Dipolemoment Studies of Ethoxy Phenyl Azo Phenyl Valerate

L Tanuj Kumar[1], B. Rupa Venkateswara Rao[2], P.Valli Rani[1], S. Sreehari Sastry[3]

[1, 2, 3]Dept of Physics
[1]Ramachandra College of Engineering, Eluru-534007, India
[2]V.R. Siddhartha Engineering College, Vijayawada-52007, India
[3]Acharya Nagarjuna University, Nagarjunanagar-522510, India

Abstract- *Polarizing optical microscopic studies reveal that the EPAP Valerate is having single phase variant nematic and it is also enantiotropy. The low frequency static dielectric constant and microwave frequency dielectric permittivity increased with increase in the concentration of the solute in non-polar solvent benzene at room temperature. There is a decrease in the relaxation time as the concentration of the EPAP Valerate is increased in solute system. Dipole moment value is calculated experimentally and theoretically (AM1 Method) and also compared with the reported value. They are also in good agreement.Dipole moment value obtained from the dilute solution method is sufficient to determine the dipole moment in liquid crystal phase.*

Keywords- EPAP Valerate, Frequency, Non- polarsolvent, Dipolemoment.

I. INTRODUCTION

The subject of liquid crystals has gained considerable momentum in recent years. This is mostly because of very useful application. The liquid crystals have found in industry and technology. Notable applications are their use in digital and analog indicators, information display devise and TV screens etc. Liquid crystal wrist watches and calculator may also be mentioned. Apart from the application point of view, the liquid crystals offer a very important and interesting study from purely academic aspect. These have properties common to both solids and liquids; As such the better understanding of liquid crystal may offer a possibility of understanding the liquid state in better way. The dielectric parameters of liquid crystals play an important role in the development of electro-optical devices[1-6]. Frequency and temperature dependent dielectric studies of different phases give information not only about bulk properties but also about molecular parameters and their mutual association and rotation under an applied electric field. Substances with high dielectric constants are widely used in the electronics industry [7-10]. The dielectric materials that are used as inter layers in electronic chips they significantly increase the speed of propagation of electric impulses and reduce dielectric losses.

The effect of frequency on dielectric properties offers valuable information about the localized charge carrier that helps to explain the mechanism responsible for charge transport phenomena and dielectric behavior.

II. EXPERIMENTAL DETAILS

Thermal Polarizing Optical Microscopy:

Liquid crystalline compounds are birefringent and exhibit different optical textures for different phases under crossed polars. To identify the different phases and to determine transition temperatures a polarizing microscope, OLYMPUS BX50 (serial number 56512, made in Japan) with computer controlled Instec (USA) temperature controller hot stage is used. To photograph the textures the polarizing microscope is provided with a DP 10 camera attachment. Accuracy of temperature measurement is $\pm\,0.1\,^{\circ}C$.

Dielectric methods:

There is no single experimental method of measuring the dielectric constant and the loss factor of the polar liquids at all frequencies. It was necessary to employ different techniques to investigate the dielectric properties of liquids over the available frequency ranges. Moreover, at a single frequency, different methods depending upon loss factor of the liquids are being investigated and also at different frequencies (optical frequency, low frequency (LCR Bridge) and at microwave frequencies). The viscosity and dipolar interaction effects usually complicate the interpretation of dielectric data in pure liquids. Also, the form of the internal field has been a subject of controversy in deriving conclusions from dielectric absorption data of pure liquids. In a polar liquid, the large electrostatic interactions between molecules modify their rotational freedom and alter the reaction fields in the medium to a large extent. In pure liquids the interactions between neighbouring molecules tend to be somewhat specific. So, there is much to recommend their investigation as solutes in dilute solutions in a polar or non-polar solvent, particularly, if the results are extrapolated towards zero concentration to

eliminate solute-solute interactions [12]. Also to avoid the much disputed ambiguity concerning the internal field correction, the dielectric relaxation time is preferably measured in dilute solutions of a non-polar solvent[2,3]. In such studies, the solute molecules will be isolated from each other depending on the concentration used, which means that the solute molecules will be in a quasi-isolated state. Further, the dipole-dipole interaction effects will be minimized. The resulting dipole moment value will be close to the gaseous value and the relaxation time will be microscopic type.

