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Acoustic and Thermodynamic Properties of Binary Mixtures of Acetophenone with Ethylcyanoacetate at 303.15, 313.15 and 323.15K

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ABSTRACT

Densities ρ, Speeds of sound u, isentropic compressibilities κ_s, intermolecular free lengths L_f, specific acoustic impedances Z, relative association R_a, intermolecular attraction α, excess molar volumes V^E, excess isentropic compressibilities κ_s^E, excess intermolecular free lengths L_f^E and excess specific acoustic impedances Z^E of acetophenone with ethyl cyanoacetate have been reported over the entire range of composition at 303.15, 313.15 and 323.15K. The excess values have been fitted to Redlich–Kister polynomial equation. The results have been analyzed in terms of molecular interactions between acetophenone and ethyl cyanoacetate. The speeds of sound in present binary mixtures have been estimated from various empirical and theoretical models.

Key words: Molecular interaction, Density, Ultrasonic velocity.

INTRODUCTION

The thermodynamic, acoustic and transport properties of non- electrolyte liquid–liquid mixtures provide information about type and extent of molecular interactions, and can be used for the development of molecular models for describing the behaviour of solutions[1-3]. They are also necessary for engineering calculation, research of mass transfer, heat transfer and fluid flow. The increasing use of acetophenone and ethyl cyanoacetate in many industrial processes, as well as theoretical interest in the nature of associated solutions have greatly stimulated the need for extensive information on properties of mixtures involving these components. Acetophenone is an important industrial chemical widely used as an ingredient of flavor and fragrance in soaps, detergents, cosmetics and perfumes. It has also been used as an important intermediate for pharmaceuticals and

agrochemicals. Ethyl cyanoacetate was used as a solvent in pharmaceuticals and organic synthesis of pharmaceuticals and drugs. In the present paper, we report densities, speeds of sound, isentropic compressibilities, intermolecular free length, specific acoustic impedance, relative association, intermolecular attraction, and calculated excess functions of binary mixtures of acetophenone with ethyl cyanoacetate at 303.15, 313.15 and 323.15 K. This study will also provide a test of Nomoto's relation[4], Van Dael and Vangeel relation[5], Junjie's relation[6], impedance relation[7] and Jacobson's free length theory[8] to estimate speed of sound in binary mixtures at different temperatures.

EXPERIMENTAL

All chemicals used in this study were of analytical grade and obtained from S.D.fine-chem., Ltd. The claimed mass fraction purity for the chemicals was >0.995. These liquids were dried over 4Å molecular sieves and partially degassed prior to use. The purity of these experimental liquids was checked by comparing the observed densities and velocities with those reported in the literature [9, 10]. The measured values are included in Table 1 along with the available literature values. Airtight stoppered bottles were used for the preparation of the mixtures. The weight of the dry bottle was first determined. The less volatile component of the binary mixtures was introduced first in the sample bottle followed by second component, and the weight at each step was taken using an electronic balance (Shimadzu Corporation. Japan-BL 2205). Densities were determined by using a 25 cm^3 bicapillary pycnometer and calibrated with deionized double distilled water with a density of 996.0 kg m^{-3} at a temperature of 303.15 K. The pycnometer was thermostatted in a transparent walled water bath (maintained constant to ± 0.01 K) for 15 min to attain thermal equilibrium, and the liquid level in the two arms was obtained with a traveling microscope which could read to 0.01 mm.

The speeds of sound in pure liquids and in their binary mixtures were measured using single-crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi) operating at 2MHz. For all the measurements, temperatures were controlled by circulating the water through an ultra thermostat (Technico,Madras. made in India) keeping temperature fluctuations within ±0.02 K. The details of the experimental procedure have been described elsewhere. The uncertainty in density and speed of sound measurements was within 0.2 kgm^{-3} and $1ms^{-1}$.

