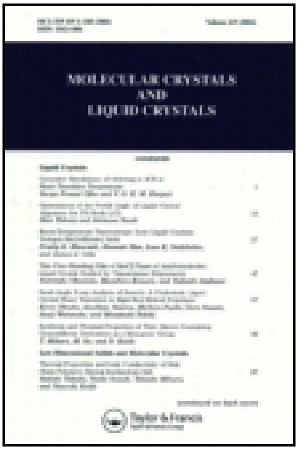


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

A Nonaqueous Lyotropic Nematic Gel

J. Campbell [a] , M. Kuzma [a] & M. M. Labes [a]

[a] Department of Chemistry, Temple University, Philadelphia, PA, 19122

Version of record first published: 20 Apr 2011.

To cite this article: J. Campbell , M. Kuzma & M. M. Labes (1983): A Nonaqueous Lyotropic Nematic Gel, Molecular Crystals and Liquid Crystals, 95:1-2, 45-50

To link to this article: http://dx.doi.org/10.1080/00268948308072406

Mol. Cryst. Liq. Cryst., 1983, Vol. 95, pp. 45–50
0026-8941/83/9502-0045/$18.50/0

Printed in the United States of America

A Nonaqueous Lyotropic Nematic Gel

J. CAMPBELL, M. KUZMA and M. M. LABES

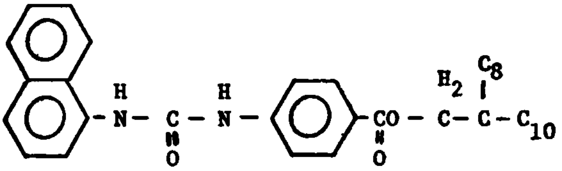
Department of Chemistry, Temple University, Philadelphia, PA 19122

(Received January 1, 1983; in final form February 25, 1983)

A nematic gel of a fatty substituted urea (3–4 Wt.%) in decane is studied optically and thermodynamically. Typical nematic schlieren textures are observed. Shear and compression forces distort these textures, but applied electric and magnetic fields are ineffective until one reaches the gel-isotropic transition temperature.

INTRODUCTION

Nematic lyotropic phases are frequently encountered in aqueous systems, but are extremely rare in other solvents. There have been, however, several recent observations of non-aqueous lamellar lyotropic phases.[1] Excluding polymeric systems,[2] the only nematic gel of which we are aware was reported by Hoppe, who observed anisotropic optical properties of gels of sunscreening substances in hydrocarbon solvents.[3,4] Although most of the preparations were lamellar phases, a "micellstructur" was reported for a solution of 2% of compound *I* (below) in heptane. In this paper, optical microscopy and differential scanning calorimetry (DSC) are applied to a study of *I* in decane.



I

4-[[(1-naphthalenylamino)carbonyl]amino]-benzoic acid, 2-octyldodecylester [Index Registry #34913-82-1]

We use the term nematic gel here to denote: (a) the occurrence of typical nematic schlieren textures in thin capillaries (~0.3 mm); (b) a system which undergoes elastic distortions in response to shear and compressive forces, or electric and magnetic fields.

EXPERIMENTAL

A small sample of *I* was kindly supplied to us by Hoppe,[3,4] 3–5 mg were weighed into polypropylene tubes and the appropriate amount of decane was then added. After sealing, the sample was heated and stirred until the solid matter dissolved. Samples for optical studies were made using 0.3 mm rectangular glass capillaries from Vitro-Dynamics, Inc., New Jersey, by heating the bulk sample to the isotropic phase and allowing capillary action to draw in the material. The sample was then sealed with a micro-torch. Reasonable consistency in transition temperatures was obtained. Some samples were made with a slide and coverslip. Only results on fresh samples made in this way are reported.

Optical observations were made between crossed polars on a Nikon microscope, whereas the thermodynamic data were obtained on a Perkin-Elmer DSC-2C differential scanning calorimeter (DSC) at relatively rapid (10–20°/min) heating rates in order to visualize the small enthalpies.

