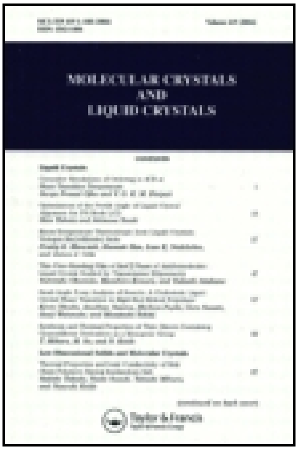

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Thermodynamic Functions of a Liquid Crystal through Density Measurements

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Thermodynamic Functions of a Liquid Crystal through Density Measurements

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Thermodynamic functions of a material are determined using ultrasonic measurements coupled with volumetric measurements at different temperatures. It is also possible to determine some of these thermodynamic functions using only volumetric measurements. Such studies are important in the case of liquid crystal as they give insight in the structural changes arising out of transition between two phases. Apart from this, these studies are also found to give clear information regarding the nature of phase transition, pre-transitional effects, and molecular ordering. Some of the thermodynamic functions calculated are adiabatic compressibility, order parameter, Sharma's number, etc. In the present study these different parameters have been determined using only volumetric measurements in case of 4,4 – azoxy anisole at different temperatures. Variations in various parameters with respect to temperature have been discussed in the light of the results obtained. In the literature the data for these parameters are available for the above said liquid crystal calculated in conjunction with ultrasound measurements. The results obtained in the present work are compared with these results. It has been shown that the variation of the properties observed with respect to temperature can be explained on the basis of Frenkal's heterophase fluctuation theory.

Keywords: liquid crystal; density measurements; thermodynamic parameters

INTRODUCTION

The study of propagation of ultrasonic waves in pure liquids, liquid crystalline materials has attracted the attention of many workers in the recent past. In particular, such a study in conjunction with density (or specific volume) determination has been found to be useful

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in drawing conclusions about intermolecular interactions, charge transfer complexions, structure of the molecules, etc. Also these studies enable one to derive several thermodynamic and acoustical parameters and their excess values. The determination of some of these parameters is also determined using only specific volume measurements [1,3].

The structural changes arising from transitions between the mesophases of liquid crystalline materials can be better understood by studying specific volume variation with temperature. In particular, these studies are found to give clear information regarding the nature of the phase transition, pretransitional effects and also molecular ordering. For example, temperature corresponding to the maximum value of adiabatic compressibility, temperature corresponding to the minimum value of order parameter, molar compressibility in thermo tropic liquid crystals [4], and some of their mixtures are very useful in understanding their structural behavior. In view of above facts, it was thought worthwhile to study using the density measurements on pure sample of a nematic, namely, 4,4′ – azoxy anisole and the variation in different thermodynamic parameters, here after referred as PAA. The results of the above work is presented in this article and discussed. The results of these are also compared with the one carried with ultrasonic measurements [1].

EXPERIMENTAL RESULTS

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 so obtained are presented in Tables 1 and 2.

DEFINING RELATIONS

The defined parameters and their relations are presented below. The values obtained at various temperatures of these parameters are presented in Tables 1 and 2.

The coefficient of volume expansion α is defined as, $\alpha = (1/V_m)(\Delta V/\Delta T)$,
where $\Delta V = (V_2 - V_1)$, $\Delta V = T_2 - T_1$, 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 obtained an expression for the isochoric temperature coefficient of internal pressure(X) is 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 Different Thermodynamic Parameters for 4,4′ – Azoxy Anisole at Various Temperatures

temp	V	α	C_1	X^1	$V^{\sim}$	$\beta^{\sim}$	X
392	0.8441	0.000473765	9.965521	−1.37143	1.164947	4.579068	−0.599
393	0.8445	0.001774623	6.697078	−2.39485	1.469714	13.18171	−0.36336
394	0.846	0.001771479	6.6966915	−2.39593	1.469955	13.19419	−0.36318
395	0.8475	0.001414927	6.867769	−2.11779	1.403073	10.2356	−0.41381
396	0.8487	0.00270636	6.6953722	−3.14344	1.611639	24.4194	−0.25745
397	0.851	0.001409112	6.8667969	−2.11884	1.403342	10.24569	−0.4136
398	0.8522	0.002228608	6.6433949	−2.77397	1.547551	18.19228	−0.30496
399	0.8529	0.000937537	7.5053484	−1.74815	1.297691	7.069511	−0.49456
400	0.8537	0.000936658	7.501947	−1.74933	1.29806	7.078341	−0.49428
401	0.8545	0.000818857	7.8165711	−1.65672	1.268121	6.402678	−0.51751
402	0.8552	0.002452555	6.6621765	−2.97185	1.583145	21.34236	−0.27849
403	0.8573	0.002562908	6.6786622	−3.0657	1.598986	22.9832	−0.26678
404	0.8595	0.00232423	6.6502939	−2.87798	1.566645	19.79758	−0.29074
405	0.8615	0.001160093	7.0881785	−1.93968	1.354922	8.610559	−0.45053
406	0.8625						

