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LYOTROPIC LIQUID CRYSTALS
II. STRUCTURAL POLYMORPHISM

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Abstract. This review presents a general description of the lyotropic polymorphism, lying on 40 international publications. The high rate of progress in the liquid crystals field, especially in phase diagram elaboration, is related to both the new techniques and methods of investigation and computer simulation, developed lately. Because the establishment of the temperature/concentration phase diagram is crucial in any study of lyotropic systems, several important binary and ternary solutions phase diagrams are presented in detail. Binary solutions polymorphism is developed in two parts, according to the surfactants polarity. Comparative evaluation between them is constantly made. Phase transition process is also discussed in the Landau-de Gennes phenomenological theory approximation.

Key words: liquid crystals, lyotropic, structure, phase transition, review.

1. INTRODUCTION

Concentration and temperature play a very important role in phase structuring and succession of different phases of lyotropic liquid crystals. Temperature coordinates both phase transitions and chain conformations (α for high values and β for low values).

Chemical composition of the amphiphilic and steric characteristics as well as concentration, are conditioning the aggregates shape and dimension and their apparition [1].

Lyotropic liquid crystals phase diagrams, in the concentration/temperature coordinates, are grouping all these proprieties. Any point in such a diagram, represents a stable phase and the curves delimitate regions of stability. Crystalline phases, which display a three-dimensional organization at the atomic level, will be included in phase diagrams too because of the large boundary they make with the liquid crystal region.

Theoretical phase diagrams for systems of particular micelle shape as hard ellipsoids, or hard-core spherocylinders, have been made by simulation programs [2, 3]. These simulations foresee new phases (columnar, for ex.) or new possible phase transitions [4].

As it is known, soaps and phospholipids are the most important amphiphilic molecules. They present typical phase diagrams as shown in Fig. 1.

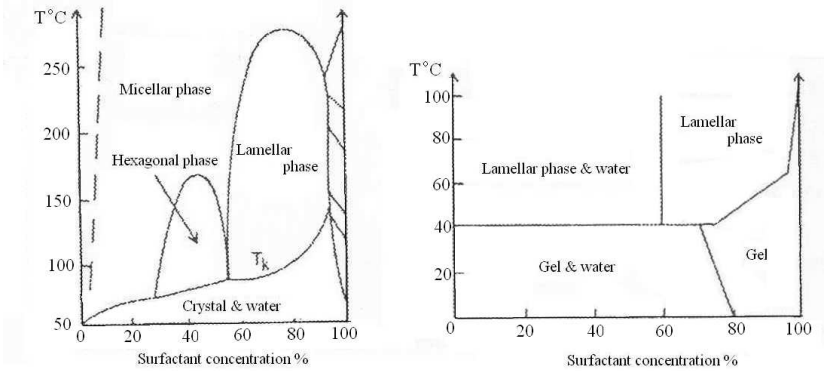

Fig. 1 - Typical phase diagrams: (a) soaps diagram, where interrupted line corresponds to the minimum concentration to form micelles and the Tk line corresponds to the Krafft boundary; (b) phospholipids diagram, where the critical concentration to form vesicles is not represented because it corresponds to very low values

All the studies made by now on usual surfactants, have revealed that the phases appearance process and their succession in diagrams, are qualitatively similar for all surfactants and are not related to the chemical structure of both the polar head and the hydrocarbon chain, thus demonstrating the validity of the packing parameter theory [1].

In Section 2, typical lyotropic binary solutions polymorphism is detailed. According to the surfactants polarity, ionic and nonionic surfactants solutions diagrams are discussed. Comparison between them is constantly made.

In Section 3, the most investigated lyotropic ternary solutions, potassium laurate (KL)/decanol/water and sodium dodecyl sulphate (SDS)/decanol/water, diagrams are presented. Apart common phases, all three nematic phases, show too and they are discussed in detail.

Phase transitions particularities are taken into account and included in both sections.

2. BINARY SOLUTIONS POLYMORPHISM

2.1. Ionic Surfactants Polymorphism

The behavior of the ionic surfactant solutions of two or more compounds has been, for a long period, under a continuous experimental observation.

Ionic surfactants solubility in water, at critical micellar concentration (CMC), is very low. It increases very slowly with the temperature since a certain value (PK) is reached, after which, the solubility has an evident improvement as Fig. 2 shows.

