INVESTIGATION OF THERMO-ACOUSTIC PROPERTIES OF WATER-ETHANOL BINARY MIXTURE AT DIFFERENT TEMPERATURES

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Abstract

The density, ultrasonic velocity and viscosity were measured using Anton Paar DSA 5000 M in the binary mixtures of ethanol with water at various mole fractions from 0.1 to 0.9 at T = (288.15, 293.15, 298.15, 303.15, 308.15, 313.15 and 318.15) K. The isentropic compressibility, relative association, free volume, relaxation time, Gibbs free energy, internal pressure, and solubility parameter were calculated using the values of experimental density, sound velocity and viscosity. Non covalent interaction taking place in the liquid mixture have been discussed on the basis of the values obtained from experimental parameters and derived parameters.

Key words: Isentropic compressibility, relative association, free volume, relaxation time, Gibbs free energy, internal pressure, solubility parameter, intermolecular non-covalent interactions.

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1. Introduction

From fundamental as well as engineering point of view, the knowledge of structure and molecular interactions of liquid mixtures is very important. For a better understanding of the non-ideal behavior of complex systems formed from liquids, fundamental thermodynamic and thermo-acoustic properties are essential and necessary sources of information because of physical and chemical effects, caused by intermolecular forces, molecular interactions *etc*. of unlike molecules. These properties are necessary from a practical point of view, for development of thermodynamic models required in adequate and optimized processes of the chemical, food processing, drugs industries, petrochemical, pharmaceutical, paint industries, fluid mechanics etc. [1,2]. The compositional dependence of thermodynamic properties has been proven to be useful as a tool in understanding the nature and extent of patterns of molecular aggregation arising from intermolecular interaction between components of mixture. Molecular interactions in liquid mixtures have been extensively studied using ultrasonic technique by many workers which are very essential for understanding the physicochemical behavior of the binary and multi-component liquid mixtures [3].

In recent years, the behavior of multi-component liquid mixtures has gained more importance rather than the single component due to their widespread range of applications. Thermodynamic parameters derived from the measurement of ultrasonic velocities, densities and viscosities for binary liquid mixtures may be found useful in understanding the nature and type of intermolecular interactions taking place in between the constituent molecules. In chemical process industries, materials are normally handled in liquid form and thus the physical, chemical and transport properties of liquids, assume importance. Thus, data on ultrasonic velocity, viscosity and density invention has found extensive applications in solution theory models and molecular dynamics [4,5].

Ultrasonic velocity in a medium is fundamentally related to the binding forces between the molecules. Ultrasonic velocities of liquid mixtures consisting of polar as well as non-polar components are of considerable importance in understanding intermolecular interaction between components molecules and are applicable in several industrial and technological processes [6,7]. Acoustical and thermodynamical study of liquid mixtures provide enough knowledge about the association of molecular packing, molecular motion and strength of intermolecular interactions. Thermodynamic and acoustical properties such as adiabatic compressibility, intermolecular free length, internal pressure, acoustic impedance, relaxation time, classical absorption and surface tension can be calculated from measured ultrasonic velocity, density and viscosity for binary mixtures and are found to be helpful in interpretation of nature and type of intermolecular interactions between the component molecules [8,9,10].

Using the measured values of sound velocity (u) and density (ρ), the thermodynamic parameters such as isentropic compressibility, internal pressure, solubility parameter, free volume and Gibbs free energy can be computed [11,12]. Thus, data on some of the properties associated with liquids and liquid mixtures like density, viscosity and ultrasonic velocity can be used to find extensive application in solution theory and molecular dynamics. Such results are necessary for interpretation of data obtained from thermochemical, electrochemical, biochemical and kinetic studies [13,14].

2. Material and methods

Literature survey showed that measurements have been previously reported for the water-ethanol binary mixture at limited range of temperature. The objective of the present investigation was to find out the density (ρ), viscosity (η) and ultrasonic velocity (U) for the binary system constituted by these components at T = (288.15, 293.15, 298.15, 303.15, 308.15, 313.15 and 318.15) K over the concentration range of 0.1 to 0.9 mole fraction. The experimental values were used to calculate isentropic compressibility (βa), relaxation time (τ), relative association (), free volume (V_f), solubility parameter (), Gibbs free energy (ΔG) and internal pressure (πi) over the entire concentration range for the binary mixtures. The results are discussed in terms of the molecular interactions.

The chemical Ethanol (CAS 64-17-5) used in present work was procured from Merck KGaA, Darmstadt, Germany with assay of 99.8%. It was absolute ethanol of analysis grade and used without further purification. The Milli-Q water (Millipore SAS 67/20 Mosheim) of 10^7 S cm^{-1} conductance was used for experimental purpose. The glassware was cleaned using standard methods and dried to absolute dryness which was further checked with anhydrous $CuSO_4$.

