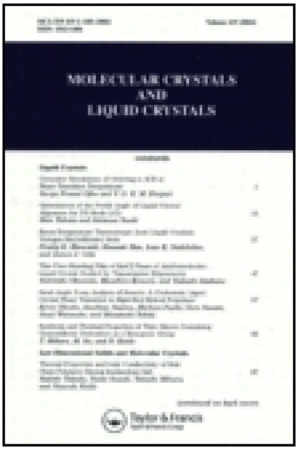

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Studies on Calorimetry, Densities and Refractive Indices of Some Smectogenic Liquid Crystalline Compounds

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Studies on Calorimetry, Densities and Refractive Indices of Some Smectogenic Liquid Crystalline Compounds[†]

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Transition heat data for five liquid crystalline compounds, three [C-5, 6 and 7] of the series: ethyl-*p*-(alkoxybenzylidene)-aminobenzoate and two [C-6 and 7] of butyl-*p*-(alkoxybenzylidene)-aminobenzoate have been obtained using a Perkin–Elmer DSC 1-B calorimeter. Two mesomorphic transitions were observed for the compounds, the lower temperature transition being monotropic in nature. Transition temperatures noted using a polarizing microscope are in agreement with those of the calorimetric data and are slightly higher than those reported by Fishel and Patel.[1]

Two pronounced discontinuities were observed in the slope of density vs temperature curves for the two representative compounds corresponding to the two series. Also, small variation in the values of refractive indices at the second phase transition have been observed for these two. Microscopic textures give clear evidence for the presence of two distinct smectic phases. It is reported[1] that the second phase is smectic A with more lines of discontinuities. However, the present studies afford the conclusion that the second phase is smectic B.

INTRODUCTION

Thermal analysis is important in characterization of mesomorphic substances and in elucidation of structure property relationship, and as such calorimetry is a valuable technique in mesophase research. It yields quantitative results indicating the magnitude of the stepwise changes in molecular order during phase transitions. Studies on refractive indices provide

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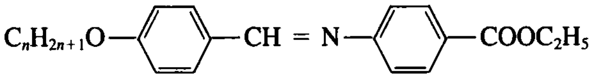
[†] Presented at the Ninth International Liquid Crystal Conference, Bangalore, 1982.

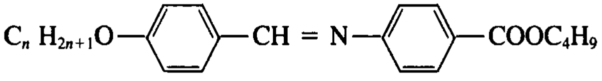
additional direct information about the molecular order, while the density measurements are essential for the determination of the order parameter. The microstructure studies, however, are of crucial importance in identification of liquid crystalline phases. Therefore, the primary aim of this work is to present the preliminary data obtained by using the above mentioned techniques for the compounds listed below,

Ethyl-*p*(alkoxybenzylidene)-aminobenzoate



where n = 5, EPAB
= 6, EH$_x$AB
= 7, EH$_p$AB; and

Butyl-*p*-(alkoxybenzylidene)-aminobenzoate



where n = 6, BH$_x$AB
= 7, BH$_p$AB .

Secondly, the other aspect of the studies is to identify the phases exhibited by these compounds.

It was noted that the three compounds of the series ethyl-*p*-(alkoxybenzylidene)-aminobenzoate show similar behavior. Therefore, we limit our discussion for only one of the compounds, EH$_x$AB, although the calorimetric data is presented for all. Similarly we choose BH$_x$AB from the other series: butyl-*p*-(alkoxybenzylidene)-aminobenzoate.

