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

Metastability in Potassium Palmitate/D_2O Phase Transitions

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Version of record first published: 20 Apr 2011.

To cite this article: L. J. Lis & P. J. Quinn (1986): Metastability in Potassium Palmitate/D_2O Phase Transitions, Molecular Crystals and Liquid Crystals, 140:2-4, 319-325

To link to this article: http://dx.doi.org/10.1080/00268948608080161

Mol. Cryst. Liq. Cryst., 1986, Vol. 140, pp. 319–325
0026-8941/86/1404–0319/$15.00/0

Printed in the United States of America

Metastability in Potassium Palmitate/D_2O Phase Transitions

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(*Received March 6, 1986*)

A perdeuterated potassium palmitate/deuterium oxide mixture (66/34% by weight respectively) was examined using time resolved x-ray diffraction. The dynamic phase initial diagram indicated that upon heating, the crystalline bilayer phase undergoes a transition to a liquid–crystalline phase at approximately 75°C via two metastable states. One of the metastable states is a disordered crystalline bilayer and the other is a liquid crystalline bilayer. Upon subsequent cooling, the liquid–crystalline bilayer transforms directly to a gel bilayer phase.

Keywords: time resolved x-ray diffraction, lyotropic liquid crystal phases, perdeuterated potassium palmitate, metastable phase transitions

INTRODUCTION

Soap-water mixtures are lyotropic liquid crystals which exhibit phase transitions as a function of water content and/or temperature. The catalogue of phases in these systems has been used to extend our knowledge about phase transitions in general, and to act as a basis for the classification of transitions observed in other liquid crystal systems. The presence of lamellar (crystal, gel and liquid crystalline), hexagonal and cubic phases are all observed in various soap/water systems.[1–3]

In this report, the transitions between lamellar phases in a perdeuterated potassium palmitate/deuterium oxide mixture (66/34 by weight) were examined using time resolved x-ray diffraction methods.[4] The temperature of the sample was varied continuously at 10°C/minute on heating and cooling, and the diffraction pattern(s) were recorded simultaneously. These data are used to determine the "dynamic" phase diagram of this system. A crystalline lamellar phase at 20°C is initially observed which transforms eventually into a liquid crystalline phase upon heating. However, a metastable "gel" lamellar phase is detected upon subsequent cooling with the eventual relaxation of the gel phase to the crystalline phase inferred. The presence of intermediate phases are also observed and characterized. The presence of these phases appears to be solely dependent on the acyl chain subcells involved. This study extends the previous NMR observations of metastability in the liquid crystalline bilayer phase.[5-7]

MATERIALS AND METHODS

Perdeuterated potassium palmitate was synthesized as previously described.[6] The material was mixed with D_2O (99+% pure) and heated to approx. 60°C to facilitate equilibration. After cooling to room temperature, the sample was mounted between mica sheets 1 mm apart in an x-ray sample holder.

The x-ray experiments were carried out by using a monochromatic (0.15 nm) focussed x-ray beam at station 7.3 of the Daresbury Synchrotron Laboratory as previously described.[8] A cylindrically bent single crystal of Ge[9] and a long float glass mirror were used for monochromatization and horizontal focussing, providing 2×10^9 photons.s^{-1} down a 0.2 mm collimator at 2.0 GeV and 100 to 200 mA of electron beam current. A Keele flat plate camera was used with a linear detector fabricated at Daresbury. The dead-time between data acquisition frames was 50 μs, with the temporal resolution of each frame 700 ms for temperature scans of 10°C/min. X-ray scattering has been plotted as a function of tan 2 θ using teflon (0.48 nm) as a calibration standard.[10] No corrections were applied to path distances from the sample to the linear detector; consequently wide-angle spacings will be slightly longer than measured directly by the detector. Indexing of the x-ray patterns has been described previously.[1]

The temperature scans were produced by water baths connected to the sample mount of the x-ray camera. The temperature of the

sample was monitored internally using a thermocouple placed adjacent to the sample region of the x-ray sample holder. We expect that the thermal diffusion through our samples was approximately the same as that observed in experiments reported by Caffrey[11] since our sample thickness was also 1 mm.

