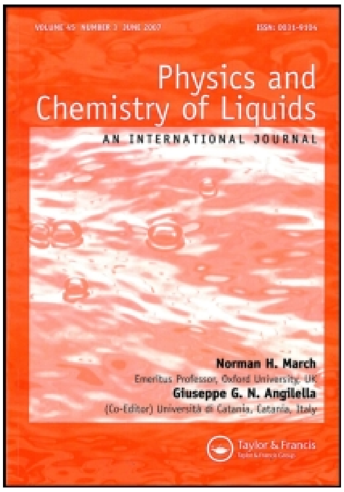

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A study on thermodynamic and sound parameters of some nematics

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A study on thermodynamic and sound parameters of some nematics

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Measurements of ultrasonic velocity and density of solutes in dilute solutions as a function of concentration and temperature can be used to obtain several thermodynamic and acoustical parameters and their excess adiabatic compressibility. The physical parameters that can be determined through these are: molar sound velocity or Rao's number (R), molar compressibility or Wada's constant (B), characteristic acoustic impedance (Z), intermolecular or free length (L_f), free volume (V_f), available volume (V_a) and adiabatic compressibility (β). These parameters play an important role in the phenomenon associated with intermolecular interaction and hence in sound transmission. For example, the parameter Z that is determined by the product of density (d) and ultrasonic velocity (c) has a greater significance as a characteristic property of the medium than does either the density or velocity individually so also in case of sound transmission the parameter of more concern is the molar sound volume (V_m) rather than molar sound velocity or Rao' number. Such studies on liquid crystals around phase transition temperature in their pure state yield important information and so also in their dilute solutions. In view of above facts, the ultrasonic velocity with density measurement studies on pure samples of nematics, namely, 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 was taken up both as a function of mole fraction (in benzene) and temperature. The results of the above work is presented in this article and discussed.

Keywords: Liquid crystals; Mesophases; Sound velocity; Volumetric measurements

1. Introduction

The structure of molecules and intermolecular interaction between the molecules can be well understood through various thermodynamic parameters calculated through velocity measurements [1–21]. The measured values of velocities along with the corresponding values of densities through volumetric measurements help in calculating some more thermodynamic parameters which in turn may help in gathering information like stabilization parameter and so on. The physical parameters that can be obtained are: molar sound velocity or Rao's number (R), molar compressibility or

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Wada's constant (B), characteristic acoustic impedance (Z), intermolecular or free length (L_f), free volume (V_f), available volume (V_a) and adiabatic compressibility (β) play an important role in the phenomenon of sound transmission. For example, the parameter Z that is determined by the product of density (d) and ultrasonic velocity (c) has a greater significance as a characteristic property of the medium than does either the density or velocity individually so also in case of sound transmission the parameter of more concern is the molar sound volume (V_m) rather than the molar sound velocity or Rao's number.

A very few studies are available in literature where the ultrasonic velocity measurements in association with density measurements are exploited to understand various aspects of liquid crystals [8] such as their structures, intermolecular interactions, pre-transitional effects etc. In view of all these considerations and also in view of the fact that ultrasonic studies are currently finding new applications in various disciplines of science, engineering and medicine, an attempt is made to carry out such studies on 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 and is taken up both as a function of mole fraction (in benzene) and temperature. Further, these studies are carried out to know whether the general conclusions arrived at by ultrasonic velocity and specific volume studies on some thermo-tropic nematogenes are still valid when studied in dilute solutions. In such, a study one, should make a proper choice of the solvent, namely, it should be non-polar to avoid the possible solvent–solute dipole–dipole interactions and that its boiling temperature should be well above that of the isotropic–nematic transition temperature of the solute nematogens [20]. In the present study, benzene is used as a solvent and has restricted the study to the crystal–nematic range if the liquid crystals under study. Butyl-*p*-(*p*-ethoxy phenoxy carbonyl)phenyl carbonate, *p*-[*N*-(*p*-methoxy benzylidene)amino]phenyl benzoate and *p*-(*p*-ethoxy phenyl azo)phenyl undecylenate and will be here after referred as BEPCP. CAR; MBAPB and EPAP. UND respectively.

