Nematic/Smectic-A Transition (NS_A), Location of Tri Critical Point (TCP) in nO.m Series – A Birefringence Study

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The tri critical point (TCP), where the second-order transition transforms to first order has been located in nO.m homologous series. The order parameter has been estimated from the birefringence δn, from the refractive indices and from birefringence data available in literature and from those obtained at our laboratory on a number of nO.m compounds. The compounds in the nO.m series exhibit both second and first-order nematic/smectic-A (NS_A) transition depending on the McMillan ratio (T_{NA}/T_{IN}) which in turn depends on the nematic and smectic-A thermal ranges. The data presented are compared with the body of the data available on this homologous series obtained with other techniques.

Key words: nO.m Compounds; NS_A Phase Transition; Tricritical Point (TCP); Birefringence.

1. Introduction

N-(*p*-*n*-alkoxybenzylidene)-*p*-*n*-alkyl anilines (nO.m) compounds exhibit a rich but subtle polymorphism not only with the change of the number of alkoxy and alkyl chains [1], but also with the change of the position of the electro negative atom on either side of the central rigid core and further, the position of the oxygen atom influences the clearing temperature [2, 3]. A number of these compounds are synthesized and characterized [4] and physical property measurements are carried out to study the nature of different phase transformations and the pretransitional effects [4] on either side of the transition.

Further, liquid crystals (LC) have attained special attention by different groups because of their multifaceted applications. These materials exhibit an anisotropy in their mechanical, electrical, and optical properties, behaving like solid crystals. Nevertheless, they have no ability to support shearing and thus they flow like ordinary liquids [5]. This particular dual property nature made these materials important in technological applications such as displays and optical switches [6].

The quantitative approach of a nematic phase is generally expressed in terms of an order parameter, which is non zero and approaches zero at the clearing temperature. This parameter to some extent determines the applicability of the material in technological applications. Several methods for the determination of the order parameter S have been developed. However, the discussion concerning the order parameter determination is inconclusive since the last four decades. Further, it is widely accepted that the most exact data can be obtained from the measurements of diamagnetic anisotropy or from the optical measurements. From these two, as the diamagnetic anisotropy measurements are, however, quite difficult to perform. Hence, the optical methods are used most frequently.

The aim of this manuscript is to describe the method of evaluation of orientational order parameter S directly from the birefringence data on a number of nO.m compounds (without considering any internal field model and thereby evaluating the order parameter from the molecular polarizability data) following the suggestion made and applied for a number of liquid crystalline compounds by Kuczynski et al. [7, 8]. Further, the purpose of the estimation of the order parameter from the birefringence study is to obtain the order parameter in liquid crystalline phases other than nematic phase as the evaluation of S is independent of any type of internal field model for the molecule. The authors employed this technique in the case of nO.m homologous compounds which exhibit a second-order and first-order NS_A transition, respectively, with varying thermal ranges of nematic and smectic-A phases. The results are utilized to locate the tri critical point (TCP) and the corresponding McMillan ratio (T_{NA}/T_{IN}) in nO.m series and compare the results with the body of the data available.

2. Method of Evaluation of *S* from Birefringence studies

It is well known that any physical property of a nematic liquid crystal and the orientational order parameter S are closely connected to one another. Further, it is pointed out that the anisotropy of any physical quantity can be a measure of orientational order. In the case of an uniaxial liquid crystal, this parameter can be defined as

$$Q = \frac{\delta A}{\Delta A}, \tag{1}$$

where δA is the anisotropy of any arbitrary physical quantity A (i.e., measured parallel and perpendicular to the nematic director, $\delta A = A_{\parallel} - A_{\perp}$), ΔA stays for a hypothetical anisotropy of A, in the case of perfect order. Among many anisotropic physical quantities which could be used for the determination of the order parameter Q, the dielectric anisotropy for optical frequencies $\delta\varepsilon = n_e^2 - n_o^2$ is useful. Thus $\delta\varepsilon$ can be used [9] for the determination of S if a particular local field is applied to the liquid crystal molecule. Further, de Jeu [10] showed that birefringence δn can be used for this purpose. Based on this, Kuczynski et al. [7, 8] proposed a simple procedure for the determination of the order parameter S from the birefringence measurements ($n_e - n_o$) without considering the local field experienced by the molecule in a liquid crystal phase. The birefringence δn which is a function of temperature is fitted to the following equation:

$$\delta n = \Delta n \left(1 - \frac{T}{T^*}\right)^{\beta}, \tag{2}$$

where T is the absolute temperature, T^* and β are constants. (T^* is about $0.1-4$ K higher than the clearing temperature and the exponent β is close to 0.20). This procedure enables one to extrapolate δn to the absolute zero temperature. In practice, the three adjustable parameters T^*, Δn, and β were obtained by fitting the experimental data for δn to the following equation written in the logarithmic form:

$$\log \delta n = \log \Delta n + \beta \log \left(\frac{T^* - T}{T^*}\right). \tag{3}$$

In the present investigations, the values of log Δn and β are calculated by the linear regression method. The parameter T^* (which is ($T_{IN} + X$) where X is varied from 0.1 to 4 K) is adjusted to get the best correlation coefficient of the linear regression and realistic values of Δn and β. Thus, S is given by

$$S = \frac{\delta n}{\Delta n}. \tag{4}$$

Following this procedure, Kuczynski et al. [7, 8] demonstrated that S determined in this way describes well the nematic order parameter. A good approximation of the order parameter S is given by the equation $S = 1/2\ (3\cos^2\theta - 1)$, where θ is the angle between the long axis of the molecule and the director 'n'. In estimating the birefringence at perfect order only the values of birefringence in nematic phase has been considered for the linear fit for all the compounds presented.

3. Experimental

The refractive indices of the liquid crystal were measured with a wedge shaped glass cell, similar to the one used to obtain the birefringence by Haller et al. [11] and a modified spectrometer. A wedge shaped glass cell was formed with two optically flat rectangular glass plates (50 mm × 25 mm) sand witched with glass plate (0.4 mm) which acts as a wedge spacer. The optical flats are uniformly rubbed along the short edge to get the alignment of the LC molecule. The cell is filled with the LC material. The LC in the cell acts as a uniaxial crystal with its optical axis parallel to the edge of the spacer glass plate. The temperature accuracy of the heating block was ±0.1 °C. The accuracy in the measured refractive indices was ±0.0005.

The other method is similar to the one used by Kuczynski et al. [7, 8] or otherwise known as Newton's rings method. The experimental setup was fabricated by the authors whose details are given elsewhere [12]. The first method provides the measurement of both refractive indices while the later method directly gives the birefringence δn. For some of the compounds, both methods are used to obtain δn either from n_e and n_o or directly. In some cases, due to the instability of Newton's rings formed, δn could not be obtained directly.

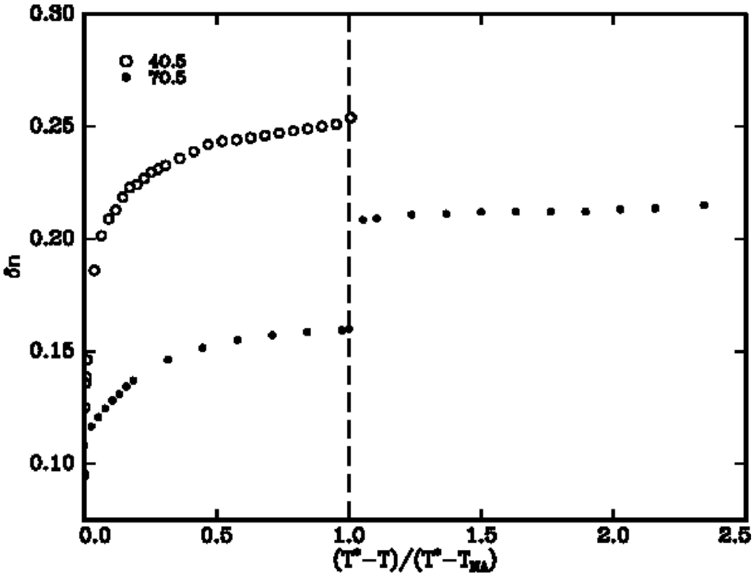

Fig. 1. Variation birefringence δn with normalized nematic range for the compounds 4O.5 (circles) and 7O.5 (dots).