EXPERIMENTAL

A. Compound preparation

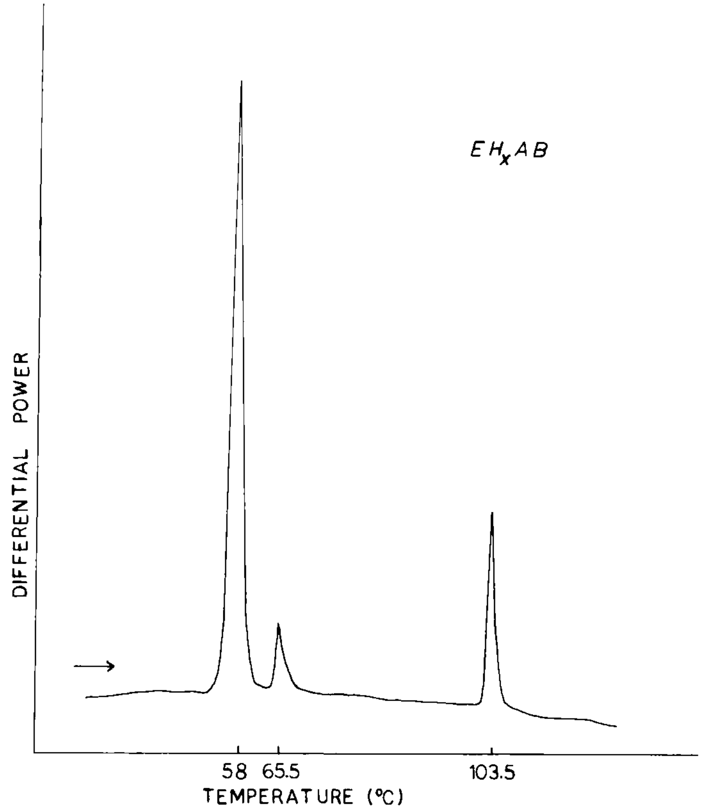
p-*n*-alkoxybenzaldehydes were prepared by the method given by Gray and Jones[2] and purified twice by distillation under reduced pressure.

The compounds were obtained[1] by condensing equimolar quantities of the appropriate aldehyde and aniline in absolute ethanol and recrystallized from absolute ethanol to constant transition temperatures.

Freshly crystallized and vacuum dried samples were used for all the measurements.

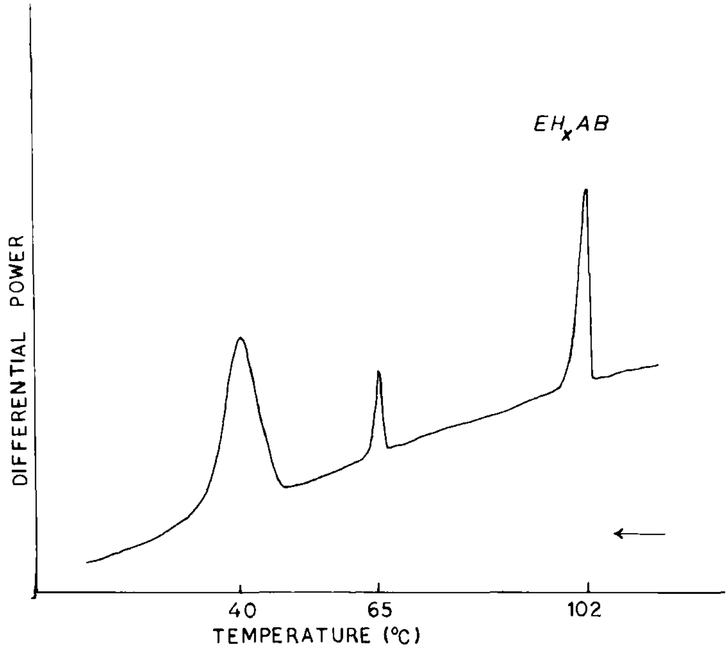
B. Calorimetry

The transition temperatures and heats were determined by using a Perkin–Elmer Differential Scanning Calorimeter DSC 1–B. Calibration of the apparatus was performed using the tabulated heats of very pure indium and tin. Samples were vacuum dried prior to weighing and about 3 mg quantities encapsuled in the standard aluminium Perkin–Elmer sample sealers. Two warming and cooling DSC scans were taken at the heating rates of 16°/min for each sample. Figure 1 shows the DSC thermograms for the compounds EH_xAB and BH_xAB.