RESULTS AND DISCUSSION

From the values of densities and speeds of sound, the isentropic compressibilities, specific acoustic impedances, intermolecular free length, relative association, intermolecular attraction, were obtained using the relations

$$\kappa_s = (\rho u^2)^{-1} \quad ...(1)$$

$$Z = u\rho \quad ...(2)$$

$$L_f = K_{jac} / U \rho^{1/2} = K_{jac} \kappa_s^{1/2} \quad ...(3)$$

$$A = (u^2/u^2_{im})-1 \quad ...(4)$$

$$R_A = (\rho/\rho_0)(u/u_0)^{1/3} \quad ...(5)$$

where $V = \Sigma(\chi_i Mi)/\rho$ in which χ_i and Mi are the molefraction and molecular mass of component i. K_{Jac} = ((91.368+0.3565T)10-8) is temperature dependent Jacobson's constant [8]. The results for the densities ρ speeds of sound u, isentropic

Table 1: Comparison of experimental density and viscosity of pure liquids with literature values at 303.15 K and 0.1 MPa

Pure liquids	ρ / g cm^{-3}		u /ms^{-1}	
	lit	Exp	lit	Exp
Acetophenone	1.0194 [12,13,14]	1.0199	1460[12]	1460
Ethyl cyanoacetate	1.0514[15]	1.0512	1396[15]	1397

Table 2: Densities (ρ), speeds of sound(u), isentropic compressibilities (k_s), specific acoustic impedances(Z) and intermolecular free lengths(L_f),inter molecular attraction(α) and relative association(R_a) for acetophenone (1)+ethyl cyanoacetate(2) mixture at 303.15,313.15and323.15 K

x_1	ρ / g·cm^{-3}	u / ms^{-1}	k_s / T Pa^{-1}	Z / Kg m^{-2}s^{-1}	L_f / 10^{-11} m	α	R_A
			303.15				
0	1.0512	1396	488	1467	4.5845	0.0000	1.0000
0.0839	1.0483	1402	485	1470	4.5712	0.0018	0.9958
0.1692	1.0455	1408	482	1472	4.5578	0.0034	0.9918
0.2558	1.0426	1414	480	1474	4.5447	0.0045	0.9876
0.3437	1.0398	1420	477	1477	4.5316	0.0054	0.9836
0.4330	1.0369	1426	474	1479	4.5189	0.0059	0.9795
0.5237	1.0341	1432	472	1481	4.5060	0.0060	0.9755
0.6159	1.0312	1438	469	1483	4.4935	0.0056	0.9714
0.7096	1.0284	1444	466	1485	4.4809	0.0049	0.9675
0.8048	1.0255	1450	464	1487	4.4687	0.0037	0.9634
0.9016	1.0227	1456	461	1489	4.4564	0.0021	0.9595
1	1.0199	1462	459	1491	4.4442	0.0000	0.9555
			313.15				
0	1.0403	1363	517	1418	4.8064	0.0000	1.0000
0.0839	1.0376	1368	515	1420	4.7937	0.0016	0.9961
0.1692	1.0349	1374	512	1422	4.7807	0.0031	0.9922
0.2558	1.0322	1379	509	1424	4.7682	0.0041	0.9883
0.3437	1.0295	1385	507	1426	4.7555	0.0050	0.9844
0.4330	1.0268	1390	504	1427	4.7433	0.0053	0.9806
0.5237	1.0241	1396	501	1429	4.7308	0.0055	0.9768
0.6159	1.0214	1401	499	1431	4.7188	0.0051	0.9729
0.7096	1.0187	1407	496	1433	4.7066	0.0045	0.9691
0.8048	1.0160	1412	494	1435	4.6945	0.0035	0.9653
0.9016	1.0133	1418	491	1436	4.6828	0.0019	0.9615
1	1.0106	1423	489	1438	4.6709	0.0000	0.9577
			323.15				
0	1.0298	1335	545	1374.8	5.0186	0.0000	1.0000
0.0839	1.0269	1339	543	1375.3	5.0095	0.0013	0.9961
0.1692	1.0241	1344	541	1376.1	4.9999	0.0025	0.9923
0.2558	1.0213	1348	539	1376.8	4.9905	0.0034	0.9886
0.3437	1.0184	1352	537	1377.3	4.9817	0.0040	0.9847
0.4330	1.0156	1357	535	1378.0	4.9723	0.0044	0.9810
0.5237	1.0128	1361	533	1378.5	4.9635	0.0044	0.9772
0.6159	1.0100	1366	531	1379.2	4.9543	0.0042	0.9735
0.7096	1.0071	1370	529	1379.6	4.9455	0.0037	0.9697
0.8048	1.0043	1374	527	1380.1	4.9369	0.0027	0.9660
0.9016	1.0015	1379	525	1380.7	4.9280	0.0015	0.9623
1	0.9987	1383	524	1381.2	4.9192	0.0000	0.9586

