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Study of molecular interactions in the mixtures of secondary alcohols with equimolar mixture of ethanol + formamide from acoustic and thermodynamic parameters

K. Sreekanth^a, D. Sravana Kumar^b, M. Kondaiah^a and D. Krishna Rao^{a*}

^aDepartment of Physics, Acharya Nagarjuna University, AP, India

^bV.S Krishna Govt. Degree College, Visakhapatnam, AP, India

ABSTRACT

Density (ρ) and ultrasonic speed (u) in the mixtures of isopropanol(IPA), isobutanol(IBA) and isoamyl alcohol(IAA) with equimolar mixture of ethanol and formamide (EMM), including those of pure liquids have been measured over the entire range of composition at temperature 308.15 K. From these experimental values, the deviations in ultrasonic speed (Δu) and isentropic compressibility (Δk_s), excess acoustic impedance (Z^E) and excess free length (L_f^E) have been calculated and reported. The variations of these properties with composition of solution are discussed in terms of molecular interactions between unlike molecules of the mixtures. Further more, the experimental values of u for afore mentioned mixtures have been compared with theoretically estimated ultrasonic speeds using different empirical relations and the relative merits of these theories and relations have been discussed in terms of percentage deviations.

Key words: Ultrasonic speed, Thermo acoustic properties, molecular interactions, Redlich – Kister polynomial, empirical velocity relations.

INTRODUCTION

Knowledge of thermo–acoustic properties is of great significance in understanding the physico chemical behaviour and molecular arrangement in various liquid mixtures and solutions. Ultrasonic study of liquids and liquid mixtures has gained much importance during the last two decades [1-4] in assessing the nature of molecular interactions and investigating the physico chemical behaviour of such systems. Speed of sound itself is highly sensitive to the structure and interactions present in the liquid mixtures as it is fundamentally related to the binding forces between the constituents of the medium [5]. For the qualitative estimation of the molecular interactions in solutions, the ultrasonic velocity approach was first studied by Lageman [6].

Measurements of ultrasonic speed and density have been used to calculate acoustic and thermodynamic parameters that are found to be very sensitive to molecular interactions [7,8]. The excess properties of the acoustic and thermodynamic parameters will give the information about the nature and strength of molecular interactions and are sensitive to the intermolecular forces as well as to size of the molecules [9,10]. Hence, such measurements are useful to study the strength of molecular interactions in liquid mixtures.

The present work is the continuation of our earlier studies [11,12] on thermodynamic properties of mixed solvents, which have relevant chemical, industrial and biological process applications [13]. The studies of physicochemical properties of amide and alkanol mixed solvents are interesting because amide is convenient model system for investigating peptide and protein - solvent interactions. Formamide is primarily used for manufacturing sulfa drugs and synthesizing vitamins and as a softener for paper and fiber [14]. Alkanols are of interest in their own right and serve as simple examples of biologically and industrially important amphiphilic materials [11,15].

Here we report the results of our studies on acoustic and thermodynamic properties of the mixtures of isopropanol or isobutanol or isoamylalcohol with equimolar mixture of ethanol and formamide (EMM) over the entire composition range expressed by the mole fraction/volume fraction of secondary alkanols at a temperature of 308.15 K. Formamide molecules are highly polar ($\mu = 3.77$ D at 298.15 K) [16] and are strongly self associated through extensive three - dimensional net work of hydrogen bonds, through its three hydrogen bond donors (3H – atoms) and three acceptors (two lone pairs of electrons at oxygen and one on nitrogen atom) [17,18]. Secondary alkanol molecules are polar and self - associated through hydrogen bonding of their hydroxyl groups [18]. Since the components of these mixtures have both proton-donating/accepting abilities, significant interaction through hydrogen bonding between unlike molecules may be expected. To the best of our knowledge, there has been no work reported on the above three systems related to the acoustic and thermodynamic investigations.

The experimental values of ultrasonic speed (u) and density (ρ) have been used to calculate various acoustic and thermodynamic properties such as the deviation in ultrasonic velocity (Δu) and deviation in isentropic compressibility (Δk_s), excess acoustic impedance (Z^E), and excess free length (L_f^E). The results of the present systems were co-related with the data obtained from Redlich –Kister type polynomial [19] equation and the corresponding standard deviations have been evaluated. The deviation and excess parameters are used to discuss the molecular interactions exist between unlike molecules through -C = O ---- H – O- hydrogen bonding in the mixtures. Besides, the experimental values of ultrasonic speed for the three systems studied have been compared with that of theoretically estimated values using different empirical relations such as, Nomoto's [20], Van Dael and Vangeel's ideal mixing relation [21], Impedance [22], Junjie's [23], Rao's specific sound velocity [24] and Jacobson's [25] equation.

EXPERIMENTAL SECTION

The chemicals ethanol-absolute (of purity 99.9%) (Changshu Yangyuan Chemicals-China make) and formamide (purity 99%), isopropanol (purity 99%), isobutanol (purity 99%), isoamyl alcohol (purity 99%) used in the present investigation are of G.R Grade obtained from LOBA Chemicals, INDIA. These were further purified by standard methods [26,27]. The purities of the liquids were checked by measuring their ultrasonic speeds and densities at 308.15 K and were in good agreement with literature values [3,28-37] and are shown in Table 1.