(*a*)

FIGURE 1 DSC thermograms obtained at the heating rate of 16°/min of compound EH_xAB for (a) heating, (b) cooling, cycle and of compound BH_xAB for (c) heating, (d) cooling, cycle, respectively.



(*b*)

FIGURE 1 (*Continued*)

The areas under the DSC peaks were measured several times by planimetry, the mean taken and the transition heats calculated. Transition temperatures and heats were presented in Table I.

The error in the determination of transition heats consists mainly of the error in the reproducibility of the base line and the peaks. The determination of the area of the peaks by planimetry introduces some error. The maximal relative error on account of these increases with decreasing enthalpy value but does not exceed 10%.

C. Microscopy

The microscopic slides and the cover slips were cleaned ultrasonically using teepol, chromic acid, acetone and twice with double distilled water and finally dried with dry-air current. Using these slides excellent textures were obtained. The hot-stage of the polarizing microscope, fabricated in our workshop, was controlled within ±0.2°C. The microscopic textures obtained under crossed polarizers with a magnification of 100× are as in Figure 2.

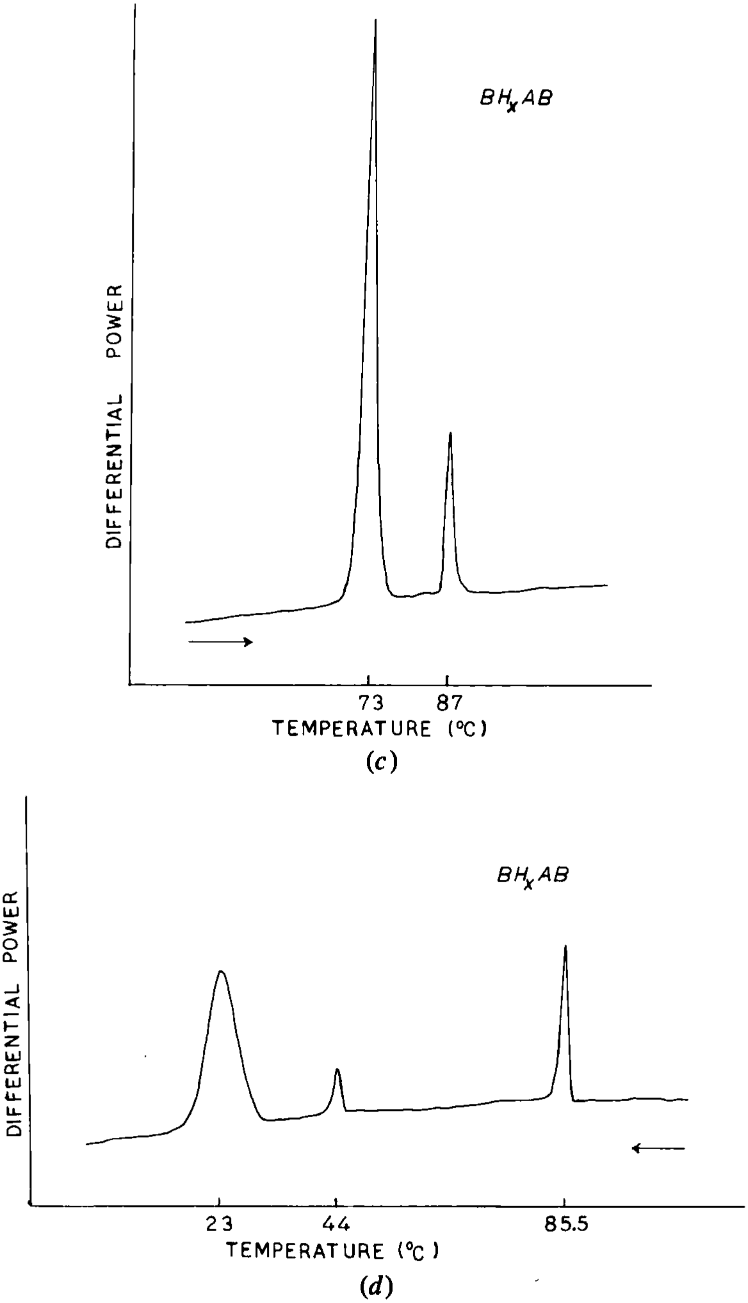


FIGURE 1 (*Continued*)