compressibilities κ_s, specific acoustic impedances Z and inter molecular free lengths L_f, relative association R_a, and intermolecular attraction α for binary mixtures of acetophenone with ethyl cyanoacetate at 303.15, 313.15, and 323.15K over the entire range of composition are given in Table 2.

Excess molar volume V^E, excess isentropic compressibility κ_s^E, excess inter molecular free length L_f^E and excess specific acoustic impedance Z^E in each mixture were calculated from ρ and κ_S of pure liquids and binary mixtures with following expression

$$Y^E = Y - Y^{id} \quad ...(6)$$

where Y represent either V, κ_s, Z, u and L_f. The density values have been used to calculate excess molar volumes V^E using the following equation

$$V^E=(x_1M_1+ x_2M_2)\ D\ \rho_m-(x_1M_1/\rho_1+ x_2M_2/ \rho_2) \quad ...(7)$$

where x_1 and x_2 refer to the mole fraction of components 1 and 2. ρ_1, ρ_2, and ρ_m refer to the density of components 1 and 2 and the density of the mixture, respectively.

The excess isentropic compressibility (k_s^E) over the entire composition range was obtained by

$$k_s^E = Ks - (x_1\ Ks_1 + x_2\ Ks_2) \quad ...(8)$$

where x_1 and x_2 refer to the mole fraction of components 1 and 2. Ks_1, Ks_2, and Ks refer to the isentropic compressibility of components 1 and 2 and the isentropic compressibility of the mixture, respectively. The change of intermolecular free length (L_f^E) on mixing were calculated by the equation

$$L_f^{\ E}= L_f - (x_1L_{f1} + x_2L_{f2}) \quad ...(9)$$

where L_{f1} and L_{f2} refer to the intermolecular free length of component 1 and 2. The excess speed of sound (u^E) over the entire composition range was obtained by

Table 3: Parameters and standard deviations (*S*) of Redlich–Kister equation for acetophenone (1) + ethyl cyanoacetate (2) *T* =(303.15, 313.15, and 323.15) K

Functions	A0	A1	A2	A3	A4	A5	S
				303.15K			
V^E / cm^3mol^{-1}	-0.0059	-0.0009	-0.0054	0.0083	0.0109	-0.0072	0.00019
Δk_s / T $Pa^{"1}$	-0.4229	0.0097	-0.5737	0.1793	0.9719	-0.1857	0.01037
ΔL_f / 10^{-11} m	-0.0182	0.0004	-0.0244	0.0074	0.0415	-0.0077	0.00058
Δu / ms^{-1}	5.2528	0.1653	7.7503	-2.0515	-12.665	1.8304	0.1879
Z^E / 10^3 kg m^{-2} s^{-1}	3.5845	-0.3526	3.588	-1.0069	-7.0234	1.3658	0.1256
				313.15K			
V^E / cm^3mol^{-1}	-0.0051	-0.0002	-0.0075	0.0018	0.0123	-0.0015	0.00026
Δk_s / T $Pa^{"1}$	-0.3973	0.0444	-0.5567	-0.0349	0.9343	-	0.0068
ΔL_f / 10^{-11} m	-0.017	0.0017	-0.0235	-0.0013	0.0397	-	0.00028
Δu / ms^{-1}	4.6343	0.0358	6.3392	-1.0881	-10.765	1.10115	0.07878
Z^E / 10^3 kg m^{-2} s^{-1}	3.0816	-0.0684	4.051	-0.6257	-7.0255	0.669	0.05179
				323.15K			
V^E / cm^3mol^{-1}	-0.0047	-0.0014	-0.0024	0.0053	0.0069	-0.0038	0.00117
Δk_s / T $Pa^{"1}$	-0.2805	0.0373	-0.2598	-0.0404	0.5324	-	0.0039
ΔL_f / 10^{-11} m	-0.0121	0.0019	-0.0103	-0.002	0.0222	-	0.00016
Δu / ms^{-1}	3.7382	-0.2743	4.3917	-0.1128	-7.9759	0.3853	0.42816
Z^E / 10^3 kg m^{-2} s^{-1}	1.6451	-0.7517	-0.4505	2.5504	-1.2632	-1.7158	0.06513

