Excess Thermodynamic Studies In Ternary Liquid Mixtures Of 2-Methyl-2-Propanol And Cyclohexane With Ketones At Varying Temperatures

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Abstract: *Densities, viscosities and speed of sound for the ternary mixtures of ketones namely, acetophenone, acetone, ethyl methyl ketone and di-ethyl ketone with 2-methyl-2-propanol and cyclohexane were measured as a function of mole fraction at 298.15, 303.15,308.15 and 313.15K at atmospheric pressure. From the these measurements, excess values such as adiabatic compressibility (β^E), excess intermolecular free length (L_f^E), excess free volume (V_f^E), excess internal pressure (π_i^E), excess Gibb's energy (ΔG^E), and excess viscosity (η^E) were determined. The excess values were found to be positive as well as negative throughout the whole range of composition for all the four liquid systems. The Grunberg's interaction parameter (d) was also evaluated in order to ascertain the conclusions drawn from these evaluated excess parameters. Eventually the variation of these excess properties with composition and temperature are discussed in terms of molecular interactions between unlike molecules of the mixtures.*

Keywords: *intermolecular free length, free volume, Gibb's Free energy, Interaction parameter, internal pressure.*

I. Introduction

Ultrasonic speed plays an important role in the investigation of intermolecular interactions. The structural arrangements are influenced by the shape of the molecules as well as by their mutual interactions [1]. Ultrasonic studies of binary mixtures or ternary mixtures have been preferred in many diversifying fields such as scattering spectroscopy and biomedical research. Furthermore, in the chemical industry, information on density and viscosity of the liquid mixtures are vital in different applications that include surface facilities, pipeline systems and mass transfer operations.

Acetone, also known as propanone, is an organic compound because carbon (C) atoms are present in its chemical formula. The physical appearance of acetone is a colorless liquid. It is a flammable liquid and it is also very volatile, and it evaporates easily. It consists of three carbon (C) atoms, 6 hydrogen (H) atoms, and one oxygen (O) atom. Acetone falls under the classification of ketones, which are organic compounds with the structure RC=OR'. The R and R' are groups containing carbon. Carbon and oxygen are bonded to each other with a double bond and this group is carbonyl group. Acetone has a carbonyl group (C=O), which is characteristic of ketones. It is a common solvent that is present in nail polish remover, and it can be identified due to its distinctive smell. Aside from its use in nail polish remover, acetone has many other uses. Acetone is also found in nail polish, bath and fragrance products, hair and skin care products, as well as skin-lightening products.

Ethyl methyl ketone (EMK) known as butanone, is an organic compound with the formula $CH_3C(O)CH_2CH_3$. This colorless liquid has a sharp, sweet odor reminiscent of butterscotch and acetone. It is produced industrially on a large scale, and also occurs in trace amounts in nature [2]. It is soluble in water and is commonly used as an industrial solvent [3]. Butanone is an effective and common solvent and is used in processes involving gums, resins, cellulose acetate and nitrocellulose coatings and in vinyl films [4]. For this reason it finds use in the manufacture of plastics, textiles, in the production of paraffin wax, and in household products such as lacquer, varnishes, paint remover, a denaturing agent for denatured alcohol, glues, and as a cleaning agent. Butanone is also used in dry erase markers as the solvent of the erasable dye. Diethyl ketone (DEK) also known as 3-pentanone is a simple, symmetrical dialkyl ketone. Diethyl Ketone (DEK) is an organic compound. This colourless liquid, belonging to a ketone group, which is widely used as a solvent. DEK has quite low solubility in water, making it useful for liquid-liquid extraction [5]. It is a colorless liquid ketone with an odor like that of acetone. It is soluble in about 25 parts water, but miscible with organic solvents. It is mainly used as a solvent in paint and a precursor to vitamin E [6]. It is easily soluble in diethyl ether and partially soluble in acetone, methanol, and water. It is very flammable, can cause irritation to the skin, and can cause redness and/or burning sensations in eyes. Acetophenone is the simplest aromatic ketone organic [7] compound and it has a sweet taste and smell that resembles that of oranges. It melts at 20.5°C which is above the melting

point of ice and freezes under cool conditions. It is able to dissolve in water but is denser than water and therefore sinks. When it is in gaseous state, its vapor is heavier than air and when inhaled in high concentrations can be narcotic. Acetophenones can react with many acids releasing heat and gases that are flammable. They have many chemical properties as they can react with oxidizing agents and reducing agents such as alkali metals and produce flammable hydrogen gas and heat. Resins that are used in the production of adhesives. Acetophenone have great value as adhesives are used vastly in industries. 2-methyl-2-propanol (2M2P), is the simplest tertiary alcohol. 2-methyl-2-propanl (2M2P), a self-associated protic liquid having a dipole moment of 1.7D and the polarizability value of 8.92×10^{-24} cm^3 It is one of the four isomers of butanol [8]. tert-Butyl alcohol is a clear liquid (or a colorless solid, depending on the ambient temperature) with a camphor-like odor. It is very soluble in water and miscible with ethanol and diethyl ether. It is unique among the isomers of butanol because it tends to be a solid at room temperature, with a melting point slightly above 25°C. It is used as a solvent, ethanol denaturant, paint remover ingredient, and gasoline octane booster and oxygenate. It is a clear, noncorrosive liquid. It is miscible with water as well as most common organic solvents and forms azeotrope. The sterically hindered tertiary butyl group imparts stability compare to primary and secondary alcohols. Cyclohexane belongs to alicyclic hydrocarbon (closed chain). The packing of carbon atoms in this even numbered alkane group and these molecules are highly inert towards an electrophile or nucleophile at ordinary temperature. Being non-polar the predominant dispersive type interactions with temporary dipolar type. As the dipole moment value of cyclohexane is zero, it can offer only dispersive type interactions. Cyclohexane is a colourless, flammable liquid with a distinctive detergent-like odor, reminiscent of cleaning products. It is a naturally occurring chemical that is also produced synthetically and used as a solvent in numerous industries [9]. Acute exposure to large doses can affect the nervous system.

Though many earlier works were available in the combined binary mixture of ketones with 2-methyl-2-propanol (2M2P), however, a detailed and a systematic approach of these ketones with 2M2P under the influence of cyclohexane, an alicyclic hydrocarbon group that are highly inert towards an electrophile or nucleophile are rarely available. Hence, the present investigation has been carried out. In this present study, the density (ρ), ultrasonic speed (u) and viscosity (η), values of pure 2-methyl-2-propanol (2M2P), cyclohexane (CH), acetone (AC), ethyl methyl ketone (EMK), acetophenone (AP) and diethyl ketone (DEK) and those of their ternary mixtures over the entire composition range have been measured and reported at 298.15, 303.15, 308.15 K, and 315.15K respectively. Excess values such as adiabatic compressibility (β^E), excess intermolecular free length (L_f^E), excess free volume (V_f^E), excess internal pressure (π_i^E), excess Gibb's energy (ΔG^E), and excess viscosity (η^E) were evaluated and using these excess properties with composition dependence are discussed in terms of molecular interactions between unlike molecules of the mixtures.

