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ULTRASONIC STUDIES OF MOLECULAR INTERACTIONS OF n-ALCOHOLS WITH DIMETHYL KETONE IN NON-POLAR SOLVENTS

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ABSTRACT

The ultrasonic velocity, density and viscosity have been measured at 301 K by the ternary mixtures of alcohols (pentanol, hexanol, heptanol, octanol and decanol) with dimethylketone in carbon tetrachloride / benzene systems. From the measured values evaluated the following acoustical parameter viz. adiabatic compressibility, acoustic impedance, relaxation time, relative association intermolecular free length, free volume, available volume, molar volume, Wadas constant and Rao's constant, Linard-John potential. The natures of intermolecular interaction in the liquid mixtures have been explained on the basis of the variation of acoustical parameter. It is found that the interaction between non-polar molecules decreases with the increase in alcohol chain length.

Keywords: Ultrasonic velocity, Adiabatic compressibility, Ternary liquid mixture, Molecular interaction, Hydrogen bonding, Non-polar solvents.

INTRODUCTION

An ultrasonic measurement gives the idea about the nature and extent of pattern molecular aggregations that exist in the multi component systems, resulting from molecular interactions[1-2]. The ultrasonic technique is used to study the properties and structures of liquids, the nature and strength of molecular interactions between the components of liquids Krishnamurthi etal[3-4.] A study of intermolecular interactions plays an important role in molecular sciences, liquids, liquid mixtures and solutions have found wide applications in chemical, textile, pharmacuetical and Nuclear industries[5-8]. The IR, Raman effect and dielectric properties also used to study the molecular interaction[9-11.] Investigated the molecular interactions by the measurements of ultrasonic velocity and density for the liquid mixtures of alcohols with ketone[12-14] at 303.15K and predicted the possible interaction between the unlike molecules.

The present work deals with ternary mixture of n-alcohol (pentanol, hexanol, heptanol, octanol, decanol) with dimethyl ketone in non-polar solvent such as carbon tetrachloride and benzene at 301K. The exact molecular interactions between the multicomponent systems have been identified.

EXPERIMENTAL

The liquid mixtures of various concentrations (0.1-0.5) in mole fraction were prepared by taking Analar grade (AR) chemicals. In all the systems, carbon tetrachloride and benzene with purity 99.99% as such without further purification. Ultrasonic velocity of pure liquids and mixtures were measured using ultrasonic interferometer (Model F: 81) at 2 MHz fixed frequency with an accuracy of ± 0.1 ms^{-1}. The densities of pure liquids and mixtures were determined from the weight measurements by using the 25ml specific gravity bottle immersed in the thermostat. An ostwald's viscometer was used for the viscosity (η) measurement of pure liquids and liquid mixtures with an accuracy of ±0.0001NSm^{-2}. The temperature was maintained at 301K with an error ±0.1K using thermostatically water bath. All the protection was taken to minimize the possible experimental error.

Using acoustical measurements evaluated the following acoustical parameters-

Adiabatic compressibility (β)

Adiabatic compressibility were calculated from the speed of sound (u) and the density of the medium (ρ) using Newton and Laplace equation as-

$$\beta = \frac{1}{U^2 \rho}$$

Free volume (V_f)

Free volume obtained from the ultrasonic velocity (u) and the viscosity (η) of the liquid as-

$$V_f = \left(\frac{M_{eff} U}{K\eta} \right)^{3/2}$$

Relaxation time (τ)

Relaxation time calculated from the adiabatic compressibility and viscosity using the relation-

$$\tau = \frac{4}{3} \eta\beta$$

Intermolecular free length (L_f)

Estimation of intermolecular free length in liquids and in liquid mixtures has been a subject of considerable interest and semi-empirical relation to achieve the concept of intermolecular free length in order to explain the ultrasonic velocity in liquids as-

$$L_f = K_T \sqrt{\beta}\,.$$

Acoustic impedance (Z)

The acoustic impedance is the product of the velocity of ultrasound in a medium and its density and can be calculated by the relation is-

$$Z = U\rho$$

Relative association

Relative association can be calculated from the relation-

$$R_a = \left(\frac{\rho}{\rho_o} \right) \left(\frac{u_o}{u} \right)^{1/3}$$

ρ and ρ_0 are the densities of the pure liquid and liquid mixture. u and u_o are the ultrasonic velocity of pure liquid and liquid mixtures.

