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

The Heterogeneity of Chain Lengths, A Factor in Lyotropic Polymorphism

J. Charvolin [a] & B. Mely [a]
[a] Laboratoire de Physique des Solides, Université Paris-Sud, 91405-ORSAY, France

To cite this article: J. Charvolin & B. Mely (1978): The Heterogeneity of Chain Lengths, A Factor in Lyotropic Polymorphism, Molecular Crystals and Liquid Crystals, 41:8, 209-215

To link to this article: http://dx.doi.org/10.1080/00268947808070302

Mol. Cryst. Liq. Cryst., Vol. 41 (Letters), pp. 209-215
©1978, Gordon and Breach Science Publishers Ltd.
Printed in the United States of America

THE HETEROGENEITY OF CHAIN LENGTHS, A FACTOR IN LYOTROPIC POLYMORPHISM.

J. CHARVOLIN and B. MELY
Laboratoire de Physique des Solides (+),
Université Paris-Sud, 91405-ORSAY (France).

(Submitted for publication: 8th March 1978)

The paraffinic medium of the lamellar phase of a potassium soap is perturbed by introducing a soap with a different chain length, while the water content of the phase is kept constant. Structural changes are observed which depend upon the concentration and the length of the solute soap.

We consider the liquid crystalline phases of potassium soap-water systems in the region of the phase diagrams where the paraffinic chains of the soap molecules are disordered, i.e. at temperatures larger than 40°C. Depending upon the water content, various phases are found which can be described as assemblies of lamellar, cylindrical, or spherical molecular aggregates (1). The sequence of structures exhibited by the system water-potassium laurate (or $C_{12}K$) for increasing water content and, correlatively, increasing mean area A per chain at the interface is sketched in fig.1. The polymorphism of the structural elements is very closely associated with a disordered state of the chains. Indeed a dense packing of rigidly extended chains can only produce lamellar aggregates and in order to fill in volumes of more complex shapes the chains have to be disordered.

(+) Laboratoire associé au C.N.R.S

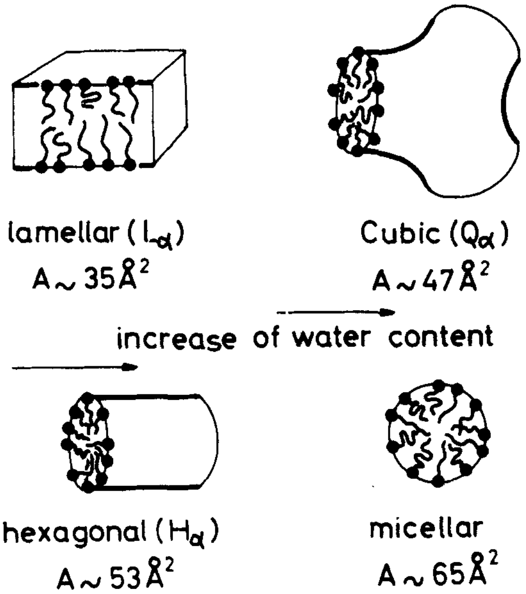

FIGURE 1: The phases with disordered chains of the $C_{12}K$-H_2O system displayed at increasing water content. The lamellar phase L_α is a periodic stacking along one dimension of soap and water lamella. In the cubic phase Q_α the soap molecules aggregates in short cylinders connected 3 by 3 in two interwoven three dimensional lattices (2)(3). In the hexagonal phase H_α infinite soap cylinders are organized in a two dimensional lattice. The micellar phase is a random dispersion of soap spherical micelles in the aqueous medium.

Our motivation is to understand the role played by the disorder of the chains in the occurrence of a given structure. As a first step we have used deuteron magnetic resonance (DMR) experiments to describe that disorder (4)(5). In a second step we study the perturbations induced when the packing of the chains is modified by mixing chains of different lengths. In this communication we describe some structural changes which may be attributed directly to differences in chain lengths and not to other parameters such as the average chain length or the water content as usually encountered.

We have studied two series of mixtures of potassium soaps, stearate (or $C_{18}K$) - myristate (or $C_{14}K$) and stearate-caprate (or $C_{10}K$) at constant temperature (70°C) and number of water molecules per soap molecule (n = 6.2). Under these conditions the pure soaps are lamellar with

A = 37 Å^2 (6). Structures and A values of our mixtures have been determined by X-ray diffraction following the method described in (1) (3), and the orientational disorder of the methylenes along the chain by DMR (4) (5). The $C_{14}K$ - $C_{18}K$ mixture exhibits a lamellar phase L_α with constant A for all relative concentrations. There is no X-ray evidence for phase separation and DMR has failed to detect any perturbation in the interfacial region. The thickness of the mixed $C_{14}K$-$C_{18}K$ lamellae is the weighted average of those of the pure lamella, as already emphasized (7). The two lamellar $C_{14}K$ and $C_{18}K$ phases appear totally miscible. Therefore one might consider the paraffinic region as an homogeneous medium of methylenes and methyl groups. However the behavior of the $C_{10}K$-$C_{18}K$ mixture is not in agreement with such a model: here the lamellar phase only exists in the narrow regions of low concentration of one soap in the other, phase separation and also new phases appear elsewhere as summarized in the Table.

