Volume 1 Issue 1

CHEMICAL PHYSICS

An International Journal

Full Paper

CPAIJ, 1(1), 2016 [001-005]

Optical studies and order parameter of lyotropic chromonic liquid crystalline phase

T.N.Govindaiah

Research Centre, Post-Graduate Department of Physics, Government College (Autonomous), Mandya-571401, (INDIA)

E-mail: tngovi.phy@gmail.com

ABSTRACT

We report the results of our studies on the optical and thermal properties of binary mixture of two compounds viz., abietic acid and poly ethylene glycol. The mixture shows a very interesting co-existent biphasic region of lyotropic nematic (N+I) and intermediate hexagonal M+I phases, sequentially when the specimen is cooled from its isotropic phase respectively at different concentrations of abietic acid in poly ethylene glycol molecule. The order parameter (S) of the co-existent biphasic region of lyotropic nematic (N+I) phase is estimated with the help of temperature dependence of optical anisotropy from the measured values refractive index and density data. The temperature variation of order parameter of the experimental curve is very well fitted with the Mayer–Saupe theoretical curve.

KEYWORDS

Lyotropic chromonic;
Molecular orientation;
Phase formation;
Optical anisotropy.

INTRODUCTION

In recent years, the existence of a second class of aqueous lyotropic mesophase termed chromonic liquid crystals, which has come to be better recognized and understood[1-3]. Unlike typical lyotropic phases formed by amphiphilic molecules having a hydrophilic head and a hydrophobic tail, chromonic liquid crystals are formed by water-soluble molecules that contain planar aromatic rings. Examples of chromonic liquid crystals-forming molecules include drugs, dyes, and nucleic acids[4, 5].

Chromonic liquid crystals are still not understood to the same extent as amphiphile-based lyotropic liquid crystals. Lydon has recently summarized the current state of knowledge on chromonics in two excellent reviews[2, 3]. Note that chromonic molecules do not show a clear separation of hydrophilic and hydrophobic parts, since the hydrophilic (ionic or hydrogen-bonding) groups that impart water solubility are distributed all around the periphery of the hydrophobic aromatic rings. Consequently, chromonic molecules do not form micelles, nor do they show any appreciable surface activity. However, the presence of some solvent, the disc, planar, cylindrical molecule leads to a weak interaction, resulting in a face-to-face stacking of the molecules, which leads to co-existent biphasic region of lyotropic chromonic liquid crystalline phases[6]. The nematic N phase corresponds to a uniaxial stacking of these columns with no positional order. At higher concentrations of the molecules, an aggregated columnar (C), hexagonal (M) phases are also occurs, with both orientational and positional order of the columns[7].

In the present investigation, we have shown the co-existent biphasic region of N+I, M+I, lyotropic nematic (N_D) and highly order hexagonal (M_H) phases respectively at different concentrations in the binary mixture of abietic acid in poly ethylene glycol. They were observed using microscopic technique and also have been verified from the results of DSC and Optical anisotropic techniques. From the experimentally measured data of ultrasonic velocity, density and refractive indices, thermodynamic and other related parameters are calculated.

EXPERIMENTAL

Mixtures of twenty five different concentrations of Abietic acid in Poly Ethylene glycol (PEG) were prepared and they were mixed thoroughly. These mixtures of concentrations were kept in desiccators for six hours. Samples were subjected to several cycles of heating, stirring and centrifuging to ensure homogeneity. Phase transition temperatures of these mixtures were measured with the help of a polarizing microscope in conjunction with a hot stage. The samples were sandwiched between the slide and cover slip and were sealed for microscopic observations. DSC thermograms were taken for mixtures of all concentrations using the Perkin-Elmer DSC II Instrument facility available at Raman Research Institute, Bangalore, India. The density and refractive indices in the optical region are determined at different temperatures by employing the techniques described by the earlier investigators[8, 9].

