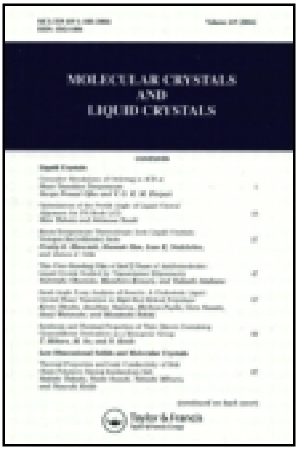

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# Orientational Order Parameter in Homogeneous Binary Mixtures of 6O.4 + 4O.6 of N-(p-n-Alkoxybenzylidene)-p-n-Alkyl Anilines, (nO.m) Series - A Birefringence Method

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# Orientational Order Parameter in Homogeneous Binary Mixtures of 6O.4 + 4O.6 of N-(*p-n*-Alkoxybenzylidene)-*p-n*-Alkyl Anilines, (nO.m) Series – A Birefringence Method

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*Different experimental methods are available to determine the order parameter in nematic liquid crystals. However, all these methods are not applicable and useful for the determination of order parameter in liquid crystalline phases other than nematic. In order to determine the order parameter in different liquid crystalline phases, we followed the extrapolation technique used by Kuczynski et al., following the suggestion made by de Gennes viz., that any anisotropic physical quantity may be a measure of orientational ordering in nematic mesophase. The order parameter can be calculated directly from a macroscopic quantity measured in the experiment. Using this idea, the authors calculated the order parameter based on birefringence measurements, which can be applied for all liquid crystalline phases, provided the birefringence data is available in those phases. The authors calculated the order parameter in nematic and smectic-A phases of a homogeneous binary mixture of two liquid crystals, 6O.4 and 4O.6 of N-(p-n-alkoxybenzylidene)-p-n-alkyl anilines, (nO.m) series. The results are discussed in the light of the available data on these binary mixtures and other compounds. In view of direct determination of order parameter, the discussion regarding the local field that a liquid crystal molecule experiences can be omitted.*

**Keywords:** nO.m series; N-SA transition; orientational order parameter; TCP

## INTRODUCTION

N-(*p*-*n*-alkoxybenzylidene)-*p*-*n*-alkyl aniline, (nO.m) compounds exhibit 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 oxygen atom on either side of the central rigid core and further, the position of the oxygen atom influences

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the clearing temperature also [2,3]. A number of these compounds are synthesized, characterized [4], and physical property measurements are carried out to study the nature of different phase transformations and the pretransitional effects [4–6] on either side of the transition. Rananavare *et al.* [7–9] and later Potukuchi *et al.* [10–12] using the differential scanning calorimeter, electron spin resonance, and optical birefringence demonstrated the crossover between second and first order behavior of the smectic-A and nematic transition ($S_AN$) in this homologous series as well as in binary mixtures of two nearly identical isomers, 4O.6 and 6O.4, by employing different field variables. Their results concur with one another that the tricitical point (TCP) to agree with the mean field prediction.

The most remarkable features of liquid crystals, crucial for their applications, are their anisotropic optical properties [13]. Further, it is well known that any of the bulk tensorial properties like electric and magnetic susceptibilities, elastic constants, refractive indices, etc. can be used to determine the order parameter. The most successful application of liquid crystals, namely, displays in wrist watches, pocket calculators, or flat screens of laptop computers, take advantage of electro-optical effects. A uniaxial liquid crystal is birefringent (for example nematic phase), meaning that it possesses two different indices of refraction parallel and perpendicular to the optic axis. As the temperature increases, the birefringence of the sample decreases and is zero at the nematic-isotropic transition. There are different methods to evaluate order parameter from the birefringence study. One such method to evaluate order parameter is the molecular polarizability, and the anisotropy of this property is one of the important properties of liquid crystals because the intermolecular interaction energies, according to several theoretical models [14–18], are based on them. The procedure for the determination of the orientational order parameter S using optical methods requires the following:

1. Measurement of both the refractive indices ($n_e$ and $n_o$, the ordinary and extraordinary indices);
2. Measurement of density, $\rho$;
3. Determination of the anisotropy of the molecular polarizability $\delta\alpha$ considering a local field model;
4. Normalization procedure for the polarizability, i.e., the determination of $\Delta\alpha$ for the perfect order; and
5. Calculating S from the equation $S = \delta\alpha/\Delta\alpha$.

Employing this procedure, S has been calculated in nematic phase for a number of compounds [19–21]. However, the results differ about

10 to 20% from one another. Recently, Kuczynski *et al.* [22,23] proposed a method to evaluate S directly from birefringence, without considering any local field thereby eliminating the determination of the density measurements as well as normalization procedures. Further, they claimed since the procedure does not consider any local field to the molecule in any liquid crystal phase, the S value can be obtained in phases like cholesteric and smectics. Following this procedure, the authors evaluated S in number of compounds which possess varying nematic thermal ranges and found that this procedure gives reliable results which fall in the middle compared to those obtained from normalization techniques [24].