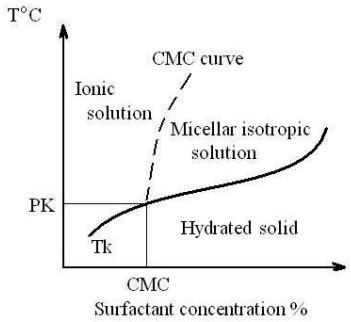

Fig. 2 - Ionic surfactants solubility dependence to temperature; the heavy line represents the Krafft boundary.

The surfactant solubility increase is generated by the monomers aggregation process that starts at CMC and improves by means of the hydrophobic effect until the apparition of the ordered structures. Ionic surfactants solubility is rather low because of the high stability of their crystals; so, an efficient way to increase solubility requires chemical changes of the amphiphilic molecules in order to modify their packing into the crystal.

The industrial applications require surfactants with a high solubility potential at low PK. Increasing the alkyl chain size or adding electrolytes in small quantities in the ionic solutions, may also considerably improve solubility.

Typical binary aqueous solutions of ionic surfactants having monovalent polar heads and short alkyl chains, usually form, at low concentration, small spherical micelles. If increasing the chain length, rod micelles may occur.

Phase succession supposes phase transitions: the usual phase succession, when increasing surfactant concentration consists in an H_1 domain, followed by an L_α domain and the location of several intermediate phases between them has to be considered too.

Phase transition phenomenon can be of the first order or of the second order, the same as the order of the first discontinuous derivatives of the Gibbs potential (or the chemical potential) in the transition point, depending on temperature or pressure.

A rather unusual phase diagram by its simplicity, have all perfluorinated surfactants mixtures with water. The most investigated compound was the anionic binary solution of cesium per-fluoro-octanoate (CsPFO). At a ratio CsPFO/water of 49/51wt% the system shows a lamellar phase up to 35.5˚C followed by a nematic phase, consisting of disc-like aggregates, which transform at 40.1˚C to an isotropic solution [5]. Nematic $\rightarrow$ lamellar phase transition is second order and can be induced by temperature variation, which do not happen very often with lyotropics. This transition is of disorder-order type, with unchanged amphiphilic aggregates. The nematic $\rightarrow$ isotropic transition is first order. Both nematic and lamellar phases are optically uniaxial and have specific textures.

Ordered mesophases of binary ionic monovalent solutions of sodium dodecyl sulphate (SDS)/water, were studied by neutron scattering techniques and a very complex phase diagram, shown in Fig. 3 [6] was found.

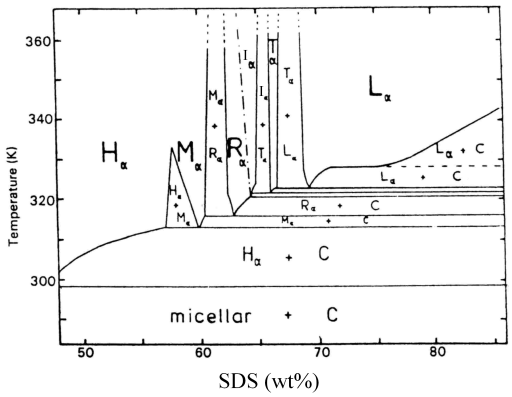

Fig. 3 - Phase diagram of SDS/water where: H_α is the hexagonal phase, M_α is the monoclinic phase, R_α is the rhombohedral phase; I_α is the cubic phase; T_α is the tetragonal phase; C refers to different polymorphic varieties

Four intermediate mesophases, monoclinic (M_α), rhombohedral (R_α), cubic (I_α) and tetragonal (T_α), are located between the hexagonal (H_α) and the lamellar (L_α) phases and have nearly vertically boundaries. Each separation zone was found to be biphasic in a very narrow domain.

Scattering patterns of the three-dimensional phases are quite different from those produced by the two-dimensional phases.

H_α phase appears at 25.7˚C and 40% SDS and consists in a two-dimensional packing of cylindrical rods in a hexagonal lattice.

At 58˚C (mixture with 57%-59% SDS) the H_α phase coexists with the two-dimensional monoclinic M_α phase which is a deformed hexagonal. In the M_α phase, aggregates become more like flat ribbons than deformed cylinders, packed in a staggered configuration analogous to that of the H_α phase. The thickness of the ribbons of about 28 Å is largely determinate by the packing constraints. For a two-dimensional phase like M_α phase, the third dimension would be infinite, but the scattering pattern indicates a modulation with a periodicity of 60 Å along the length of the ribbons [7]. The M_α phase is the phase that does not exist at temperatures higher than 100˚C (see Fig. 3).

