



STATIC ELECTRICAL CONDUCTIVITY OF LIQUID CRYSTALLINE P-BUTOXYBENZYLIDENE P-HEPTYLANILINE

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ABSTRACT

This paper reports the temperature variation of the principal components of static electrical conductivity i.e., $\sigma_{\parallel}(T)$ and $\sigma_{\perp}(T)$ in the nematic and smectic phases of p-butoxybenzylidene p-heptylaniline. The results obtained are inferred in terms of the basic understanding of nematic and smectic phases.

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INTRODUCTION

Liquid crystals are molecular fluids which are intermediate between three-dimensionally ordered (crystalline) solids and disordered liquids in structural symmetry (de Gennes and Prost, 1993). Liquid crystalline materials are broadly classified as thermotropics and lyotropics. In thermotropics, the phase transition is mainly controlled by temperature whereas in lyotropics, apart from temperature, phase transition is controlled by concentration. On the basis of molecular arrangement, thermotropics are further classified into three main types namely, nematics, smectics and cholesterics (Friedel, 1922). Nematics are characterized by orientational order (i.e., the long molecular axes are preferably oriented along a particular direction called the director, \hat{n}) while smectics have an additional positional order. There are numerous smectic phases identified as smectic A, B, C, D, etc. which possess varying degrees of positional and orientational order. Cholesterics are similar to nematics but, chiral in structure. Liquid crystals possess a combination of properties of both crystalline solids and isotropic liquids, thus, providing scientists and engineers with one of the most active and fascinating fields of scientific and industrial research. The major application of liquid crystals is in liquid crystal displays (LCDs). Apart from this, they find innumerable applications in industries, photonics, imaging technology, biomedical field and in nanoscience and nanotechnology (Pandey et al., 2009).

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To understand the suitability and applicability of liquid crystalline systems in different applications, their basic characterization is very essential. For instance, liquid crystals suitable for technical applications should be chemically and optically stable, possess wide temperature range for their liquid crystalline phases, have low melting points, low viscosities, suitable birefringence, desirable dielectric properties, low conductivities, etc (Chand and Manohar, 2010).

One of the inherent properties of liquid crystals is the rearrangement of molecules in response to external electric field which is widely explored in several practical applications. The electrical conductivity in liquid crystals, in general, arises due to ionic impurities which are present in minute concentrations, even in the samples of highest purity. Hence, conductivity is not a material property of liquid crystals. Conductivity anisotropy ($\sigma_{\parallel} - \sigma_{\perp}$) plays an important role in the electro-optical performance of liquid crystal display devices and hence ionic concentration has to be optimized to achieve best performance of the device (Seiberle and Schadt, 1994; Myrvold and Coles, 1995).

In this manuscript, we present the temperature dependence of the components of static electrical conductivity [$\sigma_{\parallel}(T)$ and $\sigma_{\perp}(T)$] of a thermotropic liquid crystalline compound, p-butoxybenzylidene p-heptylaniline (4O.7). This belongs to the class of N-(p-n-alkoxybenzylidene)-p-n-alkylanilines, popularly known as the Schiff's base nO.m compounds (where n and m denote the alkyl chain lengths on either side of the

rigid core). On account of a wide variety of polymorphism exhibited by these compounds, they have been widely explored by several investigators for the study of fundamental aspects of liquid crystals in the past few decades (Rananavare and Pisipati, 2011). The calorimetric (Meichle and Garland, 1983), X-ray studies (Ocko *et al.*, 1984), NMR (Ravindranath *et al.*, 1990), refractive index and density measurements (Rao *et al.*, 1991) of 4O.7 have been reported in literature. Electrical conductivities of several liquid crystals belonging to the nO.m series have been reported in literature (Rondelez *et al.*, 1971; Sprokel, 1974; Margerum *et al.*, 1977; Roussel and Rondelez, 1975; Heppke *et al.*, 1976; Pandey, Pandey *et al.*, 2014). Several authors have studied electrical conductivity behavior of N-(p-methoxybenzylidene)-p-butylaniline (MBBA/1O.4) (Rondelez *et al.*, 1971; Sprokel, 1974; Margerum *et al.*, 1977). Roussel and Rondelez (1975) have studied electrical conductivity of several liquid crystals including 4O.8, 6O.8, 5O.5 and 5O.7 exhibiting nematic, SmA and SmB phases. In all these compounds, it is observed that conductivity anisotropy ratio, $\sigma_R = \sigma_{\parallel} / \sigma_{\perp}$ changes sign from positive to negative close to the transition from nematic to the smectic phases due to strong pretransitional effects. Similar observations have been reported by Heppke *et al.* (1976) in nO.4 series compounds with $n = 1$ to 8 while studying their electrical conductivities using the electrolyte tetra butylammonium picrate. Recently, Pandey *et al.* (2014) have reported the effects of doping polymer poly(isobutylmethacrylate) on the dielectric and electro-optical parameters of 2O.7.

