MINOR RESEARCH PROJECT

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TITLE OF THE PROJECT

Ultrasonic studies on Molecular Interaction in Some Ternary mixtures of Alkanols at Different Temperatures

Research Work Done:

Project Title: **Ultrasonic studies on Molecular Interaction in Some Ternary mixtures of Alkanols at Different Temperatures**

Introduction:

The study of molecular interaction in Ternary mixtures of alkanols are widely used as solvent in industries and research laboratories[3].It find a wide range of applications as solubility agent in organic synthesis . When ultrasonic waves travel in medium there is a variation in pressure from particle to particle. By measuring velocity, specific impedance of the medium can be calculated thus it has relevance in physics and electronics. Ultrasonic investigations of liquid mixtures consist of polar and non-polar components have considerable importance in understanding intermolecular interactions between the components molecule and find applications in several industrial and technological process.[4] The nature and relative strength of the molecular interaction between the components of the liquid mixtures have been successfully investigated by the ultrasonic method[1].These interactions help in better understanding the nature of the solute and solvent i.e wherever the solute modifies of distorts the structure of the solvent[12].Experimental values of ultrasonic velocity (U)density (ρ), viscosity(η)are measured and these values are used to derive other parameters like free volume (Vf), free length (Lf) acoustic impedance (Z) , adiabatic compressibility (β) , Internal pressure (π) are measured which are useful in the accurate determination physico chemical properties and which are highly sensitive to molecular interactions in ternary mixtures of alkanols[3,4].

Objective:

To determine ultrasonic velocity (U) density (ρ) and viscosity(η) to study some acoustical parameter such as adiabatic compressibility(β) free volume (Vf), free length (Lf) , Internal pressure (π). The result will be analyzed and interpreted to study nature of molecular interaction such as dipole-dipole interaction through hydrogen bonding.

Methodology:

The liquid mixtures of various concentration in mole fraction can be prepared which are purified by standard method.[8]The present work deals with the measurement of ultrasonic velocity (U) density (ρ) and viscosity(η) and evaluation of the related parameters in the following binary liquid systems at different temperatures.

Chemical to be used in study of liquid ternary mixtures are

DMSO+I-Propanol+II Propanol and DMSO + I Butanol+II Butanol of different concentration in mole fraction are prepared.

An electronically digital operated constant temperature bath can be used to circulate water around the measuring cell made of steel containing the experimental solution at desired tempearure.[2]

The ultrasonic velocity can be measured using ultrasonic interferometer at fixed temperature. The density can be measured using specific-gravity bottle to an accuracy of better than ±0.1%.Viscosity by Viscometer. Studying basic parameters like ultrasonic velocity (U) density (ρ) and viscosity(η) other parameters like adiabatic compressibility(β) free volume (Vf), free length (Lf) , Internal pressure (π).calculated to study intermolecular interaction of the ternary mixture of alkanols[7,11].

2 Experimental Details:

A detail procedure for measurement of velocity , density and viscosity is described. The value of measured velocities , densities and viscosities of DMSO i.e($U_{DMSO=}$1487.0 g cm-1),(d=1.0955 gcm-3, η =1.989cp). The accuracy of densities ,Ultrasonic velocity and viscosity measurement was determined to be ±0.2 % . Chemicals of are >99.5% of purity from eMerk company were used without further purification. The ultrasonic speed was measured using Ultrasonic Interferometer 2MHz frequency. Constant Temperature Water bath from Mittal Enterprises New Delhi was used for maintaining constant temperature 300k,307K, 314K of ternary mixture. Various concentration of the trenary mixtures were prepared in terms of mole concentration of DMSO+ Propanol-I + Propanol-II and DMSO+ Butanol-1+Butano-II out of which mole concentration of DMSO was kept fixed while mole concentration of propanol-I, Propanol-II, Butanol-I and Butanol-II was changed.

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Measurements:

(i)Velocity Measurement:

The speed of sound waves was obtained by using ultrasonic interferometer from Mittal Enterprises, New Delhi. Ultrasonic speed was measured at a fixed frequency of 2MHz with an accuracy of ± 1ms-1.An electronically digital operated bath Model SSI-0.3) supplied by Mittal Enterprises with accuracy of 0.1K has been used to circulate water through the double walled measuring cell made up cell containing the experimental solution at desired temperature.

