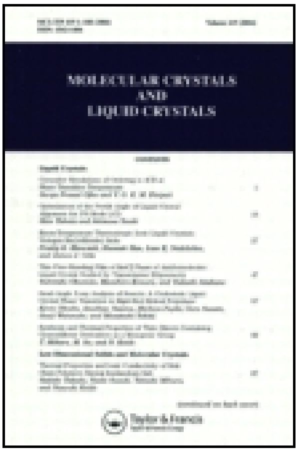


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Liquid Crystalline Beeaviour of Binary Mixtures of Two Non-Mesogenic Compounds

Nagappa [a], R. Hanumantea Nayak [a], J. Mabadeva [a], K. M. Lokanatha Rai [a] [b] & P. R. Alpati [a] [c]

[a] Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore, 570 006, INDIA

[b] Department of Chemistry, University of Southampton, SO17, IBJ, UK

[c] Department of Chemistry, University of Mysore, Mysore, 6

Version of record first published: 04 Oct 2006

To cite this article: Nagappa, R. Hanumantea Nayak, J. Mabadeva, K. M. Lokanatha Rai & P. R. Alpati (1997): Liquid Crystalline Beeaviour of Binary Mixtures of Two Non-Mesogenic Compounds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 301:1, 7-12

To link to this article: http://dx.doi.org/10.1080/10587259708041742

Mol. Cryst. Liq. Cryst., 1997, Vol. 301, pp. 7-12
Reprints available directly from the publisher
Photocopying permitted by license only

LIQUID CRYSTALLINE BEHAVIOUR OF BINARY MIXTURES OF TWO NON-MESOGENIC COMPOUNDS.

NAGAPPA, R HANUMANTHA NAYAK, J MAHADEVA, K M LOKANATHA RAI* AND P R ALAPATI[1]
Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore - 570 006, INDIA.
[1]Department of Chemistry, University of Southampton, SO17,IBJ,UK.
*Department of Chemistry, University of Mysore, Mysore-6.

Abstract: Binary mixtures of two novel amphiphilic mixtures of tetradecanol (TDC) and orthophosphoric acid (H_3PO_4) exhibit an interesting liquid crystalline phases in large range of concentration and temperature. The mixtures in the concentration range between 10 to 60% of TDC in H_3PO_4 exhibits S_A, S_D and S_E phases. The mixtures with higher concentration of TDC exhibit smectic phases. X-ray, DSC, Optical and NMR studies have been carried out.

INTRODUCTION

Studies have been carriedout by earlier investigators on the liquid crystalline behaviour of mixtures of two non-mesogenic compounds[1]. Binary and ternary mixtures of some non-mesogenic compounds exhibits lyotropic and thermotropic liquid crystalline phases[2]. H_3PO_4 has been used as solvent in forming micellar phases in lyotropic systems[3].

EXPERIMENTAL

In the present investigation we have prepared ten different concentrations of the binary mixtures of TDC in H_3PO_4 and the phase transition temperature of these mixtures were measured using the Leitz polarizing microscope in conjunction with hot stage. The mixture was sandwiched between slide and cover slip and was sealed for microscopic observations. All dynamic DSC studies were carriedout on Dupont 9900 thermal analiser with 910 DSC module. X-ray diffraction of TDC in H_3PO_4 at different temperatures were taken by using the Laue photography method described in an earlier paper[4]. ^1H and ^{13}C NMR spectra were recorded with Bruker 300 MHz NMR spectrometer at 297 K. The refractive indices were determined at different temperatures employing the technique described in our earlier paper[5].

RESULTS AND DISCUSSION

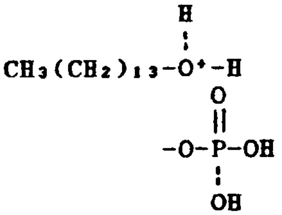
Phase diagram

The phase diagram shown in fig(1) illustrates that the mesomorphism is the thermodynamically stable for lower concentration between 10 to 40% of TDC in H_3PO_4 mixtures. The mixture with 30% of TDC exhibit I $\underline{128^\circ C}$-S_A $\underline{60^\circ C}$-S_D $\underline{49^\circ C}$-S_E phases sequentially. The values of the phase transition temperatures observed in DSC traces are agreed with the temperatures observed in microscopic method. The phase transition temperature of the mixtures of 41 to 60% of TDC decreases with increasing TDC and the mixtures exhibit S_A and S_E phases. In the concentrations from 61 to 90% of TDC, the phase transition temperature of the mixtures decreases as the TDC concentration increases, and these mixtures exhibits S_A of hexagonal columnar phase at higher temperature and lamellar phase at lower temperatures. Above 90% of TDC we get the only birefringent regions and it is difficult to associate with any of the mesophase.