As a part of systematic studies, the authors employed the above technique in the case of homogenous binary mixtures of 4O.6 and 6O.4, which exhibit a second order and first order $S_AN$ transition, respectively, with varying thermal ranges of nematic and smectic-A phases.

## METHOD

It is well known that any physical property of a nematic liquid crystal and the orientational order parameter S is closely connected to one another. Further, de Gennes [13] pointed out the anisotropy of any physical quantity can be a measure of orientational order. In the case of uniaxial liquid crystal, this parameter can be defined as

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

where $\delta A$ is the anisotropy of any arbitrary physical quantity $A = (A_{\|} - A_{\perp})$, and $\Delta A$ is the 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 [25] for the determination of S if a particular local field is applied for the liquid crystal molecule. Further, de Jeu [26] showed that birefringence $\delta n$ can be used for this purpose. Based on this, Kuczynski *et al.* [22,23] proposed a simple procedure for the determination of 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 $\delta n$ which is a function of temperature, is fitted to the following equation:

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

where T is the absolute temperature, and $T^*$ and $\beta$ are constants. ($T^*$ is about 1–4 K higher than the clearing temperature, and the exponent $\beta$ is close to 0.20). This procedure enables one to extrapolate $\delta$n to the absolute zero temperature. In practice, the three adjustable parameters $T^*$, $\Delta$n, and $\beta$ were obtained by fitting the experimental data for $\delta$n to the following equation written in the logarithmic form:

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

In the present investigations, the values of log $\Delta$n and $\beta$ are calculated by the linear regression method. The parameter $T^*$ is adjusted to get the best correlation coefficient of the linear regression. Thus, S is given by

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

The order parameter S determined in this way (Eq. (4)) describes well the nematic order parameter.

## RESULTS AND DISCUSSION

For evaluation of order parameter from birefringence data in these binary mixtures, the refractive indices data is taken from literature [11,12]. The birefringence in perfect order $\Delta$n is obtained by fitting the experimental data $\delta n$ in the equation (3) for best correlation coefficient. In the present case the values of $\Delta$n and $\beta$ are calculated by the linear regression method, treating $T^*$ as the primary adjustable parameter. The values, $T^*$, $\Delta$n and $\beta$ for all the mixtures are given in Table 1 below including the regression coefficient.

The linear fit for the mixture 20% of 6O.4 and pure compound 6O.4 are given in Fig. 1. In estimating the birefringence at perfect order only the values of birefringence in nematic phase has been considered for the linear fit, and this is the case for all mixtures. The table reveals that the $T^*$ values are within the limits as suggested by Kuczynski *et al.*, and further, the maximum (3.8 K) and minimum (0.5 K) values are for mixtures 80% and 19%, respectively. It has been observed the correlation coefficient is around 0.86 for the case of pure 4O.6 compound and the first three mixtures which exhibit second order $S_AN$ transition and for the rest of the mixtures, and in the case of 6O.4 which exhibits first order $S_AN$ transition, the correlation factor is ~0.99. The $\Delta n$ values are slightly higher for the first three mixtures compared to the other mixtures. The coefficient $\beta$ is around 0.2 for all

**TABLE 1** Parameters for the Best Fit through Linear Regression for the Equation $\log \delta n = \log \Delta n + \beta \cdot \log\left(\frac{T^{*}-T}{T^{*}}\right)$

| % of 6O.4 (x) in 4O.6 + 6O.4 | $T^{*} = (T_{NI} + -)$ | $\beta$ | $\Delta n$ | R |
|---|---|---|---|---|
| 0.00 (4O.6) | 3.5 | 0.198 | 0.385 | 0.8263 |
| 13.45 | 3.0 | 0.201 | 0.385 | 0.8679 |
| 19.00 | 3.0 | 0.198 | 0.385 | 0.8545 |
| 20.00 | 1.8 | 0.206 | 0.363 | 0.9906 |
| 22.50 | 2.4 | 0.206 | 0.336 | 0.9974 |
| 28.50 | 3.3 | 0.204 | 0.332 | 0.9940 |
| 39.00 | 2.0 | 0.200 | 0.322 | 0.9928 |
| 50.00 | 2.3 | 0.204 | 0.324 | 0.9330 |
| 66.00 | 2.1 | 0.201 | 0.333 | 0.9991 |
| 80.00 | 0.5 | 0.202 | 0.354 | 0.9879 |
| 89.90 | 2.0 | 0.204 | 0.350 | 0.9988 |
| 100.00 (6O.4) | 3.5 | 0.204 | 0.337 | 0.9977 |

the cases. The order parameter calculated using Eq. (4) for the two pure compounds 6O.4 (which exhibits a first order nematic – smectic-A transition) and 4O.6 (which exhibits a second order nematic – smectic-A transition) in both nematic and smectic-A phases are depicted in Fig. 2.