2. Experimental

For the measurement of sound velocity an ultrasonic interferometer type M81 supplied by Mittel enterprises, New Delhi, India was used. With this instrument the ultrasound velocity through the measurement of wavelength can be measured at several spot frequencies in the mega hertz region and in the present work the measurements are carried out at 1–4 MHz. The measuring cell (in the form of a hollow cylinder) was appropriately thermostated (electrical heating) by winding heating element on its surface and the temperature of the medium inside the cell was controlled by using temperature control unit – thermocouple arrangement. With this, the temperature could be controlled accurately to within $\pm 1^\circ$C and the measured sound velocities are accurate to $\pm 5\%$. The density measurements were carried out using a specially designed pycnometer with necessary heating arrangement. (The pycnometer which is a specially designed specific gravity measuring instrument had two capillaries of length 19 cm with a radius of 0.363 mm with a bulb with total volume up to a reference point being 1.49398 cc and volume per unit length being 0.004154 cc.) This pycnometer was calibrated using several liquids. The pycnometer was filled with required samples in and change in its volume was noted as a function of temperature using appropriately designed oven controlled by a digital temperature indicator/controller of an accuracy ±0.2°C. Densities of some standard liquids like benzene, cyclohexane etc. as in case of ultrasonic studies was measured using the above equipments and the results were compared. The estimated values of the densities are accurate to within fourth decimal place. Arrangement for maintaining the temperature uniformly around the pycnometer was achieved with specially built oven with one face being transparent to measure the change in position of the sample in one of the arms of the pycnometer through a microscope of list count 0.0005 cm.

3. Defining relations

For the derivation of several acoustical and thermo dynamical parameters, the following defining relations reported in the literature are used.

(1) Molar volume $(V_m) = \{(M_1 f_1 + M_2 f_2)/d_{12}\}$
where, M, f and d refer to molecular weight, mole fraction and density, while suffixes 1, 2 and 12 indicate the relevant quantity for the solute and solvent respectively.
(2) Adiabatic compressibility $\beta = 1/(C^2 d_{12})$
(3) Intermolecular free length $(L_f) = K(\beta)^{1/2}$
where, K is a temperature-independent constant given by 6.25 EXP-04.
(4) Available volume (V_a: Schaff's) $= V_m \cdot \{1 - (C/C_\infty)\}$ where, $C_\infty = 1600\,\mathrm{m\,s^{-1}}$.
(5) Available volume (V_a: Kittel) $= \{V_m \cdot C_g \cdot 3^{1/2}/C\}$
where, $C_g = \{\gamma$ (ratio of specific heats) $\cdot RT/M\}^{1/2}$.
(6) Free volume $(V_f) = \{V_m \cdot (C_g/C)^3\}$
(7) Molar sound velocity or Rao's number $(R) = V_m \cdot (C)^{1/3}$
(8) Molar compressibility or Wada's number $(B) = V_m \cdot (\beta)^{-1/7}$
(9) Thermal expansion coefficient $(\alpha) = (1/V_n)\,(\Delta V/\Delta T)$
where, $V_n = \{(V_1 + V_2)/2\}$; $\Delta V = (V_2 - V_1)$; $\Delta T = (T_2 - T_1)$.
(10) Characteristic acoustic impedance $(Z) = C \cdot d_{12}$ Rayls.

4. Results and discussion

The analysis of the data in case of solute molecules in a solvent can be carried out by noting the variation with respect the observations and analysis made for pure solvent. Hence, in the present study the studies on benzene were also carried out along with BEPCP. CAR; MBAPB and EPAP. UND. The variation of the physical parameters as a function of temperature in the case of benzene and as a function of mole fraction or weight fraction as well as temperature in the case of BEPCP. CAR; MBAPB and EPAP. UND molecules dissolved in benzene can be explained in the following paragraphs. The maximum temperature attained in the case of dilute solution measurements is around 323 K, which is nearer to the K–N transition temperature of the molecules BEPCP. CAR and EPAP. UND. Because of some experimental limitations, measurements could not be carried out in the entire K–N–I temperature intervals of these nematic compounds. The measured values of '*c*' and '*d*' at different

Table 1. Benzene.

T (K)	C ($\mathrm{m\,s^{-1}}$)	d_{12} ($\mathrm{kg\,l^{-1}}$)	$V_m \times 10^3$ ($\mathrm{l\,mole^{-1}}$)	$\beta \times 10^{11}$ ($\mathrm{m^2\,N^{-1}}$)	L_f (Å)	$V_a \times 10^3$ (Schaff's) ($\mathrm{l\,mole^{-1}}$)	$V_a \times 10^3$ (Kittle) ($\mathrm{l\,mole^{-1}}$)	$V_f \times 10^3$ ($\mathrm{l\,mole^{-1}}$)	R	B	$Z \times 10^{-6}$ Rayls
298	1294	0.8679	90.00	68.81	0.518	17.21	25.50	0.394	981	2547	1.12
303	1280	0.8637	90.44	70.67	0.525	18.09	26.13	0.419	982	2550	1.11
308	1269	0.8532	91.55	72.78	0.533	18.94	26.89	0.446	991	2570	1.08
313	1231	0.8523	91.65	77.43	0.550	21.14	27.98	0.549	983	2552	1.05
318	1207	0.8459	92.34	81.15	0.563	22.68	28.98	0.549	983	2552	1.02
323	1183	0.8451	92.43	84.55	0.574	24.09	29.83	0.597	978	2540	1.00

Table 2. The values of various physical parameters as a function of temperature as well as mole fraction (weight fraction) of the molecule BEPCP. CAR.