The accuracy of measurement of dielectric constant (ε') and the dielectric loss (ε'') in dilute solutions is of primary importance in deriving molecular parameters. The two most widely used methods of Von Hippel[4] and Heston e*t.al*[5] for dilute solution measurements involve mathematical expressions derived with approximations of the theoretical formula, apart from the time-consuming standing wave ratio measurements. Although curve fitting methods have been reported for the evaluation of ε' and ε'' in pure liquids [11-13], reports of similar techniques are not available for dilute solution measurements. The present chapter deals with a simplified plunger technique for the precise evaluation of the attenuation constant (α) and the phase constant (β) in dilute solutions in X-band region.

III. RESULTS AND DISCUSSION

Preparation of samples:

EPAP Valerate was supplied by M/s Eastman Organics, USA. Benzene was supplied by M/s Qualigens and it is ExcelaR grade and was double distilled before use. Benzene is used as solvent, and EPAP Valerate is used as the solute in the preparation of solution. EPAP Valerate is dissolved in benzene in various concentrations, the various weights of EPAP Valerate for each concentration is given in Table 1 for 25.0 ml (volume of plunger) of benzene. All the weights are measured using a single pan electronic balance Dhona make, model 100 DS with an accuracy of 0.01 mg.

Table .1: Mole fraction and weights of EPAP Valerate

Mole fraction of EPAP Valerate in benzene	Weight of EPAP Valerate (gm)
0.02 %	1.78132
0.03 %	3.63686
0.04 %	5.57137
0.05 %	7.58998

Ethoxy Phenyl Azo Phenyl Valerate (EPAP Valerate, whose structure is shown in **Plate 3.1)** in benzene for different concentrations are also given.
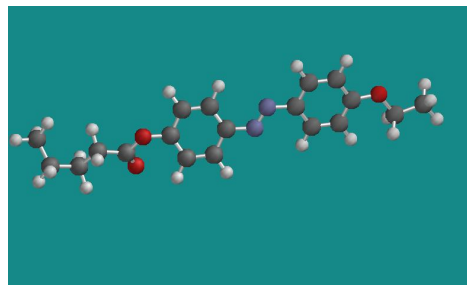
RED-OXYGEN, VIOLET-NITROGEN, WHITE-HYDROGEN, BLACK-CARBON ATOM

PLATE 3.1: STRUCTURE OF EPAP VALERATE

POLARISING MICROSCOPIC STUDY **:-**

The compound EPAP Valerate, which belongs to the azo compounds family [14-18], exhibits a single phase variant in between solid crystal (**Plate 3.2**) and isotropic phase. The observed phase is enantiotropic
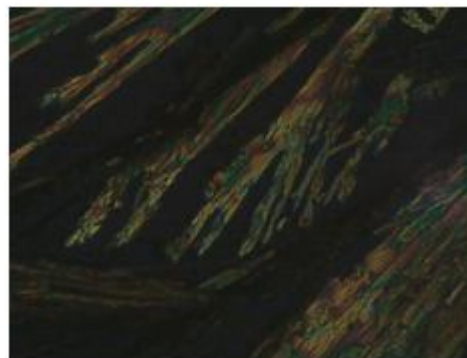

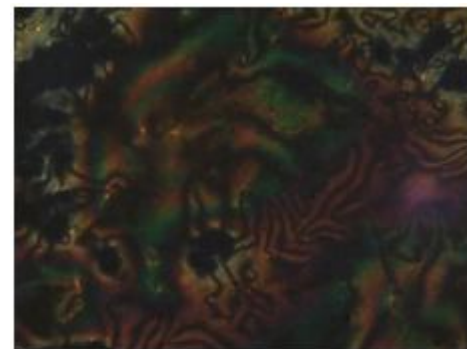Plate 3.2: Solid phase of EPAP Valerate

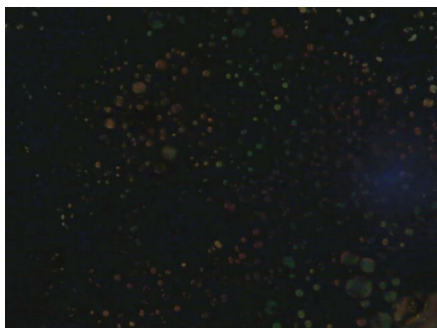Plate 3.3: Nematic phase of EPAP Valerate

