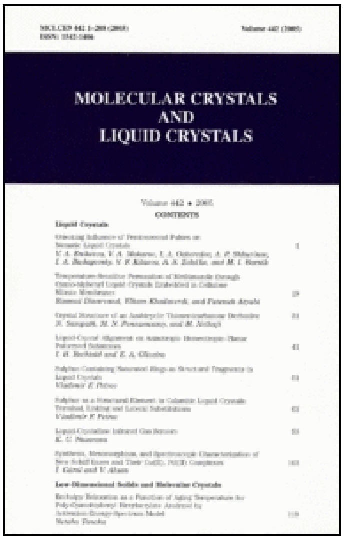

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Density Measurements and Thermodynamic Parameters of 4,4′-Dibutoxyazoxybenzene

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Thermodynamic functions using the coefficient of volume expansion (α*) of a system, a number of thermoacoustic and anharmonic parameters such as the isochoric temperature coefficient of internal pressure (*X*), isochoric temperature coefficient of volume expansivity (*X′*), reduced compressibility (*$\tilde{\beta}$*), reduced volume (*$\tilde{V}$*), isothermal microscopic Gruneisen parameter (*Γ*), fractional free volume (*f*), and Sharma parameter (*So*) can be investigated. The temperature dependence of these parameters gives a basic understanding about the intermolecular interactions in general. These studies also can applied to a solute in dilute solutions. In the present study these different parameters have been determined using volumetric measurements in the case of a liquid crystal, namely, 4,4′-dibutoxy azoxy benzene (HPOAB), which is a typical liquid crystal with a nearly linear structure, in dilute solutions at different temperatures. Variations in various parameters with respect to temperature are discussed in the light of the results obtained. The variation of the properties is analyzed and discussed in this article.*

Keywords 4,4′-Dibutoxy azoxy benzene; liquid-crystalline materials; thermodynamic parameters

Introduction

Investigation of the propagation of ultrasonic waves in pure liquids, liquid-crystalline materials, and dilute solutions in polar and nonpolar solvents provides insight into molecular structure and association with the surrounding molecules and hence has attracted the attention of many researchers recently [1–4] and references cited therein. In this direction, work is being reported from this laboratory. In particular, this type of study in combination with density (or specific volume) determination at different temperatures on pure materials and on both temperature and weight fraction in dilute solutions [1] has been found to be useful in drawing conclusions about intermolecular interactions, charge transfer complexations, structure of the molecules, etc. Some such parameters can also be obtained using only density measurements.

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In general, nematics are studied under various environments (both temperature and dilution in various solvents) with an interest in finding the relation between chemical constitutions and different conditions like temperature, pressure etc. 4,4′-Dibutoxy azoxy benzene, hereafter referred to as HPOAB, is a typical liquid crystal with a nearly linear structure. The benzene rings are nearly planar and great numbers of nematics have the same basic structure. Thus, HPOAB is a useful liquid crystal for many physical experiments. In solids, the orientation of polar molecules is rigidly fixed in a typical manner. Therefore, the solution study of liquid-crystalline substances is needed to find the solute–solvent interactions. In view of the above facts, density measurements were carried out on a pure sample of a HPOAB in dilute solutions at different temperatures (around its phase transition temperature (K—93°C—N—124°C—I) in its pure form), with different weight fractions in dilute solutions. These were carried out with the intention to determine the qualitative behavior of HPOAB with variation in temperature, as the samples involve a nematic phase. The results of the above work are presented and discussed in this article.

Defining Relations

The values of specific volume obtained and reported in earlier work [1] for HPOAB are used for the calculation of the different parameters as defined later. The values for different parameters like isochoric temperature coefficient of internal pressure (X), isochoric temperature coefficient of volume expansivity (X'), reduced compressibility ($\beta^{\sim}$), reduced volume ($V^{\sim}$), isothermal microscopic Gruneisen parameter (Γ), fractional free volume (f), and Sharma parameter (So) calculated through coefficient of volume expansion (α) at different temperatures so obtained are presented in Table 1. The defined parameters and their relations are presented below.

The coefficient of volume expansion, α, is defined as

$$\alpha = \frac{1}{V_m}\frac{\Delta V}{\Delta T}$$

where $\Delta V = (V_2 - V_1)$, $\Delta V = T_2 - T_1$, and $V_m = (V_1 + V_2)/2$; V_1 and V_2 are molar volumes at temperatures T_2 and T_1, respectively.

