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

Micellar Nematic Lyophase in the Mixture of Sodium Oleate and Glacial Acetic Acid

R. Hanumantha Nayak Nagappa [a] , K. N. Jagadish [a] , A. Siva Prasad [a] , R. Somashekar [a] & K. M. Lokanath Rai [b]

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

[b] Department of Chemistry, University of Mysore, Manasagangotri, Mysore, 570 006, INDIA

Version of record first published: 23 Sep 2006.

To cite this article: R. Hanumantha Nayak Nagappa , K. N. Jagadish , A. Siva Prasad , R. Somashekar & K. M. Lokanath Rai (1995): Micellar Nematic Lyophase in the Mixture of Sodium Oleate and Glacial Acetic Acid, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 260:1, 631-640

To link to this article: http://dx.doi.org/10.1080/10587259508038736

Mol. Cryst. Liq. Cryst. 1995, Vol. 260, pp. 631–640
Reprints available directly from the publisher
Photocopying permitted by license only

MICELLAR NEMATIC LYOPHASE IN THE MIXTURE OF SODIUM OLEATE AND GLACIAL ACETIC ACID.

NAGAPPA, HANUMANTHA NAYAK. R., JAGADISH. K.N.,* SIVA PRASAD. A.,SOMASHEKAR. R. AND LOKANATH RAI. K.M.*
Department of Physics, University of Mysore, Manasagangotri, Mysore - 570 006, INDIA.
*Department of Chemistry,University of Mysore, Manasagangotri, Mysore - 570 006, INDIA.

ABSTRACT Lyotropic micellar nematic and smectic phases observed in the mixture of sodium oleate and glacial acetic acid has been studied by X- ray and optical methods. It is found that a nematic phase is observed with small concentration of sodium oleate at higher temperatures. Smectic A and Smectic E phases also occur at lower temperatures and with low concentration of sodium oleate. Optical anisotropy of lyotropic nematic phase has been estimated using experimental values of density and refractive index data. The order parameter of the micellar nematic phase is calculated from the optical data. X - ray diffraction study was carried out in smectic phase. Many striking optical textures like fan, focal conic and drops with low concentration of sodium oleate are also illustrated.

INTRODUCTION

Lyotropic nematic liquid crystals are frequently observed in samples with the high concentration of some surfactant solutions of anisometric micelles which possessing long range orientational order[1-4]. Generally stable micellar nematic phases occur over a wide temperature and composition in a two component system between isotropic micellar solution and smectic phase[5,6]. Nematic phase of disc shaped micelles N_D and cylindrical shaped micelles N_C occur in some of the lyotropic systems. Example, Caesiumpentadecafluoro octanoate (CsPFO)/water[7] system exhibits a nematic phase N_D which occurs intermediate to a lamellar phase and an isotropic micellar solution[8].

The lyotropic phase transitions I-N_D-L correspond with the thermotropic isotropic (I) - Nematic (N) - Smectic A (S_A) exhibited by rod shaped molecules. A similar correspondence in symmetries exist between the phases involved in the lyotropic I - N_C - H transitions and those in the thermotropic I - N - columnar transitions exhibited by disc shaped molecules. Our aim is to emphasize on the possibilities of the general and simple method which permits not only of obtaining the micellar nematic phase but also smectic A and smectic E phases in the mixture of sodium oleate and glacial acetic acid.We present here the results of x-ray studies in smectic E phase which appears at room temperature and birefringence and texture studies for micellar nematic phase N_D at higher temperatures. In the light of the above investigations we are able to understand the coupling between aggregate structure and mesophase order.

EXPERIMENTAL

The material used in this investigation viz., sodium oleate is obtained from The British Drug house Ltd., England and glacial acetic acid from Kodak Ltd., Kodak house, Bombay. Sodium oleate is further purified twice by recrystallisation method using benzene as asolvent. The concentrations were prepared by mixing sodium oleate with acetic acid in a sealed container which were then heated to 100°C for about six hours. The samples were subjected to several cycles of heating, stirring and centrifuging to ensure homogenity.

