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Free Volume and Internal Pressure of Binary Liquid Mixtures from Ultrasonic Velocity at 303.15 K

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Abstract

Ultrasonic velocity (u), density (ρ), and viscosity (η) measurements have been taken in six binary liquid mixtures ethyl acetate + methanol, ethyl acetate + ethanol, ethyl acetate + propanol, ethyl acetate + butanol, ethyl acetate + hexanol and ethyl acetate + octanol at 303.15 K over the entire mole fraction range. The experimental data has been used to calculate the free volume, internal pressure and their excess values. Excess values of free volume (V_f^E) and internal pressure (p_i^{E}) were plotted against the mole fraction of ethyl acetate over the whole composition range at 303.15 K. They have been analyzed to discuss the nature and strength of intermolecular interactions in these mixtures.

Keywords: *Ultrasonic velocity; binary liquid mixtures; internal pressure; free volume; intermolecular interactions.*

1. Introduction

In recent years, ultrasonic investigation of binary liquid mixtures has revolutionized the pharmaceutical industries to great extent [1-6]. Ultrasonic technique has become a powerful tool for studying the molecular behavior of liquid mixtures [7-9]. This is because of its ability of characterizing physic-chemical behavior of liquid medium. Fundamental thermodynamic and thermo-physical properties are essential sources of information necessary for a better understanding of the non-ideal behavior of complex system. Excess thermodynamic functions have been used to explain the formation of complexes in liquid mixtures. These deviations have been interpreted as arising from the presence of strong or weak interactions. The free volume is an important fundamental factor to be considered in explaining variations in the physic-chemical properties many workers have studied this parameter for liquid and liquid mixtures. An-another thermodynamic property internal pressure was recognized many year ago by Hildebrand [10]. The main use of this property has for a long time been limited to descriptive or qualitative purpose. In recent year, it has been found to be an important tool in the study of molecular interactions in liquid and liquid mixtures. An internal pressure of liquid is highly useful in understanding molecular interactions, internal structure and the clustering phenomenon. Now days, many investigations have been carried out to evaluate it in pure and binary liquid mixtures.

The measurement of ultrasonic velocity has been adequately employed in understanding the molecular interactions in liquid mixtures. Ultrasonic velocity and viscosity measurements have been widely used in the field of molecular interactions and structural aspect evaluation studies.

Internal pressure and free volume has been a subject of active interest among several researchers during recent past [11]. Several attempts have been made by a number of investigators to calculate the internal pressure of liquids and liquid mixtures theoretically.

Fundamental thermodynamic and thermo physical properties are essential source of information necessary for a better understanding of the non-ideal behavior of complex systems because physical and chemical effects which are caused by molecular interactions, intermolecular forces etc. of unlike molecules [12] .

In order to examine molecular interactions, we report have the ultrasonic velocity (u), density (ρ), and viscosity (η) of binary liquid mixtures of ethyl acetate with alkanols over entire composition range at 303.15 K. The experimental value of u, ρ and η were used to calculate free volume (V_f)**,** internal pressure (p_i) and their excess values. These parameters are quite sensitive towards the intermolecular interactions between the component molecules in the mixtures. The dependence of these parameters on composition of the mixtures reveals the nature and extent of interaction between component molecules.

2. Experimental

2.1 Material

The chemicals used in the present work were high purity laboratory reagent grade samples of ethyl acetate, methanol, ethanol, propanol, butanol, hexanol, octanol purchased from Merck Chem. Ltd India. All chemicals was stored over sodium hydroxide pellets for several days. All the chemicals were stored in dark bottles over freshly activated molecular sieve to minimize adsorption of moisture. The purity of the solvent was ascertained by comparing the measured density, dynamic viscosities and

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sound velocity of the pure component at 303.15K with the available literature [13-22] as shown in Table 1.