Increasing SDS concentration between 59% and 69% the succession of the phases is: M_α (40.1˚C), M_α + R_α (biphasic), R_α (43˚C), I7.8˚C), I_α + T_α (biphasic), T_α (48.5˚C) and T_α + L_α (49.8˚C).

Because both three-dimensional phases, I_α and R_α, give the same scattering pattern, the rhombohedra R_α phase can be interpreted as a deformation of the cubic phase I_α [8].

The cubic phase I_α consist in rods that form pseudolamellar planes with a particular arrangement, convenient to the way in which a cubic three-dimensional structure can built a lamellar two-dimensional one [9].

The T_α phase consists in rods, which orthogonally meet at the vertices and form square lattices presenting a long-range order [10].

The L_α phase consists in parallel amphiphilic bilayers separated by water layers which thickness is about 12 Å for the most hydrated regions and about 7 Å for the least hydrated ones.

Using different ionic surfactants, it has been found that many other transformations from a hexagonal phase to a lamellar phase are possible [11, 12].

The cubic phase I_1 may not appear at all for some ionic monovalent surfactant, but it always does for ionic divalent ones. Surfactants with divalent polar groups, dodecyl-1, 3-propylene-bis (ammonium chloride) (DoPDAC) for example, have phase diagram in the limits of a normal behavior. DoPDAC presents two amino groups in the polar head, separated by a propylene group. The phase diagram of the water solution of this amphiphilic is shown in Fig. 4 [13].

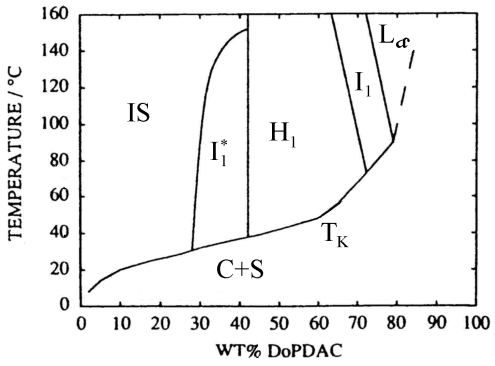

Fig. 4 - Phase diagram of DoPDAC/water solution with the following phase succession: Micellar isotropic solution, discontinuous cubic, hexagonal cubic, lamellar; C + S region indicates the presence of solid surfactant

The isotropic micellar solution (IS) consists in spherical micelles with the maximum radius of about 20 Å [14]. By means of fluorescence quenching measurements, it was found that the aggregation number is about 75, the same with theoretical predictions for C_{15} surfactants as DoPDAC.

A discontinuous cubic phase I_1^* appear at 30% surfactant, in the 30-150˚C-temperature range. The lattice parameter is 105 Å and the aggregation number is 90. I_1^* phase consists in two different types of cubic phases [15] and is considered to be of a discontinuous cubic type. After Fontell *et al* [16] each cubic cell contains 8 micelles that orient with respect one to each other in a T-shape (crossed way).

Taking into account that the presence of counter-ions screens the electrical charge of divalent polar groups, with an average charge of less than +1.75 per polar head, no cubic phase is usually formed. In this case, the hexagonal phase is formed directly from the micellar isotropic solution. But, this is not the case of the DoPDAC/water solution, because pH measurements confirms that the fraction of singly charged amphiphilic molecules generated by counter-ions, is very low and an average charge of at least +1.75 per molecule is expected. That prevents the micelles from growing and keeps them spherical.

Both the aggregation number and the existence of the cubic phase I_1^* demonstrate that micelles are small and have a rather spherical shape. This particular phase is formed at a rather low concentration as compared to monovalent surfactants.

The hexagonal phase H_1 appears at 42% surfactant in the 38-160˚C ranges and was investigated by microscopy and by X-ray measurements. They revealed the existence of rods with a radius of 17 Å and a two-dimensional hexagonal unit parameter of 44 Å.