The equipment used for measurements of density, viscosity and ultrasonic velocity was Anton Paar DSA 5000 M having range, up to 3g/cc with 0.000007 g/cc accuracy for density, 1000 to 2000 m/s with 0.01 m/s accuracy for ultrasonic velocity, 0.2 to 30,000 mm^2/s range for viscosity with 0.1% accuracy and temperature range from 0^0C to 100^0C with repeatability of 0.001^0C. This equipment works based on oscillation periods of quarts U tube with air, solvent and solutions [15].

For each experimental measurement, the tube was cleaned with acetone first and then dried by passing dried air through the tube using air pump. This process of drying the tube was continued till a constant oscillation period was obtained as was done during the initial instrument calibration.

The literature and experimental density, speed of sound and viscosity value of pure water and ethanol with standard deviation at T = (288.15, 293.15, 298.15, 303.15, 308.15, 313.15 and 318.15) K, are given in table 2.1 which shows accuracy and calibration of instruments.

Table 2.1

T/K	Lit	$\rho/(g\ cm^{-3})$	б	Lit	$u/(m\ s^{-1})$	б	Lit	η(mPa.s)	б
Ethanol									
293.15	0.78950[16]	0.790173	6.73×10^{-4}	1161.78[18]	1161.82	0.04	1.1870[20]	1.18635	6.5×10^{-4}
298.15	0.78520[17]	0.785885	6.85×10^{-4}	1144.00[19]	1144.03	0.03	1.0820[20]	1.08135	6.5×10^{-4}
303.15	0.78070[16]	0.781576	8.76×10^{-4}	1127.58[18]	1127.62	0.04	0.9870[20]	0.98628	7.2×10^{-4}
308.15	0.77690[17]	0.777233	3.33×10^{-4}				0.9015[20]	0.90056	9.4×10^{-4}
313.15	0.77210[16]	0.772851	7.51×10^{-4}	1094.07[18]	1094.09	0.02	0.8306[20]	0.83051	9.0×10^{-5}
318.15	0.76840[17]	0.768422	2.2×10^{-5}				0.7642[20]	0.76332	8.8×10^{-4}
Water									
288.15							1.1381[22]	1.13960	1.5×10^{-3}
293.15	0.99820[20]	0.998297	9.7×10^{-5}				1.0020[22]	1.00370	1.7×10^{-3}
298.15	0.99705[20]	0.997141	9.1×10^{-5}	1496.60[21]	1496.51	0.09	0.8903[22]	0.89234	2.04×10^{-3}
303.15	0.99565[20]	0.995748	9.8×10^{-5}	1509.10[21]	1509.06	0.04	0.7976[22]	0.80107	3.47×10^{-3}
308.15	0.99400[20]	0.994137	1.37×10^{-4}	1519.80[21]	1519.72	0.08	0.7195[22]	0.72593	6.43×10^{-3}
313.15	0.99220[20]	0.992326	1.26×10^{-4}	1528.89[21]	1528.85	0.03	0.6531[22]	0.66384	1.07×10^{-2}
318.15							0.5963[22]	0.61060	1.43×10^{-2}

3. Theory and calculations

The various acoustical parameters computed from experimental parameters using the following relations,

Isentropic Compressibility [23] $\beta_a = (U^2\rho)^{-1}$ (1)

Relative Association [24] $R_A = \rho/\rho_o\,(U_o/U)^{1/3}$ (2)

Free Volume [25] $V_f = (M_{eff}\,U/\eta K)^{3/2}$ (3)

Relaxation Time [26] $\tau = 4/3\,\eta\,\beta_a$ (4)

Gibb's Free Energy [27] $\Delta G = K_b.T.\mathrm{Log}_e h/(\tau.K_b.T)$ (5)

Internal Pressure [28] $\pi_i = bRT(K\eta/U)^{1/2}\left(\rho^{2/3}/M_{eff}\right)^{7/6}$ (6)

Solubility Parameter [29] $\delta s = \sqrt{p*}/V$ (7)

Where, K is the temperature independent Jacobson's constant

The evaluation of theoretical values of ultrasonic velocity, viscosity and density in binary mixture those obtained experimentally in the binary mixture is expected to interpret the nature of interaction between components of the mixture. Such theoretical study is useful in the wide-ranging theoretical modeling for the liquid mixtures [30].