II. Materials And Methods

All the chemicals used in present investigation were of analytical grade and were kept in sealed dark bottle dried over molecular sieves for 2 to 3 weeks prior to their use. The chemicals were manipulated under a nitrogen atmosphere and degassed. Binary mixtures were prepared by mass in air-tight stopper glass bottles using an analytical balance (AX-180, Shimadzu, Japan) with a readability of 0.0001g. Binary solvent mixtures were prepared with 2-methyl-2-propanol (2M2P) and cyclohexane (CH) respectively in the fixed ratio of 2:1 by molefraction. Ketones such as acetone (AC), ethyl-methyl ketone (EMK), di-ethyl ketone (DEK) and acetophenone (AP) were added as solutes on different molar concentrations. Care was taken to avoid evaporation and solvent contamination during mixing. The mole fraction was accurate up to fourth power of decimal. The densities of pure and experimental liquids were measured with a 5ml capillary specific gravity bottle. An Oswald U-tube viscometer of 10ml capacity with sufficient long efflux time was used for viscosity measurements. An electronic digital stopwatch (Racer-10) with a readability of ±0.01s was used for flow time measurement. At least three repetitions of each data point were obtained and the results were averaged. All measurements were carried out in a thermostatic water bath (Ragaa Industries-Chennai) controlled to ±0.01K. Speed of sound was measured by using a 2 MHz ultrasonic interferometer (Model: F-81, Mittal Enterprises, NewDelhi) with the accuracy of ±2 ms^{-1}. The purity of organic chemicals used in the present investigation were tested by measuring its corresponding density values and later ascertained with earlier works.

III. Results and Discussion

In the present study, all the four ternary liquid systems, the density (ρ) and the ultrasonic velocity (U) increase with increasing molar concentrations of ketones, namely acetophenone (AP), acetone (AC), ethyl methyl ketone (EMK), di-ethyl ketone (DEK). Whereas the viscosity (η) shows a decreasing trend, which are tabulated in Table-1. The variation of ultrasonic velocity in a mixture depends upon the increase (or) decrease of intermolecular free length after mixing the components. According to Eyring and Kincaid for sound projection [10], ultrasonic velocity should decrease, if the intermolecular free length increase and vice-versa. This is

ascertained in the present investigation for all the four liquid systems. Further, it is interesting to note that density, viscosity and ultrasonic velocity values decrease with increase of temperature.

Mole fraction(X_1)	Density(ρ) (kg/m^3)				Viscosity(η) ($\times 10^{-3}$ Nsm^{-2})				Ultrasonic Velocity(U) (m/s)			
	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
SYSTEM-I Acetone + 2-Methyl- 2-Propanol + Cyclohexane												
0.0000	774.75	768.35	761.32	754.85	1.8858	1.6135	1.3596	1.1492	1117.71	1104.53	1091.36	1078.18
0.1000	776.36	769.96	763.06	756.59	1.3396	1.1560	1.0144	0.8769	1121.28	1110.15	1099.02	1087.88
0.3140	778.37	771.71	764.67	758.47	0.8714	0.7828	0.6979	0.6257	1128.38	1117.26	1106.13	1094.97
0.5000	780.25	773.99	766.68	760.48	0.5850	0.5417	0.4944	0.4631	1135.52	1124.34	1113.17	1102.01
0.7000	782.53	776.00	768.53	762.49	0.4500	0.4051	0.3666	0.3144	1142.68	1131.51	1120.34	1109.16
0.9000	784.55	776.94	770.84	764.64	0.3787	0.3225	0.2841	0.2504	1148.83	1138.33	1127.14	1115.96
SYSTEM-II EMK + 2-Methyl- 2-Propanol + Cyclohexane												
0.0999	777.70	773.05	768.03	763.16	1.4058	1.2626	1.0492	0.9519	1132.00	1118.82	1105.64	1092.46
0.3002	781.06	776.40	771.38	766.38	0.9446	0.8664	0.7806	0.7151	1143.57	1130.39	1117.21	1104.03
0.4999	784.41	779.63	774.47	769.46	0.7009	0.6406	0.5763	0.5214	1154.03	1140.85	1127.67	1113.88
0.7000	787.90	783.12	778.09	773.09	0.5179	0.4625	0.4232	0.3842	1164.64	1151.46	1138.28	1125.10
0.9000	791.39	786.60	781.44	776.44	0.4426	0.4069	0.3676	0.3269	1175.12	1161.94	1148.76	1135.58
SYSTEM-III DEK + 2-Methyl- 2-Propanol + Cyclohexane												
0.1000	779.45	774.66	769.37	764.50	1.5530	1.3910	1.1755	1.0362	1138.45	1125.34	1113.69	1100.94
0.2999	783.21	778.28	772.99	767.86	1.0135	0.9237	0.8436	0.7693	1150.96	1137.88	1124.64	1113.75
0.4999	786.96	782.04	776.75	771.75	0.7802	0.7219	0.6550	0.5988	1163.08	1151.09	1138.23	1126.11
0.7000	790.85	785.93	780.64	775.63	0.5929	0.5481	0.4989	0.4652	1176.22	1164.47	1152.66	1140.19
0.9000	794.61	789.69	784.39	779.39	0.4896	0.4446	0.4058	0.3610	1189.41	1177.28	1165.55	1154.71
SYSTEM-IV Acetophenone + 2-Methyl 2-Propanol + Cyclohexane												
0.1052	811.12	806.07	800.63	795.35	2.0216	1.8743	1.6581	1.4376	1156.32	1133.62	1110.22	1088.32
0.3000	861.85	856.93	851.60	846.32	1.8139	1.6832	1.4531	1.2281	1219.42	1196.62	1173.72	1151.92
0.5000	912.85	907.93	902.72	897.55	1.6072	1.4779	1.2468	1.0164	1281.50	1259.49	1237.10	1215.20
0.7000	963.44	958.66	953.29	948.12	1.4081	1.2784	1.0312	0.9812	1340.64	1318.24	1295.34	1272.74
0.9011	1014.44	1009.53	1004.00	998.68	1.2156	1.0836	0.9886	0.9476	1395.81	1372.71	1349.19	1327.33

Table-1 values of Density (ρ), viscosity (η) and ultrasonic velocity (U) at 298.15, 303.15, 308.15 and 313.15K

The thermodynamic excess properties of organic liquid mixtures depend on the chemical structure, size and shape of their constituent molecules. The excess functions which are a measure of deviation from ideal behaviour are found to be highly sensitive to intermolecular interactions between component molecules of the mixtures. The sign and magnitude of these functions depend on the strength of interaction between dissimilar molecules in the mixture.