MATERIALS AND METHODS

The sample 4O.7 studied in this work was procured from M/s Frinton Laboratories Inc., USA and used without any further purification. Its molecular structure is shown in Figure 1. The phase sequence and transition temperatures of the compound were determined from optical polarizing microscopy and DSC. Optical observations were made using an optical polarizing microscope (model SDTECHS-SD-VPM2727) in conjunction with an electrically controlled hot stage. The sample temperature was maintained to an accuracy of $\pm 1^{\circ}\text{C}$.

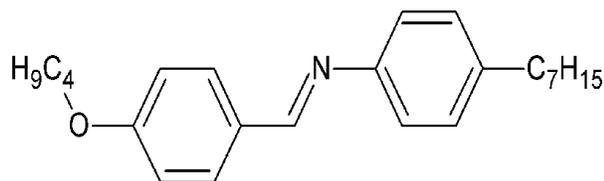


Figure 1: Molecular structure of 4O.7

For the measurement of electrical conductivity, the sample was taken in a sample cell which is of sandwich type, made of passivated Indium Tin Oxide (ITO) coated glass plates. Planar and homeotropic alignment of the sample were achieved by spin coating the ITO electrodes with polyimide and Octa Decyl Triethoxy Silane (ODSE) respectively. Planar alignment of the sample gives the conductivity component σ_{\perp} with the applied electric field perpendicular to the director (i.e., $\vec{E} \perp \hat{n}$) while

homeotropic alignment gives σ_{\parallel} with the applied electric field parallel to the director (i.e., $\vec{E} \parallel \hat{n}$). The electrical conductivity data of the samples were recorded using Novocontrol Alpha-A frequency analyzer at a constant frequency of 1 kHz. The data were collected in the cooling mode, the sample being cooled from the isotropic phase. The thickness of the empty sample cell was measured precisely using fiber optic spectrometer (Ocean Optics Model S2000) employing interferometric technique. The sample temperature was controlled with an accuracy of $\pm 0.1^{\circ}\text{C}$ using Instec hot stage (model FS1) connected to the Eurotherm 2416 PID Controller. Temperature of the sample was measured using 100 Ω Platinum (Pt100) Resistance Temperature Device (RTD).

RESULTS

The DSC scan of the compound 4O.7 is shown in Figure 2. The figure shows two sharp peaks around 46°C and 81°C and a weak peak around 54°C indicating the occurrences of phase transitions at these temperatures. Observations with polarizing microscope during the cooling cycle showed in sequence the threaded texture [Figure 3(A)], appearance of focal conic texture [Figure 3(B)], appearance of transition bars on focal cones [Figure 3(C)] and reappearing of focal conic texture [Figure 3(D)] indicating the characteristic change from nematic (N) \rightarrow smectic A (SmA) \rightarrow smectic C (SmC) \rightarrow smectic B (SmB) phase. The same phases were observed in the heating cycle also. The sample was observed to be in the SmB phase at room temperature and melted into the isotropic (I) phase around 81°C . From these observations, the phase sequence of 4O.7 was inferred as given below:

(Sm B) 45.9°C (Sm C) 47°C (Sm A) 54°C (N) 80.8°C (I)

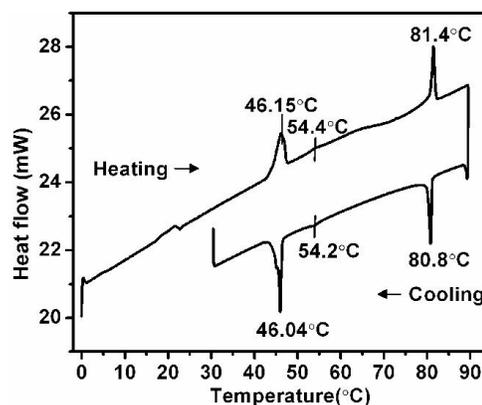


Figure 2: DSC thermogram of 4O.7 (scanning rate: $5^{\circ}\text{C}/\text{min}$)

