

in nearly linear lattice dynamics.

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## Observation of a Biaxial Nematic Phase in Potassium Laurate-1-Decanol-Water Mixtures

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The phase diagram of the ternary system potassium laurate-1-decanol-D<sub>2</sub>O was studied over concentration ranges where nematic phases are likely to occur. Two uniaxial nematic phases which are separated by a biaxial nematic phase are found. In limited concentration range the following phase sequence may be observed reversibly on heating and on cooling: isotropic-uniaxial nematic (positive optical anisotropy)-biaxial nematic-uniaxial nematic (negative optical anisotropy)-biaxial nematic-uniaxial nematic (positive optical anisotropy)-isotropic.

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The existence of a uniaxial nematic phase with negative diamagnetic anisotropy in aqueous solutions of potassium laurate (KL) containing some 1-decanol and potassium chloride was first reported by Long and Goldstein.<sup>1,2</sup> The properties indicate that the phase has micelles of a bilayer structure. We denote this phase as  $N_L$  (see Refs. 3 and 4 for a discussion of structures and relations to Type-I and Type-II phases<sup>5</sup>). In studying the phase diagram of the ternary system KL-1-decanol-D<sub>2</sub>O, we found that besides  $N_L$  two additional nematic phases occur. One of the additional phases is also uniaxial but of negative optical and positive diamagnetic anisotropy. It corresponds probably to a phase with cylindrical micelles and we denote it as  $N_C$ .<sup>4</sup> The third nematic phase occurs in concentration and temperature ranges that separate  $N_L$  and  $N_C$ . It is a biaxial nematic phase that we will denote as  $N_{bx}$ . To our knowledge this is the first time that the existence of a biaxial nematic phase has been clearly established.

The phases were classified by microscopic studies and by deuteron resonances as described in the following sections. Figure 1 shows part of

the phase diagram of the KL-1-decanol-D<sub>2</sub>O system. The 1-decanol concentration is constant at 6.24 wt. % while the weight concentration ratio of D<sub>2</sub>O to KL varies from 2.67 to 2.56. For D<sub>2</sub>O concentrations higher than 68 wt. % only one nematic phase  $N_L$  is formed. Upon cooling it transforms to a viscous isotropic phase and upon heating to an isotropic phase of a relatively low viscosity. The biaxial nematic phase  $N_{bx}$  is formed at 68 wt. % D<sub>2</sub>O concentration. It transforms on cooling and on heating to  $N_L$  ( $N_L \leftrightarrow N_{bx} \leftrightarrow N_L$ ). The  $N_C$  phase forms when the D<sub>2</sub>O concentration is lowered to 67.8 wt. %. All three nematic phases occur near this concentration and the sequence by which they transform into each other is  $N_L \leftrightarrow N_{bx} \leftrightarrow N_C \leftrightarrow N_{bx} \leftrightarrow N_L$ . The range of  $N_C$  widens with decreasing water concentration whereas those of  $N_L$  and  $N_{bx}$  are narrowed. The  $N_C$  phase of the mixture with 67.4 wt. % D<sub>2</sub>O transforms on heating directly to the isotropic micellar solution. Upon further heating a formation of batonnets takes place which may belong to a lamellar smectic phase.

Microscopic observations were made on the films sealed in flat capillaries. In general some