4. Result and discussion

Table 4.1 Density Vs. Concentration

	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.1	967.460	964.347	961.110	958.108	954.551	951.035	946.807
0.2	941.175	937.317	933.460	929.543	925.612	920.941	915.934
0.3	914.482	910.335	906.034	901.950	897.071	892.715	887.949
0.4	889.539	885.436	881.284	877.078	872.812	868.481	864.084
0.5	869.076	864.855	860.581	856.247	851.854	847.399	842.883
0.6	849.549	845.266	840.934	836.547	832.106	827.612	823.053
0.7	832.626	828.314	823.953	819.544	815.088	810.576	806.000
0.8	818.453	814.142	809.788	805.396	800.957	796.465	791.911
0.9	805.852	801.565	797.239	792.885	788.489	784.043	779.544

Table 4.2 Viscosity Vs Concentration

	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.1	0.002722	0.002244	0.001881	0.001601	0.001374	0.001202	0.001059
0.2	0.003464	0.002827	0.002344	0.001972	0.00168	0.001449	0.001262
0.3	0.003425	0.002843	0.002368	0.002015	0.001736	0.001508	0.001321
0.4	0.0031147	0.0026164	0.0022212	0.0019047	0.0016473	0.0014378	0.0012732
0.5	0.0026749	0.0022866	0.001972	0.0017134	0.0014991	0.0013209	0.0011707
0.6	0.0023282	0.0020162	0.0017593	0.0015439	0.0013631	0.0012098	0.0010795
0.7	0.0020094	0.001765	0.001558	0.001381	0.0012304	0.0011009	0.0009899
0.8	0.0017623	0.0015625	0.0013915	0.0012441	0.0011171	0.0010072	0.000911
0.9	0.0015429	0.0013834	0.0012441	0.0011225	0.0010163	0.0009228	0.0008402

Table 4.3 Ultrasonic Velocity Vs Concentration

	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.1	1632.10	1626.40	1620.28	1613.80	1606.84	1599.41	1591.44
0.2	1581.56	1569.45	1557.19	1544.71	1532.06	1519.24	1506.27
0.3	1496.36	1484.37	1470.06	1456.56	1442.84	1428.88	1414.73
0.4	1423.12	1409.34	1395.36	1381.18	1366.77	1351.98	1336.89
0.5	1372.74	1357.73	1342.51	1327.20	1311.58	1295.90	1279.98
0.6	1323.78	1307.98	1292.07	1276.13	1259.95	1243.64	1227.16
0.7	1282.58	1265.94	1249.27	1232.57	1215.90	1199.21	1182.36
0.8	1246.28	1229.30	1212.35	1195.36	1178.31	1161.33	1144.35
0.9	1211.91	1194.78	1177.62	1160.64	1143.73	1126.86	1110.02

Table 4.4 Isentropic Compressibility Vs Concentration

	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.1	-6.819E+12	-6.772E+12	-6.721E+12	-6.667E+12	-6.610E+12	-6.549E+12	-6.484E+12
0.2	-6.403E+12	-6.306E+12	-6.208E+12	-6.108E+12	-6.009E+12	-5.909E+12	-5.808E+12
0.3	-5.732E+12	-5.641E+12	-5.532E+12	-5.431E+12	-5.329E+12	-5.227E+12	-5.124E+12
0.4	-5.185E+12	-5.085E+12	-4.984E+12	-4.884E+12	-4.782E+12	-4.679E+12	-4.575E+12
0.5	-4.824E+12	-4.719E+12	-4.614E+12	-4.509E+12	-4.404E+12	-4.299E+12	-4.194E+12
0.6	-4.486E+12	-4.380E+12	-4.274E+12	-4.169E+12	-4.064E+12	-3.959E+12	-3.855E+12
0.7	-4.211E+12	-4.103E+12	-3.995E+12	-3.889E+12	-3.785E+12	-3.682E+12	-3.579E+12
0.8	-3.976E+12	-3.869E+12	-3.763E+12	-3.658E+12	-3.554E+12	-3.453E+12	-3.352E+12
0.9	-3.760E+12	-3.654E+12	-3.550E+12	-3.449E+12	-3.349E+12	-3.251E+12	-3.154E+12

Table 4.5 Relative Association Vs Concentration

	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.1	0.934226	0.936633	0.938758	0.941019	0.942605	0.944201	0.945095
0.2	0.918424	0.921261	0.923902	0.926377	0.928664	0.930131	0.931195
0.3	0.909001	0.911519	0.914134	0.916657	0.918211	0.920242	0.921809
0.4	0.899123	0.902050	0.904755	0.907310	0.909656	0.911923	0.914117
0.5	0.889057	0.892108	0.894945	0.897610	0.900095	0.902441	0.904712
0.6	0.879666	0.882819	0.885749	0.888504	0.891078	0.893545	0.895925
0.7	0.871278	0.874586	0.877663	0.880581	0.883270	0.885829	0.888306
0.8	0.864682	0.868080	0.871243	0.874267	0.877090	0.879770	0.882337
0.9	0.859343	0.862822	0.866092	0.869184	0.872053	0.874791	0.877421