The transition temperatures of the mixtures in different phases were obtained in the course of heating or cooling using hot stage and polarizing microscope. The partial phase diagram of sodium oleate in glacial acetic acid shown in

fig.1 and indicates that by increasing the sodium oleate concentration the nematic range decreases and finally ceases to exist for a mole fraction X > 0.096. The phase transition from N_D -L is very well accounted with the help of Mcmillan s mean field theory[9], which explains the general features of N-S_A transition in thermotropic liquid crystals. Chandrasekhar et.al.,[10] also elucidated the experimental studies on N-S_A transition of the nematic mixtures and located the tricritical point where the change of phase occurs from first order to second order. In the present study we conclude that I-N_D transition is first order and N_D - L transition is second order because of coexistence of phases near I - N_D transition. The second order transition of N_D - L phase indicates that there is a continuity in the structure of the amphiphile aggregate. Therefore, it infers that at N_D - L transition, the nematogenic disc shaped micelles condense on the lamellar planes instead of aggregate into infinitely extending molecular lamellae[8,11]

TEXTURE STUDIES

Optical texture studies have been carried out using Leitz orthoplan polarizing microscope. All the textures obtained here are at low concentration of sodium oleate from 2 to 10%. The schlieren texture[12,13] obtained at higher temperature of the samples between 2 to 10% of sodium oleate correspond to the micellar nematic phase is shown in fig. 2(a), 2(b) and 2(c). On further cooling, N_D phase changes to L phase which is characterised by the focal conic and fan texture is shown in Fig 3(a), 3(b). Before crystallising the smectic A phase changes over to smectic E phase which is characterized by radial crosses on the ellipses shown in fig 4. Occasionally in some regions we get drops and maltase

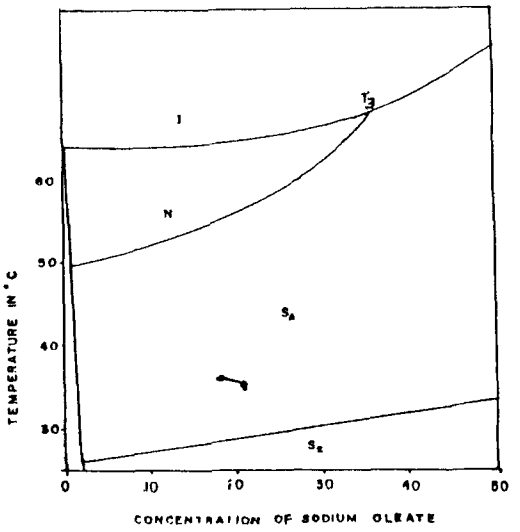


Fig.1. Partial phase diagram of binary mixture of sodium oleate and glacial acetic acid.

(b)

(c)

Fig.2. Microphotographs of Schlieren texture of micellar nematic phase between the concentration 2 to 10% of Sodium oleate at higher temperature. Crossed polars. a).120x. b) 150x. c) With only polarizer 150x.

