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Liquid Crystals

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Online publication date: 06 August 2010

To cite this Article Galyametdinov, Yury G. , Jervis, Helen B. , Bruce, Duncan W. and Binnemans, Koen(2001) 'Lyotropic mesomorphism of rare-earth trisalkylsulphates in the water-ethylene glycol system', Liquid Crystals, 28: 12, 1877 — 1879
To link to this Article: DOI: 10.1080/02678290110093219
URL: http://dx.doi.org/10.1080/02678290110093219

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LIQUID CRYSTALS, 2001, VOL. 28, NO. 12, 1877–1879

Preliminary communication

Lyotropic mesomorphism of rare-earth trisalkylsulphates in the water–ethylene glycol system

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(*Received 20 April 2001; in final form 29 July 2001; accepted 2 August 2001*)

Lyotropic mesophases were observed for rare-earth trisdodecylsulphates, $Ln(C_{12}H_{25}SO_4)_3$ ($Ln = Y$, La, Ce–Lu, except Pm) in the presence of ethylene glycol or water (or mixtures thereof) as the solvent. In ethylene glycol, a normal hexagonal phase and a cubic phase could be detected, whereas in water a normal hexagonal phase and a lamellar phase were found. Thus by changing the solvent, it is possible to obtain different supramolecular organizations within a series of lanthanide-containing metallomesogens.

Due to the presence of paramagnetic rare-earth ions, rare-earth-containing magnetic liquid crystals can have a high magnetic moment and a large magnetic anisotropy. Large values of the magnetic anisotropy are desirable for the design of liquid crystals which are switchable by a weak external magnetic field. Magnetic alignment was observed for rare-earth-containing liquid crystals containing Schiff's base ligands [1]. Although these thermotropic liquid crystals have moderate transition temperatures, the relatively high viscosity of the mesophase is a severe disadvantage which prevents short switching times. Because of the need for a low viscosity mesophase at temperatures close to room temperature, we are looking for lyotropic mesophases incorporating rare-earth ions. In lyotropic systems the formation of a mesophase depends on two parameters: the solvent and the temperature (in contrast to thermotropic systems in which the temperature is the only parameter which can be varied). Magnetic alignment of lyotropic liquid crystals was demonstrated by Ramos *et al.* [2]. To date, there exists only limited evidence for lyotropic mesomorphism in rare-earth compounds. Gin and coworkers used an inverted hexagonal mesophase formed by metal complexes of 3,4,5-substituted benzoic acid as a template for the creation of nanostructured materials [3]. Yada and coworkers made mesostructured rare-earth oxides templated by lamellar and hexagonal mesophases formed by yttrium trisdodecylsulphate [4]. Their mesophase was shown to exist as a mixture of rare-earth oxide, hydroxide, carbonate and dodecylsulphate species. Closely related to lyotropic systems are rare-earth-containing bilayered micelles [5]. In this paper we report on the lyotropic mesomorphism of rare-earth trisdodecylsulphates in ethylene glycol, water or mixtures thereof.

The rare-earth trisdodecylsulphates, $Ln(C_{12}H_{25}SO_4)_3$ [abbreviated to $Ln(DOS)_3$], are starting materials for the synthesis of thermotropic liquid crystals of the type $[Ln(LH)_3(DOS)_3]$, where Ln is a trivalent rare-earth ion and LH is a salicylaldimine Schiff's base [6]. The rare-earth trisdodecylsulphates can be synthesized by a metathesis reaction between sodium dodecylsulphate and a rare-earth salt (hydrated chloride or nitrate). We prepared

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Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2001 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290110093219

$Ln(DOS)_3$ compounds for all the rare-earth elements, except scandium and promethium. The $Ln(DOS)_3$ compounds do not shown a thermotropic mesophase, but melt with decomposition between 150 and 175°C (depending on the rare-earth ion). The $Ln(DOS)_3$ compounds can be considered as anionic surfactants, with the trivalent rare-earth ions as counter ions. Earlier work by some of us on lyotropic ruthenium complexes [7], inspired us to check the presence of lyotropic mesophases in the $Ln(DOS)_3$–ethylene glycol system. Initially ethylene glycol was chosen, because it is a better solvent for $Ln(DOS)_3$ than water. Although ethylene glycol is totally miscible with water, it is known that lyotropic mesomorphism in ethylene glycol sometimes differs from that in water. For example, cubic mesophases are stabilized in ethylene glycol [8].