The temperature dependence of the principal components of electrical conductivity, $\sigma_{\parallel}(T)$ and $\sigma_{\perp}(T)$ and the anisotropy ratio, $\sigma_R (= \sigma_{\parallel} / \sigma_{\perp})$ are presented in Figure 4. From the figure, it is observed that the conductivity components vary between 2×10^{-9} and $9 \times 10^{-8} \text{ Sm}^{-1}$ in the entire liquid crystalline phase and between 9×10^{-8} and $11 \times 10^{-8} \text{ Sm}^{-1}$ in the isotropic phase. Further, it may be noticed that σ_R which is greater than

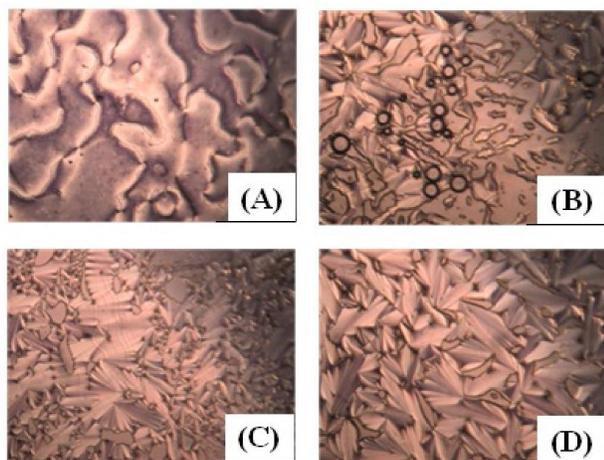


Figure 3: Microphotographs of the optical textures of 4O.7 showing (A) nematic phase at 75.6°C, (B) SmA phase transition at 54.7°C, (C) SmC phase at 47.5°C and (D) SmB phase at 35°C. [crossed polarizers, 40x]

unity near N-I phase transition slightly increases and then starts decreasing with decrease in temperature down to unity a few degrees above the N-SmA phase transition. It decreases further in the SmA phase, shows a slight increase in the SmC phase, reaches minimum in the SmB phase and again starts increasing. Thus, the conductivity anisotropy is positive over certain range in the nematic phase and becomes negative in the smectic phases. However, this sign reversal occurs slightly below the N-SmA transition temperature due to pretransitional effects. It is also observed that σ_{\parallel} decreases continuously with decrease in temperature and saturates in smectic phase. On the other hand, σ_{\perp} decreases with decrease of temperature in the nematic phase, increases slightly near N-SmA phase transition, becomes almost constant in the SmA phase, drops a little in the SmC phase and gradually decreases in the SmB phase. Conductivity anisotropy ratio is maximum in the SmA phase. Throughout the isotropic phase, the conductivity components are equal i.e., $\sigma_{\parallel} = \sigma_{\perp}$ as expected and they increase slightly with increase in temperature.

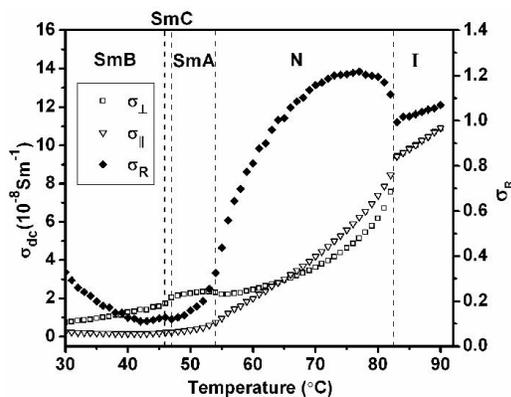


Figure 4: Variation of dc conductivity components and conductivity ratio with temperature in different phases of 4O.7

DISCUSSION

The results obtained can be understood in terms of molecular arrangement in the smectic and nematic phases. In the nematic phase, the long axes of the molecules are preferably oriented parallel to the director whereas in smectic phases, the molecules are arranged in layers. In the nematic phase, movement of ions is easier in the ordering direction (parallel to the director) than in the perpendicular direction and hence, $\sigma_{\parallel} > \sigma_{\perp}$. Formation of smectic layers favors movement of ions in a direction perpendicular to the smectic layers only and hence, $\sigma_{\perp} > \sigma_{\parallel}$ in all the smectic phases (Jadżyn and Kedziora, 1987). The variation of σ_{\parallel} and σ_{\perp} in different smectic phases of 4O.7 (i.e., SmA, SmC and SmB) is attributed to varying degrees of orientational order and positional order in these phases.