A qualitative clarification over the behaviour of excess values may be interpreted as the ternary liquid mixtures reported in this present work consisting of a common component. The ketone groups taken for the present investigation are acetone, acetophenone, ethyl methyl ketone and di-ethyl ketone were added as solutes in this study have a common functional group C = O. While acetone, ethyl methyl ketone (EMK), diethyl ketone (DEK) falling under the category of aliphatic series, acetophenone is an aromatic component. All these ketones are aprotic molecules having large dipole moment values [AP =3.02 D, Acetone =2.88D, EMK =2.78 D, DEK=2.71D,][11]. In addition to this, acetone is known to be extensively self associated through H-bonding in the pure state [12].
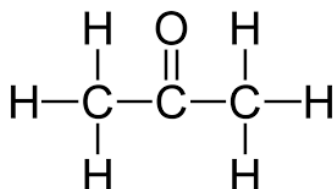
2-METHYL- 2-PROPANOL

When ketones are mixed with binary solvent mixture containing 2M2P and cyclohexane, the strength of interaction between the participating molecules depends on the polarizability and geometry of the interacting molecules. The overall interaction between ketones and binary solvent mixture containing 2M2P and cyclohexane and combination of of both of these effects which are opposing each other. Generally, ketones are

electron acceptors [13], but 2M2P is protic and strongly associated due to H-bonding ability of the –OH group [14] as the hydroxyl group in 2M2P possesses one hydrogen bond donor (the H atom) and two acceptors (the two lone pairs of electrons on the oxygen atom). When ketones as solutes are added with binary solvent mixture containing 2M2P and cyclohexane, there could be a possibility of dissociation of hydrogen bonding of like molecules [8].
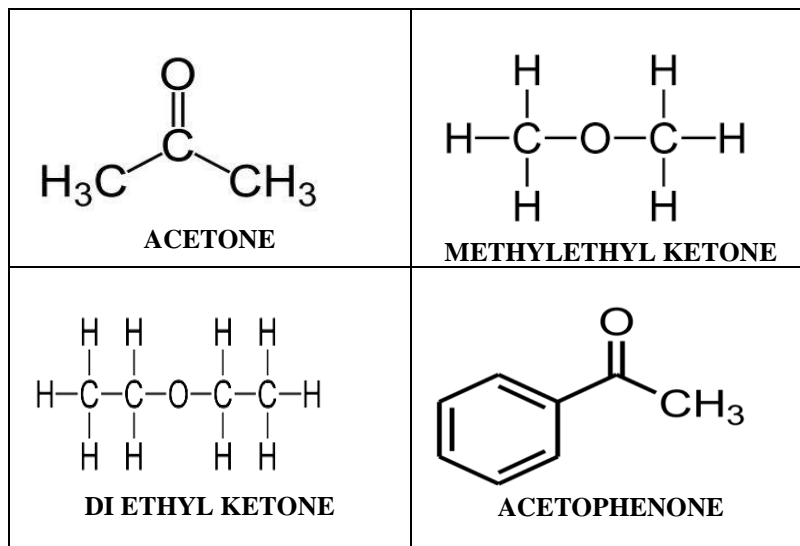

Structure of Ketones

An examination of data in Table -2 shows that the excess adiabatic compressibility (β^E) and excess intermolecular free length (L_f^E) are positive in all of the four ternary liquid systems (except the system-IV, where a reverse trend is noticed) over the entire range of composition. According to Sri Devi et al. [15], negative excess values are due to closely packed molecules which accounts for the existence of strong molecular interactions, whereas positive excess values reflect weak interactions between unlike molecules. The sign of the excess adiabatic compressibility (β^E) and excess intermolecular free length (L_f^E) are useful in assessing the compaction due to molecular interactions in liquid mixtures through hydrogen-bonding, charge transfer, dipole–dipole and dipole-induced dipole interactions, interstitial accommodation and orientational ordering [16], which lead to a more compact structure, leading to negative values of the excess adiabatic compressibility and excess intermolecular free length. From the perusal of the Figs-1 and 2 the positive values of the excess adiabatic compressibility (β^E) and excess intermolecular free length (L_f^E) in the present systems suggesting a weak molecular interactions present between unlike molecules in the liquid mixtures.

Table-2 Excess Values of Adiabatic Compressibility (β^E), Free Length(L_f^E), and Free Volume(V_f^E) at 298.15, 303.15, 308.15,313.15K