RESULTS AND DISCUSSION

Table I summarizes data on optically and thermodynamically observed transitions. Nematic to isotropic transition temperatures (T_{NI}) were difficult to obtain optically because of the small birefringence and represent the visual observation of $\Delta n \rightarrow 0$. The DSC measurements along with macroscopic observation of samples in a stirred water bath confirm the existence

TABLE I

Sample compositions, transition temperatures, and enthalpies of I in decane

Wt. % I	Molar ratio $\frac{\text{decane}}{\text{I}}$	T_{NI} Optical °C	T_{GF} DSC °C	ΔH Kcal mole^{-1}
3.0	135.1	71	81	.17
3.5	114.9	71	80	.10
4.0	100.0	73	78	.08
5.0	79.4	74	76	.24

of a gel-fluid transition T_{GF} which does not appear to coincide with T_{NI} observed optically.

Figure 1 demonstrates the typical nematic schlieren textures obtained. These textures typically developed when the sample was quenched from the isotropic phase to room temperature rapidly.[3] When stored at room temperature, the texture did not relax over a three-week period of observation. The brushes around the singularities did not move in response to $\pm 10°$ temperature changes within the nematic gel phase. Even close ($T_{NI} - T \cong 2°$) to the transition, mobility of the brushes was very small in comparison with ordinary thermotropic nematics. As $T \rightarrow T_{NI}$ the already small birefringence ($\Delta n \sim 10^{-4}$) decreases uniformly over the sample. Figure 2 shows a nematic-isotropic transition under strong illumination.

Figure 3 shows the result of a shear applied to a sample with a coverslip. The textures in Figure 4 arise from shear induced orientation as the isotropic liquid of low viscosity is drawn into a cold capillary. Noticeable in both Figures 3 and 4 are faint striations running perpendicular to the direction of shear, and are possibly hydrodynamically induced defects. In general, the director field appears "locked" to the amorphous gel lattice. At room temperature, the director does not reorient in a magnetic field of 25 k Gauss applied in any of three orthogonal directions over a period of three days. In a large applied electric field of $\sim 10^7$ V/cm on a 23 μm

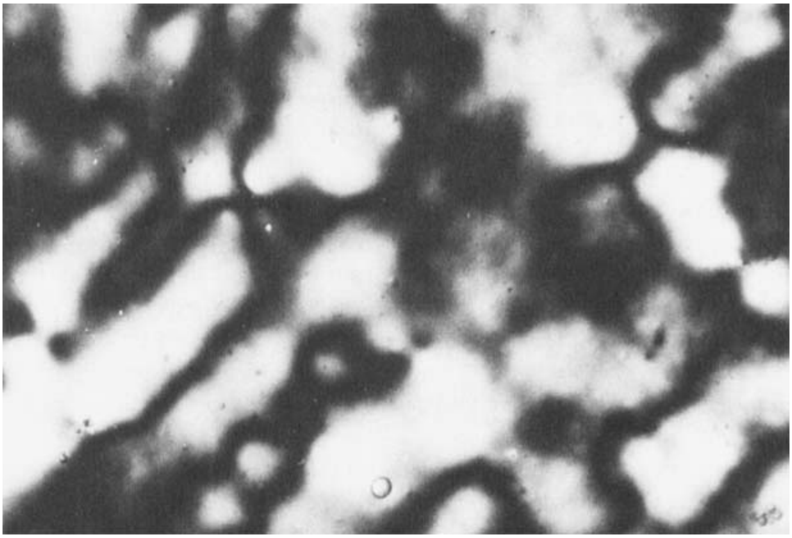


FIGURE 1 Nematic schlieren texture of 3.5% *I* in decane at 22°. Magnification 130X; crossed polars.