Table 4: Experimental and Theoretical values of Speeds of Sound in Acetophenone+ Ethyl cyanoacetate system at different temperatures

χ_1	u_{exp}	u^{Nom}	u^{IDR}	u^{VAN}	u^{FLT}	u^{RAO}	% Deviation				
	ms^{-1}	ms^{-1}	ms^{-1}	ms^{-1}	ms^{-1}	ms^{-1}	u^{Nom} ms^{-1}	u^{IDR} ms^{-1}	u^{VAN} ms^{-1}	u^{FLT} ms^{-1}	u^{RAO} ms^{-1}
					303.15K						
0	1396	1396.0	1396.0	1396.0	1396	1396.0	0.000	0.00	0.00	0.00	0.00
0.0839	1402	1401.9	1401.4	1400.7	1402	1401.5	0.005	0.04	0.09	0.00	0.04
0.1692	1408	1407.9	1406.9	1405.7	1408	1407.0	0.008	0.08	0.17	0.00	0.07
0.2558	1414	1413.8	1412.5	1410.8	1414	1412.7	0.011	0.11	0.22	0.00	0.09
0.3437	1420	1419.8	1418.2	1416.2	1420	1418.5	0.013	0.12	0.27	0.00	0.11
0.4330	1426	1425.8	1424.1	1421.9	1426	1424.3	0.014	0.13	0.29	0.00	0.12
0.5237	1432	1431.8	1430.1	1427.8	1432	1430.3	0.013	0.13	0.29	0.00	0.12
0.6159	1438	1437.8	1436.2	1434.0	1438	1436.4	0.012	0.13	0.28	0.00	0.11
0.7096	1444	1443.9	1442.4	1440.5	1444	1442.6	0.010	0.11	0.24	0.00	0.10
0.8048	1450	1449.9	1448.8	1447.3	1450	1449.0	0.007	0.08	0.19	0.00	0.07
0.9016	1456	1455.9	1455.3	1454.5	1456	1455.4	0.004	0.05	0.10	0.00	0.04
1	1462	1462.0	1462.0	1462.0	1462	1462.0	0	0.00	0.00	0.00	0.00
					313.15 K						
0	1363	1363.0	1363.0	1363.0	1363	1363.0	0.000	0.00	0.00	0.00	0.00
0.0839	1368	1368.4	1367.9	1367.3	1368.4	1368.0	0.001	0.04	0.08	0.00	0.03
0.1692	1374	1373.8	1372.9	1371.8	1373.9	1373.0	0.008	0.07	0.15	0.00	0.06
0.2558	1379	1379.2	1378.0	1376.5	1379.3	1378.2	0.006	0.09	0.20	0.00	0.08
0.3437	1385	1384.6	1383.2	1381.4	1384.8	1383.4	0.011	0.11	0.25	0.00	0.10
0.4330	1390	1390.1	1388.6	1386.5	1390.2	1388.8	0.008	0.12	0.26	0.00	0.10
0.5237	1396	1395.5	1394.0	1391.9	1395.7	1394.2	0.012	0.12	0.27	0.00	0.11
0.6159	1401	1401.0	1399.5	1397.6	1401.1	1399.8	0.007	0.11	0.25	0.00	0.10
0.7096	1407	1406.5	1405.2	1403.5	1406.6	1405.4	0.008	0.10	0.22	0.00	0.09
0.8048	1412	1412.0	1411.0	1409.7	1412.1	1411.2	0.009	0.08	0.17	0.00	0.07
0.9016	1418	1417.5	1416.9	1416.2	1417.5	1417.0	0.001	0.04	0.09	0.00	0.03
1	1423	1423.0	1423.0	1423.0	1423	1423.0	0.000	0.00	0.00	0.00	0.00
					323.15 K						
0	1335	1335.0	1335.0	1335.0	1335.3	1335.0	0.000	0.00	0.00	-0.02	0.00
0.0839	1339	1339.3	1338.9	1338.4	1339.6	1339.0	-0.002	0.03	0.06	-0.02	0.02
0.1692	1344	1343.7	1342.9	1342.0	1344.0	1343.0	0.002	0.06	0.12	-0.02	0.05
0.2558	1348	1348.0	1347.0	1345.8	1348.4	1347.2	0.006	0.08	0.17	-0.02	0.07
0.3437	1352	1352.4	1351.2	1349.7	1352.7	1351.4	0.003	0.09	0.20	-0.02	0.08
0.4330	1357	1356.7	1355.4	1353.9	1357.1	1355.6	0.006	0.10	0.22	-0.02	0.09
0.5237	1361	1361.1	1359.8	1358.2	1361.4	1360.0	0.001	0.10	0.22	-0.02	0.08
0.6159	1366	1365.5	1364.2	1362.7	1365.8	1364.4	0.003	0.09	0.21	-0.02	0.08
0.7096	1370	1369.8	1368.8	1367.4	1370.2	1368.9	0.005	0.08	0.18	-0.02	0.07
0.8048	1374	1374.2	1373.4	1372.4	1374.5	1373.5	-0.001	0.06	0.13	-0.02	0.05
0.9016	1379	1378.6	1378.1	1377.6	1378.9	1378.2	0.000	0.03	0.08	-0.02	0.03
1	1383	1383.0	1383.0	1383.0	1383.3	1383.0	0.000	0.00	0.00	-0.02	0.00

