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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. In the present study, these different parameters have been determined using only volumetric measurements in the case of a liquid crystal, namely, Butyl-p-(p-ethoxy-phenoxy carbonyl)-phenyl carbonate (BEPCP)at different temperatures. Variations in various parameters with respect to temperature have been discussed in the light of the results obtained. The variation of the properties is analyzed on the basis of Frenkal's heterophase fluctuation theory.

Keywords Butyl-p-10-(p-ethoxy-phenoxy carbonyl)-phenyl carbonate; liquid crystal; thermodynamic functions; ultrasonic measurements; volumetric measurements

Introduction

The study of the propagation of ultrasonic waves in pure liquids and liquid crystalline materials has attracted the attention of many workers in the recent past. In particular, such a study in conjunction with density (specific volume) determination has been found to be useful 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. In view of above facts, it was thought worthwhile to study the density measurements on a pure sample of a nematic, namely, 4 Butyl-p-(p-ethoxy-phenoxy carbonyl)-phenyl carbonate (BEPCP) and the variation in different thermodynamic parameters. The results are presented and discussed in this article. The results of these are also compared with those carried at with ultrasonic measurements [1].

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Defining Relations and Results

The values of specific volume obtained and reported in earlier work [1] for BEPCP are used for the calculation of the different parameters as defined in the later section. The values for some parameters 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 $\Delta V = (V_2 - V_1)$, $\Delta T = T_2 - T_1$, 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 $X = (d\ln P_i/d\ln T)|_v = [(2/\beta)\ (d\ln\alpha/d\ln T)]|_v = [-2(1+2\ \alpha T)]/V_m^{C1}$, where P_i is the internal pressure, $\beta^{\sim}$ is reduced compressibility, and $V^{\sim}$ is reduced volume. These are expressed as $V^{\sim} = (V/V^*) = [1 + \alpha T/3(1+\alpha T)]^3$ and $\beta^{\sim} = (\beta/\ \beta^*) = (V^{-})^{C1}$. Here V, V^* and β, β^* are the hard core volume and compressibility at temperature T and 0°K, respectively. The other different parameters calculated are: the isochoric temperature coefficient of volume expansivity $X^1 = (d\ln\alpha/d\ln T)|_v = -(1+2\alpha T)$;

Table 1. Values of some parameters at different temperatures

T in K	$\alpha \times 10^4$	C_1	Γ	X	S_0	F
331	9.35	7.98	1.35	−0.51	1.08	2.51
332	8.17	8.38	1.17	−0.54	1.1	2.54
333	13.98	7.1	1.82	−0.46	1.12	2.46
334.5	27.9	6.65	2.47	−0.3	1.01	2.3
335.5	17.4	6.82	2.04	−0.4	1.07	2.4
336.5	11.58	7.42	1.63	−0.48	1.09	2.48
337.5	11.57	7.41	1.64	−0.48	1.09	2.48
338.5	11.58	7.41	1.64	−0.48	1.1	2.48
339.5	12.7	7.23	1.75	−0.47	1.11	2.47
340.5	14.58	7.01	1.89	−0.44	1.1	2.44
341.5	14.93	6.97	1.91	−0.43	1.08	2.43
343	15.04	6.96	1.93	−0.43	1.09	2.43
344	16.47	6.85	2.02	−0.41	1.08	2.41
345	17.6	6.79	2.08	−0.39	1.06	2.39
346	18.73	6.74	2.14	−0.38	1.06	2.38
347	19.42	6.72	2.17	−0.37	1.05	2.37
348	19.38	6.72	2.17	−0.37	1.05	2.37
349	11.38	7.38	1.66	−0.49	1.12	2.49
350	22.73	6.65	2.32	−0.33	1.02	2.33
351	22.24	6.66	2.3	−0.33	1.01	2.33
352	22.54	6.65	2.32	−0.33	1.02	2.33
353.5	17.99	6.75	2.12	−0.39	1.08	2.39
354.5	14.6	6.96	1.93	−0.43	1.09	2.43
355.5	12.33	7.2	1.76	−0.46	1.09	2.46
356.5	10.08	7.6	1.54	−0.5	1.11	2.5
357.5	7.83	8.28	1.22	−0.53	1.09	2.53
358.5	12.3	7.19	1.77	−0.46	1.1	2.46
360	16.74	6.8	2.07	−0.39	1.06	2.39

MOELWYN-HUGES parameter $C_1 = (\mathrm{dln}\,\beta/\mathrm{dlnT})|_T = (13/3) + (1/\alpha T) + (4\alpha T/3)$; the SHARMA parameter $S_0 = (-X/2)(3 + 4\alpha T)$; HUGGINS parameter of a liquid crystal is related to S_0 as $F = (1 + (2\alpha T/3) + (\mathrm{dln}\,\beta/\mathrm{dlnT})|_T = 2[1 + S_0/3 + 4\alpha T)] - (3 + 4\alpha T)/3$; the isothermal microscopic Gruneisen parameter $\Gamma = -(\mathrm{dln}\upsilon/\mathrm{dlnV})|_T = (2/3)\alpha T + (2 - F + 4\alpha T)/(2\alpha T)$; 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 $\Delta = -(XT)/2$ and $\Gamma_p = (2/3)(\alpha T) + (1/2\alpha T) + 2$. The importance of these different parameters is discussed in the article by 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 of several parameters are presented in Table 1. The variation of each physical parameter with temperature can be observed from the table. The specific volume increases linearly with increasing temperature in BEPCP 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 the 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 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.

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 temperatures being K–56°C–N– 87°C–I for BEPCP. 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 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 the 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 consistent with the inferences drawn in earlier work of the authors [1], using sound measurements.

The variation in the other parameters, which are not reported in the table, follows the same trend as reported in the Table 1.

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