Between 65-72% DoPDAC the H_1 phase coexists with the cubic phase I_1, which appears at 70˚C. Over 72% surfactant, I_1 phase coexists with the lamellar phase L_α. At 79% DoPDAC and 90˚C, only L_α was found. I_1 and L_α phases have not been X-rayed since the temperature is so high and were identified between crossed polarizes.

In the region between hexagonal and lamellar phases, other intermediate phases may exist together with the cubic one.

As it results from Fig. 4, the Krafft boundary between the hydrated solid phase (C+S) and the micellar phases has a large slope, while for the monovalent surfactants the Krafft boundary is rather flat or has only a small slope. An explanation may be that a divalent molecule will contribute with two counterions to the solution and the counterions entropy will decrease more rapidly for DoPDAC than for a monovalent surfactant, as the concentration is increased.

The shape of the aggregates involved in this multitude of mesophases, vary nearly continuously throughout the concentration range whereas the symmetry of their packing cannot evolve in such a continuous way During the transitional process, a specific class of defects appears each time; this could be interpreted in terms of comparable inter- and intra-aggregate forces.

For both monovalent and divalent surfactants, the electrostatic interactions [17] are often the dominating factor in determining the proprieties of the lyotropic systems, like CMC or the size and shape of the aggregates.

Many different monovalent surfactant/water systems have been investigated, but only a few data of divalent surfactants are available, in spite of their importance from technical point of view.

2.2. Nonionic Surfactants Polymorphism

Nonionic surfactants have amphiphilic molecules with nonionic hydrophilic group. Theoretically, their proprieties, especially the solubility, must be easier to investigate than for ionic surfactants, because of the lack of long-range electrostatic interactions.

Inter- and intra-micellar interactions, localized at the head group level, operate only at short range and allowed the tight packing required by amphiphilic aggregation in *reversed* micelles or in micelles with high interfacial curvature [18].

Nonionic surfactants solubility in water decreases when temperature increases till reaching a *critical point* (CP) also named "cloud" temperature. Over this point, the nonionic solution separates in two different phases: one phase is very reach in amphiphilic molecules, while the other one is highly aqueous. This phase separation is generated by the very strong micellar interactions and not by the high aggregation number, as expected. Such behavior is specific for all nonionic lyotropics and this region will be found in all phase diagrams, as the "miscibility gap" (MG).

Some particular nonionic surfactants of the poly (ethyleneoxide) alkylethers group, denoted by $C_n EO_x$ have been systematically investigated [19]. The "cloud" temperature value depends on concentration and on the length of the polyethylenoxide chain (EO).

Nonionic surfactants solutions can be investigated as liquid crystals up to the CP only; adding nonpolar molecules or short chain alcohols, in order to decrease the CP value, can make improvements of their solubility in water.

Up the CP temperature, when increasing concentration in nonionic surfactants solutions, amphiphilic molecules began to aggregate in micelles at the CMC (table 1 [1]) and then, usual phases observed in ionic solutions appear too.

But, at a sufficiently high temperature, phases have a different succession, depending on concentration: at low concentration, micelles usually form and brake-out then, at a specific concentration value, while the lyotropic system reaches the MG region; on increasing concentration, the micellar aggregation process begins once more, to form the isotropic micellar solution (IS) and different other phases.

The $C_{12}EO_6$/water solution has the most usual behavior and shows a common phase succession: hexagonal H_1, cubic V_1, lamellar L_α and a relatively large MG region, as in Fig. 5 (a) [20].

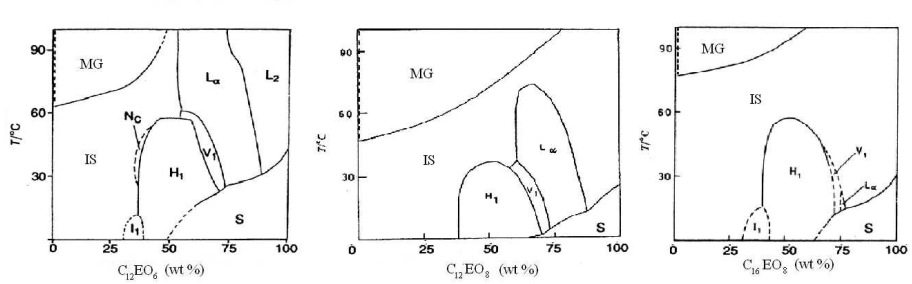

Fig. 5 - Nonionic surfactants diagrams where: MG is the miscibility gap; IS is the isotropic solution; S indicates the presence of solid surfactant; H_1 is the normal hexagonal phase;

