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RESEARCH ARTICLE

A DILATOMETRIC INVESTIGATION OF PHASE TRANSITION IN LIQUID CRYSTAL DIMERS

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Abstract

We report here the variation of density across the phase transitions Isotropic – Nematic, Isotropic – Smectic A, Nematic – Smectic A and Smectic A – Smectic B exhibited by the two homologue of Schiff base liquid crystal dimeric compounds of α,ω-bis(4-alkylanilinebenzylidene-4′-oxy)alkane (m.OnO.m). The compounds studied are 4.O4O.4 and 4.O5O.4. The compound 4.O4O.4 illustrates Smectic A and Smectic B phases, whereas the compound 4.O5O.4 illustrates Nematic and Smectic A phases. The density jumps and peak in thermal expansion coefficient at the transitions confirm the first order nature of the transitions with a density jumps compared to the similar kind of dimeric liquid crystals. The calculated pressure dependence of the transition temperatures using Clausius- Clapeyron equation is also discussed.

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Introduction:-

There has been considerable interest in the experimental investigation of liquid crystal dimers due to its unusual properties compared to low molar mass liquid crystals. The liquid crystal dimers consist of two mesogenic groups linked by a flexible spacer are considered to be the precursor of semi flexible main chain liquid crystal polymers [1]. In addition, the dimers exhibits quite attractive properties which include the strong alternation in transitional properties especially in the nematic – isotropic transition temperature, the change of entropy and the orientational order parameter. At a superficial it has been attributed to the difference of shape of dimers with odd and even numbers of atoms in the flexible spacers [2].

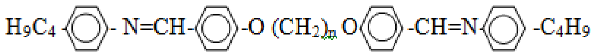
As these kinds of liquid crystal dimers are gaining importance, and also, we have been carrying various experimental techniques with variable degree of sophistication on different alkyl and spacer lengths for understanding the unusual properties of these dimers for last few years, we report here the phase transition studies of lower homologues of two liquid crystal dimers viz. 4.O4O.4 and 4.O5O.4 using the DSC and density investigation as a function of temperature across the Isotropic – Nematic, Isotropic – Smectic A, Nematic – Smectic A and Smectic A – Smectic B phase transitions.

Experimental:-

The compounds were synthesized as reported [2] earlier. The crude product was repeatedly recrystallized from ethyl acetate until the transition temperatures were found to be constant and reproducible. The differential scanning calorimetric studies (DSC) were carried out on Perkin – Elmer DSC – 7. The sharpness of melting transition indicates the purity of the compounds. The observed phases were identified from their standard characteristic textures under a polarizing microscope attached with a custom built hot stage. The temperature resolution in these microscopic studies was 0.1°C. The transition temperatures and entropy change at different phase transitions are found to be in excellent agreement with literature values [2]. Dilatometric studies were carried out using a U shaped bicapillary pyknometer in conjunction with a cathetometer containing a sample of approximately 3ml. The diameter of the capillary was about 0.35 mm and the accuracy in the density measurements was ±0.1 Kg. m^{-3}. The permitted cooling rate during the experiment was 2°C hr^{-1} and the temperature accuracy is ±0.1°C. The experimental details are described elsewhere [10]

Results and Discussion:-

The general molecular formula and phase sequence and transition temperatures in microscopic studies of the dimers viz. 4.O4O.4 and 4.O5O.4 are shown below.



4.O4O.4 (n=4) and 4.O5O.4 (n=5)

4.O4O.4 :

$$\begin{tikzcd} K \arrow[r, leftrightarrow, "144.2^\circ C"] & Sm\ B \arrow[r, leftrightarrow, "150.5^\circ C"] & Sm\ A \arrow[r, leftrightarrow, "212.5^\circ C"] & I \end{tikzcd}$$

4.O5O.4 :

$$\begin{tikzcd} K \arrow[r, "112.6^\circ C"] & N \arrow[r, leftrightarrow, "122.7^\circ C"] \arrow[d, "106.7^\circ C"] & I \\ & Sm\ A \arrow[ul, "96^\circ C"] & \end{tikzcd}$$

The variation of density as a function of temperature and the variation of estimated thermal expansion coefficient ($\alpha = dlnV/dT$ where V is molar volume) with temperature for 4.O4O.4 and 4.O5O.4 are shown in Figure 1[(a) and (b)] and Figure 2[(a) and (b)] respectively. The density in both the compounds increases as the temperature decreases, except in the vicinity of the phase transitions. No hysteresis was observed in density in heating and cooling cycles in all the phase transitions

