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Thermodynamic parameters and their variation with temperature and chain length in a number of symmetric dimeric liquid crystals

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ABSTRACT

Different thermodynamic parameters are estimated for the first time in the case of a number of symmetric dimeric liquid crystals, (DLCs), from the thermal expansion coefficient, α computed from the density data in isotropic as well as in liquid crystalline phases. Further, the parameters like the molecular free length, L_f, the molecular radius, M_r and the nonlinearity parameter, B/A are also estimated from α in the above compounds. All these parameters are obtained either with the temperature in an individual compound or either with the spacer length or with the end alkyl chain number. The results are discussed with the body of the data available on the corresponding monomers and other monomer liquid crystalline compounds. The molecular radius is estimated from both the density and the birefringence data.

1. Introduction

Liquid crystal dimers (LCDs) discovered by Vorlander [1] are found that the transitional properties of these compounds depend both on the length of the spacer and the parity of the number of atoms in it. In contrast to the monomers, the LCDs contain two mesogenic units either identical or non-identical connected through a flexible central spacer and are called symmetric and non symmetric DLCs respectively. Further, it is also found from the earlier studies from various researchers [2–4] that there exists a remarkable difference in the mesomorphic behaviour exhibited by these group compounds viz., the DLCs and the corresponding monomers. The mesogenic properties of these DLCs depend on many factors such as size of the mesogenic unit, length of the spacer and terminal units [5–7]. The study of density measurements helps to understand the nature of phase transitions in the mesomorphic compounds at the phase transitions. By employing the density data and in turn thermal expansion coefficient many thermo dynamic parameters can be estimated. The estimation of thermodynamic parameters is mostly dealt in pure liquids, binary, ternary mixtures of liquids and liquid crystal monomers (LC) at ambient and at different temperatures [8]. To the best of our knowledge for the first time we are trying to extend the work to dimeric liquid crystals in the present manuscript.

The nature of molecular interactions in LC compounds can be studied from different phase transformations and pretransitional effects [9]. Further, the study of thermo acoustic, anharmonic parameters provides information regarding the physico-chemical behaviour of the molecules. The Moelwyn-Hughes [10] parameter is of great importance because of its close relationship with the Gruneisen parameter and some thermo-acoustic parameters. The Gruneisen parameter [11] is an important quantity of current interest that has been found very useful in studying the internal structure, molecular order, anharmonicity, and other thermo-acoustic properties of different liquids, liquefied gases etc. Moreover, the Beyer's non linearity parameter (B/A) provides information regarding physical attributes of a liquid such as internal pressure, intermolecular spacing and acoustic scattering [12]. Sehgal [13] has reported a set of relations involving the parameter B/A for the determination of molecular properties such as internal pressure, cohesive energy, effective Van der waals constant, distance of closest approach of molecules, diffusion coefficient and rotational correlation time of pure liquids such as water, alcohols and fluorocarbons.

In view of the importance of these parameters in the present manuscript the thermodynamic parameters such as reduced molar volume ($V^{\sim}$), Moelwyn–Hughes parameter (C_1), reduced compressibility (β), fraction free volume (f), etc., are estimated from volume expansion (α). In addition to these, parameters like molecular free length (L_f), molecular radius (M_r) and the nonlinearity parameter (B/A) are also estimated. As the data on symmetric DLCs is not available, the authors have carried out extensive studies on the estimation of the above parameters for number of symmetric DLCs utilizing the available dilatometric and birefringence data from the literature over the past few years. From these studies, the authors are trying to address the following aspects (1) how will these parameters vary in a particular phase of the DLC material? (2) How do these parameters behave in

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the total DLC molecule? (3) What will be the behavior of these thermodynamic parameters at and around the phase transformation? (4) What will be their behavior in a particular homologous series? That is, how does the magnitude vary with either with the spacer length, n or the end chain length, m chain number? and (5) are there any parameters that are independent of both temperature and material in DLCs like their monomer counterparts? Finally the aim is to see whether the values of these thermo dynamic parameters for the symmetric dimeric LCs are different from their corresponding monomers or not. For some of the DLCs, where there is no density data, (in the case of 3.O11O.3, 3O.12O.3, 4.O7O.4, 4.O10O.4, 4.O11O.4, 4.O12O.4, 5.O11O.5, 5.O12O.5), the value in isotropic phase is estimated following the rule that the molar volume varies around 15 to 17 × 10^{-6} mole^{-1} per CH_2 unit at $T_{IN} + 5$ values in the isotropic phase.