V_1 is the normal bicontinous cubic phase; I_1 is the spherical micelle cubic phase; L_α is the normal lamellar phase; L_2 is the reversed lamellar phase N_c is the rod nematic phase

The maximum temperatures of the H_1 and V_1 phases are 37˚C and 38˚C, respectively; only the L_α phase exists up to 73˚C. The MG region arises above about 49˚C and is caused by EO-EO strong interactions between adjacent micelles [21]. On increasing the EO size, some particularities show up in the phase succession. $C_{12}EO_8$ for example, shows a supplementary cubic phase I_1 between 30-43wt% surfactant, as in Fig. 5(b) [20], but both I_1 and L_α phases occupy regions reduced to a smaller temperature and concentration range, which totally disappear when the EO size increases more. Thus, for $C_{12}EO_{10}$ nonionic surfactant, I_1 and H_1 phases subsist only. With a further increase in EO size, the phase diagram of the $C_{12}EO_{12}$ surfactant, look the same, but the I_1 phase concentration range increases too between 35-53wt%.

The phase diagram in Fig. 5(c) [22] refers to the $C_{16}EO_8$ nonionic surfactant, that has the same EO size as $C_{12}EO_8$, but an increased carbonic size.

It is interesting to remark, when comparing diagram (b) and (c), a supplementary nematic calamitic phase N_c in a very narrow concentration range (about 34 wt%) and a temperature range between 28-54˚C. It consists of short rod-like micelles and has a very low viscosity.

Note that, the first nematic phase observed in a binary nonionic solution, was reported as a discotic one (N_d). It was formed by the surfactant $H_2C{=}CHCH_2OBiphenyl\text{-}EO_7$ /water solution and has been found between the IS region and L_α phase, in a narrow concentration range of 34-38% surfactant and between 7.5-23.4˚C as it is shown in Fig. 6 [23].

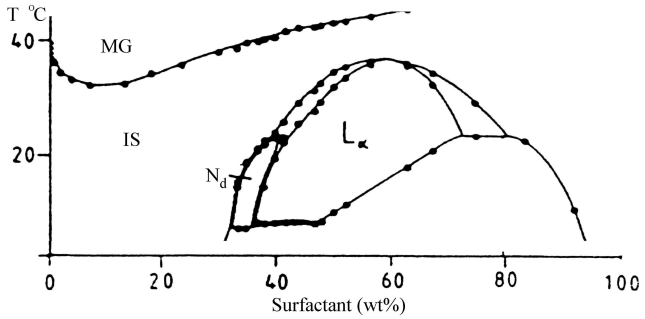

Fig. 6 - Partial phase diagram of $H_2C{=}CHCH_2OBiphenyl\text{-}EO_7$ /water solution showing the nematic phase N_d location between isotropic micellar solution IS and lamellar phase L_α; the miscibility gap MG is very large.

The L_α phase exists up to both 72% and 80% surfactant, in biphasic regions with water. The CP temperature of 33.2°C is rather low and the MG region is extended over a large concentration range, up to 90% surfactant.

3. TERNARY SOLUTIONS

When adding an adequate third component to the binary lyotropic solutions, the phase diagrams are essentially modified. The third components usually are electrolytes, oils or cosurfactants.

Electrolytes can either be adsorbed to surfactants increasing their solubility, or desorbed from the aggregates, raising the chemical potential that decreases solubility. For nonionic surfactants, these two effects are known as "salting in" and "salting out", respectively and are observed at high electrolyte level in the solutions [24]. For ionic surfactants, there are two additional effects, depending on the quality and quantity of the electrolyte; the first effect is the raising of the Krafft temperature in the presence of an electrolyte counter-ion, that produces an insoluble surfactant salt; the second effect consists of reducing the relatively high CMC values of the ionic surfactants, meaning an improvement of the solubility level. Very often, the electrolyte presence induces in ionic solutions, a region of coexistence between a dilute aqueous phase and a micellar one, similar to the MG region that appears in nonionic solutions. The influence of the electrolytes may be explained by dispersion interactions for nonionic solutions and by electrostatic repulsions for ionic solutions.