Plate 3.4: Nematic droplets

In heating cycle the EPAP Valerate exhibits nematic phase [2] as shown in **Plate 3.3** in between the temperatures 77.1°C and 125°C. On further heating the nematic phase becomes isotropic above 125° C . In cooling cycle , the nematic phase appears at 125.5 °C and this phase is up to 76.9 °C. On further cooling it becomes as solid below 76.9 °C . In heating and cooling cycles nematic droplets are observed as shown in **Plate 3.4**.The transition temperature corresponding to EPAP Valerate given by M/s Frinton Laboratories, Inc., USA [3] is also given in **Table 3.1**. Sharma reported [4] on their laboratory prepared compound, the nematic phase appears in between 78 °C and 126 °C. The values are depicted in Table 3.1. The measured phase transition temperatures are in good agreement with the reported literature [3,4]. For further confirmation of the phase, miscibility studies [5] are also carried out. The compound EPAP Valerate is mixed with EPAP Hexanoate which also exhibits phase variant nematic. This phase of EPAP Valerate is co-miscible with the phase of EPAP Hexanoate. This confirms that the identified phase of EPAP Valerate is nematic and it is enantiotropic.

Table:3 Phase transition temperatures

Study	Crystal to Nematic	Nematic to Isotropic
PRESENT [HEATING]	77.1 °C	125 °C
PRESENT[COOLING]	76.9 °C	125.5 °C
FRINTON LABS [3]	78 °C	126 °C
P.B.K.SHARMA[4]	78 °C	126 °C

Dipole moment:

The Significance of the dipole moment studies in understanding the structure of the molecules has been realized by Debye [12] and it had also been observed that the values of the dipole moment could be connected with the geometrical arrangement of the atoms in the molecules.

The importance of Debye's method was understood and the determination the dipole moment had been given due consideration by smyth [13,14] and his co-workers.Dipole moment [15] measurements had been carried out by many workers on the dilute solutions of polar substances in non polar solvents. These results obtained from these measurements were comparable with those obtained from the gases phase. Maier and Maier [16] extended the onsagar's theory to nematic liquid crystals with some approximations. The zero dipole moment value for central azo group has been confirmed by Bergmann and Weizmann [17] and Hartly and Le Fevre [18]. In this work the dipole moments are calculated from Higasi method [7]

$$\mu^2 = \frac{27\,kTM_2}{4\pi Nd_1} \cdot \frac{(a_0 - a_\infty)}{(\varepsilon_1 + 2)^2}$$

where M_2 is molecular weight of solute, d_1 is density of solvent, ε_1 is the dielectric constant of solvent (benzene), a_0 and a_∞ are respectively the slopes of ε_0 and ε_∞ with respect to the concentration. The other constants have the usual meaning.The data required for calculating dipole moment are given along with the dipole moment at each concentration in Table 3.

The values of a_0 and a_∞ are found from the graphs of ε_0 (static dielectric constant) and ε_∞, Vs concentration respectively which are shown in Figure 1 and 2. ε_0 (static dielectric constant) is measured at 1 kHz using LCR meter. ε_∞ is the dielectric constant measured at optical frequency using Abbe refractometer.

Table 3.9 : Dipole moment study of EPAP valerate

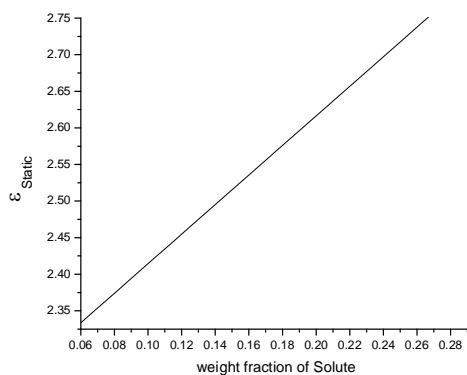| Weight fraction of solute (W_1/ W_1+ W_2)	ε_{static}	n^2 (Optical frequency)	a_0	a_∞	Dipole moment (μ) Debye
0.075 0.142 0.202 0.256	2.357 2.504 2.642 2.714	2.28 2.26 2.25 2.23	1.944	0.282	2.18