Using the coefficient of thermal expansion, one can obtain an expression for the isochoric temperature coefficient of internal pressure (X), defined as

$$X = (\mathrm{dln}P_i/\mathrm{dln}T)|v = [(2/\beta^{\sim})(\mathrm{dln}\alpha/\mathrm{dln}T)]|_v \text{ and}$$

$$X = \frac{-2(1+2\alpha T)}{(V^{\sim})^{c_1}}$$

where P_i is the internal pressure, $\beta^{\sim}$ is reduced compressibility, and $V^{\sim}$ is reduced volume.

Further,

$$V^{\sim} = \frac{V}{V^*} = \left[1 + \frac{\alpha T}{3(1+\alpha T)}\right]^3$$

and $\beta^{\sim} = (\beta/\beta^{*})$ with

$$\beta^{\sim} = (V^{\sim})^{c_1}$$

Here V, V^{*} and β, β^{*} are the hard core volumes and compressibilities at temperature T and 0 K.

The other different parameters calculated are as below.

- The isochoric temperature coefficient of volume expansivity

$$X^1 = (\mathrm{dln}\alpha/\mathrm{dln}T)|_v = X' = -(1 + 2\alpha T)$$

- Moelwyn-Hugles parameter

$$C_1 = (\mathrm{dln}\beta/\mathrm{dln}T)|_T \text{ with}$$

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

- The Sharma parameter

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

- Huggins parameter of a liquid crystal, related to S_0 as

$$F = (1 + (2\alpha T/3)) + (\mathrm{dln}\beta/\mathrm{dln}\ T)|_T, \text{ that is,}$$

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

- The isothermal microscopic Gruneisen parameter Γ as

$$\Gamma = -(\mathrm{dln}\upsilon/\mathrm{dln}V)|_T$$

$$\Gamma = \frac{2}{3}\alpha T + \frac{(2 - F + 4\alpha T)}{2\alpha T}$$

- The fraction of free volume (f) as

$$f = (V_a/V)$$

$$f = \frac{1}{\Gamma + 1}$$

where V_a is defined as available volume of a liquid crystal.

- Thermal parameter (A^*), a dimensionless parameter as

$$A^* = (1+f^2)(1-f)$$

$$A^* = 1+\frac{f}{\Gamma}$$

- The isochoric acoustical parameter Δ and Gruneisen parameter Γ_p are given by

$$\Delta = -\frac{XT}{2}$$

$$\Gamma_p = \frac{2}{3}\alpha T + \frac{1}{2\alpha T} + 2$$

The importance of these different parameters are discussed in the article by Reddy *et al.* [3].

Results and Discussion

As stated in the earlier work [1], benzene was chosen as solvent because it is a well-tested non-polar solvent in which the nematic chosen was found to be readily solvable. In the present work, studies were restricted to only low concentrations of solutes in the solvent in view of the very small amount of the samples available of spectroscopic-grade purity although it is desired to extend the work up to the benzene solubility limit of each liquid crystal. However, it was felt that the studies presented here provide enough information about the behavior for the studied systems. The values obtained at various temperatures of these parameters are presented in Table 1.

Using the measured values of the molar volumes (reported in an earlier work [1]) various physical parameters are derived with the help of their defining equations listed above and the results of all parameters are presented in Tables 1a, 1b, 1c and 1d. The variation of each of the physical parameter can be observed from the table with temperature at different weight fractions of the solute (HPOAB) in solvent (benzene).

It can be inferred from the data that the variation of all the parameters with weight fraction or temperature is not linear. It is seen that the values of different parameters do not show any definite trend of variation with temperature, particularly around the transition temperature. This is due to the fact that in the process of heating, there is a structural change in the liquid crystal involved.