Available Volume and molar volume

The available volume is a direct measure of compactness and the strength of attraction between the molecules of a liquid or a mixture. It can be calculated from Schiff's relation as-

$$V_a = V\left[1 - \left(\frac{u}{u_\infty} \right) \right]$$ and molar volume $$V_m = \frac{m}{\rho}$$

Rao's constant

Rao's noted that the ratio of temperature coefficient of sound velocity u to the expansion coefficient V is virtually same for all but it is not associated with organic liquids. According to the Rao-

$$R = u^{1/3} V$$

Wada's constant

In the study of sound velocity in liquids, another constant has been suggested by Wada. According to Wada's constant –

$$w = \frac{m_{eff}}{\rho} \beta^{-1/7}$$

Lenard Jones Potential

The Lenard Jones potential is given by-

$$LJP=\frac{6v_m}{V_a}$$

Where, V_m represents the molar volume and V_a represents the available volume.

RESULTS AND DISCUSSION

The Tables-1 to 5 present the experimental values of ultrasonic velocity (u), density(ρ) and viscosity (η) for the ternary mixtures n-alcohols with dimethyl ketone in carbon tetrachloride or benzene systems at 301K. The variation of these experimental values depending on the values of pure components, solute-solvent interaction and hydrogen bonding of the solute etc., From the table 1 to 5, the ultrasonic velocity and viscosity increases with increasing the concentration of n – alcohols where as the density shows the decreasing trend[7] in all the ternary systems. The variation of ultrasonic velocity in a ternary mixtures depends upon the increase or decrease of inter molecular free length after mixing the components. On the basis of a model for sound propagation proposed by Eyiring and Kincaid, ultrasonic velocity should increases, if the intermolecular free length increase and vice-versa. The values of all the parameters are evaluated and are plotted in figures-1 to 12.

The ultrasonic velocity (u) increase with increase in mole fraction of alcohol[15-16]with dimethyl ketone keeping constant in carbon tetrachloride or benzene used as mixed solvent; this suggests that there are different types of molecular interactions between the components in these mixtures. The value of ultrasonic velocity is reported (fig.- 1 to 5). The variations in the ultrasonic velocity values in these systems behave almost ideal. This indicate weak induced dipole-induced dipole exist in these systems.

The adiabatic compressibility (β) values for various mole fractions of ternary mixtures have been computed and the values are plotted (fig.-2). In all the cases the value of adiabatic compressibility decreases with increasing concentration of alcohols[17-19] over a range of concentration (0 to 0.5). This indicates that weak induced dipole – induced dipole interactions exist. A comparison of the value of β in these 10 ternary mixtures consist of dimethyl ketone in carbon tetrachloride suggests that there are compressibility are in the order pentanol > hexanol > heptanol > octanol> decanol and dimethyl ketone as one components. Similar order observed other systems consists of alcohols with dimethylketone with benzene. The variations in the adiabatic compressibility (β) values in these systems behave almost ideal. This indicate that weak induced dipole-induced dipole exist in these systems.