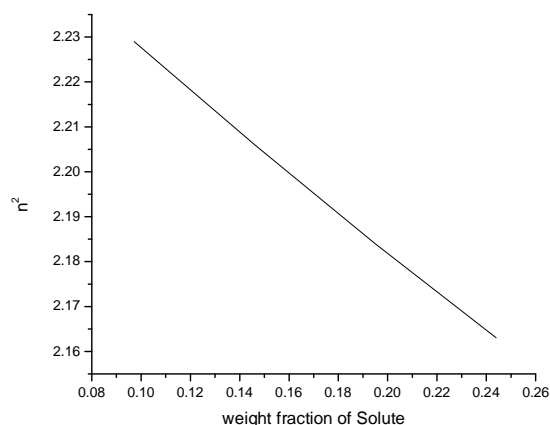Figure1: Weight fraction of Solute Versus Static dielectric constant

Figure2:. Weight fraction of Solute Versus Optic dielectric constant

It is evident from the data given in the Table 2, the dielectric constant increases with the increased frequency. The microwave data show that these compounds are polar in nature and correspondingly the dielectric constant is a complex quantity. The relaxation time is found to decrease in magnitude for a given concentration of EPAP Valerate in benzene with the increase of dilution in benzene.   However from the present study the dipole moment is obtained 2.18.

From the above results, it is observed that with the increase of frequency dielectric constant is decreasing at room temperature and also for any concentration. The reason is obvious and the contributions from the polarizations are decreasing with the increase of frequency [19].it is observed that the optical refractive index value decreased with increase in the concentration of the solute EPAP Valerate in a non polar solvent benzene at room temperature which shows that the angle of refraction may be increasing.The microwave and low frequency static dielectric constants increased with the increase in the concentration of the solute in a non-polar

solvent benzene at room temperature which shows that the dielectric constant of the solute EPAP Valerate is higher and also polar in nature.

Dielectric constant at microwave frequency is same with in the experimental limitations obtained in plunger technique [22-24] and cavity perturbation technique [11].There is a decrease in the relaxation time as the concentration of the EPAP Valerate is increased in non-polar solvent benzene which reflects that the strength of dipole is increasing. The dipole moment value from the experimental study is 2.18 D   and this value is nearly in good agreement 2.04 with the molecular structural   calculation in Austin Model 1(AM1) [9].   The Austin Model 1 method is parameterized for modeling organic systems. This method is a popular method as it predicts energies and geometries better than many semi empirical methods, which belong to the Modified Neglect of Differential Overlap (MNDO) group.The study of the magnitude and direction of the dipole moment gives   important   information   regarding   the   molecular alignment [20]. Work on the dipole moment determination and also the dispersion studies has been undertaken by Maier [21] in alkoxy azoxy benzenes and also on alkoxy azo benzenes. The contribution of the permanent dipole moment to the mesomorphic behaviour has been discussed by handrasekhar *et al* [2].   From the work of Sarma who followed the Guggenheim method [23] the value of the dipole moment of the liquid crystal EPAP Valerate obtained from radio and microwave frequency measurements agree fairly well with the estimated values.   Estimating the value of refractive index (which is an average value of the ordinary and extraordinary rays-obtained from extrapolation method using benzene as a solvent) and measuring the dielectric constant in the liquid crystalline range for the compound, the dipole moment in the liquid crystalline state has been determined by Sarma The value obtained is in a fair agreement with the value determined from other methods. This comparison is shown in the table 3 Thus it can be concluded that the values obtained from the dilute solution data are sufficient [4] to determine the dipole moment of liquid crystals however this is true as far as the determination of dipole moment is concerned.

Table 3: Dipole moments of various studies

	Dipole moment (D)
Present study	2.18
Present Theoretical study	2.03
P.B.K.Sharma	2.30
theoretical [4]	2.34

It is worthwhile to mention that Sarma [4] reported the results on EPAP Valerate liquid crystalline compound using plunger method (according to Guggenheim method) and theoretical considerations of modified Kirkwood equation. In this study on the same compound EPAP Valerate, the plunger method is used to standardize the instrument at microwave frequency and then repeated the experiment using cavity perturbation technique at the same frequency, which requires less sample when compared to plunger. Theoretically AM1 method is used to calculate the dipole moment. Though the work is different from experimental and theoretical considerations, the results are equal with in the limitations of the experimental conditions.

