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

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Abstract : In Present studies we have calculated molecular parameters such as available volume (V_a) molecular radius (M_r) intermolecular free length (L_f) and Beyer's acoustic nonlinearity parameter (B/A) of homologoues series of 4-(hexyloxybenzylidene)-4'alkoxy anilines, 6O.Om with m = 4 to 10 liquid crystalline (LC) compounds by employing thermal expansion coefficient obtained from variation of density with temperature in liquid crystal and isotropic phases. The intermolecular free - length of liquid crystalline compuned is computed in six different ways and the data obtained is compared with the available literature.

Key words: Liquid crystals, density studies, Acoustic Nonlinearity parameter, molecular radius and free length.

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1. INTRODUCTION

The study of physical properties, optical properties and thermal properties, density, viscosity refractive indices, and specific heat etc, are very muchnecessary for understanding the basic nature of liquid crystals and its application in terms of technical aspects. In addition to these properties, Knowledge of thermodynamic al behavior and internal structure of the molecules of liquid crystalline compounds is also important for understanding the behavior 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. Present studies we have attempted to enhance the same and estimated the intermolecular free length (L_f) for the liquid crystalline materials which belong to nO.Om class of compounds. All these compounds are synthesized and Charecterized by using POM and DSC and also the physical properties of liquid crystal compounds Such as Refractive Indices, density are calculated by using modified spectrometer and Pyknometer. In this work it is proposed to measure the thermo dynamical and an harmonical parameters using the coefficient of volume expansion are isochoric temperature coefficient of internal pressure (X),volume expansivity (X′),the reduced volume ($V^{\sim}$) and the reduced compressibility ($\beta^{\sim}$) in the crystalline and isotropic phases. In addition this we also estimated available volume (V_a), intermolecular freelength (L_f) parameters in different ways and Beyer's nonlinearity parameter (B/A) and molecular radius (M_r) for the homologoseries of 4-hexyloxybenzylidene)-4'-alkyloxy anilines, 6O.Om liquid crystalline phases where m = 4 to 10.

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Expressions for computation in various thermoacoustic parameters are using the thermal expansion coefficient (a) [2-4] are explained further.

Coefficient of volume expansion (α) =1/ V_m (dV_m/dT)
Where $dV_m=V_{m2}-V_{m1}$ and $dT=T_2-T_1$, For the evaluaiton of following parameters
we are taken $dV_m=V_{m2}-V_{m1}$ and $dT=T_2-T_1$ values from our recent publication [5].

Available volume and Intermolecular freelength

The Moelwyns-Hughes parameter (C_1):

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

Reduced molar volume ($V^{\sim}$):

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

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

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

where $V^{\sim C}{}_1 = \beta$ is the reduced compressibility
From equations 1, 2 and 3 we obtained
The isochoric acoustical parameter

$$K'' = 1 + (\frac{X}{2\alpha T}) \quad (4)$$

The isobaric acoustical paramters

$$K = \frac{1}{2}[1 + (\frac{S^*(1+\alpha T)}{\alpha T})] \quad (5)$$

$$\text{where } S^* = 1 + (\frac{4\alpha T}{3}) \quad (6)$$

The isothermal acoustical patameter $K' = K + K''$

$$= \frac{1}{2}[3 + \frac{(S^*(1+\alpha T) + X)}{\alpha T}] \quad (7)$$

The relation between isothermal acoustical parameter (K') and available volume (Va) of the compoundas

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

Here V_m is the molar volume (molecular weight/density)

The available volume $V_a = \frac{V_m}{K'+1}$ (9)

The relations [5,6] are used to write the available volume in C_1

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

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

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

Where Y is surface area per mole given by

$$Y = (36\pi N V_0^{\,2})^{1/3} \quad (12a)$$

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

Where V_0 is themolar volume at 0 K

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

$V^{\sim}$ is reduced molar volume and N is Avogadro number

.Thermal expansion (□□□ can be gained by the density data and Thermodynamical parameters such as isochoric temperature coefficient of internal pressure (X),

It is observed that with the effect of temperature the variations of parameters, reduced volume ($V^{\sim}$) reduced compressibility ($V^{\sim c1}$) and isochoric temperature coefficient of internal pressure (X) is same that of coefficient of thermal expansion (α), and is accepted these parameters for all compounds are proportional to α. All these parameters exhibit a constant value at a particular phase except around the phase transition where they exhibit singularity, all these values in different Liquid crystal phases in all the compounds given in Table 1.

Using Eq. (9) and Eq. (10) we estimated the available volume, Va. It is observed that the available volume increased for one methylene unit is about 3.5. In isotropic phase the change in available volume, V_a with chain length is found to be less and it is increased 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.