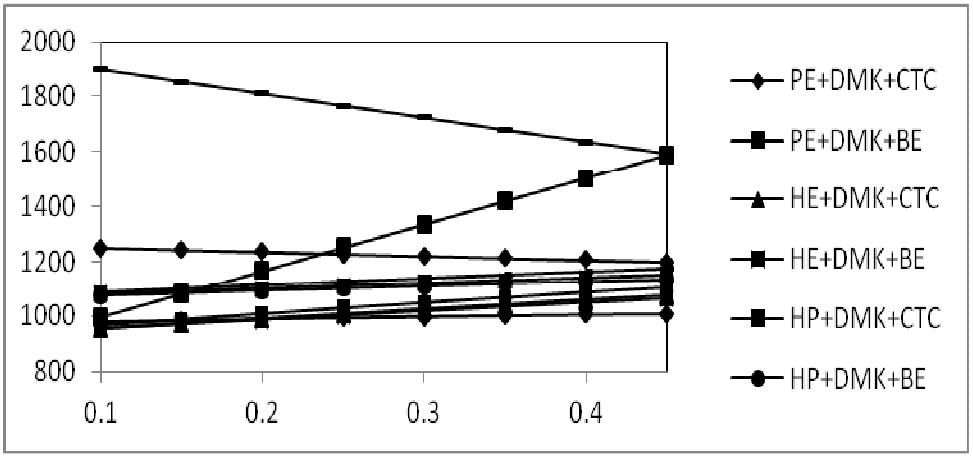

Fig.- 1:Plots of X_2 Vs ultrasonic velocity (u) of ternary liquid mixtures at 301 K

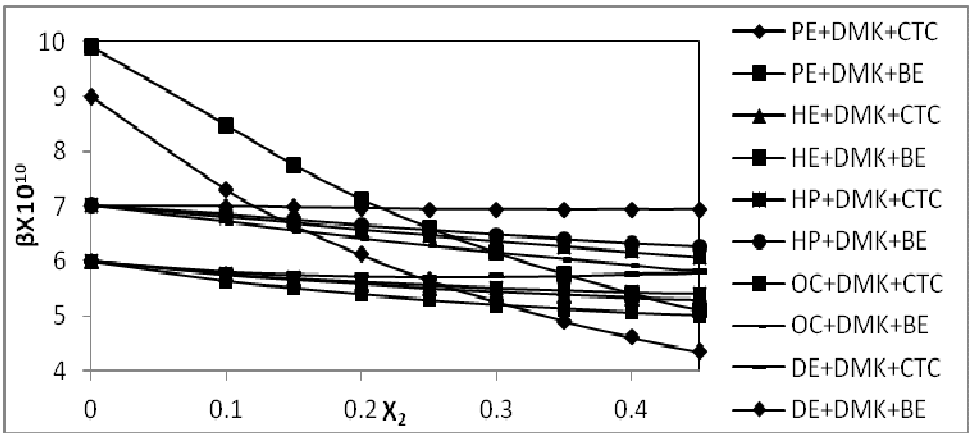

Fig.- 2:Plots of X_2 Vs adiabatic compressibility (β) of ternary liquid mixtures at 301 K

Table-1: Experimental ultrasonic velocity (u ms^{-1}), density (ρ Kgm^{-3}) and viscosity (η $X10^{-3}Nsm^{-2}$) values for the ternary mixtures of pentanol with dimethylketone with solvent at 301K

Mole fraction		U ms^{-1}	ρ Kgm^{-3}	η x10^{-3} Nsm^{-2}	U ms^{-1}	ρ Kgm^{-3}	η^{-3} Nsm^{-2}
X_1	X_3	Carbon tetrachloride			Benzene		
0.10	0.4	1005	1835	1.11	1130	1190	1.17
0.15	0.35	1020	1797	1.28	1138	1188	1.34
0.20	0.3	1034	1758	1.45	1146	1185	1.5
0.25	0.25	1049	1720	1.62	1154	1182	1.67
0.30	0.20	1064	1681	1.79	1162	1179	1.84
0.35	0.15	1079	1642	1.96	1170	1177	2
0.40	0.10	1094	1604	2.13	1178	1174	2.17
0.45	0.05	1108	1565	2.30	1186	1171	2.33

Table-2: Experimental ultrasonic velocity (u ms^{-1}), density (ρ Kgm^{-3}) and viscosity (η $X10^{-3}Nsm^{-2}$) values for the ternary mixtures of hexanol with dimethylketone with solvent at 301K

