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Intermolecular Free Length and Molar Volume of Binary Liquid Mixtures of Ethyl Acetate with 1-Alkanol At 303.15K

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ABSTRACT

The ultrasonic velocity (u) and density (ρ) have been measured for ethyl acetate with 1-alkanols at 303.15K, over the entire range of composition. The thermodynamic parameter such as intermolecular free length (Lf), molar volume (V_m), isentropic compressibility (β_s) and internal pressure (P_i) have been obtained for all mixtures from experimental data with a view to investigating the exact nature of the molecular interaction. The excess values of the said parameter have also been calculated. The deviation from ideality of these parameters is explained on the basis of molecular interactions between the constituent components of the mixture.

Keywords: Internal pressure; Isentropic compressibility; Ultrasonic velocity; Density; Mole fraction; Binary mixtures; Molecular interaction

INTRODUCTION

During last three decades [1,2], studying thermo acoustical parameters have gained much importance. These parameters include intermolecular free length (L_f), molar volume (V_m), isentropic compressibility (β_s) and internal pressure (P_i) [3,4], has been made to study the intermolecular interaction in mixtures. Fundamental thermodynamic and thermo physical properties are essential sources of information necessary for a better understanding of the non-ideal behaviour of complex systems because physical and chemical effects which are caused by molecular interactions, intermolecular forces etc. of unlike molecules. In recent years the ultrasonic study of properties of liquid mixtures and solvation find direct application in chemical and biochemical industry. Thermodynamic and transport properties of liquid of liquid mixtures have been extensively used to study the departure of a real liquid mixture behavior from ideality. The measurements of ultrasonic velocity, viscosity and density have been adequately employed in understanding the molecular interactions in liquid mixtures.

Investigations on binary liquid mixtures of ethylacetate with 1- alkanols at 303.15K by calculation excess thermodynamic parameters are found to be highly useful in understanding the solute-solvent interactions in these mixtures. The measured ultrasonic parameters are being extensively used to study intermolecular process in liquid system [5,6].The sign and magnitude of non-linear deviations from ideal values of velocities and inter molecular free length are attributed to the difference in molecular size and strength of interaction between unlike molecules[7-10].Ultrasonic velocity and density of the six binary mixtures are measured at 303.15K for different composition of the components. Intermolecular free length (L_f), molar volume (V_m), isentropic compressibility (β_s) and internal pressure (P_i) and excess values are calculating using the standard equation.

The present note deals with the study of ultrasonic velocity (u) , density (ρ), Intermolecular free length (L_f), molar volume (V_m), isentropic compressibility (β_s) and internal pressure (P_i) and excess values of excess intermolecular free length (L_f^E), excess molar volume (V_m^E), excess isentropic compressibility (β_s^E) and excess internal pressure (P_i^E) for six binary liquid mixtures. The results were analyzed in terms of changes in intermolecular free spaces between the pairs of molecules due to addition of second component.

EXPERIMENTAL

Material

The chemicals used in the present work were high purity laboratory reagent grade samples of ethyl acetate, 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol, 1-octanol purchased from Merck Chem. Ltd India. The purity of the chemicals is shown in table-1. All the chemicals were kept in tightly sealed bottles to minimize the absorption of atmospheric moisture

Table 1: Provenance and purity of the materials used.

Component	CAS number	Source	Initial mass fraction purity
Ethyl acetate	141-78-6	Merck Chem. Ltd India	0.998
1-Methanol	67-56-1	Merck Chem. Ltd India	0.995
1-Ethanol	64-17-5	Merck Chem. Ltd India	0.995
1-Propanol	71-23-8	Merck Chem. Ltd India	0.995
1-Butanol	71-36-3	Merck Chem. Ltd India	0.995
1-Hexanol	111-27-3	Merck Chem. Ltd India	0.995
1-Octanol	111-87-5	Merck Chem. Ltd India	0.995

The purity of the solvent was ascertained by comparing the measured density, and sound velocity of the pure component at 303.15K with the available literature [11-18], as shown in Table 2. The reported experimental values of density (ρ) and sound velocity (u) conform closely to their corresponding literature values.

Table 2: Physical properties of pure components at 303.15K.