2.2 Measurements

Six binary system viz. ethyl acetate + methanol, ethyl acetate + ethanol, ethyl acetate + propanol, ethyl acetate + butanol, ethyl acetate + hexanol and ethyl acetate + 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.) with an accuracy of ± 0.00001×10^{-3} kg as described elsewhere [23]. 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.

2.2.1 Density

Densities of pure liquids and their binary mixtures were determined by using a double-arm pycnometer [24] 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 is calibrated by using conductivity water (having specific conductance less than 1×10^6 ohm^{-1}) with 0.9970 and 0.9940 gcm^{-3} as its densities at T = 303.15 K, respectively. 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, methanol, ethanol, propanol, butanol, hexanol and octanol at 303.15K were 0.8820, 0.7840, 0.7720, 0.8070, 0.8040, 0.8128 and 0.8242 $g.cm^{-3}$ which compare well with corresponding literature values of respectively.

2.2.2 Sound velocity

The ultrasonic velocities were measured using a multifrequency ultrasonic interferometer (Model F-80D, Mittal Enterprise, New Delhi, India) working at 3 M.Hz. The meter was calibrated with water and benzene at 303.15K. The measured values of ultrasonic velocities of pure ethyl acetate, methanol, ethanol, propanol, butanol, hexanol and 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.

2.2.3 Viscosity

The viscosity of pure liquids and their binary mixture were measured using suspended ubbelohde type viscometer [25-26] having a capacity of about 15 ml and the capillary having a length of about 90 mm and 0.5 mm internal diameter has been used to measure the flow time of pure liquids and liquid mixtures and it was calibrated with triply distilled water, methanol and benzene at 303.15 K. The details of the methods and techniques have been described by researchers [27-28]. The efflux time was measured with an electronic stop watch (Racer) with a time resolution (±0.015), and an average of at least four flow time readings was taken. Glass stopper was placed at the opening of the viscometer to prevent the loss due to evaporation during measurements. The two bulbs reservoir, one at the top and other at the bottom of the viscometer linked to each other by U type facilitate the free full of liquid at atmospheric pressure.

The measured values of viscosities of pure ethyl acetate, methanol, ethanol, propanol, butanol, hexanol and octanol at 303.15 K were 0.4402, 0.4949, 1.1399, 1.5477, 2.2045, 4.5642 and 7.8512 C.P. which compare well with the corresponding literature values.

Table 1. Physical properties of pure components at 303.15K.

Component	Density (ρ) $g.cm^{-3}$		Ultrasonic Velocities (u) $m.s^{-1}$		Viscosity (η) CP	
	Observed	Literature	Observed	Literature	Observed	Literature
Ethyl acetate	0.8820	0.8885 [14]	1125	1115.0 [12]	0.4402	0.4000 [17]
Methanol	0.7840	0.7817 [14]	1084	1084.0 [21]	0.4949	0.5040 [15]
Ethanol	0.7720	0.7807 [13]	1141	1144.3 [15]	1.1399	1.3560 [13]
Propanol	0.8070	0.8003 [20]	1182	1182.6 [15]	1.5477	1.6626 [15]
Butanol	0.8040	0.8020 [15]	1196	1196.6 [15]	2.2045	2.2740 [16]
Hexanol	0.8128	0.8118 [15]	1298	1282.0 [22]	4.5642	4.5930 [18]
Octanol	0.8242	0.8187 [19]	1327	1330.8 [19]	7.8512	7.6630 [18]

3 Theoretical Aspects

3.1 Free Volume (V_f)

Liquid viscosity has been treated as free volume problem by a number of workers. Suryanarayana and Kuppusami derived a formula for the free volume based on one dimensional analysis of the situation. When a ultrasonic wave passes through a liquid medium.

$$V_f = (M\,U/\,k\,\eta)^{3/2} \quad (1)$$

Where, M is the molecular weight, u is the ultrasonic velocity, η is the viscosity, V_f , the free volume is in milliliters per mole and K is a constant, independent of temperature and it's value is 4.28×10^9 for all liquids.