Table 1 Comparison of experimental values of ultrasonic velocity (u) and density (ρ) of pure liquids with the corresponding literature values at 308.15 K

Liquid	u/ m.s ⁻¹		ρ / kg.m ⁻³	
	Present work	Literature	Present work	Literature
ethanol	1109.76	111.00[28]	776.49	776.41
formamide	1582.96	1580.00[3] 1577.20[30]	1120.10	1121.10[31]
isopropanol	1107.80	1105.90[32]	771.66	772.20[33] 772.88[34]
isobutanol	1166.50	1166.50[32]	790.79	789.70[35] 790.10[36]
isoamylalcohol	1210.42	1212.20[32]	800.54	800.70[37]

Equimolar mixture of ethanol and formamide (EMM) is first prepared and this solution has been used to prepare the liquid mixtures with isopropanol/isobutanol/isoamylalcohol so that the entire composition range is covered (i.e. 0-100% of the secondary alcohol). All the mixtures have been prepared by weight and kept in airtight bottles. The samples have been weighed using METLER TOLEDO (Switzerland make) AB135-S/FACT Digital balance with an accuracy of $\pm 10^{-5}$ g.

The ultrasonic speed of the pure liquids and the solutions has been measured using a multi-frequency ultrasonic interferometer (M-82 Model) supplied by Mittal enterprise, New Delhi. In the present work, a steel cell fitted with a quartz crystal of 2MHz has been used to measure the ultrasonic speed with an estimated accuracy of $\pm 0.2\%$. In this method, the wavelength of ultrasonic wave was determined accurately at the working frequency. In the present study the constant temperature water bath (digital electronic) supplied by Concord Instruments Co. Ltd., Chennai (RAAGA type) has been used. The instrument can maintain temperature to ± 0.01 K as per its specifications.

The measurement of density of pure liquids and liquid mixtures presented already in our previous paper [12]. The estimated accuracy of this method is 3 in 10^5 parts.

RESULTS AND DISCUSSION

The experimentally measured values of ultrasonic speed, density and evaluated values of deviation in ultrasonic speed and isentropic compressibility, excess free length and excess acoustic impedance for all the systems studied have been presented in Table 2. The ultrasonic speed and density decreased non-linearly with increasing concentration of isopropanol or isobutanol or isoamylalcohol. This non-linear variation is attributed to the deviation from ideal behaviour that suggests interactions between molecules of component liquids of the mixtures.

The deviations and excess functions, which are a measure of deviation from ideal behavior, are found to be highly sensitive to intermolecular interactions amongst the component molecules of the liquid mixture. The presence of dispersion forces, specific interactions such as dipole – dipole and hydrogen bonding interaction has been understood from the sign and magnitude of the values of the mixtures.

Table 2 Experimental values of ultrasonic velocity (u), densities (ρ), deviation in ultrasonic velocity (Δu), deviation in isentropic compressibility (Δk_s), excess acoustic impedance (z^E) and excess free length (L_f^E) for all the systems at 308.15 K

mole fraction (x)	volume fraction (Φ)	u / m.s ⁻¹	ρ / kg.m ⁻³	Δu /m.s ⁻¹	Δk_s /10 ⁻¹⁰ pa ⁻¹	z^E /10 ⁶ kg m ⁻² s ⁻¹	L_f^E /10 ⁻¹⁰ m
EMM+isopropanol							
0.0000	0.0000	1331.50	932.48	0.00	0.0000	0.0000	0.0000
0.0645	0.0649	1307.37	910.43	-9.70	0.0845	-0.0264	0.0051
0.1410	0.1422	1278.26	891.42	-21.70	0.1752	-0.0476	0.0103
0.2136	0.2152	1255.42	877.54	-28.30	0.2106	-0.0573	0.0127
0.3070	0.3113	1230.32	861.30	-32.50	0.2169	-0.0632	0.0141
0.3884	0.3898	1211.81	848.62	-32.80	0.2171	-0.0630	0.0139
0.4783	0.4789	1193.50	835.85	-31.00	0.1895	-0.0590	0.0127
0.5975	0.5980	1171.04	818.82	-26.80	0.1590	-0.0516	0.0110
0.7183	0.7182	1149.10	803.44	-21.72	0.1372	-0.0405	0.0090
0.8481	0.8470	1129.00	788.88	-12.78	0.0749	-0.0229	0.0050
1.0000	1.0000	1107.80	771.66	0.00	0.0000	0.0000	0.0000
EMM+isobutanol							
0.0000	0.0000	1331.50	932.48	0.00	0.0000	0.0000	0.0000
0.0562	0.0566	1311.43	910.89	-10.80	0.1508	-0.0291	0.0071
0.1182	0.1192	1290.80	896.02	-21.20	0.2628	-0.0473	0.0124
0.1941	0.1953	1269.40	882.39	-30.07	0.3506	-0.0596	0.0164
0.2584	0.2596	1253.96	871.52	-34.90	0.4061	-0.0663	0.0188
0.3418	0.3430	1238.63	858.62	-36.47	0.4297	-0.0690	0.0198
0.4389	0.4398	1223.08	845.30	-36.00	0.4326	-0.0677	0.0197
0.5504	0.5517	1207.43	831.22	-33.25	0.4134	-0.0623	0.0187
0.6791	0.6807	1191.45	816.90	-28.00	0.3664	-0.0516	0.0162
0.8217	0.8231	1179.02	803.84	-16.90	0.2303	-0.0317	0.0101
1.0000	1.0000	1166.50	790.79	0.00	0.0000	0.0000	0.0000
EMM+isoamylalcohol							
0.0000	0.0000	1331.50	932.48	0.00	0.0000	0.0000	0.0000
0.0436	0.0439	1315.80	914.68	-10.42	0.1570	-0.0262	0.0070
0.0940	0.0945	1300.00	901.54	-20.12	0.2804	-0.0440	0.0124
0.1607	0.1617	1282.46	887.23	-29.58	0.4034	-0.0599	0.0177
0.2281	0.2293	1268.22	875.13	-35.66	0.4877	-0.0696	0.0211
0.3050	0.3065	1255.80	862.54	-38.77	0.5435	-0.0753	0.0233
0.3995	0.4016	1243.94	848.81	-39.19	0.5699	-0.0768	0.0243
0.5052	0.5075	1232.50	836.79	-37.83	0.5611	-0.0725	0.0236
0.6455	0.6490	1219.70	821.97	-33.64	0.5214	-0.0631	0.0216
0.8380	0.8195	1214.35	808.40	-15.68	0.3097	-0.0315	0.0107
1.0000	1.0000	1210.42	800.54	0.00	0.0000	0.0000	0.0000