Mole fraction		U ms^{-1}	ρ Kgm^{-3}	η x10^{-3} Nsm^{-2}	U ms^{-1}	ρ Kgm^{-3}	η^{-3} Nsm^{-2}
X_1	X_3	Carbon tetrachloride			Benzene		
0.10	0.4	1010	1836	1.1	1134	1191	1.16
0.15	0.35	1027	1798	1.27	1144	1189	1.33
0.20	0.3	1044	1760	1.43	1154	1186	1.49
0.25	0.25	1061	1721	1.6	1163	1184	1.65
0.30	0.20	1077	1683	1.76	1173	1181	1.81
0.35	0.15	1094	1645	1.93	1182	1179	1.97
0.40	0.10	1110	1606	2.1	1192	1176	2.14
0.45	0.05	1126	1568	2.26	1201	1174	2.3

The values of relaxation time (τ) was calculated (fig.-3). There was an only slight variation in relaxation time value of alcohols-dimethylketone-carbon tetrachloride/benzene systems. This indicates that relatively weak interactions exist between the molecules of the three components and stronger intermolecular interactions exist between the molecules of each component.

The free length (L_f) of a system follows a measure of intermolecular attraction between the components in ternary mixtures. The increase in free length indicates that weakening of intermolecular interaction (fig.-

4). It is seen that the free length values increase with increase in concentration of alcohols[20].This shows that the intermolecular attraction weakens at higher concentration.

Table-3: Experimental ultrasonic velocity (u ms^{-1}), density (ρ Kgm^{-3}) and viscosity (η $X10^{-3}Nsm^{-2}$) values for the ternary mixtures of heptanol with dimethylketone with solvent at 301K

Mole fraction		U ms^{-1}	ρ Kgm^{-3}	η x10^{-3} Nsm^{-2}	U ms^{-1}	ρ Kgm^{-3}	η^{-3} Nsm^{-2}
X_1	X_3	Carbon tetrachloride			Benzene		
0.10	0.4	1008	1836	1.02	1130	1191	1.08
0.15	0.35	1024	1797	1.14	1139	1188	1.2
0.20	0.3	1040	1758	1.27	1146	1185	1.32
0.25	0.25	1055	1720	1.39	1154	1182	1.44
0.30	0.20	1065	1681	1.51	1162	1180	1.56
0.35	0.15	1084	1643	1.64	1169	1177	1.68
0.40	0.10	1098	1604	1.76	1176	1174	1.8
0.45	0.05	1112	1565	1.88	1183	1171	1.92

Table-4: Experimental ultrasonic velocity (u ms^{-1}), density (ρ Kgm^{-3}) and viscosity (η $X10^{-3}Nsm^{-2}$) values for the ternary mixtures of octanol with dimethylketone with solvent at 301K

Mole fraction		U ms^{-1}	ρ Kgm^{-3}	η x10^{-3} Nsm^{-2}	U ms^{-1}	ρ Kgm^{-3}	η^{-3} Nsm^{-2}
X_1	X_3	Carbon tetrachloride			Benzene		
0.10	0.4	1018	1837	1.36	1140	1192	1.42
0.15	0.35	1039	1799	1.66	1152	1190	1.71
0.20	0.3	1058	1761	1.95	1164	1187	2
0.25	0.25	1078	1723	2.24	1176	1183	2.3
0.30	0.20	1097	1685	2.54	1187	1185	2.59
0.35	0.15	1115	1647	2.83	1198	1183	2.88
0.40	0.10	1133	1609	3.13	1209	1179	3.17
0.45	0.05	1150	1571	3.42	1219	1177	3.46

Table-5: Experimental ultrasonic velocity (u ms^{-1}), density (ρ Kgm^{-3}) and viscosity (η $X10^{-3}Nsm^{-2}$) values for the ternary mixtures of decanol with dimethylketone with solvent at 301K