T (K)	W_2 ($\times 10^2$)	C ($\mathrm{m\,s^{-1}}$)	d_{12} ($\mathrm{kg\,l^{-1}}$)	$V_m \times 10^3$ ($\mathrm{l\,mole^{-1}}$)	$\beta \times 10^{11}$ ($\mathrm{m^2\,N^{-1}}$)	L_f (Å)	$V_a \times 10^3$ (Schaff's) ($\mathrm{l\,mole^{-1}}$)	$V_a \times 10^3$ (Kittle) ($\mathrm{l\,mole^{-1}}$)	$V_f \times 10^3$ ($\mathrm{l\,mole^{-1}}$)	R	B	$Z \times 10^{-6}$ Rayls
299	0.7824	1293	0.8659	90.94	69.08	0.5195	17.45	25.75	0.3974	991	2572	1.12
	1.5163	–	0.8674	91.12	–	–	–	–	–	–	–	–
	2.2560	–	0.8683	91.57	–	–	–	–	–	–	–	–
	2.9746	1309	0.8712	91.78	66.99	0.5115	16.69	25.45	0.3768	1004	2607	1.14
	3.7693	–	0.8736	92.14	–	–	–	–	–	–	–	–
303	0.7824	1269	0.8629	91.05	71.96	0.5302	18.84	26.45	0.4294	986	2560	1.10
	1.5163	1279	0.8642	91.46	70.74	0.5257	18.35	26.28	0.4177	993	2578	1.11
	2.2560	1288	0.8657	91.85	69.63	0.5215	17.91	2614	0.4073	999	2595	1.12
	2.9746	1295	0.8683	92.09	68.67	0.5179	17.56	2599	0.3983	1004	2607	1.13
	3.7693	1302	0.8707	92.44	67.75	0.5144	17.22	25.86	0.3895	1009	2622	1.13
308	0.7824	1251	0.8561	91.78	74.64	0.5400	20.02	27.27	0.4633	989	2567	1.07
	1.5163	1261	0.8608	91.82	73.06	0.5342	19.45	26.98	0.4482	992	2576	1.09
	2.2560	1274	0.8626	92.18	71.43	0.5282	18.78	26.73	0.4326	999	2595	1.10
	2.9746	1281	0.8646	92.48	70.48	0.5247	18.44	26.60	0.4234	1004	2608	1.11
	3.7693	1287	0.8677	92.76	69.58	0.5213	18.15	26.47	0.4146	1009	2621	1.12
313	0.7824	1239	0.8491	92.53	76.72	0.5474	20.88	27.98	0.4923	994	2578	1.05
	1.5163	1247	0.8578	92.14	74.97	0.5412	20.33	27.61	0.4769	992	2576	1.07
	2.2560	1256	0.8588	92.58	73.81	0.5370	19.91	27.44	0.4644	999	2594	1.08
	2.9746	1261	0.8610	92.87	73.04	0.5342	19.68	27.35	0.4565	1003	2606	1.09
	3.7693	1271	0.8640	93.16	71.53	0.5286	19.10	27.11	0.4418	1009	2622	1.10
318	0.7824	1213	0.8451	92.97	80.42	0.5605	22.49	28.94	0.5397	992	2573	1.03
	1.5163	1229	0.8528	92.68	77.63	0.5507	21.49	28.40	0.5130	993	2578	1.05
	2.2560	1236	0.8555	92.94	76.51	0.5467	21.14	28.22	0.5009	997	2591	1.06
	2.9746	124	0.8581	93.18	75.18	0.5419	20.67	28.01	0.4873	1002	2604	1.07
	3.7693	1249	0.8607	93.52	74.48	0.5394	20.52	27.93	0.4797	1007	2617	1.08
323	0.7824	1180	0.8415	93.37	85.35	0.5774	24.51	30.11	0.6026	987	2562	0.99
	1.5163	1186	0.8502	92.97	83.62	0.5715	24.06	29.75	0.5862	984	2559	1.01
	2.2560	1198	0.8528	93.23	81.70	0.5649	23.42	29.44	0.5649	990	2574	1.02
	2.9746	1208	0.8545	93.58	80.20	0.5597	22.93	29.22	0.5485	997	2591	1.03
	3.7693	1225	0.8575	93.87	77.71	0.5517	22.00	28.81	0.5225	1004	2611	1.05

temperatures in the case of benzene molecules and the values of derived sound parameters there from are presented in table 1.