(Molecular radius) M_r

In Density and refractive index results [8] the appropriate expressions of Molecular radius ((M_r) of Liquid Crystal molecule is given by Molecular radius $M_r = \frac{1}{2}3\sqrt{\frac{M\sqrt{2}}{\rho N}}$ (14)

Here M is the molecular weight of a liquid crystal compound

Acoustic Nonlinearity parameter, **B/A**

The Acoustic non-linearity parameter, B/A can be obtained from coefficient of the thermal expansion, α and ultrasonic velocity, u is given as

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

By, using the equation Moelwyns-Hughes parameter (C_1), the acoustical parameter for liquids and polymers is given by

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

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

The expressions for B/A from density are given as reference [9,10]

Results and discussion

In the present study the liquid crystal (LC's) compounds were synthesized and characterized with 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 thermal expansion coefficient(C_1), reduced volume ($V^{\sim}$), and isobaric (K) isothermal (K'), isochoric (K") acoustical parameters are estimated by the coefficient of thermal expansion . In addition to this molecular free length (L_f), nonlinearity parameter (B/A) reduced compressibility (□), Moelwyn-Hughes parameter and molecular radius (M_r) are also evaluated using equations (1) - (16).

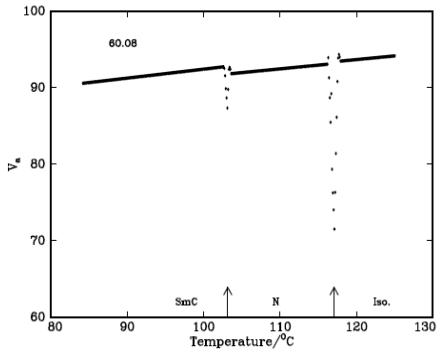

Figure 1

Figure1: *Variation of available volume (Va) with temperature in 6O.O8 compound*

Figure 1 shows the available volume varies with various temperatures in 6O.O8 compound and it is observed that available volume increases with temperature. Thus, by the change in temperature change in available volume quite

natural phenomenon and it is attributed due to increase the motion of molecules 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. From the experimental studies on the TBnA compounds [11], benzoic acids [12] as well as in a number of nO.O5 [13] compounds and observed that the slope value should be around 8×10^{-4} is good agreement with experimental value. The agreement between these results clearly demonstrates the clear interrelation between V_a, C_1 and B/A . The change in molecular radius (M_r) with temperature in all the compounds of 6O.Om homologues is shown in Figure 2.

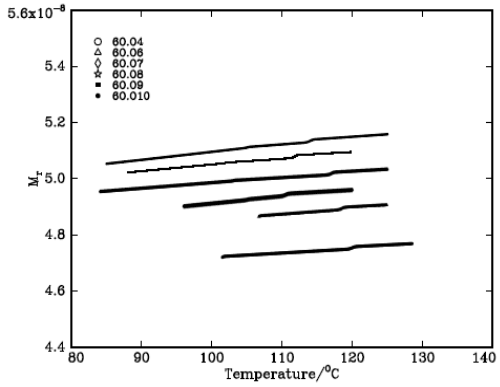

Figure 2

***Figure 2**: Variation of molecular radius (M_r) with temperature in all 6O.Om compounds*

The values of M_r and B/A in various Liquid Crystal phases shown in Table 3. Variation of M_r, Beyers nonlinearity parameter, B/A in 6O.Om compounds in isotropic, nematic and smectic phases. The data reveals that the increased value of molecular radius for methylene unit is found to be 0.064 Å.

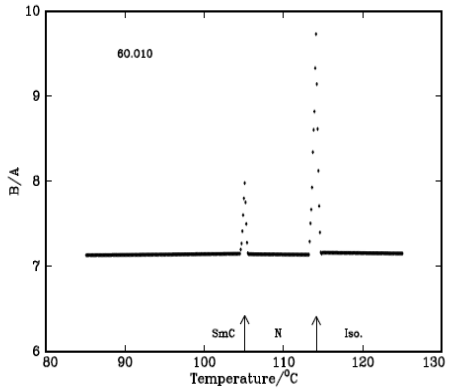

Figure 3

***Figure 3:** Variation of Acoustic nonlinearity parameter (B/A) with temperature in 6O.O10 compound*

Figure 3 shows that non linearity parameter, B/A with variation of temperature for 6O.O10 compound. In this case the value of B/A almost constant at a particular phase except around the phase transition and the peak value depends on the coefficient α. On the other hand, the value of B/A is slightly smaller in Liquid Crystal phases than in isotropic phase. In general this parameter, lies in the range 5.5 to 9.5, with extreme variations of 2 and 13 [10].

CONCLUSIONS

It has been concluded that. All the molecular parameters are almost constant than 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).

1. Regarding the free length it increases linearly with the increase of the chain length with one or two exceptions.
2. This is the first time that free length is calculated six different ways in liquid crystals.
3. The free length increases with the decrease of temperature i.e., it is higher in LC
4. phases with the exception of V_a from K and V_0 calculated from equation (12).

ACKNOWLEDGEMENTS

The Author thank the Department of Engineering Physics, Andhra University college of Engineering (A) and also the author thank the management & Principal of Chaitanya Engineering College, Kommadi, Visakhapatnam for their tremendous and continuous support to carry out the research work.