Component	Density (ρ)		Ultrasonic Velocities (u)	
	$kg\text{-}m^{-3}$		$m.s^{-1}$	
	Observed	Literature	Observed	Literature
Ethyl acetate	0.882	0.8885[13]	1125	1115.0[11]
1-Methanol	0.784	0.7817 [13]	1084	1084.0 [17]
1-Ethanol	0.772	0.7807 [12]	1141	1144.3 [14]
1-Propanol	0.807	0.8003 [16]	1182	1182.6 [14]
1-Butanol	0.804	0.8020 [14]	1196	1196.6 [14]
1-Hexanol	0.8128	0.8118 [14]	1298	1282.0 [18]
1-Octanol	0.8242	0.8187 [15]	1327	1330.8 [15]

Measurements

Six binary system viz. ethyl acetate + 1-methanol, ethyl acetate + 1-ethanol, ethyl acetate +1- propanol, ethyl acetate + 1-butanol, ethyl acetate + 1-hexanol and ethyl acetate + 1-octanol were studied. Each sample mixture was prepared, on mass basis, by mixing the calculated volume of liquid components in specially designed glass stoppered bottles. All binary mixtures were prepared by weight covering the entire mole fraction range. The components of binary mixtures were injected by means of syringe in to the glass vials of sealed with rubber stopper in order to check evaporation losses during sample preparation. The mass measurements were carried out using an single pan analytical balance (Model K-15 Deluxe, K Roy Instruments Pvt. Ltd. Varanasi, India.) with an accuracy of $\pm\ 0.00001\times10^{-3}$ kg as described elsewhere [19]. The possible error in the mole fraction was estimated to be less than 1×10^{-4}. Five samples were prepared for one system, and their density and sound velocity were measured on the same day.

Density

Densities of pure liquids and their binary mixtures were determined by using a double-arm pycnometer made of Borocil glass [12], with a bulb of 25 cm^3 and a capillary of an internal diameter of about 1 mm is used to measure the densities (ρ) of pure liquids and binary mixtures. The pycnometer was calibrated by using conductivity water (Conductance less than $1\times10^{-6}\omega^{-1}$) with 0.99705 g cm^{-3} as its density at 303.15K. The pycnometer was kept for about 30 min. in an electronically controlled thermostated water bath (303.15 + 0.02K) and the position of the liquid level

on the capillary was noted. The volume of the pycnometer at each mark was calculated by using the literature value of the density of pure water at 303.15K. The pycnometer filled with air bubbles free liquids is kept in a thermostate water bath (MSI Goyal Scientific, Meerut, India) controlled with a thermal equilibrium. The precision of the density measurements was estimated to be ±0.0002 g cm^{-3}. The observed values of densities of pure ethyl acetate, 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15K were 0.8820, 0.7840, 0.7720, 0.8070, 0.8040, 0.8128 and 0.8242 $kg.m^{-3}$ which compare well with corresponding literature values of respectively.

Sound velocity

The ultrasonic velocities were measured using a multi frequency ultrasonic interferometer (Model F-80D, Mittal Enterprise, New Delhi, India) working at 3 MHz. that has reproducibility of + 0.5 m s^{-1} at 30^0C. The meter was calibrated with water and benzene at 303.15K. For all the measurements, temperature was controlled by circulating the water through a thermo state water bath (MSI Goyal Scientific, Meerut, India) controlled with a thermal equilibrium keeping temperature accuracy within + 0.02K. The measured values of ultrasonic velocities of pure ethyl acetate,1- methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15K were 1125, 1084, 1141, 1182, 1196, 1298 and 1327 $m.s^{-1}$ respectively, which compare well with the corresponding literature values.

Theoretical

In the year 1952, Jacobson [15,16], suggested an empirical relation for calculating the free length (L_f) of liquids. Intermolecular free length (L_f), can be calculated from the isentropic compressibility (β_s) by the relation given below

$$L_f = K\beta_s^{1/2}$$

Where K is temperature dependent constant, called the Jacobson constant. Jacobson determined the value of K empirically between 0 to 50ºC and β_s is the isentropic compressibility. The isentropic compressibility (β_s) has been calculated from the sound velocity (u) and the density (ρ) of the medium using the equation as

$$\beta_s = u^{-2}\rho^{-1}$$

The molar volume V_m calculated from the measured values of density (ρ), molar volume (V_m) was calculated using the relation

$$V_m = \frac{X_1M_1 + X_2M_2}{\rho}$$

Where X_1, X_2 and M_1, M_2 are the mole fraction and molecular weight of the component 1 and 2 respectively.

Suryanarayana and Kuppuswami [20,21], suggested a method for evaluation of internal pressure from the knowledge of ultrasonic velocity, u, density, ρ, and viscosity, η, the relation proposed is expressed as

$$pi = bRT\left(\frac{kn}{u}\right)^{\frac{1}{2}}\frac{p^{2/3}}{M_{eff}^{7/6}}$$

Where b is packing factor, which is assumed to be 2 for all liquid and solution. k is a constant, independent of temperature and its value is 4.28×10^9 for all liquids, R is universal gas constant and T is absolute temperature.