Mole fraction		U ms^{-1}	ρ Kgm^{-3}	η x10^{-3} Nsm^{-2}	U ms^{-1}	ρ Kgm^{-3}	η^{-3} Nsm^{-2}
X_1	X_3	Carbon tetrachloride			Benzene		
0.10	0.4	1004	1826	2.09	1120	1181	2.15
0.15	0.35	1017	1783	2.75	1123	1174	2.81
0.20	0.3	1029	1740	3.41	1125	1166	3.46
0.25	0.25	1041	1696	4.07	1128	1159	4.12
0.30	0.20	1051	1653	4.73	1130	1151	4.78
0.35	0.15	1061	1610	5.39	1132	1144	5.43
0.40	0.10	1070	1566	6.05	1134	1136	6.09
0.45	0.05	1079	1523	6.71	1136	1129	6.74

The mathematical relations for acoustic impedance and adiabatic compressibility show that they exhibit opposite behaviour and the behaviour is observed in all the liquid mixtures are studied (fig.-5). Out of all the ternary systems none exhibited a maximum in velocity curve and dip in compressibility curve.

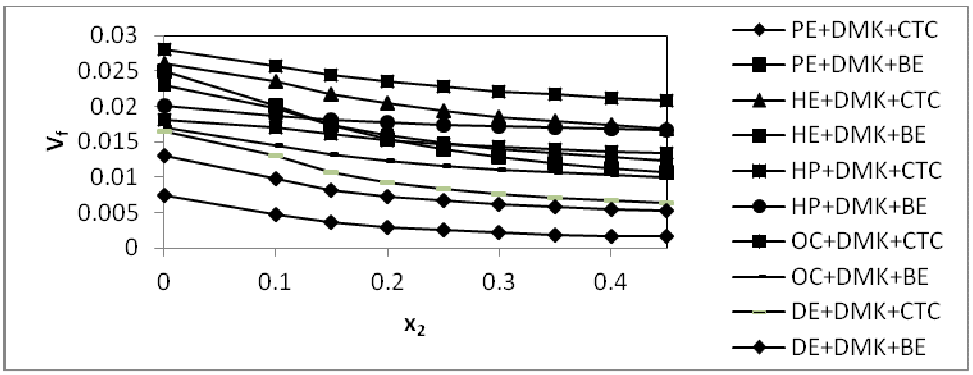

Fig.- 3:Plots of X_2 Vs free volume (V_f) of ternary liquid mixtures at 301 K

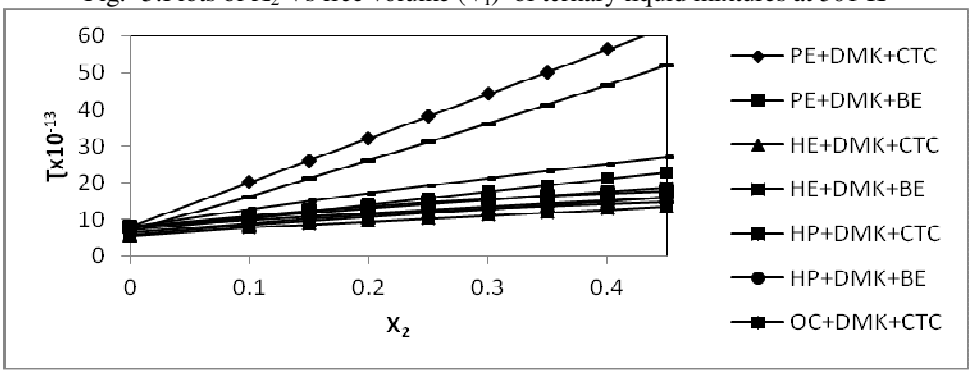

Fig.-4: Plots of X_2 Vs relaxation time (τ) of ternary liquid mixtures at 301 K

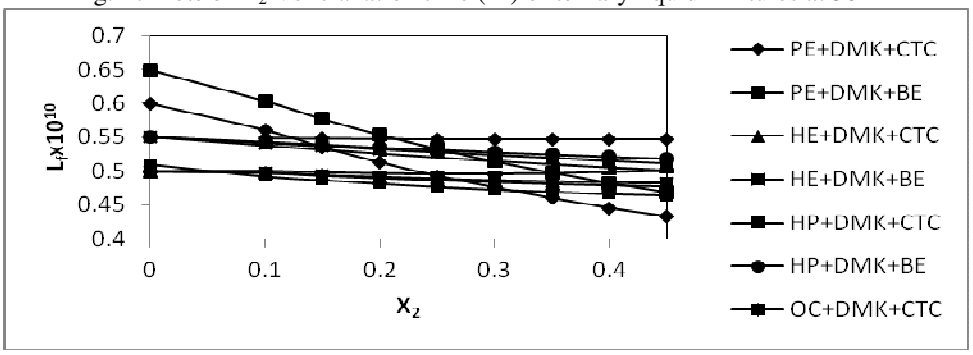