(ii)Density Measurement:

The density was measured using 50ml specific gravity bottle.The specific gravity bottle with the experimental mixtures was immersed in a digital temperature controlled water bath. The measurements of mass for different liquid concentration were performed on an electronic balance. Digital balance with .001gm accuracy was used to measure it's weight. The density was measured using the formula

1. $\rho_2 = (W2/W1).\rho_1$

Where W1= weight of distilled water. W2= Weight of experimental liquid.ρ_1=Density of water. ρ_2= Density of liquid mixture.

(iii)Viscosity Measurement:

The viscosity of the ternary mixture were measured an Ostwakd.s viscometer calibrated with double distilled water having time of effulix 0.01s and accuracy was found to be ± Nm-2s. The Oswald's *viscometer* with the experimental mixture was immersed in digitally temperature controlled water bath. The time of flow was measured using a digital racer stop watch with an accuracy of 0.1 sec.To reduce error

The viscosity was determined using the relation,

$$3.\eta_2 = \eta_1(t2/t1)(\rho 2/\rho 1)$$

Where η_1= Viscosity of distilled water, η_2 = Viscosity of ternary mixture, t1= time of flow of distilled water, t2 = time of flow of mixture solvent.ρ2 = density of ternary mixture, ρ1= density of distilled water,

Isontropic compressibility is a characteristic property and central importance in the ultrasonic study of liquids and liquid mixtures of intermolecular arrangement and orientation of constitution of consistence molecules.[6]

Speed in ternary liquid mixtures given by Nomonto can be written as [6]

$$U^{nom} = \left\{ \frac{X_1R_1 + X2R_2 + X_3R_3}{X_1V_1 + X2V_2 + X_3R_3} \right\}_3$$

Where X1,X2,X3 are the mole fraction of the liquid mixture R1,R2,R3 the molar sound velocities and V1,V2,V3 are molar volume.

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1. Adiabatic Compressibility(β) Adiabatic Compressibility is the fractional decrease of volume per unit increase of pressure, when no heat in or out [9,10] .It is calculated from the Ultrasnic speed of sound (U) and the density (ρ). It is calculated by equation

$$\beta = 1/U2.\rho$$

(ii) Intermolecular free length (Lf) :- The intermolecular free length is the distance between the surfaces of the neighboring molecules[11]. It is calculated by using the relation

$$Lf = KT\beta 1/2$$

Where KT is the temperature dependent constant and 'β' is the adiabatic compressibility.

(iii) Free Volume (Vf) :- Free volume in terms of ultrasonic velocity(U) and the viscosity(η) of liquid is

$$Vf = (Meff.U / K.\eta)1/2$$

Where 'Meff' is the effective mass of the mixture, 'K' is a dimensionless constant independent of temperature and liquid. Its value is 4.281 x 109.

(iv) Internal Pressure (Πi):- The measurement of internal pressure is important in the study of the thermodynamic properties of liquids. The internal pressure is the cohesive force, which is a resultant o force of attraction and force of repulsion between the molecules[12 ,13]. It is calculated by using the relation,

$$\Pi i = bRT\,(k\eta/U)\,1/2\,(\rho 2/3/Meff7/6)$$

Where 'b' stands for cubic packaging, which is assuemd to be '2' for all liquids, ' k' is a dimensionless constant independent of temperature and nature of liquids. Its value is 4.281 x 109. ' T ' is the absolute temperature in Kelvin, 'Meff' is the effective molecular weight, 'R' is the Universal gas constant, 'η' is the viscosity of solution in N.S.m-2, 'U' is the ultrasonic velocity in m.s-1 and 'ρ' is the density in Kg.m-3 of solution.

System:I DMSO+I-Propanol+II Propanol

DMSO Mole Concentration = 0.70346

Table:I **Table:1 Densities (ρ), Viscosites ,experimental ultrasonic speed equations for the System-I at temperature Temperature :300K**

Mole Concentration	Density	Viscosity	Velocity	(U)^2
0.66892 0.0000	0.949	1.4289	1356	1838736
0.60203 0.06522	0.942	1.2016	1324	1752976
0.40135 0.26089	0.941	1.2643	1304	1700416
0.33446 0.29567	0.951	1.3159	1272	1617984
0.26756 0.33045	0.785	1.0868	1159	1343281
0.13378 0.43045	1.003	1.3205	1271	1615441
0.13378 0.5200	1.036	1.5246	1420	2016400
0.03389 0.6523	1.041	1.4754	1269	1610361