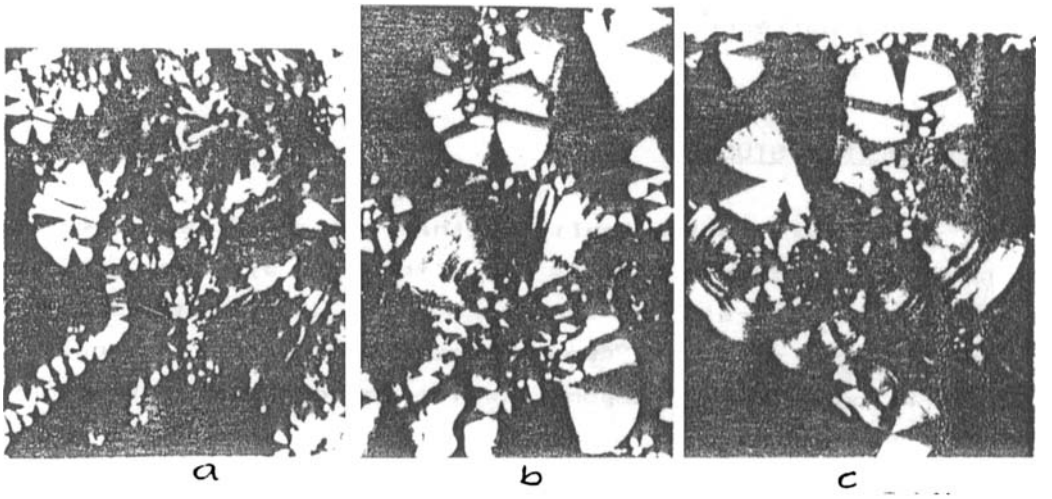
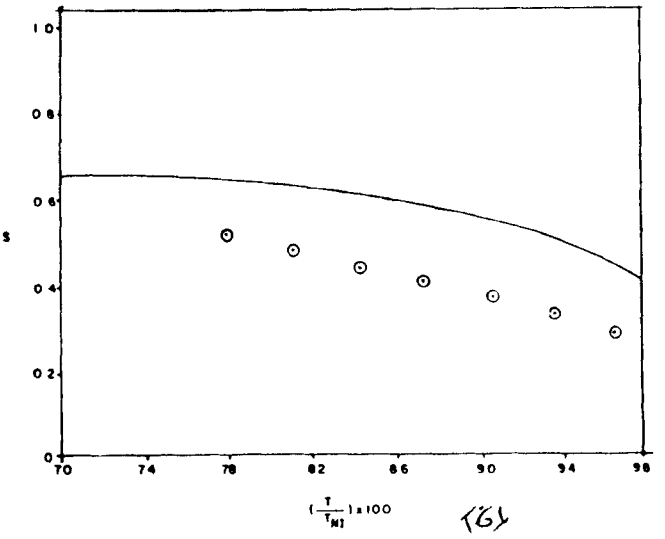


Fig.3. Microphotographs of a) focal conic with Schlieren texture for phase transition from nematic to smectic. Crossed polars 500x. b) Focal conic fan shaped texture. Crossed polars 500x.

Fig.4. Microphotograph of focal conic texture with radial crosses.Crossed polars 400x.



(5)

Fig.5. Microphotograph of drops with crossed polars 400x.

Fig.6. Temperature variation of order parameter of micellar nematic phase. The solid line represents Maier-Saupe curve.

crosses as shown in fig. 5. The drops exhibit H_v and V_v scattering patterns.

BIREFRINGENCE STUDIES

It is very well established that the micellar nematic phase in lyotropic system is formed by amphiphilic aggregation with bilayer structure[14]. As in nematic phase the bilayer micelles show some degree of parallel orientation which is responsible for macroscopic anisotropy of the phase[15].

The birefringence studies are useful forthe estimation of the order parameter and also helpful to understand the degree of orientation of the micelles[11,15]. In the present investigation we have measured the temperature variation of two refractive indices n_1 and n_2 of the mixture for lower concentration of sodium oleate using Abbe refractometer for the wavelength 589.3 nm in the nematic and smectic phases. The refractive index n_1 due to extraordinary ray is polarized parallel to the length of the specimen and n_2 due to ordinary ray is polarized perpendicular to the length of the specimen and lying in the plane of the specimen. Saupe[13] used the modified Lorenz.-Lorentz formula[16] for the calculation of orientational orderparameters. The ordinary and extraordinary indices n_1 and n_2 are

$$(n_1^2 - 1)/(n_1^2 + 2) = 4\pi/3\ N[W_{AC}\alpha_o(AC) + W_{SO}\alpha_o(SO) + 2/3\ W_{so}\Delta\alpha\ (SO)S] \quad \text{------ (1).}$$