Oils are solubilized either inside the micelles, increasing their radius and giving rise to cubic (I_1) and hexagonal (H_1) phases, or at the micelles surface, reducing micelle curvature and giving rise to the lamellar (L_1) phase. All phases may appear in both *normal* and *reversed* structures.

Cosurfactants as alcohols, fatty acids and long chain aldehydes**,** are substances that are insufficiently hydrophilic to form micelles in aqueous solutions. An insoluble substance in a certain solvent can be "solubilized" when adding an amphiphilic component to the solution that becomes an isotropic ternary solution, thermodynamically stable.

This process can happen only in the presence of *normal* micelles in aqueous solutions and of *reversed* micelles in nonpolar solutions. Only micellar solutions remain fluid and isotropic in the presence of the solubilized substances. The liquid crystal phases are anisotropic and conserve a relatively high viscosity.

Hence, the presence of the association micelles is determinant for the solubilization process; if the insoluble substance is amphiphilic too, then mixed micelles form and a lyotropic ternary solution results.

If association micelles are of a nonionic surfactant aqueous solution, then there is a supplementary possibility to solubilized cosurfactants in the EO zone of the amphiphilic molecules.

The NMR technique has been extensively used to investigate the existence of different phases in lyotropic solutions. Spectroscopic studies of spectral lines shape provide information about the symmetry of the mesophase, the sign of the magnetic susceptibility anisotropy and the orientation ordering of the micelles.

Yu and Saupe [25], investigated by NMR techniques, the ternary system potassium laurate/decanol/deuterated water, (KL/DeOH/D_2O), and found that beside the N_d (nematic discotic) phase, there are two other nematic phases. One of them is uniaxial negative and has positive magnetic susceptibility anisotropy and was supposed to correspond to a cylindrical micelles phase, so it was denoted by N_c, (nematic calamitic). The other one appeared in a narrow zone situated between the two other phases and is biaxial, so it was denoted by N_{bx}. They have the same ordering as the nematic phases founded in binary solutions and have been found at 6.24 wt% DeOH, between 25.6-26.4-wt% KL and 67.4-68.2 wt% D_2O in the 15-40˚C temperature range.

The existence of all three nematic phases has been reported in potassium laurate/decylammonuim hydrochloride/water (KL/DaCl/D_2O) ternary solution too and was found using advanced investigation techniques. Lyotropic mesomorphism as a function of temperature was obtained by NMR [26] and optical [27] techniques. Small angle neutron scattering (SANS) experiments were performed with the same solution on fully deuterated compounds and revealed the micellar shape anisotropy evolution with temperature [28]. The transition temperature between the three-nematic phases was found to be dependent of the relative molar ratio R = [DaCl]/[KL]. SANS investigation revealed the possibility to have reentrant biaxial and reentrant disc nematic phase, as it follows: $N_d \rightarrow N_{bx} \rightarrow N_c \rightarrow N_{bx} \rightarrow N_d$. Authors used the phase diagram in Fig. 7 and studied the KL/DaCl/D_2O ternary solution at the relative molar ratio of the two amphiphilic R = 0.145, R = 0.142 and R = 0.150.

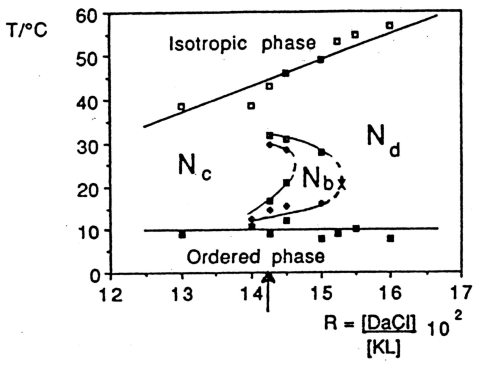

Fig. 7 - KL/DaCl/water solution diagram focused on the nematic region; the arrow shows the location of the investigated samples.

Another intensively investigated ternary solution is sodium dodecyl sulphate (SDS)/decanol/water that presents interesting phases illustrated by the partial phase diagram in Fig. 8, [29]. Author used water mixture with 10-wt% D_2O.