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Table 1: *Variation of thermoacoustic parameters and available volume Va in different LC phases of all the 6O.Om compounds*

Table 1

Comp.	phase	Temp.	C1	V~	β	X_1	K”	K	K’	Va(K)	Va(C_1)
6O.O4	Iso.	124.1	7.90	1.26	6.26	-0.52	0.179	3.449	3.628	79.574	82.82
	N	106.5	7.67	1.28	6.68	-0.51	0.270	3.337	3.607	78.312	83.22
6O.O5	Iso.	115.0	6.70	1.47	12.97	-0.37	0.72	3.06	3.780	81.36	98.49
	N	105.0	6.64	1.54	17.27	-0.31	0.80	2.89	3.690	80.80	----
6O.O6	Iso.	123.5	7.73	1.28	6.57	-0.51	0.246	3.366	3.612	87.10	92.21
	N	112	7.18	1.34	8.16	-0.46	0.479	3.090	3.569	86.52	96.70
6O.O7	Iso.	120	7.69	1.28	6.65	-0.51	0.268	3.339	3.607	90.281	95.82
	N	111.2	7.24	1.33	7.93	-0.47	0.454	3.118	3.572	90.270	98.29
	SmC	105	6.95	1.71	42.28	-0.18	0.610	2.953	3.562	89.435	98.73
6O.O8	Iso.	121.8	7.78	1.27	6.47	-0.52	0.226	3.391	3.617	93.874	98.76
	N	111.8	7.75	1.27	6.53	-0.51	0.239	3.375	3.614	92.662	97.77
	SmC	97.6	7.17	1.34	8.21	-0.46	0.483	3.085	3.568	92.164	103.11
6O.O9	Iso.	116.1	7.68	1.28	6.66	-0.51	0.266	3.341	3.607	97.518	103.11
	N	106.1	7.48	1.30	7.14	-0.49	0.350	3.239	3.589	96.445	104.46
	SmC	97.6	6.94	1.39	9.59	-0.43	0.590	2.972	3.562	95.775	110.27
6O.O10	Iso.	119	7.36	1.31	7.49	-0.48	0.400	3.180	3.580	101.502	111.28
	N	109	7.24	1.33	7.93	-0.47	0.454	3.118	3.572	100.072	111.16
	SmC	100	6.76	1.44	11.73	-0.39	0.695	2.879	3.574	98.599	116.31

Table 2: *Variation of molecular free length L_f obtained in six different ways in all the 6O.Om compounds in isotropic, nematic and smectic phases.*

Com.	phase	Temp.	Intermolecular freelength (L_f) in angstrom units					
			V_a from K			V_a from C_1		
			V_o eq.(13)	V_o eq.(12)	V_o(graph)	V_o eq.(13)	V_o eq.(12)	V_o(graph)
6O.O4	Iso.	124.1	0.907	0.892	0.981	0.944	0.929	1.01
	N	106.5	0.914	0.891	0.964	0.971	0.947	1.02
6O.O6	Iso.	123.5	0.944	0.923	1.03	0.99	0.976	1.09
	N	112	0.979	0.928	1.03	1.09	1.04	1.14
6O.O7	Iso.	120	0.957	0.934	1.05	1.02	0.992	1.11
	N	111.2	0.975	0.938	1.05	1.06	1.02	1.14
	SmC	105	1.070	0.826	0.932	1.33	1.02	1.15
6O.O8	Iso.	121.8	0.964	0.945	1.05	1.01	0.994	1.11
	N	111.8	0.962	0.941	1.04	1.02	0.993	1.09
	SmC	97.6	1.000	0.948	1.03	1.12	1.06	1.15
6O.O9	Iso.	116.1	0.983	0.959	1.08	1.04	1.02	1.14
	N	106.1	0.992	0.958	1.07	1.07	1.04	1.15
	SmC	97.6	1.031	0.961	1.06	1.19	1.11	1.22
6O.O10	Iso.	119	1.011	0.976	1.17	1.12	1.07	1.28
	N	109	1.020	0.973	1.15	1.14	1.08	1.27
	SmC	100	1.070	0.968	1.13	1.26	1.14	1.33

Table 3

Comp.	Phase	Temp.	M_r	B/A	B/A
6O.O4	Iso.	124.1	4.763	7.257	6.899
	N	106.5	4.731	7.213	6.673
6O.O6	Iso.	123.5	4.905	7.223	6.724
	N	112	4.877	7.137	6.180
6O.O7	Iso.	120	4.960	7.214	6.678
	N	111.2	4.943	7.227	6.749
	SmC	105	4.925	7.130	5.839
6O.O8	Iso.	121.8	5.029	7.234	6.782
	N	111.8	5.006	7.228	6.750
	SmC	97.6	4.981	7.137	6.170
6O.O9	Iso.	116.1	5.096	7.215	6.682
	N	106.1	5.096	7.179	6.478
	SmC	97.6	5.096	7.124	5.939
6O.O10	Iso.	119	5.148	7.160	6.359
	N	109	5.121	7.144	6.236
	SmC	100	5.096	7.147	5.758