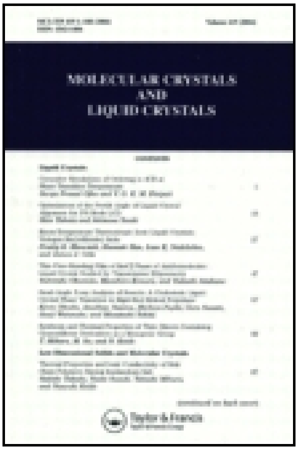

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 13 Dec 2006.

To cite this article: R. Somashekar (1987): Mesomorphic Behaviour of N-4-hexadecylpyridinium Chloride, Molecular Crystals and Liquid Crystals, 146:1, 225-233

To link to this article: http://dx.doi.org/10.1080/00268948708071815

Mol. Cryst. Liq. Cryst., 1987, Vol. 146, pp. 225–233
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Printed in the United States of America

Mesomorphic Behaviour of N-4-hexadecylpyridinium Chloride

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(*Received September 24, 1986*)

In this paper we report the mesomorphic behaviour of anhydrous N-4-hexadecylpyridinium chloride (HDPCl). DTA, X-ray and optical studies show that HDPCl exhibits smectic A phase above 76°C. Existence of lamellar phase in the mixtures of HDPCl and water, is reported using X-ray and optical studies.

Keywords: N-4-hexadecylpyridinium chloride, thermotropic, lyotropic, smectic A

INTRODUCTION

Knight and Shaw[1] have reported that the long chain of N-n-alkyl pyridinium chloride shows liquid crystalline properties. However, it was found that the detailed studies have not been carried out so far on the mesomorphic behaviour of N-4-hexadecylpyridinium chloride (HDPCl). The chemical formula is given by CH:CHCH: CHCH:N(Cl)$(CH_2)_{15}CH_3$. Liquid crystalline phases that can be observed in anhydrous amphiphiles have been reported.[2] Following the method of investigating an organic compound exhibiting liquid crystalline properties reported earlier,[3–7] here we investigate the phase transition and nature of thermotropic mesmorphism in anhydrous HDPCl in part I as well as lyotropic liquid crystalline phase of HDPCl with water in part II.

Part I

EXPERIMENTAL

N-4-hexadecylpyridinium chloride (>98% purity) was obtained from M/s Fluka, AG Buchs, S G Switzerland. HDPCl was dried by keeping it at 70°C in a temperature bath and also in a desiccator containing calcium sulfate, until no further loss in weight was observed. The transition temperature from solid to liquid crystalline phase was determined to be 76°C using a polarizing microscope in conjunction with a hot stage. Temperature was measured to an accuracy of ±0.5°C. The clearing point from liquid crystalline to the isotropic phase could not be determined as the substance decomposes around 237°C.[8] This transition was further confirmed by differential thermal analysis. Figure 1 shows the transition from solid to liquid crystalline phase at 76°C as obtained by DTA recording. Using standard procedure,[9] we have estimated the change in enthalpy (ΔH) the area under the corresponding peak in DTA curve and it turns out to be 9.13 Kcals/mole. The calibration of the instrument was carried out using semiconductor grade Indium. The deviation in the calculation of ΔH from sample to sample is of the order of ±0.06 Kcals/mole. The estimated

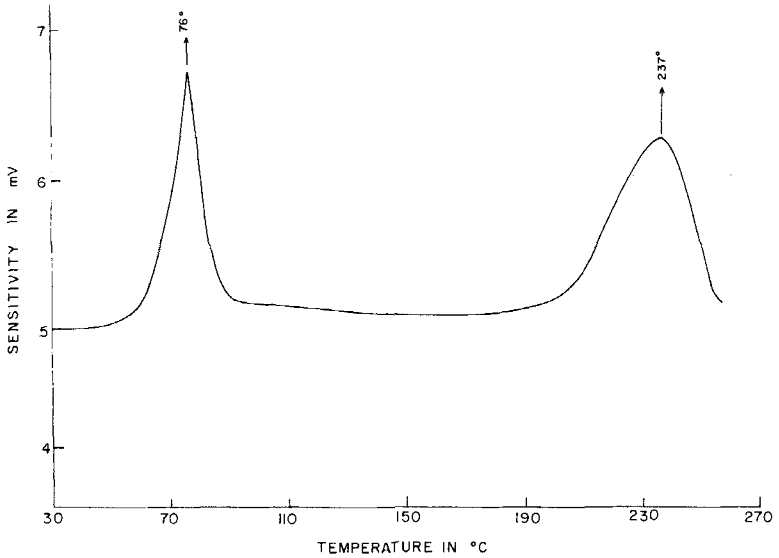

FIGURE 1 DTA recording of anhydrous HDPCl on heating at 5°/min, x-axis $-T$, y-axis $-\Delta T$.

value of ΔH for solid to smectic phase is of the same order as reported by earlier investigators[10] for compounds exhibiting smectic phase.