Fig.- 5:Plots of X_2 Vs Intermolecular free length (L_f) of ternary liquid mixtures at 301 K

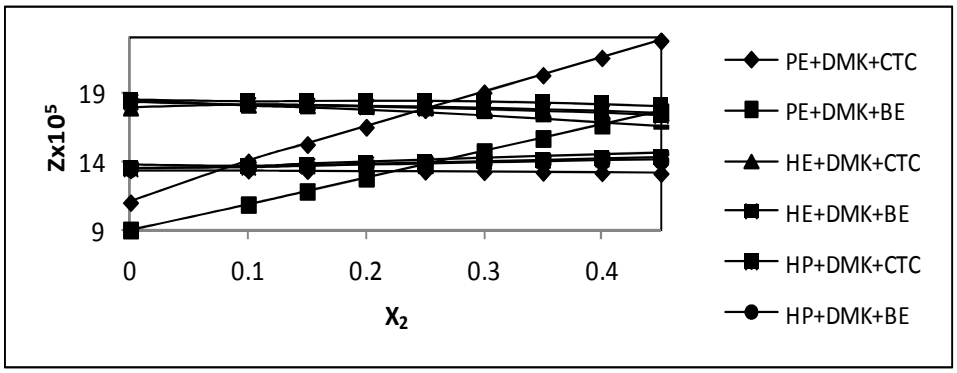

Fig.- 6: Plots of X_2 Vs acoustic impedance (Z) of ternary liquid mixtures at 301 K

This indicates the absence of complex formation[21-22]. The poor complex formation is also confirmed by the linear variation of specific acoustic impedance. So the specific acoustic impedance is linear, hence no indication of complex formation in the systems.

The relative association (RA) values in a system can be used to ascertain the variation in intermolecular attraction and also to establish the existence of similar types of interaction in different ternary systems. The relative association values are increase with increase in the mole fraction of the alcohols (fig 6). The values are increase from unity[23]. This trend suggests that induced dipole–induced dipole types of molecular interaction exist in all these ternary systems.

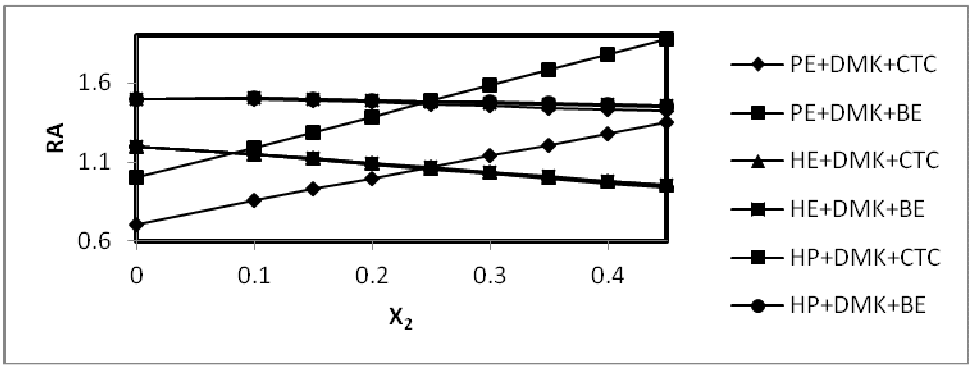

Fig.- 7: Plots of X_2 Vs relative association (RA) of ternary liquid mixtures at 301 K