It is clear from the results in table 1 that the parameters '*c*', '*d*', R, V_m and '*B*' fluctuate. The parameters β, L_f and V_a and V_f increase with increase of temperature and the sound impedance parameter (Z) fluctuates and the value centres around 1 Rayl.

Table 3. The values of various physical parameters as a function of temperature as well as mole fraction (weight fraction) of the molecule MBAPB.

T (K)	W_2 ($\times 10^2$)	C (m s^{-1})	d_{12} (kg l^{-1})	$V_m \times 10^3$ (l mole^{-1})	$\beta \times 10^{11}$ (m^2 N^{-1})	L_f (Å)	$V_a \times 10^3$ (Schaff's) (l mole^{-1})	$V_a \times 10^3$ (Kittle) (l mole^{-1})	$V_f \times 10^3$ (l mole^{-1})	R	B	$Z \times 10^{-6}$ Rayls
299	0.1871	1284	0.8697	89.93	69.74	0.5220	17.76	25.70	0.4042	977	2540	1.12
	0.2314	–	0.8712	89.80	–	–	–	–	–	–	–	–
	0.2896	–	0.8723	89.72	–	–	–	–	–	–	–	–
	0.2923	1302	0.8733	89.61	67.55	0.5137	16.69	25.25	0.3858	979	2543	1.14
	0.3170	1316	0.8760	89.35	65.92	0.5074	15.86	24.91	0.3726	980	2544	1.15
	0.3630	1332	0.8773	89.39	64.25	0.5010	14.97	24.60	0.3584	984	2555	1.17
303	0.1871	1269	0.8675	90.16	71.58	0.5288	18.65	26.25	0.4282	976	2537	1.10
	0.2314	1284	0.8685	90.08	69.84	0.5223	17.79	25.92	0.4130	979	2544	1.12
	0.2896	1290	0.8693	90.03	69.13	0.5196	17.44	25.78	0.4070	980	2546	1.12
	0.2923	1295	0.8707	89.88	68.48	0.5172	17.13	25.64	0.4016	980	2545	1.13
	0.3170	1309	0.8736	89.60	66.81	0.5108	16.30	25.28	0.3871	980	2546	1.14
	0.3630	1324	0.8741	89.72	65.26	0.5049	15.48	25.00	0.3736	985	2558	1.16
308	0.1871	1236	0.8644	90.48	75.73	0.5439	20.58	27.27	0.4769	971	2526	1.07
	0.2314	1241	0.8662	90.31	74.96	0.5411	20.26	27.10	0.4696	971	2525	108
	0.2896	1248	0.8671	90.26	74.05	0.5378	19.96	26.93	0.4615	972	2528	1.08
	0.2923	1260	0.8680	90.16	72.57	0.5324	19.16	26.65	0.4479	974	2532	1.09
	0.3170	1273	0.8709	89.87	70.86	0.5261	18.37	26.29	0.4330	974	2533	1.11
	0.3630	1291	0.8716	89.97	68.84	0.5186	17.38	25.93	0.4144	980	2546	1.13
313	0.1871	1199	0.8627	90.66	80.63	0.5612	22.72	28.39	0.5360	963	2508	1.03
	0.2314	1214	0.8647	90.47	78.47	0.5536	21.83	27.98	0.5153	965	2513	1.05
	0.2896	1224	0.8657	90.40	77.10	0.5488	21.24	27.72	0.5017	967	2517	1.06
	0.2923	1232	0.8664	90.33	76.04	0.5450	20.78	27.52	0.4916	968	2520	1.07
	0.3170	1258	0.8676	90.21	72.83	0.5334	19.28	26.91	0.4611	974	2532	1.09
	0.3630	1265	0.8685	90.29	71.95	0.5302	18.91	26.76	0.4526	977	2539	1.10
318	0.1871	1171	0.8575	91.21	85.05	0.5764	24.46	29.48	0.5926	961	2504	1.00
	0.2314	1188	0.8600	90.97	82.39	0.5673	23.43	28.98	0.5660	964	2509	1.02
	0.2896	1208	0.8611	90.88	79.58	0.5576	22.27	28.47	0.5378	968	2519	1.04
	0.2923	1221	0.8618	90.81	77.83	0.5514	21.51	28.15	0.5204	971	2526	1.05
	0.3170	1237	0.8638	90.63	75.67	0.5437	20.56	27.73	0.4995	973	2530	1.07
	0.3630	1257	0.8660	90.55	73.08	0.5343	19.41	27.22	0.4736	977	2541	1.09
323	0.1871	1134	0.8535	91.64	91.11	0.5966	26.69	30.82	0.6710	956	2491	0.97
	0.2314	1157	0.8562	91.37	87.25	0.5838	25.30	30.12	0.6299	959	2499	0.99
	0.2896	1164	0.8578	91.23	86.04	0.5797	24.86	29.89	0.6176	960	2501	1.00
	0.2923	1176	0.8589	91.12	84.19	0.5735	24.15	29.55	0.5982	962	2505	1.01
	0.3170	1183	0.8598	91.03	83.11	0.5698	23.73	29.35	0.5871	963	2508	1.02
	0.3630	1190	0.8637	90.80	81.76	0.5651	23.27	29.07	0.5737	962	2507	1.03

