

A STUDY ON NEMATIC-SMECTIC PHASE TRANSITION OF OCTYLCYANOBIIPHENYL-CYCLOHEXANE BINARY MIXTURES

Purna Chandra Barman
Assistant Professor
Department of Physics
Raiganj University, West Bengal, India

ABSTRACT: In this paper the phase transition temperature at the nematic-smectic A region of the binary mixtures of cyclohexane, and octylcyanobiphenyl (8CB) has been conferred. A non-mesogenic, low molecular weighted solvent, Cyclohexane is used. The high resolution optical transmission technique has been employed to study the phase transition temperatures at nematic-smectic A region. The variation of transition temperature is shown and discussed for several concentrations of mixtures.

Keywords- *Liquid crystal, Binary mixture, Cyclohexene, Octyl-cyanobiphenyl.*

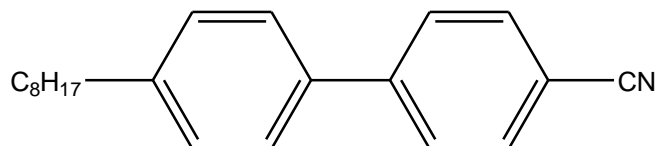
I INTRODUCTION

Several experimental as well as theoretical consents about the order of the transitions were adopted accordingly. Gray and his co-workers [1] confer point in time for synthesis this type of liquid crystal molecules for a long time ago. The nematic-smectic A (N-SmA) phase transition has been intensively deliberated for octylcyanobiphenyl (8CB) by means of several experimental techniques till now. Thoen and co-workers [2, 3] evidently signified that (N-SmA) phase transition was a second-order transition by explaining a specific-heat critical exponent. By various kind of experimental procedures such as volumetric measurements completed by Zywocki and Wiczorek [4, 5], it was predicted that the transition is second order. Marynissen et al. [6, 7] ensured the existence of a tricritical point (TCP) to verify the order of the N-SmA transition from very precise adiabatic scanning measurements (ASC). Assuming these findings Kobayashi [8], McMillan [9] and de Gennes and Prost [10] were capable to explain the order of N-SmA transition. Assuming a coupling between nematic and smectic order parameters, they predicted that the N-SmA transition should belong to second-order 3D-XY transition as well as the tricritical point (TCP). And first order nature is observed for N-SmA transition beyond the tricritical point (TCP). In addition, McMillan, through McMillan's ratio defined as T_{AN}/T_{NI} (T_{NI} is the nematic-to-isotropic transition temperature, and T_{AN} is the nematic to smectic transition temperature), suggested that the N-SmA transition may change from the second-order transition to a first-order one for strong coupling and this ratio nearly equal to one. On contrary, when the coupling is weak enough or the McMillan ratio is small, the 3D-XY model may be considered. The nematic order parameter completely saturated when the 3D-XY model is applicable. Moreover, Halperin, Lubensky, and Ma [11, 12] predicted by a theory, known as HLM theory, that N-SmA transition always a weak first order. Nevertheless, this fact has not yet been strictly proved. In this case the concept of tricritical point (TCP) is not considered.

In the present work the phase diagram of a binary system of octylcyanobiphenyl (8CB) and solvent (cyclohexene) as obtained by using the high resolution optical transmission method is presented. The critical behaviour in the vicinity of the nematic-smectic A (N-SmA) phase transition of various mixtures having concentration range of $0.024 < x_{\text{hex}} < 0.19$ of cyclohexene along with pure 8CB has been explored by measuring the temperature dependence of optical birefringence (Δn). The extraction of critical exponent (α) has been successfully done by using optical birefringence data at the nematic-smectic A (N-SmA) phase transition, which is mainly important to determine character of order at that phase transition. The nature of the N-SmA phase transition dramatically changes with addition of cyclohexane on 8CB. The heat capacity peak associated with the N-SmA transition increases toward lower temperature region as concentration of solvent increases.