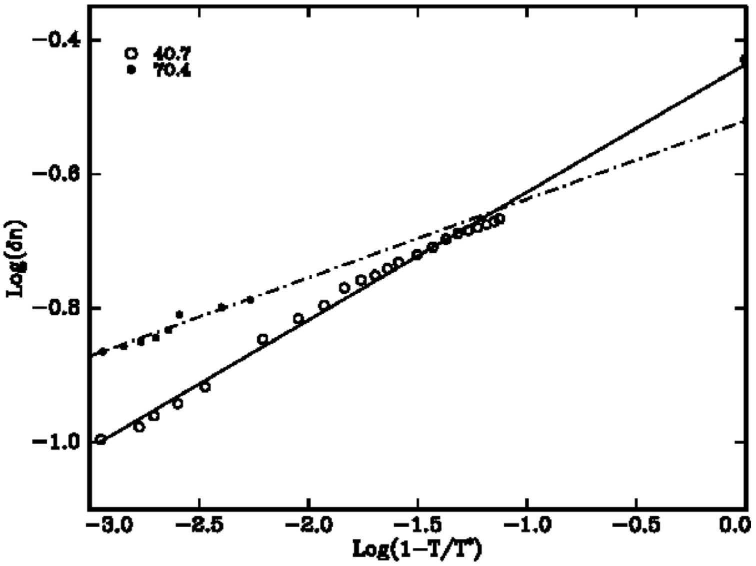

Fig. 2. log-log plot of birefringence δn versus reduced temperature for the compounds 4O.7 (circles) and 7O.4 (dots).

In such cases, the first method is employed to obtain δn from n_e and n_o.

4. Results and Discussion

The refractive indices in some of the compounds studied are obtained using the experimental procedure described above. For the other compounds the data is taken from literature for the computation of Δn, the birefringence at perfect order, and in turn the order parameter S. Figure 1 illustrates the variation of the birefringence in 4O.5 and 7O.5 compounds with temperature (nematic range normalized where $T^* = T_{IN}$). In the former case $\delta n = (n_e - n_o)$ and in the later case δn is directly obtained from the second method. Since δn is obtained from refractive indices difference in 4O.5, birefringence only in the nematic range is depicted. However, while illustrating S with temperature the variation of S in smectic-A phase is also shown in this compound (Fig. 5). Figures 2 and 3 show the log-log fit curves for some compounds as representative cases. Figure 2 shows the log-log fit in the case

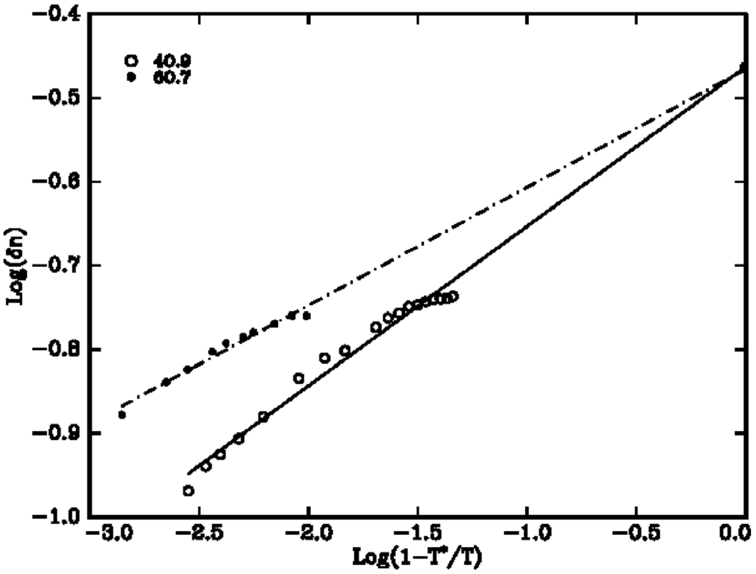

Fig. 3. log-log plot of birefringence δn, versus reduced temperature for the compounds 4O.9 (circles) and 6O.7 (dots).