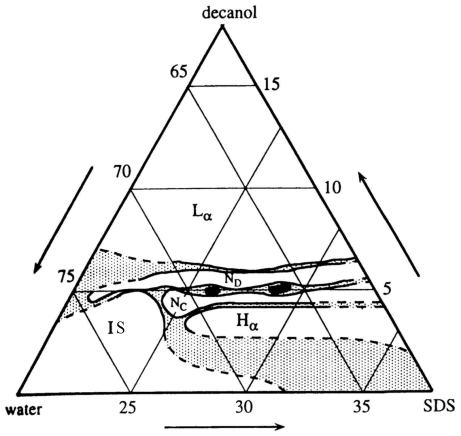

Fig. 8 - SDS/DeOH/water solution partial phase diagram (in wt%, at 25 ˚C) shows: isotropic solution IS, lamellar phase L_α, hexagonal phase H_α, nematic calamitic N_c, nematic discotic N_d, nematic biaxial N_{bx} in the black regions and polyphasic in the shaded regions.

Investigations performed by NMR techniques [30] furnish information about micelle size in the nematic and isotropic regions. The results for the micellar axial ratio are in agreement with a recent small-angle X-ray scattering study [31] of the isotropic region in the same ternary solution at 22˚C and similar water content. The micelle shape was reported to be spherocylindrical rather than disc-like. Progression from a more curved spherocylindrical to a less curved disc-like micellar shape was also detected in the isotropic solution, with increasing decanol content. This micellar shape evolution is very similar to the progression from calamitic to discotic nematic phase revealed by NMR techniques and agreed with theoretical predictions [32]. Experimental NMR measurements confirm a major change in micelle size at the $N_d \rightarrow$ IS transition, in contrast to the insignificant change found at the same transition in KL/DaCl/water ternary system [28].

The X-ray dimensional evaluation of the calamitic micelles of SDS/DeOH/water solution, respective KL/DeOH/water solution, shows for both the same pattern as in the hexagonal phase; aggregates diameter is about 26 Å and 36 Å, respectively, the length is about 60 Å and 66 Å, respectively, and the aggregation number is about 90 and 190, respectively [33].

All nematic phases are characterized by an order parameter *S*, which is a second rank, symmetric, traceless tensor with two eigenvalues in the uniaxial phases and three in the biaxial one. NMR investigations [30] have found that the temperature dependence of

the order parameter is very much stronger than that predicted by the classical mean-field theory [34].

Transition between uniaxial phases, as well as between uniaxial and biaxial phase in SDS ternary solution is first order [29]. Temperature (determined by optical microscopy or calorimetric methods) [35] and density (determined by dilatometer methods) [36], are parameters frequently used to test phase transition theories.

Phase transition between uniaxial phases is first order, but uniaxial to biaxial phase transition in KL ternary solution, is considered to be second order [37].

Landau, made the supposition that near a second order transition, the free energy density *f*, can be expanded in function of the order parameter and its spatial derivatives, the coefficients being temperature dependent [38].

De Gennes, applied the theory to nematic liquid crystals which is known to present weak first order nematic $\longrightarrow$ isotropic transition [39].

Sufficiently near the transition temperature, only the first terms in the free energy density are important, so that:

$$f(T,V) = f_0(T,V) + \frac{1}{2}A(T)S^2 - \frac{1}{3}BS^2 + \frac{1}{4}CS^4 \qquad (1)$$

A(T), B>0, C>0, are phenomenological coefficients. T and V are the system temperature and volume, respectively.

The theory supposes $A(T) = a(T-T_c)$ where T_c is the transition temperature.

Minimizing equation (8) leads to two stable states, the isotropic one, for $T>T_c^*$ and the nematic one, for $T<T_c^*$ where $T_c^* = T_c - B^2/27aC$.

In a new attempt to apply this phenomenological theory to lyotropic nematic phase transitions [40], beside the critical temperature T_c^*, a critical concentration x_c is introduced in the phenomenological coefficient A, in order to describe the appearance of the ordered phase as function of concentration x, too. This concentration dependence is given by:

$$A(T, x) = a(T - T_c^*) + b(x_c^* - x) \qquad (2)$$

The theory succeeds to give a good description of temperature and concentration dependence of the order parameter for the cesium per-fluoro-octanoate (CsPFO) lyotropic solution.

X-ray scattering using oriented samples in a magnetic field too extensively studded Nematic phases. It has been found that aggregates have different dimensions along the three axes, confirming that micelles are ellipsoids, but the micelles shape still remains insufficiently clear.

Because of the great complexity of lyotropics domain, it still remains many unsolved questions. No doubt; improvement of both experimental investigation and computer simulation techniques will get the answer.

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