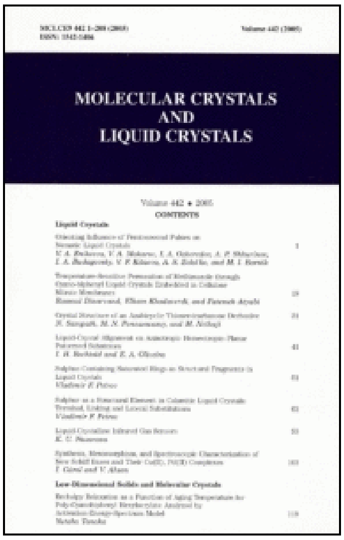

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Computation of Molecular Free Length (L<i>f</i>) and Molecular Radius (M<i>r</i>) of *p*-*n*-Alkoxy Benzoic Acids

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Computation of Molecular Free Length (L_f) and Molecular Radius (M_r) of *p-n*-Alkoxy Benzoic Acids

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Dilatometric (density, ρ) and optics (refractive index, n*) studies are utilized for the computation of thermoacoustic parameters, molecular radius, and intermolecular free length of* p-n-*alkoxy benzoic acids (nbas). For the estimation of* L_f*, the parameters like* V_0*, molar volume at absolute zero, and (*V_a*), the available volume is calculated from thermodynamic parameters. Further,* V_0 *can be obtained by the extrapolation of temperature variation of molar volume in isotropic phases to absolute zero. The molecular radius (*M_r*) is obtained from the density and refractive index. The computed values using different methods are compared with one another as well as with the body of the data available. The temperature variation of different thermoacoustic parameters like Moelwyn-Hughes (*C_1*), reduced molar volume (*$V^{\sim}$*), isochoric temperature coefficient of internal pressure (*X*), etc., calculated using different expressions are also presented. The increment in the molecular radius per methylene group in this homologous series is found to be 0.084 Å from density data and 0.054 Å from optics data. Further, it is observed that the* M_r *values obtained from optics data are found to be less compared to those obtained from density results. The* L_f *values estimated from different methods are found to show a similar type of variation with the chain length. However, the values differ slightly from one another and refinement is needed in the expressions to get concurrent results from different experimental data.*

Keywords Alkoxy benzoic; molecular free length; molecular radius; thermodynamic parameters

Introduction

Alkoxy benzoic acids are well-known and extensively studied liquid-crystalline (LC) compounds [1–5]. As a part of systematic studies involving phase transitions across different LC phases, isotropic to first LC phase, orientational order parameter estimation, and its variation with temperature in different LC phases, the authors

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have undertaken density [6] and refractive index measurements [7] of *p*-*n*-alkoxy benzoic acids with chain number $n = 3$ to 12 and 16.

The evaluation of thermoacoustic parameters of different liquids and liquid mixtures has gained much interest in the last decade [8–12]. Different methods are proposed for the evaluation of thermoacoustic parameters [9–11] in liquids, polymers, and liquid crystals. However, the data on LC materials is meager and to the best of our knowledge this is the first time V_0 is obtained from the extrapolation technique, which is used in the estimation of L_f, in addition to the methods proposed in the literature. The aim of this manuscript is to estimate the thermoacoustic parameters, L_f and M_r, in homologous series and to study their behavior with chain length.

Theory

The different expressions for the estimation of various thermoacoustic parameters using the coefficient of thermal expansion (α) [9–11] are described below.

The Moelwyns-Hughes parameter (C_1) and reduced molar volume ($V^{\sim}$) may be expressed as

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

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

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

$$X = -\frac{2(1 + 2\alpha T)}{V^{\sim}_{c1}} \tag{3}$$

Expressions of isothermal (K'), isochoric (K'') and isobaric (K) acoustical parameters are

$$K' = K + K'' = \frac{1}{2}\left[3 + \frac{(S^*(1 + \alpha T) + X)}{\alpha T}\right] \tag{4}$$

$$K'' = 1 + \left(\frac{X}{2\alpha T}\right) \tag{5}$$

and

$$K = \frac{1}{2}\left[1 + \left(\frac{S^*(1 + \alpha T)}{\alpha T}\right)\right] \tag{6}$$

where

$$S^* = 1 + \left(\frac{4\alpha T}{3}\right) \tag{7}$$

The isothermal acoustical parameter (K') is related to the available volume (V^a) of the compound as