The variation of different parameters with weight fraction at a temperature indicates that the variation is not linear. The nature of the interaction between the components in the mixture (or dilute solution) can be understood by knowing whether the parameters vary linearly (weak interaction) or nonlinearly (molecular association). This observation thus supports strong interaction between the molecules. This strong interaction between the molecules is contradictory to expectation

Table 1a. Coefficient of volume expansion and other thermoacoustic parameters for W12 = 6.2520E-03

W12	T	α	$V^{\sim}$	C_1	$\beta^{\sim}$	X'	X
6.2520E-03	266	0.000074859	1.020	54.580	2.893	−1.040	−0.719
	305.5	0.0018759	1.410	6.842	10.513	−2.146	−0.408
	310.5	0.0064374	1.826	7.499	91.241	−4.998	−0.110
	315.5	0.0010058	1.261	7.908	6.248	−1.635	−0.523
	320.5	0.0014675	1.355	7.087	8.619	−1.941	−0.450

W12	T	α	So	F	Γ	f	A^*	Γp	Δ
6.2520E-03	266	0.000074859	1.107	1.692	9.737	0.093	1.010	27.123	95.622
	305.5	0.0018759	1.080	0.644	3.565	0.219	1.061	3.255	62.366
	310.5	0.0064374	0.602	−1.556	4.222	0.191	1.045	3.583	17.007
	315.5	0.0010058	1.117	1.100	3.629	0.216	1.060	3.787	82.543
	320.5	0.0014675	1.099	0.823	3.565	0.219	1.061	3.377	72.164

because the solvent used is benzene. This type of observation is also seen in some other nematics [1].

This nonlinearity observed in liquid crystals under study in the present case and earlier works [1] (butyl-p-(p-ethoxy phenoxy carbonyl) phenyl carbonate, p-(p-ethoxy phenyl azo) phenyl undecylenate and p-[N-(p-methoxy benzylidene) amino] phenyl benzoate in dilute solutions in benzene) probably indicates strong interaction due to liquid crystals rather than benzene. As per reports [3], the value of the Sharma parameter (*So*) is a constant for any system existing either in the liquid or solid state. It can be seen from the present investigations that even in the present study the value of the Sharma parameter is also a constant.

The studies indicate that it is likely that if a liquid-crystalline material is studied in dilute solution using an appropriate solvent, such that the solvent used is nonpolar

Table 1b. Coefficient of volume expansion and other thermoacoustic parameters for W12 = 2.3730E-02

W12	T	α	$V^{\sim}$	C_1	$\beta^{\sim}$	X'	X
2.3730E-02	266	0.000076339	1.020	53.607	2.896	−1.041	−0.719
	305.5	0.0012958	1.311	7.387	7.403	−1.792	−0.484
	310.5	0.00092349	1.240	8.203	5.832	−1.573	−0.540
	315.5	8.56898E-05	1.027	41.358	2.956	−1.054	−0.713
	320.5	0.00017127	1.053	22.624	3.213	−1.110	−0.691

W12	T	α	So	F	Γ	f	A^*	Γp	Δ
2.3730E-02	266	0.000076339	1.107	1.692	9.608	0.094	1.010	26.637	95.579
	305.5	0.0012958	1.109	0.956	3.582	0.218	1.061	3.527	73.944
	310.5	0.00092349	1.119	1.157	3.661	0.215	1.059	3.935	83.778
	315.5	8.56898E-05	1.108	1.677	7.991	0.111	1.014	20.512	112.491
	320.5	0.00017127	1.112	1.618	5.519	0.153	1.028	11.145	110.706

Table 1c. Coefficient of volume expansion and other thermoacoustic parameters for W12 = 3.1060E-02

W12	T	α	$V^{\sim}$	C_1	$\beta^{\sim}$	X'	X
3.1060E-02	266	0.000092322	1.024	45.087	2.934	−1.049	−0.715
	305.5	0.0016146	1.368	7.018	9.019	−1.987	−0.441
	310.5	0.00094118	1.244	8.145	5.905	−1.584	−0.537
	315.5	0.00025592	1.096	14.237	3.677	−1.205	−0.655

W12	T	α	So	F	Γ	f	A^*	Γp	Δ
3.1060E-02	266	0.000092322	1.108	1.682	8.483	0.105	1.012	22.377	95.112
	305.5	0.0016146	1.095	0.783	3.563	0.219	1.062	3.343	67.288
	310.5	0.00094118	1.119	1.147	3.654	0.215	1.059	3.906	83.314
	315.5	0.00025592	1.115	1.563	4.757	0.174	1.037	8.246	105.866
	320.5	0.00031944	1.117	1.519	4.419	0.185	1.042	6.952	105.001

so as to minimize solvent–solute interaction, and that it has a boiling temperature well above the N-I transition of the solute molecule used, then the solute would exhibit a behavior reminiscent of a liquid-crystalline material even in dilute solution phase. This observation is consistent with some earlier work on nematic liquid crystals in dilute solution using other methods like microwave using an X band and ultrasonic propagation [4–6]. However, in the present work, because of certain experimental limitations, the measurements could not be performed on the solutions in the entire temperature interval of K-N-I transition. Further, the above studies have shown that, if a sufficient quantity of sample for carrying out such studies is not available, the molecular characterization information can be obtained much better with its interaction with the surroundings of a different environment, with a view to understanding their qualitative trends.