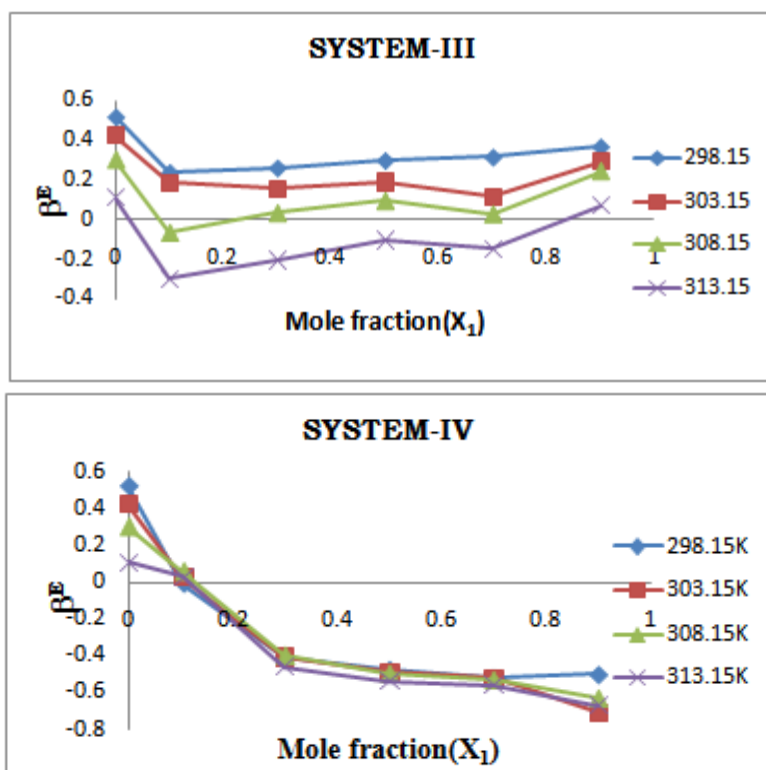| Mole fraction(X_1)	Adiabatic compressibility(β^E) ($\times10^{-10}$m^{2}N^{-1})				Free Length(L_f^E) ($\times10^{-10}$ m)				Free Volume(V_f^E) ($\times10^{-7}$m^{3}mol^{-1})			
	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
SYSTEM-I Acetone + 2-Methyl- 2-Propanol + Cyclohexane												
0.0000	0.5212	0.4253	0.2994	0.1088	0.0168	0.0138	0.0098	0.0037	-0.0323	-0.0029	0.0365	0.1028
0.1000	0.4750	0.3385	0.1689	-0.0662	0.0153	0.0090	-0.0096	-0.0171	-0.1518	-0.0820	-0.0396	0.0635
0.3140	0.3328	0.1886	0.0249	-0.2147	0.0108	0.0062	0.0012	-0.0072	-0.3785	-0.2882	-0.2225	-0.0972
0.5000	0.3219	0.1731	0.0224	-0.2073	0.0105	0.0057	0.0011	-0.0061	-0.3388	-0.2340	-0.1558	-0.0723
0.7000	0.2439	0.0927	-0.0495	-0.2766	0.0080	0.0031	0.0013	-0.0083	-0.3612	-0.0865	0.1011	0.7280
0.9000	0.2055	0.0529	-0.0993	-0.3179	0.0067	0.0018	0.0003	-0.0097	-0.5678	0.0480	0.4809	1.1546
SYSTEM-II EMK + 2-Methyl- 2-Propanol + Cyclohexane												
0.0999	0.3273	0.2068	0.0680	-0.1206	0.0109	0.0071	0.0022	-0.0036	-0.4779	-0.4686	-0.7748	-0.4637
0.3002	0.2783	0.1773	0.0411	-0.1833	0.0094	0.0058	0.0012	-0.0015	-0.4169	-0.4162	-0.3740	-0.3676
0.4999	0.2609	0.1720	0.0317	-0.1217	0.0090	-0.0135	0.0011	-0.0025	-0.5452	-0.5105	-0.4020	-0.3143
0.7000	0.2605	0.1633	0.0266	-0.1390	0.0095	0.0067	0.0030	-0.0031	-0.3590	-0.1623	-0.0260	0.1858
0.9000	0.2438	0.1613	0.0162	-0.1452	0.0085	0.0059	0.0027	-0.0044	-0.4077	-0.2972	-0.0227	0.3951
SYSTEM-III DEK + 2-Methyl- 2-Propanol + Cyclohexane												
0.1000	0.2349	0.1854	-0.0682	-0.2977	0.0081	0.0043	-0.0014	-0.0084	-0.2660	-0.2609	-0.2149	-0.1759
0.2999	0.2591	0.1534	0.0309	-0.2056	0.0122	0.0088	0.0051	-0.0063	-0.5202	-0.5031	-0.5239	-0.4906
0.4999	0.2971	0.1890	0.0922	-0.1035	0.0104	0.0070	0.0040	-0.0073	-0.7164	-0.7009	-0.6843	-0.6090
0.7000	0.3140	0.1147	0.0250	-0.1488	0.0037	0.0040	-0.0026	-0.0083	-0.5469	-0.4658	-0.3740	-0.2903
0.9000	0.3672	0.2948	0.2424	0.0707	0.0027	-0.0102	-0.0184	0.0027	-0.3329	-0.0863	0.0878	0.6126
SYSTEM-IV Acetophenone + 2-Methyl- 2-Propanol + Cyclohexane												
0.1052	-0.0067	0.0284	0.0584	0.0296	0.0035	0.0048	0.0060	0.0014	-0.1258	-0.1596	-0.1822	-0.1858
0.3000	-0.4073	-0.4043	-0.3986	-0.4581	-0.0063	-0.0076	-0.0090	-0.0168	-0.1043	-0.1427	-0.1252	-0.0776
0.5000	-0.4733	-0.4868	-0.4972	-0.5358	-0.0078	-0.0098	-0.0070	-0.0256	-0.0159	-0.0389	0.0608	0.2509
0.7000	-0.5173	-0.5226	-0.5319	-0.5580	-0.0112	-0.0107	-0.0194	-0.0345	-0.1931	0.2156	0.4086	0.4238
0.9011	-0.0503	0.0767	0.1317	0.6698	-0.0163	-0.0178	-0.0195	-0.0206	-0.5972	0.7255	0.8040	0.6661
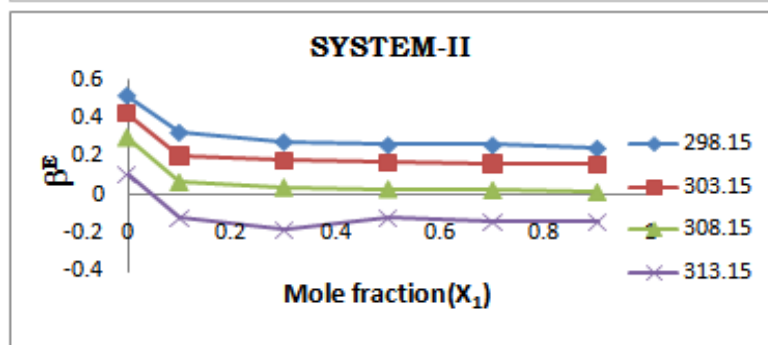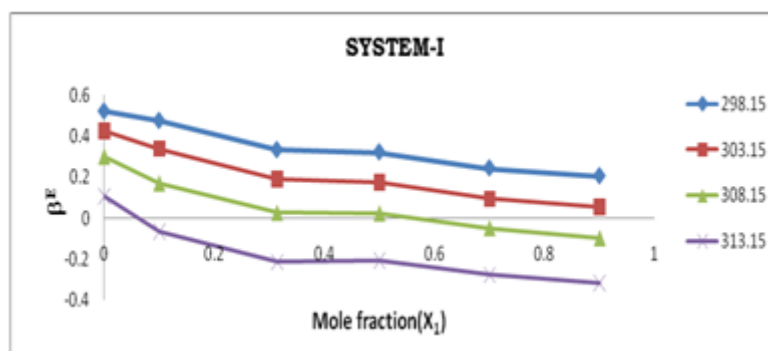
SYSTEM-I