The excess value of ultrasonic related parameters have been calculated by using the following relation

$$A^E = A_{exp} - \left(X_1A_1 + X_2A_2\right)$$

Where A represents the parameter such as intermolecular free length, molar volume, isentropic compressibility and internal pressure and X_1 and X_2 are the mole fractions of components whose parameters.

RESULT AND DISCUSSION

The experimental values of density and ultrasonic velocity and calculated values of intermolecular free length, isentropic compressibility, molar volume and internal pressure at 303.15K over the entire composition range are presented in table 3. The excess function, excess intermolecular free length (L_f^E), excess molar volume (V_m^E), excess isentropic compressibility (β_s^E), and excess internal pressure ($P_i{}^E$) for six binary liquid mixtures evaluated using equation (5) are summarized in table 4. The excess parameters, excess intermolecular free length (L_f^E), excess molar volume (V_m^E), excess isentropic compressibility (β_s^E) and excess internal pressure ($P_i{}^E$) have been plotted against mole fraction of ethylacetae in figures 1,2,3,4. It is evident from table 3 density, molar volume and sound velocity increases while intermolecular free length, isentropic compressibility and internal pressure decrease with increase in concentration of ethylacetae in all the mixtures. The pronounced increase or decrease in these parameters with composition of the mixtures indicates the presence of interaction between the component molecules in the binary liquid mixture. The resultant interaction an a liquid mixture is not solely dependent on the molecular structure of component liquids but is also influenced by other factors like

dispersion forces, dipole-dipole interaction, dipole-induced dipole interaction, hydrogen bonding, charge transfer interaction and a complex formation. Normally dispersion forces make a positive contribution to excess values, while other makes a negative contribution.

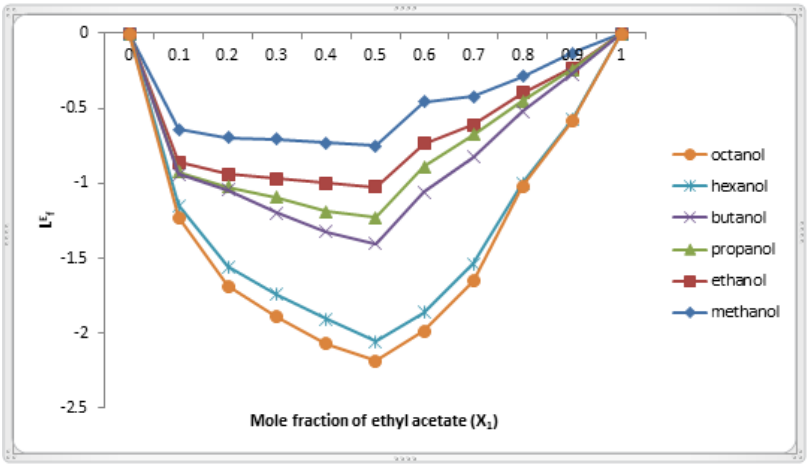


Figure 1: Plots of excess free length (L_f^E) versus mole fraction of ethyl acetate (X_1) at 303.15 K for binary mixtures of ethyl acetate with 1-methanol, 1-ethanol, 1- propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15 K.

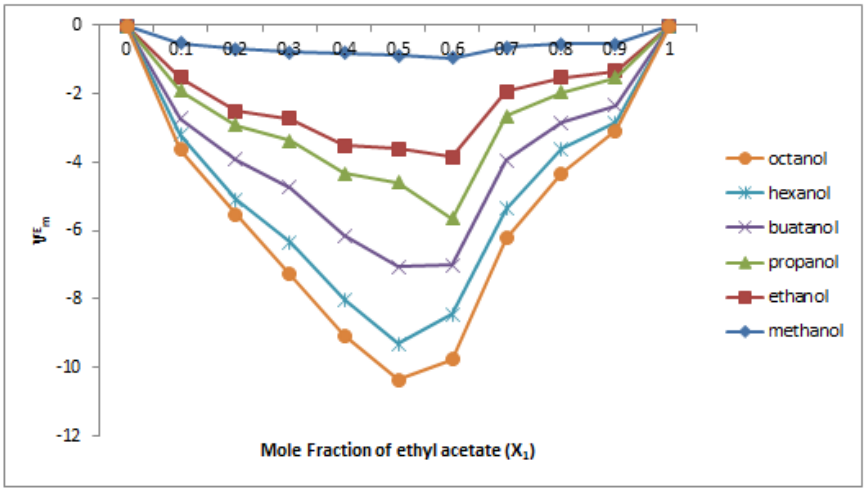


Figure 2: Plots of excess molar volume (V_m^E) versus mole fraction of ethyl acetate (X_1) at 303.15 K for binary mixtures of ethyl acetate with 1-methanol, 1-ethanol, 1- propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15 K.