Some of these trends of variations can be conveniently explained on the basis of L_f values. The increase in the value of L_f with temperature implies that the mean distance between the molecules increases there by decreasing the potential energy of interaction between them thus leading to the decrease in '*c*' and '*d*' values. Further an increase in L_f value means the V_a or V_f also increases. The increase in the value of β with temperature is obvious since '*c*' and '*d*' decreases with temperature. The increase in the value of the adiabatic compressibility and molar volume is an indication of weak interaction between the molecules of the components [2].

The benzene was chosen as the solvent as it is a well-tested non-polar solvent in which the nematics chosen were found to be readily solvable. In present work, studies at only low concentrations of solutes in solvent could be done in view of very small amount

Table 4. The values of various physical parameters as a function of temperature as well as mole fraction (weight fraction) of the molecule EPAP. UND.

T (K)	W_2 ($\times 10^2$)	C ($\mathrm{m\,s^{-1}}$)	d_{12} ($\mathrm{kg\,l^{-1}}$)	$V_m \times 10^3$ ($\mathrm{l\,mole^{-1}}$)	$\beta \times 10^{11}$ ($\mathrm{m^2\,N^{-1}}$)	L_f (Å)	$V_a \times 10^3$ (Schaff's) ($\mathrm{l\,mole^{-1}}$)	$V_a \times 10^3$ (Kittle) ($\mathrm{l\,mole^{-1}}$)	$V_f \times 10^3$ ($\mathrm{l\,mole^{-1}}$)	R	B	$Z \times 10^{-6}$ Rayls
302	0.7614	1280	0.8682	90.54	70.30	0.5240	18.11	26.02	0.4137	983	2551	1.11
	1.5009	1285	0.8721	90.57	69.44	0.5208	17.85	25.86	0.4060	986	2561	1.12
	2.2506	1291	0.8759	90.83	68.50	0.5173	17.54	25.74	0.3977	989	2572	1.13
	2.9505	1299	0.8781	91.14	67.49	0.5135	17.15	25.56	0.3878	994	2588	1.14
	3.6811	1308	0.8789	91.02	66.50	0.5097	16.72	25.47	0.3786	1001	2609	1.15
308	0.7614	1272	0.8605	91.35	71.83	0.5297	18.73	26.68	0.4381	990	2569	1.10
	1.5009	1276	0.8645	91.36	71.05	0.5265	18.52	26.56	0.4305	992	2576	1.10
	2.2506	1285	0.8733	91.10	69.35	0.5205	17.94	26.18	0.4161	990	2575	1.10
	2.9505	1290	0.8751	91.45	68.67	0.5179	17.72	26.10	0.4094	996	2589	1.13
	3.6811	1296	0.8771	91.80	67.99	0.5153	17.50	26.03	0.4025	1001	2602	1.14
313	0.7614	1240	0.8585	91.57	75.76	0.5440	20.60	27.67	0.4860	964	2556	1.07
	1.5009	1245	0.8620	91.73	74.84	0.5407	20.35	27.51	0.4764	967	2565	1.07
	2.2506	1250	0.8725	91.19	73.35	0.5353	19.95	27.17	0.4640	982	2557	1.09
	2.9505	1260	0.8730	91.67	72.15	0.5309	19.48	27.00	0.4510	990	2577	1.10
	3.6811	1268	0.8753	91.99	71.06	0.5268	19.09	26.85	0.4404	996	2591	1.11
318	0.7614	1216	0.8568	91.75	78.93	0.5553	22.02	28.49	0.5287	979	2546	1.04
	1.5009	1219	0.8593	92.02	78.32	0.5531	21.91	28.41	0.5213	983	2556	1.05
	2.2506	1225	0.8693	91.52	76.66	0.5472	21.45	28.04	0.5066	979	2558	1.07
	2.9505	1233	0.8707	91.92	75.55	0.5432	21.08	27.89	0.4942	986	2567	1.07
	3.6811	1253	0.8731	92.22	72.95	0.5378	20.00	27.46	0.4685	994	2588	1.09
323	0.7614	1204	0.8552	91.92	80.66	0.5613	22.75	29.05	0.5585	978	2543	1.03
	1.5009	1209	0.8571	92.25	79.82	0.5584	22.54	28.94	0.5483	983	2556	1.04
	2.2506	1216	0.8686	91.60	77.86	0.5515	21.98	28.50	0.5307	978	2547	1.06
	2.9505	1228	0.8693	92.06	76.28	0.5459	21.40	28.27	0.5129	986	2567	1.07
	3.6811	1240	0.8705	92.05	74.71	0.5402	20.81	28.05	0.4964	994	2587	1.08