TABLE I

Heats of transition

Compound	Transition	ΔH K cal/mol	ΔS K cal/ mole/°K	ΔH Total K cal/mol	ΔS Total K cal/ mol/°K	Temperature °C DSC	microscopy
EPAB	I-Sm 1	1.38	0.00382			99.5	99
	Sm 1-Sm 2	0.49	0.00146	6.98	0.02155	72	70.5
	Sm 2-C	5.11	0.01627			53	59
EH$_x$AB	I-Sm 1	1.10	0.00302			102	101.5
	Sm 1-Sm 2	0.42	0.00130	6.25	0.02003	65	63
	Sm 2-C	4.73	0.01571			40	48
EH$_p$AB	I-Sm 1	1.25	0.00344			101.5	102
	Sm 1-Sm 2	0.29	0.00090	3.75	0.01231	60.5	60
	Sm 2-C	2.21	0.00797			26	40
BH$_x$AB	I-Sm 1	1.07	0.00297			85.5	85
	Sm 1-Sm 2	0.21	0.00067	5.77	0.01958	44	42.5
	Sm 2-C	4.53	0.01594			23	36
BH$_p$AB	I-Sm 1	1.27	0.00368			85	84
	Sm 1-Sm 2	0.25	0.00084	3.68	0.01250	42	42
	Sm 2-C	2.16	0.00798			20	37

I-Isotropic liquid, C-Solid.

D. Density

Capillary method was used for density measurements. Standard Top syringe capillaries with 1 mm bore were carefully cleaned and oven dried overnight at a temperature of 120°C. The samples were inserted in the capillaries in liquid form by capillary action to a length of about 3 cm, and the amount was weighed on a microbalance. The oven temperature was controlled to ±0.5°C, and the sample length was measured to the accuracy of 1×10^{-5} cm. The method was calibrated using distilled water, benzene and mercury. The density variations are shown in Figure 3.

E. Refractive indices

Refractive indices were measured by the hollow-prism method, the prism angles ranging between 1° to 1.5°. The glass plates forming the prisms were cleaned ultrasonically as mentioned earlier, and the prisms were calibrated using double distilled water, benzene and acetone.

The samples were inserted in liquid state along the edge of the prism by capillary action and subsequently subjected to a magnetic field of 8 K Gauss for alignment. The prisms were contained in a copper block and the temperature of which was controlled to ±0.5°C. The spectrometer used