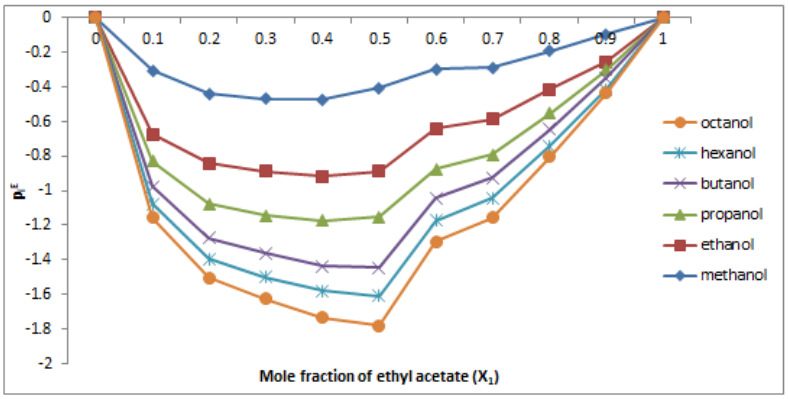


Figure 3: Plots of excess internal pressure versus mole fraction of ethyl acetate (X_1) at 303.15 K for binary mixtures of ethyl acetate with 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15 K.

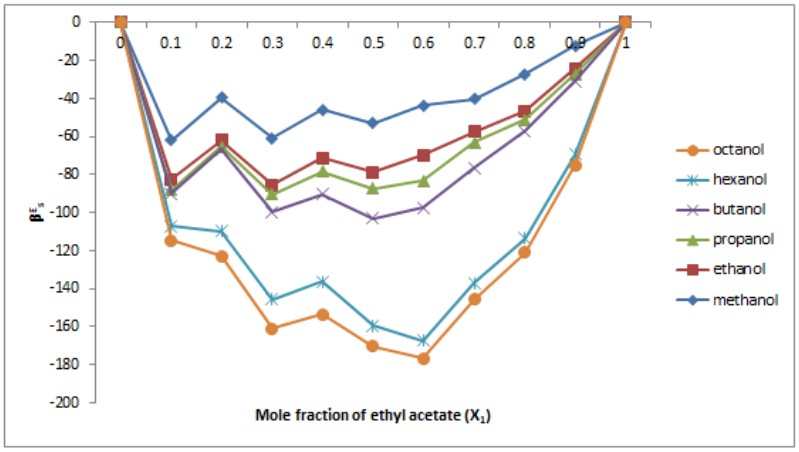
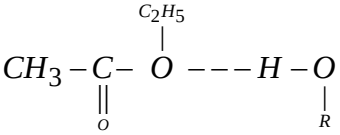


Figure 4: Plots of excess isentropic compressibility β_S^E versus mole fraction of ethyl acetate (X_1) at 303.15 K for binary mixtures of ethyl acetate with 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15 K.

Alkanols are liquids which are associated through the hydrogen bonding and in the pure state; they exhibit an equilibrium between the monomer and multimer species. Also, they can be associated with any other group having some degree of polar attraction [22]. Due to polar nature of ethyl acetate and alkanols, the dipole-dipole interaction prevail in these mixtures. When the compounds are mixed the changes the occur in association equilibria are evidently repture of the hydrogen bonds [17] in pure ethyl acetate and alkanols, dipole-dipole interactions and the formation of O − H----O hydrogen bonds between the components.

The 1-alkanols are associated through hydrogen bonding.

and ethyl acetate – 1-alkanols interactions are due to hydrogen bonding between the oxygen atom of the ethyl acetate and the proton of hydrogen group of alkanols.



The result present in Table 3, show non-linear behaviour of isentropic compressibility, intermolecular free length, molar volume and internal pressure which is further substantial by their excess values (Table 4). All the seven organic compounds namely ethyl acetate, methanol, ethanol, propanol, butanol, hexanol and octanol are a polar organic compounds having dipole moment 1.78 D, 1.70 D, 1.69 D, 1.68 D, 1.66 D, 1.60 D and 1.68 D respectively. Normally more the dipole moment, stronger is the intermolecular attraction, which results in decreasing of free space between molecules and increase in the ultrasonic velocity (Table 4).

Table 3: Values of density, ultrasonic velocity, isentropic compressibility, intermolecular free length, molar volume, and internal pressure properties for binary liquids mixtures of ethyl acetate +1- methanol, ethyl acetate + 1-ethanol, ethyl acetate + 1-propanol, ethyl acetate +1-butanol, ethyl acetate +1- hexanol and ethyl acetate +1- octanol at 303.15 K.