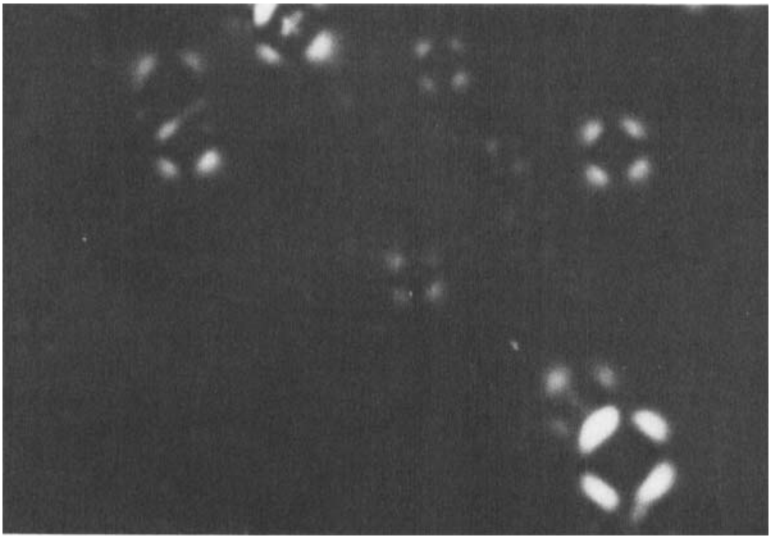
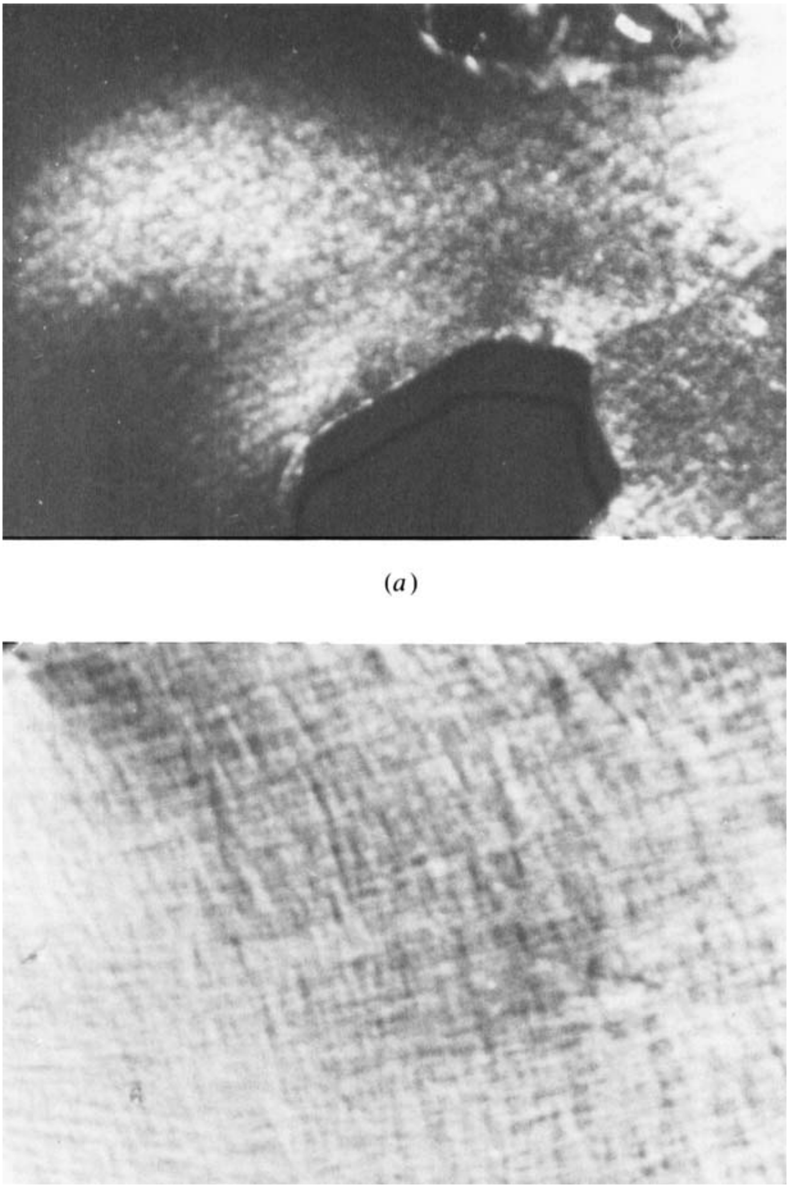


FIGURE 2 Nematic → isotropic transition of 3.5% *I* in decane at 71.4°. Magnification 130×; crossed polars.

thick cell no observable instability occurred until $T \approx T_{GF}$ when electrohydrodynamically induced turbulence occurred. By periodically varying an applied pressure of ~0.5 Kg cm^{-2} on the coverslip or the voltage in the electrooptical cell (condenser forces causing the compression), the elastic response of the system was qualitatively verified to quite low frequencies (~1 − .1 sec^{-1}) by observing the relative distances between dust particles and bubbles.