The lyotropic mesomorphism of the rare-earth trisdodecylsulphates was investigated via polarizing optical microscopy, by performing *Lawrence Penetration Experiments* [9]. In a typical experiment, a sample of solid $Ln(DOS)_3$ was placed on a microscope slide and a cover slip placed on top. A drop of ethylene glycol was put at the end of the cover slip and proceeded from one end to the other by capillary action, creating a concentration gradient across the sample. At any given temperature it was possible to view a snapshot of the phase diagram. The temperature range of investigation was from 26 to 70°C. For $Dy(DOS)_3$, we observed a fanlike texture, which is typical for the normal hexagonal phase (H_1) [8]. The hexagonal phase consists of micellar cylinders of indefinite length, packed into a hexagonal arrangement. Between the hexagonal phase and the crystalline phase, an optically extinct region was detected. This points to the presence of a cubic phase (although we were unable yet to determine its exact nature). Indeed, the only other regions in the phase diagram that can give rise to isotropic optical textures, are at low surfactant concentrations, where monomeric surfactant molecules or micelles exist. We observe an optically isotropic region at surfactant concentration, higher than required for the formation of the normal hexagonal phase. The cubic phase is most likely a type I bicontinuous structure, possible of spacegroup *Ia*3*d*. However further work is necessary to establish this. Figure 1 shows an optical texture formed by $Dy(DOS)_3$ in contact with ethylene glycol. Similar lyotropic mesomorphism in ethylene glycol was observed for all the rare-earth trisdodecylsulphates synthesized, although it was sometimes difficult to obtain good optical textures.

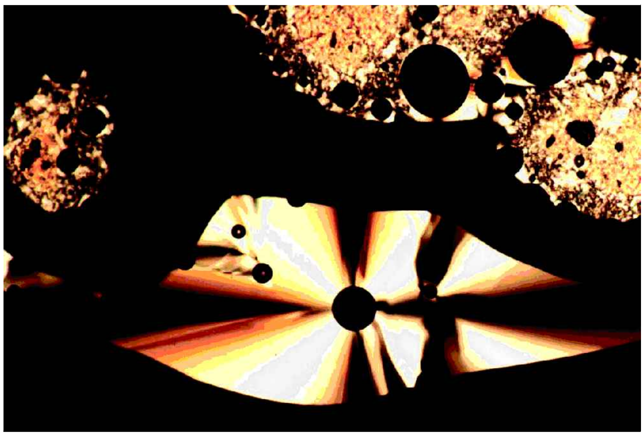

Figure 1. Optical texture of lyotropic mesophases in the system $Dy(DOS)_3$–ethylene glycol at 40°C. Solid $Dy(DOS)_3$ is present in the upper right corner and in the middle of the left side.

Although the $Ln(DOS)_3$ compounds have quite low solubilities in water at room temperature, we also tested the existence of lyotropic mesophases in the $Ln(DOS)_3$–water system. The first experiments were unsuccessful, but after heating $Ln(DOS)_3$ in contact with water to 85°C, lyotropic mesophases were observed, which remained present even after cooling the mixtures to room temperature. The reason why the mesophases could only be observed after heating the system to 85°C, is because the dissolution rate of the $Ln(DOS)_3$ compounds is low. The suggestion that the limiting factor for observing a lyotropic mesophase in water at room temperature is a kinetic one, is supported by the fact that when the time of contact between $Ln(DOS)_3$ and water is sufficiently long at a temperature just above room temperature (waiting times of more than 12 h were used), lyotropic mesophases could be observed without a preceding heating step. In contrast to the behaviour in ethylene glycol, there is to date no evidence for the existence of a cubic mesophase in water. Besides the normal hexagonal phase (H_1), a lamellar phase (L_α) was detected also at high surfactant concentrations. The lamellar phase gives a texture with mosaic oily streaks [8]. As expected, lyotropic mesomorphism was detected also in water–ethylene glycol mixtures. For a 50–50 (v/v) mixture, the lyotropic mesophase behaviour was similar to that observed in pure ethylene glycol. Other solvents (hydrophilic or hydrophobic) which were tested, but for which no lyotropic mesomorphism was observed, include: isopropanol, pentanol, decanol, decane, pentadecane, acetone, acetonitrile, benzene, DMF and DMSO.

In conclusion, lyotropic mesomorphism was observed for the rare-earth trisdodecylsulphates, $Ln(C_{12}H_{25}SO_4)_3$ in the presence of ethylene glycol or water (or mixtures thereof) as the solvent. In ethylene glycol, a normal hexagonal phase and a cubic phase could be detected, whereas in water a normal hexagonal phase and a lamellar phase were found. Thus, by changing the solvent it is possible to obtain a different supramolecular organization for a series of rare-earth compounds. This is the first description of lyotropic mesomorphism for a whole series of rare-earth compounds containing the same counter-ion. Further work is now in progress to characterize the mesophases, to determine the temperature dependence of the lyotropic mesomorphism and to investigate their physical properties (magnetic and optical). Differences can be expected, depending on the rare-earth ion. We are also considering alkylsulphates other than dodecylsulphate.

K. B. is a Postdoctoral Fellow of the Fund for Scientific Research Flanders (Belgium) and he thanks Prof. C. Görller-Walrand for laboratory facilities. Yu. G. G. and K. B. are indebted to the NATO for financial support (Collaborative Linkage Grant PST.CLG.974907). Financial support by the K. U. Leuven (GOA 98/03) and by the F. W. O.-Flanders (G.0243.99) is gratefully acknowledged.

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