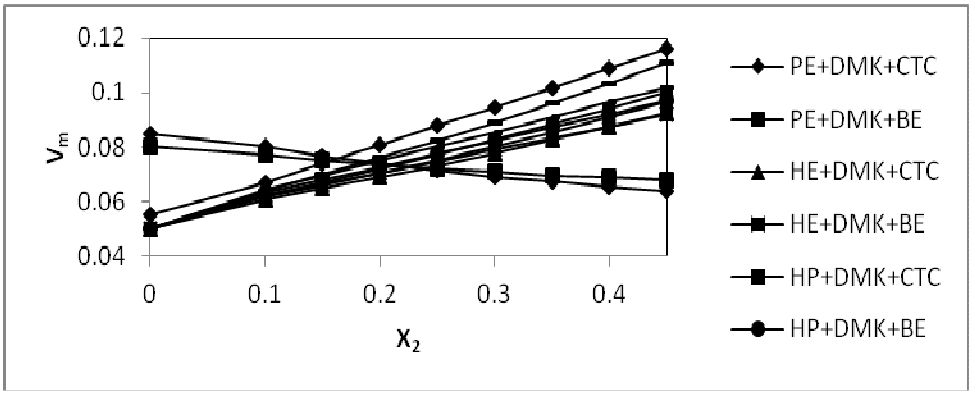

Fig.- 8: Plots of X_2 Vs molar volume (V_m) of ternary liquid mixtures at 301 K

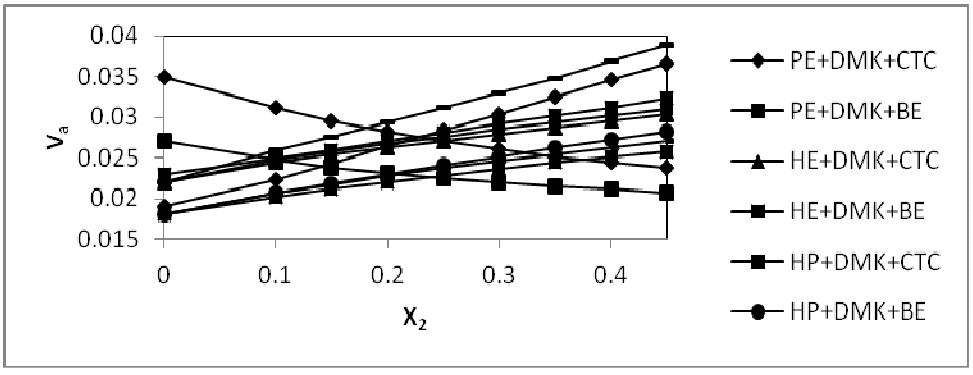

Fig.- 9: Plots of X_2 Vs available volume (V_a) of ternary liquid mixtures at 301 K