Table 1d. Coefficient of volume expansion and other thermoacoustic parameters for W12 = 1.5790E-02

W12	T	α	$V^{\sim}$	C_1	$\beta^{\sim}$	X'	X
1.5790 E-02	266	0.0001119900	1.029	37.942	2.981	−1.060	−0.711
	305.5	0.0006721200	1.180	9.477	4.808	−1.411	−0.587
	310.5	0.0015739000	1.366	7.031	8.939	−1.977	−0.442
	315.5	0.0011349600	1.288	7.603	6.831	−1.716	−0.502
	320.5	0.0002987300	1.090	14.906	3.610	−1.191	−0.660

W12	T	α	So	F	Γ	f	A^*	Γp	Δ
1.5790 E-02	266	0.0001119900	1.109	1.671	7.540	0.117	1.016	18.804	94.543
	305.5	0.0006721200	1.121	1.313	3.810	0.208	1.055	4.572	89.631
	310.5	0.0015739000	1.096	0.791	3.563	0.219	1.062	3.349	68.689
	315.5	0.0011349600	1.113	1.025	3.600	0.217	1.060	3.635	79.260
	320.5	0.0002987300	1.116	1.532	4.506	0.182	1.040	7.286	105.771

Density studies on HPOAB have been reported by Ayachit [7] in its liquid-crystalline state over a range of temperatures. In this work it has been noted that the variation of different parameters with respect to temperature is not systematic over the whole range of temperature, although it shows a clear phase transition, with the transition temperatures being K–119°C—N—133°C—I for HPOAB. In some parameters, the order of values in these parameters being very large, the small variations may lead to a large variation in the parameters reported. The value of order parameters being small, the same type of variation is not to be seen, which is consistent with the above observations. The behavior of non-crystalline material in dilute solution with variation in weight fraction is linear, whereas in the present work the observation is not only non-linear, it is found that the variation is not smooth. The same is consistent with earlier observations [1,6]. This behavior in dilute solution may probably be correlated with the behavior of HPOAB in its liquid-crystalline state. Although no logical argument can be made, the consistent experimental observations of liquid crystals in dilute solution at different temperatures are in favor of some agreement between behavioral aspects in dilute solution and the liquid-crystalline state.

Conclusions

It is clear that the variations of the different thermodynamic parameters with respect to the temperature indicate that the transitional and pre-transitional effects observed in the liquid-crystalline state of HPOAB also affect the behavior of these parameters in dilute solution. The variation of various parameters that are expected to be linear are found to be non-linear, which is attributed to the transitional and pre-transitional effects. These observations are found to be consistent with the earlier work discussed.

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References

[1] Ayachit, N. H., Vasan, S. T., Sannaningannavar, F. M., & Deshpande, D. K. (2007). *J. Mol. Liq.*, *133*, 134–138.

[2] Ranga Reddy, R. N. V., Suryanarayana, A., & Murthy, V. R. (1999). *Cryst. Res. Tech.*, *34*, 1299–1307.

[3] Reddy, R. P., Venkatesulu, A., Ram Gopal, K., & Neelakanteswara Reddy, K. (2007). *J. Mol. Liq.*, *130*, 112–118.

[4] Johri, G. K., Rishishwar, R. P., & Saxena, D. (1985). *IEEE Trans. Electr. Insul.*, *EI-20*(2), 469–473.

[5] Bhatia, A. B. (1985). *An Introduction to Absorption and Dispersion in Gases, Liquids and Solids*, Dover: New York.

[6] Sannaningannavar, F. M., Ayachit, N. H., & Deshpande, D. K. (2006). *Phys. Chem. Liq.*, *44*, 217–225.

[7] Ayachit, N. H. *Mol. Cryst. Liq. Cryst.*