SYSTEM-II

Fig-1. Variation of Excess Adiabatic Compressibility (β^E) with Mole fraction (X_1) of ternary liquid systems at different temperatures
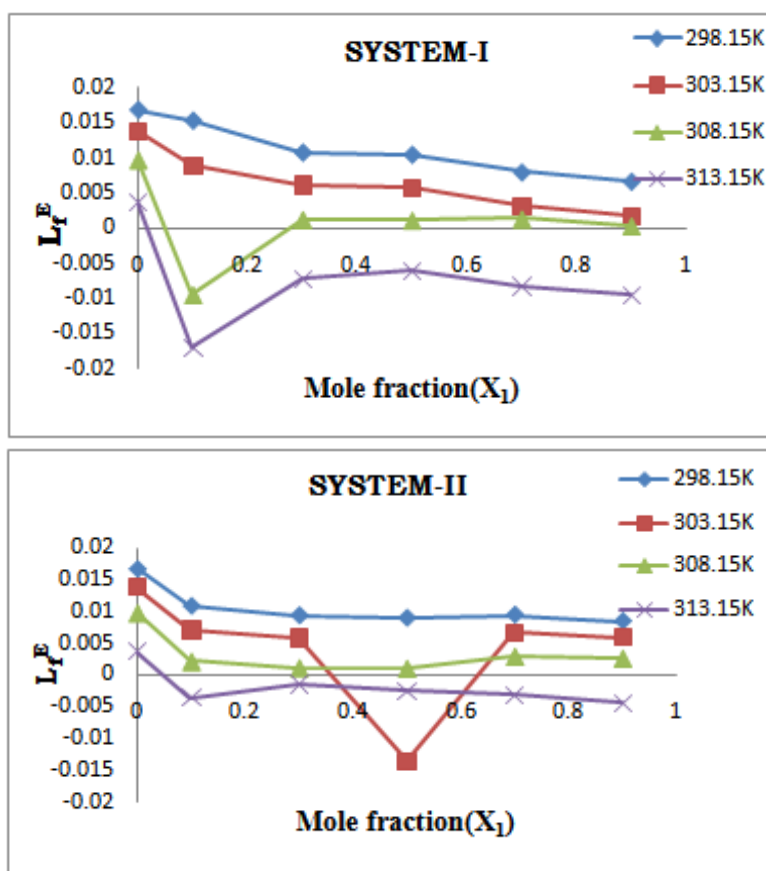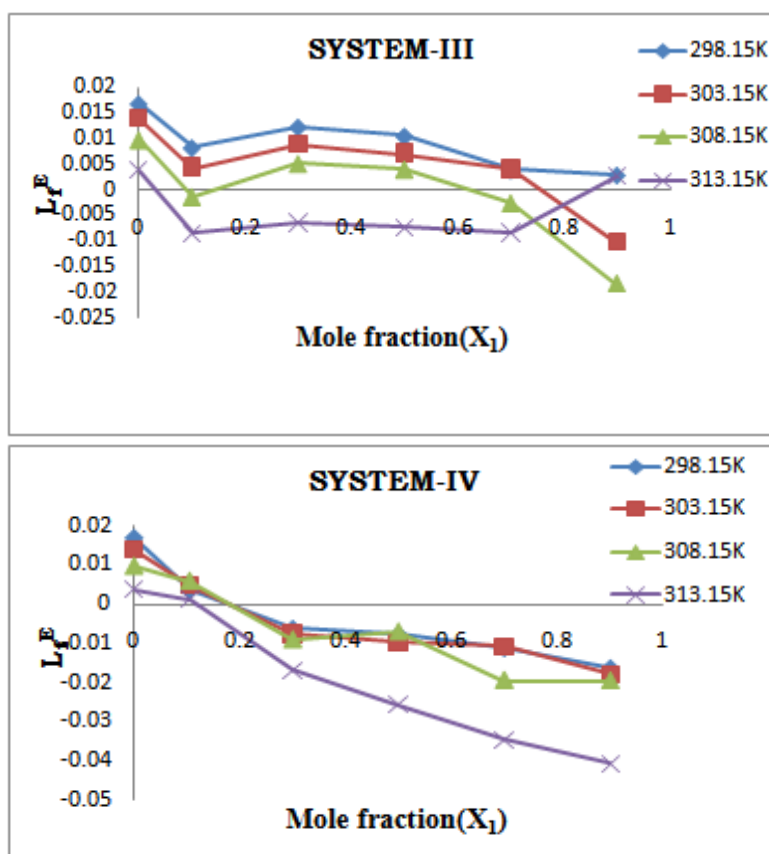
Fig-2. Variation of Excess Free length (L_f^E) with Mole fraction (X_1) of ternary liquid systems at different temperatures

However in system-IV, 2-methyl-2-propanol (2M2P) with an aromatic ketone acetophenone, there lies a possibility of formation of some complexes due to the hydrogen bonding between the oxygen atom of acetophenone (AP) with the hydrogen atom of the hydroxyl group of 2M2P and the π.......H interaction between π electron and hydrogen atom of the hydroxyl group of 2M2P, which may result in negative deviation in β^E and L_f^E. Reddy et.al., [17] reported that AP showed a stronger interaction with alcohols, giving rise to negative deviation.