$$(n_2^2 - 1)/(n_2^2 + 2) = 4\pi/3\ N[W_{AC}\alpha_o(AC) + W_{SO}\alpha_o(SO) - 1/3\ W_{so}\Delta\alpha(SO)S] \quad \text{------ (2).}$$

where N is the number of molecules per unit volume and W_{AC} and W_{SO} are mole fractions of the acetic acid and sodium oleate respectively. α_os are the mean polarizabilities of sodium oleate and acetic acid. For the estimation of the orientational order parameters we assume the contribution of birefringence (Δn) is only due to sodium oleate[17] because the polarizability tensor of sodium oleate can be approximated with principal polarizibility α_1 parallel to the long axis and α_2 perpendicular to it. The optical anisotropy ($\Delta\alpha$) contribution from acetic acid is neglected. Therefore, only ($\Delta\alpha$) of sodium oleate molecule is considered. $(\Delta\alpha) = (\alpha_1 - \alpha_2)$ and $S = 1/2\ (3\cos^2\theta - 1)$ is the degree of order of sodium oleate molecule where θ is the angle between long molecular axis and the optic axis of the nematic phase. $\cos^2\theta$ is the average over the molecular motion.

Subtracting equation (2) from (1) and using $\Delta n = (n_1 - n_2) \ll 1$ we obtain

$$\Delta n = [2\pi\ (n_2^2+2)^2 N\Delta\alpha\ W_{so} S]/9n_2 \qquad \text{---------} \quad (3)$$

In order to estimate the value of optical anisotropy ($\Delta\alpha$) of sodium oleate molecule, the values of $(\alpha_{\parallel})_{eff}$ i.e., polarizability along the long axis of the molecule and $(\alpha_{\perp})_{eff}$ the polarizability perpendicular to the long axis of the molecule are to be determined. The value of $(\alpha_{\parallel})_{eff}$ of each methylene group is calculated from the optical anisotropy of the bond polarizability for 5893 Å[18,19] assuming that the molecules have all transcofiguration. And hence $(\alpha_{\perp})_{eff}$ may also be calculated. Using the values of $(\alpha_{\parallel})_{eff}$, $(\alpha_{\perp})_{eff}$ and α the mean polarizability, the value of $(\Delta\alpha)$ is estimated[20] The value of $(\Delta\alpha)$ for sodium oleate molecule turns out to be 11.55×10^{-24} cm^3. The order parameter S of the micellar

nematic phase is calculated with the help of ($\Delta\alpha$) value. Temperature variation of order parameter is shown in fig 6. Boden et.al, pointed out in their study that the variation of the birefringence with temperature is dependent upon both the size and shape of the micelles in addition to their dependence on orientational order. However, we also notice that order parameter varies with mole percent in the micellar nematic phase. It is observed that the order parameter decreases with decreasing sodium oleate concentration. Maier-Saupe curve is also shown in fig.6. The values of birefringence are in good agreement with that measured by interference technique explained in one of our earlier paper[21].

NMR and IR studies are also carried out to show the existence of smectic E phase at room temperature.

X-RAY DIFFRACTION STUDIES

Order parameter of micellar nematic phase is very well documented from X-ray diffraction studies by earlier investigators[8,9]. Unfortunately we are unable to carry out X-ray diffraction studies at higher temperature range where the micellar nematic phase exists.

X-ray recording for the mixture at room temperature is carried out using Joel (Japan) make with the following settings - 35Kv, 15mA, TC 4, CPS 400, Channel Centre 100, Channelwidth100, λ=1.934 Å. This recording indicates reflections which correspond to E phase. The cell parameters were obtained by using a multidimensional minimization (simplex) programme. Here the programme starts with an initial set of parameters ($a,b,c,\alpha,\beta,\gamma$) and refines these set of parameters until all the observed reflections are accounted to within ±1% of the experimental d spacings. The parameters thus obtained are given in table (1).It also

gives the volume of the unit cell as $183.67\times10^{-23}cm^3$ which is the approximate volume of the micelle.