X-ray Studies

X-ray diffractometer (JEOL, JAPAN) recording of this substance at different temperatures were obtained by varying the scanning angle from 0 to 30° (2 θ) with the following settings: 30kv; 15ma; 2°/min; channel centre 100; channel width 50 and chart speed 10 mm/min. Recording of HDPCl taken at a temperature of 120°C is shown in Figure 2. The geometry of the XRD is such that a diverging beam is incident on the sample and the scattered beam is focussed on the detector. XRD recordings were taken at different temperatures 80, 86, 98, 102, 125, 135 and 145°C and it was found that there was only one sharp inner ring and outer ring was very weak. The weak outer ring at large angles is due to very large thermal agitation factor and not due to the absence of short range order.[11] The spacings determined for low angle scattering using $2d \sin \theta = \lambda$, for different temperatures are given in Table I. It is clear from the Table I that there is no significant variation in the layer spacing indicating that there is no major change in molecular ordering with increase in temperature.

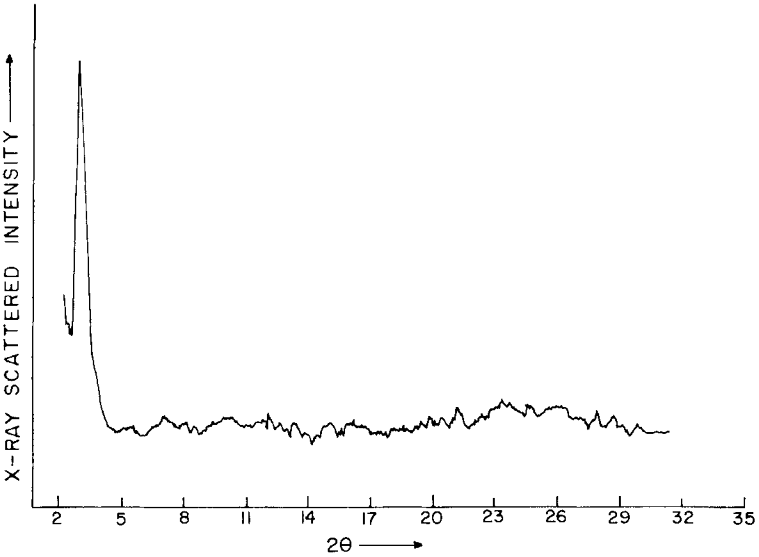

FIGURE 2 X-ray diffractometer recording of anhydrous HDPCl obtained at 120°C (λ = 1.934 Å)

TABLE I

Bragg spacings obtained from X-ray diffractometer recordings of anhydrous HDPCl

(Spacings in Å)	Temperature in °C	80	86	90	98	102	112	125	135	145
d		36.9	36.9	36.9	36.9	34.6	34.6	34.6	34.6	33.5

Using bond length data, the estimated length 'l' of the molecule (HDPCl) is about 28 A and the ratio of the effective spacing determined from the inner ring to the estimated length of HDPCl including the correction for thermal expansion[12] turns out to 1.3. A number of examples and explanations are now known where 'd' is greater than the estimated length (l).[13,14] It is possible to explain this difference (d—l) using a modified bilayer structure which arises due to steric effects or inter-molecular dipoles.[15]

OPTICAL STUDIES

Anhydrous HDPCl, a white powder, was taken in the form of a thin film between a microscope slide and a cover glass. When observed at a temperature above 76°C under a polarizing microscope in conjunction with a hot stage, HDPCl becomes transparent without any polarizers but shows birefringent textures between crossed polarizers, characteristic of the smectic phase. The characteristic texture is fan-like and is shown in Figure 3. This texture remained till the substance starts decomposing indicating that there is no major change in molecular ordering with increase in temperature as mentioned earlier from X-ray studies. We have also observed conoscopic figures of this sample in mesomorphic phase which clearly indicates that the phase is uniaxial positive.