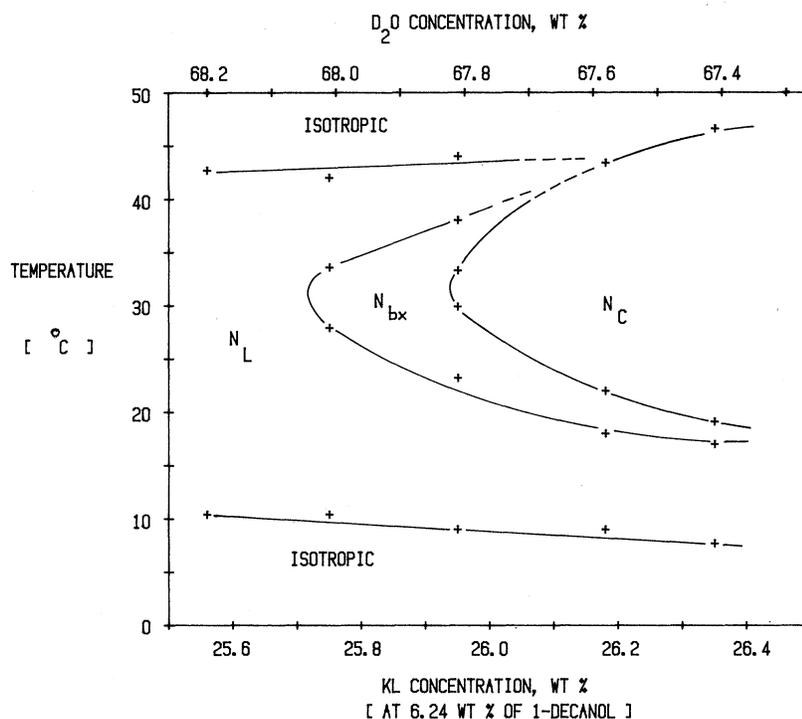


FIG. 1. Phase diagram of the potassium laurate (KL)-1-decanol- $D_2O$  system.

loss of materials occurred during sealing. The transition temperatures observed with these samples deviated, therefore, somewhat from the transition temperature observed on the original mixtures (NMR samples). Another disturbing factor is that the glass of the capillaries showed in general some strain birefringence.

The surface alignment of  $N_L$  is perpendicular to the glass surface so that the relaxed film shows a pseudoisotropic texture. Conoscopic observations show that the system is uniaxially positive. At the  $N_L$ - $N_{bx}$  transition the uniaxial cross splits into two arcs which move rapidly out of the field of vision. The micrographs (Fig. 2) demonstrate the change of the splitting with temperature. There is still some splitting observable in  $N_L$  [Fig. 2(a)]. It is caused by the strain birefringence of the glass. The temperature dependence of the splitting is similar for both  $N_L$ - $N_{bx}$  transitions at the lower and the upper limits. The surface alignment of  $N_C$  is parallel and its uniaxial properties cannot be directly demonstrated.

The pseudoisotropic texture of  $N_L$  turns to a nematic schlieren texture at the  $N_L$ - $N_{bx}$  transition. The texture may contain half-integer-numbered singularities but integer-numbered singularities which are common in many uniaxial ne-

matics were not observed by us. A uniform alignment could be achieved with use of a magnetic field. The occurrence of a schlieren texture and the response to the magnetic field clearly demonstrate the presence of curvature elastic properties and the absence of a translational periodicity. It is, therefore, justified to classify this biaxial phase as nematic.

The  $D_2O$  signal of an amphiphilic nematic phase splits into a doublet due to the orientation of the water associated with the surfactant aggregates. There is a rapid exchange between the associ-

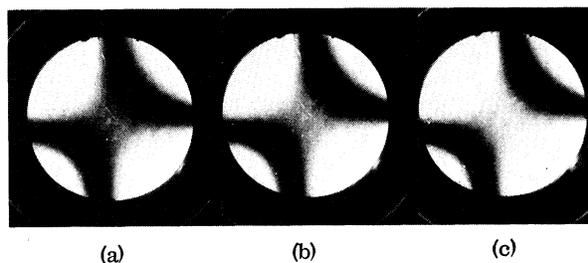


FIG. 2. Conoscopic observation of  $N_L$ - $N_{bx}$  transition. (a) 11.25°C, (b) 11.38°C, (c) 11.40°C. Approximate sample composition of (KL, 1-decanol,  $D_2O$ ) is (28.09, 6.02, 65.89) wt.%.

ated and free water so that only one doublet with relatively sharp lines is observed.

Figure 3 gives the temperature dependence of the  $D_2O$  splitting in the nematic phases for samples of different compositions. The sample with the highest water concentration 68.19 wt. % has only an  $N_L$  phase. The splitting follows a smooth convex curve. Its temperature dependence is strongest near the ends where the transitions to isotropic phases occur. The curves for all other samples show discontinuities in the temperature derivations at the  $N_L-N_{bx}$  transitions. The  $N_{bx}-N_C$  transitions cannot be determined from these curves but it can be clearly identified by observing the change of the splitting under rotation of the sample.