II Materials

The pure compound 8CB were purchased from Merck, U.K. and was synthesized and purified by Professor Dabrowsky in the Institute of Chemistry, Military University of Technology, Warsaw, Poland. By chromatography, the purity was stated to be higher than 99.9% and no further purification was carried out. Liquid crystal homogeneous binary mixtures of 8CB+Cyclohexene were prepared at room temperature by weighing the pure in compounds in selected proportions and heated up to the isotropic phase. Cyclohexane is a cycloalkane with the molecular formula C_6H_{12} . It is a colourless, flammable liquid with a distinctive detergent-like odor and is used for the industrial production of adipic acid and caprolactam, which are precursors to nylon. The general structural formula and the chemical name with transition temperature of the compound 8CB are given below:



Octyl-cyanobiphenyl (8CB): Cr 21.5°C SmA 33.5° N 40.2°C I

III Experimental

A solid state green laser of wave length 532 nm was directed onto a homogeneously aligned (planar) liquid crystal cell of thickness 5.1 mm (purchased from AWAT Co. Ltd., Warsaw, Poland). The cell is placed between two crossed linear polarizer's. The temperature of the cell was regulated and measured with a temperature controller (Eurotherm PID 2404) with an accuracy of ± 0.1 °C by placing the cell in a custom built heater made of brass. The transmitted light intensity was measured by a photo diode at an interval of 3 seconds. When the heater temperature is varied at a rate of $0.5^{\circ}\text{C min}^{-1}$, this translates into a temperature difference of 0.025°C between two readings [13,14].

IV NEMATIC TO SMECTIC A (N-SmA) PHASE TRANSITION

In order to settle on the critical behaviour appeared in the vicinity of nematic to smectic A (N-SmA) phase transition, the transition temperature of that phase has been considered as a worth factor.

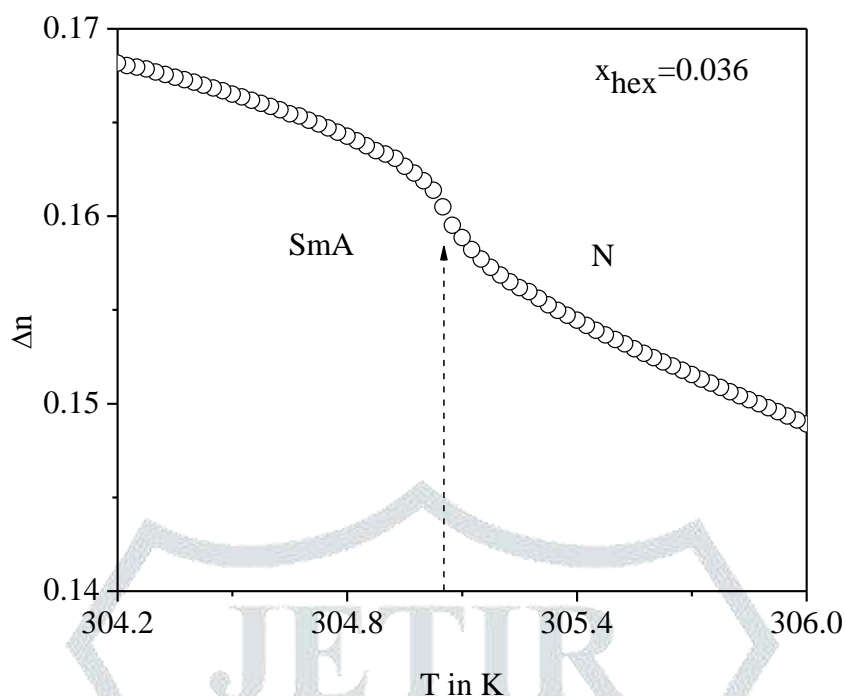


Figure 1. The temperature dependence of birefringence (Δn) for mixtures of mole fraction of cyclohexane. $x_{\text{hex}} = 0.036$.