$C_{10}K/C_{18}K$	∞	10	4	1 0.25	0.1	0
Optical	aniso.	aniso.	iso.	anisotropic	aniso.	aniso
X-rays A(Å^2)	L_α 37	L_α 36,9	Q_α 43,4	one L_α plus other phases	L_α 37,4	L_α 36,9
DMR typical of	L_α	L_α	iso. liquid	superimposed spectra	L_α	L_α

Results from three different experiments on several $C_{10}K$-$C_{18}K$ mixtures with 6,2 H_2O molecules per soap molecule. The relative soap concentrations are expressed as the numbers of $C_{10}K$ molecules with respect to those of $C_{18}K$.

We propose to analyse these results in the light of a model of chains strongly stretched because of steric requirements (8)(9), hence considering the paraffinic medium of a pure lamellae to be heterogeneous with its methyl ends concentrated in the central zone of the bilayer. In the case of a mixed lamellae the ends of short chains cannot be in register with those of long ones and their abrupt endings introduce defects of density around which the long chains have to reorganize, either locally or through a structural change. The concentration of defects, their position within the host lamellae with respect to its disorder profile, as shown on fig. 2, are certainly important terms.

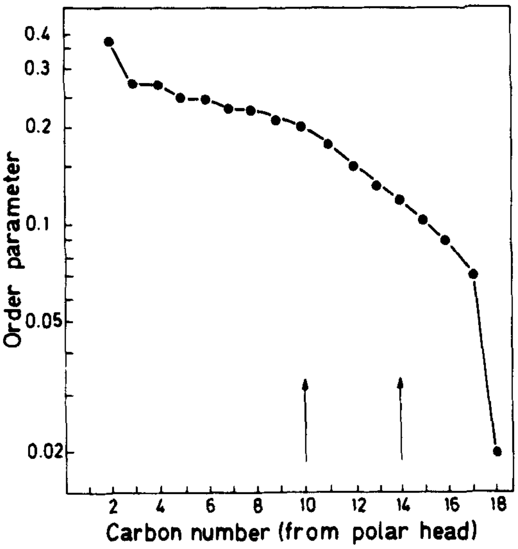

FIGURE 2: Orientational order parameter curve of a $C_{18}K$-H_2O lamellar phase, the disorder increases moving towards the end of the chain. The arrows suggest the positions of the ends of C_{10} and C_{14} chains diluted in the C_{18} matrix. The C_{14} chain end is in a more disorder region than the C_{10} one.

Table I shows three types of behavior according to the relative number of short chains versus long ones and the difference of chain lengths. Thus the $C_{14}K$-$C_{18}K$ mixture keeps an unaltered lamellar structure whatever the relative soap concentrations are. This behavior seems to indicate that the C_{14} and C_{18} chain lengths are close enough so that the disordered regions of their methyl ends overlap. The local decrease of density associated with a short chain amongst long ones may easily be filled by the disordering of the latter while in the opposite case of a long chain outnumbered by short ones the local increase of density may be absorbed by the surrounding disorder of the matrix of short chains. On the other hand, in the case of the $C_{10}K$-$C_{18}K$ mixture the lamellar phase is present, as an homogeneous phase, only in the extreme regions of the concentration range close to the pure lamellar phases. This behavior indicates that, when one chain is about twice as long as the other, the defect of density can no longer be accomodated by a lamellar structure. Presumably the disordered regions of both chains no longer overlap, in other words a short chain introduces a hole in the paraffinic medium which is too far from the disordered region of the long chains to be filled in by them. Therefore as soon as the defect concentration is too high their total energy can alter the lamellar structure. A trivial alteration is the separation of the two types of molecules, the corresponding lamellar phases coexist in a wide central region of the concentration diagram. But at about 1 $C_{18}K$ for 4 $C_{10}K$, just before the phase separation, the system adapts itself in a more subtle way: the anisotropic lamellar phase evolves to an isotropic homogeneous phase. This mixed isotropic phase presents all the structural, optical and DMR characteristics of a pure cubic Q_α phase. Indeed the X-ray diagram of the $C_{18}K$-$4C_{10}K$ mixture is compared, in fig. 3, with that of a cubic phase of $C_{12}K$(3); the similarity of small angle patterns is evident.