The above studies clearly indicate that the phase is Smectic A phase.

Part II

Lamellar mesophase of HDPCl in water

The existence of different mesophases in two component systems was observed by McBain.[16,17] Luzzati et al.,[18-20] have reported X-ray diffraction studies of various mesomorphic structure in these systems.

FIGURE 3 Microphotograph of anhydrous HDPCl in mesophase showing fan-like texture at 90°C 55x.

Using the standard procedures described in earlier review articles by Ekwall,[2] Luzzati,[21] Mandell[22] and Fontell,[23] we report here the lyotropic mesomorphism of HDPCl in water.

Preparation of samples for optical microscopy and X-ray diffraction studies

The components, HDPCl and water were weighed into small glass vials closed with air tight tops. All samples were centrifuged at 7000 rpm and no separation of layers was noticed. Finally they were left to equilibrate for 3 days in a temperature bath at 22°C. The samples were examined, sealed between microscope slide and cover slip, on a microscope between crossed polarizers, to study their optical patterns. In conjunction with a hot stage, the transition temperature to isotropic phase for all the samples were determined and is given in Figure 4. A small amount of the equilibrated, well mixed sample was drawn into a fine, flattened capillary and sealed for X-ray Laue diffraction studies. Ni-filtered Cu-radiation was used.

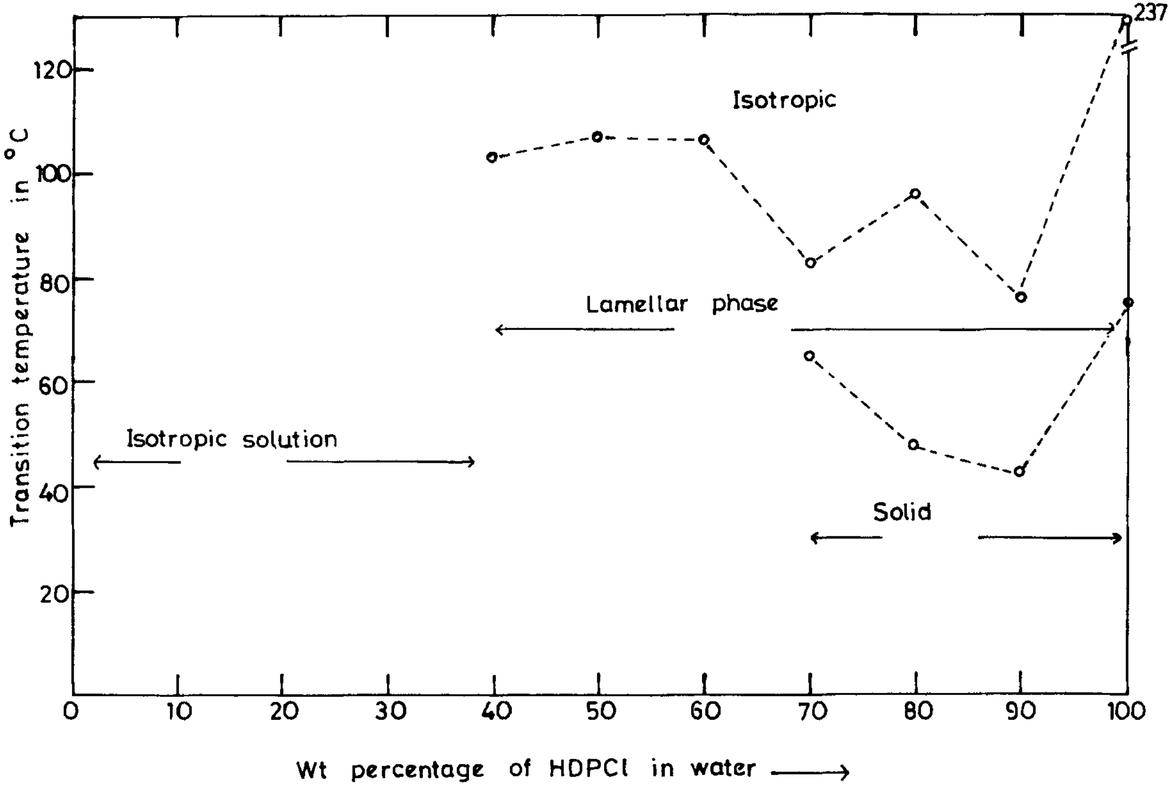

FIGURE 4 Transition temperatures of mixtures of anhydrous HDPCl and water.