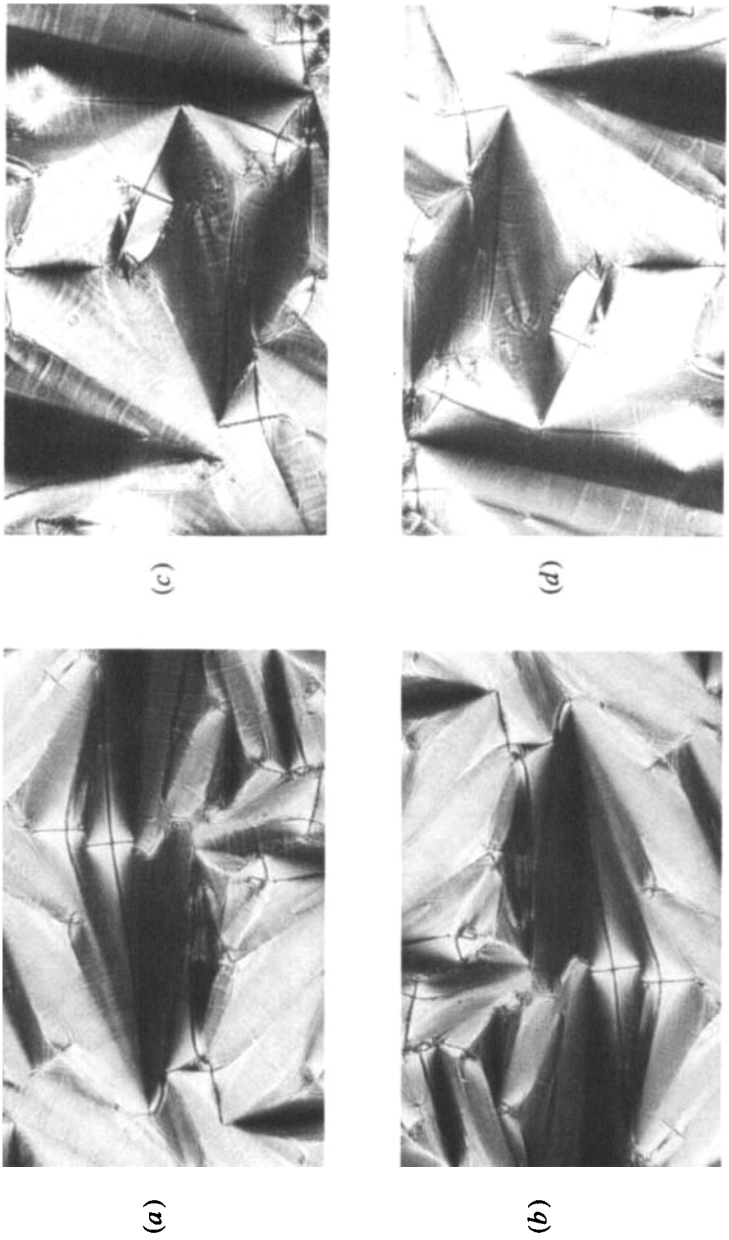
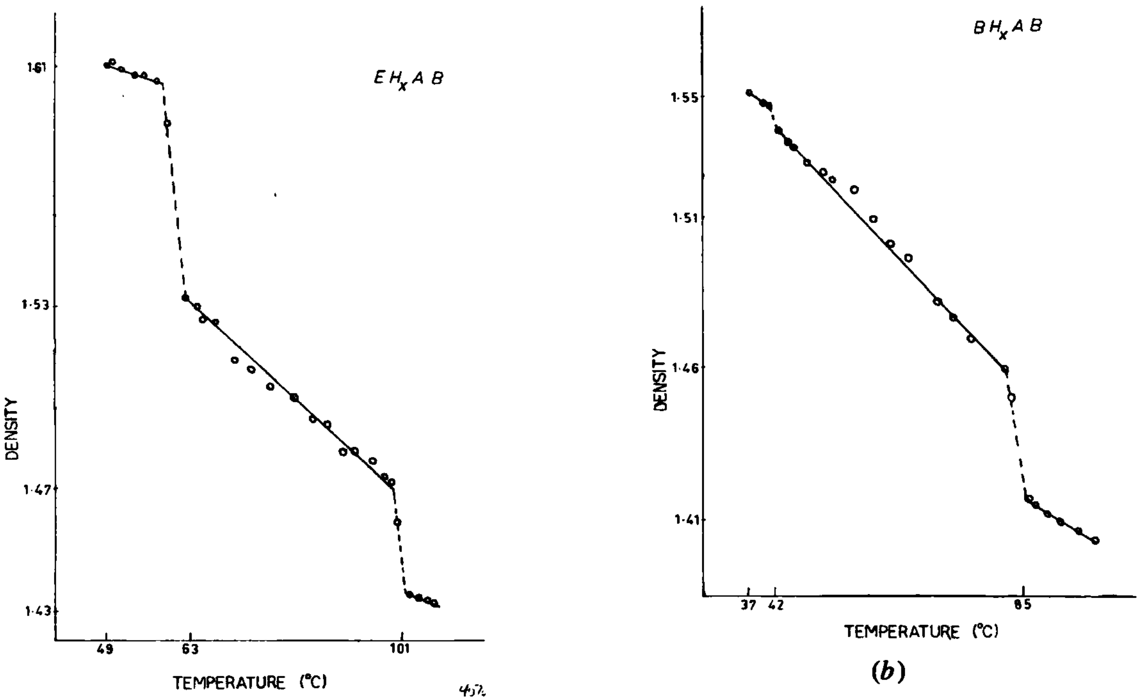