3.2 Internal Pressure (p_i)

Suryanarayana and Kuppuswami [29-30] 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

$$p_i = bRT\left(\frac{k\eta}{u}\right)^{\frac{1}{2}}\frac{\rho^{2/3}}{M_{eff}^{7/6}} \quad (2)$$

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.

3.3 Excess Thermodynamic Parameters

The excess thermodynamic function (Y^E) provide a way to represent directly the deviation of a solution from ideal behavior. The difference between the thermodynamic function of mixing for a real system and the value corresponding to a perfect solution at the same temperature, pressure and composition is called the thermodynamic

excess function, denoted by Y^E. Excess values for all the parameters are computed using the general formula

$$Y^E = Y_{exp} - (X_1 Y_1 + X_2 Y_2) \quad (3)$$

4. Result and Discussion

The experimental determinate values of density (ρ), viscosity (η) and sound velocity (u) of all the pure liquids at 303.15 K are presented in Table 1 and the same for the six binary systems are listed in Table 2. The excess value of viscosity (η^E), sound velocity (u^E), free volume (V_f^E) and internal pressure (p_i^E) at 303.15 K are reported in Table 3.

The result present in Table 2 show non-linear behavior of viscosity, sound velocity, free volume and internal pressure, which is further substantial by their excess values (Table 3). 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 interaction, which result is decreasing of free space between molecules and increase in the ultrasonic velocity.

Table 2. Values of density, sound velocity, viscosity, free volume and internal pressure properties for binary liquids mixtures of ethyl acetate + methanol, ethyl acetate + ethanol, ethyl acetate + propanol, ethyl acetate + butanol, ethyl acetate + hexanol and ethyl acetate + octanol at 303.15 K.