Table-2:System-1 Adiabatic compressibility, Intermolecular free length (Lf)**, Free volume Vf and Internal pressure** Πi **at temp.300K**

β=1/(U)^2ρ	Lf=KT*β^1/2	Meff	Vf=Meff*U/η*K	πi
5.16E-07	1104.545	95.007	3.86E+14	1.61E-05
5.37E-07	1149.488	94.905	4.48E+14	1.38E-05
5.53E-07	1184.235	34.605	1.53E+14	0.017136
5.88E-07	1257.451	86.685	3.59E+14	3.02E-05
5.85E-07	1250.937	78.753	3.59E+14	3.65E-05
6.21E-07	1328.673	70.725	2.91E+14	0.00014
5.14E-07	1099.309	62.895	2.51E+14	0.000351
6.46E-07	1382.783	62.793	2.31E+14	0.000388

Table3; Densities (ρ), Viscosities ,experimental ultrasonic speed (Uexpt) for the System-I at temperature Temperature :307K

Mole Concentration	Density	Viscosity	Velocity	(U)^2
0.66892 0.0000	0.949	1.4289	1356	1838736
0.60203 0.06522	0.942	1.2016	1324	1752976
0.40135 0.26089	0.941	1.2643	1304	1700416
0.33446 0.29567	0.951	1.3159	1272	1617984
0.26756 0.33045	0.785	1.0868	1159	1343281
0.13378 0.43045	1.003	1.3205	1271	1615441
0.13378 0.5200	1.036	1.5246	1420	2016400
0.03389 0.6523	1.041	1.4754	1269	1610361

Table:4System-1

Adiabatic compressibility, Intermolecular free length (Lf)
Free volume Vf and Internal pressure Πi at temp.307K

β=1/(U)^2ρ	Lf=KT*β^1/2	Meff	Vf=Meff*U/η*K	πi
5.16E-07	1104.545	95.007	3.86E+14	1.61E-05
5.37E-07	1149.488	94.905	4.48E+14	1.38E-05
5.53E-07	1184.235	34.605	1.53E+14	0.017136
5.88E-07	1257.451	86.685	3.59E+14	3.02E-05
5.85E-07	1250.937	78.753	3.59E+14	3.65E-05
6.21E-07	1328.673	70.725	2.91E+14	0.00014
5.14E-07	1099.309	62.895	2.51E+14	0.000351
6.46E-07	1382.783	62.793	2.31E+14	0.000388

Table:5 Densities (ρ), Viscosities ,experimental ultrasonic speed for the System-I at temperature :314K

Mole Concentration	Density	Viscosity	Velocity	(U)^2
0.66892 0.0000	0.9300	0.82780	1308	1710864
0.60203 0.0652	0.9312	0.82427	1272	1617984
0.13378 0.0000	1.0229	0.97090	1385	1918225
0.26756 0.13045	0.7858	0.66848	1178	1387684
0.33446 0.19567	0.9471	0.83831	1252	1567504
0.40135 0.26089	0.9272	0.75689	1277	1630729
0.13378 0.13045	0.9875	0.80155	1256	1577536
0.03389 0.0652	1.0269	1.17156	1240	1537600

Table:6 System-1Adiabatic compressibility β, Intermolecular free length (Lf) Free volume Vf and Internal pressure IIi at temp.314K

β=1/(U)^2ρ	Lf=KT*β^1/2	Meff	Vf=Meff*U/η*K	πi
5.436E-07	1163.309416	95.007	6.42509E+14	9.727E-06
5.755E-07	1231.635084	94.905	6.26834E+14	1.006E-05
5.332E-07	1141.151116	62.895	3.84005E+14	0.0002339
5.662E-07	1211.747141	78.753	5.93976E+14	2.315E-05
6.042E-07	1292.966543	86.685	5.54096E+14	2.027E-05
5.686E-07	1216.764094	34.605	2.49884E+14	0.010646
6.26E-07	1339.643343	70.725	4.74326E+14	8.73E-05
6.679E-07	1429.20671	62.793	2.84454E+14	0.0003214

Temperature :300K

System-II DMSO+ Butanol-I+Butanol-II Temperature :300K

Table:7 **System-II Densities (ρ), Viscosities ,experimental ultrasonic speed for the System-I at temperature**