Using measured data of ultrasonic speed and density acoustic parameters [38-40] such as the isentropic compressibility (k_s), acoustic impedance (Z), the intermolecular free length (L_f) have been determined.

$$k_s = 1/u^2 \rho \quad (1)$$

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

$$L_f = K k_s^{1/2} \quad (3)$$

where K is Jacobson temperature dependent constant and is equal to $K = (93.875 + 0.375T) \times 10^{-8}$, where T is absolute temperature

The deviation in ultrasonic speed [41] in the mixtures has been calculated using the relation.

$$\Delta u = u - x_1 u_1 - x_2 u_2 \quad (4)$$

here 'x' is the mole fraction of the liquid mixture and the subscripts 1 and 2 stands for equimolar mixture and secondary alcohol.

Pertinent to the calculation of deviation and excess parameters, equimolar mixture is considered as one component of the binary liquid mixture [11].

The deviation in isentropic compressibility has been calculated from the equation [3,42,43].

$$\Delta k_s = K_s - \Phi_1 K_{s1} - \Phi_2 K_{s2} \quad (5)$$

Since K_s is not additive on mole fraction but these are additive on volume fraction. Hence, such values are calculated using volume fraction $\Phi_i = \frac{x_i V_i}{\sum x_i V_i}$.

The excess functions such as Z^E and L_f^E have been calculated [42] using,

$$Z^E = z - x_1 z_1 - x_2 z_2 \quad (6)$$

$$L_f^E = L_f - x_1 L_{f1} - x_2 L_{f2} \quad (7)$$

The values of deviation in ultrasonic velocity and isentropic compressibility, excess acoustic impedance, excess free length have been fitted to a Redlich-Kister [19] type polynomial equation.

$$Y^E = x(1-x) \sum A_i (1-2x)^{i-1} \quad (8)$$

Where Y^E is Δu or Z^E or L_f^E . The subscript 'i' in the summation of the above equation takes values from 1 to 5.

The values of Δk_s have been fitted to Redlich – Kister type polynomial with volume fraction [42] instead of mole fraction in the polynomial.

$$\Delta k_s = (1-\Phi) \sum A_i (1-2\Phi)^{i-1} \quad (9)$$

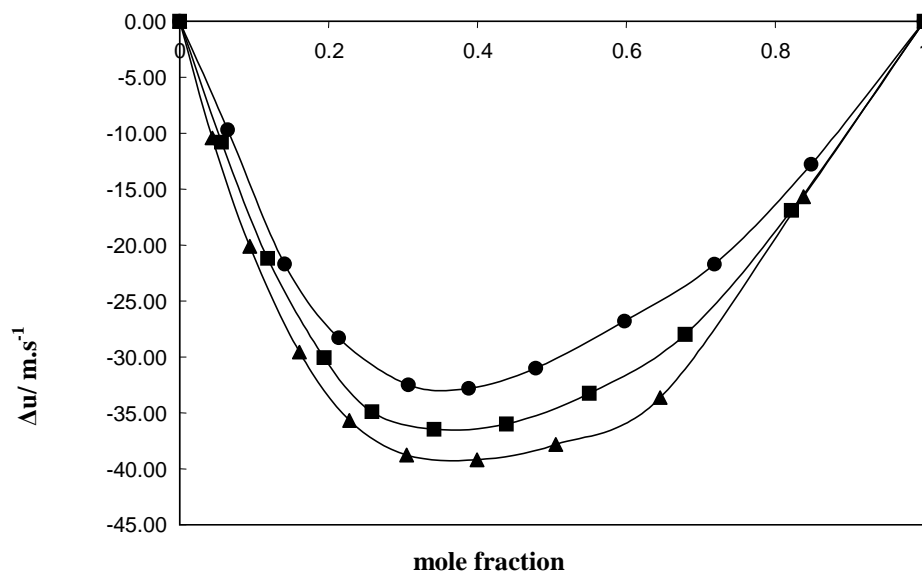
The values of coefficients A_i in the above equations have been determined using the least square method and are compiled in Table 3 along with the standard deviations $\sigma(Y^E)$ calculated using the expression.

$$\sigma(Y^E) = [\sum (Y_{\text{exp}}^E - Y_{\text{cal}}^E)^2 / (m-n)]^{1/2} \quad (10)$$

where 'm' is the total number of experimental points and 'n' is the number of coefficients in the Eq. (8). The value of n in the present study is 5.