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

where V_m is molar volume (mol · wt/density) and the available volume can be deduced using the thermoacoustical parameter K' as

$$V_a = \frac{V_m}{K' + 1} \tag{9}$$

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

$$L_f = \frac{2V_a}{Y} \tag{10}$$

where V_a represents the available volume per mole and Y is surface area per mole given by

$$V_a = V - V_0 \qquad \text{and} \qquad Y = (36\pi N V_0^2)^{1/3} \tag{11}$$

Also

$$V_0 = \frac{V}{V^{\sim}} \tag{12}$$

Here, N is the Avogadro number and V_0 and V are the molar volumes at absolute zero and at temperature T, respectively. Refractive index data can be utilized in conjunction with molar volume to compute the molecular radius (M_r) using the following relation [12,13]:

$$M_r = \left[\left(\frac{3}{4\pi N}\right)\frac{(n^2 - 1)}{(n^2 + 2)} V_m\right]^{1/3} \tag{13}$$

The molecular radius (M_r) can also be obtained from density data from the relation [12,14]

$$M_r = \frac{1}{2} 3\sqrt{\frac{M\sqrt{2}}{\rho N}} \tag{14}$$

Results and Discussion

Thermodynamic Parameters and Molecular Radius

Alkoxy benzoic acids with alkoxy chain number $n = 3$ to 12 and 16 were chosen to evaluate different thermoacoustic parameters, molecular radius (M_r), and the molecular free length (L_f). The necessary experimental values to evaluate thermoacoustic

Table 1. Thermoacoustic parameters of benzoic acids in different phases

	Thermoacoustic parameters									
Compound	Phase	C_1	$V^{\sim}$	$V^{\sim}_{C_1}$	X	S^*	K''	K	K'	V_a
3bacid	Isotropic (157.0)	8.76	1.20	5.26	−0.56	1.32	−0.16	3.88	3.72	39.18
	Nematic (150.1)	10.33	1.15	4.43	−0.60	1.23	0.75	4.67	3.91	37.44
4bacid	Isotropic (165.1)	7.50	1.29	7.04	−0.49	1.49	0.33	3.25	3.59	43.95
	Nematic (155.0)	6.73	1.44	12.06	−0.38	1.86	0.70	2.87	3.57	43.17
5bacid	Isotropic (156.4)	8.01	1.25	6.07	−0.53	1.40	0.13	3.50	3.64	46.99
	Nematic (147.5)	7.32	1.31	7.58	−0.47	1.54	0.41	3.16	3.57	47.15
6bacid	Isotropic (159.0)	8.99	1.19	5.09	−0.57	1.30	−0.24	4.00	3.75	49.56
	Nematic (151.3)	8.11	1.24	5.93	−0.53	1.39	0.09	3.55	3.65	50.23
7bacid	Isotropic (151.8)	7.45	1.30	7.18	−0.49	1.50	0.35	3.23	3.587	54.84
	Nematic (140.1)	7.17	1.34	8.16	−0.46	1.59	0.47	3.08	3.56	54.10
	Smectic C (96.1)	7.30	1.32	7.66	−0.47	1.55	0.42	3.15	3.57	51.47
8bacid	Isotropic (152.5)	7.57	1.29	6.901	−0.50	1.48	0.31	3.28	3.59	58.15
	Nematic (143.1)	7.28	1.32	7.73	−0.47	1.55	0.43	3.14	3.57	57.58
	Smectic C (96.9)	7.62	1.28	6.77	−0.50	1.47	0.28	3.31	3.60	54.71
9bacid	Isotropic (147.9)	8.44	1.22	5.55	−0.55	1.35	−0.03	3.72	3.68	59.94
	Nematic (140.1)	8.31	1.23	5.68	−0.54	1.36	0.01	3.66	3.67	59.54
	Smectic C (114.1)	8.12	1.24	5.92	−0.53	1.39	0.08	3.56	3.65	58.74

(*Continued*)