of samples available of spectroscopic grade purity although it is desirous to extend the work till benzene solubility limit of each liquid crystal. However, it is felt that the studies presented here give enough information regarding systems under study.

In tables 2–4 are given the values of various physical parameters as a function of temperature as well as mole fraction (weight fraction) of the molecules BEPCD. CAR; MBAPB and EPAP. UND, respectively.

It is observed that as the weight fraction of the solute component in all the three cases increases, the value of C, d_{12}, increase and those of β, L_f, V_a and V_f exhibit decreasing trend, although the differences in values from solution to solution may not be very well outside the experimental errors. The increase in the values C and d_{12} as the weight fraction increases indicate that under the limiting case of the mixture i.e. for benzene content zero, these values are more in each case of the molecule than that compared to benzene values. The decrease in the values of L_f with the increase in the solute component means the distance between the molecules in the mixture decreases and thereby increasing the potential energy of the interaction between the molecules which leads to observed increase in the value of C. Judging from the results in these tables 2–4, it is also clear that as the temperature is varied, the L_f increases and therefore the potential energy of interaction decreases and this leads to an observed decrease in the values of C and d_{12}.

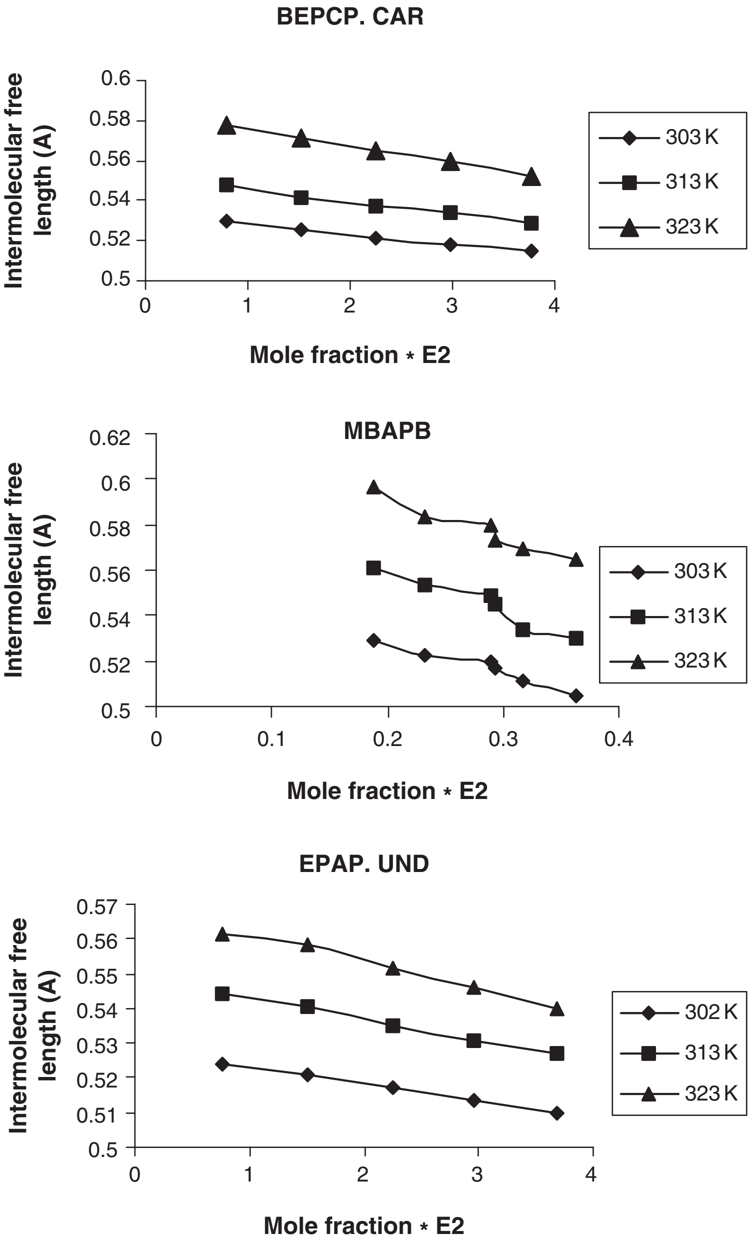

Figure 1. Plots showing variation of intermolecular free length with weight fraction of solutes in solvent at various temperatures.

The variation of L_f with weight fraction in case of three liquid crystals at a given temperature is demonstrated in figure 1 while with its variation with temperature at a given weight fraction in few cases is demonstrated in figure 2. From the figure it is clear that the variation of L_f with weight fraction or temperature is

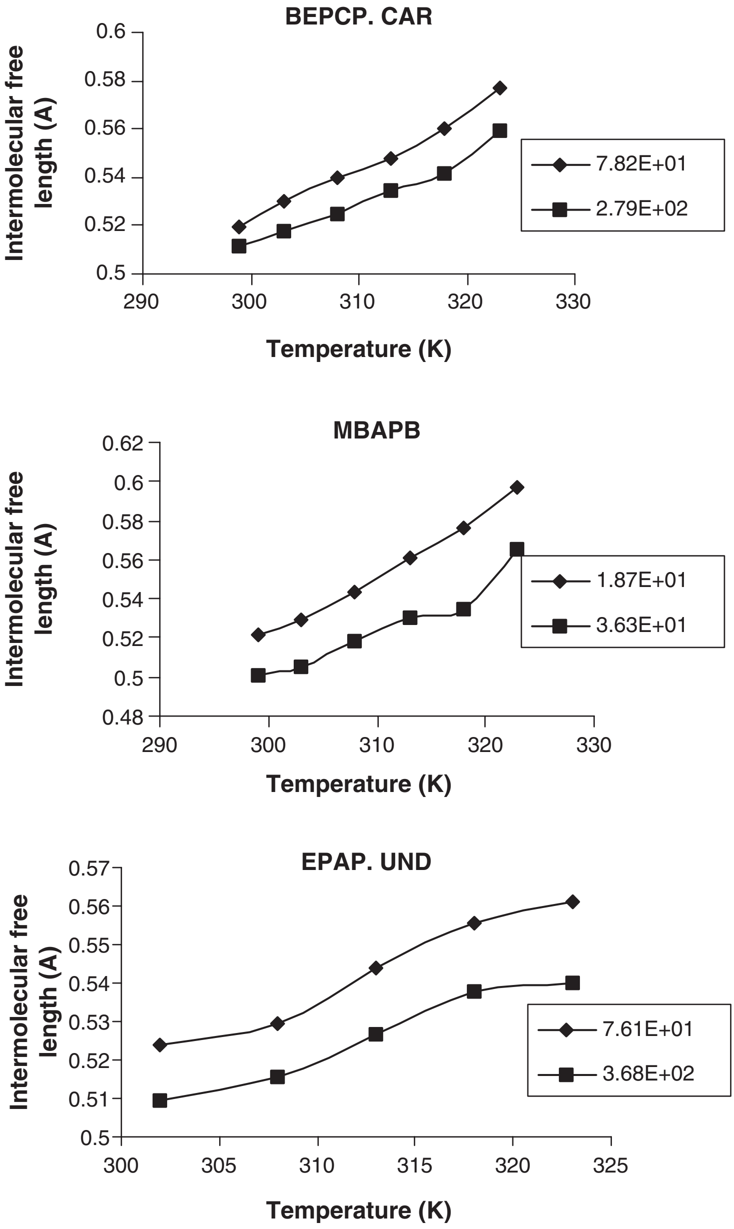

Figure 2. Plots showing variation of intermolecular free length with temperature of solutes in solvent at various weight fractions.

not linear, however, the variation is in accordance with expected lines as discussed earlier.