Mole Concentration	Density	Viscosity	Velocity	(U)^2
0.66892 0.0000	0.949	1.4289	1356	1838736
0.60203 0.06522	0.942	1.2016	1324	1752976
0.40135 0.26089	0.941	1.2643	1304	1700416
0.33446 0.29567	0.951	1.3159	1272	1617984
0.26756 0.33045	0.785	1.0868	1159	1343281
0.13378 0.43045	1.003	1.3205	1271	1615441
0.13378 0.5200	1.036	1.5246	1420	2016400
0.03389 0.6523	1.041	1.4754	1269	1610361

Table:8 **System-II Adiabatic compressibility β, Intermolecular free length (Lf) Free volume Vf and Internal pressure IIi at temp.314K**

β=1/(U)^2ρ	Lf=KT*β^1/2	Meff	Vf=Meff*U/η*K	πi
5.16E-07	1104.545	95.007	3.86E+14	1.61E-05
5.37E-07	1149.488	94.905	4.48E+14	1.38E-05
5.53E-07	1184.235	34.605	1.53E+14	0.017136
5.88E-07	1257.451	86.685	3.59E+14	3.02E-05
5.85E-07	1250.937	78.753	3.59E+14	3.65E-05
6.21E-07	1328.673	70.725	2.91E+14	0.00014
5.14E-07	1099.309	62.895	2.51E+14	0.000351
6.46E-07	1382.783	62.793	2.31E+14	0.000388

System-II DMSO+ Butanol-I+Butanol-II Temperature :307K

Table-9 **System-II Densities (ρ), Viscosities ,experimental ultrasonic speed for the System-I at temperature 307**

Mole Concentration	Density	Viscosity	Velocity	(U)^2
0.66892 0.0000	0.937	1.406	1348	1817104
0.60203 0.06522	0.937	1.039	1324	1752976
0.40135 0.26089	1.032	1.235	1420	2016400
0.33446 0.2956	0.789	0.875	1156	1336336
0.26756 0.3304	0.953	1.080	1288	1658944
0.13378 0.4304	0.934	1.004	1322	1747684
0.13378 0.5200	0.996	1.081	1234	1522756
0.03389 0.6523	1.035	1.147	1244	1547536

Table:10 **System-II Adiabatic compressibility β, Intermolecular free length (Lf) Free volume Vf and Internal pressure IIi at temp.307K**

β=1/(U)^2ρ	Lf=KT*β^1/2	Meff	Vf=Meff*U/η*K	πi
5.16E-07	1103.895	95.007	3.9E+14	1.59E-05
5.35E-07	1144.311	94.905	5.17E+14	1.21E-05
5.12E-07	1095.15	62.895	3.1E+14	0.000289
5.9E-07	1263.644	78.753	4.45E+14	3.05E-05
5.75E-07	1229.758	86.685	4.43E+14	2.51E-05
5.35E-07	1144.081	34.605	1.95E+14	0.013545
6.54E-07	1399.839	70.725	3.45E+14	0.000119
6.69E-07	1430.655	62.793	2.91E+14	0.000311

System-II Densities (ρ), Viscosities ,experimental ultrasonic speed for the System-I at temperature 314K

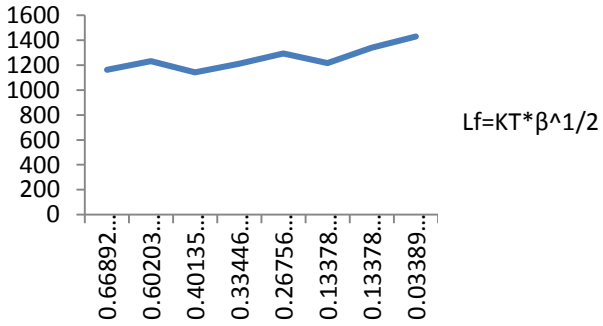
Mole Concentration	Density	Viscosity	Velocity	(U)^2
0.66892 0.0000	0.9300	0.828	1308	1710864
0.60203 0.0652	0.9312	0.824	1272	1617984
0.40135 0.2609	1.0229	0.971	1385	1918225
0.33446 0.2959	0.7858	0.668	1178	1387684
0.26756 0.3360	0.9471	0.838	1252	1567504
0.13378 0.4234	0.9272	0.757	1277	1630729
0.13378 0.5191	0.9875	0.802	1256	1577536
0.03389 0.6499	1.0269	1.172	1240	1537600