Mole fraction of ethyl acetate (X_1)	Density (ρ) g.cm^{-3}	Sound velocity (u) m.s^{-1}	Viscosity (η) CP	Free volume (V_f) ml mol^{-1}	Internal pressure ($p_i \times 10^4$) atm
Ethyl Acetate + Methanol					
0.0000	0.7840	1084	0.4949	0.06639	1.85827
0.1039	0.7968	1099	0.4832	0.08953	1.39542
0.2248	0.8192	1103	0.4810	0.11699	1.07580
0.3129	0.8395	1105	0.4792	0.13807	0.91572
0.4370	0.8483	1110	0.4720	0.17316	0.73366
0.5474	0.8675	1114	0.4684	0.20581	0.62282
0.6409	0.8709	1117	0.4618	0.23810	0.53580
0.7128	0.8790	1118	0.4601	0.26139	0.49096
0.8164	0.8792	1122	0.4538	0.30139	0.43096
0.9104	0.8805	1123	0.4506	0.33654	0.38473
1.0000	0.8820	1125	0.4402	0.38161	0.34494
Ethyl Acetate + Ethanol					
0.0000	0.7720	1141	1.1399	0.03536	1.48567
0.1049	0.8025	1137	0.6563	0.09237	0.99503
0.2090	0.8157	1135	0.6096	0.11781	0.84487
0.3105	0.8278	1134	0.5420	0.15538	0.71041
0.4166	0.8392	1133	0.5298	0.17907	0.62822
0.5094	0.8496	1132	0.5059	0.20957	0.56071
0.6076	0.8604	1131	0.4743	0.25199	0.49618
0.7150	0.8639	1130	0.4667	0.28264	0.44587
0.8069	0.8776	1128	0.4472	0.32369	0.40652
0.9030	0.8827	1126	0.4461	0.34887	0.37581
1.0000	0.8820	1125	0.4402	0.38161	0.34494
Ethyl Acetate + Propanol					
0.0000	0.8070	1182	1.5477	0.03511	1.12536
0.1074	0.8133	1173	1.1104	0.06146	0.88659
0.2086	0.8262	1169	0.8458	0.09824	0.72795
0.3145	0.8321	1161	0.7144	0.13382	0.62680
0.4099	0.8428	1159	0.6106	0.17883	0.54900
0.4758	0.8509	1154	0.5718	0.20368	0.51357
0.5430	0.8609	1150	0.5071	0.25201	0.46810
0.6127	0.8647	1142	0.4850	0.27686	0.44151
0.7564	0.8685	1138	0.4593	0.32271	0.39664
0.9126	0.8788	1134	0.4510	0.35690	0.36363
1.0000	0.8820	1125	0.4402	0.38161	0.34494
Ethyl Acetate + Butanol					
0.0000	0.8040	1196	2.2045	0.02879	0.93886
0.1063	0.8056	1194	1.4102	0.05784	0.72809
0.2151	0.8168	1184	1.0541	0.09105	0.61710
0.3213	0.8269	1180	0.8149	0.13714	0.53084
0.4327	0.8322	1176	0.8129	0.14106	0.51618
0.5192	0.8420	1170	0.5978	0.22702	0.43625
0.6266	0.8424	1167	0.5290	0.27918	0.39871
0.7124	0.8581	1154	0.4890	0.31567	0.38101
0.8127	0.8666	1142	0.4611	0.34790	0.36421
0.9044	0.8742	1134	0.4533	0.36108	0.35557
1.0000	0.8820	1125	0.4402	0.38161	0.34494
Ethyl Acetate + Hexanol					
0.0000	0.8128	1298	4.5642	0.01768	0.76533
0.0996	0.8214	1292	2.8302	0.03523	0.62247
0.2225	0.8338	1287	2.0351	0.05597	0.54978
0.3149	0.8355	1275	1.5522	0.08122	0.49429
0.4151	0.8406	1257	1.2032	0.11401	0.45038
0.5186	0.8466	1247	0.9528	0.15624	0.41469
0.6083	0.8544	1240	0.7949	0.19927	0.39077
0.7096	0.8617	1222	0.6724	0.24487	0.37353
0.8066	0.8672	1210	0.5862	0.28991	0.36080
0.9041	0.8780	1192	0.5216	0.33007	0.34774
1.0000	0.8820	1125	0.4402	0.38161	0.34494
Ethyl Acetate + Octanol					
0.0000	0.8242	1327	7.8512	0.01165	0.66872
0.1056	0.8259	1312	4.7776	0.02292	0.55668
0.2095	0.8300	1294	3.2258	0.03838	0.49024
0.3174	0.8318	1275	2.2206	0.06206	0.43728
0.4286	0.8387	1239	1.5414	0.09634	0.37509
0.5083	0.8400	1225	1.2853	0.11928	0.38467
0.6196	0.8444	1214	0.9417	0.17562	0.35719
0.7090	0.8586	1192	0.8858	0.17723	0.37519
0.8064	0.8651	1164	0.6239	0.27175	0.34396
0.9044	0.8716	1148	0.5565	0.29587	0.35364
1.0000	0.8820	1125	0.4402	0.38161	0.34494

The measured values density (ρ), viscosity (η) and sound velocity (u) and the evaluated parameters are presented in Table 2. For the binary system ethyl acetate + methanol, ethyl acetate + ethanol, ethyl acetate + propanol, ethyl acetate + butanol, ethyl acetate + hexanol and ethyl acetate + octanol at 303.15 K. From Tables it can be noticed that, at the 303.15 K temp. The value of viscosity, sound velocity and internal pressure decease with increase in mole fraction of ethyl acetate (X_1) but the value of density (ρ) and free volume (V_f) increase with increase in mole fraction of ethyl acetate (X_1). It is evident that the pronounced increase or decrease in these parameters with composition of mixtures indicates the presence of interaction between the component molecules in the binary mixtures. It can also be observed that the ultrasonic velocity is decreasing with increase in mole fraction of ethyl acetate. This trend indicates specific interactions among the constituents of the mixtures. This behavior can be attributed to intermolecular interaction [31-32]. The chemical interaction may involve the association due to hydrogen bonding order to dipole-dipole interaction or may be due to the formation of charge-transfer complexes. All these process may lead to strong interaction forces [33]. The decrease in velocity in these liquid mixtures suggest that molecular interactions among the molecules of the components of liquid mixture.