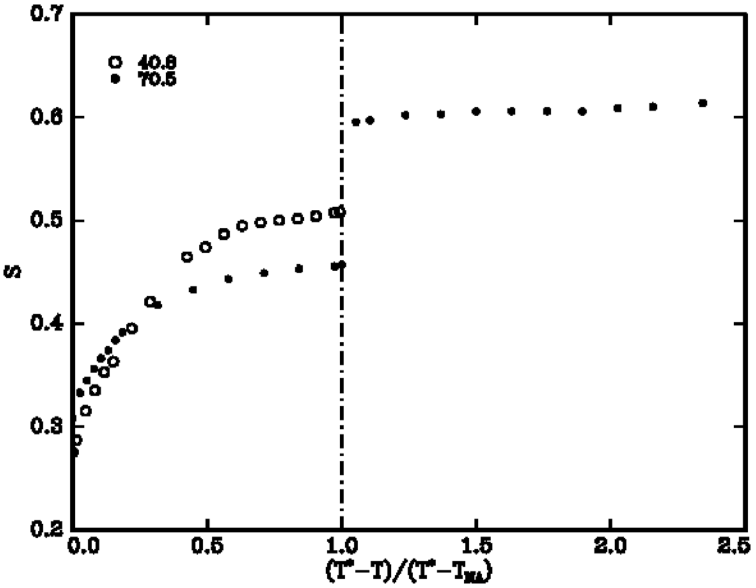

Fig. 4. Variation of order parameter S with normalized nematic range for the compounds 4O.8 (circles) and 7O.5 (dots).

of 4O.7 and 7O.4 compounds while Figure 3 exhibits the fits for the compounds 4O.9 and 6O.7, respectively. Table 1 gives the data regarding the log-log fit that has been used to obtain Δn using the equation (3). The table provides the fit parameters viz. β, X values and the regression coefficient R. Further, these parameters are adjusted to get the value of Δn from a better fit. The birefringence in the case of perfect order, Δn estimated from the log-log fits is used to obtain the order parameter in liquid crystalline phases of the compounds listed in Table 1 using (4). In some cases, due to the non-resolution of the lines representing n_e and n_o, in the first experiment or the instability in the formation of Newton's rings in the later experiment (instability in the sense that it is not possible to measure the radius of the ring and in turn the value Δn), the authors could not obtain the birefringence data in liquid crystalline phases other than the nematic phase.

Figure 4 exhibits the variation of the order parameter with the normalized nematic range in the case

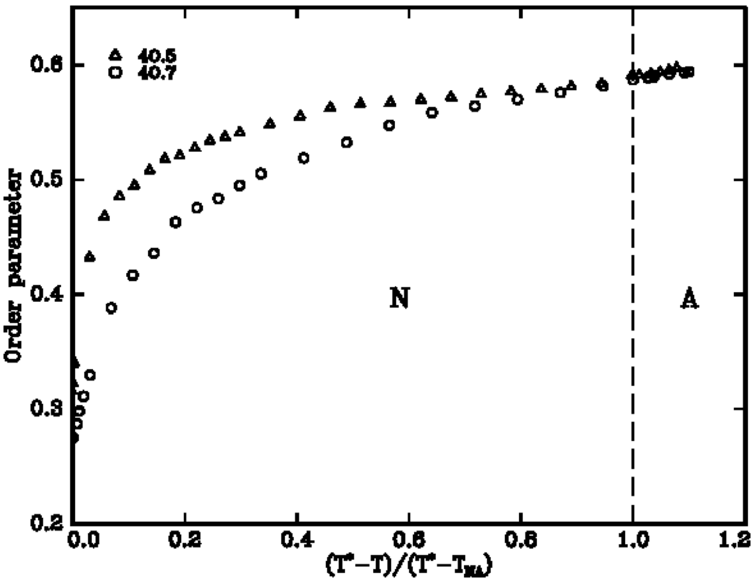

Fig. 5. Variation of order parameter S with normalized nematic range for the compounds 4O.5 (circles) and 4O.7 (dots).