Table 4.6 Free Volume Vs Concentration

	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.1	4.982E-09	6.620E-09	8.578E-09	1.086E-08	1.357E-08	1.647E-08	1.977E-08
0.2	4.001E-09	5.365E-09	7.023E-09	8.991E-09	1.129E-08	1.392E-08	1.691E-08
0.3	4.432E-09	5.790E-09	7.507E-09	9.432E-09	1.163E-08	1.415E-08	1.701E-08
0.4	5.514E-09	7.058E-09	8.889E-09	1.102E-08	1.349E-08	1.628E-08	1.921E-08
0.5	7.531E-09	9.372E-09	1.151E-08	1.396E-08	1.676E-08	1.991E-08	2.342E-08
0.6	9.961E-09	1.214E-08	1.462E-08	1.746E-08	2.065E-08	2.421E-08	2.816E-08
0.7	1.331E-08	1.585E-08	1.874E-08	2.200E-08	2.563E-08	2.967E-08	3.406E-08
0.8	1.728E-08	2.028E-08	2.364E-08	2.737E-08	3.148E-08	3.598E-08	4.092E-08
0.9	2.237E-08	2.579E-08	2.960E-08	3.379E-08	3.837E-08	4.337E-08	4.880E-08

Table 4.7 Relaxation Time Vs Concentration

	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.1	1.408E-12	1.173E-12	9.940E-13	8.555E-13	7.433E-13	6.588E-13	5.888E-13
0.2	1.962E-12	1.633E-12	1.381E-12	1.185E-12	1.031E-12	9.089E-13	8.097E-13
0.3	2.230E-12	1.890E-12	1.613E-12	1.404E-12	1.239E-12	1.103E-12	9.911E-13
0.4	2.305E-12	1.984E-12	1.726E-12	1.518E-12	1.347E-12	1.208E-12	1.099E-12
0.5	2.178E-12	1.912E-12	1.695E-12	1.515E-12	1.364E-12	1.238E-12	1.130E-12
0.6	2.085E-12	1.859E-12	1.671E-12	1.511E-12	1.376E-12	1.260E-12	1.161E-12
0.7	1.956E-12	1.773E-12	1.615E-12	1.479E-12	1.361E-12	1.259E-12	1.171E-12
0.8	1.848E-12	1.693E-12	1.559E-12	1.441E-12	1.339E-12	1.250E-12	1.171E-12
0.9	1.738E-12	1.612E-12	1.500E-12	1.401E-12	1.314E-12	1.236E-12	1.166E-12

Table 4.8 Gibb's Free Energy Vs Concentration

	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.1	8.481E-21	7.958E-21	7.483E-21	7.050E-21	6.639E-21	6.295E-21	5.972E-21
0.2	9.798E-21	9.295E-21	8.834E-21	8.414E-21	8.030E-21	7.685E-21	7.370E-21
0.3	1.031E-20	9.887E-21	9.472E-21	9.122E-21	8.812E-21	8.522E-21	8.257E-21
0.4	1.044E-20	1.008E-20	9.752E-21	9.448E-21	9.166E-21	8.913E-21	8.712E-21
0.5	1.021E-20	9.935E-21	9.678E-21	9.439E-21	9.219E-21	9.018E-21	8.834E-21
0.6	1.004E-20	9.820E-21	9.619E-21	9.429E-21	9.256E-21	9.097E-21	8.953E-21
0.7	9.787E-21	9.628E-21	9.480E-21	9.339E-21	9.211E-21	9.093E-21	8.991E-21
0.8	9.562E-21	9.443E-21	9.333E-21	9.232E-21	9.142E-21	9.062E-21	8.990E-21
0.9	9.317E-21	9.244E-21	9.176E-21	9.114E-21	9.060E-21	9.012E-21	8.972E-21

Table 4.9 Internal Pressure Vs Concentration

	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.1	3624125768	3346357499	3114935844	2921737307	2750480729	2613960882	2491565764
0.2	3518503531	3237329623	3001653444	2802795453	2633050959	2487094872	2359684723
0.3	3095587031	2872151251	2670488795	2508760018	2369677338	2248073630	2140697372
0.4	2641804067	2467709440	2316798817	2185581611	2070207717	1969666788	1887306101
0.5	2205517965	2079241124	1968454739	1870064165	1782510295	1704664187	1634731797
0.6	1871321423	1776332189	1692177230	1616192282	1548050298	1486390831	1430763199
0.7	1592137724	1522745345	1459611670	1401669813	1349144541	1301059062	1257578617
0.8	1375119977	1321708343	1272853003	1227950119	1186934064	1149358918	1114494564
0.9	1194212200	1154538668	1117597612	1083292217	1051595698	1022056384	994485825

Table 4.10 Solubility Parameter Vs Concentration

	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.1	60,200.7	57,847.7	55,811.6	54,053.1	52,445.0	51,126.9	49,915.6
0.2	59,317.0	56,897.5	54,787.3	52,941.4	51,313.3	49,870.8	48,576.6
0.3	55,638.0	53,592.5	51,676.8	50,087.5	48,679.3	47,413.9	46,267.7
0.4	51,398.5	49,676.0	48,133.1	46,750.2	45,499.5	44,380.9	43,443.1
0.5	46,962.9	45,598.7	44,367.3	43,244.2	42,219.8	41,287.6	40,431.8
0.6	43,258.8	42,146.6	41,136.1	40,201.9	39,345.3	38,553.7	37,825.4
0.7	39,901.6	39,022.4	38,204.9	37,438.9	36,730.7	36,070.2	35,462.4
0.8	37,082.6	36,355.3	35,677.1	35,042.1	34,451.9	33,902.2	33,384.0
0.9	34,557.4	33,978.5	33,430.5	32,913.4	32,428.3	31,969.6	31,535.5