Results and Discussion

The low angle X-ray Laue diffraction patterns ($\theta < 10°$) gave two reflections at room temperature for 50 and 60 weight percentage of HDPCl in water, which enabled the structure to be identified as lamellar phase (G).[23] Lower concentrations gave no reflections except for a diffused outer ring. X-ray diffraction studies for higher concentrations could not be carried out because of experimental difficulties, as these showed lyotropic liquid crystalline phase at higher temperatures. The Bragg spacings obtained from X-ray studies for inner and outer rings for 50 and 60 wt percentage of HDPCl in water are given in Table II, along with the area per polar group. The area per polar group (S) was calculated using the X-ray layer spacings of the mixtures and densities, molecular weight and wt concentrations of the constituents.[24] The optical patterns agreed with the earlier X-ray observations; patterns showed ellipses and fan-like textures which are shown in Figures 5(a) and 5(b). Oily streaks were also observed by disturbing the coverslip of the specimen. These textures are characteristics of lamellar phase (G).[25] The optical textures like ellipses, spherulites and fan-like textures are observed both for lamellar and hexagonal phases.[25] The presence of low angle reflections in the ratio 1:1/2, conclusively indicates that the phase here is lamellar structure.

Conclusions

DTA, X-ray and Optical microscopy studies clearly indicate that the anhydrous HDPCl exhibits smectic A phase above 76°C. Lamellar

TABLE II

Bragg spacings (d in Å) and area per polar group (S in Å^2) in the lamellar phase of the HDPCl-water system.

Wt percentage of HDPCl in water	d	S	d_{hc} in Å
50	27.40 13.69 7.04 5.60 4.70	86.7	26.1
60	29.56 14.80 7.30 5.78 4.80	55.6	26.8

d_{hc} = hydro carbon spacing.