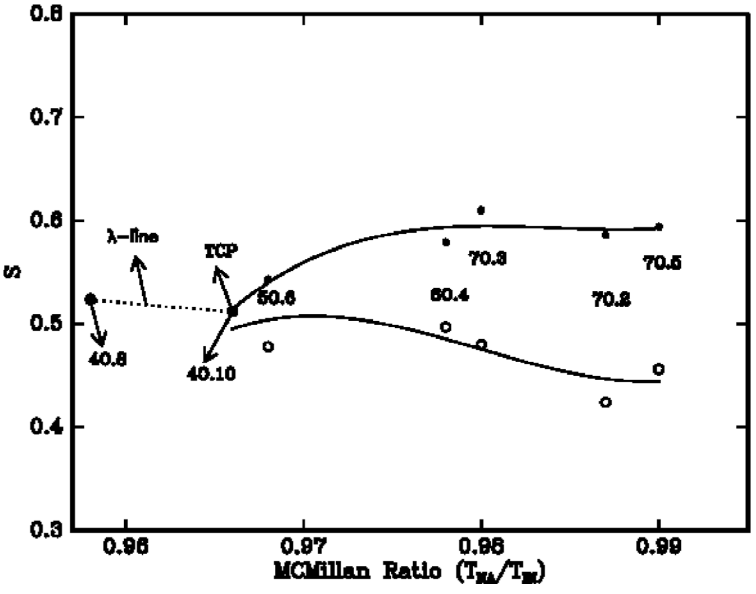

Fig. 6. Variation of order parameter S with McMillan ratio for nO.m homologous series. The coexistence region and λ-line are shown (the difference of magnitude between the filled and open circles represent the jump of S across NA transition).

of 4O.8 and nematic and smectic-A phases in 7O.5, respectively. In the case of 7O.5 there is a clear jump of the order parameter at the NS_A transition. A similar type of results are obtained for the other compounds which exhibit first-order NS_A transition in this series of compounds. However, in the case of compounds which exhibits second-order transition no order parameter jump is observed at this transition [13]. This is clearly observed in the case of 4O.5 and 4O.7 compounds which exhibit second-order NA transition, viz. the smooth changeover of the parameter S at the NS_A phase transformation (Fig. 5).

Table 1 envisages that the β values are very near to 0.2 (suggested by Kuczynski et al. [7, 8]) in most of the cases except in few cases. X is adjusted from 0.1 to 4 K from T_{IN} to obtain a better fit which provides realistic values for Δn, β, and R. In the case of 5O.6, 7O.1, and 7O.5, the β values are 0.13, 0.15 and 0.17, respectively (which are smaller than 0.2), but at the same time giving realistic β and R values. The

Table 1. Parameters for the best fit through linear regression for the equation $\log \delta n = \log \Delta n + \beta \cdot \log\left(\frac{T^{*}-T}{T^{*}}\right)$ in the case of nO.m compounds.