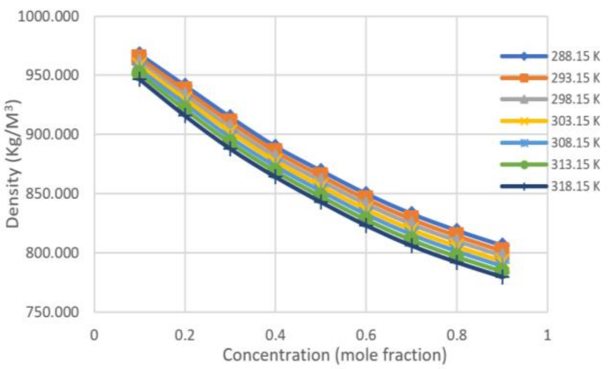

Fig. 4.1 : Variation of Density Vs. Concentration of ethanol at different temp., water-ethanol system

4.1 - From the Fig. 4.1, it is observed that density of water-ethanol solution decreases smoothly with increase in concentration of ethanol in water. When solute is added to the solvent, solute molecules may get strongly or weakly associated with solvent molecules, changing the packing of the medium and affecting its density. In this case of water and ethanol, there must be a weak association taking place between component molecules thereby decreasing the density with increase in concentration of ethanol. It can be concluded that the hydrogen bonding initially existing between water molecules decreases with addition of ethanol, thereby increasing the intermolecular distance, hence density decreases. Thus, hydrogen bonding shows the order water-water > water-ethanol > ethanol-ethanol.

The density of water-ethanol solution is found to decrease with increase in temperature. As the temperature increases, the noncovalent interactions like Van der Waals forces and dipole-dipole become weak resulting due to thermal agitation of the components of the mixtures. The medium becomes loosely packed leading to decrease in density of the medium with increase in temperature [31].

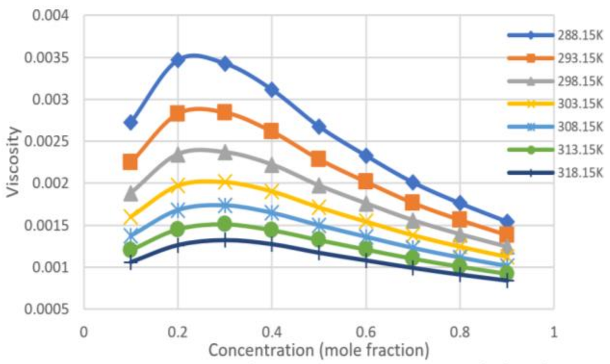

Fig. 4.2 : Variation of Viscosity Vs. Concentration of ethanol at different temp., water-ethanol system

4.2 - From the Fig. 4.2, the viscosity of water-ethanol solution is first found to increase up to 0.3M concentration and then decrease with increase in ethanol concentration. The variation of viscosity is a consequence of the variation in surface area, relative velocity and the structure (shape, size and geometry) of the molecules of the liquid medium. When polar solute molecules like ethanol are added to a solvent (water), these ethanol molecules can polarize the water molecules. This polarization depends on the strength of polarity of solute molecules. Ethanol molecules can exert high electric fields on the surrounding water molecules if the magnitude of its dipole moment is high, resulting in the production of additional order of water molecules beyond first hydration shell. As a result of this effect, the viscosity of solution increases. This effect is maximum at 0.3M concentration, hence the viscosity.

As the temperature of water-ethanol solution increases, the cohesion and frictional forces get reduced due to thermal motion of component molecules increasing the relative velocity and hence the viscosity gets decreased with rise in temperature [32-35].

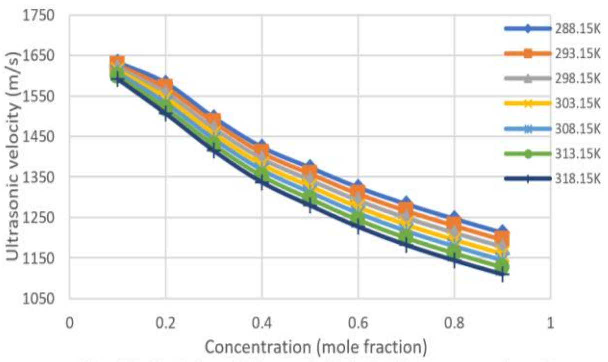

Fig. 4.3 : Variation of Ultrasonic Velocity Vs. Concentration of ethanol at different temp., water-ethanol system

4.3 - From the Fig. 4.3, it can be observed that the ultrasonic velocity decreases with increase in ethanol concentration. The decrease in ultrasonic velocity in any solution suggests the lesser association among the components of the solution. The lesser association is due to decreased intermolecular hydrogen bonding between component molecules. In the water-ethanol solution, a slow but steady decrease of ultrasonic velocity is observed as the concentration of ethanol increases. This indicates steady decrease in interactive forces existing between the component molecules.