Table 3 Coefficients A_i of Redlich-Kister type polynomial equation Eqs. [(8)-(9)] and the corresponding Standard deviations of all the systems under investigation

	A0	A1	A2	A3	A4	σ
EMM +isopropanol						
$\Delta u/ m.s^{-1}$	-120.5809	-61.2277	-85.3229	14.4392	107.0853	0.3083
$z^E/10^6 kg.m^{-2}.s^{-1}$	-0.2323	-0.1107	-0.1246	-0.0734	0.0542	0.0004
$\Delta k_s/10^{-10} pa^{-1}$	0.7347	0.4678	0.9883	0.2091	-1.0022	0.2701
$L_f^E/10^{-10} m$	0.0497	0.0271	0.0457	0.0085	-0.0476	0.0001
EMM +isobutanol						
$\Delta u/ m.s^{-1}$	-138.4729	-50.1996	-88.528	-30.1979	113.643	0.1638
$z^E/10^6 kg.m^{-2}.s^{-1}$	-0.2626	-0.0947	-0.0773	-0.1118	-0.0791	0.0006
$\Delta k_s/10^{-10} pa^{-1}$	1.7082	0.2927	0.8475	0.6701	-0.5932	0.0044
$L_f^E/10^{-10} m$	0.0774	0.0181	0.0373	0.0311	-0.022	0.0002
EMM +isoamylalcohol						
$\Delta u/ m.s^{-1}$	-151.1614	-34.4935	-91.8466	-94.0727	125.07	0.0938
$z^E/10^6 kg.m^{-2}.s^{-1}$	-0.2957	-0.0881	-0.0757	-0.1562	-0.0507	0.0009
$\Delta k_s/10^{-10} pa^{-1}$	2.2786	0.1785	0.9225	1.1709	0.8069	0.0043
$L_f^E/10^{-10} m$	0.096	0.0129	0.0361	0.0578	-0.0324	0.0002

**Figure 1.** Variation of deviation in ultrasonic speed with mole fraction of (●) isopropanol, (■) isobutanol,(▲)isoamylalcohol with EMM

The variation of deviation in ultrasonic speed with mole fraction of secondary alcohols as shown in Figure 1. The deviation in ultrasonic speed is negative in all the systems studied. The negative values of deviation in ultrasonic speed, generally, indicate dispersion forces due to weak

interactions [44-46]. The addition of secondary alcohol to the mixture is disrupting the existing hydrogen bonding between ethanol and formamide. The addition of secondary alcohol molecules to the equimolar mixture of ethanol and formamide increases monomers in the structures and dispersion forces in the system. This might be the possible reason for the observed negative values of deviation in ultrasonic speed over the entire composition range.

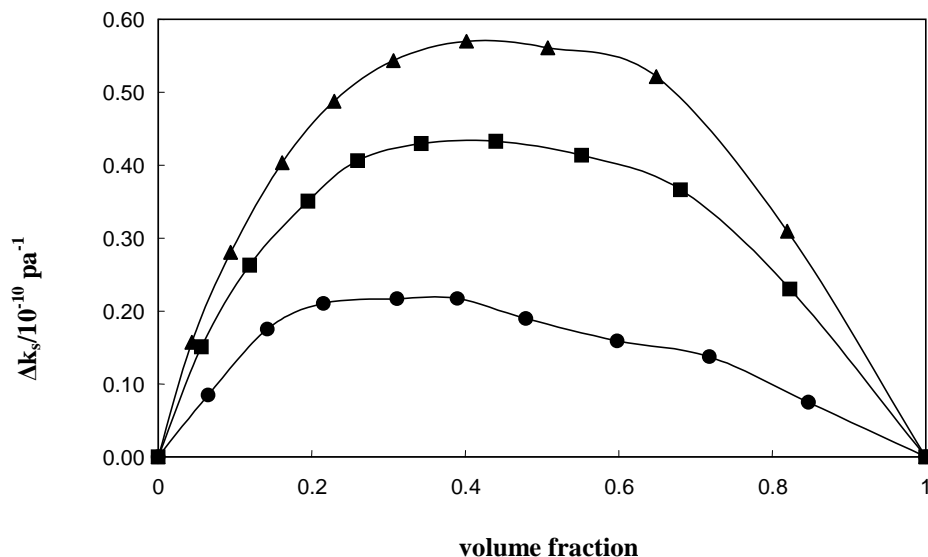


Figure 2. Variation of deviation in isentropic compressibility with volume fraction (●) isopropanol, (■) isobutanol, (▲) isoamylalcohol with EMM

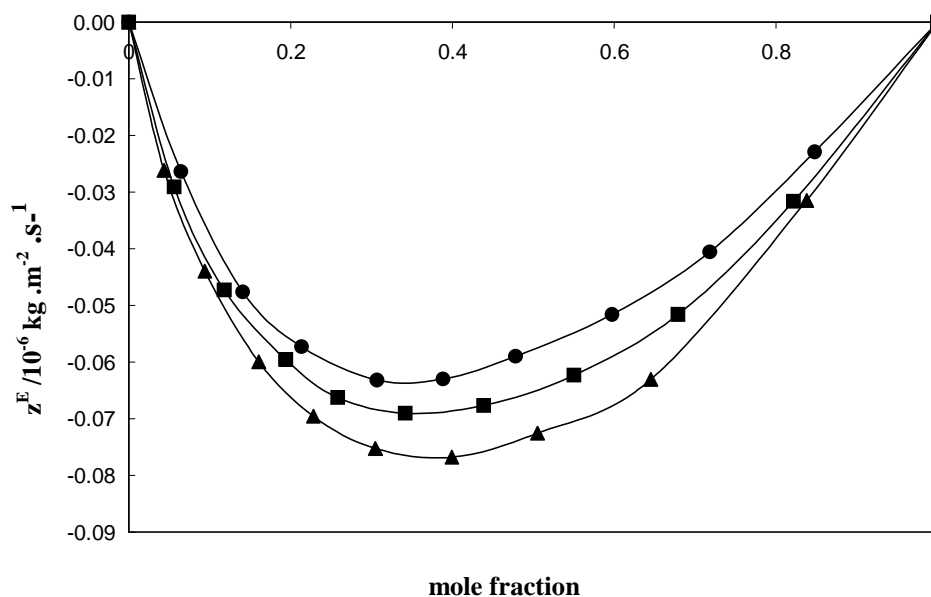


Figure 3. Variation of excess acoustic impedance with mole fraction of (●) isopropanol, (■) isobutanol, (▲) isoamylalcohol with EMM

