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RESEARCH ARTICLE

Temperature dependence of the orientational order parameter for Anisaldazine, p-Azoxyanisole and p-Azoxyphenetole close to the Nematic-Isotropic liquid Transition

* H. Yurtseven and O. Ay

Department of Physics, Middle East Technical University, 06531 Ankara-TURKEY

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Abstract

The orientational order parameter in the nematic phase of anisaldazine, p-azoxyanisole and p-azoxyphenetole has been analysed using a power-law formula close to the nematic-isotropic liquid transition. From our analysis, we find the value of $\beta \approx 0.1$ for the orientational order parameter, which is close to $1/8$ predicted from the two-dimensional Ising model. This indicates that the existence of long range order can be described by this model in the nematic phase of the liquid crystals studied.

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1. Introduction

Phase transitions in anisaldazine, p-azoxyanisole(PAA) and p-azoxyphenetole have been the subject of a number of studies. The volume was measured at various temperatures and the thermal expansion was calculated for PAA by Maier and Saupe[1] some years ago. The specific heat of PAA and anisaldazine, in particular, has been measured at various temperatures by the differential scan calorimetry(DSC) for the phases of solid-nematic-isotropic liquid[2]. The thermal expansivity α_p in PAA has also been measured as a function of pressure along the isotherm 413K across the nematic-isotropic transition[3]. Recently, we have analyzed the experimental data[1] for the specific heat C_p in PAA[4] and anisaldazine[5]. We have also analyzed the experimental data[2] for the thermal expansivity in PAA[6]. We have reported [7] the analysis of the C_p in the supercooled solid phase of PAA.

Experimental data on viscosity [8,9], magnetic susceptibility[4], dielectric constant[8,10] and thermal conductivity[11-13] on PAA were reported. Measurements of the dielectric constant of anisaldazine in the presence of the electric and magnetic fields were conducted[14]. In regard to the spectroscopic techniques used for p-azoxyanisole, small angle x-ray measurements close to the phase transitions in this liquid crystal[15] were made and

the Raman spectra of p-azoxyanisole in the nematic and isotropic phases were obtained[16]. Using Raman spectroscopy and differential scanning calorimetry(dsc), phase transitions of PAA and p-azoxyanisole in confined geometries have been investigated[17].

Some theoretical models, firstly, the Maier-Saupe model[1] was introduced for the nematic-isotropic(NI) transition and some other models[18,20] have been reported in the literature for the NI transition. In the Maier-Saupe theory, the attractive energy due to dipolar moments predicts the NI transition, as pointed out previously[20]. Monte-Carlo computer simulation techniques were used[18] to study the orientational phase transitions (NI) in the Lebwohl-Lasher model[21].

Transitions among the phases of the isotropic liquid, nematic and smectic can be studied in terms of the order parameters in liquid crystals. In particular, orientational order parameter in the nematic phase of the liquid crystals, namely, anisaldazine, p-azoxyanisole and p-azoxyphenetole has been studied as a function of temperature in a previous study[22]. From the measurements of the refractive indices of those liquid crystals, the orientational order parameter in the nematic phase has been calculated using Vaks formula by the molecular polarizability[22]. Also, from the proton spin-lattice relaxation measurements, temperature dependence of the degree of orientational long range order was

Corresponding author: hamit@metu.edu.tr

studied for nematic anisaldazine[23]. Small angle measurements for p-azoxyanisole in the isotropic liquid, nematic and solid regions provided the temperature dependence of the coherence lengths and the ordering parameters in this liquid crystal[15].

In this study, we analyze the temperature dependence of the orientational order parameter in nematic phase of anisaldazine, p-azoxyanisole and p-azoxyphenetole using a power- formula. We determine the values of the critical exponent β for the orientational order parameter and interpret its critical behaviour for the liquid crystals studied here.

Below, we give our analysis and results in section 2. In section 3, we discuss our results. Conclusions are given in section 4.

2. Analysis and Results

The temperature dependence of the orientational order parameter S was analyzed here according to a power-law formula

$$S = A(T_c - T)^\beta \quad (1)$$

for the nematic-isotropic liquid transition of the three liquid crystals, namely, anisaldazine, p-azoxyanisole and p-azoxyphenetole. In Eq.(1), β is the critical exponent for the order parameter and A is the amplitude. T_c represents the transition temperature between the nematic phase and the isotropic liquid. For this analysis of the three liquid crystals, we used the values of the orientational order parameter calculated from the molecular polarizabilities of the nematic medium[22]. By taking the logarithm of both sides in Eq.(1), we get

$$\ln S = \ln A + \beta \ln(T_c - T) \quad (2)$$

A plot of $\ln S$ against $\ln(T_c - T)$ gives the critical exponent β for the orientational order parameter of the liquid crystals studied here. Table 1 gives the β values for the orientational order parameter S and the amplitude A for the three liquid crystals indicated for the temperature intervals from our analysis. Fig.1 gives the temperature dependence of the orientational order parameter S in a log-log scale(Eq.2) in the nematic phase for the three liquid crystals studied here.