The ultrasonic velocity of water-ethanol solution is found to decrease with increase in the temperature. This is because, at higher temperatures, kinetic energy of system increases and medium becomes loosely packed, increasing the spacing among the molecules due to weakening of the weak electrostatic forces of attraction as mentioned above thereby decreasing the ultrasonic velocity at elevated temperatures [36-38].

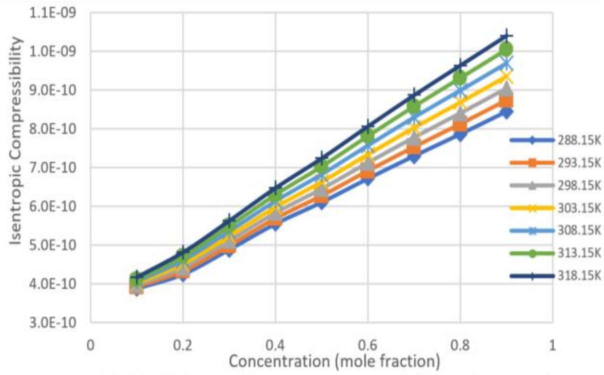

Fig. 4.4 : Variation of Isentropic Compressibility vs. Concentration of Ethanol at different temp., Water-Ethanol system

4.4 - From the Fig. 4.4, the isentropic compressibility of water-ethanol solution is found to increase with increase in ethanol concentration. The increase in isentropic compressibility implies the decrease in molecular association in this system upon increment of ethanol. The new complex structure formed, due to lesser molecular association become less compact and more compressible. This suggests that the compressibility of the solution is more than that of solvent (water). The magnitude of compressibility depends on the electrostriction. It gives insight to the hydrophobic-hydrophilic interactions in the mixture. Positive values indicate hydrophilic interaction and gain in structural compressibility due to decreased population of hydrogen bonded water molecules. This increasing trend in compressibility with increase in concentration of ethanol indicates diminution of solute-solvent interaction through intermolecular hydrogen bonding.

As the temperature of water-ethanol solution increases, the isentropic compressibility of water-ethanol solution also increases. This is because, as temperature increases less ordered structure is formed and spacing between the molecules increase due to increase in thermal motion of the components of the solution. Due to thermal motion of molecules, the volume expansion takes place. Hence, compressibility must increase [39-42].

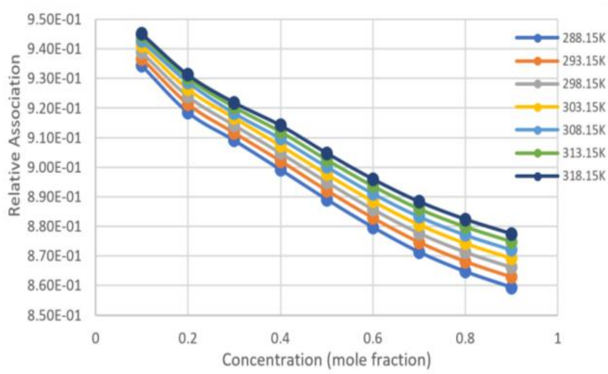

Fig. 4.5 : Variation of Relative Association vs. Concentration of ethanol at different temp., water-ethanol system

4.5 - Relative association measures the extent of association of the components in the medium. Increasing trend in this parameter suggests the strengthening of molecular association in the medium. This parameter depends on the density of mixture. Solute-solute and solute-solvent interaction can be explained on the basis of relative association. After addition of solute, if relative association increases in very small proportions, it attributes solute-solvent interaction. If variation of relative association is significant then it is considered to be solute-solute interaction. Weak or strong molecular interaction is confirmed by relative association.

It can be observed from Fig. 4.5, that relative association of ethanol-water solution is found to decrease with increase in concentration of ethanol suggesting decreasing trend of molecular association between solute and solvent molecules. This lesser association may be due to decreased intermolecular hydrogen bonding between solute and solvent molecules.

At higher temperature, association between solute and solvent molecules become weak due to rupture of hydrogen bonding among the components of the medium and thus, at higher temperatures relative association is lowered appreciably. But in this case as temperature increases, hydrogen bonding among solute and solvent may rupture but simultaneously the freed water molecules may form hydrogen bonding among themselves which is stronger compared water-ethanol hydrogen bonding thereby increasing the relative association at elevated temperatures [43-45].