NMR studies

The proton NMR spectrum was recorded in a Jeol MHz spectrometer at 297 K. The ^1H NMR spectrum for the mixture of 60% TDC in H_3PO_4 is shown in Fig(2). The spectrum illustrates that broad triplet, singlet, a broad multiplet at δ 0.9, 1.25 & 1.55 ppm and they correspond to CH_3, CH_2 and $-CH_2-CH_2OH$ respectively. The triplet peak at 3.65 ppm is due to $-CH_2-O-$group. The broad peak at 8.5 ppm correspond to $-^{+}OH_2$. ^{13}C NMR spectrum recorded at 297 K give quite weak signals. The main peak is broad around δ 0.1 ppm since the H_3PO_4 is in the emulsion. These results fully justified with those from mass spectral analysis. Mass spectrum gives more fragmentation, but basically the main peaks for alcohol are MH^{+}, $MH^{+}-18[M-17]$ and these fragments have less and less CH_2 units.

When the mixture of TDC in H_3PO_4 is heated one can expect the interaction of the long chain hydroxyl group of TDC with a free H_3PO_4 molecule.



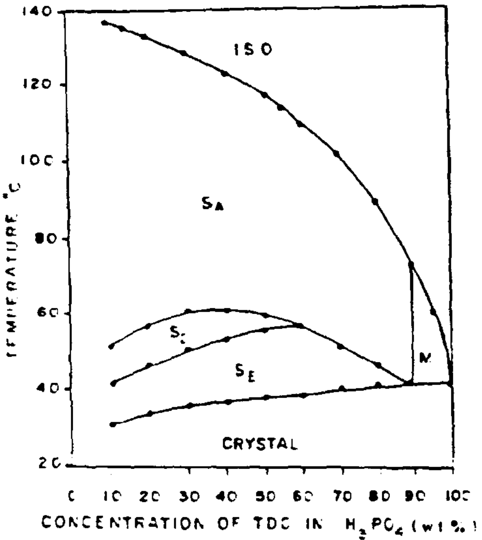
$$\begin{array}{c} H \\ \vdots \\ CH_3(CH_2)_{13}{-}O^{+}{-}H \\ O \\ \| \\ {-}O{-}P{-}OH \\ \vdots \\ OH \end{array}$$

But from the above spectroscopic studies it is evident that there is no esterification reaction or dehydration of alcohol.

Optical studies

On cooling the specimen of the 30% of TDC in H_3PO_4 from its isotropic liquid phase a focal conic texture is observed which is the characteristic of S_A phase as shown in fig(3a). Further it changed over to an isotropic viscous S_D phase[6]. see fig(3b). The S_D phase changes to S_E phase on further cooling and which remains upto room temperature. The S_E phase is characterized by fan shaped focal conic texture, which are crossed by a number of arcs as shown in fig(3c).

The refractive indices for the extraordinary ray(n_e) and the ordinary ray(n_o) of the mixtures of concentration

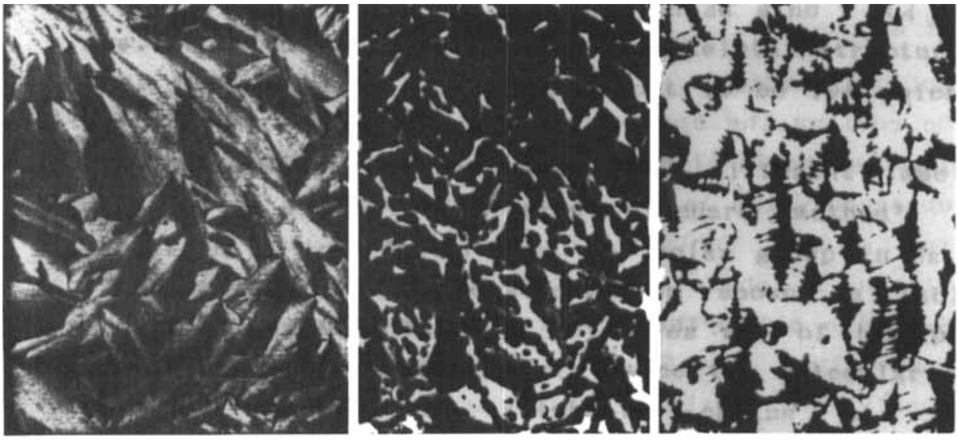


fig(1)

fig(2)

FIGURE 1 Partial phase diagram of binary mixture of TDC and H_3PO_4

FIGURE 2 ^1H NMR Spectrum for 60 % of TDC



(3a) (3b) (3c)

FIGURE 3 Microphotographs of a) S_A phase (150X)
b) Isotropic viscous S_D phase (150X)
c) S_E phase (185X)

30% to 50% of TDC were determined using Goniometer spectrometer. The values of n_e is greater than n_o indicating that the material is uniaxial positive. The electrical susccptibility is related to $N\alpha$ i.e. equal to $N\alpha_e$ and $N\alpha_o$, here α_e and α_o are the effective polarisabilities of extraordinary and ordinary rays. N is the number of molecules per unit volume. The values of χ_e and χ_o at various temperatures are calculated by using Neugebauer's relation[7]. The plot of $\Delta\chi$ as a function of temperature is shown in fig(4).