The temperature variation of conductivity components is usually described by Arrhenius law $\sigma = \sigma_0 \exp(-E_a/k_B T)$ where σ_0 is a constant, k_B is the Boltzmann constant and E_a is activation energy for ionic transport. Hence, activation energies $E_{a\parallel}$ and $E_{a\perp}$ can be computed from the slopes of the straight line graphs obtained on plotting $\ln(\sigma_{\parallel})$ and $\ln(\sigma_{\perp})$ against $1/T$ (Arrhenius plots). Arrhenius plots of the sample are shown in Figures 5 and 6. The activation energies hence determined for the nematic phase of 4O.7 are $E_{a\parallel} = 0.69 \pm 0.04$ eV and $E_{a\perp} = 0.44 \pm 0.03$ eV. Thus, $E_{a\parallel} > E_{a\perp}$ within the limit of experimental error which further justifies that movement of ions is favored in the ordering direction in the nematic phase. These results are in conformity with those reported earlier for other liquid crystalline compounds belonging to the same series (Roussel and Rondelez, 1975; Heppke *et al.*, 1976). Activation energies have not been estimated in the smectic phases due to high non-linearity of the Arrhenius plots which is attributed to pretransitional effects and narrow temperature range of these phases.

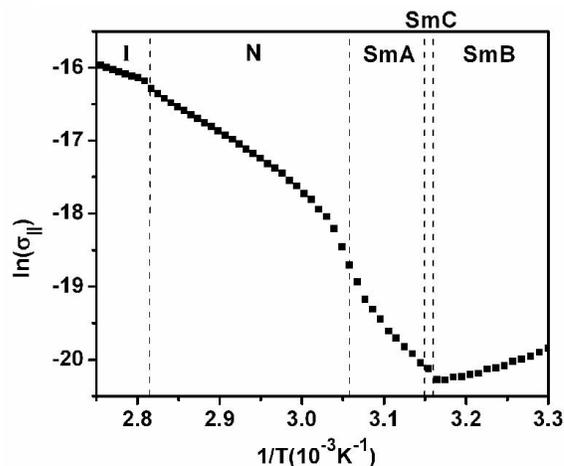


Figure 5: Arrhenius plot for σ_{\parallel} in 4O.7

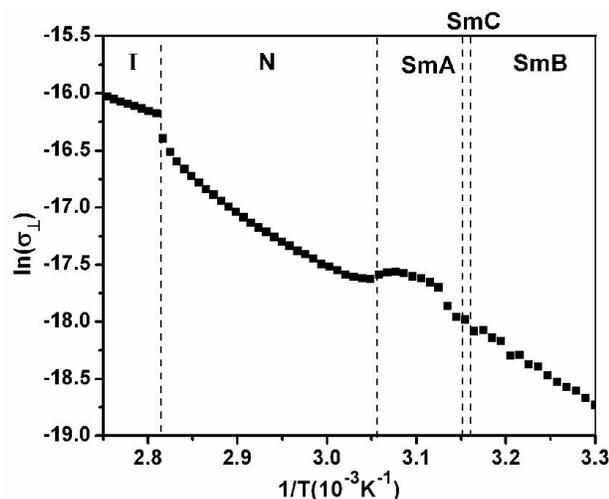


Figure 6: Arrhenius plot for σ_{\perp} in 4O.7

In conclusion, we have reported the static electrical conductivity of the liquid crystalline compound p-butoxybenzylidene p-heptylaniline (4O.7) in its nematic, smectic and isotropic phases. Its conductivity components, σ_{\parallel} and σ_{\perp} , lie in the range of 2×10^{-9} – 9×10^{-8} Sm^{-1} in liquid crystalline phase, which is within the normal range (10^{-9} – 10^{-6} Sm^{-1}) observable for liquid crystalline materials. The parallel component of conductivity dominates in the nematic phase while the perpendicular component dominates in the smectic phases. The former is due to orientational order prevalent in the nematic phase and the latter is attributed to layered arrangement in the smectic phases.

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