01 Jan 1981

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Magda A. El-nokaly

Larry D. Ford

Stig Friberg
Missouri University of Science and Technology, stic30kan@gmail.com

David W. Larsen

Recommended Citation

M. A. El-nokaly et al., "The Structure Of Lamellar Lyotropic Liquid Crystals From Lecithin And Alkanediols," *Journal of Colloid And Interface Science*, vol. 84, no. 1, pp. 228 - 234, Elsevier, Jan 1981.
The definitive version is available at https://doi.org/10.1016/0021-9797(81)90279-4

The Structure of Lamellar Lyotropic Liquid Crystals from Lecithin and Alkanediols

MAGDA A. EL-NOKALY, LARRY D. FORD, AND STIG E. FRIBERG

Department of Chemistry, University of Missouri–Rolla, Rolla, Missouri 65401

AND

DAVID W. LARSEN

Department of Chemistry, University of Missouri–St. Louis, St. Louis, Missouri 63121

Received February 25, 1981; accepted April 6, 1981

Lamellar liquid crystals from lecithin and alkanediols were studied to determine the composition range of stability and geometrical dimensions using low-angle X-ray scattering. An estimation of the dislocation pattern was made from the optical pattern in polarized light. The ethylene glycol gave the widest range of stability for the lamellar structure, the range being reduced toward heptanediol, the longest member to give liquid crystals. The interlayer spacing was reduced with increasing chain length of the diol and the dislocation pattern remained identical.

INTRODUCTION

Lyotropic liquid crystals are formed by the action of a solvent on an amphiphilic substance which may be a solid or a liquid in its pure form (1, 2). Thus far (3–6) the solvent used in combination with an amphiphilic compound has been water, which is a natural choice because of the importance of the liquid crystals as models for biomembranes (7, 8). It has even been suggested (9–11) that the ordered structure of water should be a decisive factor for this kind of structure.

Examples of nonaqueous lyotropic liquid crystals have so far been limited to solvent/polymer systems. These have a variety of interesting features (12, 13); the extensive and careful investigations on polypeptide/hydrocarbon systems (14) deserve special mention.

Nonaqueous lyotropic liquid crystals for which the directive forces originate from an amphiphilic compound were discovered independently by Moucharafieh (15) and Larsson (16). We found this new field of lyotropic mesomorphism sufficiently interesting from a scientific and technical point of view to institute a research program in this area.

With this publication we report our investigations on alkane diols with terminal hydroxide groups using low angle X-ray diffraction and optical microscopy.

EXPERIMENTAL

I. Preparation of Materials

(a) *Lecithin.* The lecithin, Epikuron 200 (Lucas Meyer, Hamburg) have four spots on silica-gel-precoated plates and was purified according to the following procedure.

Epikuron 200 (17 g) dissolved in a minimum amount of chloroform (≈75 ml) was fractionated on a 4 × 87-cm alumina (625 g) column (17). The sample was washed in the column with chloroform (500 ml) and eluted

0021-9797/81/110228-07$02.00/0

with chloroform:methanol (9:1 by vol.). The progress of the fractionation was followed by TLC and a qualitative test with Dragendorff's reagent (18). The first fractions (400 ml) were clear. The following 175 ml were turbid, yellow, and positive to Dragendorff's reagent. TLC showed this fraction to contain neutral fat and some lecithin. The next 300 ml of eluate were cloudy and contained only lecithin. The final 200 ml were clear and contained a decreasing amount of eluted material. The fractions containing only lecithin were vacuum distilled (<50°C) under nitrogen atmosphere to recover pure translucent and colorless lecithin giving one spot on TLC.

An antioxidant Progallin P (NIPA Labs, Ltd., Pontypridd, Glam) was added in the proportions of 2 mg/10 g lecithin to the lecithin fractions before distillation.

(b) *Solvents: Diols.*

1,2-Ethanediol, 0.04% water (Fisher certified);
1,3-Propanediol, 0.07% Water (Aldrich);
1,4-Butanediol, 0.08% water (Aldrich);
1,5-Pentanediol, 0.05% water (Aldrich);
1,6-Hexanediol, melting point 41–43°C (Aldrich);
1,7-Heptanediol, 0.09% water (Aldrich);
1,8-Octanediol, melting point 59–61°C (Aldrich).

Karl Fischer titration showed the original water content of the solvents to be high, ≈0.3%. Hence they were dried over sodium sulfate, and fractionally distilled under vacuum with dry nitrogen repeatedly until stable levels as given were obtained. The dehydrated solvents flushed with dry nitrogen were sealed and stored in a desiccator over anhydrous calcium sulfate.