$$u^E = u - (x_1 u_{---1} + x_2 u_2) \quad ...(10)$$

The excess specific acoustic impedance Z^E on mixing were calculated by the equation

$$Z^E = Z - (x_1 Z_1 + x_2 Z_2) \quad ..(11)$$

where Z_1 and Z_2 refer to the intermolecular free length of component 1 and 2.

Excess molar volume, excess isentropic compressibility, excess ultrasonic velocity, excess specific acoustic impedance and excess intermolecular free length were fitted to a Redlich–Kister equation[11] of the type

$$Y = \chi_1 \chi_2 \Sigma A_i (x_1 - x_2)^i \quad ...(12)$$

where *Y* is either V^E, κ_s^E, u^E, L_f^E, Z^E and *n* is the degree of polynomial. Coefficients A_i were obtained by fitting equation 12 to experimental results using a least-squares regression method. In each case, the optimum number of coefficients is ascertained from an examination of the variation in standard deviation (*S*).*S* was calculated using the relation

$$S(Y) = [\Sigma(A_{exp} - A_{cal})^2 / (N-n)]^{1/2} \quad ...(13)$$

where *N* is the number of data points and *n* is the number of coefficients. The calculated values of coefficients along with the standard deviation S are given in table 3.

It is observed that the values of ρ, u, Z and R_a increase, whereas those of k_s, L_f and α

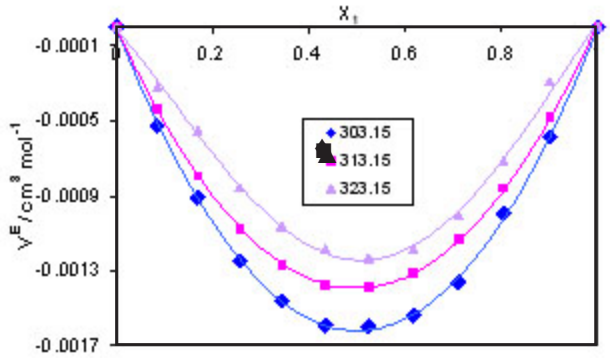

Fig. 1: Excess molar volume for [acetophenone (1) + ethyl cyanoacetate (2)]: T=303.15 K; T=313.15 K; T=323.15K