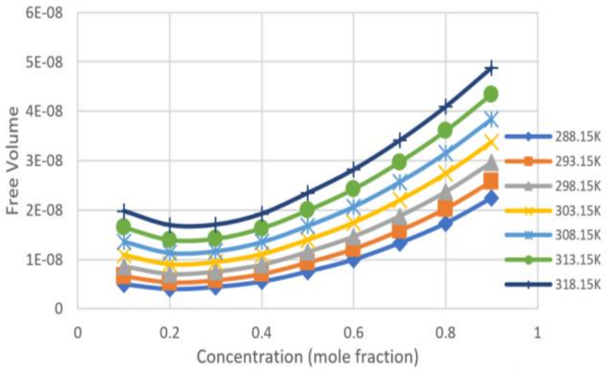

Fig. 4.6 : Variation of Free Volume vs. Concentration of ethanol at different temp., water-ethanol system

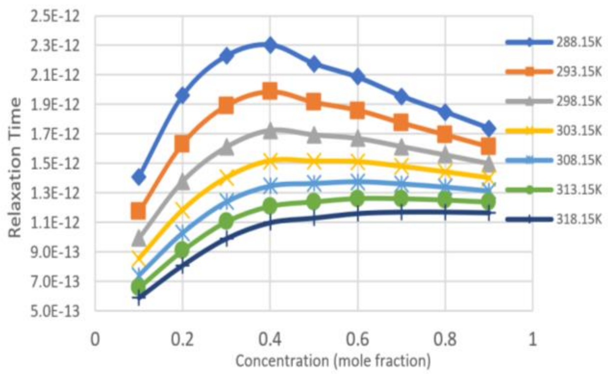

Fig. 4.7 : Variation of Relaxation Time vs. Concentration of Ethanol at different temp., Water-Ethanol system

4.6 - Free volume is an average volume in which central molecule can move inside the hypothetical cell under the repulsive interaction caused by neighboring molecules. Monomer size space present in the system due to uneven packing of solvent molecules is also referred as free volume.

From the Fig. 4.6, it is observed that the free volume of water-ethanol solution initially decreases up to 0.3M concentration and then increases with increase in ethanol concentration, suggesting decrease in molecular association between constituent molecules after 0.3M concentration. The increase in free volume after 0.3M may be due to weakening of cohesive forces which result into breaking the structure of water-ethanol complex making it loosely packed. So, it can be concluded that interaction shows the order as water-water > water-ethanol > ethanol-ethanol. This may be due to the fact that, water forms stronger hydrogen bond with itself than it forms with ethanol or ethanol forms with ethanol itself. This is because ethanol has lower dipole moment as compared to water due to its larger size. Also, water is capable of forming two hydrogen bonds while ethanol can form only one.

The increase in the free volume of water-ethanol solution with increase in temperature also confirms reduced molecular association with rise in temperature [46-47].

4.7 - The relaxation time (τ) measures the closed packing of the medium. If the medium is loosely packed, it is easy to disrupt the medium thereby changing the equilibrium of the system. For such system, the relaxation time is short. If the medium is closely packed, it is difficult to disrupt and to change the equilibrium. The relaxation time for such system is long. If the relaxation time increases for any system, it is supposed to be close packed.

From the Fig. 4.1(h), it is observed that the relaxation time increases with increase in ethanol concentration up to 0.4M, suggesting the formation of complex clusters between ethanol and water molecules is maximum at this concentration. As concentration of ethanol is further increased, intermolecular interaction in the solution decreases. This may lead to decrease in relaxation time. Relaxation time measures the strength of association of molecules of the medium.

As temperature increases, association between the molecules become weak due to thermal motion (rotation, vibration and translational). In some extent due to decreased association, molecules in the medium becomes loosely packed. It is easy to disturb the order the molecules of the medium. As a result, relaxation time value decreases with increase in temperature in water-ethanol solution. It is also noted that the solution at 0.4 mol fraction shows wide spread for temperature. It may be due to more pronounced associational changes with temperature [48-49].

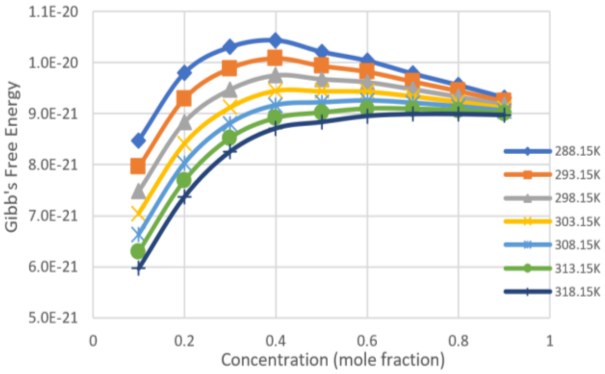

Fig. 4.8 : Variation of Gibb's Free Energy vs. Concentration of ethanol at different temp., water-ethanol system

4.8 - From the Fig. 4.8, it is observed that Gibbs' free energy of activation of water-ethanol solution is found to first increase up to 0.4M and then decrease with increase in ethanol concentration. Decrease in Gibbs' free energy in any solution suggests the weaker association among the components of the solution. The weak association is due to less intermolecular interaction between component molecules. Hence it can be concluded that, in water-ethanol solution, molecular association increases up to 0.4M and then decreases for concentration of ethanol. This may be due to decrease in hydrogen bonding. Hence it can be suggested that, strength of hydrogen bonding in ethanol-water system may be highest at around 0.4M concentration of ethanol.