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

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

$$\beta^{\sim} = (\beta/\beta^{*}) = (V)^{c1}$$

TABLE 2 Different Thermodynamic Parameters for 4,4′ – Azoxy Anisole at Various Temperatures

S_0	F	Γ	f	A^{*}	Δ	Γ_p
1.120989	1.351379	3.870082	0.205335	1.053057	117.4041	4.816094
1.051875	0.433458	3.588038	0.217958	1.060746	71.40028	3.181872
1.051739	0.432562	3.588175	0.217952	1.060742	71.54625	3.181679
1.083267	0.668614	3.563682	0.219121	1.061487	81.72733	3.267218
0.938018	−0.1715	3.727573	0.211525	1.056746	50.97591	3.181019
1.083163	0.667715	3.563724	0.219119	1.061486	82.10059	3.266732
0.998435	0.122313	3.649789	0.215064	1.058925	60.68733	3.155031
1.111851	0.995792	3.591632	0.217787	1.060637	98.66504	3.586008
1.111788	0.994725	3.591347	0.217801	1.060646	98.85519	3.584307
1.116125	1.079694	3.620268	0.216438	1.059785	103.7607	3.741619
0.966889	−0.03608	3.689854	0.213226	1.057787	55.97719	3.164422
0.951251	−0.11036	3.710185	0.212306	1.057222	53.75573	3.172664
0.982115	0.038755	3.670331	0.214118	1.058337	58.72957	3.15848
1.099157	0.824084	3.564632	0.219076	1.061458	91.23315	3.377423

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

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

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 is related to S_0 as

$$F = (1 + (2\alpha T/3) + (\mathrm{dln}\,\beta/\mathrm{dln}\,T)|_T = 2[1 + S_0/3 + 4\alpha T)] - (3 + 4\alpha T/3).$$

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 the 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 is given as

$$\Delta = -(XT)/2\Gamma_p = (2/3)(\alpha T) + (1/2\alpha T) + 2.$$

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

RESULTS AND DISCUSSIONS

Using the measured values of the density d (reported in an earlier work [1]), various physical parameters are derived with the help of their defining equations listed above, and the results are presented in Tables 1 and 2. The variation of the each of the physical parameter, can be observed from the tables. The specific volume increases linearly with increase in temperature in PAA molecule. This value suddenly increases at the temperature corresponding to transition temperature. In other words, the value of specific volume is maximum at the nematic-isotropic transition. This can be attributed to the change in the structure, from the partially ordered nematic to the disordered isotropic liquid state.

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: fully ordered (crystal) to quasi ordered (nematic) to disordered (isotropic) phase. Most of the properties of physical parameters can be explained on the basis of Frenkel's hetero phase fluctuation theory. According to this theory as the temperature of the first order transition is approached an ever increasing concentration of small elements of second phase can exist in the first phase. This may lead to rigorous fluctuations resulting in pretransitional vibrations in all the physical properties. In the present work for the values around the transition temperature for the molecule studied the variation of the parameters can be explained on the basis of the theory, but the values fluctuate to a large extent and this behavior seems to be difficult to account for. However, such observations are available in the literature [4].

Further, from the above observations, it may be noted that the variation of different parameters with respect to temperature is although not systematic over the whole range of temperature, it shows a clear phase transition, with transition temperature 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 large variation in the parameters reported. The value of order parameters being small the same type of variations is not to be seen, which is in consistent with above observations.

In the present work, the variation of different parameters in the entire range of temperature, namely, K-N-I transitions could not be mapped because of certain experimental difficulties well below K-N transition and higher temperatures above N-I transition, however, this has not come in way of this study which is intended to be carried around phase transition.

The results obtained here are in consistent with the inferences drawn in earlier work of the authors [1], using sound measurements.

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