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Computation of Available Volume (Va) And Intermolecular Free Length (Lf) In 4- Hexyloxybenzylidene)-4'alkoxy Anilines, 6o.Om Schiff's Compounds

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Abstract (10pt)

The molecular parameters like available volume(Va) intermolecular free length (Lf), molecular radius (Mr) and Beyer's non-linearity parameter (B/A) are computed for the homologues series of 4-hexyloxybenzylidene)-4'alkoxy anilines, 6O.Om liquid crystalline (LC) compounds with m = 4 to 10 by employing thermal expansion coefficient obtained from density variation with temperature in isotropic and liquid crystalline phases. The intermolecular free length (Lf), is computed in six different ways and the data obtained is compared with the available literature data.

Keywords:

Liquid crystal compounds, density studies, thermodynamic parameters, molecular radius and free length.

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1. Introduction

In order to understand the fundamental aspects and the usage of liquid crystalline compounds (LCs) in technological applications, the study of physical properties such as density, viscosity, refractive indices, specific heat, etc. is necessary and they will provide more information. In addition to these properties, the study of internal structure and thermodynamical behavior of the Liquid Crystal (LC) molecule is also important to understand the behaviour of the material. Recently, R.R. Reddy etal [1] has done extensive studies on some binary mixtures to test the interrelation between Va, C_1 and B/A. In the present manuscript we attempted to extend the same and estimated the intermolecular free-length (L_f) for the liquid crystalline materials which belong to nO.Om

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class of compounds. All these compounds are synthesized and characterized using POM and DSC and also the physical properties such as density and refractive indices are measured using Pyknometer and modified spectrometer. In the present investigation it is proposed to estimate thermo dynamic parameters and the anharmonic parameters such as the isochoric temperature coefficient of internal pressure (X), isochoric temperature coefficient of volume expansivity (X′), the reduced compressibility ($\beta^{\sim}$), the reduced volume ($V^{\sim}$) from the data of the coefficient of volume expansion in the isotropic and liquid crystalline phases. In addition to these we also estimated the parameters like available volume (V_a), intermolecular freelength (L_f) in different ways, molecular radius (M_r) and Beyer's nonlinearity parameter (B/A) for the homologues series of 4-hexyloxybenzylidene)-4'-alkyloxy anilines, 6O.Om liquid crystalline compounds with m = 4 to 10 in isotropic and liquid crystalline phases.

2. Theory and expressions

The various expressions for the estimation of different thermoacoustic parameters using the coefficient of thermal expansion (a) [2-4] are described below. The values of coefficient of volume expansion (α) =1/ Vm (dVm /dT) Where dT=T2-T1, dVm=Vm2-Vm1 are taken from our recent publication [5] for the evaluation the following parameters.

2.1. Available volume and Intermolecular freelength

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

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

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

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

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

where $V^{\sim C_1} = \beta$ is the reduced compressibility

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

$$K' = K + K'' \qquad (4)$$

$$= \frac{1}{2}\left[3 + \frac{(S^*(1+\alpha T) + X)}{\alpha T}\right]$$

$$K'' = 1 + \left(\frac{X}{2\alpha T}\right) \text{ and} \quad (5)$$

$$K = \frac{1}{2}\left[1 + \left(\frac{S^*(1+\alpha T)}{\alpha T}\right)\right] \quad (6)$$

$$\text{where } S^* = 1 + \left(\frac{4\alpha T}{3}\right) \quad (7)$$

The isothermal acoustical parameter (K') is related to the available volume (Va) of the compound as

$$\frac{V_a}{V_m} = \frac{1}{(K'+1)} = \frac{1}{(K''+K+1)} \quad (8)$$

where V_m is molar volume (molecular weight/density) and the available volume, (Va) can be deduced using the thermo acoustical parameter K' as

$$V_a = \frac{V_m}{K'+1} \quad (9)$$

R.R.Reddy et al [6,7] computed the available volume using $C_1$with the following relation

$$V_a = V[2/(C_1+1)] \quad (10)$$

Then the intermolecular free-length[2] (L_f) is given by the relation

$$L_f = \frac{2V_a}{Y} \quad (11)$$

Where V_a represents the available volume per mole and Y is surface area per mole given by

$$V_0 = V - V_a \quad (12a)$$

$$\text{where } Y = (36\pi N V_0^2)^{1/3} \quad (12b)$$

The molar volume at 0 K (V_0) can also be obtained by as

$$V_0 = \frac{V}{\tilde{V}} \quad (13)$$

N is the Avogadro number and $\tilde{V}$ is taken from equation (2).

Further, V_0 can be obtained directly from molar volume data by extrapolating isotropic data to 0 K.