In general the spin Hamiltonian that determines the NMR spectrum is a function of the molecular properties and a generalized order matrix<sup>6,7</sup> defined by

$$S_{\nu\mu}^{ik} = \frac{1}{2} \langle 3\beta_{i\nu}\beta_{k\mu} - \delta_{ik}\delta_{\nu\mu} \rangle. \quad (1)$$

The angular brackets indicate the average over the molecular motions and  $\beta_{i\nu} = \cos\theta_{i\nu}$ , where  $\theta_{i\nu}$  denotes the angle between the  $x_i$  axis of the lab system and the  $x_\nu'$  axis of the molecular system. It can be shown readily that, with the  $x_1$  axis parallel to the magnetic field, the spin Hamiltonian can be written in the same format

for uniaxial and biaxial systems. For a generalization it is only necessary to replace  $S_{\nu\mu}$  by  $S_{\nu\mu}^{ii}$  in the commonly used equations for uniaxial nematics.<sup>8-10</sup>

We are interested in the quadrupole splitting of  $D_2O$ . The electric field gradient at the deuteron has practically cylindrical symmetry around the bond axis. The splitting is accordingly proportional to the degree of order of the bond axis<sup>8-10</sup> and choosing the  $x_1'$  axis parallel to O-D we can write for the splitting  $\nu = \frac{3}{2}DS_{11}$ , where  $D$  is the quadrupole coupling constant.<sup>9</sup>

It is useful to express  $S_{11}$  in terms of an order matrix that refers to a local system for which the axes coincide with the symmetry axes of the liquid crystal. We are interested in a system with  $D_{2h}$  symmetry. In the local system all axes correspond to twofold symmetry axes and therefore  $S_{\nu\mu}^{ik} = 0$  for  $i \neq k$ . With  $\alpha_i$  denoting the direction cosines between the  $x_i$  axis of the local system and the magnetic field, we have

$$S_{11} = \sum_{i=1}^3 \alpha_i^2 S_{11}^{ii}. \quad (2)$$

A sample of biaxial nematic phase with principal diamagnetic susceptibilities  $\chi_1 > \chi_2 > \chi_3$  aligns in a magnetic field so that  $x_1$  is parallel to the field and  $\nu = \frac{3}{2}DS_{11}$ <sup>11</sup>. Rotating the sample repeatedly around an axis perpendicular to the field

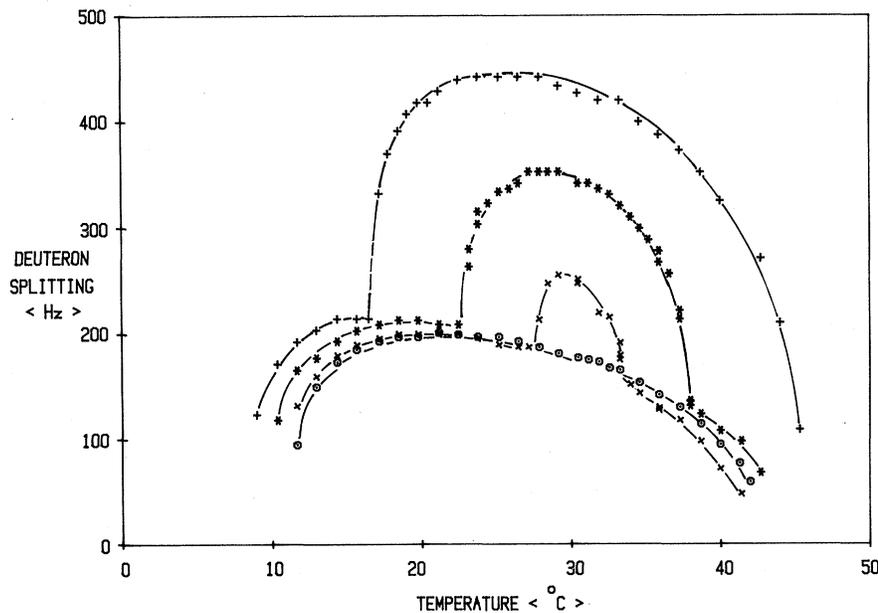


FIG. 3. Temperature dependence of the deuteron resonance splittings of  $D_2O$ . Sample compositions in wt. % (KL, 1-decanol,  $D_2O$ ): pluses, (26.35, 6.24, 67.41); asterisks, (25.95, 6.25, 67.80); crosses, (25.75, 6.24, 68.01); circles, (25.56, 6.25, 68.19).