Table 1. Continued

	Thermoacoustic parameters									
Compound	Phase	C_1	$V^{\sim}$	$V^{\sim}_{C_1}$	X	S^*	K''	K	K'	V_a
10bacid	Isotropic (143.3)	8.50	1.22	5.50	−0.55	1.34	−0.05	3.75	3.69	63.08
	Nematic (133.3)	8.01	1.25	6.06	−0.53	1.40	0.12	3.51	3.64	63.23
	Smectic C (110.2)	7.89	1.26	6.25	−0.52	1.42	0.17	3.45	3.62	62.28
11bacid	Isotropic (145.7)	7.42	1.30	7.27	−0.48	1.51	0.37	3.21	3.58	68.31
	Nematic (135.7)	6.99	1.37	9.17	−0.43	1.67	0.56	2.99	3.56	67.26
	Smectic C (115.4)	6.83	1.41	10.51	−0.40	1.76	0.64	2.92	3.56	65.34
12bacid	Isotropic (142.2)	12.00	1.12	3.99	−0.63	1.17	1.37	5.50	4.12	64.29
	Nematic (133.5)	9.43	1.18	4.82	−0.58	1.27	−0.41	4.21	3.80	67.64
	Smectic C (125.5)	8.16	1.24	5.87	−0.53	1.38	0.07	3.58	3.65	69.24
16bacid	Isotropic (155.3)	7.90	1.26	6.24	−0.52	1.42	0.17	3.45	3.62	85.36
	Nematic (146.4)	7.49	1.29	7.08	−0.49	1.50	0.34	3.24	3.59	85.10
	Smectic C (118.6)	7.52	1.29	6.99	−0.49	1.49	0.32	3.26	3.59	82.87

parameters are taken from Datta Prasad *et al.* [6]. The thermoacoustic parameters estimated are C_1 (Moelwyns-Hughes parameter), reduced molar volume ($V^{\sim}$), isochoric temperature coefficient of internal pressure (X), isothermal (K'), isochoric (K''), and isobaric (K) acoustical parameters and the available volume (V_a). The data regarding the above parameters at different temperatures covering different phases that a liquid crystal exhibits are presented in Table 1. In Fig. 1, the molecular radius estimated using refractive index [7] and density data using Eqs. (13) and (14) respectively are presented. The data evaluated from both density and refractive index differ from one another. Our systematic studies on a number of LC systems also showed the same trend [15]. The variation with temperature of the molecular radius follows that of molar volume in all cases. It exhibits jumps at the phase transition temperature. Figure 1 reveals that the molecular radius, M_r, increases with the increase of alkoxy chain number, with a core molecular radius of 3.58 and 2.68 Å and the increment for methylene unit is 0.084 and 0.054 Å in the case of density and refractive index data respectively. From our systematic studies it is concluded that the expressions used for the estimation of molecular radius from density and refractive index need refinement to get concurrent results from these two experimental results.

The variation of different thermoacoustic parameters with the chain length showed an even–odd effect like clearing temperature. However, as expected, the variation of $V^{\sim}$, $V^{\sim}_{C_1}$, and S^* with the chain length is similar, whereas in the case of C_1 the variation is opposite, even though this parameter also exhibits the even–odd effect with the chain number. These features are depicted in Figs. 2 and 3.

Available Volume and Molecular Free Length

The available volume, V_a, is estimated using Eq. (9). It is found that the available volume increment for one methylene unit is about 3.5. Using the values of V_a and V_0 (molar volume at 0 K), the molecular free length can be estimated. However,

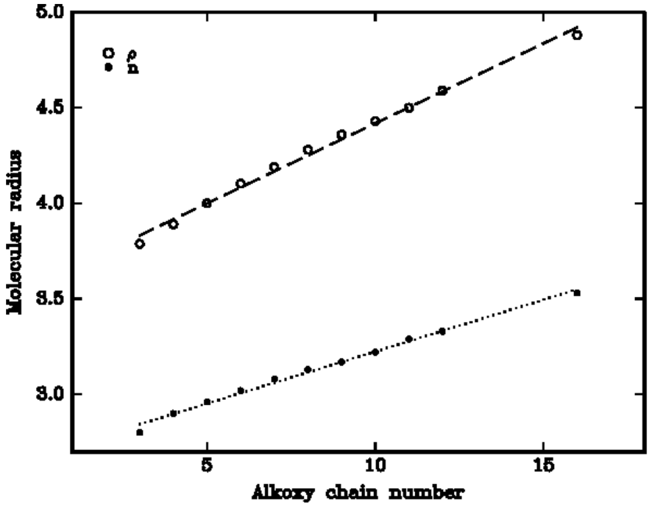

Figure 1. Variation of molecular radius (Å) with chain number in benzoic acids estimated from ρ and n.