The perusal of Table-2 provides a qualitative picture of excess free volume (V_f^E) values for all the four ternary liquid systems. The excess values for all the four ternary liquid systems are negative. These negative deviations found to be increased on increasing the molar concentration of ketones (solutes) as well as rise of temperature. This can be ascribed as molecular interaction, structural effect and interstitial accommodation along with the changes in free volume. The sign of the V_f^E depends on the relative strength between the contractive forces and expansive forces. The factors responsible for volume contraction are (i) specific interactions between the component molecules and (ii) weak physical forces, such as dipole-dipole or dipole-induced dipole interactions or Vanderwaal's forces. The factors that cause expansion in volume are dispersive forces, steric hindrance of component molecules, unfavourable geometric fitting and electrostatic repulsion. The increasing trend of negative values of excess free volume from the fig-3 in the present study in all the systems assert that the effect of the factors responsible for volume expansion [18]. Adgaonkar et al. [19] advocated the positive deviations may result in existence of weak molecular interactions in the liquid mixtures. Further, the observed negative values suggesting the existence of dipole-dipole interactions between unlike molecules and also the formation of H-bonds between the oxygen atom of the carbonyl group [20] of ketones and the hydrogen atom of the 2M2P.
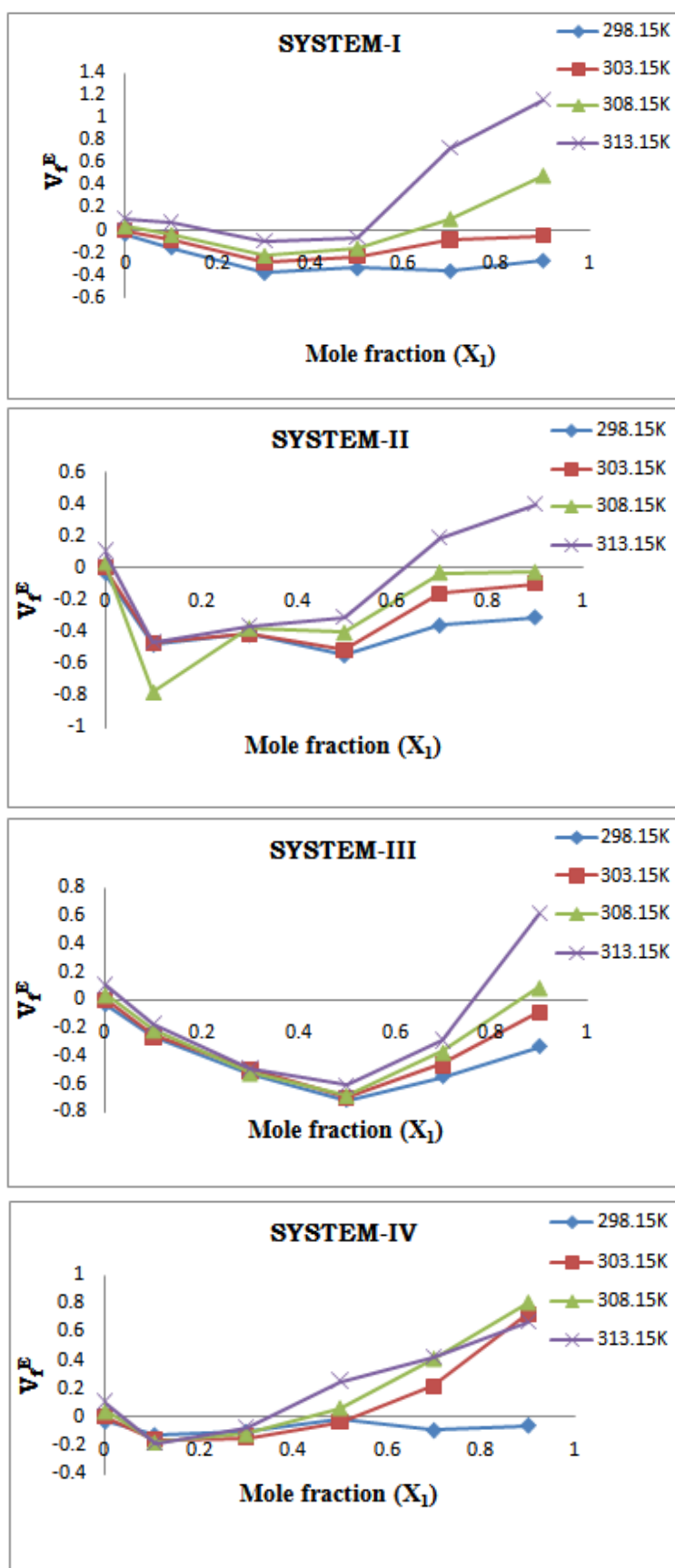
Fig-3. Variation of Excess Free Volume (V_f^E) with Mole fraction(X_1) of ternary liquid systems at different temperatures
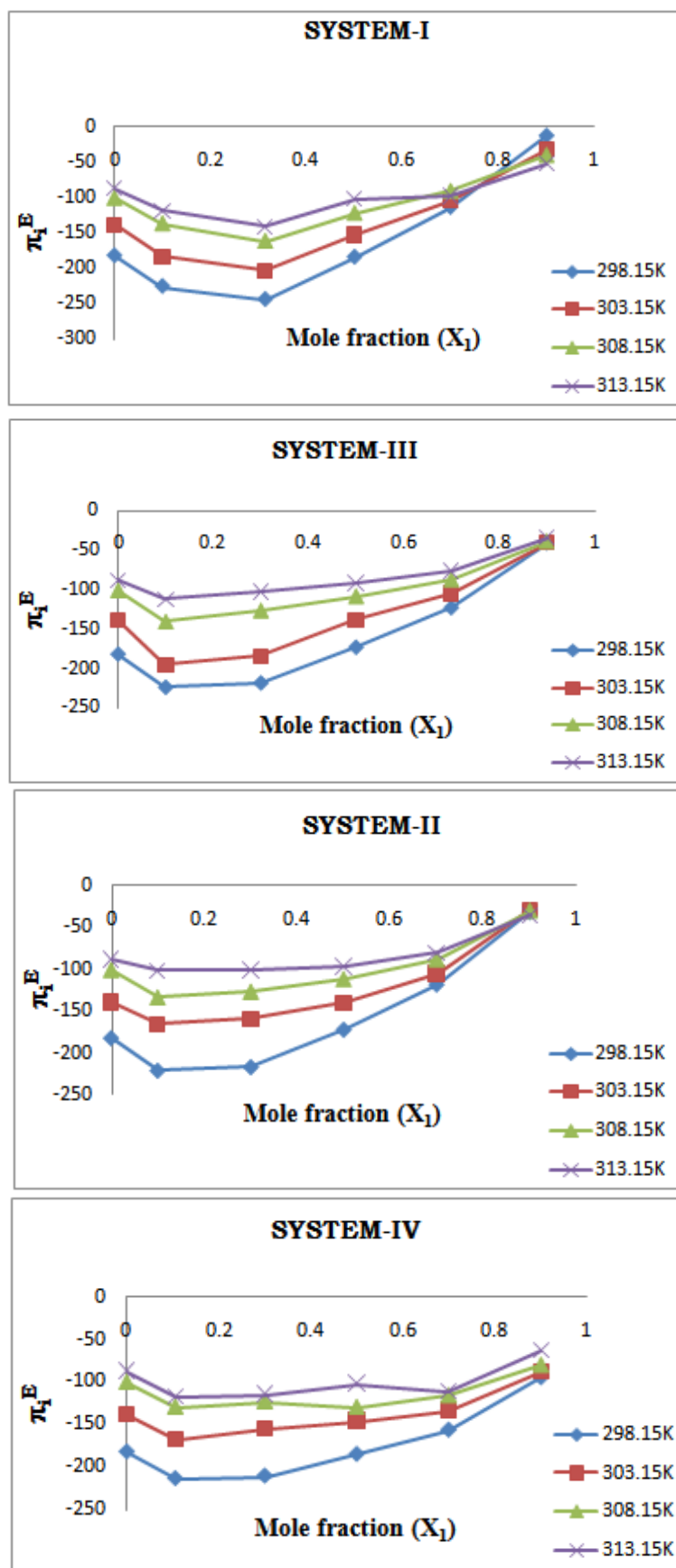
Fig-4. Variation of Excess Internal Pressure (π_i^E) with Mole fraction(X_1) of ternary liquid systems at different temperatures

In the study of liquid mixtures, the variation of internal pressure may give some suitable information regarding the nature and strength of the forces existing between the molecules. In fact, the internal pressure is a broader concept and it is a measure of the totality of forces of the dispersion, ionic and dipolar interaction that contribute to be overall cohesion of the liquid systems. The perusal of Fig-4 with composition dependence with excess internal pressure depicts the values are negative in all the four liquid systems and are increasing with further addition of solutes (ketones) indicating that only dipolar forces are operating between the unlike molecules. Further, the observed increasing negative values of excess internal pressure values instructing that the weakening of cohesive forces.
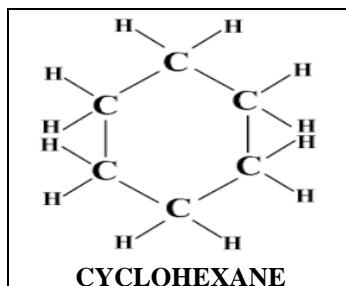
CYCLOHEXANE