FIGURE 2 Smectic transition bars illustrating focal conic contour lines. Magnification 100×. Compound EH$_x$AB at 62.8°C, S$_A$S$_B$ transition (a) and at 62°C, S$_B$ phase (b). Compound BH$_x$AB at 42.5°C, S$_A$S$_B$ transition (c) and at 42°C, S$_B$ phase (d).



(*a*)

(*b*)

FIGURE 3 Plot of density variation with temperature for EH_xAB (a) and for BH_xAB (b).

has a least count of 20″. The variation with temperature of refractive indices (n_e, n_0) is graphically represented in Figure 4.

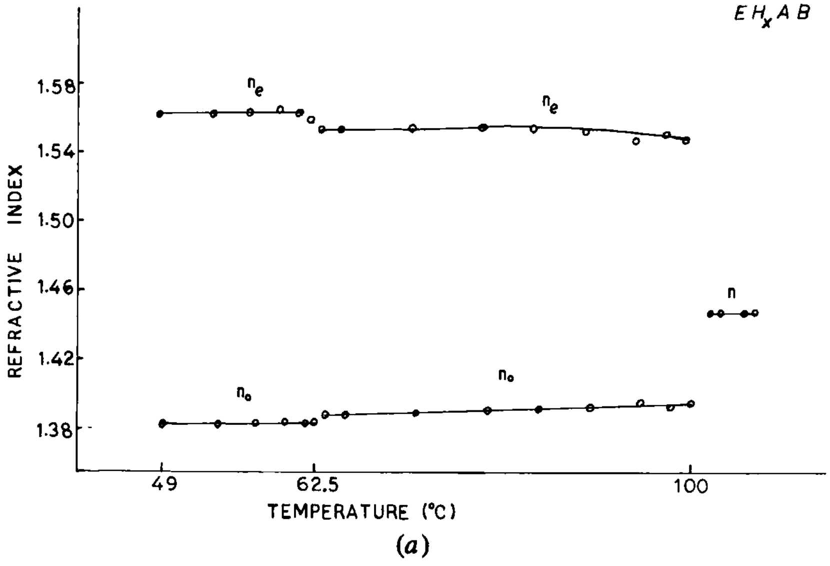
All the chemicals and solvents used were purified and of A. R. grade.

RESULTS AND DISCUSSION

The transition temperatures obtained from optical microscopy and DSC are in good agreement at the smectic-smectic, and smectic-isotropic transitions, and are slightly higher than those reported in literature,[1] especially at the clearing points, indicating the purity of the samples. From the DSC thermograms it is observed that considerable supercooling takes place for the mesophase-solid transition as compared to the transition temperature obtained from optical microscopy.