Although, no distinct alteration of temperature dependence birefringence (Δn) resembling to nematic to isotropic phase transition has been observed yet we have easily envisaged the exact value of transition temperature by analyzing the minimum value of the first order temperature derivative of Δn i.e., $d(\Delta n)/dT$ which has been made to be associated to the specific heat capacity anomaly [15]. The derivative of Δn is found to be relatively scattered is shown in the Figure 1. This is due to may be for the small temperature range between consecutive data. In view of appropriate insight of the critical aspects as well as to reduce the scattering, a new quotient is to be introduced in the following form [16-18].

$$Q(T) = - \frac{\Delta n(T) - \Delta n(T_{NA})}{T - T_{NA}} \quad (1)$$

where $\Delta n(T_{NA})$ is the birefringence value at the nematic-smectic A phase transition temperature (T_{NA}) determined from the minimum of the $d(\Delta n)/dT$ curve. A diverging behaviour of the $Q(T)$ values has been seen in the vicinity of N-SmA phase transition. To minimize this type of manner a new expression is to be made in the following form [16] by which straightforwardly the nature of the N-SmA phase transition can be explained.

$$Q(T) = A_{\pm} |\tau|^{-\alpha} + B \quad (2)$$

where A^+ and A^- are the critical amplitudes and B^+ and B^- are the background terms above and below the nematic-smectic A phase transition temperature (T_{NA}), α is the critical exponent similar to specific heat critical exponent and $t = |(T - T_{NA})/(T_{NA})|$ is the reduced temperature. The temperature dependence of $Q(T)$ values for the different mixtures ranging from 0.024 to 0.19 in weight percentage of cyclohexene are demonstrated in Figure 1 and the related values of the critical amplitude, background term and the critical exponent (α) describing the critical behavior on both sides of the N-SmA transition have been gathered in Table 1. The solid line within the presented figures indicates the fitting curves.

The reduced χ^2 values on either sides of the investigated transition have been used to establish the features of the fittings whether it is ideal or good. Theoretically, the ideal or good fittings had to be suggested by testing the value of χ^2 . Corresponding to the ideal fits the value of χ^2 is equal to unity and the values lying between 1 and 1.5 indicates good fits. The reduced χ^2 has been determined by evaluating the ratio of variance of the fit (s^2) to the variance of the experimental data (σ^2) and can be expressed as follows, [19]

$$\chi^2 = \frac{s^2}{\sigma^2} = \frac{1}{\sigma^2} \sum_i (y_i - f_i)^2 \quad (3)$$

where N is the total number of data points, p is the number of adjustable parameter and f_i is the i th fit value corresponding to the measurement y_i . For our present fits, the χ^2 value have been found to lie between 1.00 and 1.45 which indicate the satisfactory fits to the Q(T) data for the considered model expression.

Before investigating the critical exponent (α) for each fit, which be a sign of the nature of the N-SmA phase transition we have identified the transition temperature exactly by introducing the temperature dependence of $d(\Delta n)/dT$. In our study, it is found that the Q(T) value increases as the nematic region of the mixtures decreases describing the stronger coupling between the nematic and smectic ordering. The critical exponent (α) value increases corresponding to the increase of sharpness of Q(T) value. For these mixtures we have obtained the α value lie in between 0.330 to 0.403. Nearly the same value for the exponent α above and below the N-SmA phase transition has been obtained from fitting procedure taking a range of 1–2 K above and below of T_{NA} . According to theoretical interpretation, for a tricritical point the ratio of critical amplitude (A_-/A_+) requires value very close to 1. But, it should be noted that the results for the pure compound and the mixtures dealt with in this work, the amplitude ratio A_-/A_+ is obtained ranging from 0.94 to 1.44. For the pure compound 8CB we have used the α values nearly equal to 0.32 ± 0.03 . The critical exponent values (α) for the investigated mixtures and pure compound are found to exhibit a definite pattern when plotted against the McMillan ratio as shown in Figure 3. Nonlinear critical exponent (α) dependence on McMillan ratio of mixtures and pure compound is not unique as compared to that seen by K. Denolf *et.al.* [20, 21].