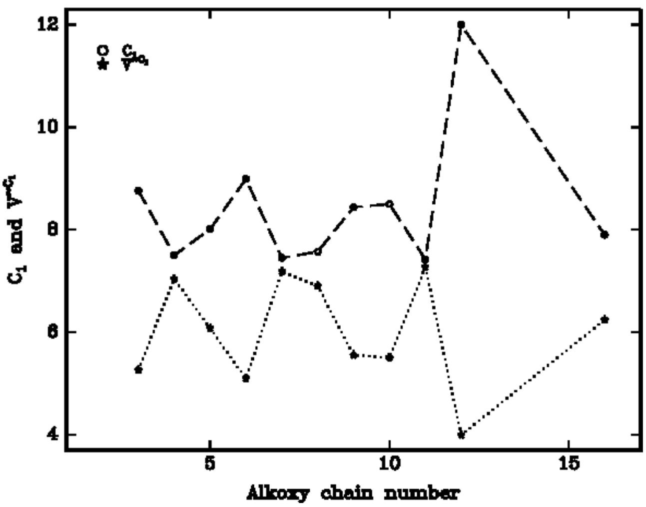

Figure 2. Variation of C_1 and $V^{\sim}_{C_1}$ with chain number in benzoic acids.

V_0 can be evaluated differently by using different expressions as well as extrapolating the molar volume in isotropic phase to 0 K. The authors estimated V_0 in three ways and the values at different temperatures in LC phases are given in Table 2. The values in Table 2 reveal that V_0 values estimated using Eqs. (11) and (12) show agreement with one another, whereas the values obtained from extrapolation exhibit divergence, as expected. This discrepancy depends on the slope of the density curve with temperature in the isotropic phase. Further, the authors, from their systematic studies on these compounds as well as in a number of nO.m [15] compounds found that the slope value should be around 8×10^{-4} to obtain reasonable agreement with the values obtained using Eqs. (11) and (12).

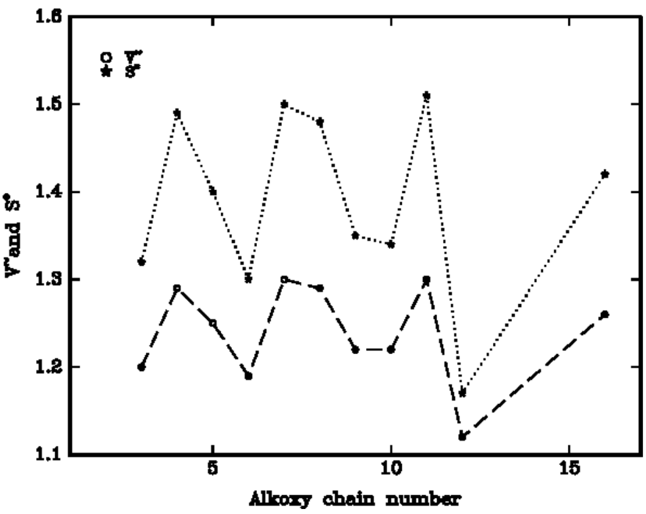

Figure 3. Variation of $V^{\sim}$ and S^* with chain number in benzoic acids.

Table 2. V_0 values evaluated in three different ways in the case of benzoic acids

Compound	Phase	Molar volume at absolute zero V_0		
		V_0 from Eq. (12)	V_0 from Eq. (11)	V_0 from extrapolation
3acid	Isotropic (157.0)	153.13	145.91	164.48
	Nematic (150.1)	159.38	146.63	164.48
4acid	Isotropic (165.1)	155.60	157.86	126.75
	Nematic (155.0)	136.53	154.42	126.75
5acid	Isotropic (156.4)	174.06	171.03	151.33
	Nematic (147.5)	163.67	168.69	151.33
6acid	Isotropic (159.0)	196.51	185.92	181.56
	Nematic (151.3)	187.58	183.38	181.56
7acid	Isotropic (151.8)	193.14	196.75	151.71
	Nematic (140.1)	184.47	193.07	151.71
	Smectic C (96.1)	178.22	184.06	151.71
8acid	Isotropic (152.5)	207.08	209.15	170.21
	Nematic (143.1)	198.89	205.84	170.21
	Smectic C (96.9)	195.90	197.05	170.21
9acid	Isotropic (147.9)	229.28	221.00	205.79
	Nematic (140.1)	225.77	218.69	205.79
	Smectic C (114.1)	219.52	214.50	205.79
10acid	Isotropic (143.3)	242.26	232.98	218.31
	Nematic (133.3)	234.34	230.19	218.31
	Smectic C (110.2)	228.54	225.96	218.31
11acid	Isotropic (145.7)	239.72	244.89	191.37
	Nematic (135.3)	223.50	239.45	191.37
	Smectic C (115.4)	211.44	232.92	191.37
12acid	Isotropic (142.2)	293.78	265.44	285.80
	Nematic (133.5)	274.97	257.30	285.80
	Smectic C (125.5)	259.51	253.13	285.80
16acid	Isotropic (155.3)	313.44	309.77	269.64
	Nematic (146.4)	300.76	305.52	269.64
	Smectic C (118.6)	294.00	297.81	269.64

