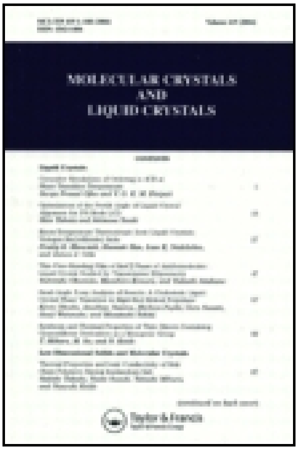

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Density Measurements and Thermodynamic Parameters of a Nematic Liquid Crystal

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Density Measurements and Thermodynamic Parameters of a Nematic Liquid Crystal

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Thermodynamic functions using the coefficient of volume expansion (α) of a system, a number of thermo acoustic and an harmonic parameters such as the isochoric temperature coefficient of internal pressure (X), isochoric temperature coefficient of volume expansivity (X|), the reduced compressibility (β∼), the reduced volume (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 be 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′–azoxy anisole (PAA) 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′–azoxy anisole; liquid crystalline materials; thermodynamic parameters

INTRODUCTION

Investigation of the propagation of ultrasonic waves in pure liquids, liquid crystalline materials, and in dilute solutions in polar and non-polar solvents, gives an insight into molecular structure and association with the surrounding molecules and hence has attracted the attention of many workers in the recent past [1–4, and the cited references]. In particular, such a study in combination with density (or specific volume) determination at different temperature 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

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of the molecules, etc. Some such parameters can also be obtained using only density measurements.

In general, nematics are studied under various environments (both temperature and dilution in various solvents) with an interest to find the relation between chemical constitutions and different conditions like temperature, pressure, etc. 4,4′–azoxy anisole, hereafter referred to as PAA, is a typical liquid crystal with a nearly linear structure. The benzene rings are nearly planar and great numbers of nematics have the basic structure like this. Thus, PAA is a useful liquid crystal for many physical experiments. In solids, 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 PAA, in dilute solutions at different temperatures (around its phase transition temperature (K − 119°C- - -N- - - 133°C- - -I) in its pure form), with different weight fractions in dilute solutions. These were carried out with the intention to know the qualitative behavior of PAA with variation in temperature, as the samples involved are in a nematic phase. The result of the above work is presented in this article and discussed.

DEFINING RELATIONS

The values of specific volume obtained and reported in earlier work [1] for PAA are used for the calculation of the different parameters as defined in the later section. The values for different parameters like isochoric temperature coefficient of internal pressure (X), isochoric temperature coefficient of volume expansivity (X^1), the reduced compressibility ($\beta\sim$), the reduced volume ($V\sim$), isothermal microscopic Gruneisen parameter (Γ), fractional free volume (f), and Sharma parameter (S_o) 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 $\alpha = (1/V_m)(\Delta V/\Delta T)$, where $\Delta V = (V_2 - V_1)$, $\Delta T = T_2 - T_1X$, 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

$$X = (\mathrm{dln}P_i/\mathrm{dln}T)\,|_v = [(2/\beta)(\mathrm{dln}\ \alpha/\mathrm{dln}T)]\,|_v = [-2(1+2\alpha T)]/V_m^{C1},$$

TABLE 1 Coefficient of Volume Expansion (a) and Other Thermo Acoustic Parameters

$W \times 10^2$	T in K	$\alpha \times 10^4 K_{-1}$	C1	V^-	X	S_0
0.7862	298	0.00064	9.83	1.17	−0.59	1.11
	303	0.001897	6.84	1.41	−0.41	1.09
	308	0.00081	8.67	1.21	−0.57	1.14
	313	0.001025	7.88	1.26	−0.53	1.14
	318	0.000565	10.14	1.16	−0.6	1.12
1.5335	298	0.000953	8.23	1.24	−0.53	1.1
	303	0.001892	6.84	1.41	−0.41	1.09
	308	0.001136	7.66	1.28	−0.51	1.12
	313	0.000999	7.95	1.26	−0.52	1.11
	318	0.000627	9.61	1.18	−0.57	1.08
2.2931	298	0.000641	9.82	1.17	−0.59	1.11
	303	0.001254	7.47	1.3	−0.5	1.13
	308	0.000678	9.4	1.18	−0.6	1.15
	313	0.000807	8.63	1.22	−0.54	1.08
	318	0.00804	8.13	1.9	−0.07	0.46
3.0166	298	0.000638	9.85	1.17	−0.59	1.11
	303	0.001293	7.41	1.31	−0.48	1.1
	308	0.000545	10.51	1.15	−0.61	1.12
	313	0.000913	8.21	1.24	−0.54	1.12
	318	0.000757	8.81	1.21	−0.55	1.09
3.704	298	0.000549	10.66	1.15	−0.6	1.1
	303	0.001071	7.85	1.27	−0.51	1.1
	308	0.001087	7.77	1.27	−0.52	1.13
	313	0.000779	8.76	1.21	−0.56	1.11
	318	0.000712	9.05	1.2	−0.56	1.09