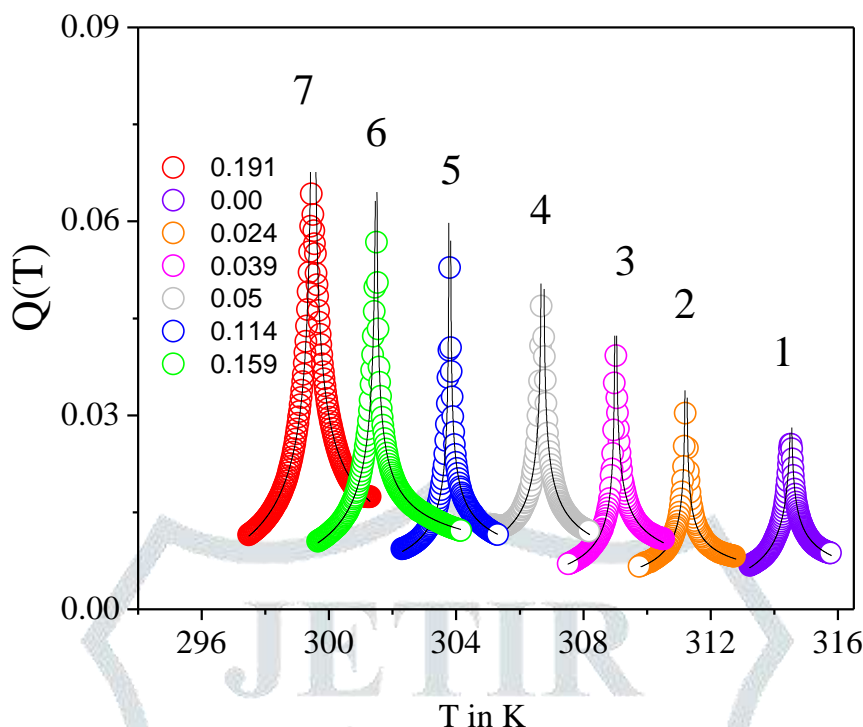


Figure 2. The temperature dependence of $Q(T)$ in the vicinity of the N -SmA transition for different mixtures of 8CB and cyclohexane. For clarity the $Q(T)$ curves have been shifted in temperature to make the view clearer. 1: $x_{cyhex} = 0.0$ ($\Delta T_{shift} = 8.0$ K); 2: $x_{cyhex} = 0.024$ ($\Delta T_{shift} = 6.0$ K); 3: $x_{cyhex} = 0.039$ ($\Delta T_{shift} = 4.0$ K); 4: $x_{cyhex} = 0.05$ ($\Delta T_{shift} = 2.0$ K); 5: $x_{cyhex} = 0.114$; 6: 0.159 ($\Delta T_{shift} = -2.0$ K); 7: 0.191 . Open circles (\circ) represent the calculated $Q(T)$ values and the solid lines are fit to equation

It also to be noted that for the binary systems the calculated critical exponent values (α) is much lower than the reported values [20] of corresponding concentrations.