RESULTS AND DISCUSSION

The system of potassium palmitate in water or D_2O has been extensively studied.[1-3,5-7] Previous x-ray diffraction studies by Luzzati and coworkers[1] probed the formation of hexagonal and lamellar mesophases. Recent NMR studies[6,7] have indicated that there are metastable liquid crystalline bilayer states in this system. Previous reports of metastability in lipid systems,[12-15] however, were limited to the gel or crystalline bilayer systems. However, all of these observations have relied on static measurements of these structures, which, in the case of x-ray diffraction, would need to be extremely long lived.

The static x-ray diffraction pattern of 66 wt% perdeuterated potassium palmitate in D_2O at 20°C is shown in Figure 1. The pattern

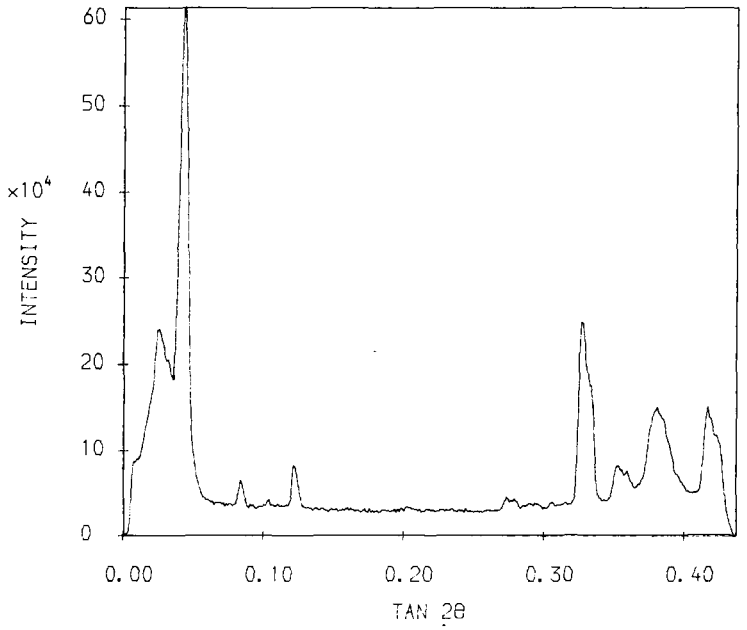

FIGURE 1 X-ray scattering intensity as a function of scattering angle for a dispersion of perdeuterated potassium palmitate in D_2O at 20°C. The pattern was obtained during 100 s exposure to the X-ray beam.

can be indexed for a bilayer with a lamellar repeat spacing of 6.1 nm and acyl chains packed in a monoclinic two dimensional array. The subcell is indexed from four diffraction peaks of 0.47, 0.44, 0.41 and 0.38 nm. The sample was driven to undergo a phase transition by a temperature scan of 10°C/min and the diffraction patterns recorded as a function of real time (Figure 2). The data indicates that the sample experiences a number of pre-transitions involving reorganization of the acyl chain subcells. Specifically, at approx. 35°C, the 0.41 nm peak in the wide angle scattering region loses intensity and broadens, indicating a disorder in the monoclinic sub-cell packing. At approx. 40°C, the 0.38, 0.41 and 0.44 nm peaks are reduced in height and broadened into the background scattering. The 0.47 nm peak is the main feature and is diagnostic of disordered acyl chains in an hexagonal subcell. At approx. 48°C, the main transition occurs as indicated by changes in relative intensity of the diffraction maxima in small angle scattering region, and the broadening of the 0.47 nm peak upon disordering of the acyl chain subcell. The position of the latter peak does not shift appreciably in the second more disordered liquid crystal lamellar phase. The static x-ray pattern for perdeuterated potassium palmitate in the liquid crystal phase at 75°C (Figure 3) also indicates the presence of a bilayer with a repeat of 4.11 nm.