3. Discussion

We analyzed in this study the temperature dependence of the orientational order parameter S for the nematic phase of the anisaldazine, p-azoxyanisole and p-azoxyphenetole according to Eq.1, as plotted in a log-log scale in Fig.1. For the three liquid crystals, we obtained the value of $\beta \approx 0.1$ for the critical exponent of the orientational order parameter S in the

nematic phase within the temperature intervals studied (Table 1). Our β value is close to the value of $1/8 (=0.125)$ as expected from the two-dimensional Ising model. The β value (≈ 0.1) which we obtained from our analysis indicates that the nematic-isotropic transition is a weak first order for liquid crystals of anisaldazine, p-azoxyanisole and p-azoxyphenetole.

TABLE 1 Values of the critical exponent β and the amplitude A for the liquid crystal indicated in the temperature intervals according to Eq.(1).

Liquid Crystal	β	A	Temperature Interval (K)
p-azoxyanisole	0.14	0.35	$1.2 < (T_c - T) < 36$
anisaldazine	0.11	0.41	$0.5 < (T_c - T) < 26.7$
p-azoxyphenetole	0.11	0.47	$1.2 < (T_c - T) < 43.2$

Experimentally, the curves for the order parameter versus temperature $(T_c - T)$ have been found nearly parallel to each other for the three liquid crystals studied[22]. As expected at the nematic-isotropic (N-I) transition, when the order parameter drops suddenly the transition is of first order, which is not the case for anisaldazine, p-azoxyanisole and p-azoxyphenetole as studied here.

Our β value of ≈ 0.1 for the orientational order parameter S is not in agreement with the predicted value of $\beta=0.5$ from the mean field theory. In fact, we calculated the temperature dependence of the orientational order parameter S from the mean field theory[24] according to the relation

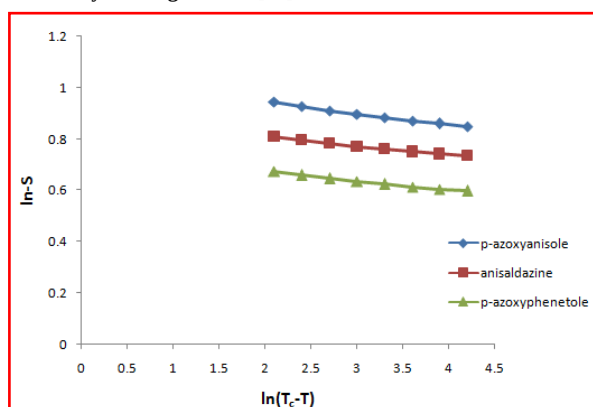
$$S = [3(1 - T/T_c)]^{1/2}, \quad 0 < (T_c - T) \ll T_c \quad (3)$$

for the nematic-isotropic liquid transition of the three liquid crystals studied here. With this exponent value of $\beta=1/2$ (Eq.3), our calculated values for the orientational order parameter S were not in agreement with those obtained from the molecular polarizabilities[22] for the liquid crystals considered here. This concludes that the mean field theory is inadequate to describe the critical behaviour of the orientational order parameter at various temperatures in the nematic phase of anisaldazine, p-azoxyanisole and p-azoxyphenetole.

As observed in various liquid crystals experimentally for a first order transition there occurs the temperature shift at the nematic-isotropic transition (two-phase region). As expected, the order parameter does not vary in the nematic part of the two-phase region. In the coexistence region, the degree of molecular alignment increases largely in the nematic phase, whereas in the isotropic phase random molecular orientations become important [25]. Experimentally, transition temperatures in the phase change region and the temperature range of the

heterophase intervals need to be determined within the high accuracy for the nematic-isotropic liquid (NI) transition of anisaldazine, p-azoxyanisole and p-azoxyphenetole, as we have measured for the NI transition of H-126 and H-134 liquid crystalline materials [26].

FIGURE 1 Orientational order parameter S in a log-log scale (Eq.2) as a function of the temperature with respect to the transition temperature T_c for the liquid crystals indicated from our analysis using the data[22].



4. Conclusions

The orientational order parameter was analysed in the nematic phase of anisaldazine, p-azoxyanisole and p-azoxyphenetole using a power-law formula. The three liquid crystals exhibit similar critical behaviour of a weak first order, as obtained from our analysis. As Ising model seems to explain the critical behaviour of the orientational order parameter close to the nematic-isotropic liquid transition. Experimental measurements can be compared with our analysis given here.

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