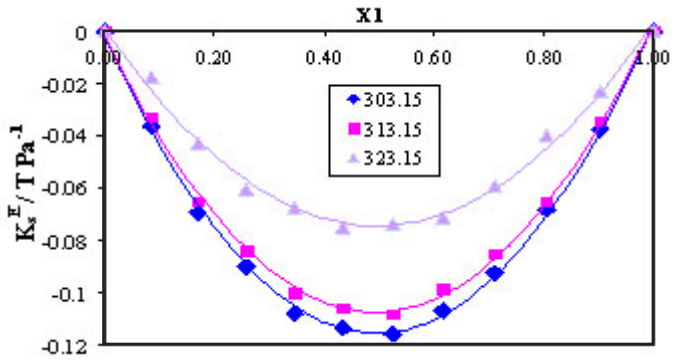

Fig. 2: Excess isentropic compressibility for[acetophenone(1)+ethyl cyanoacetate (2)]: ♦ T=303.15 K; T=313.15 K; T=323.15K

decrease with increasing mole fraction of acetophenone for the studied temperatures. In general, u and L_f have been reported to vary as the inverse of each other as in the present systems. The decrease of k_s and L_f, and also the increases in R_a and Z, with increasing mole fraction of acetophenone indicates the presence of molecular interactions between unlike molecules.

The decreases in κ_s and L_f with increase in molar concentration indicate significant interaction between the component molecules of the mixtures through dipole-dipole interaction. An increase in the value of Z is in agreement with the requirements given as per eq.2.relatively higher values of the relative association R_a signifies that unlike interactions are strong compared to like interactions.

Variation of excess molar volume *V*E versus mole fraction (χ1) of the binary liquid mixtures of acetophenone with ethyl cyanoacetate is depicted in Fig.1. The observed values of excess molar volumes in the present investigation may be explained in terms of several effects, which may

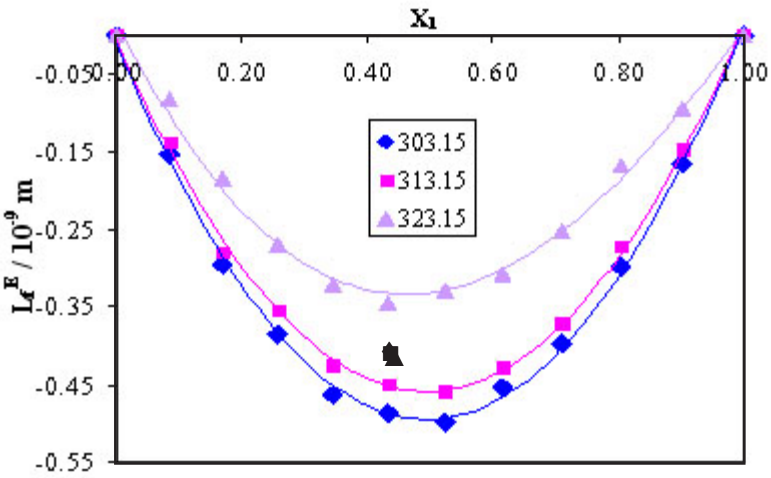

Fig. 3: Excess inter molecular free length for[acetophenone(1)+ethyl cyanoacetate(2)] : T=303.15 K; T=313.15 K; T=323.15K