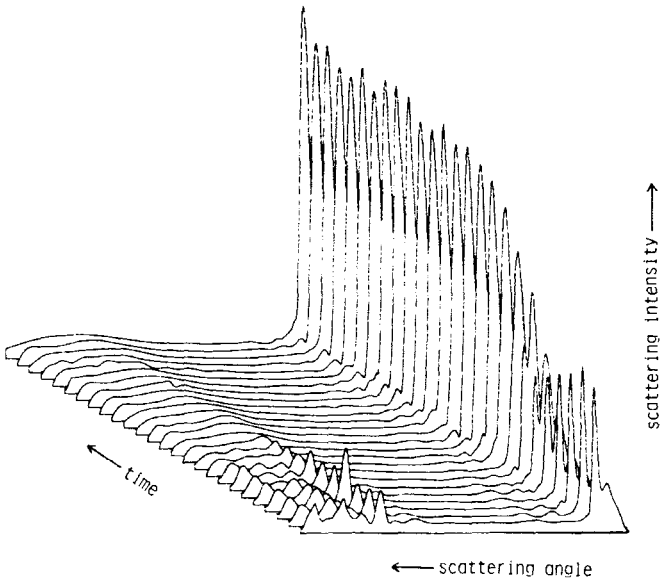

FIGURE 2 Three dimensional plot of X-ray scattering intensity versus scattering angle in which successive 700 ms. time frames were recorded during a temperature scan of $10° \cdot min^{-1}$ starting at 28°C for perdeuterated potassium palmitate in D_2O. Every tenth frame of the data set is plotted in this figure.

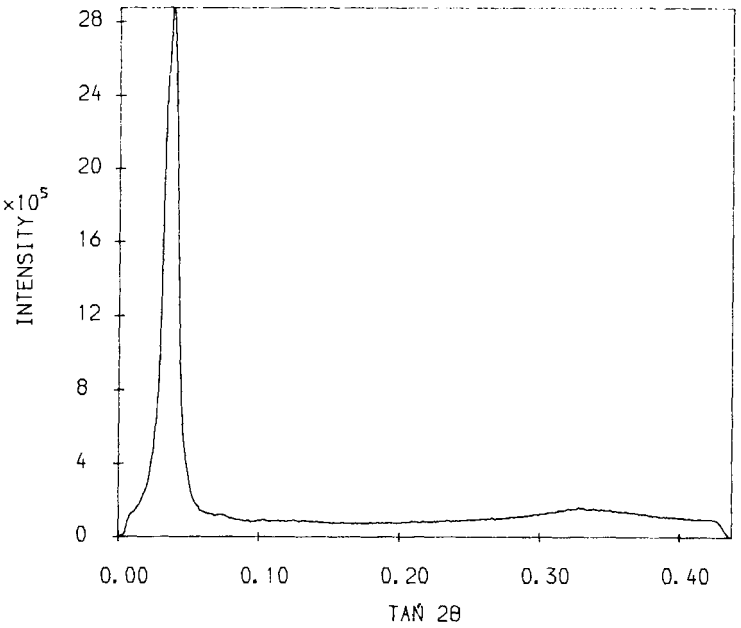

FIGURE 3 X-ray scattering intensity as a formation of scattering angle for a dispersion of perdeuterated potassium palmitate in D_2O at 75°C. The pattern was obtained during a 100 s. exposure to the X-ray beam.

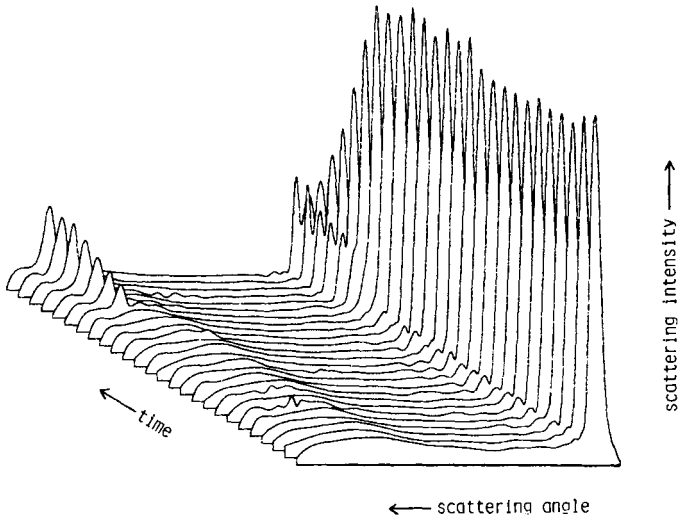

FIGURE 4 Three dimensional plot of X-ray scattering intensity versus scattering angle in which successive 700 ms. time frames were recorded during a temperature scan of $10° \cdot min^{-1}$ starting at 60°C for perdeuterated potassium palmitate in D_2O. Every tenth frame of the data set is plotted in this figure.