Mole fraction x_1	**Density(ρ) k.gm^{-3}**	**Sound Velocity(u) m / s**	**isentropic compressibility $\beta_s \times 10^{-8}$ m^{2}N^{-1}**	**intermolecular free length $L_f \times 10^{-9}$ m**	**Molar volume $V_m \times 10^6$ m^3 mol^{-1}**	**Internal pressure ($p_i \times 10^4$) atm**
Ethyl acetate+ 1-Mehanol						
0.0000	784.0	1084	108.54	2.22022	40.8673	1.85827
0.1039	796.8	1099	100.39	2.13515	47.5245	1.39542
0.2248	819.2	1103	100.33	2.13451	54.4992	1.07580
0.3129	839.5	1105	96.54	2.09380	59.0643	0.91572
0.4370	848.3	1110	95.67	2.08435	66.6542	0.73366
0.5474	867.5	1114	92.88	2.05373	72.3090	0.62282
0.6409	870.9	1117	92.02	2.04420	78.0508	0.53580
0.7128	879.0	1118	91.01	2.03295	81.9179	0.49096
0.8164	879.2	1122	90.34	2.02545	88.5081	0.43096
0.9104	880.5	1123	90.05	2.02220	94.3665	0.38473
1.0000	882.0	1125	89.58	2.01695	99.8979	0.34494
Ethyl acetate+ 1-Ethanol						
0.0000	772.0	1141	99.49	2.12563	59.6761	1.48567
0.1049	802.5	1137	96.38	2.09216	62.9054	0.99503
0.2090	815.7	1135	95.16	2.07882	67.2489	0.84487

0.3105	827.8	1134	93.93	2.06531	71.4184	0.71041
0.4166	839.2	1133	92.81	2.05305	75.7609	0.62822
0.5094	849.6	1132	91.84	2.04230	79.4294	0.56071
0.6076	860.4	1131	90.85	2.03118	83.2250	0.49618
0.7150	863.9	1130	90.65	2.02893	88.1223	0.44587
0.8069	877.6	1128	89.54	2.01653	91.1441	0.40652
0.9030	882.7	1126	89.35	2.01434	95.1972	0.37581
1.0000	882.0	1125	89.58	2.01695	99.8979	0.34494
Ethyl acetate + 1-Propanol						
0.0000	807.0	1182	88.68	2.00681	74.4563	1.12536
0.1074	813.3	1173	89.35	2.01439	77.5792	0.88659
0.2086	826.2	1169	88.56	2.00541	79.7993	0.72795
0.3145	832.1	1161	89.15	2.01209	82.8013	0.62680
0.4099	842.8	1159	88.33	2.00280	84.9257	0.54900
0.4758	850.9	1154	88.24	2.00185	86.2868	0.51357
0.54307	860.9	1150	87.82	1.99707	87.4748	0.46810
0.6127	864.7	1142	88.67	2.00668	89.3453	0.44151
0.7564	868.5	1138	88.90	2.00933	93.5897	0.39664
0.9126	878.8	1134	88.48	2.00458	97.4750	0.36363
1.0000	882.0	1125	89.58	2.01695	99.8979	0.34494
Ethyl acetate + 1-Butanol						
0.0000	804.0	1196	86.95	1.98712	92.1902	0.93886
0.1063	805.6	1194	87.06	1.98837	93.8435	0.72809
0.2151	816.8	1184	87.33	1.99147	94.4294	0.61710
0.3213	826.9	1180	86.85	1.98595	95.0707	0.53084
0.4327	832.2	1176	86.88	1.98633	96.3355	0.51618
0.5192	842.0	1170	86.75	1.98486	96.6507	0.43625
0.6266	842.4	1167	87.16	1.98949	98.3882	0.39871
0.7124	858.1	1154	87.50	1.99344	97.9889	0.38101
0.8127	866.6	1142	88.47	2.00441	98.6404	0.36421
0.9044	874.2	1134	88.94	2.00981	99.2555	0.35557
1.0000	882.0	1125	89.58	2.01695	99.8979	0.34494
Ethyl acetate +1- Hexanol						
0.0000	812.8	1298	73.02	1.82102	125.6914	0.76533
0.0996	821.4	1292	72.92	1.81983	122.6634	0.62247
0.2225	833.8	1287	72.40	1.81331	118.7742	0.54978
0.3149	835.5	1275	73.62	1.82849	116.9760	0.49429
0.4151	840.6	1257	75.29	1.84907	114.5933	0.45038
0.5186	846.6	1247	75.95	1.85723	112.0864	0.41469
0.6083	854.4	1240	76.11	1.85917	109.5595	0.39077
0.7096	861.7	1222	77.70	1.87853	106.9770	0.37353
0.8066	867.2	1210	78.75	1.89111	104.7255	0.36080
0.9041	878.0	1192	80.15	1.90786	101.8771	0.34774
1.0000	882.0	1125	89.58	2.01695	99.8979	0.34494
Ethyl acetate + 1-Octanol						
0.0000	824.2	1327	68.89	176878	158.0052	0.66872
0.1056	825.9	1312	70.33	1.78718	152.2800	0.55668
0.2095	830.0	1294	71.94	1.80754	146.2509	0.49024
0.3174	831.8	1275	73.94	1.83249	140.4730	0.43728
0.4286	838.7	1239	77.66	1.87799	133.7374	0.37509
0.5083	840.0	1225	79.32	1.89800	129.5386	0.38467
0.6196	844.4	1214	80.35	1.91025	123.3172	0.35719
0.7090	858.6	1192	81.96	1.92927	145.9131	0.37519
0.8064	865.1	1164	85.31	1.96830	111.2675	0.34396
0.9044	871.6	1148	87.05	1.98825	105.7013	0.35364
1.0000	882.0	1125	89.58	2.01695	99.89795	0.34494