An analysis of the viscosity values from the Table 2 it can be observed that the viscosity is in decrease trend with increase in mole fraction of ethyl acetate. Similar trend is also observed for the internal pressure values. This kind of non-linearity indicates the presence of molecular interactions.

It is observed that for the binary liquid mixtures, the density (ρ) and free volume (V_f) increase with increase in concentration of ethyl acetate. The increases the density (ρ) and free volume (V_f) in these liquid mixtures suggest that molecular interaction among the molecules of the components of liquid mixture.

4.1 Excess Acoustical and Thermodynamic Parameters

In order to understand the nature of molecular interactions between the components of the liquid mixtures, it is of interest to discuss the same in terms of excess parameters rather than actual values. Non-ideal liquid mixtures show considerable deviation from linearity in their concentrations and this can be interpreted as the presence of strong or weak interactions. The extent of deviation depends upon the nature of the constituents and composition of the mixtures. The thermodynamic excess properties are found to be more sensitive towards intermolecular interaction among the component molecules of liquid mixtures. The sign and extent of deviation of excess parameters depend on the strength of interaction between unlike molecules [34]. So various excess acoustic and thermodynamic parameters have been evaluated and corresponding graphs are also given.

Table 3. Excess values of sound velocity (u^E), viscosity (η^E), free volume(V_f^E) and internal pressure (P_i^E) properties for binary liquids mixtures of ethyl acetate + methanol, ethyl acetate + ethanol, ethyl acetate + propanol, ethyl acetate + butanol, ethyl acetate + hexanol and ethyl acetate + octanol at 303.15 K.