II. Preparation of Samples for Optical Microscopy and X Ray Diffraction

Lecithin was dried each time over phosphorous pentoxide by continuous pumping *in vacuo* at room temperature until no further loss in weight was observed. The components, lecithin and the nonaqueous solvents, were weighed into small glass vials with screw tops, flushed with nitrogen and centrifuged. They were mixed in a Vortex vibromixer with intermittant heating (<50°C) to facilitate mixing and centrifuged (7000 rpm) to remove air bubbles. Finally, they were left to equilibrate overnight in a water bath slowly cooling from 50 to 21°C. The samples were examined, between slide and cover, on a microscope between crossed polarizers, for proper mixing and absence of air, and to study their optical patterns.

A small amount of the equilibrated, well-mixed sample was drawn into a fine, flattened glass capillary and sealed for X-ray diffraction by a Kiessig low-angle camera from Richard Seifert. Ni-filtered Cu radiation was used and the reflections determined by a Tennelec position sensitive detection system (Model PSD-1100).

RESULTS

The results will be described with respect to the following considerations. The low angle X-ray diffraction patterns gave two reflections for most of the samples, which enabled the structure to be identified as lamellar (19). For those cases for which only a single reflection was observed, the optical pattern was used to give an unambiguous assignment of the basic structure of the liquid crystal.

The interlayer spacings calculated for the lamellar structures (19) were plotted against the solvent weight ratio, which gave straight lines for all the diols involved (Fig. 1). The values for the ethylene glycol agreed with those published by Moucharafieh (15). The present values are slightly higher due to a different batch of the lecithin. Liquid crystals with propanediol in turn gave interlayer spacings identical to those with ethylene glycol, the extrapolated interlayer spacing at zero solvent content being 36 Å and the onset of constant spacing indicating a two-phase area being at a solvent weight ratio of 1.45.

The structures with butanediol and pentanediol also gave an identical extrapolated interlayer spacing of 36 Å. The onset of the two-phase area occurred at lower solvent weight ratio with increased chain length, the value for butanediol being 1.1 and for pentanediol 0.75. The increase of interlayer spacing with solvent content was also lowered. The stability range of the liquid crystals containing heptanediol was too small to enable a reliable extrapolation; however, the data indicate that lower values exist both for the observed interlayer spacings and for the highest solvent content for stability.

Hexanediol and octanediol are solids at room temperature and although liquid crystalline patterns were produced after heating mixtures with lecithin, the question of stability could not be answered immediately. If thermodynamically stable structures do exist, they are present in an extremely limited composition range.

The values for the interlayer spacings extrapolated to zero solvent content were smaller than the value for dried lecithin in noncrystalline form $\simeq$ 42.5 Å.

III. Optical Microscopy

Observations under polarized light confirmed the phase transition which was indicated by the constant interlayer spacing at high solvent content. Samples in the two-phase area showed spots of isotropic material embedded into an anisotropic matrix.

The optical patterns for liquid crystals with ethylene glycol agreed with earlier observations; the pattern of "oily streaks" at low solvent concentrations was replaced by one with fine striations at high solvent ratios for structures stressed by shear. Long-time equilibration gave oily streaks also for the latter compositions.

For higher alkanediol homologs, the fine striations were not observed. Instead (see Fig. 2) the oily streaks existed also at the highest solvent ratios. In addition closed figures and Maltese crosses were observed.

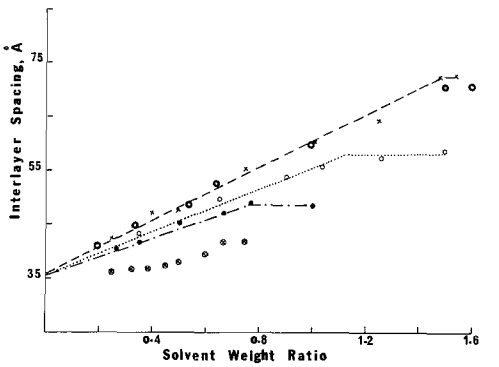

FIG. 1. The interlayer spacing as function of the solvent weight ratio. (– – –) ●, 1,2-ethanediol; (– – –) ×, 1,3-propanediol; (· · · · ·) ○, 1,4-butanediol; (–·–) ●, 1,5-pentanediol; ⊗, 1,7-heptanediol.

DISCUSSION

The results gave evidence that the specifics of an ordered water structure are not necessary in order to obtain the liquid crystalline state of lecithin. The O–O distance in ethylene glycol coincides with the corresponding distance in the wurzite-ordered water structure and the results from ethylene glycol only (15) could not be used to test the importance of the water structure. However, the present results with a series of alkanediols prove that the specifics of the water structure are not decisive in order to obtain the liquid crystalline state.