Three exothermic peaks were observed on the DSC thermograms during cooling cycles for all the compounds. During heating cycles, two endothermic peaks were observed for EPAB, BH_xAB and BH_pAB, whereas three endothermic peaks were observed for EH_xAB and EH_pAB. The solid-mesophase transition enthalpy is an order of magnitude greater than the enthalpy changes associated with the loss of order at other transitions as expected. The enthalpies of the smectic-isotropic liquid transitions lie in the expected limit[3] between 1 to 3 K cal/mole. The total transition entropy decreases as the carbon number increases (Table I). The entropy changes for the smectic-isotropic transitions for the compounds EPAB, EH_xAB, EH_pAB account for 13%, 15%, 28% and that for BH_xAB, BH_pAB 15%, 29%, respectively, of the total entropy change. It is noticeable that the percentage entropy change for smectic-isotropic transitions amount to the same extent for EH_xAB–BH_xAB and EH_pAB–BH_pAB, the pairs with the same carbon number in the alkyl chains of the respective series. The smectic-isotropic transition entropy in 4,4′-di-*n*-dodecyloxyazoxybenzene accounts for 20% of the solid-isotropic liquid transition entropy.[4,5]

Our texture identification is based on comparison with the microphotographs given in the literature.[6,7] Cooling from the isotropic liquid state gives rise to a phase exhibiting simple fan texture characteristic of smectic A for all the compounds. We see the transition bars in Figures 2(a) and (c) formed by the coexistence of the alternate layers of smectic A and smectic B phases (both in fan textures) at the S_AS_B transition temperature. Transition bars can be formed in the vicinity of the transition either on cooling from S_A to S_B or warming from S_B to S_A. It is possible to maintain



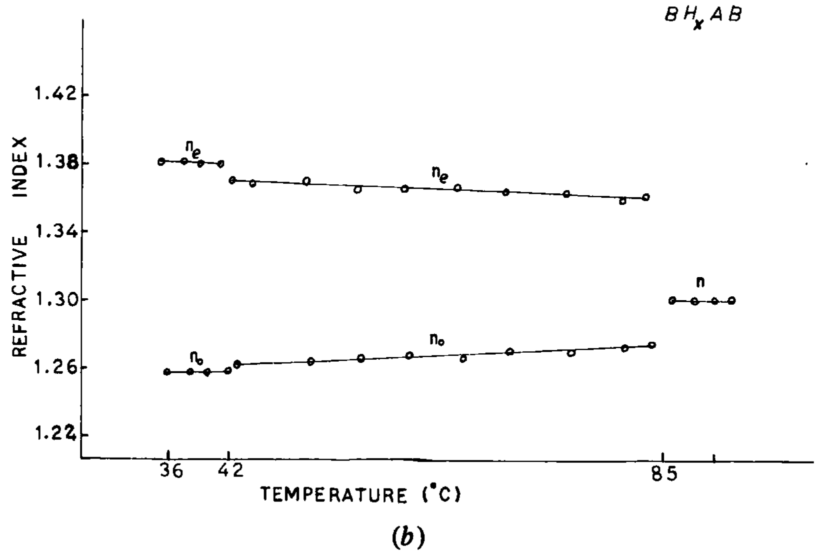


FIGURE 4 Refractive indices variation with temperature for EH_xAB (a), and for BH_xAB (b).

the coexistence of the two phases and the bars indefinitely, if the temperature is controlled at the transition point. However, a slight cooling or warming produces the growth of the equilibrium phase and reduces the coexistence regions, leading to disappearance of the bars. Although the bars themselves disappear upon cooling to S_B, remanent indications of their presence can still be seen in the fans with reduced discontinuities characteristic of S_B,[6] Figures 2(b) and (d).

The plots of density variation with temperature give two pronounced discontinuities in the slopes of the density curves for EPAB, EH_xAB [Figure 3(a)], EH_pAB and relatively less pronounced but clear discontinuities for BH_xAB [Figure 3(b)], BH_pAB indicating the presence of two distinct phases. A small noticeable change in the values of refractive indices is also observed at the smectic-smectic phase transitions, Figures 4(a) and (b). This change in the optical property reflects the change in the molecular anisotropy and hence the distinction of one phase from the other. These experimental evidences confirm the existence of two smectic mesophases and the microstructure study helps for their identification, the high temperature phase being smectic A and the low temperature one being smectic B.

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