RESULTS AND DISCUSSION

Optical texture studies

The detail phase diagram of binary system of Abietic acid in Poly Ethylene glycol has been reported in our earlier publication[10]. For the purpose of optical texture studies the sample was sandwiched between the slide and cover glass and then the optical textures were observed using Leitz-polarizing microscope in conjunction with specially constructed hot stage. Mixture of 5% to 48% of abietic acid is cooled from its isotropic liquid phase, a genesis of nucleation starts in the form of molecular orientations, which grow and segregate the molecules, which identified as co-existent biphasic region of nematic (N+I) phase and the texture as shown in Figure 1. On further cooling, N+I phase changes over to lyotropic nematic (N_D) phase and this phase produces a schlieren texture with disclinations (characterized by two dark brushes of extinction) and

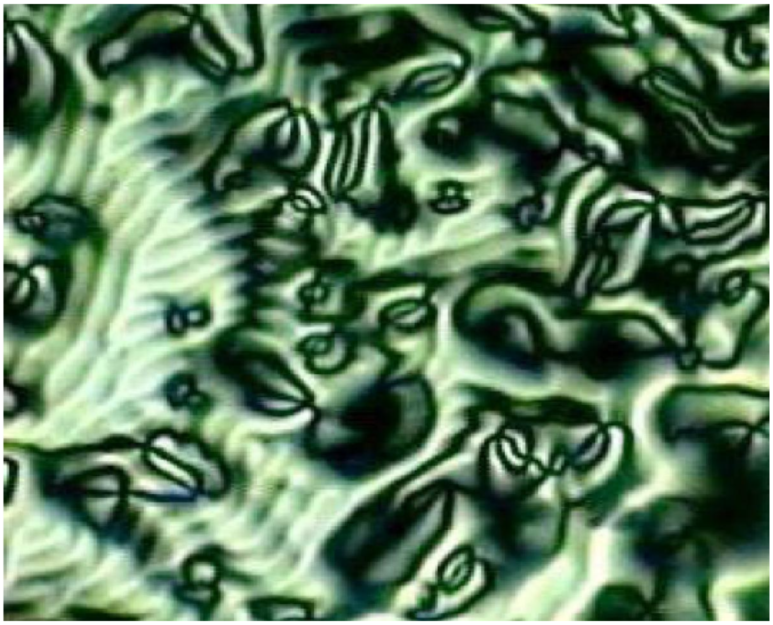

Figure 1 : Microphotographs obtained in between the crossed polars, Co-existent biphasic region of nematic (N+I) phase (250X)

point defects-boojums (with four brushes of extinction)[11]. Above 48% of abietic acid, the binary mixture exhibits a biphasic region of aggregated intermediate hexagonal (M+I) phase. In this phase, molecules are stack to form hexagonal order. There is long-range positional order among the oriented molecules. On further cooling at different temperatures, co-existent biphasic region of intermediate hexagonal (M+I) phase slowly changes over to aggregation of M_H phase respectively. Due to exhibition of this behavior, chromonic liquid crystals hold great promise to applications as optical materials and devices[12–24]. Here it is pertinent to remark that low concentrations of abietic acid with poly ethylene glycol molecule exhibits N+I phase and high concentrations of abietic acid with poly ethylene molecule show M+I phases. This type of behavior observed only in chromonic liquid crystal system[25]. For samples having the concentration 48% of abietic acid, the optical textures are not clear. In this region, the sample shows viscous nature.

Birefringence studies

The co-existent biphasic region of nematic (N+I) phase in lyotropic system is generally formed by amphiphilic aggregation with bilayer structure[26]. As in biphasic region of nematic phase of lyotropic system, the bilayer micelles show some degree of parallel orientation, which is responsible for the macroscopic anisotropy of the phase. The birefringence study helps us to understand the optical anisotropic properties of the samples. The orientational order parameter of the co-existent biphasic region of nematic (N+I) phase is essential to understand the degree of orientations of the micelles[27].