Figure 2 represents the variation of deviation in isentropic compressibility with the mole fraction of the secondary alcohols in the mixture investigated over the entire composition range. In general, the negative values of deviation in isentropic compressibility indicate strong and specific interactions such as H-O, -dipole interactions etc., on the other hand, the positive values of deviation in isentropic compressibility indicate weak interactions and dispersion forces operating between the molecules of the components of the mixtures [47,48]. The greater excess isentropic compressibility values for (ethanol+formamide)+isoamylalcohol than the other systems are in accordance with the fact that the strength of hydrogen bonds formed by secondary alcohols decreases with the increase in the carbon chain length [49]. From Figure 2 it is observed that the deviation in isentropic compressibility is positive over the entire composition range in all the mixtures investigated. This supports the inferences made from the variation of deviation in all ultrasonic speeds.

The variations of excess acoustic impedance and excess free length with mole fraction of secondary alcohols in the mixtures have been presented in the Figures 3 and 4 respectively. The observed negative values of excess acoustic impedance and positive excess free length values over the entire composition range of the liquid mixtures supporting the variation of deviation in ultrasonic velocity as well as deviation in isentropic compressibility [4,50].

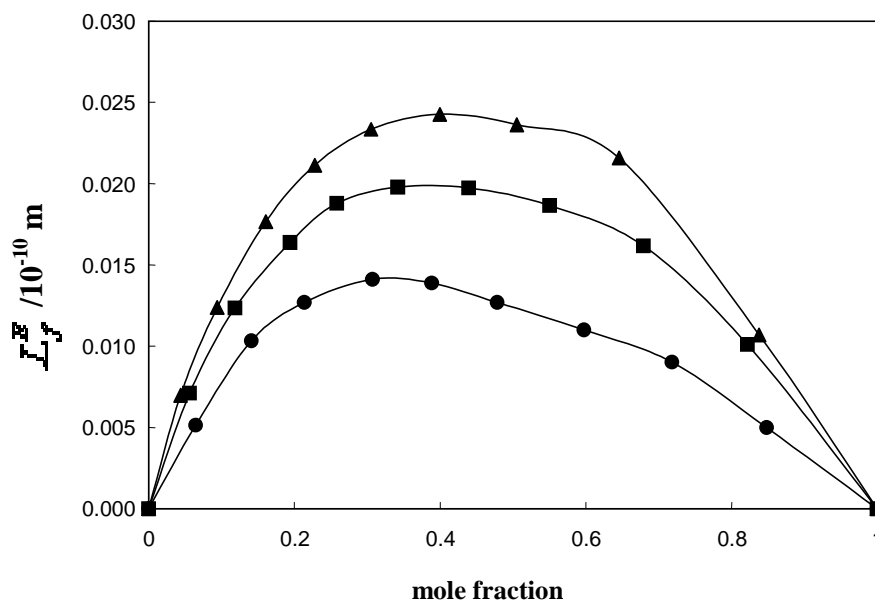


Figure 4. Variation of excess frelength with molefraction of (●) isopropanol,(■)isobutanol,(▲)isoamylalcohol with EMM

The experimental values of ultrasonic speed in the liquid mixtures investigated and the speeds calculated using various theories [20-25] along with percentage of deviation between theoretical and experimental values have been presented in Tables 4 and 5 respectively. Various theoretical formulae used for evaluating sound velocity are hereafter given. Such an evaluation offers a simple method to investigate molecular interactions besides verifying the applicability of various theories to liquid mixtures. In the present study, theoretical speeds have been also evaluated by considering equimolar mixture of ethanol and formamide as one component and secondary alcohol as the other component in the binary mixture.

On assuming additivity of molar sound velocity, Nomoto [20] established the following equation for sound velocity:

$$U_N = \{(\sum x_i R_i) / (\sum x_i V_i)\}^3 \quad (11)$$

where x_i is the molefraction, $R_i = u_i^{1/3} V_i$ the molar sound velocity, V_i the molar volume and u_i is the sound velocity of the i^{th} component.

Van Dael and Vangeel [21] obtained the relation

$$\sum (x_i M_i / u_i^2) = \{1 / \sum x_i M_i\} \{1 / U_V\}^2 \quad (12)$$

where M_i is the molecular weight of i^{th} component in the liquid mixture
Impedance relation [22] is given by

$$U_{imp} = \sum x_i Z_i / \sum x_i \rho_i \quad (13)$$

Junjie's equation [23] is given by

$$U_{Jun} = \{\sum x_i V_i / (\sum x_i M_i)^{1/2}\} \{\sum (x_i V_i / \rho_i u_i^2)\}^{-1/2} \quad (14)$$

where Z_i is the acoustic impedance and ρ_i is the density of the i^{th} component of the mixture.
Rao's (specific sound velocity) relation [24] is given by

$$U_R = (\sum x_i r_i \rho)^3 \quad (15)$$

where $r_i = u_i^{1/3} / \rho_i$ is the Rao's specific sound velocity of the i^{th} component of the mixture
Jacobson's equation [25] is given by

$$U_J = K \rho^{-1/2} L_f^{-1} \quad (16)$$

where L_f is the ideal free length of the mixtures.