Table 4: Excess values of isentropic compressibility(β_s^E), intermolecular free length (L_f^E), molar volume (V_m^E) and internal pressure (p_i^E) properties for binary liquids mixtures of ethyl acetate + 1-methanol, ethyl acetate + 1-ethanol, ethyl acetate + 1-propanol, ethyl acetate +1- butanol, ethyl acetate + 1-hexanol and ethyl acetate + 1-octanol at 303.15 K.

Mole Fraction x_1	$\beta_s^E \times 10^{-7}$ $m^2\ N^{-1}$	$L_f^E \times 10^{-10}$ m	V_m^E $m^3\ mol^{-1}$	$p_i^E \times 10^4$ atm.
Ethyl acetate + 1-Methanol				
0.0000	0.00	0.0000	0.00000	0.0000
0.1039	-61.8	-0.6391	-0.52201	-0.3055
0.2248	-39.4	-0.6993	-0.66072	-0.4421

0.3129	-60.6	-0.7077	-0.77383	-0.4689
0.4370	-45.8	-0.7300	-0.80962	-0.4732
0.5474	-52.8	-0.7517	-0.87129	-0.4070
0.6409	-43.6	-0.4569	-0.95002	-0.2967
0.7128	-40.1	-0.4232	-0.62853	-0.2885
0.8164	-27.1	-0.2876	-0.55257	-0.1923
0.9104	-12.2	-0.1289	-0.54600	-0.0956
1.0000	0.00	0.0000	0.00000	0.0000
Ethyl acetate+ 1-Ethanol				
0.0000	0.00	0.0000	0.00000	0.0000
0.1049	-20.6	-0.2204	-0.99258	-0.3708
0.2090	-22.6	-0.2408	-1.83336	-0.4023
0.3105	-24.8	-0.2654	-1.94880	-0.4209
0.4166	-25.4	-0.2722	-2.67661	-0.4438
0.5094	-25.9	-0.2794	-2.73675	-0.4821
0.6076	-26.2	-0.2839	-2.88955	-0.3438
0.7150	-17.5	-0.1896	-1.31421	-0.2963
0.8069	-19.4	-0.1137	-0.99000	-0.2240
0.9030	-11.9	-0.1013	-0.79942	-0.1585
1.0000	0.00	0.0000	0.00000	0.0000
Ethyl acetate + 1-Propanol				
0.0000	0.00	0.0000	0.00000	0.0000
0.1074	-5.75	-0.0650	-0.39267	-0.1542
0.2086	-3.10	-0.0849	-0.43678	-0.2345
0.3145	-4.85	-0.1210	-0.64416	-0.2530
0.4099	-7.22	-0.1873	-0.84248	-0.2564
0.4758	-8.65	-0.1978	-0.97433	-0.2640
0.5430	-13.4	-0.1524	-1.80306	-0.2334
0.6127	-5.62	-0.0634	-0.69878	-0.2056
0.7564	-4.57	-0.0515	-0.41016	-0.1384
0.9126	-3.16	-0.0148	-0.19909	-0.0495
1.0000	0.00	0.0000	0.00000	0.0000
Ethyl acetate + 1-Butanol				
0.0000	0.00	0.0000	0.00000	0.0000
0.1063	-1.69	-0.0190	-0.83451	-0.1476
0.2151	-1.84	-0.0204	-0.98179	-0.1939
0.3213	-9.46	-0.1073	-1.38436	-0.2171
0.4327	-12.0	-0.1368	-1.81050	-0.2656
0.5192	-15.6	-0.1772	-2.45928	-0.2942
0.6266	-14.3	-0.1630	-1.36900	-0.1679
0.7124	-13.1	-0.1491	-1.30851	-0.1347
0.8127	-6.17	-0.0693	-0.88668	-0.0919
0.9044	-3.81	-0.0286	-0.79466	-0.0460
1.0000	0.00	0.0000	0.00000	0.0000
Ethyl acetate + 1-Hexanol				
0.0000	0.00	0.0000	0.00000	0.0000
0.0996	-17.4	-0.2069	-0.45637	-0.1009
0.2225	-43.0	-0.5129	-1.17608	-0.1219
0.3149	-46.1	-0.5421	-1.59146	-0.1386
0.4151	-46.0	-0.5828	-1.88840	-0.1404
0.5186	-56.5	-0.6538	-2.25452	-0.1623
0.6083	-69.8	-0.8103	-1.43844	-0.1326
0.7096	-60.6	-0.7152	-1.40800	-0.1187
0.8066	-56.2	-0.4784	-0.75911	-0.0934
0.9041	-38.4	-0.3028	-0.49263	-0.0654
1.0000	0.00	0.0000	0.00000	0.0000
Ethyl acetate + 1-Octanol				
0.0000	0.00	0.0000	0.00000	0.0000
0.1056	-7.43	-0.0781	-0.42861	-0.0778
0.2095	-12.8	-0.1323	-0.43692	-0.1106
0.3174	-15.1	-0.1505	-0.92541	-0.1286
0.4286	-16.97	-0.1684	-1.04906	-0.1548
0.5083	-10.81	-0.1308	-1.07905	-0.1694
0.6196	-9.50	-0.1229	-1.32444	-0.1194
0.7090	-8.90	-0.1146	-0.85666	-0.1109
0.8064	-7.65	-0.0160	-0.72863	-0.0632
0.9044	-5.53	-0.0096	-0.25366	-0.0222
1.0000	0.00	0.0000	0.00000	0.0000