In the present investigation we have measured the temperature variation of the refractive indices (n_1 and n_2) and densities for the mixture of different concentrations of Abietic acid in Poly Ethylene glycol by using Abbe Refractometer and Precision Goniometer spectrometer using the wavelength 589.3 nm in the co-existent biphasic region of nematic (N+I) phase and biphasic region of aggregated intermediate hexagonal (M+I) phases. The refractive index n_1 due to extraordinary ray and n_2 due to ordinary ray have been determined. Saupe[28] used the modified Lorentz-Lorentz[29] formula for the calculation of orientational order parameters of the lyotropic mixture. The refractive indices n_1 and n_2 are given by

$$\frac{n_1^2-1}{n_2^2+2}=4\frac{\pi}{3N}\left[W_{PEG}\alpha_{PEG}+W_{Abieticacid}\alpha_{Abieticacid}-\left(\frac{2}{3}\right)W_{Abieticacid}\Delta\alpha_{Abieticacid}S\right] \quad \textbf{(1)}$$

$$\frac{n_1^2-1}{n_2^2+2}=4\frac{\pi}{3N}\left[W_{PEG}\alpha_{PEG}+W_{Abieticacid}\alpha_{Abieticacid}-\left(\frac{1}{3}\right)W_{Abieticacid}\Delta\alpha_{Abieticacid}S\right] \quad \textbf{(2)}$$

where, N is the number of molecules per unit volume of the mixtures and W_{PEG} and $W_{\text{Abietic acid}}$ are the mole fractions of PEG and Abietic acid respectively, α is the mean polarizability of the respective compounds. For the estimation of orientational order parameter of the co-existent biphasic region of nematic (N+I) phase, we assume only the birefringence Δn of the Abietic acid molecules[30]. Because the polarizability tensor of Abietic acid can be approximated with principle polarizability $_1$ parallel to the long axis of the molecule and $_2$ is perpendicular to it. The optical anisotropy ($\Delta\alpha$) contribution from acetic acid is neglected. Therefore, only of Abietic acid molecules is considered, $\Delta\alpha = (\alpha_1 - \alpha_2)$ =and $S=\frac{1}{2}[3\cos^2\theta-1]$ is the degree of order of the Abietic acid molecules, where is the angle between the long molecular axis and optic axis of the molecular disc in the co-existent biphasic region of nematic (N+I) phase phase and $\cos^2\theta$ is the average over the molecular motion.

From the equations 1 and 2, and using $\Delta n = (n_e - n_o) << 1$ we obtain

$$\Delta n = \frac{\left[2\pi(n_2^2+2)^2 N\Delta\alpha W_{Abieticacid} S\right]}{9n_2} \quad \textbf{(3)}$$

In order to estimate the value of optical anisotropy ($\Delta\alpha$) of Abietic acid molecule, the value of $(\alpha_{||})_{eff}$ i.e., the polarizability along the axis of the molecules and $(\alpha_{\perp})_{eff}$ the polarizability perpendicular to the long axis of the molecule, the value of $(\alpha_{||})_{eff}$ of each group is calculated from the optical anisotropy of bond polarizability data for the wavelength 5893 ú[31] assuming that the molecules have all trans-configuration and hence $(\alpha_{\perp})_{eff}$ may also be calculated. Using the values of $(\alpha_{||})_{eff}$, $(\alpha_{\perp})_{eff}$ and α the mean polarizability, the value of $\Delta\alpha$ is estimated[32]. The value of ($\Delta\alpha$) for Abietic acid molecules turns out to be 37.358x10^{-24} cm^3. The order parameter (S) of the lyotropic micellar nematic phase is calculated with the help of ($\Delta\alpha$) value. The order