Cyclohexane belongs to alicyclic hydrocarbon (closed chain). The packing of carbon atoms in this even numbered alkane group allows the maximum intermolecular attractions and therefore these molecules are highly inert towards an electrophile or nucleophile at ordinary temperature. Being non-polar, the predominant dispersive type interactions with temporary dipolar type are existing as a net result of intermolecular forces. As the dipole moment value of cyclohexane is zero, it can offer only dispersive type interactions. Being itself a ring type molecule, it exhibits conformation and exists either in rigid chain form or in boat form and also in skew-boat form, all can undergo rapid interconversion at room temperature. Due to the presence of bowspirit-flagpole interaction in the boat cyclohexane breaking of hydrogen bonds are highly favoured. A reduction in density and viscosity with increase in mole fraction of cyclohexane in the present study suggests that the existing intermolecular interactions are weakening in magnitude [21].
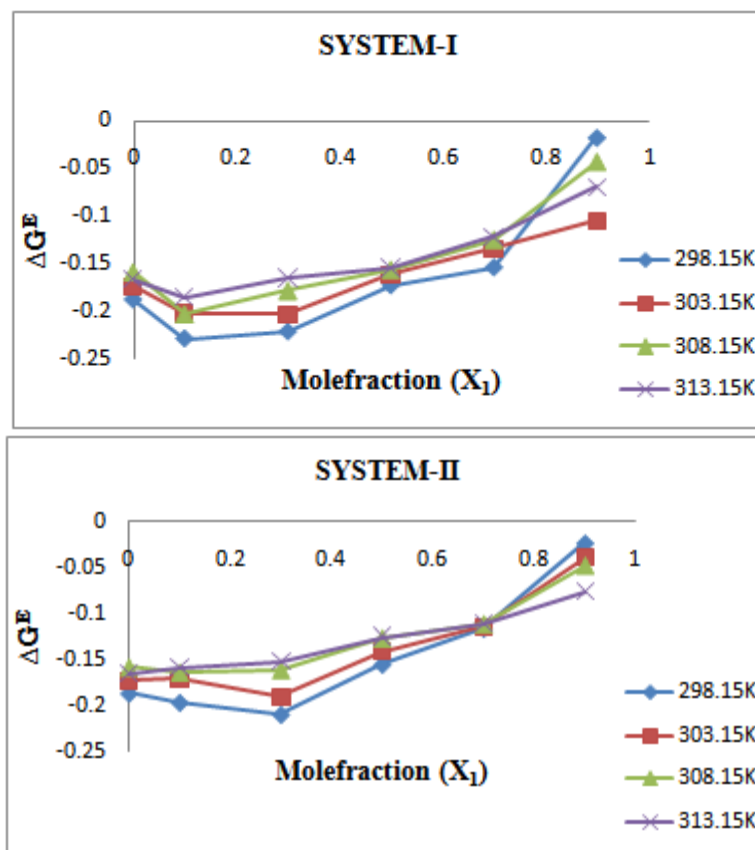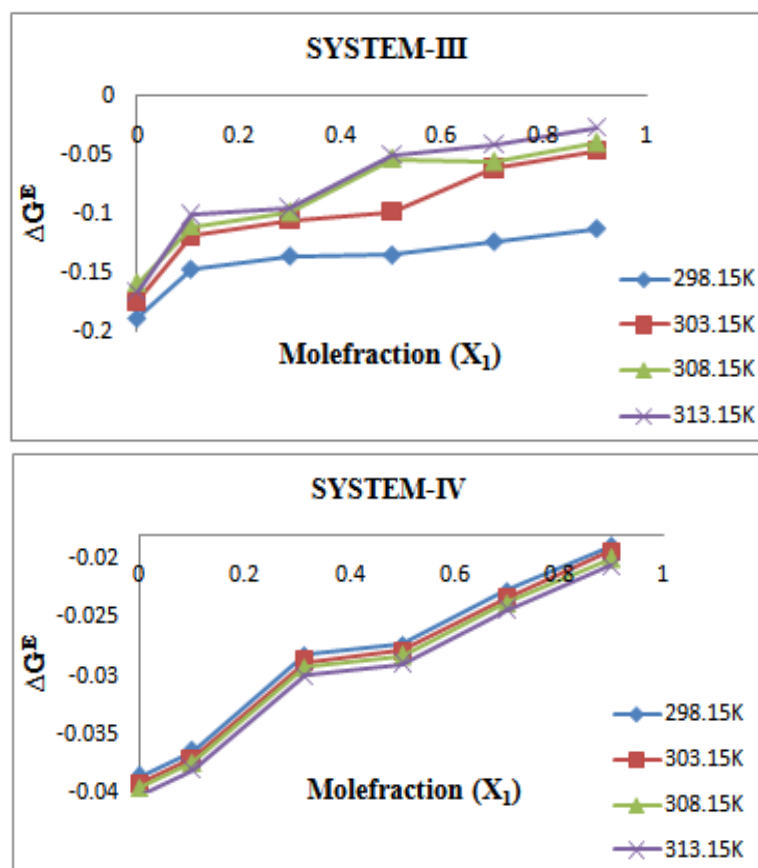
Fig-5. Variation of Excess Gibb's Free Energy (ΔG^E) with Mole fraction(X_1) of ternary liquid systems at different temperatures

The evaluated values in Table-3 shows the variation of excess Gibbs free energy (ΔG^E) for the four ternary liquid systems. The values of ΔG^E are all negative in all the liquid systems concerned and increase with molar concentration of ketones as well as rise of temperature. According to Read et al. [22], the positive values of excess Gibbs energy values may be attributed to specific interactions like hydrogen bonding and charge transfer, while negative ΔG^E values may be due to the dominance of dispersion forces [23]. In the present investigation, from the perusal of Fig-5, it is noticed that the increasing negative values of ΔG^E suggesting the strength of interaction gets weakened on further addition of solutes (ketones). It is also learnt from the present study that the increasing trend of negative deviation over the elevation of temperature paving the way for weakening of the molecular association as it causes rupture of more and more hydrogen bonded and hetero-association between unlike molecules.

According to Fort et al. [16] the study of excess viscosity (η^E) gives the strength of molecular interaction between the molecules. For the liquid systems, where dispersion, induction, and dipolar forces which are operated by the values of excess viscosity are found to be negative, whereas the existence of specific interactions leading to the formation of complexes and hydrogen bonding in liquid mixtures tends to make excess viscosity positive. The evaluated excess viscosity values are reported in Table-3 depicting the negative values in all the four ternary liquid systems and increase with the further addition of ketones as well as elevation of temperature. The present observation predicts that the trend of excess viscosity's reveals the presence of weak dipolar forces in the liquid mixtures. The increasing negative values of η^E also suggests that the dominance of dispersive interaction resulting from the breaking up of the hydrogen bonds of 2-methyl-2-propanol. Further, the increasing negative deviations over the elevation of temperature in all the four liquid systems clearly suggesting the strength of interaction gets weakened as thermal dispersion forces are highly operative in the liquid mixtures.