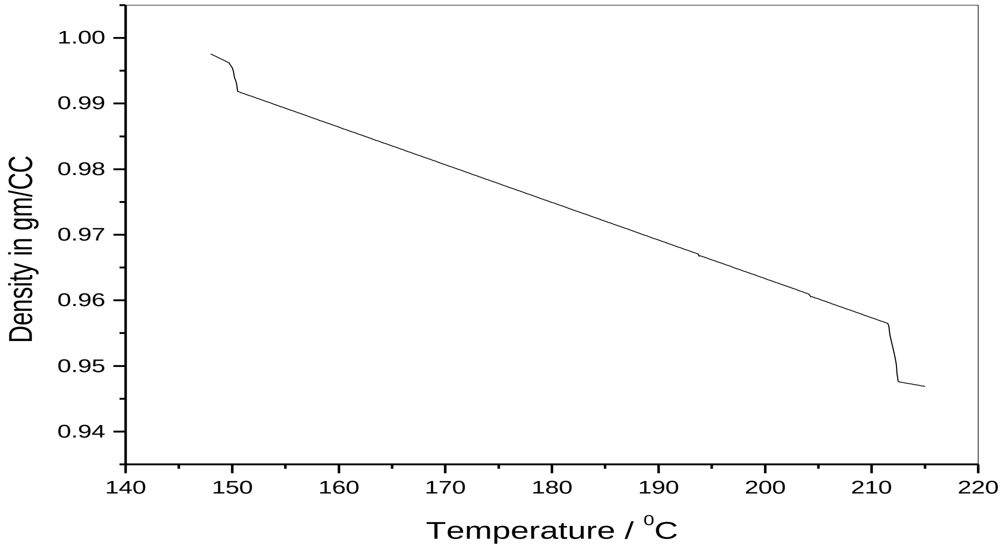


Figure 1: (a) Variation of density as a function of temperature in 4.O4O.4

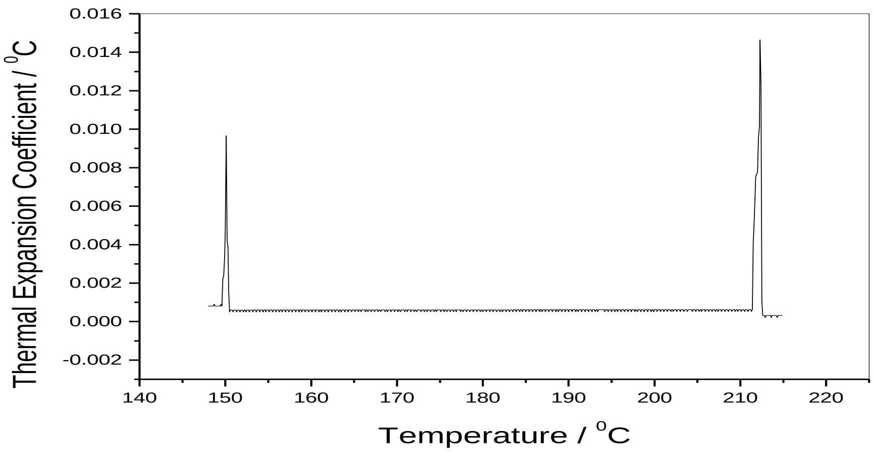


Figure 1:(b) Variation of thermal expansion coefficient 4.O4O.4

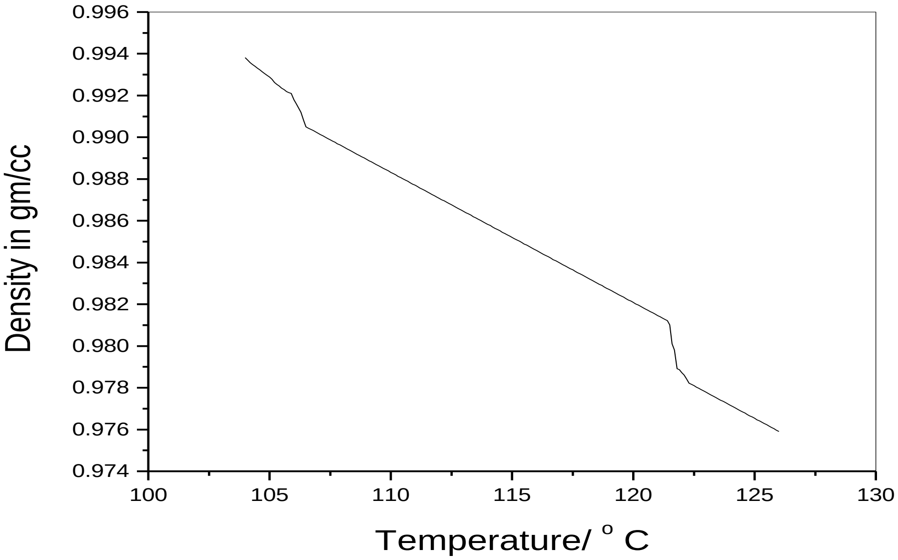


Figure 2: (a) Variation of density as a function of temperature in 4.O5O.4

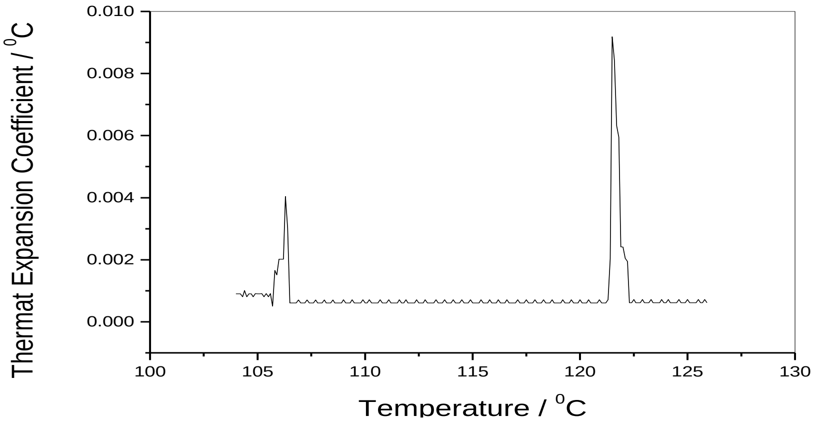


Figure 2: (b) Variation of thermal expansion coefficient 4.O5O.4

Isotropic toNematic Transition(4.O5O.4):-

The Isotropic to Nematic (I –N) phase transition was confirmed from the development of optical textures of nematic phase under the crossed polarizer. As the rotational symmetry of the isotropic phase is broken at the I – N phase transition, this transition is expected to be a first order transition. The I - N transition of the compound, 4.O5O.4 is indicated by a small but significant jump in density ($\Delta\rho/\rho\% = 0.28\%$) and a peak in the thermal expansion coefficient 91.6 x 10^{-04}°C^{-1}) at the transition. The discontinuous change in density and peak in the thermal expansion coefficient at the I – N transition confirmed this to be a first order transition. It was also noticed that the density slope increased from the isotropic to nematic phase which indicates the relatively closer packing of orientationally ordered molecules in the lower temperature nematic phase. Further, co-existence of isotropic to nematic phase is observed for 0.8°C, but the large part of the density jump is completed within 0.3°C.

An estimate of the pressure dependence of transition temperatures can be obtained using Clausius-Clapeyron equation.

$$\frac{dT_t}{dP} = T_t\left(\frac{\Delta V}{\Delta H}\right)$$

Where T_t - Transition temperature
ΔV – Molar volume change associated with the transition
ΔH – Heat of transition