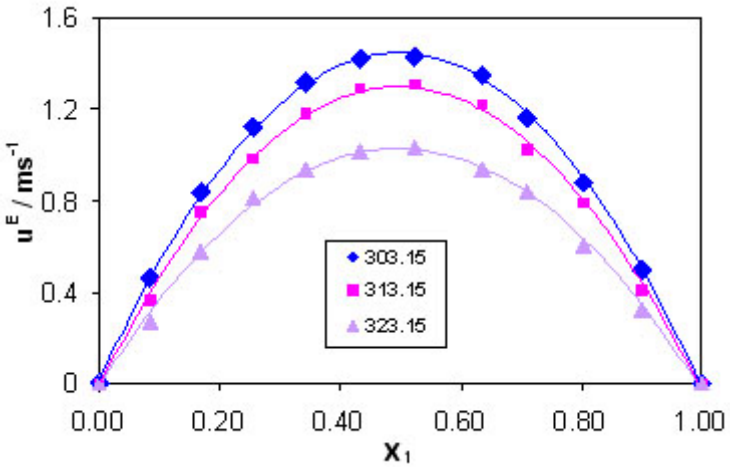

Fig. 4: Excess ultrasonic velocity for [acetophenone (1) + ethyl cyanoacetate (2)]: T=303.15 K; T=313.15 K; T=323.15K

arbitrarily be divided into physical, chemical and geometrical contributions[1]. Chemical interaction between constituent molecules, such as hetero molecular association through the formation of H-bond, known as strong specific interaction[2]. Accommodation of molecules of one component into the interstitials of the molecules of the other component[3]. Geometry of the molecular structure that favors fitting of the component molecules with each other. In all the mixtures, the observed negative[18,19] values of V^E are attributed to the interstitial accommodation of ester molecules with in the associated structure of acetophenone, formation of weak molecular complexes through hydrogen bonds, π-π interactions and dipole- dipole interactions. The negative V^E values are due to formation of weak molecular complexes like hydrogen bonds and dipole-dipole interactions

Examinations of excess isentropic compressibility (κ_s^E) data in figure.2 suggest that the quantity is negative[16,17] over the entire composition range for the binary mixtures of acetophenone with ethyl cyanoacetate. These may be attributed to the relative strength of effects which influenced the free space between component molecules. The negative ΔKs values arise from change of free volume in the real mixture and presence of π-electrons in acetophenone resulting in the formation of weak intermolecular complexes leading to positive deviation in sound velocity and negative deviation in isentropic compressibility.

As expected, the trend of negative L_f^E value (Fig. 3) is similar to κ_s^E in all three studied temperatures. The negative values of L_f^E are generally observed in systems with specific interactions between unlike molecules. Fig. 5 shows that Z^E is positive for all the systems. Specific acoustic impedance is a quantity, which depends on the molecular packing of the systems. The positive values of Z^E are in accordance with the presence of strong interactions between the unlike molecules.

The speed of sound u from the Nomoto's relation[4], Van Dael and Vangeel relation[5], Junjie's relation[6]] impedance relation[7] and Jacobson's free length theory[8] have also been estimated for the present binary mixtures. The pertinent relations in these calculations and their theoretical basis have been outlined several times and will not be repeated here. The speeds of sound u_{exp} in the binary mixture over the entire range of composition were estimated.

On assuming additivity of molar sound velocity Nomoto[4] established the following equation for sound velocity

$$U_N = [\Sigma(\chi_i R_i)/\Sigma(\chi_i V_i)]^3 \qquad ...(14)$$

Speeds of Sound by Jacobson's free length theory [8] are calculated using the following formula.

$$u^{FLT\text{----}} = K / L_{f(mix)} \rho^{1/2}_{exp} \qquad ...(15)$$

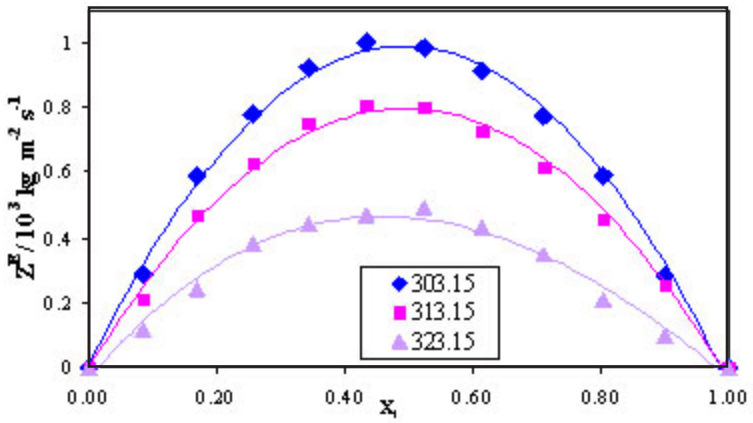

Fig. 5: Excess specific acoustic impedance for [acetophenone (1)+ ethyl cyanoacetate (2)]: T=303.15 K; T=313.15 K; T=323.15K