X-Ray Studies

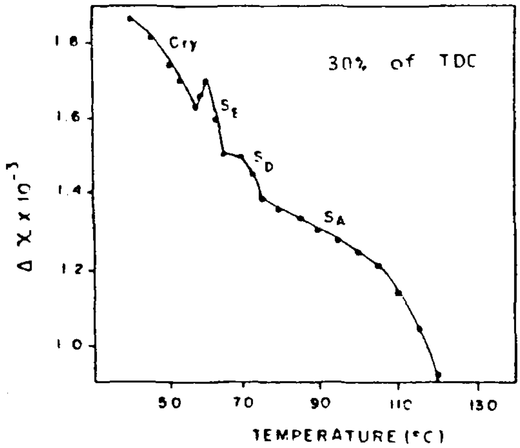
The X-ray diffraction photograph shown in fig.5. taken at 299 K for the 40% of TDC in H_3PO_4 exhibit two sharp outer and inner rings which are characteristics of S_E phase[8]. The outer rings are sharp owing to the fact that with in each smectic layers, there is an exactly regular arrangement of molecules in the lateral direction laying in the plane of the each layers. The sharp inner ring correspond to the first ordered diffraction from the set of smectic layer like planes. The effective d spacings are calculated by using the equation $2d \sin\theta = n\lambda$ which are tabulated in table 1. From the skeletal structure of TDC, the molecular length turns out to be 19Å which is half of the effective d spacing.

The area per polar group(S) in different lamellar phases was calculated using standard method[9]. The variation of interfacial area per polar group in S_E and S_A phases with Bulk concentration shown in table-1 clearly indicates that the molecules are of the polar head at higher temperatures is twice the molecular area of the crystallized aliphatic chains at lower temperature[10].

TABLE I: Calculated values of d, S and d_{hc}, average thickness of the hydrogen layers obtained for different concentrations

Content wt% TDC	d Å	D_1 Å	D_2 Å	d_{hc} Å	S(Å):	
					S_E	S_A
30	31.63	4.97	4.66	26.23	19.82	43.35
40	32.89	4.78	4.23	27.98	18.57	41.91
50	34.15	4.56	4.10	28.07	17.23	40.49
60	35.53	4.39	4.02	29.73	16.87	39.44
70	37.08	4.21	3.98	30.14	15.46	38.67

d_0=4.53 Å, minimum thickness of H_3PO_4



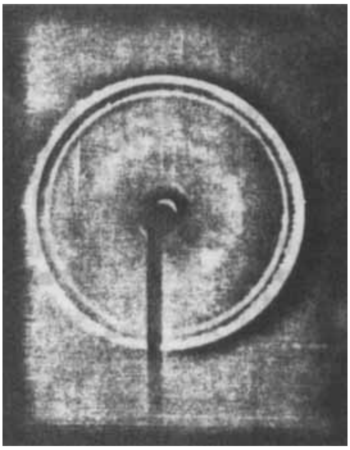


FIGURE 4 Dependence of $\Delta\chi$ on T°C
FIGURE 5 Laue X-ray photographs of 30 % TDC

REFERENCES

1. M. Marthandappa, Nagappa, K. M. Lokanatha Rai; J. Phys.Chem 95 6369 (1991)
2. W J Benton and C A Millar J.Phys.Chem 82 1981 (1983)
3. M. Acimix Liquid crystal 4(2) 549 (1987)
4. D Krishnamurti, K S Krishnamurthy and R Shashidhar Mol. Cryst. Liq. Cryst. 8 339 (1969)
5. Nagappa, S K Nataraju and D Krishanamurthi Mol. Cryst. Liq. Cryst. 133 31 (1986)
6. K Fontel, L Mandell, P Ekwall Acta Chem Scand 22 3209 (1968)
7. H E J Neugebauer Can. J. Phys. 32 1 (1954)
8. A De Vries Pramana Suppl 1 93 (1975)
9. V A Parsigian Scienc 156 939 (1967)
10. J Franeois J. Phys. Radium 30 89 (1967)