A perusal of table 4 shows that the values of excess intermolecular free length for all the six binary system are negative. These negative values of excess intermolecular free length are shown in figure 1. From figure 1 shows that the excess intermolecular free length (L_f^E) values are negative for all binary systems but the magnitude of the negative values increase with increasing chain length of alcohols, the order are given below-

1-Methanol < 1-Ethanol < 1-Propanol < 1-Butanol < 1-Hexanol < 1-Octanol

The above order indicates the strength of interactions between component molecules decreases due to decrease in polarizability of alkanol molecules.

The negative values of excess intermolecular free length (L_f^E) play a very important role in description of molecular interaction in liquid mixtures through dipole-dipole interaction and hydrogen bonding. Due to polar nature of ethyl acetate and alkanols, the dipole-dipole interactions prevail in these mixtures. When the compounds are mixed the changes the occur in association equilibria are evidently rapture of the hydrogen bonds in pure ethyl acetate and alkanols, dipole-dipole interactions and the formation of O − H----O hydrogen bonds between the components. This suggests the existence of strong interaction between the components in all the binary systems. The values of L_f^E suggest that strong specific interaction like the formation of H- bond association through weaker physical forcers of attraction [23].

A perusal of Table 4 reveal that the value of excess molar volume (V_m^E) are negative in all binary liquid system over the entire range of composition at 303.15 K. The value of V_m^E are plotted against the mole fraction of ethyl acetate (X_1) and are shown in Figure 2. In the present investigation the negative V_m^E values for binary mixtures of ethyl acetate with 1- alkanols may be attributed to hydrogen bond formation through dipole-dipole interaction between 1- alkanol and ethyl acetate molecule or to structure contribution arising from geometrical fitting of one component (1-alkanol) in to the other (ethyl acetate) due to differences in the molar volumes between components. Excess molar volume value of all binary liquid systems increases with an increases of concentration of ethyl acetate (X_1). This is attributed to decreased ester-ester and alkanol-alkanol contacts with an increase the concentration of ethyl acetate (X_1).

The excess internal pressure (p_i^E) is another important parameter through which molecular interactions can be explained. In the present investigation for the six binary systems it is observed that, as the mole fraction of ethyl acetate increase, the p_i^E values decreases. The values of p_i^E are almost negative and gradually decrease and move towards the positive values by the increase of mole fraction of ethyl acetate. More over the p_i^E decrease with increase in X_1. This situation is observed for all six binary system under study and can be viewed from plots Figure 3.