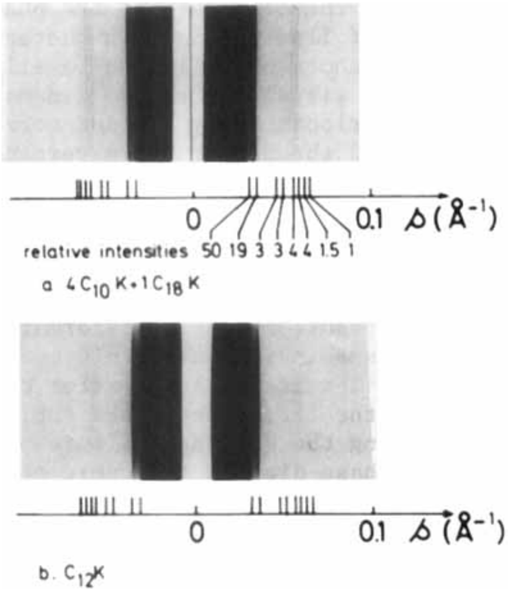

FIGURE 3: X-ray diffraction diagrams at 70°C of the isotropic phase of the $4C_{10}$-$1C_{18}K$ mixture (a), of the cubic phase of a $C_{12}K$ sample (b).
(The camera is of the Guinier type; the relative intensities, obtained from a microdensitometer trace, are only indicative).

The optical isotropy of the phase is due to its cubic symmetry

The"liquid" behavior in the NMR results comes from the averaging out of all quadrupolar interactions by the translational diffusion of the molecules throughout the three-dimensional rod structure (10). Furthermore this phase has a mean area per chain at the interface (A = 43 Å^2) which is larger than that of the lamellar phase of pure $C_{10}K$ (A = 36,5 Å^2) but slightly smaller than that of the cubic phase of pure $C_{12}K$ (A = 47 Å^2) observed at higher water content. The occurrence of a cubic phase here is quite noteworthy because the pure system with equivalent chain length (i.e. $C_{12}K$ since our mixture has an average length of 11.6 carbons) is lamellar at similar temperature and water content (11). Both the appearance of the cubic phase and the phase separation of two lamellar phases show that it is not correct to treat the paraffinic medium as an homogeneous liquid.

A more detailed interpretation of the effects of the density defects on the structure of the phases might be attempted along the following line. The defect of density associated with the short chain in the lamellar matrix of long ones might be visualized in two dimensions as the section of an edge dislocation by a plane normal to the dislocation line. Around the defect the divergence of the chain stretching vectors (8) is no longer null as in the pure lamellar phase. The chains being not fully flexible their splay in the core of the defect might impose a curvature of the interface to relax the stresses in the paraffinic medium. In this respect the mixed cubic phase, if it is looked at as the result of the transformation of a lamellar phase under stresses in its paraffinic medium, would have a slightly curved interface. As a matter of fact a similar conclusion about the interface of the cubic phase might be drawn reconsidering the sequence of pure phases shown on fig. 1. In this phase diagram the cubic phase is located in between the lamellar and hexagonal phases the interfaces of which have respectively null and finite curvatures. Therefore the cubic phase might be thought of here as a phase of intermediate curvature originating from stresses created by the increase of the mean area A per polar group on the interface. This is reminiscent of the attempt at systematization proposed by Winsor (11) who considered the evolution of the convexity of the interface with water content, although ignoring the model of the cubic phase described in (1).

In conclusion we think that by mixing chains of different lengths, we have brought some clues about the structural role played by the limited disordering ability of the chains at a given temperature and their cohesion in the paraffinic region of the liquid crystal. Obviously a clear understanding of these aspects requires exhaustive investigations of the phase diagrams of soap mixtures.

REFERENCES AND NOTES

1. Luzzati V., in "Biological Membranes", D. Chapman Editor, Academic Press, New York 1968.
2. Luzzati V., Spegt P.A., Nature, 215, 701 (1967).
3. Luzzati V., Tardieu A., Gulik-Krzywicki T., Rivas E., Reiss-Huqqon F., Nature, 220, 485 (1968).
4. Mely B., Charvolin J., Keller P., Chem. Phys. Lip. 15, 161 (1975).
5. Mely B., Thèse, Orsay, June 1977.
6. Gallot B., Skoulios A., Kolloïdzeitschrift, 208, 37 (1966).
7. Harkins W.D., J. Am. Chem. Soc. 68, 220 (1946).
8. de Gennes P.G., Phys. Letters 47A, 123 (1974).
9. Alexander S., J. de Physique 38, 983 (1977).
10. Charvolin J., Rigny P., J. Chem. Phys. 58, 3999 (1973).
11. This stems from four comparisons of pure and mixed phases each time prepared from freshly neutralized fatty acids.
12. Winsor P.A., Chem. Rev. 68, 1 (1968).