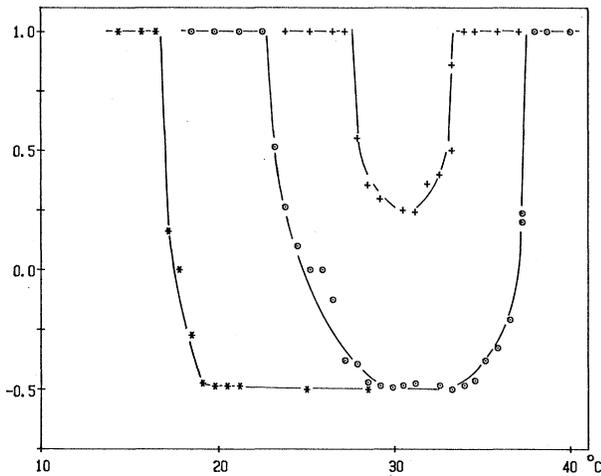


FIG. 4. Ratio of  $D_2O$  splittings of  $90^\circ$  rotated and relaxed samples [see Eq. (4)]. Compositions as in Fig. 3.

results in a complete alignment with the  $x_3$  axis parallel to rotation axis. When the relaxed sample is rotated anew by an angle  $\theta$  the splitting changes to

$$\nu(\theta) = \frac{3}{2}D(\cos^2\theta S_{11}^{11} + \sin^2\theta S_{11}^{22}). \quad (3)$$

The ratio of the splittings at  $\theta = 90^\circ$  and  $\theta = 0^\circ$  is equal to the ratio between two principal  $S$  values:

$$\nu(90^\circ)/\nu(0^\circ) = S_{11}^{22}/S_{11}^{11}. \quad (4)$$

For a uniaxial nematic phase of a positive diamagnetic anisotropy, like  $N_C$ , we have  $\chi_2 = \chi_3$  and  $S_{11}^{22} = S_{11}^{33} = -\frac{1}{2}S_{11}^{11}$ . The splitting under a  $90^\circ$  rotation changes accordingly to  $-\frac{1}{2}\nu(0^\circ)$ . (We set the sign of the  $90^\circ$  splitting negative when the splitting passes through zero during the rotation.) For a negative uniaxial phase we have  $\chi_1 = \chi_2$  and  $S_{11}^{11} = S_{11}^{22} = -\frac{1}{2}S_{11}^{33}$ . In that case the splitting does not change under rotation. For a biaxial phase it is accordingly  $1 > \nu(90^\circ)/\nu(0^\circ) > -\frac{1}{2}$ .

The relaxation times for reorientation in magnetic fields are relatively long for the nematic KL-1-decanol- $D_2O$  mixtures. The splitting under  $90^\circ$  rotation can, therefore, be relatively well determined. The results of the measurements are presented in Fig. 4. The phase bound-

aries between the nematic phases show up clearly in particular also the boundaries between  $N_C$  and  $N_{bx}$  which are not recognizable in Fig. 3.

Theoretical investigations<sup>10-15</sup> have predicted that a biaxial nematic phase is likely to form as an intermediate phase between two uniaxial nematic phases. This and other predictions obtained by Alben<sup>14</sup> are in good agreement with our observations as will be shown in a forthcoming publication. In view of the present findings we studied again the transition between the uniaxial nematics of sodiumdecylsulfate system<sup>4,5</sup> and found that an intermediate biaxial phase is also formed for a certain concentration range while the observations in other ranges indicate a direct first order  $N_C$ - $N_L$  transition.

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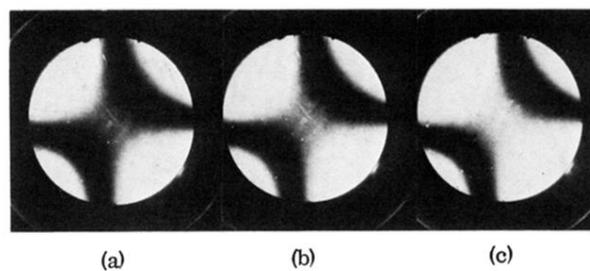


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