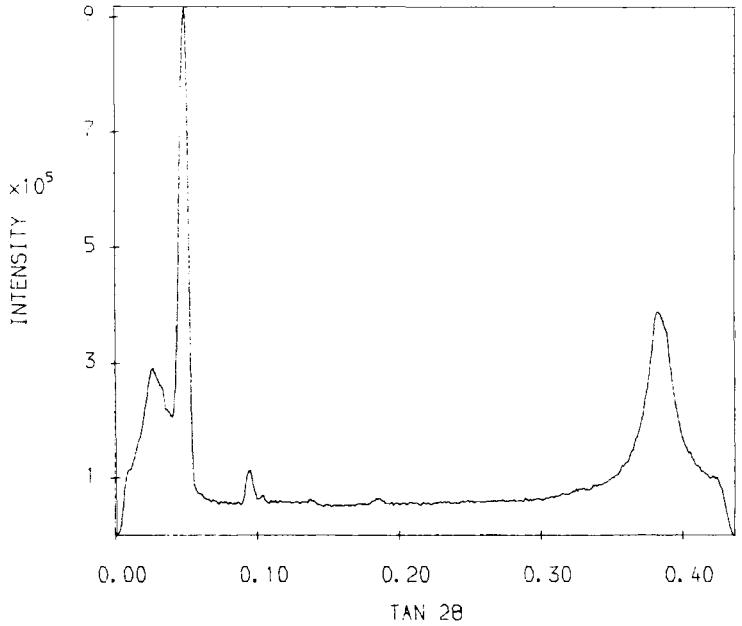

FIGURE 5 X-ray scattering intensity as a function of scattering angle for a dispersion of perdeuterated potassium palmitate in D_2O at 3°C. The pattern was obtained during a 100 s. exposure to the X-ray beam.

During subsequent cooling, the diffraction patterns were once again recorded as a function of time and therefore temperature (Figure 4). The potassium palmitate bilayer transforms from the liquid crystal to the gel bilayer phase at approx. 32°C. The gel phase bilayer can be indexed for a 5.71 nm bilayer with acyl chains packed in an hexagonal subcell with a dimension of 0.41 nm (Figure 5).

The transition scheme for 66 wt% perdeuterated potassium palmitate in D_2O in the temperature range 20° to 75°C as deduced from

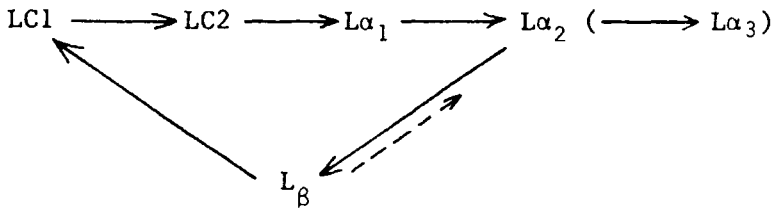

FIGURE 6 Schematic of lamellar phase transitions for perdeuterated potassium palmitate in D_2O. Back reactions (indicated by broken arrows) are inferred by comparison with other lyotropic liquid-crystal systems. The transition to a third liquid crystalline state is described in References 6 and 7.

the x-ray data is illustrated in Figure 6. The crystalline bilayer is the equilibrium state at low temperatures, and can irreversibly transform into a liquid crystalline lamellar phase after passing through two intermediate (metastable) phases. The liquid crystalline lamellar phase can transform upon cooling into a gel-state bilayer. The gel state can isothermally transform during prolonged storage (i.e. hours) at 20°C into the crystalline bilayer phase. The latter fact we can infer since our samples were initially heated to above their transition temperature (determined visually) to facilitate water flow between the bilayers and cooled to room temperature (20°C). The samples then equilibrated at room temperature for a number of hours. The result of this sample preparation was the crystalline bilayer phase characterized by the x-ray diffraction pattern in Figure 1. The liquid crystalline phase transition reported at 80°C[6,7] was not observed because of limitations with our sample heating system.

Acknowledgments

We would like to thank Dr. Mary Neubert for synthesizing the perdeuterated potassium palmitate used in this study. This research was partially funded by a grant from the SERC (U.K.). L.J.L. was a Burroughs Wellcome Travelling Fellow.

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