Table-4 Excess Values of Molar volume (V_m^E) and Interaction parameter(d) at 298.15, 303.15, 308.15, 313.15K								
Mole fraction(X_1)	**Molar volume(V_m^E)**				**Interaction parameter (d)**			
	298.15K	**303.15K**	**308.15K**	**313.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**

SYSTEM-I Acetone + 2-Methyl- 2-Propanol + Cyclohexane								
0.0000	-0.0385	-0.0391	-0.0395	-0.0401	-1.4134	-1.2723	-1.1151	-1.0984
0.1000	-0.0364	-0.0370	-0.0374	-0.0380	-20.738	-19.319	-16.636	-16.108
0.3140	-0.0282	-0.0288	-0.0292	-.02995	-14.515	-13.267	-11.079	-11.174
0.5000	-0.0273	-0.0278	-0.0283	-0.0290	-11.311	-10.348	-9.2100	-8.3041
0.7000	-0.0227	-0.0233	-0.0238	-0.0244	-13.710	-14.498	-14.046	-17.219
0.9000	-0.0189	-0.0194	-0.0200	-0.0206	-10.234	-9.567	-8.389	-7.573
SYSTEM-II EMK + 2-Methyl- 2-Propanol + Cyclohexane								
0.0999	-0.0366	-0.0372	-0.0376	-0.0382	-19.963	-17.109	-16.279	-14.052
0.3002	-0.0325	-0.0330	-0.0335	-0.0341	-10.523	-9.108	-7.805	-6.818
0.4999	-0.0284	-0.0289	-0.0294	-0.0300	-9.823	-8.871	-8.128	-7.723
0.7000	-0.0241	-0.0245	-0.0251	-0.0257	-5.647	-6.044	-5.328	-5.250
0.9000	-0.0202	-0.0206	-0.0213	-0.0218	-2.383	-2.668	-3.642	-4.9841
SYSTEM-III DEK + 2-Methyl- 2-Propanol + Cyclohexane								
0.1000	-0.0369	-0.0374	-0.0378	-0.0384	-17.068	-14.336	-12.901	-11.670
0.2999	-0.0332	-0.0337	-0.0341	-0.0346	-10.099	-8.840	-7.211	-6.350
0.4999	-0.0295	-0.0300	-0.0304	-0.0309	-9.0703	-7.926	-6.825	-6.311
0.7000	-0.0273	-0.0277	-0.0282	-0.0286	-7.219	-6.460	-5.710	-4.946
0.9000	-0.0222	-0.0225	-0.0230	-0.0234	-3.1086	-3.947	-4.2325	-5.7629
SYSTEM-IV Acetophenone + 2-Methyl- 2-Propanol + Cyclohexane								
0.1052	-0.0353	-0.0358	-0.0362	-0.0368	-28.2	-30.03	-30.49	-28.92
0.3000	-0.0266	-0.0271	-0.0273	-0.0279	-27.75	-30.15	-31.68	-31.65
0.5000	-0.0180	-0.0186	-0.0190	-0.0192	-30.97	-33.06	-35.66	-37.4
0.7000	-0.0112	-0.0118	-0.0123	-0.0128	-54.39	-57.05	-61.37	-65.12
0.9011	-0.0014	-0.0021	-0.0026	-0.0031	-48.25	-52.37	-59.26	-64.3

The perusal of Table-4 exhibits the excess molar volume (V_m^E) are all negative over the entire range of concentration range of the solutes (ketones). According to V_m^E data for ternary mixtures of 2-methyl-2-propanol, cyclohexane with ketones depend upon the balance between two opposing contributions [24, 25].

(a) A positive term from the rupture of hydrogen bonds and physical dipole-dipole interactions between alkanol monomers and multimers, and

(b) A negative term from the formation of the OH π-electron hydrogen bonded complexes, changes of free volume and interstitial accommodation.

The experimental data in the present investigation suggest that factor (b) which is responsible for the negative excess volume is dominant over the entire composition range in the liquid mixtures. According to Awwad et al. [26] measured excess molar volume obtained in the present study can be qualitatively explained as arising to due to differences in the sizes of the component molecules and in the interactions between them. Differences are mainly due to positive contributions arising from changes of free volume in the real mixtures, comprising alkanol monomers and multimers and cyclohexane and ketone molecules. The experimental data in the present study suggest that the factors which account for the existence of dipole-dipole interactions present in the liquid mixtures. One can understand from Table-4 that the excess molar volume (V_m^E) values are exhibiting negative deviations in all the four liquid systems. The negative deviations are found to be increased with the increase of molar concentration of ketones and rise of temperature. The increasing trend of negative values of V_m^E for the further addition of solutes (ketones) clearly predicting the existence of weak dipolar forces. When solutes (ketones) are added with binary solvent mixture containing 2-methyl-2-propanol (2M2P) and cyclohexane, there could be a possibility of dissociation of hydrogen bonds of like molecules which may result in positive excess molar volume (V_m^E). However, if a new hydrogen bond is formed between 2M2P and ketone molecules, it will be reflected in a negative trend.

The evaluated excess values of free volume (V_f^E), internal pressure (π_i^E), Gibb's free energy (ΔG^E) and viscosity (η^E) increase with increase in temperature for all the four ternary liquid mixtures under study. Such an increase may be attributed to the breaking of Hydrogen bonded associates formed between unlike molecules with rise in temperature leading to an expansion in volume. As the thermal energy increases, the intermolecular interactions between the unlike molecules decrease.

The existence of weak intermolecular interaction between unlike molecules in the present study further confirmed by evaluating the interaction parameter d in the Gruenberg and Nissan equation which is a measure of strength of interaction between the mixing components. d-values were said to indicate various types of interactions [27]. Large and positive d-values indicate strong specific interaction, small positive values indicate weak specific interaction. It is evident from Table-4 the d-values are negative and increase with increasing of mole fraction of ketones (solutes) as well as rise of temperature. The increasing negative behaviour of d-values advocates weaker interaction between the unlike molecules, and also their increasing behaviour over the rise of temperature clearly advocating the weakening of intermolecular interaction due to thermal dispersion forces.

IV. Conclusion

In the present investigation, the density, ultrasonic speed and the viscosity data have been reported for ternary liquid mixtures of 2-methyl-2-propanol (2M2P) and cyclohexane (CH) with ketones namely acetophenone (AP), ethyl methyl ketone (EMK), di-ethyl ketone (DEK) and acetone (AC) at varying temperatures. The evaluated excess thermodynamic parameters predicting the presence of weak interaction between aliphatic ketones (AC, DEK and EMK) and binary solvent mixture containing 2M2P and CH. However, aromatic ketone (AP) exhibits a strong molecular association in the binary solvent mixture. The elevation of temperature in all the liquid systems in the present study may be attributed to the breaking of Hydrogen bonded associates formed between unlike molecules leading to weakening of intermolecular interactions in the liquid mixtures.

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