The authors tried to fit experimental data to two types of polynomial equations described below, so that these empirical fittings described qualitatively and quantitatively use experimental speed data even in the specific interaction predominant region where non-ideal behavior of the system is observed.

The polynomial equations used are [51,52]

$$f(x) = U(x) = \sum a_k x^k \quad \text{and} \quad (17)$$

$$g(x) = \ln U(x) = \sum (\ln U_k) x^k \quad (18)$$

where k in the summation assumes values from 1 to 5, x is the molefraction of the secondary alcohol and a_k , $\ln U_k$ are constant co-efficients to be determined using numerical methods. The values of sound velocities and percentage deviation, (after determining the co-efficients in the above polynomial equations by applying least squares method) have been compiled in Table 4 and Table 5 respectively.

Table 4 Experimental and theoretical values of ultrasonic velocity from Eq.s [(11)-(18)]

x	U_N	U_V	U_{imp}	U_{Jun}	U_R	U_J	f(x)	g(x)
EMM +isopropanol								
0.0000	1331.50	1331.50	1331.50	1331.50	1331.50	1331.47	1332.01	1332.08
0.0645	1308.12	1313.98	1319.43	1296.02	1272.29	1307.39	1306.18	1306.10
0.1410	1282.84	1293.87	1304.74	1261.90	1231.73	1278.16	1278.75	1278.57
0.2136	1261.01	1275.42	1290.44	1235.49	1209.71	1255.52	1255.88	1255.64
0.3070	1235.58	1252.54	1271.48	1207.85	1186.83	1230.37	1230.53	1230.53
0.3884	1215.54	1233.35	1254.42	1188.16	1171.90	1211.74	1211.54	1211.72
0.4783	1195.38	1212.92	1234.97	1170.05	1159.41	1193.60	1193.04	1193.45
0.5975	1171.40	1186.96	1208.15	1150.49	1140.70	1171.03	1170.96	1171.45
0.7183	1149.81	1161.90	1179.69	1134.59	1127.68	1149.09	1149.93	1150.21
0.8481	1129.16	1136.26	1147.55	1120.77	1120.00	1128.92	1128.45	1128.34
1.0000	1107.80	1107.80	1107.74	1107.80	1107.80	1107.74	1107.90	1107.77
EMM +isobutanol								
0.0000	1331.50	1331.50	1331.50	1331.50	1331.50	1331.47	1331.92	1331.95
0.0562	1313.91	1316.04	1323.57	1306.57	1268.18	1311.51	1310.74	1310.81
0.1182	1296.56	1300.16	1314.67	1284.11	1235.91	1290.87	1290.57	1290.52
0.1941	1277.78	1282.25	1303.53	1261.95	1214.66	1269.42	1269.72	1269.65
0.2584	1263.65	1268.30	1293.88	1246.62	1198.81	1254.06	1254.79	1254.76
0.3418	1247.34	1251.70	1281.07	1230.24	1182.35	1238.70	1238.37	1238.31
0.4389	1230.74	1234.34	1265.72	1214.91	1169.05	1222.98	1222.46	1222.43
0.5504	1214.26	1216.73	1247.48	1200.92	1157.38	1207.47	1207.20	1207.13
0.6791	1197.96	1199.18	1225.58	1188.22	1150.21	1191.47	1192.31	1192.13
0.8217	1182.61	1182.84	1200.16	1177.23	1152.19	1179.06	1178.56	1178.15
1.0000	1166.50	1166.50	1166.55	1166.66	1166.50	1166.59	1166.56	1166.78
EMM +isoamylalcohol								
0.0000	1331.50	1331.50	1331.50	1330.92	1331.50	1331.47	1331.97	1332.08
0.0436	1319.89	1315.97	1326.94	1314.94	1277.92	1315.75	1315.33	1315.27
0.0940	1307.96	1299.70	1321.60	1299.67	1247.40	1300.11	1299.45	1299.45
0.1607	1294.19	1280.68	1314.41	1283.39	1219.37	1282.58	1282.58	1282.54
0.2281	1282.17	1264.09	1307.00	1270.28	1200.18	1268.28	1268.94	1268.89
0.3050	1270.33	1248.04	1298.37	1258.28	1182.50	1255.90	1256.21	1256.27
0.3995	1257.94	1232.12	1287.49	1246.67	1166.86	1243.89	1243.34	1243.27
0.5052	1246.29	1218.76	1274.95	1236.56	1161.84	1232.54	1231.72	1231.76
0.6455	1233.54	1207.65	1257.67	1226.38	1158.02	1219.72	1220.70	1220.72
0.8380	1219.71	1203.75	1232.68	1216.30	1178.77	1214.30	1213.96	1214.03
1.0000	1210.42	1210.42	1210.43	1210.08	1210.42	1210.47	1210.50	1210.51

Table 5 Percentage deviations of theoretical velocities from experimental velocities