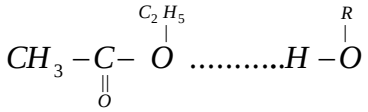
The negative values of excess internal pressure (p_i^E) indicate the presence of strong molecular interaction. We may conclude that alkanols, which is a self – associating polar organic liquid has a tendency to form complexes with ethyl acetate and the increase in its dilution causes disruption of aromatic C – H bond stretching as the self – association of alkanes is disrupted. It is also concluded that suryanarayana approach for estimating internal pressure of binary liquid mixtures, based on dimensional analysis using thermodynamic consideration is very well applicable in the present case.

A perusal of Table 4 also reveal that the values of excess isentropic compressibility (β_s^E) are negative over the entire range of concentration in all the six binary system at 303.15 K. The value of excess isentropic compressibility (β_s^E) are plotted against the mole fraction of ethyl acetate and are shown in Figure 4.

The sign of excess isentropic compressibility play a vital role in assessing the compactness due to molecular interaction in liquid mixtures through charge transfer, dipole-dipole interaction and dipole induced dipole interactions interstitial accommodation and orientational ordering leading to more compact structure making, which enhances excess isentropic compressibility to have negative values. Fort and Moore [18] suggested that the liquid having different molecular size and shape mix well there by reducing the volume which causes the values of β_s^E to be negative. It is also suggested that liquids are less compressible when compared to their ideal mixtures signifying the chemical effects including charge transfer forces, formation of hydrogen bond and other complex forming interactions. It can also be said that the molecular interaction are strong in these binary liquid mixtures and that the medium is highly packed. Similar results were obtained by earlier worker [24]. The negative value of β_s^E in these mixtures can be associated with a structure forming tendency.

The charge in intermolecular free length, molar volume and internal pressure with change in composition in these systems, indicate the variations in cohesive forces of these system. A perusal of the sign and magnitude of the excess values of the parameters (L_f^E), (V_m^E), (β_s^E) and (p_i^E) show that the strength of the molecular interaction between the component molecules. The present study point at clearly that in all six binary systems ethyl acetate is involved in the charge transfer interaction with alcohols. The oxygen atom of ethyl acetate being strongly electronegative would have tendency to attract electropositive hydrogen of alcohols resulting in the formation of new species, showing the negative value of excess thermodynamic properties.

The negative deviations of high magnitude lead to the unstable complex formation between the hetero molecules of the mixtures. In the present study the negative excess volume indicates the breaking of hydrogen bond of alcohols polymers as alcohol is diluted with ethyl acetate and association between unlike molecules causing contraction with increasing concentration of ethyl acetate. Therefore it can be concluded that AB type strong specific interaction take place leading to a bonding like (− H---O−) Which results in the formation of a complex of the type



The results reveal that the intermolecular interaction decreases with the increasing size of the alcohol molecules. Hydrogen bonding strength also decreases with decreasing dipole moment of the alcohol molecules.

CONCLUSIONS

The ultrasonic method is powerful tool for characterizing physic-chemical properties and existence of molecular interaction in the mixture. In this paper, an attempt is made to measure densities (ρ) and ultrasonic velocity (u) at 303.15 K over the entire range of mixture composition of ethyl acetate with 1-methanol, 1-ethanol, 1- propanol, 1-butanol, 1-hexanol and 1-octanol out of these measured data, excess intermolecular free length (L_f^E), excess molar volume (V_m^E), excess isentropic compressibility (β_s^E) and excess internal pressure (p_i^E) have been calculated.

The negative deviations are observed in the case of excess intermolecular free length (L_f^E), excess molar volume (V_m^E), excess isentropic compressibility (β_s^E) and excess internal pressure (p_i^E) are observed for all binary mixtures of ethyl acetate with 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol, 1-octanol.The results are analyzed in the sight of molecular interactions between the components. It may be concluded that the interaction resulting in the interstitial accommodation of ethyl acetate in to 1-alkanols are the predominant factor over dipole-dipole interaction. All the experimental determinations of excess intermolecular free length (L_f^E), excess molar volume (V_m^E) excess isentropic compressibility (β_s^E) and excess internal pressure (p_i^E) are strongly correlated with each other.

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Declarations conflict of interest

The authors have no competing interests to declare that are relevant to the content of this article.

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Author Contribution Statement

Dhirendra Kumar Sharma, Research design, Investigation, Writing-Original draft preparation and Manuscript correction.
Seema Agarwal, Data Analysis and Mathematical Calculation
Akil Khan, Tables and Graph preparation.

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