REFERENCES

[1] Sreehari Sastry.S , Vindhya Kumari.T, Mallika.K, Gowri Sankara Rao.B, Sie-Tiong Ha & Lakshminarayana.S, (2012). *"Order parameter studies on EPAP alkanoate mesogens"*, Liq. Cryst., **39(3),** 295.

[2] Priestley.B, Wojtowicz.P.J, Sheng.P, (1975). *Introduction to Liquid Crystals"* RCA Laboratories, Plenum Press, Princeton, New Jersy.

[3] Sreehari Sastry.S, Sandeep Kumar,Vindhya Kumari.T, Mallika. K, Gowri Sankara Rao.B & Sie Tiong Ha,(2012). *"Liquid crystal parameters through image analysis"*, Liq. Cryst., 39(12), 1527.

[4] Bahadur.B (1991). *"Liquid Crystals: Applications And Uses*,*"* World Scientific Publishers, Singapore.

[5] Collings. P.J. (2000). *"Liquid crystals: Nature'sDelicate Phase of Matter"* 2nd Edition, Princeton University Press, Princeton, New Jrsey.

[6] Collings. P.J., Hird. M.J.(1997) *"Introduction to Liquid Crystals: Chemistry and Physics"* Taylor and Francis.

[7] Meier.G, Sackmann.E, Grabmaier. J.G.(1975) in *"Applications of Liquid Crystals"* Springer Verlag, Berlin- Heidelberg, Newyork

[8] P.G.de Gennes, (1975). *"The Physics of Liquid Crystals"* Clarendon Press, Oxford.

[9] Reinitzer.F (1988), *Montasch. Chem.*, **9**, 421.

[10] O.Lehmann, *Z. Krist*, **18**, 464, (1890).

[11] Collings. P.J. Patel. ,J.S. (1997) *"Handbook of Liquid Crystal Research"* Oxford University Press, New York.

[12] Dunmur. D, Sluckin.T(2011), *"Soap, Science and Flat-Screen TVs: A History of L*iquid Crystals*"* Oxford, UK: Oxford UniversityPress.

[13] Rosevear. F.B(1968), *J. Soc. Cosmetic Chemists*, **19**, 581, (1968).

[14] Cumper. C.W.N ,Langley. P G(1971), *J. Chem.Soc. Faraday trans. II*, **67**, 35.

[15] Symth. C P (1955) "Dielectric Behaviour and Structure", Mc Graw-Hill Book CoINC, New York.

[16] Raman Kumar and V.S.Rangra,(2005) "Dielectric relaxation studies of binary mixtures of NMA and Acetonitrile in Benzene solutions using microwave absorption Studies", *Z.Phy.Chem*, **219,** 169.

[17] Von Hippel. A.R. (1954) "Dielectric materials and applications", MIT Press, Cambridge.

[18] Heston. W H, Franklin. A D, Hennelly. E J and Smyth C P, (1950) *J. Amer. Chem. Soc.,* **72**, 3443.

[19] Debye.P (1929) " Polar Molecules" Chem. Cat. Co. Inc. New York .Collective papers inter science NY1954 "Polar Molecules".

[20] SmythC.P (1931) " Dielectric constant and molecular structures" Chemical Catalogue, New York .

[21] SmythC.P. (1955) " Dielectric behaviour and structure, McGraw Hill, New York .

[22] SmythJ.W. (1955) " Electric Dipole moments", Butterworths, London.

[23] Maier.W ,Maier.G (1961), *Z. Naturforschung* **16a**, 262

[24] Heston N.H, Franklin. A. D., Hennelly. E.J. Smyth. C.P.(1950) *J. Am, Chem. Soc.,* **72**, 3443.

[25] Viswanathan.B, Raman. R , Raman. N.S. and Murthy. V.R.K.(1988), *Solid. State Commn.,* **66,** 409.