x	% ΔU_N	% ΔU_V	% ΔU_{imp}	% ΔU_{Jun}	% ΔU_R	% ΔU_J	% $\Delta f(x)$	% $\Delta g(x)$
EMM +isopropanol								
0.0000	0.000	0.000	0.000	0.000	0.000	0.000	0.038	0.044
0.0645	0.057	0.506	0.922	-0.868	-2.683	0.002	-0.091	-0.100
0.1410	0.358	1.221	2.072	-1.28	-3.64	-0.010	0.038	0.024
0.2136	0.445	1.593	2.79	-1.588	-3.641	0.008	0.037	0.018
0.3070	0.428	1.806	3.345	-1.826	-3.535	0.004	0.017	0.017
0.3884	0.308	1.778	3.516	-1.952	-3.293	-0.010	-0.022	-0.010
0.4783	0.158	1.627	3.475	-1.965	-2.856	0.008	-0.039	0.000
0.5975	0.031	1.359	3.169	-1.755	-2.591	0.000	-0.007	0.035
0.7183	0.062	1.114	2.662	-1.263	-1.864	0.000	0.072	0.097
0.8481	0.014	0.643	1.643	-0.729	-0.797	-0.010	-0.049	-0.060
1.0000	0.000	0.000	-0.010	0.000	0.000	-0.010	0.009	0.000
EMM +isobutanol								
0.0000	0.000	0.000	0.000	0.000	0.000	0.000	0.032	0.034
0.0562	0.189	0.352	0.926	-0.371	-3.298	0.006	-0.053	-0.050
0.1182	0.446	0.725	1.849	-0.518	-4.252	0.005	-0.018	-0.020
0.1941	0.660	1.012	2.689	-0.587	-4.312	0.002	0.025	0.020
0.2584	0.773	1.144	3.184	-0.585	-4.398	0.008	0.066	0.064
0.3418	0.703	1.055	3.426	-0.677	-4.544	0.006	-0.021	-0.030
0.4389	0.626	0.921	3.486	-0.668	-4.418	-0.010	-0.051	-0.050
0.5504	0.566	0.770	3.317	-0.539	-4.145	0.003	-0.019	-0.020
0.6791	0.546	0.649	2.865	-0.271	-3.461	0.002	0.072	0.057
0.8217	0.304	0.324	1.793	-0.152	-2.276	0.003	-0.039	-0.070
1.0000	0.000	0.000	0.004	0.014	0.000	0.008	0.005	0.024
EMM +isoamylalcohol								
0.0000	0.000	0.000	0.000	-0.044	0.000	0.000	0.035	0.044
0.0436	0.311	0.013	0.847	-0.065	-2.879	0.000	-0.036	-0.040
0.0940	0.612	-0.020	1.662	-0.025	-4.046	0.008	-0.042	-0.040
0.1607	0.915	-0.140	2.491	0.073	-4.919	0.009	0.009	0.006
0.2281	1.100	-0.330	3.058	0.162	-5.365	0.005	0.057	0.053
0.3050	1.157	-0.620	3.390	0.197	-5.837	0.008	0.033	0.037
0.3995	1.125	-0.950	3.501	0.219	-6.196	0.000	-0.048	-0.050
0.5052	1.119	-1.110	3.444	0.329	-5.733	0.003	-0.063	-0.060
0.6455	1.135	-0.990	3.113	0.548	-5.057	0.002	0.082	0.084
0.8380	0.441	-0.870	1.509	0.161	-2.930	0.000	-0.032	-0.030
1.0000	0.000	0.000	0.000	-0.028	0.000	0.004	0.007	0.007

The standard deviations corresponding to ultrasonic speed values calculated using the polynomial equations from that of experimental values of speeds have been evaluated using the relation:

$$\sigma = \{\Sigma(U_E - U_P)^2 / n\}^{1/2} \quad (19)$$

where U_E is the experimental value of ultrasonic speed. U_P the value of sound velocity calculated using the polynomial equations $f(x)$ and $g(x)$ and n is the number of mole fractions at which experimental and theoretical velocities have been determined.

Table 6 Standard deviation of sound velocity calculated using polynomial equations from experimental values

Name of the system	Polynomial form	Standard deviation σ / m.s^{-1}
EMM+isopropanol	f(x)	0.56119
	g(x)	0.60191
EMM+isobutanol	f(x)	0.51842
	g(x)	0.54609
EMM+isoamylalcohol	f(x)	0.32619
	g(x)	0.37902

The percentage errors shown in Table 5 are extremely small. The standard deviations presented in Table 6 are very low obtained from the polynomial Eqs. (17) and (18). From the above tables, the agreement between theoretical and experimental values is better in the case of EMM+isopropanol system. On comparison, the Jacobson's velocity equation gives better estimate of experimental values in the present study.

CONCLUSION

1. Dispersion forces are operative in the systems studied.
2. The strength of hydrogen bond follows the order EMM+IPA>EMM+IBA>EMM+IAA in the systems investigated.
3. The Jacobson's velocity equation gives good agreement between the experimental and theoretical ultrasonic speed values for all the systems employed.

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REFERENCES

- [1] D Venkatesulu; P Venkatesu; MV Prabhakararao. *Phys. Chem. Liq.*, **1996**, 32, 127-132.
- [2] NV Sastry; MC Patel; SR Patel. *Fluid Phase Equilib.*, **1999**, 155, 261-276.
- [3] A Ali; Abida; AK Nain; S Hyder. *J. Solution Chem.*, **2003**, 32, 865-877.
- [4] A Moses Ezhil Raj; LB Resmi; V Bena Jothy; M Jaychandran; C Sanjeeviraja. *Fluid Phase Equilib.*, **2009**, 282, 78-86.
- [5] G Arul; L Palaniappan. *Indian J. Pure Appl. Phys.*, **2001**, 39, 561-564.
- [6] RT Lagemann; WS Dunbar. *J. Phys. Chem.*, **1945**, 49, 428-436.
- [7] RK Dewan; SK Mehta; R Parashar; K Bala. *J. Chem. Soc., Faraday Trans.*, **1991**, 87, 1561-1568.
- [8] Rose Venis; Rosario Rajkumar. *J. Chem. Pharm. Res.* **2011**, 3(2), 878-885
- [9] S Rodriguez; C Lafuente; H Artigal; FM Royo; JS Urieta. *J. Chem. Thermodyn.* **1999**, 31, 139-149.
- [10] M Aravinthraj; S Venkatesan; D Meera. *J. Chem. Pharm. Res.* **2011**, 3(2), 623-628.
- [11] D Sravan Kumar; K Srikanth; D Krishna Rao. *J. Mol. Liq.*, **2007**, 136, 90-93.
- [12] K Sreekanth; D Sravan Kumar; M Kondaiah; D Krishna Rao. *Phys. B*, **2011**, 406, 854-858.
- [13] C Yang; H Lai; Z Liu; P Ma. *J. Chem. Eng. Data*, **2006**, 51, 1345-1351.
- [14] H Iloukhani; R Ghorbani. *J. Solution Chem.*, **1998**, 27, 141-149.