With increase in temperature, intermolecular forces existing in components of the medium will be weaken and less amount of energy will be required to distort and rupture these weak bonding. Thus, increase in temperature of ethanol-water solution decreases the Gibb's free energy, indicating that less time is required for cooperative process or rearrangement of molecules in the solution. It is interesting to note that, at high temperatures, Gibbs' Free Energy shows almost no change with concentration after 0.4M. This suggests that, in water-ethanol system, molecular association (intermolecular forces) shows very small or almost no change at high temperatures above 0.4M concentration of ethanol [50].

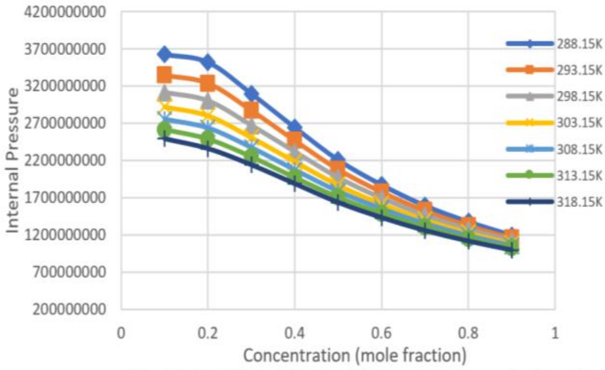

Fig. 4.9 : Variation of Internal Pressure vs. Concentration of ethanol at different temp., water-ethanol system

4.9 - From the Fig. 4.9, it is observed that internal pressure of water-ethanol solution is found to decrease with increase in ethanol concentration, which indicates decrease in cohesive forces. Internal pressure is the results of the forces of attraction and repulsion among the molecules of solution. As the values of ultrasonic velocity, density, and isentropic compressibility shows the weakening of solute-solvent interaction, the decrease in internal pressure with increase in concentration also indicates the diminishing solute-solute interaction.

Internal pressure of water-ethanol solution at concentration higher than 3.0M shows very small change with increase in temperature compared to lower concentrations. This may be because of the thermal agitation of molecules due to increase in thermal energy (rotational, vibrational and translational), is slightly able to diminish the interaction between the molecules in the system. Thus, very small change in cohesive forces resulting into less variation in internal pressure. The opposite is possible for the solutions having concentrations up to 0.3M [51-52].

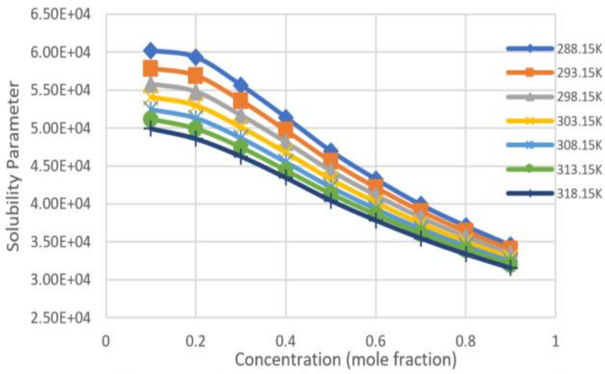

Fig. 4.10 : Variation of Solubility Parameter vs. Concentration of Ethanol at different temp., Water-Ethanol system

4.10 - It is observed from fig. 4.10, that solubility parameter of ethanol-water solution is found to decrease with increase in concentration of ethanol. This suggests the decrease in heat of vaporization which is due to dominancy of amount of ethanol in solution. This decrease in solubility parameter is due to decrease in hydrogen bonding and Van der Walls forces between solute and solvent molecules which in turns indicate decrease in intermolecular association solute and solvent molecules**.** As the temperature increases, solubility parameter should also increase (less negative) (due to thermal motion of molecules which reduces strength of the intermolecular forces thereby decreasing its vaporization energy). But this is not observed in current system. This may be due to the fact that, ethanol has lower boiling point compared to water, which makes it easy to vaporize, thereby increasing the vapor pressure of the solution and decreasing the amount of ethanol in solution. This results in lowering of solubility parameter at high temperatures [53-54].

5. Conclusion

It has been observed that the inter molecular interactions depends not only on Van-der-Waal forces and hydrogen bonding but also on the size of the molecules and cohesive forces among them.

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Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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