Mole fraction of ethyl acetate (X_1)	Excess sound velocity (u^E)	Excess Viscosity (η^E) CP	Excess Free volume (V_f^E) ml mol^{-1}	Excess internal pressure ($p_i^E \times 10^4$) atm
Ethyl Acetate + Methanol				
0.0000	0.00	0.0000	0.0000	0.0000
0.1039	+7.57	-0.0610	-0.0096	-0.3055
0.2248	+8.10	-0.0841	-0.0202	-0.4421
0.3129	+8.19	-0.1153	-0.0269	-0.4689
0.4370	+9.81	-0.2102	-0.0309	-0.4732
0.5474	+10.51	-0.2374	-0.0331	-0.4070
0.6409	+6.74	-0.1346	-0.0303	-0.2967
0.7128	+4.79	-0.1292	-0.0297	-0.2885
0.8164	+4.54	-0.0813	-0.0223	-0.1923
0.9104	+1.69	-0.0561	-0.0168	-0.0956
1.0000	0.00	0.0000	0.0000	0.0000
Ethyl Acetate + Ethanol				
0.0000	0.00	0.0000	0.0000	0.0000
0.1049	+0.83	-0.4101	-0.0206	-0.3708
0.2090	+1.32	-0.4321	-0.0257	-0.4023
0.3105	+2.01	-0.4805	-0.0312	-0.4209
0.4166	+2.30	-0.5123	-0.0389	-0.4438
0.5094	+2.64	-0.6432	-0.0412	-0.4821
0.6076	+1.84	-0.2704	-0.0495	-0.3438
0.7150	+1.76	-0.2475	-0.0325	-0.2963
0.8069	+1.73	-0.1280	-0.0246	-0.2240
0.9030	+0.76	-0.0615	-0.0211	-0.1585
1.0000	0.00	0.0000	0.0000	0.0000
Ethyl Acetate + Propanol				
0.0000	0.00	0.0000	0.0000	0.0000
0.1074	+1.04	-0.3182	-0.0108	-0.1542
0.2086	+1.37	-0.4707	-0.0191	-0.2345
0.3145	+1.87	-0.4848	-0.0216	-0.2530
0.4099	+1.90	-0.5026	-0.0369	-0.2564
0.4758	+2.86	-0.5618	-0.0486	-0.2640
0.5430	+3.05	-0.4390	-0.0512	-0.2334
0.6127	+1.88	-0.3840	-0.0416	-0.2056
0.7564	+1.50	-0.2506	-0.0315	-0.1384
0.9126	+0.96	-0.1659	-0.0186	-0.0495
1.0000	0.00	0.0000	0.0000	0.0000
Ethyl Acetate + Butanol				
0.0000	0.00	0.0000	0.0000	0.0000
0.1063	+3.29	-0.6066	-0.0084	-0.1476
0.2151	+5.57	-0.7707	-0.0134	-0.1939
0.3213	+6.83	-0.8224	-0.0150	-0.2171
0.4327	+10.74	-0.8880	-0.0404	-0.2656
0.5192	+10.88	-0.8905	-0.0450	-0.2942
0.6266	+15.51	-0.5698	-0.0512	-0.1679
0.7124	+8.60	-0.4585	-0.0355	-0.1347
0.8127	+3.72	-0.3094	-0.0131	-0.0919
0.9044	+2.24	-0.1552	-0.0108	-0.0460
1.0000	0.00	0.0000	0.0000	0.0000
Ethyl Acetate + Hexanol				
0.0000	0.000	0.0000	0.0000	0.0000
0.0996	+11.26	-1.3229	-0.0187	-0.1009
0.2225	+27.52	-1.6113	-0.0426	-0.1219
0.3149	+31.50	-1.7131	-0.0516	-0.1386
0.4151	+32.50	-1.8488	-0.0547	-0.1404
0.5186	+38.84	-1.9126	-0.0398	-0.1623
0.6083	+30.27	-1.4724	-0.0310	-0.1326
0.7096	+28.79	-1.2602	-0.0213	-0.1187
0.8066	+20.56	-0.9649	-0.0166	-0.0934
0.9041	+13.87	-0.6514	-0.0120	-0.0654
1.0000	0.000	0.0000	0.0000	0.0000
Ethyl Acetate + Octanol				
0.0000	0.00	0.0000	0.0000	0.0000
0.1056	+6.36	-2.2921	-0.0278	-0.0778
0.2095	+9.36	-3.0735	-0.0508	-0.1106
0.3174	+12.14	-3.2790	-0.0670	-0.1286
0.4286	+13.42	-3.4681	-0.0738	-0.1548
0.5083	+14.73	-4.2162	-0.0804	-0.1694
0.6196	+12.18	-2.7995	-0.0967	-0.1194
0.7090	+8.25	-2.3178	-0.0652	-0.1109
0.8064	+5.07	-1.7108	-0.0503	-0.0632
0.9044	+3.72	-1.1250	0.0315	-0.0222
1.0000	0.00	0.0000	0.0000	0.0000

The sign and magnitude of excess ultrasonic velocity (u^E) play an important role in describing molecular rearrangement as a result of the molecular interaction between the component molecules in the mixtures. The excess ultrasonic velocity (u^E) curves at 303.15 K varying with mole fraction of ethyl acetate are represented in Figure-1 for the six binary systems. The excess ultrasonic velocity values exhibiting positive in all six binary systems. Generally, the value of the excess function (u^E) depend upon several physical and chemical contributions [35-36]. The physical contribution depends mainly on two factors, namely:

1. The dispersion forces or weak dipole-dipole interaction that leads to positive values.
2. The geometrical effect allowing the fitting of molecules of two different sizes in to each other's structure resulting in negative values.

The chemical contributions include breaking up of the associates present in pure liquids, resulting in positive u^E. In the present mixture the graphical representation of excess sound velocity (u^E) are positive, presented in Figure 1. The positive values reveal that there are present weak interactions in the mixture.