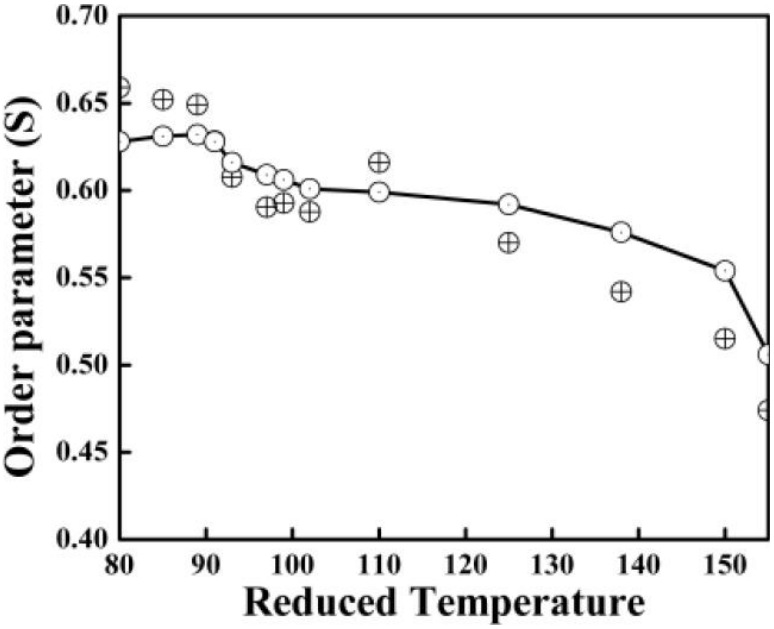

Figure 2 : Temperature variations of order parameter of co-existent biphasic region of nematic (N+I) phase

parameter (S) value of the mixture was estimated at different temperatures for different concentrations. Boden et al[33] have pointed out in their study that the variation of birefringence with temperature is dependent upon both the size and shape of the micelles, in addition to their dependence on the orientational order. However, we also notice that the order parameter varies with mole percent of Abietic acid in the co-existent biphasic region of nematic (N+I) phase. It is observed that the order parameter (S) decreases with decreasing the concentrations of Abietic acid. The temperature variations of order parameter of the co-existent biphasic region of nematic (N+I) phase are as shown in Figure 2, the experimental values of the order parameters are compared with the Maier-Saupe theoretical curve. It is observed that, the trend of the variation of order parameter (S) values agrees with the Maier-Saupe theoretical curve. The values of birefringence are in good agreement with the values measured using the interference techniques[34].

CONCLUSIONS

Microscopic investigation of the binary mixture of Abietic acid in Poly Ethylene glycol shows the existence co-existent biphasic region of lyotropic nematic (N+I) and intermediate hexagonal M+I phases for different concentrations and at different temperatures. Birefringence study shows the contribution of birefringence of the given mixture is mainly due to Abietic acid. From the optical anisotropic technique it has been observed that: the variation of order parameter values are in good agreement with the Maier-Saupe theoretical curve.

REFERENCES

[1] T.K.Attwood, J.E.Lydon, C.Hall, G.J.T.Tiddy; Liq.Cryst., **7**, 657-668 **(1990)**.

[2] J.E.Lydon; Curr.Opin.Colloid Interface Sci., **3**, 458-466 **(1998)**.

[3] J.E.Lydon; Curr.Opin.Colloid Interface Sci., **8**, 480-490 **(2004)**.

[4] T.K.Attwood, J.E.Lydon; Mol.Cryst.Liq.Cryst., **108**, 349-357 **(1984)**.

[5] T.N.Govindaiah, H.R.Sreepad, Nagappa, J.Mahadeva, Mol.Cyst.Liq.Cryst., **593**, 43-50 **(2014)**.

[6] Y.A.Nastishin, H.Liu, S.V.Shiyanovskii, O.D.Lavrentovich, A.F.Kostko, M.A.Anisimov; Phys.ReV.E., **70**, 051706, **(2004)**.

[7] Luana Tortoraa, Oleg D.Lavrentovich; PNAS., **108(13)**, 5163-5168 **(2011)**.

[8] Nagappa, D.Revanasiddaiah, D.Krishnamurti; Mol.Cryst.Liq.Cryst., **101**, 103 **(1983)**.

[9] J.Thiem, V.Vill, F.Fischer; Mol.Cryst.Liq.Cryst., **170**, 43 **(1989)**.