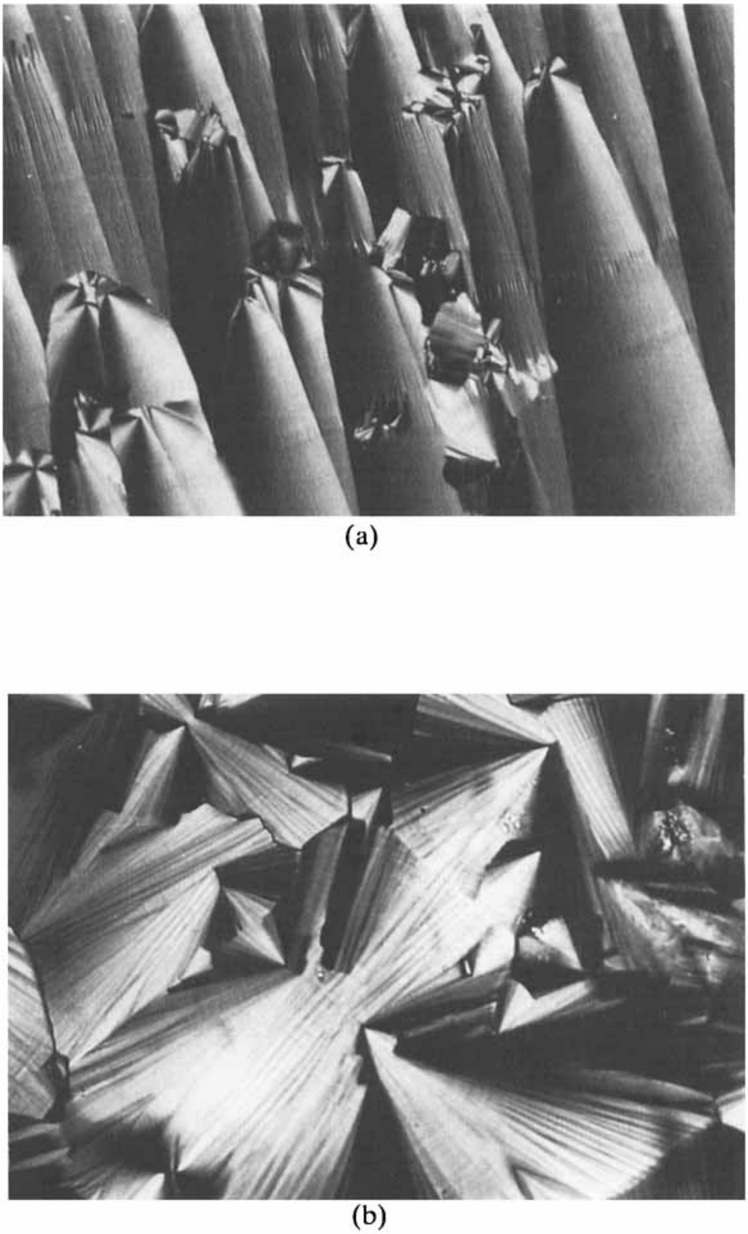

FIGURE 5 Microphotographs of HDPCl in water in lyotropic mesophase, at room temperature
a) ellipses 225x.
b) fan-like 55x. observed in the same slide but different region.

structure in the lyotropic mesophase behaviour of HDPCl in water has been established by X-ray and Optical studies.

References

1. G. A. Knight and B. D. Shaw, *J. Chem. Soc.*, 682 (1938).
2. P. Ekwall, "*Adv. in Liquid Crystals*" Ed. G. H. Brown, Academic Press, New York, London 1975, Vol. 1, pl.
3. I. A. Shanks, *Contemporary Physics*, **23**, 65 (1982).
4. E. Faneth, P. Giovanni, B. Marie and R. Ginseppe, *Mol. Cryst. Liq. Cryst.*, **87**, 77 (1982).
5. R. Dabrowski and E. Zytynski, *Mol. Cryst. Liq. Cryst.*, **87**, 109 (1982).
6. A. Malliaris, C. Christas, G. Margomeaoni, Leaonidopoulow and C. M. Paleos, *Mol. Cryst. Liq. Cryst.*, **82**, 161 (1982).
7. S. Chandrasekhar, "*Liquid Crystals*" (London) University Press, 1977, p. 8.
8. Handbook of Chemistry and Physics, Published by the Chemical Rubber Co., Cleveland, Ohio (1964), p. 2088.
9. R. F. Porter and J. M. Johnson Eds., "*Analytical Calorimetry*" New York; Plenum, p. 200 (1968).
10. D. Coates and G. W. Gray, "*The microscope*," **24**, 117 (1976).
11. J. Doucet, Chapter 14, "*The Molecular Physics of Liquid Crystals*," Eds. G. R. Luckhurst and G. W. Gray, 330 (1979).
12. A. de Vries, A. Ekachai and N. Spielberg, *Mol. Cryst. Liq. Cryst.* (letters), **49**, 143 (1979).
13. J. E. Lydon and C. J. Coakley, *J De Physique.*, **36**, C1-44 (1975).
14. W. L. McMillan, *Phys. Rev.*, **A7**, 1419 (1973).
15. A. J. Leadbetter, J. P. Gaughan, B. Kelly, G. W. Gray and J. Goodby, *J de Physique.*, **40**, C3-178 (1979).
16. J. W. McBain and M. C. Field, *J. Am. Chem. Soc.*, **55**, 4776 (1948).
17. J. W. McBain and W. C. Sierichs, *J. Am. Chem. Soc.*, **25**, 221 (1948).
18. V. Luzzati, H. Mustacchi, S. Skoulios, *Dis. Farad. Soc.*, **25**, 43 (1958).
19. V. Luzzati, H. Mustacchi and S. Skoulios, *Nature*, **180**, 600 (1957).
20. V. Luzzati, H. Mustacchi, S. Skoulios and F. Husson, *Acta. Cryst.*, **13**, 660 (1960).
21. V. Luzzati, in "*Biological Membranes*" Ed. D. Chapman, Academic Press, London (1968), p. 71–123.
22. L. Mandell, K. Fontell and P. Ekwall, "*Ordered Fluids and Liquid Crystals*" Ed. by R. S. Porter and J. F. Johnson, Adv. in Chemistry, Washington, 1967, p. 89.
23. K. Fontell, "*Liquid Crystals and Plastic Crystals*," Eds. G. W. Gray and P. A. Winsor, Vol. 2, 1974.
24. V. A. Parsegian, *Science*, **156**, 939 (1967).
25. N. H. Hartshorne, "*Liquid Crystals and Plastic Crystals*" Eds. G. W. Gray and P. A. Winsor, Vol. 2, p. 55 (1974).