Calculation of the thickness of the layers and the area per molecule of the amphiphilic molecules using the standard equations (20, 21) showed a linear dependence on the solvent weight ratio. We describe the results in the following manner

$$\phi = \phi_0 + \zeta \cdot \rho,$$

in which ϕ is the function described, ϕ_0 is its value extrapolated to zero solvent content, and ζ is the slope of the function versus the solvent weight ratio ρ. These values are given in Table I.

The data in Table I provide information about the packing conditions that merits further consideration. A straightforward, but probably oversimplified, approach would

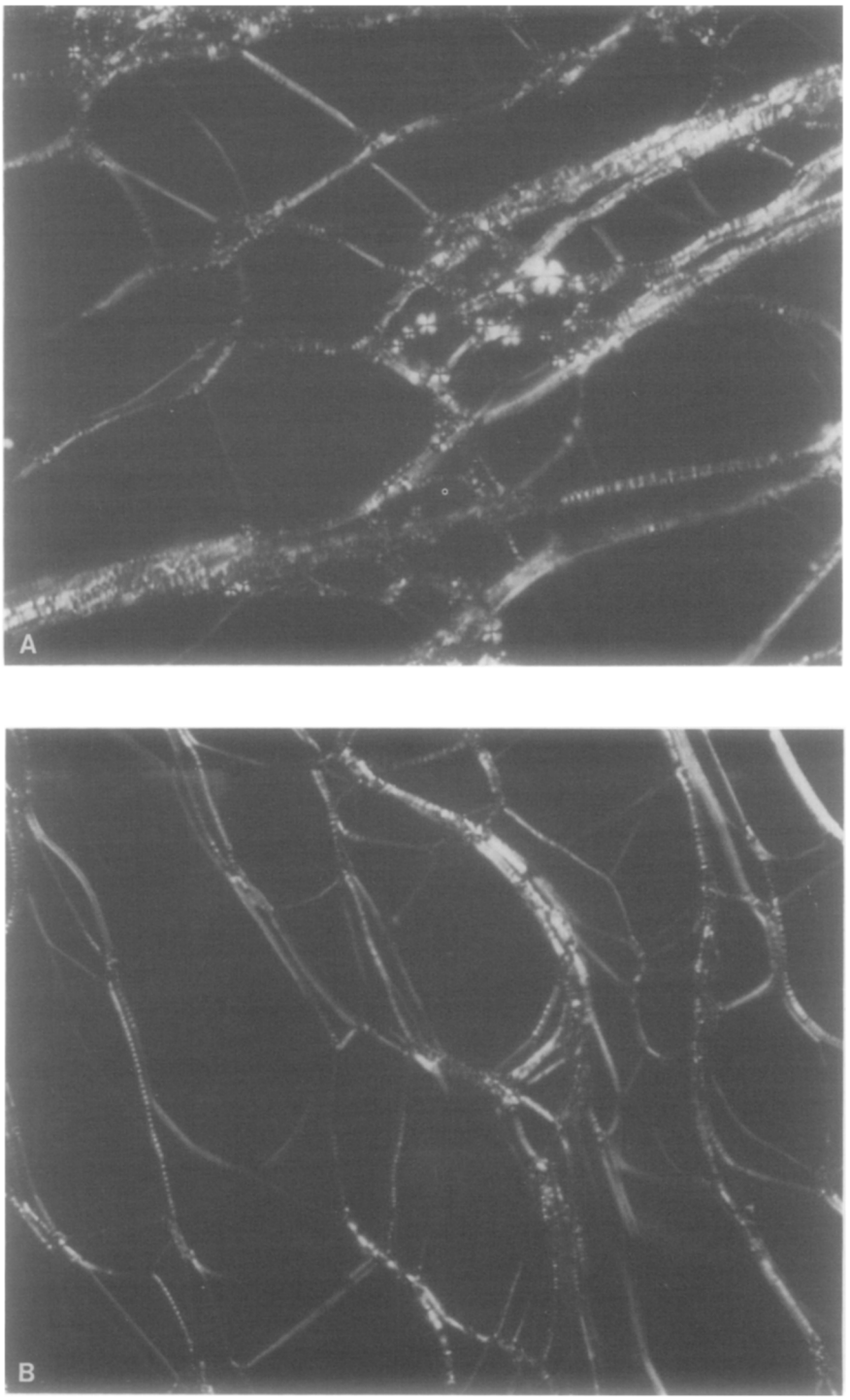

FIG. 2. The optical pattern of propanediol/lecithin liquid crystals. (A) The pattern at solvent ratio = 0.25; (B) the pattern observed at solvent ratio = 1.0.

attribute the value of the interlayer spacing extrapolated to zero solvent content to the state of the lecithin molecules at the lowest solvent content consistent with stability of the lamellar liquid crystalline phase. The value was 36 Å for all diols except heptanediol. The values for this latter compound were judged less reliable as discussed above and they are given in parentheses in Table I. The value 36 Å is considerably lower than the value, 42 Å, for the dry, solvent-free lecithin. The reduction may be due either to a change in the angle of the lecithin molecule with respect to the lamellar plane or to an enhanced disorder of the hydrocarbon chains.