The observed positive trends in excess sound velocity indicate that the effect due to the breaking up of self-associated structure of the components of the mixtures is dominant over the effect of hydrogen bonding and dipole-dipole interaction between unlike molecule. The excess sound velocity values in the sequence methanol < ethanol < propanol < butanol < hexanol < octanol which also reflects

the decreasing strength of interaction unlike molecule in the mixture.

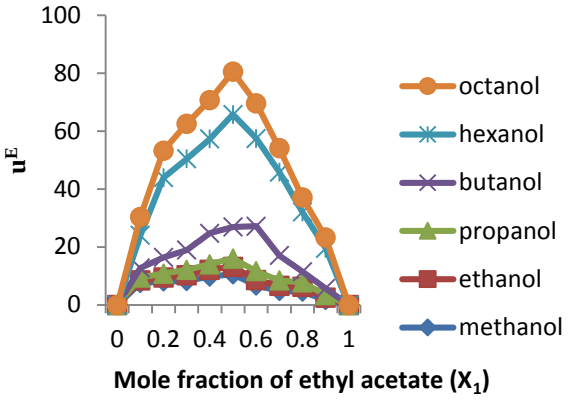

Figure 1. Plots of excess sound velocity versus mole fraction of ethyl acetate (X_1) at 303.15 K for binary mixtures of ethyl acetate with methanol, ethanol, propanol, butanol, hexanol and octanol at 303.15 K.

The measurement of viscosity in binary liquid mixture gives some reliable information in the study of intermolecular interaction. The molecules of one or more components forming the temarise are either polar, associating or accordingly show non-ideal behavior's in mixtures. Negative values of η^E in most of the cases are the consequence of lower viscosity contributions of similar non-specific interaction and hydrogen bonding effect of molecular species in real mixtures rather than those in the corresponding ideal mixtures.

In the present study, it is observed that, for the six binary systems the η^E values gradually decrease up to the mole fraction around 0.5 and then begins to increase Figure 2 more over it is observed that the η^E values decrease as the concentration of X_1 increase. The negative values imply the presence of dispersion forces between the mixing components in the mixtures.

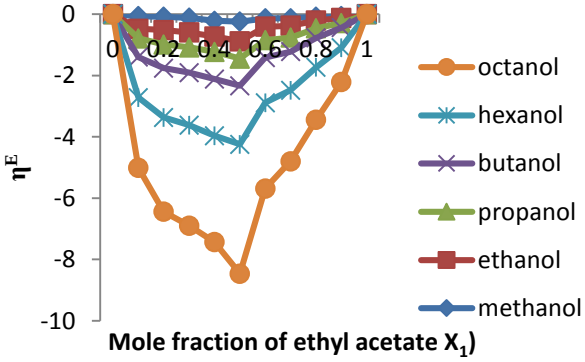

Figure 2. Plots of excess viscosity versus mole fraction of ethyl acetate (X_1) at 303.15 K for binary mixtures of ethyl acetate with methanol, ethanol, propanol, butanol, hexanol and octanol at 303.15 K.

The excess free volume (V_f^E) is another important parameter through which molecular interactions can be explained.

In the present investigation the negative excess free volume (V_f^E) for binary mixtures of ethyl acetate with alkanols may be attributed to hydrogen bond formation through dipole-dipole interaction between alkanol and ethyl acetate molecule or to structural contributions arising from the geometrical fitting of one component (alkanol) into the other (ethyl acetate) due to difference in the free volume between components.

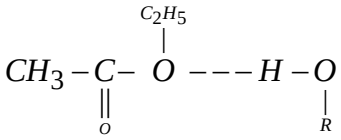

Figure 3. Hydrogen bonding between ethyl acetate and 1-alkanol molecule.