Table 2 illustrates the $T_{NA}$, the order parameter S, (values $S_N$ and $S_A$ in coexistence at $T_{NA}$(x)) along with the % of 6O.4 (x) in 4O.6 + 6O.4.

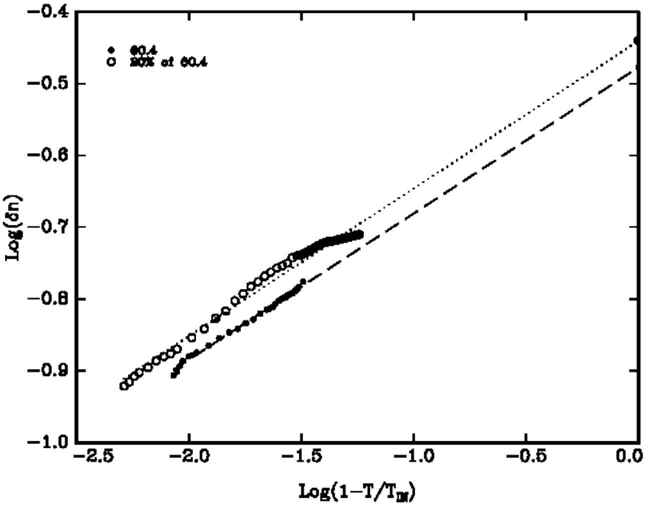

**FIGURE 1** The log-log plot of birefringence $\delta n$, against reduced temperature for the mixture 20% of 6O.4 and 6O.4.

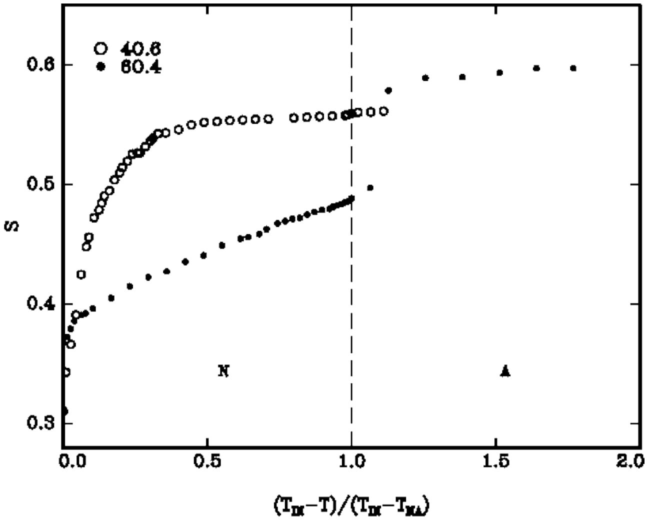

**FIGURE 2** Variation of order parameter S with temperature in 4O.6 and 6O.4.

Figure 3 shows the order parameter measured at the NA phase transformation for all the x values. The plot to the right of tricritical point (TCP) (where a second order transition transforms to first order) shows the values of $S_N$ and $S_A$ in coexistence at $T_{NA}(x)$ corresponding to first order NA transition, while the single line to the left of TCP is the $\lambda$-line associated with the second order transition. This figure may

**TABLE 2** Orientational Order Parameter Values at N-SA Interface, for all Compositions and N-SA Transition Temperatures

| $T_{NA}$(°C) | % of 6O.4 (x) in 4O.6 + 6O.4 | Order parameter, $S_N$ | Order parameter, $S_A$ | ΔS |
|---|---|---|---|---|
| 53.8 | 0.00 (4O.6) | 0.558 | 0.559 | 0.001 |
| 55.4 | 13.45 | 0.548 | 0.549 | 0.001 |
| 56.2 | 19.00 | 0.544 | 0.546 | 0.002 |
| 57.1 | 20.00 | 0.536 | 0.558 | 0.022 |
| 58.5 | 22.50 | 0.541 | 0.585 | 0.044 |
| 58,6 | 28.50 | 0.543 | 0.591 | 0.048 |
| 60.1 | 39.00 | 0.549 | 0.617 | 0.068 |
| 62.3 | 50.00 | 0.542 | 0.610 | 0.068 |
| 64.5 | 66.00 | 0.516 | 0.589 | 0.073 |
| 66.5 | 80.00 | 0.496 | 0.571 | 0.075 |
| 67.1 | 89.90 | 0.489 | 0.564 | 0.075 |
| 67.5 | 100.00 (6O.4) | 0.497 | 0.579 | 0.082 |