The latter phenomenon may be modeled into "kinks" in a straight chain. An $n/n + 3$ *cis* position will shorten the chain by 1.215 Å, and thus any increased disorder in the observed samples would correspond to at least four "kinks." This number appears relatively high and an assumption of the reduced interlayer spacing being caused by a combination of enhanced disorder and a changed lecithin/lamellar plane angle appears justified. This assumption is supported by a comparison with the interlayer spacings in the corresponding liquid crystals with water as a solvent (15). For these the extrapolated value at zero water solvent was lowered to only 40 Å. It is difficult to envision such a drastic increase of disorder in the system by shifting from water to ethylene glycol followed by no change of disorder throughout the series of alkanediols considering the variation of geometric dimensions with solvent content. If the increased disorder of the lecithin hydrocarbon chains occurred only when substituting ethylene glycol for water, one should find a sign of constant penetration between the lecithin molecules by the diols investigated. In fact the variations within the series of diols were much greater than between the water and the ethylene glycol systems. Table I shows the values of interlayer spacing variation with solvent content to be more than doubled from ethylene glycol to pentanediol. The following discussion on the thickness of the amphiphilic part of the layer illustrates this behavior.

TABLE I

Parameters Relating Geometric Dimensions (ϕ) to Solvent Weight Ratio (ρ), Assuming $\phi = \phi_0 + \zeta\rho$

	Interlayer spacing, Å		Amphiphilic layer thickness, Å		Area per amphiphilic molecule, Å²	
	ϕ_0	ζ	ϕ_0	ζ	ϕ_0	ζ
Water	39	32.5	39	−3	64	7
Ethanediol	36	29	36	−5	70	12
Propanediol	36	29	36	−5	70	12
Butanediol	36	21	36	−8	70	25
Pentanediol	36	18	36	−12	70	26
Heptanediol[a]	(33)	(9)	(33)	(−15)	(75)	(54)

[a] The values for heptanediol are less accurate and are given in parentheses.

All the solvents gave a formal reduction of the thickness of the amphiphilic part of the layer (Table I). This reduction of the thickness with increased amount of solvent and the fact that higher homologs caused a more pronounced reduction may partially be ascribed to increased penetration of the solvent between the lecithin molecules. The penetration can be formally calculated if no changes in the amphiphile/lamellar plane angle nor in the lecithin hydrocarbon chain order are assumed. The penetration is the ratio of the difference between calculated values of interlayer spacing assuming no penetration nor angle changes and the experimental value, divided by the calculated value. The algebra is elementary after assuming

$$d = d_0(1 + \phi_\rho),$$

in which ϕ_ρ means solvent/amphiphile volume ratio. The final expression is

$$p = 100\left[1 + \frac{1}{\rho \cdot \rho_d}\left(1 - \frac{d}{d_0}\right)\right], \qquad [1]$$

TABLE II

Percentage Penetration of the Solvent

Solvent	Penetration (%)
Water	22
Ethylene glycol	14
Propanediol	18
Butanediol	22
Pentanediol	52
Heptanediol	74

in which p is the percentage of the solvent molecules located between the lecithin molecules, ρ is defined, Eq. [1], and ρ_d is solvent/amphiphile density ratio. These values, (see Table II) certainly are entirely formal and also artificial but give an indication of the location of the solvent molecule. The difference between the values for water and the lower diol homologs is probably not of a magnitude to be significant. On the other hand the conclusion of considerable fraction of the pentanediol molecules as located between the lecithin *molecules* appears justified. As a contrast the ethylene glycol molecules are mostly found between the lecithin *layers*.

These values are a good illustration of the fact that the differences in geometric dimensions are more pronounced within the series of diols than between the water and the ethylene glycol system.

They also appear to have a bearing on the stability of the lamellar structure. Increased chain length of the solvent molecule and enhanced penetration gave a reduction in the maximum amount of solvent that could be accommodated in the structure (see Fig. 1). The liquid crystals with ethanediol and propanediol accommodated 60% by weight of the solvents; for butanediol and pentanediol the numbers were 52 and 43. This result means that solvents which are mainly accommodated between *the layers* are accepted at higher levels without destabilizing the lamellar structure than are the ones located between the lecithin *molecules*.

A more complete description of the destabilization mechanism can probably be obtained only after a detailed determination of the variation of the order parameter along the chain of the lecithin and solvent molecules, however, the assumption of a critical disorder of the lecithin chains from the perturbation by partially penetrating solvent molecules appears reasonable.

ACKNOWLEDGMENT

This research was supported by NSF Grant DMR 8010690.

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