The estimated pressure dependence of transition temperature of I – N transition is 31.22 K/k bar, which is lower than that of TB5A and TB6A but comparable with other dimeric and monomeric compounds [10 - 15]. A comparison of density jump and estimated pressure dependence of transition temperature of different compounds are presented in Table 1.

Table 1: Density jump ($\Delta\rho/\rho\%$) and pressure dependence of transition temperature (dT_t/dP) of some compounds at I – N transition.

COMPOUND	$\Delta\rho/\rho\%$	dT_t/dP K/k bar	REFERENCE
4.O5O.4	0.28	31.22	Present study
CB.O10O.10	1.04	26.83	14
Terephthalylidene-bis-p-n-pentylaniline (TBPA)	0.356	56.05	11
Terephthalylidene-bis-p-n-hexylaniline (TBHA)	0.351	60.07	11
N(4-n-pentyloxybenzylidene)-4′-n-pentylaniline (5O.5)	0.34	36.5	13
N(4-n-pentyloxybenzylidene)-4′-n-hexylaniline (5O.6)	0.30	33.0	13
N(4-n-pentyloxybenzylidene)-4′-n-octylaniline (5O.8)	0.25	26.3	10
N(4-n-hexyloxybenzylidene)-4′-n-octylaniline (6O.8)	0.43	37.0	13

Isotropic to Smectic A Transition(4.O4O.4):-

The Isotropic – Smectic A transition of 4.O4O.4 is inferred as a first order transition with a significant jump in density as well as indicated by a peak in thermal expansion coefficient. Further, coexistence of isotropic and smectic A phases is observed for 0.9°C. However, significant jump in density at the transition is completed within 0.3°C. The observed density jump ($\Delta\rho/\rho$ %) across the Isotropic – Sm A transition is found to be 0.88% and is in agreement with the values of other similar dimers [11,16]. These density jumps and a thermal expansion coefficient peak value of 146.5 x 10^{-4} °C^{-1} confirm the Isotropic – Sm A transition to be first order transition. . However, the density jumps across the Isotropic – Sm A transition in both of these compounds is significantly smaller than that for the transition exhibited by monomers. A comparison of density jumps and transition enthalpy at Isotropic – Sm A transition in different mesogenic dimers is presented in Table 2.