DSC measurements rarely show a peak on cooling. On slowly cooling samples from $T > T_{GL}$ to room temperature, the samples remained optically isotropic but the gel properties were retained. After 24 hours at room temperature they were still optically isotropic. The samples were then placed in an oven at 55° and within three days the samples became uniformly birefringent. Textures obtained in this way showed little structure except for an occasional +½ singularity with broad brushes along the capillary edge. Supercooling into an isotropic gel is the most likely explanation of these effects.

It seems most likely that the nematic gel is composed of extended inverse micelles held together by dispersion and dipolar forces. If this is true, the existence of textures with splay deformations implies either the micelles are finite in extent, or break apart and reform easily in response to thermal fluctuations and diffusive processes. Why such a small amount of a rela-



(*a*)

(*b*)

FIGURE 3 Shear induced birefringence of 3.5% *I* in decane at 22°. Magnification 62X; crossed polars. Sample is sheared in horizontal direction by moving coverslip ~1 mm. (a) Before shearing; (b) After shearing.

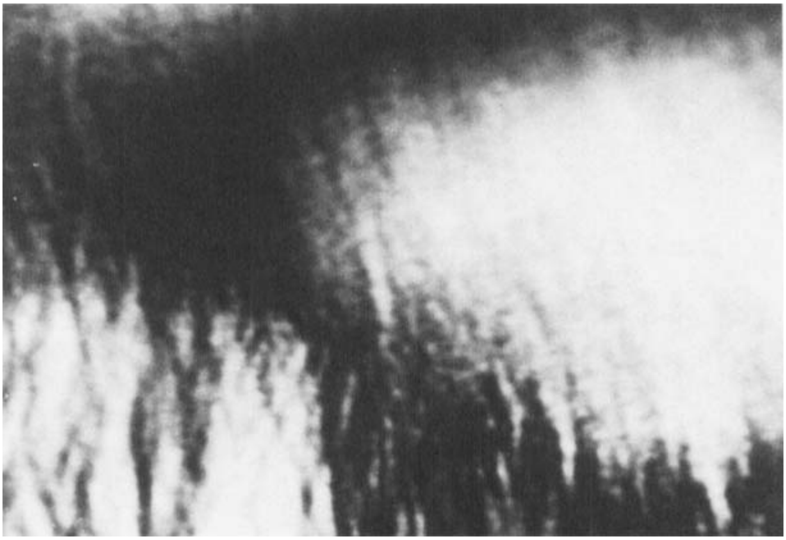


FIGURE 4 Striated birefringent texture of 3.5% *I* in decane at 22°. Magnification 62X; crossed polars. Sample flow into the capillary occurred in the horizontal direction.

tively low molecular weight amphiphile is able to establish an extended micellar phase with a high viscosity is the interesting materials question which remains unanswered.

Acknowledgment

We wish to thank Dr. U. Hoppe for furnishing us samples of these compounds. This work was supported by the U. S. Army Research Office under Contract No. DAAG29-81-K-0003.

References

1. See, for example, L. Gan-zuo, M. El-Nokaly and S. E. Friberg, *Mol. Cryst. Liq. Cryst. Letters*, **72**, 183 (1982) and earlier references cited therein.
2. For a review, see H. Kelker and R. Hatz, "*Handbook of Liquid Crystals*," Verlag Chemie, Weinheim, pp. 543–549 (1980).
3. U. Hoppe, *J. Soc. Cosmetic Chem.*, **24**, 317 (1973).
4. U. Hoppe, DBP 2,009,600 (16-9-1971).