Compound	Nematic range (°C)	X	β	Δn	R
4O.5 [22]	37.2	1.2	0.200	0.420	0.9246
4O.6 [22]	23.4	3.5	0.198	0.385	0.9330
4O.7 [22]	26.2	0.5	0.197	0.367	0.9945
4O.8 [22]	14.6	0.6	0.205	0.425	0.9942
4O.9 [22]	15.5	1.0	0.193	0.350	0.9888
4O.10 [22]	12.0	1.3	0.199	0.330	0.9987
4O.12 [22]	8.0	1.5	0.201	0.320	0.9888
5O.1 [23]	5.4	1.6	0.199	0.398	0.9994
5O.2 [23]	5.3	0.5	0.205	0.378	0.9999
5O.4 [23]	16.8	1.0	0.195	0.257	0.9850
5O.5 [24]	22.4	1.2	0.198	0.350	0.9617
5O.6 [24]	11.2	4.0	0.130	0.265	0.9901
5O.7 [24]	13.3	1.0	0.192	0.354	0.9962
5O.8 [25]	8.0	1.0	0.210	0.360	0.9924
5O.9	11.0	4.0	0.170	0.310	0.9764
5O.10 [26]	8.8	0.5	0.180	0.320	0.9846
60.2 [27]	10.3	0.2	0.170	0.365	0.9854
6O.4 [27]	7.8	3.5	0.204	0.337	0.9977
6O.5	10.0	4.0	0.191	0.326	0.9061
6O.7	4.0	1.0	0.201	0.440	0.9978
7O.1 [27]	12.0	1.0	0.151	0.290	0.9878
7O.2	4.4	1.1	0.201	0.390	0.9785
7O.3	6.1	3.5	0.200	0.295	0.8417
7O.4	2.1	0.3	0.120	0.302	0.9750
7O.5	3.8	0.5	0.170	0.350	0.9951

minimum and maximum values obtained for Δn, the birefringence at perfect order, are 0.265 for 5O.6 and 0.440 for 6O.7, respectively (Table 1). Further, it is observed that the R values obtained in these cases are low compared to those obtained in other compounds. The authors systematic studies on alkoxy benzoic acids [14] and nO.O.m [15] compounds also show a similar type of compromising situation regarding the four adjustable parameters given in equation (3).

Rananavare et al. [16, 17] have shown that the McMillan ratio (T_{NA}/T_{IN}) is useful in analyzing the crossover between second and first-order behaviour of nematic/smectic-A transition in the nO.m homologous series as well as in the homogeneous mixture of two liquid crystals 6O.4+4O.6, which exhibit first and second-order NS_A transition, respectively, from the ESR and DSC data. Rao et al. [18] worked on the similar lines in case of above homogeneous mixture and they have shown similar results based on the refractive indices data obtained for different mixtures. However, the order parameter obtained from birefringence data has not been used for this purpose. Recently, Pisipati et al. [13] have used the order parameter obtained from birefringence using the procedure of Kuczynski et al. [7, 8] in the case of 6O.4+4O.6 mixture and obtained the TCP which concurred with the reported data within the experimental errors.

Figure 6 shows the order parameter measured at the NA phase transformation with the McMillan ratio for all the compounds studied. The plot to the right of the tri critical point (TCP) (where a second-order transition transforms to first order) shows the values of S_N and S_A in coexistence at T_{NA} corresponding to first-order NA transition, while the single line to the left of the TCP is the λ-line associated with the second-order transition. This plot is similar to those obtained by Rannavare et al. [16, 17] and Pisipati et al. [13] in the case of nO.m series and in the case of mixture 6O.4+4O.6, respectively. However, Rananavare et al. utilized different data. The figures given in references [13, 16, 17] may be compared with the results for ^{3}He-^{4}He mixture [19]. In the later case the mole fraction (mf) was plotted against T(mf), the transition temperature. Brisbin et al. [20] has pointed out that S_A-$S_N = \Delta S$ is the non-ordering density for the NA transition analogous to the mf difference in the ^{3}He-^{4}He case. In the case of ^{3}He-^{4}He, it is well known that the two branches of the phase separation curve are linear near the TCP and are meeting at a finite angle. The λ-line starts from this peak [19]. This is clearly seen in Figure 6 for the NA transition. It is to be mentioned in the present case that the λ-line is horizontal.

The results on a number of compounds and the conclusions drawn from these reveal that this method of evaluating the order parameter is useful for obtaining the order in the liquid crystalline phases other than nematic. The extrapolation procedure for $\delta n(T)$ does not undergo restrictions resulting from the local field model for the molecule, due to the extrapolation procedure is not applied for the polarizability anisotropy but directly to the birefringence δn. However, one disadvantage of this method is the adjustment of T^{*} for the estimation of Δn, the birefringence in perfect order, for getting better values of β and R in linear regression analysis.

Further, the McMillan ratio obtained from different methods differs slightly from one another. However, these values are higher compared with the value suggested by McMillan [21] in his theory.

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