2.2 Molecular radius (M_r)

M_r for the LC molecule can be obtained from density and refractive index results and the relevant expressions are given below [8]

(i). From density, ρ

$$M_r = \frac{1}{2}3\sqrt{\frac{M\sqrt{2}}{\rho N}} \quad (14)$$

where M is the molecular weight.

2.3 Acoustic Nonlinearity parameter, B/A

There are number of reports in literature describing in detail the theoretical and empirical approach for the estimation of B/A from the thermal expansion coefficient, α and ultrasonic velocity, u respectively, the relevant expressions of .the non-linearity parameter, B/A is given as

$$B/A = 2u\rho[du/dp]_T \quad (15)$$

General formalism for B/A in terms of the acoustical parameters for liquids and polymers has been made using Moelwyns-Hughes parameter (C_1), isobaric acoustic parameter (K) and the isothermal acoustic parameter (K") (the detailed method of calculation of K and K" from α is given elsewhere obtained from the thermal expansion coefficient, α, and from the ultrasonic velocity, u respectively. The expressions for B/A from density are given as [9,10]

$$B/A = C_1 - 1 \quad (16a)$$

$$B/A = 2K+2\gamma K" \quad (16b)$$

3. Results and discussion

The compounds in the present study were synthesized and characterized also the properties such as density and refractive indices were calculated. The density data which is published very recently [5] is taken for the estimation of coefficient of thermal expansion**.**

The thermal expansion coefficient, α obtained from density data is used to estimate the thermodynamic parameters such as Moelwyn-Hughes parameter (C_1), reduced volume ($V^{\sim}$), reduced compressibility (β), isochoric temperature coefficient of internal pressure (X), and acoustical parameters like isothermal (K'), isobaric (K),isochoric (K") acoustical parameters. In addition to these, the parameters like molecular free length (L_f),

molecular radius (M_r) and nonlinearity parameter, (B/A) are also evaluated using equations (1) - (16).

It is observed that all the parameters exhibit a constant value in a particular phase except in the vicinity of phase transition where they exhibit singularity, The parameters such as reduced volume, $V^{\sim}$, reduced compressibility, $V^{\sim c1}$, and the isochoric temperature coefficient of internal pressure, (X) and their variation with temperature is similar to that of thermal expansion coefficient α, as excepted in all compounds as these parameters are proportional to α. Table 1 represents all these values in different Lc phases in all the compounds.

The available volume, Va, is estimated using Eq. (9) and Eq. (10). It is found that the available volume increment for one methylene unit is about 3.5. The variation of available volume, V_a with chain length is found to be less in isotropic phase and also it is observed that the increment for methylene unit is 3.75 (from K) and 3.61 (from C1) in isotropic phase in 6O.Om series. Using the values of V and V_0 (molar volume at 0 K), which is obtained in three ways is used to calculate the molecular free length in six different ways. Figure 1 shows the variation of available volume with temperature in 6O.O8 compound and it is observed that available volume increases with temperature. Thus, the increase in available volume with raising temperature is quite natural phenomenon and it is attributed due to increase in molecular motion and decrease in intermolecular attraction at higher temperatures [1]. Table 2 depicts the values of intermolecular freelength (L_f) in all the compounds obtained in different ways in different LC phases. It is found that all values are in agreement with each other. It is reported earlier, from the systematic studies on the TBnA compounds [11], benzoic acids [12] as well as in a number of nO.O5 [13] compounds and found that the slope value should be

around 8×10^{-4} to obtain reasonable agreement. The agreement between these values clearly demonstrates the clear interrelation between V_a, C_1 and B/A

Figure 2 shows the variation of molecular radius (M_r) with temperature in all the compounds of 6O.Om homologues and Table 3 shows the values of M_r and B/A in different Lc phases.. Further, the increment of molecular radius for methylene unit is found to be 0.064 Å from density in this case.

The variation of non linearity parameter, B/A with temperature for 6O.O10 compound is shown in Figure 3. The data reveals that the B/A value almost remains constant in a particular phase except at the vicinity of the phase transition where it shows a peak and the peak magnitude depends on α, and further, the magnitude of B/A is slightly smaller in LC phases compared to that in isotropic phase. Generally this parameter, lies in the range 5.5 to 9.5, with extreme variations of 2 and 13 [10].

4. Conclusions

The salient features observed from the study are.

1. All the parameters are almost constant except at the phase transition where it shows an elevation or the dip depending whether α is directly or indirectly proportional to the quantity under consideration including B/A (this can be seen from the graphs).
2. Regarding the free length it increases linearly with the increase of the chain length with one or two exceptions.
3. This is the first time that free length is calculated six different ways in liquid crystals.
4. The free length increases with the decrease of temperature i.e., it is higher in LC phases with the exception of Va from K and V0 calculated from equation (12).

5. Molecular radius increases with the decease of temperature except in the vicinity of the transition.

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