Table 1. Parameters values for the quantity $Q(T)$ near N-SmA transition obtained from Equation (1) and the corresponding value of χ^2 associated with the fit.

x_{hex}		A. or A_+	T	α	B. or B_+	χ^2	No. of points
0.00	$T < T_{NA}$	0.0023 ± 0.0006	306.56 ± 0.842	0.319 ± 0.075	-0.0061 ± 0.0006	1.38	48
	$T > T_{NA}$	0.0016 ± 0.0001	306.51 ± 0	0.320 ± 0.006	-0.0011 ± 0.0003	1.36	65
0.024	$T < T_{NA}$	0.0014 ± 0.0002	305.20 ± 1.117	0.330 ± 0.077	-0.0022 ± 0.0015	1.06	54
	$T > T_{NA}$	0.0013 ± 0.0001	305.24 ± 0.97	0.329 ± 0.010	0.0003 ± 0.0004	1.45	58
0.039	$T < T_{NA}$	0.0016 ± 0.0003	304.99 ± 1.527	0.335 ± 0.094	-0.0028 ± 0.0029	1.01	31
	$T > T_{NA}$	0.0017 ± 0.0002	305.02 ± 0.19	0.338 ± 0.014	-0.0001 ± 0.0007	1.33	49
0.05	$T < T_{NA}$	0.0020 ± 0.0004	304.69 ± 1.496	0.345 ± 0.092	-0.0020 ± 0.0038	1.02	41
	$T > T_{NA}$	0.0019 ± 0.0001	304.73 ± 1.1	0.346 ± 0.007	-0.0006 ± 0.0004	1.11	51

0.11	$T < T_{NA}$	0.0016 ± 0.0001	303.78 ± 0.53	0.355 ± 0.037	-0.0021 ± 0.0009	1.37	56
	$T > T_{NA}$	0.0015 ± 0.0001	303.81 ± 0.85	0.356 ± 0.011	0.0015 ± 0.0005	1.27	53
0.16	$T < T_{NA}$	0.0023 ± 0.00065	303.49 ± 0.67	0.378 ± 0.071	-0.0059 ± 0.0007	1.02	72
	$T > T_{NA}$	0.0016 ± 0.0001	301.48 ± 0.001	0.377 ± 0.006	0.0025 ± 0.0003	1.38	98
0.19	$T < T_{NA}$	0.0028 ± 0.00001	299.50 ± 0.0163	0.403 ± 0.007	-0.0099 ± 0.0001	1.0	76
	$T > T_{NA}$	$0.0023 \pm 4.8679E-6$	299.51 ± 0.002	0.406 ± 0.011	-0.0021 ± 0.0005	1.15	49

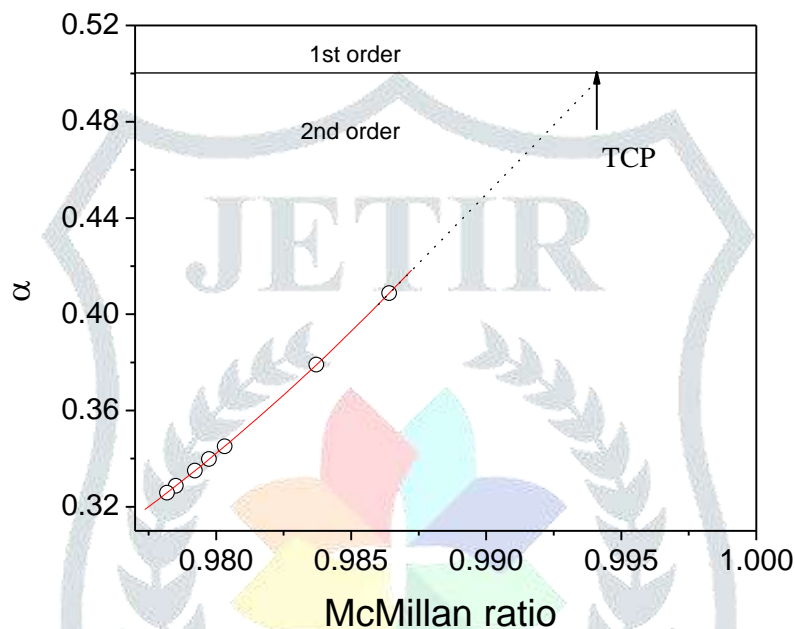


Figure 3. Variation of critical exponent (α) with McMillan ratio (T_{NA}/T_{NI}). The vertical bar represents the error associated with α value. The solid line shows polynomial fit to the data and the dotted line represent the linear extension on fitted line.