F	Γ	f	A^*	Δ	Γp	X_1
2.59	0.58	0.63	2.09	87.91	4.75	−1.38
2.41	2.03	0.33	1.16	62.12	3.25	−2.15
2.57	1.02	0.5	1.49	87.78	4.17	−1.5
2.53	1.39	0.42	1.3	82.95	3.77	−1.64
2.6	0.45	0.69	2.53	95.4	4.9	−1.36
2.53	1.26	0.44	1.35	78.97	3.95	−1.57
2.41	2.02	0.33	1.16	62.12	3.25	−2.15
2.51	1.5	0.4	1.27	78.54	3.66	−1.7
2.52	1.38	0.42	1.3	81.38	3.81	−1.63
2.57	0.7	0.59	1.84	90.63	4.64	−1.4
2.59	0.58	0.63	2.09	87.91	4.74	−1.38
2.5	1.6	0.38	1.24	75.75	3.57	−1.76
2.6	0.7	0.59	1.84	92.4	4.53	−1.42
2.54	1.1	0.48	1.44	84.51	4.15	−1.51
2.07	3.69	0.21	1.06	11.13	3.9	−6.11
2.59	0.58	0.63	2.09	87.91	4.76	−1.38

(*Continued*)

TABLE 1 Continued

F	Γ	f	A^*	Δ	Γp	X_1
2.48	1.65	0.38	1.23	72.72	3.54	−1.78
2.61	0.29	0.78	3.69	93.94	5.09	−1.34
2.54	1.25	0.44	1.35	84.51	3.94	−1.57
2.55	1.02	0.5	1.49	87.45	4.24	−1.48
2.6	0.28	0.78	3.79	89.4	5.17	−1.33
2.51	1.43	0.41	1.29	77.27	3.76	−1.65
2.52	1.45	0.41	1.28	80.08	3.72	−1.67
2.56	1.01	0.5	1.5	87.64	4.21	−1.49
2.56	0.91	0.52	1.57	89.04	4.36	−1.45

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

These are expressed as

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

$$\beta^{\sim} = (\beta/\beta^*) = (V^{-})^{C1}.$$

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

The other different parameters calculated are as shown below.

The isochoric temperature coefficient of volume expansivity:

$$X_1 = (\mathrm{dln}\ \alpha/\mathrm{dln}T)\,|_v = -(1 + 2\alpha T).$$

MOELWYN-HUGES parameter:

$$C_1 = (\mathrm{dln}\ \beta/\mathrm{dln}T)\,|_T = (13/3) + (1/\alpha T) + (4\alpha T/3)$$

The SHARMA parameter $S_0 = (-X/2)(3 + 4\alpha T)$.

HUGGINS parameter of a liquid crystal, related to S_0 as

$$F = (1 + (2\alpha T/3) + (\mathrm{dln}\ \beta/\mathrm{dln}T)|_T = 2[1 + S0/(3 + 4\alpha T)] - (3 + 4\alpha T)/3.$$

The isothermal microscopic Gruneisen parameter Γ as

$$\Gamma = -(\mathrm{dln}\ \upsilon/\mathrm{dln}V)\,|_T = (2/3)\alpha T + (2 - F + 4\alpha T)/(2\alpha T).$$

The fraction of free volume (f) as

$$f = (V_a/V) = 1/(\Gamma + 1),$$

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

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

$$A^* = (1 + f^2)(1 - f) = 1 + (f/\Gamma).$$

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

$$\Delta = -(XT)/2$$

$$\Gamma_p = (2/3)(\alpha T) + (1/2\alpha T) + 2$$

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 give 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 Table 1. The variation of the each of the physical parameter can be observed from the table with temperature at different weight fractions of the solute (PAA) 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 liquid crystal involved.

The variation of different parameters with weight fraction at a temperature indicates that the variation is not linear. The nature of 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 once expectation because the solvent used is benzene. This type of observation in some more nematics is available in the literature [1].

This nonlinearity observed in liquid crystals under study in 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 the reports [3], the value of the Sharma parameter (S_o) is a constant for any system existing either in 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 phase using an appropriate solvent, such that the solvent used is non-polar 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 its behavior reminiscent to 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 different environment, with a view to understand their qualitative trends.

The density studies on PAA has been studied and reported by Ayachit [7] in its liquid crystalline state over a range of temperatures. In this work, may be noted that the variation of different parameters with respect to temperature is not systematic over the whole range of temperature, but does show a clear phase transition, with the transition temperatures being K – 119°C- - -N- - -133°C- - -I for PAA. 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 seen, which is consistent with above observations. The behavior of noncrystalline material in dilute solution with variation in weigh fraction is linear, while in the present work the observation is not only nonlinear, but it is found that the variation is not smooth. The same is consistent with earlier observation [1,6]. This behavior in dilute solution may probably be correlated with the behavior of PAA in its liquid crystalline state. Although no logical argument can be put, 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 liquid crystalline state.

CONCLUSIONS

According to this article, it is clear that the variations of the different thermodynamic parameters with respect to the temperature indicate that the transitional and pretransitional effects observed in the liquid crystalline state of PAA affects also the behavior of these parameters in dilute solution. The variation of various parameters which are expected to be linear are found to be nonlinear which are attributed to the transitional and pretransitional effects. These observations are found to be consistent with earlier work.

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