In order to substantiate the presence of interaction between the molecules, it is essential to study the excess parameter such as free volume. The deviation of physical property of the liquid mixtures from the ideal behavior is a measure of the interaction between the molecules which is attributed to either adhesive or cohesive forces [37]. In the present study, alkanols in a polar and has self - association character in other polar organic solvents.

Figure 4. Self association of 1-alkanol molecule.

The negative values of excess free volume (V_f^E) indicate the presence of strong molecular interaction [38-39]. 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 alkanols is disrupted. It is also concluded that suryanarayana approach for estimating free volume of binary liquid mixtures, based on dimensional analysis using thermodynamic consideration is very well applicable in the present case.

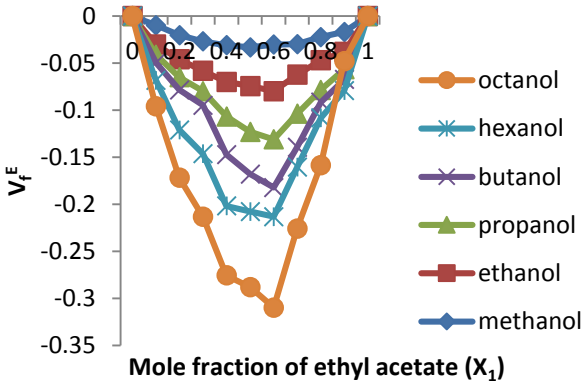

Figure 5. Plots of excess free volume versus mole fraction of ethyl acetate (X_1) at 303.15 K for binary mixtures of ethyl acetate with methanol, ethanol, propanol, butanol, hexanol and octanol at 303.15 K.

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 6.

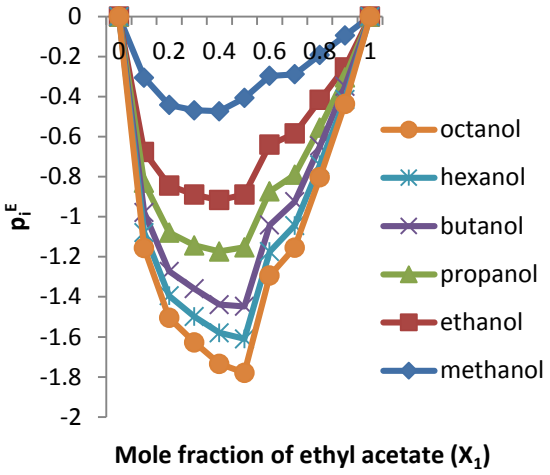

Figure 6. Plots of excess internal pressure versus mole fraction of ethyl acetate (X_1) at 303.15 K for binary mixtures of ethyl acetate with methanol, ethanol, propanol, butanol, hexanol and octanol at 303.15 K.

This suggests that dipole and dispersion force are operative in these systems, when the ethyl acetate concentration low. When the concentration of ethyl acetate leads to specific interactions, i.e. the interactions move from weak to strong which supports the above arguments is case of other parameters

5. Conclusions

From the observed thermodynamic studies of six binary liquid mixtures of six binary liquid mixtures ethyl acetate + methanol, ethyl acetate + ethanol, ethyl acetate + propanol, ethyl acetate + butanol, ethyl acetate + hexanol and ethyl acetate + octanol at 303.15 K are shown negative values of excess free volume and excess internal pressure may given information about the considerable interactions among the molecules of the between these binary mixtures, so we concludes that interactions are exist may be due to dipole-dipole interactions. It is also concluded that Suryanarayana [40] approach for estimating free volume and internal pressure of binary liquid mixtures, based on dimensional analysis using thermodynamic considerations is very well applicable in the present case.

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Nomenclature

ρ Densities of liquid
u, Ultrasonic velocity
u^E, excess ultrasonic velocity
η, Viscosity
η^E, excess viscosity
V_f, Free Volume
V_f^E, Excess values of free volume
P_i, Internal pressure
P_i^E, Excess internal pressure
X_1, Mole fraction of ethyl acetae
Y^E, Thermodynamic excess function

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