Standard deviation is < 1%

$a=12.38\times10^{-8}cm$	$b=10.66\times10^{-8}cm$	$c=14.18\times10^{-8}cm$
$\alpha=97.98$	$\beta=86.57$	$\gamma=94.07$

Table(1)

CONCLUSION

The nematic lyomesophases are useful solute hosts. These general micellar properties are combined with anisotropic orientational effects arising from aggregates shapes and magnetic properties. The microscopic investigation allows us to differentiate the three phases $I-N_D-S_A-S_E$. The phase diagram exhibits the phase behaviour and reveals that micellar nematic phase exists at low concentration and high temperature and smectic A and E phases at lower temperature. Birefringence study reveals that the contribution of birefringence is mainly due to sodium oleate. The above facts are also supported by NMR, IR, X-ray and Optical texture studies.

ACKNOWLEDGEMENTS

One of us (Hanumantha Nayak) is thankful to the University Of Mysore for the award of Junior Research Fellowship and principal investigator Prof.Nagappa thank DST, Govt.Of India for financial support and also thank Prof.N.V.Madhusudana, Raman Research Institute for his valuable suggestions.

REFERENCES

1. B.J.Forrest, L.W.Reeves. Chem. Rev. 81, 1 (1981)
2. A.Saupe. Navo Cemento 3, 16 (1984)
3. V.Ramesh, M.M.Labes. J.Am.Chem.Soci. 108, 4643 (1986)
4. Y.Hendrikx, J.Marvolin. J.Phys.(Paris) 42, 1427 (1981)
5. N.Boden, R.J.Bushby, K.W.Jolley, M.C.Holmes, Sixl.Mol.Cryst.Liq.Cryst. 152, 37 (1987)
6. N.Boden, K.Radly, M.C.Holmes. Mol. Phys. 42, 493 (1981)
7. N.Boden, M.C.Holmes.Chem.Phys.Letts.109, 176 (1984)
8. N.Boden, P.P.H.Jackson, K.Mcmillan, M.C.Holmes. Chem.Phys.Letts.65, 476 (1979)
9. N.Boden, M.C.Holmes. Chem.Phys.Letts. 109, 1 (1984)
10. V.N.Raja, S.KrishnaPrasad, D.S.Shankar Rao, S.Chandrasekhar. Liq. Cryst. 12, 2239 (1992)
11. B.D.Larson, J.D.Litster. Mol. Cryst. Liq.Cryst. 113, 13 (1984)
12. L.J.Yu, A.Saupe. Phys. Rev. Letts. 45, 1000 (1980)
13. A.Saupe, P.Boonbrahm, L.J.Yu. J.Chem.Phys. 80, 7 (1983)
14. Tom Haven, Keith Radley, A.Saupe. Mol. Cryst. Liq. Cryst. 75, 87 (1981)
15. P.Boonbrahm, A.Saupe. J.Chem.Phys. 81(4), 2076 (1984)
16. J.Chavolin, A.M.Leveleiet, E.T.Samulski. J.Phys. Letts.(Paris) 40L, 587 (1979)
17. Tomhaven, Keith Radely, A.Saupe. Mol.Cryst. Liq. Cryst. 75, 87 (1987)
18. G.Leferve, R.J.W.Leferve. Phys. Methods Of Chemistry Ed. A.Weissberger and B.W.Rositer (Weily International Science, New York) 1972, Part-2 Page-437
19. C.W.Bunn. Chem.Crystallography (Clarendon press, Oxford 1961) Second Edn.
20. R.Somashekar, D.Krishnamurti. Mol.Cryst. Liq. Cryst 85 (1981)
21. Nagappa, D.Revannasiddaiah, D.Krishnamurti. Mol.Crys. Liq. Cryst. 103, 1113 (1983)