- [15] CD Eads. *J. Phys. Chem. B*, **2000**, 104, 6653-6661.
- [16] JA Dean. Lange's Hand book of chemistry. Mc Graw Hill, New York, **1956**.
- [17] Y. Marcus. Introduction to Liquid state chemistry, wiley interscience, New York, **1977**.
- [18] GA Krestov. Thermodynamics of salvation, Ellis-Horwood Ltd, England, **1991**.
- [19] O Redlich; AT Kister. *Ind. Eng. Chem.*, **1948**, 40, 345-348.
- [20] O Nomoto. *J. Phys. Soc. Jpn.*, **1958**, 13, 1528-1532.
- [21] W Van Dael; Vangeel. Proceedings of the first International conference on calorimetry and thermodynamics, Warsaw, **1969**; 556.
- [22] Shipra Baluja; PH Parrania. *Asian J. Chem.*, **1995**, 7, 417-423.
- [23] Z Junjie. *J. Chem. Univ. Sci. Technol.*, **1984**, 14, 298-300.
- [24] VD Gokhale; NN Bhagavat. *J. Pure Appl. Ultrason.*, **1989**, 11, 21-24.
- [25] B Jacobson. *J. Phys. Chem.*, **1952**, 20, 1927-1928.
- [26] AI Vogel. A Text Book of Practical Organic Chemistry (English Language Book Society London), **1983**.
- [27] JA Riddick; W Bunger; TK Sakana. Techniques of Chemistry, Organic solvents, physical properties and methods of purification, vol.II, fourth edition, WileyInterscience, NewYork, **1986**.
- [28] UB Kdam; AP Hiray; AB Sawant; M Hasan. *J. Chem. Thermodyn.*, **2006**, 38, 1675-1683.
- [29] PS Nikam; NL Shirsat; M Hasan. *J. Chem. Eng. Data*, **1998**, 43, 732-737
- [30] A Ali; AK Nain; N Kumar; M Ibrahim. *Acoustic Letters.*, **2001**, 24, 199-205.
- [31] A Ali; AK Nain. *Indian J. Chem.*, **1996**, 35, 751-757.
- [32] D Sravana Kumar. Ph.D Thesis, Acharya Nagarjuna University, NagarjunaNagar,Guntur, A.P., India, **2007**.
- [33] M Sakurai. *J. Solution Chem.*, **1988**, 17, 267-275.
- [34] Fong-Meng Pang; Chye-Eng Seng; Tjoon-Tow Teng; MH Ibrahim. *J. Mol. Liq.*, **2007**, 136, 71-78.
- [35] TRC Thermodynamic Tables, Thermodynamics Research Center, Texas A&M University . College Station, Texas, **1994**.
- [36] R Riggio; JF Ramos; MH Ubeda; JA Espindola. *Can. J.Chem.*, **1981**, 59, 3305-3308.
- [37] M Rafiqul Islam; SK Quadri. *Thermochim. Acta*, **1987**, 115, 335-344.
- [38] K Tiwar; C Patra; V Chakravorthy. *Acoustic Letters.*, **1995**, 19, 53.
- [39] BK Rout; V Chakravorthy; K Samal. *Acoustic Letters.*, **1994**, 10, 203.
- [40] S Velmourougane; TK Nambinarayanan; AS Rao; B Krishnan. *Indian J. Phys.*, **1987**, 61, 105.
- [41] K Rajagopal; S Chenthilnath. *J. Chem. Thermodyn.*, **2010**, 42, 675-683
- [42] H Iloukhani; Z Rostami. *J. Solution Chem.*, **2003**, 32, 451- 462.
- [43] DS Wankhede; NN Wankhade; MK Lande; BR Arbad, *Indian J. Pure Appl. Phys.*, **2006**, 44, 909-916.
- [44] Anil kumar Nain. *Fluid Phase Equilib.*, **2008**, 265, 46-56.
- [45] Anil kumar Nain. *J. Mol. Liq.*, **2008**, 140, 108-116.
- [46] F Kawaizumi; M Ohno; Y Miyahara. *Bull. Chem. Soc. Jpn.*, **1977**, 50, 2229-2233.
- [47] RD Rai; RK Shukla; AK Shukla; JD Pandey. *J. Chem. Thermodyn.*, **1989**, 21, 125-129.
- [48] S Thirumaran; S Sudha. *J. Chem. Pharm. Res.* **2010**, 2(1), 327-337.
- [49] GA Krestove. Thermodynamics of Solution, Ellis-Horwood Ltd. England, **1991**.
- [50] S Thirumaran; R Murugan; N Prakash. *J. Chem. Pharm. Res.* **2010**, 2(1), 53-61.
- [51] D Sravana Kumar; D Krishna Rao. *Indian J. Pure Appl. Phys.*, **2007**, 45, 210-220.
- [52] A Ali; AK Nain; N Kumar; M Ibrahim. *J. Pure Appl. Ultrason.*, **2002**, 24, 27-32.