Where K is the Jacobson's constant (K= (93.875+0.375T) 10^{-8}) and depends only on temperature and $L_{f(mix)}$ is intermolecular free length of mixture. Vandeal vangeal [5] ideal mixing relation is compared from the following formula.

$$u^{VAN}= [(\chi_1/M_1u_1^2+ \chi_2/M_2u_2^2) (\chi_1m_1+ \chi_2m_2)]^{-1/2} \quad ...(16)$$

where x_1 and x_2 are mole fractions and u_1 and u_2 is speed of sound of acetophenone and ethyl cynoacetate respectively. The sound speed in the mixture is given by impedance dependence relation [7] as

$$u^{IDR}=[(\chi_1Z_1+\chi_2Z_2)/ (\chi_1 \rho_1+\chi_2 \rho_2)] \quad ...(17)$$

Where χ_i, Z_i and ρ_i are the mole fractions ,impedance and density of the i^{th} component respectively. Rao's (specific sound velocity) relation [22] is given by

$$U_R=(\Sigma\chi_i\rho_i\rangle)^3 \quad ...(18)$$

Where $r_i= u_i^{1/3}/\rho i$ is the Rao's specific sound velocity of the i^{th} component of the mixture.

Theoretical values of the speeds of sound were calculated by using the theoretical and empirical relations (14)-(18) and are presented in table.4 along with the experimental values. The percentage of deviation of the theoretical values from experimental values are also shown in table 4.The validity of different theoretical formulae is checked by percentage deviation for all the mixtures at all the temperatures and is given in table.4.The limitations and approximation incorporated in these theories is responsible for the deviations of theoretical from experimental values. In Nomoto's theory, no interaction between components of liquid mixtures has been taken into account as it is supposed that the volume does not change on mixing. Similarly the assumption for the formation of ideal mixing relation is that, the ratios of specific heats of ideal mixtures and the volumes are equal by not taking into the consideration of molecular interactions. Various types of forces such as dispersion forces, charge transfer, hydrogen bonding [20], dipole-dipole [21] and dipole-induced dipole interactions are operative due to interactions when two liquids are mixed. Thus the observed deviation of theoretical values of velocity from the experimental values shows that the molecular interactions is taking place between the unlike molecules in the liquid mixture. Data reveal that sound speed computed from FLT exhibit more satisfactory agreement with the experimental values in the temperature range 303.15 -323.15 K than other empirical relations. On the whole, all of the predicted speeds of sound from these experimental values for the studied binary mixtures, thus showing the validity of the theoretical models described above. The order of applicability of the theories on acetophenone+ ethyl cyanoacetate mixture from 303.15-323.15K is as follows.

$$u^{FLT} > u^{NOM} > u^{IDR} > u^{RAO} > u^{VAN}$$

CONCLUSION

Ultrasonic velocity measurements in binary mixtures of acetophenone in ethyl cyanoacetate media throw some light on the nature of solute-solvent interactions in the systems. The increase in ultra sonic velocity indicates association among the molecules of a solution. This association between acetophenone and ethyl cyanoacetate molecules forms a more compact structure. This effect favors a decrease in compressibility. It confirms the presence of strong interaction through dipole-dipole interactions. It has been observed that the intermolecular free length decreases on increasing the concentration of acetophenone. All of the theoretical models predict ultrasonic velocities that are reasonably close to the experimental values. This shows the validity of these theoretical models for binary mixtures. The excess isentropic compressibility and inter molecular free length of the system decreases as the molar concentration of acetophenone increases.

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