Table 2: Density jump, heat of transition and pressure dependence of transition temperature at Isotropic – Sm A transition of few mesogenic dimers.

COMPOUND	$\Delta\rho/\rho$%	ΔH/J mol^{-1}	dT_t/dP (K/k bar)	References
4.O4O.4	0.88	11670	21.70	Present study
6.O5O.6	0.78	7511.33	26.89	16
6.O6O.6	1.80	14342.48	39.60	16
7.O4O.7	1.57	17665.73	29.08	11
7.O5O.7	0.95	9046.68	30.07	11
10.O10O.10	2.26	20515.34	39.71	12

The estimated value of pressure dependence of transition temperature from the molar change and heat of transition, (dT_t/dP) is found to be 21.70 K/k bar and is in reasonable agreement with the reported values estimated for Isotopic – Sm A transition as compared in Table 2.

Nematic to Smectic A transition (4.O5O.4):-

On cooling the nematic phases of many members of the m.OnO.m family, the schlieren texture changed to give regions of focal-conic fan and homeotropic textures. The presence of focal-conic fans implied a layer structure, while a homeotropic alignment indicated an orthogonal arrangement of the director with respect to the layer planes. In consequence, this lower temperature phase is assigned as a smectic A phase. On cooling the isotropic liquid, batonnets developed which coalesced to form a focal-conic fan texture co-existing with regions of homeotropic texture and thus concluded as an Isotropic – SmecticA transition.

At the N – Sm A transition, a small but measurable density jumps at the transition temperature indicate this to be first order transition. The observed density jump ($\Delta\rho/\rho$ %) across the Nematic – Sm A transition is found to be 0.16% and is in agreement but lower than the values of other similar dimers [11,12]. This is found to be in good agreement with the prediction of the Mc Millan's theory. The Mc Millan's parameter T_{NA}/T_{IA} is found to be 0.912 and far higher than the value of 0.87 to predict the nature of Nematic to smectic A phase transition. It also noticed that the thermal expansion coefficient peak value of 40.40 x 10^{-4} °C^{-1} in this transition. The estimated value of pressure dependence of transition temperature from the molar volume change and heat of transition, (dT_t/dP) is found to be 100 K/k bar and higher than the values of similar dimeric compounds. The small density jump, volume expansion coefficient maxima and small change of enthalpy value suggest the first order N – Sm A transition. Further, the observed higher slope of density plot in the Sm A phase are argued due to the growth of layer order in addition to orientational order.

Smectic A to Smectic B Transition(4.O4O.4):-

Microscopic textural studies revealed that further cooling of smectic A phase results in the appearance of transient bars across the smectic A focal conic fans at the transition. This is the indication of SmA – SmB phase transition. In SmA – SmB phase ttransition it involves the growth of positioning ordering in the smectic B phase from the layered molecular arrangement of smectic A is justified from the sudden density jump at the transition. The density jump and peak in thermal expansion in the Sm A – Sm B transition of 4.O4O.4 inferred as a first order transition. Besides the higher slope of the density value for Sm B phase compared to the Sm A phase indicates the dense packing and higher structural ordering in the Sm B phase than in the Sm A phase. The observed density jump ($\Delta\rho/\rho$%) across the Sm A – Sm B transition is 0.43% and peak in the expansion coefficient is 96.6 x 10^{-4} °C^{-1} . The estimated value of pressure dependence of transition temperature from the molar volume change and heat of transition, (dT_t/dP) is found to be 20.32 K/k bar is reasonably in good agreement with available literature values.[13,17,18].

Conclusion:-

In conclusion, we have studied the Isotropic – Nematic, Isotropic – Smectic A, Nematic – Smectic A and Smectic A – Smectic B phase transitions exhibited by two liquid crystal dimers using density measurement technique and all the transitions are found to be first order in nature but density jumps are smaller than the monomers [13] in terms of changes in enthalpy across the phase transitions.

Acknowledgements:-

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