V Summary of the results and conclusions

In this paper detailed studies of birefringence on the continuous second order nematic-smectic A phase transition of 8CB doped with nonmesogenic, low-molecular weight solvent, cyclohexene, has been undertaken. A dramatic change in pretransitional effect at the nematic-smectic A (N-SmA) phase transition is detected. In addition to coupling between the nematic and smectic order parameter, the pretransitional effect is stronger when the concentration of cyclohexene is increased. The second order nature of N-SmA phase transition of all mixtures along with pure 8CB is verified by analyzing the critical exponent (α).

VI Acknowledgement

All of this work has been done at Experimental Liquid Crystal Laboratory, Department of Physics, University of North Bengal. Author is thankful to Professor Malay Kumar Das, Department of Physics, University of North Bengal, for completing the work.

References

[1]

G. W. Gray,

Molecular structure and the properties of Liquid Crystals, Academic Press (1962).

- [2] J. Thoen, T. Bose, Handbook of Low and High Dielectric Constant Materials and Their Applications, edited by H. S. Nalwa, Vol. 1, Academic, London, 1999.
- [3] J. Thoen, G. Menu, *Mol. Cryst. Liq. Cryst.*, 97, 163 (1983).
- [4] Zywocinski, A.; Wieczorek, S. A. *Phys. Rev. A* **1985**, 31, 479.
- [5] Zywocinski, A.; Wieczorek, S. A. *Mol. Cryst. Liq. Cryst.* **1987**, 151, 399.
- [6] Marynissen, H.; Thoen, J.; van Dael, W. *Mol. Cryst. Liq. Cryst.* **1985**, 124, 195.
- [7] Marynissen, H.; Thoen, J.; van Dael, W. *Mol. Cryst. Liq. Cryst.* **1983**, 97, 149.
- [8] Kobayashi, K. *Phys. Lett. A* 1970, 31, 125–126.
- [9] McMillan, W. L. *Phys. Rev. A* **1971**, 4, 1238.
- [10] De Gennes, P.G.; Prost, J.; *The Physics of Liquid Crystals*; Oxford University Press: Oxford (UK), 1994.
- [11] Halperin, B. I.; Lubensky, T. C.; Ma, S. *Phys. Rev. Lett.* 1974, 32, 292.
- [12] Halperin, B. I.; Lubensky, T. C. *Solid State Commun.* 1974, 14, 997.
- [13] S. K. Sarkar, P. C. Barman and M. K. Das, *IMPACT-IJRANSS*, 1, 4, Pp. 1-8, (2013), (2013).
- [14] S. K. Sarkar, P. C. Barman and M. K. Das, *Physica B* **446**, 80-84, (2014).
- [15] A.V. Kityk, P. Huber, *Appl. Phys. Lett.* 97 (2010) 153124.
- [16] S. Erkan, M. Cetinkaya, S. Yildiz, H. Ozbek, *Phys. Rev. E* 86 (2012) 041705.
- [17] S. Yildiz, H. Ozbek, C. Glorieux, J. Thoen, *Liq. Cryst.* 34 (2007) 611.
- [18] M.C. Cetinkaya, S. Yildiz, H. Ozbek, P. Losada-Perez, J. Leys, J. Thoen, *Phys. Rev. E* 88 (2013) 042502
- [19] P.R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*, 1st edn., McGraw-Hill, New York, 1969.
- [20] K. Denolf, G. Cordoyiannis, C. Gloriénx, and J. Thoen, *Phys. Rev. E*, vol. 76, p. 051702, 2007.
- [21] K. Denolf, B. V. Roie, C. Gloriénx, and J. Thoen, *Phys. Rev. Lett.*, vol. 97, p. 107801, 2006.