[10] T.N.Govindaiah, H.R.Sreepad; Phase Transition, **88(2)**,183-191 **(2015)**.

[11] M.Kleman, O.D.Lavrentovich; Soft Matter Physics, Springer-Verlag New York.P, 36 **(2003)**.

[12] S.V.Shiyanovskii, O.D.Lavrentovich, T.Schneider, T.Ishikawa, I.I.Smalyukh, C.J.Woolverton, G.D.Niehaus, K.J.Doane; Mol.Cryst.Liq.Cryst., **434**, 259/587-270/598 **(2005)**.

[13] S.V.Shiyanovskii, T.Schneider, I.I.Smalyukh, T.Ishikawa, G.D.Niehaus, K.J.Doane, C.J.Woolverton, O.D.Lavrentovich; Phys.Rev.E, **71**, 020702/1(R) **(2005)**.

[14] S.L.Helfinstine, O.D.Lavrentovich, C.J.Woolverton; Lett.Appl.Microbiol., **43**, 27-32 **(2006)**.

[15] K.Ichimura, M.Momose, K.Kudo, Haruhisa Akiyama, N.Ishizuki; Langmuir, **11(7)**, 2341-2343 **(1995)**.

[16] K.Ichimura, T.Fujiwara, M.Momose, D.Matsunaga; J.Mater.Chem., **12**, 3380-3386 **(2002)**.

[17] C, Ruslim, M.Hashimoto, D.Matsunaga, T.Tamaki, K.Ichimura; Langmuir, **20(1)**, 95-100 **(2004)**.

[18] S.W.Tam-Chang, W.Seo, I.K.Iverson, S.M.Casey; Angew.Chem.Int.Ed., **42**, 897-900 **(2003)**.

[19] S.W.Tam-Chang, L.Huang; Chem.Commun., **17**, 1957-1967 **(2008)**.

[20] M.Lavrentovich, T.Sergan, J.Kelly; Liq.Cryst., **30**, 851-859 **(2003)**.

[21] M.Lavrentovich, T.Sergan, J.Kelly; Mol.Cryst.Liq.Cryst., **409**, 21-28 **(2004)**.

[22] T.Fujiwara, K.Ichimura; J.Mater.Chem., **12**, 3387-3391 **(2002)**.

[23] Christian Ruslim, Daisaku Matsunaga, Masanori Hashimoto, Takashi Tamaki, Kunihiro Ichimura; Langmuir, **19(9)**, 3686-3691 **(2003)**.

[24] Heung-Shik Park, Oleg D.Lavrentovich, Edited by Quan Li, John Willey, Sons; 449 **(2012)**.

[25] T.N.Govindaiah, H.R.Sreepad, Nagappa; Mol.Cryst.Liq.Cryst., **570**, 101-108 **(2013)**.

[26] T.Haven, K.Radley, A.Saupe; Mol.Cryst.Liq.Cryst., **75**, 87 **(1981)**.

[27] P.Boonbrahm, A.Saupe; J.Chem.Phy., **81**, 2076 **(1984)**.

[28] A.Saupe, P.Boonbrahm, L.J.Yu; J.Chem.Phys., **80**, 3 **(1983)**.

[29] J.Chavolin, A.M.Leveveiet, E.T.Samulski; J.Phys.Letts.(Paris)., **40(L)**, 587 **(1979)**.

[30] A.Saupe, P.Boonbrahm, L.J.Yu; J.Chem.Phys., **80**, 7 **(1983)**.

[31] C.W.Bunn; Chemical Crystallography, 2nd Edtion, Clarendon Press: Oxford, **(1961)**.

[32] R.Somashekar, D.Krishnamurti; Mol.Cryst.Liq.Cryst., **65**, 3 **(1981)**.

[33] N.Boden, P.P.Jackson, K.Mc Mullen, M.C.Holmes; Chem.Phys.Lett., **65**, 476 **(1979)**.

[34] Nagappa, D.Revannasiddaiah, D.Krishanamurti; Mol.Cryst.Liq.Cryst. **103**,101 **(1983)**.