2. Experimental

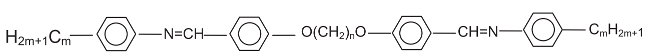
2.1. Density studies

The compounds are synthesized following the standard procedure reported in literature [14]. The crude products are repeatedly recrystallized from ethyl acetate until the transition temperatures remain constant. DSC studies are carried out using a differential scanning calorimeter (Perkin – Elmer, Diamond). Nematic and SmA phases exhibited by the compounds are identified by observing their characteristic optical textures under a polarizing microscope attached with an indigenous hot stage. The temperature resolution of the microscopic studies is ± 0.1 °C. The density measurements are carried out using a bicapillary pycnometer [5]. The capillary diameter of the pycnometer is of the order of 3.5 × 10^{-4} m and accuracy in density measurements is ± 0.1 kg m^{-3}. The permitted cooling rate was 1 °C per hour and temperature accuracy is ± 0.1 °C.

2.2. Refractive index

The refractive indices of a liquid crystal are measured with a wedge shaped glass cell, similar to the one used to obtain birefringence by Haller et al. [15], using a modified spectrometer. A wedge shaped glass cell was formed with two optically flat rectangular glass plates (50 mm × 25 mm) sandwiched 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 nematic liquid crystal in the cell acts as a uniaxial crystal with its optic 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 molecular structure of the compounds studied is given below.



with m = 3, 4, 5, 6, 7, 8 and 10 and n = 4, 5, 6, 7, 8, 9, 10, 11 and 12.

3. Thermodynamic parameters

The procedure for the estimation of different thermodynamic parameters, molecular free length, L_f and molecular radius from both α and birefringence, δn are described in detail using the coefficient of thermal expansion (α) [16–25] is described below.

The values of coefficient of volume expansion $(\alpha) = 1/V_m\,(dV_m/dT)$ Where $dT = T_2 - T_1$, $dV_m = V_{m2} - V_{m1}$ are taken from literature [17–20] for the evaluation the following parameters.

The Moelwyns–Hughes parameter (C_1) and reduced molar volume ($V^{\sim}$) are evaluated from the following expressions.

$$C_1 = \left(\frac{13}{3}\right) + \left(\frac{1}{\alpha T}\right) + \left(\frac{4\ \alpha T}{3}\right) \tag{1}$$

$$V^{\sim} = \left\{\frac{\left(\frac{\alpha T}{3}\right)}{(1+\alpha T)} + 1\right\}^3 \tag{2}$$

The isochoric temperature coefficient of internal pressure (X) is given by

$$X = -\frac{2(1+2\ \alpha T)}{V^{\sim C_1}} \tag{3}$$

where $V^{\sim C}{}_1 = \beta$ is the reduced compressibility

Sharma parameter [17–24] S_O is given by the expression

$$S_0 = \left(-\frac{X}{2}\right)\ (3+4\ \alpha T). \tag{4}$$

The Huggins parameter [22] F of a liquid crystal is related to S_O by the equation

$$F = 2\left[1+\left(\frac{S_0}{(3+4\ \alpha T)}\right)\right]-\left(3+\frac{4\alpha T}{3}\right). \tag{5}$$

Isothermal microscopic Gruneisen parameter (Γ) is a measure of volume dependence of the hormonicity of the normal mode frequency (ν) of molecular vibrations of a material is related to F and So as

$$\Gamma = \left(\frac{2}{3}\right)\alpha T + \left(\frac{2-F+4\ \alpha T}{2\ \alpha T}\right). \tag{6}$$

The fraction free volume (f), is a measure of disorder due to increase of mobility of molecules in a liquid crystal and can be expressed in terms of isothermal Gruneisen parameter (Γ) as

$$f = \frac{1}{(\Gamma+1)} = \frac{V_a}{V} \tag{7}$$

where V_a is the available volume. The estimation of V_a is described below.

Thermal parameter A^* is a dimensionless parameter which shows that at low temperatures, a liquid crystal tends to be ordered, thereby makes A^* equal to unity

$$A* = 1 + \left(\frac{f}{\Gamma}\right). \tag{8}$$

The Gruneisen parameter (Γ_p) for liquid crystals can be obtained from

$$\Gamma_p = \left(\frac{2}{3}\right)\alpha T + \left(\frac{1}{2\alpha T}\right) + 2. \tag{9}$$

The isochoric acoustical parameter, Δ is given as

$$\Delta = \left(\frac{-\alpha T}{2}\right)\ . \tag{10}$$

3.1. Inter molecular free length (L_f)

The estimation of L_f is described below using the thermodynamic parameters. Using the Eqs. (1) to (3), the isothermal (K′), isochoric (K″) and isobaric (K) acoustical parameters are obtained from the following expressions

$$\begin{aligned} K' &= K + K'' \\ &= \frac{1}{2}\left[3+\frac{(S*(1+\ \alpha T)+X)}{\alpha T}\right] \end{aligned} \tag{11}$$