In figure 3 the variation *R* with weight fraction at a temperature are presented for three liquid crystals under study. From this figure it may be noted that the variation is not linear, although *R* increases gradually as weight fraction increases. The nature

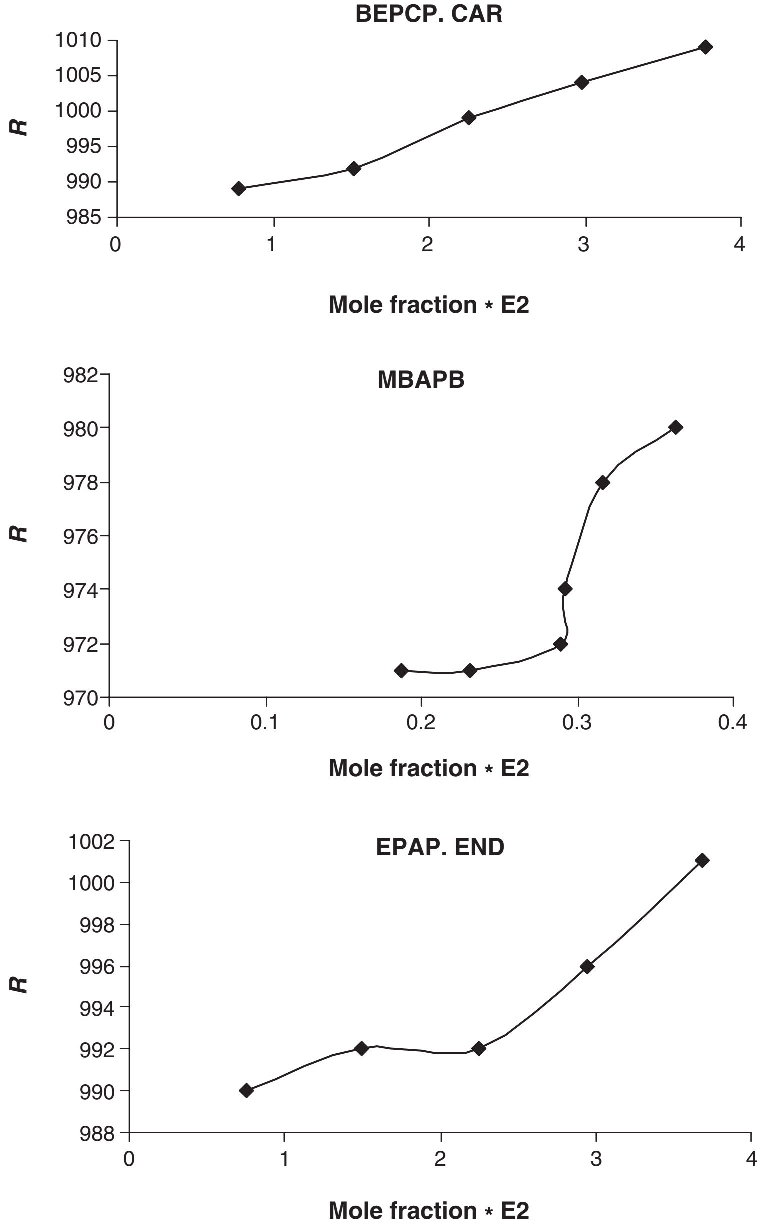

Figure 3. Variation of R with mole fraction at 308 K of solutes in solvent at various weight fractions.

of interaction between the components in the mixture (or dilute solution) can be understood by knowing whether R and B very linearly (week interaction) or non-linearly (molecular association) or by calculating the excess values of β, namely, if β_{excess} is positive it indicates week interaction or strong interaction between the molecules if β_{excess} is negative. In the present work, the value of β for individual components of the mixture at a single temperature are not determined. But a rough estimate of the quantity β_{excess} can be made as follows:

$$\text{Value of } \beta \text{ for benzene at } 50^\circ\text{C} = 84.55\ 10^{-11}\ \text{m}^2\,\text{N}^{-1}$$

$$\text{Value of } \beta \text{ for BEPCP. CAR at } 50^\circ\text{C (Ref. [21])} = 44.15\ 10^{-11}\ \text{m}^2\,\text{N}^{-1}$$

$$\text{Value of } \beta \text{ for mixture of BEPCP. CAR (0.038) and benzene (0.962) at } 323\,\text{K} = 77.71\ 10^{-11}\ \text{m}^2\,\text{N}^{-1}$$

Therefore, $\beta_{\text{excess}} = \beta_{\text{expt}} - (X_1\beta_1 + X_2\beta_2)$ and hence is negative indicating a strong interaction between the molecules. This observation is supported by the non-linear variation of R and β values with temperature or with weight fraction. Further, a disagreement between the values of V_a calculated by two different approaches may also support this point. This strong interaction between the molecules is contradictory to one's expectation because of the solvent used being benzene.

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