on micellar systems are already clear, but points of interest still remain to be resolved for micellar systems with lyonematic phases. We have shown that the Landau point at higher temperatures, joining I, N_C, N_D and N_B phases in the KL system can be modelled using a mixture of uniaxial shapes under exchange conditions [22]. The possibility of continuous change of form passing through a biaxial shape also remains open. But such a continuous change in form would probably in fact be statistically equivalent to a mixture of changing composition. Very recently, a molecular dynamics simulation of amphiphilic molecules in solution has shown conditions for the dynamic coexistence of different micellar forms [89]. A complete understanding of the KL phase diagram would require a definition of the gel phases existing at lower temperatures, and of the intersection of the boundaries of I, G and N domains, which may be sensitive to differences in water. It seems clear that the main characteristics of the biaxial phase do not depend on the use of H_2O or D_2O, but the exact details may depend both on the type of water and on the pH. The O–H bond is easier to break than the O–D bond, and the delicate equilibrium of H-bond networks might be different. For instance, studies of relaxation kinetics of SLS micelles have shown differences in H_2O and D_2O [91]. A completely new direction would open up if lyomesophases became a tool for exploring the differences between H-bond and D-bond networks, which are known to have important effects for life.

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