In calculating molecular free length, L_f, all three different V_0 values are utilized in Eq. (10). The variation of L_f with temperature is evaluated in all the compounds. Figure 4 shows the variation of L_f with temperature in 7Oba from V_0 evaluated from density data. The figure reveals that L_f shows a slight decrease with the decrease of temperature in a particular phase. However, at the phase transformations the L_f exhibited a peak value for thermal expansion coefficient as expected. For the sake of comparison, the L_f values estimated in three different ways in isotropic phase are plotted against the chain number in Fig. 5. The L_f values showed an even–odd effect with the chain number. However, the values estimated from V_0 obtained from an extrapolation technique showed higher values compared to those obtained from the other two methods. Further, the L_f values evaluated from V_0 using Eqs. (11) and (12) concur with one another. Similar results are obtained in the case of a number of

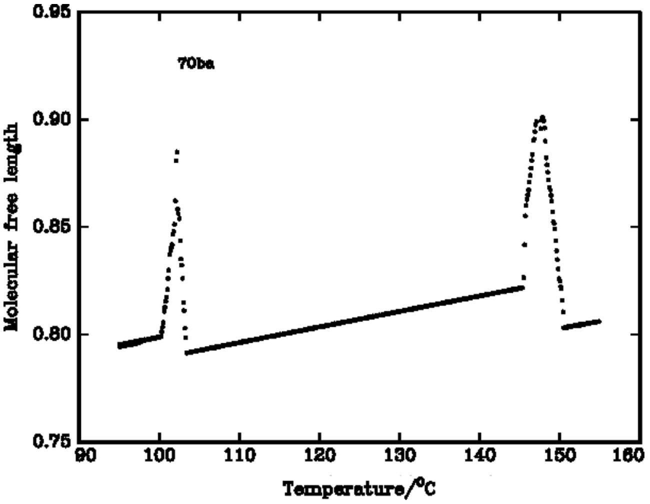

Figure 4. Variation of L_f (Å) with temperature in 7Oba compound.

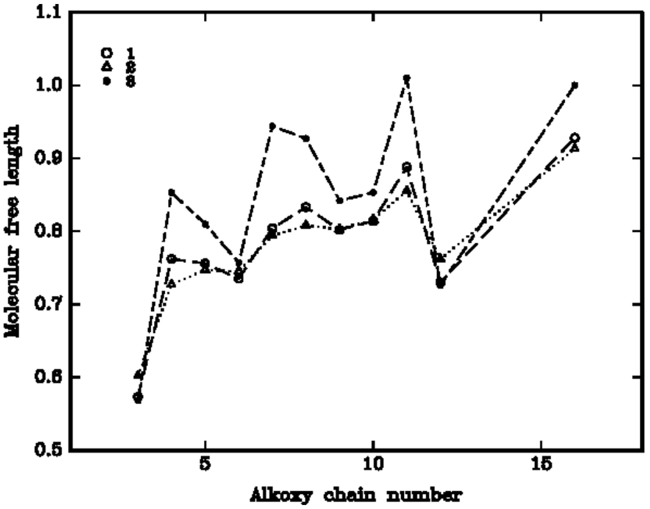

Figure 5. Variation of L_f (Å) with chain number in benzoic acids estimated in three different ways.

nO.m compounds also [15]. The correlation between these values is expected if the $d\rho/dT$ is around 8×10^{-4}. This can be observed in the case of compounds with $n = 3$, 6, and 12 where the values concur with one another.

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