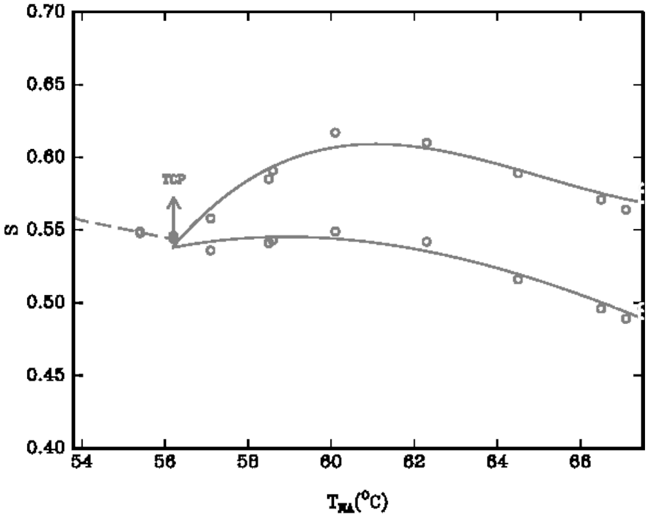

**FIGURE 3** The variation of order parameter, S with $T_{NA}$(x). The coexistence and $\lambda$-line are shown.

be compared with the results for the $^3He$-$^4He$ mixture [27]. In the later case, mole fraction (m.f) was plotted against T(m.f), the transition temperature. Brisbin [28] has pointed out $S_A - S_N = \Delta S$ is the non-ordering density for the NA transition analogous to the m.f difference in the $^3He$-$^4He$ case. In the case of $^3He$-$^4He$, it is well known that the two branches of the phase separation curve are linear near the (TCP) and meeting at a finite angle, and that the $\lambda$-line starts from this peak [27]. This is clearly seen in Fig. 3 for the NA transition. It is to be mentioned in the present case the $\lambda$-line is horizontal.

These studies and the experimental results on other compounds such as nO.Om, nO.m, n.Om, and n.m, and alkoxy benzoic acid compounds [24] reveal that:

1. For the compounds which exhibit a second order $S_AN$ transition, the correlation coefficient is always around 0.86, and the $T^*$ value is around 3 to 4 K from the clearing temperature. Irrelevant values are obtained for both $\Delta n$ and $\beta$, if $T^*$ is adjusted for a better regression coefficient;
2. For the compounds which exhibit first order $S_AN$ and possessing reasonably long thermal nematic range, the correlation coefficient is around 0.99, and $\Delta n$ and $\beta$ are reasonably good;
3. In the case of compounds which exhibit only nematic phase, the above argument holds good and

4. In the case of compounds which exhibit a small nematic thermal range, the $T^*$ range is only from 0.01 to 0.1°C (except in some cases where this value exceeds 0.5°C) for which the obtained $\beta$ value is around 0.12 to 0.15 for getting better $\Delta$n value and regression coefficient;
5. The order parameter, S can be considered as tool to predict a TCP either in homologous series or in mixtures.

In conclusion, the value of the birefringence $\Delta$n for a hypothetical, ideally ordered nematic could be extrapolated from the temperature dependence of $\delta$n. This value can be also used for the determination of the order parameter in cholesteric and smectic liquid crystals. The extrapolation procedure for $\delta n(\mathrm{T})$ does not undergo restrictions resulting from the choice of the local field model, because the extrapolation procedure is applied not for the polarizability anisotropy (where a particular local field model either isotropic [14] or anisotropic [15] is to be considered) but directly for the birefringence. In the present case, the birefringence $\delta$n has been taken from the difference of the two refractive indices that an anisotropic phase possesses. However, accurate methods are available [22,23] to measure $\delta$n directly. Our experimental observations on a number of LC materials [24] reveal that $\delta$n obtained from $n_e$–$n_o$ and $\delta$n measured directly from different methods (such as rotating polarization technique, Newton's ring method etc.,) are in close agreement with one another within the experimental error. In some compounds it is possible to get $\delta$n in crystalline phase also. When the birefringence for crystalline state $\Delta$n (where orientational order is equal to 1—as it would be in a perfectly ordered nematic liquid crystal), S can be determined from the ratio $\delta n(\mathrm{T})/\Delta n$. Otherwise, $\Delta$n can be evaluated by extrapolation procedure fitting $\delta n(\mathrm{T})$ in the Eq. (3).

In some cases, (where $\delta n$ in crystalline phase is obtained), *p*-*n*-butyloxy benzoic acid (for example), the $\delta$n value obtained in crystal state is in good agreement with the value obtained through extrapolation method. This result suggests that the anisotropy of the local field in both the nematic and the crystalline phase is negligible.

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