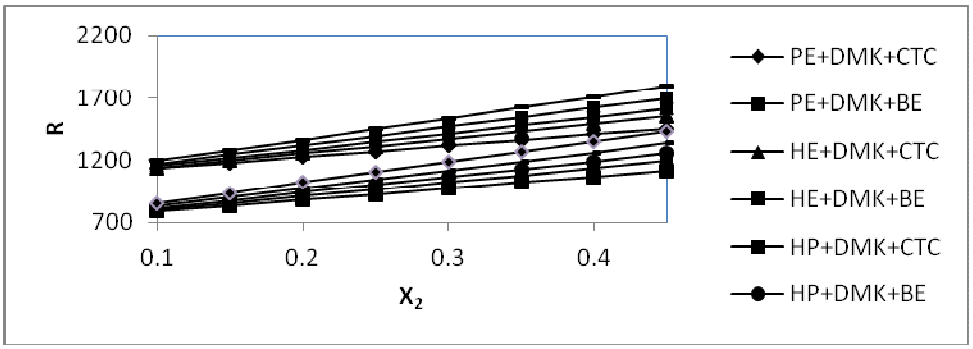

Fig.- 10: Plots of X_2 Vs Rao constant (R) of ternary liquid mixtures at 301 K

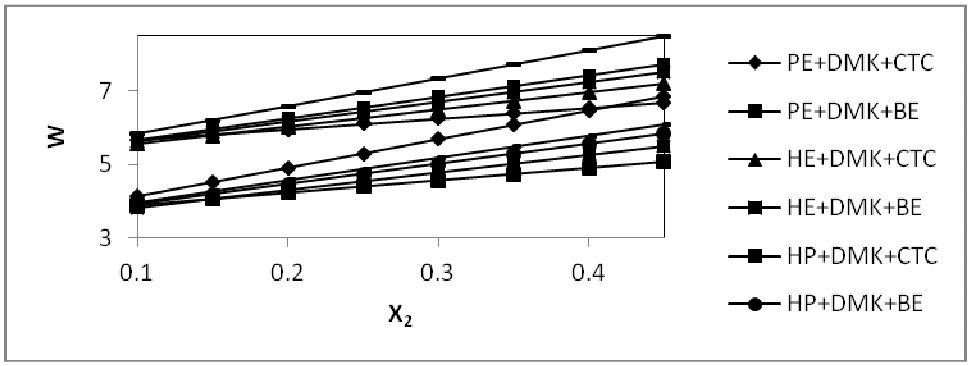

Fig.- 11: Plots of X_2 Vs Wadas constant (W) of ternary liquid mixtures at 301 K

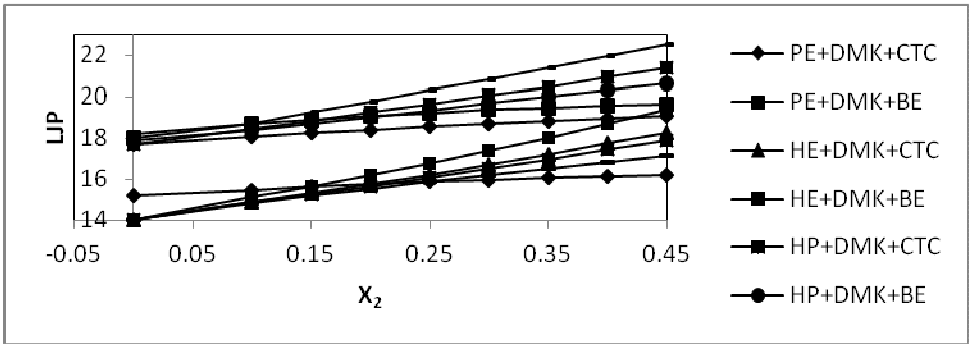

Fig.- 12: Plots of X_2 Vs Linard -John potential (LJP) of ternary liquid mixtures at 301 K

The free volume (V_f) and available volume (V_a) values are calculated (fig.-7 and fig.-8). It is found that for all the systems at 301 K, free volume is increases with increase in concentration[24-25]. But the calculated available volume increases with increase concentration for all the systems.

The values of these constants for the present ternary systems are evaluated (fig.- 9). It is clear that the variations of these constants with mole fractions of alcohols are linear. It is reported that in a ternary liquid mixtures of one component indicate weak induced dipole-induced dipole interaction.

The Lenard-John Potential (LJP) values are calculated (fig.- 10). The LJP values indicate that dipole-dipole attractions are stronger than induced dipole-induced dipole attractions.

CONCLUSION

Generally, solute-solvent association arise due to slightly polar solute and polar nature of the solvent. The natures of intermolecular interaction in the liquid mixtures have been explained on the basis of the

variation of acoustical parameter. It is found that the interaction between unlike molecules decreases with the increase in alcohol chain length. It is concluded that ultrasonic studies provide a comprehensive investigation of molecular association between dimethylketone with pentanol, hexanol, heptanol, octanol and decanol in carbontetrachloride and benzene arising from the hydrogen bonding between the solute and solvent molecules, the order of interactions is found to be in the solvent CCl_4 is octanol>hexanol>heptanol>pentanol>decanol. The order of interactions in the solvent benzene is octanol>hexanol>pentanol>heptanol>decanol. Thus it can be concluded that the interaction of alcohol with benzene is stronger than Carbon tetrachloride.

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