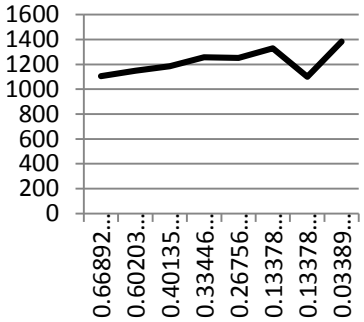
Table:10 **System-II Adiabatic compressibility β, Intermolecular free length (Lf) Free volume Vf and Internal pressure IIi at temp.314K**

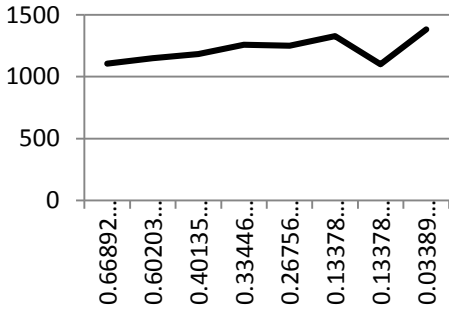
β=1/(U)^2ρ	Lf=KT*β^1/2	Meff	Vf=Meff*U/η*K	πi
5.44E-07	1163.309	95.007	6.43E+14	9.73E-06
5.76E-07	1231.635	94.905	6.27E+14	1.01E-05
5.33E-07	1141.151	62.895	3.84E+14	0.000234
5.66E-07	1211.747	78.753	5.94E+14	2.32E-05
6.04E-07	1292.967	86.685	5.54E+14	2.03E-05
5.69E-07	1216.764	34.605	2.5E+14	0.010646
6.26E-07	1339.643	70.725	4.74E+14	8.73E-05
6.68E-07	1429.207	62.793	2.84E+14	0.000321

Graphs For System-I DMSO+Propanol-I+ Proponol-II

Graph1 : System1: DMS) +propanol-1+Propanol-2Molecular Concentration Vs free length

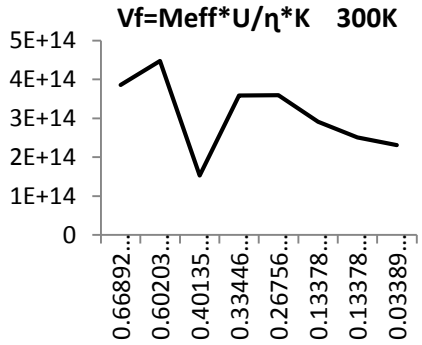


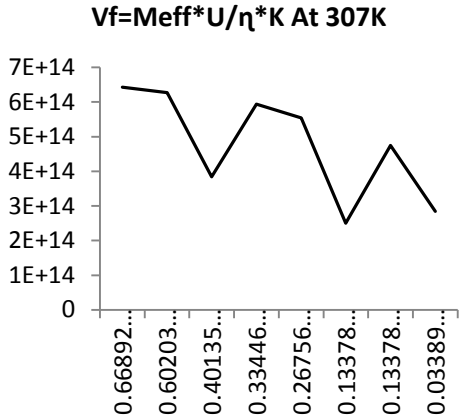


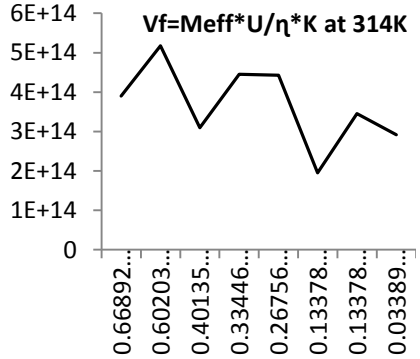


Graph2 : System1:

DMSO +propanol-1+Propanol-2Molecular Concentration Vs Free Volume **Vf=Meff*U/η*K At 314K**



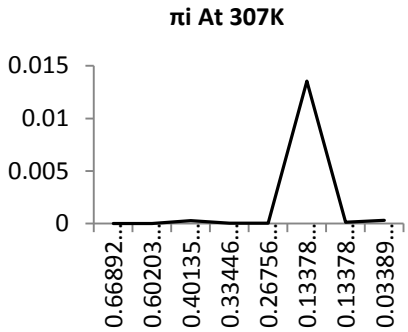


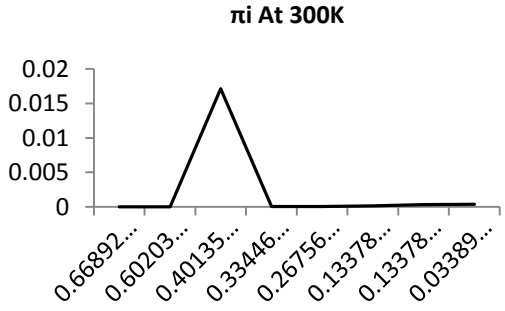


Graph2 : System1:

DMSO +propanol-1+Propanol-2

Molecular Concentration Vs Internal Pressure πi

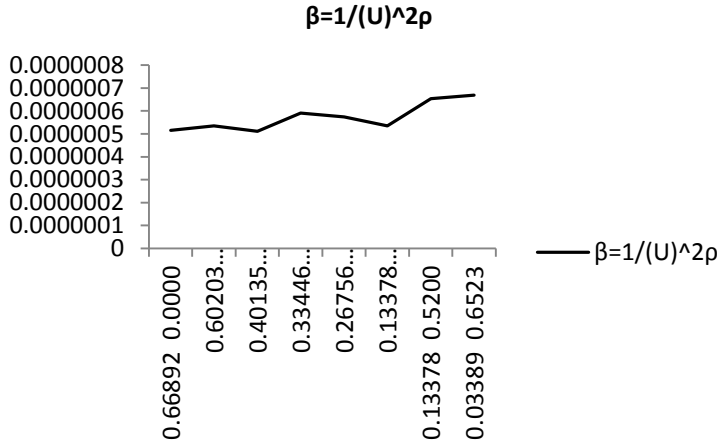


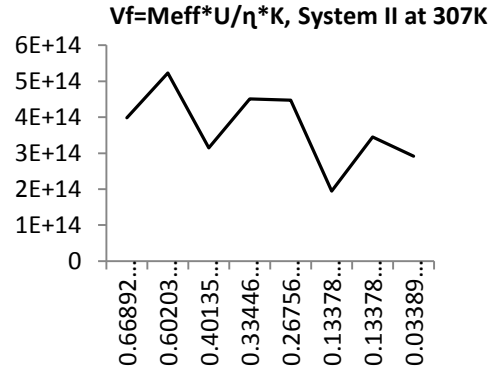


Graph2 : System-2

DMSO +Butanol-1+Butanol-2

Molecular Concentration Vs Adiabatic Compressibility at Temperature 307K





Result and Conclusion:

Ultrasonic velocity studies on the system of ternary mixture of DMSO with Propanol-1+ propanol-2 and system-2 DMSO with Butanol-1+Butanol--2 shows that, when concentration of DMSO increases, structure is formed due to bonding between the unlike molecules through dipole-dipole and dipole-induced dipole interaction. Ultrasonic velocity decreases with increase in concentration of Propanol in DMSO and decreases with increase in temperature, adiabatic compressibility decreases with concentration of Alkanols The same variation also occur in case of free length and free volume. Internal pressure, decreases with increase in concentration of proponal and butanol and decreases with increase in temperature. So acoustic parameters are highly affected at different temperatures due to dipole-dipole

and dipole-induced dipole interaction between molecules. The intermolecular interaction seems to be stronger than the intra-molecular interaction thus leading to a decrease of Free volume. Hence free volume decreases with increase in mole fraction. When the temperature is increased there is reduction in

Dispersive forces are also found to exist between the components of the mixture. molecular interaction as they move away from each other. This reduces the cohesive force. Thus a decrease in internal pressure and increase in free volume occurs with increases in temperature .

Internal Pressure: Internal Pressure explain the interaction in the liquid solution. Internal pressure vary due to intermolecular interactions.[7 ,10] The variation in internal pressure play significant role in understanding intermolecular interactions. For system-1 (DMSO+ Propanol-1+propanol2)at Mole Concentration = 0.70346 0.33446 0.2956 internal pressure is maximum .This indicates that these compound have structure making property at this concentration.

For system-2 (DMSO+Butanp-1+Butano-2) at mole concentration 0.70346 0.26756 0.33045 internal pressure is maximum .This indicates that these compound have structure making property at this concentration.

Free volume: Free volume decreases with decrease I mole concentration of DMSO . This indicates that with increase of concentration of propanol in DMSO

Free length: Free length decreases When temperature is increased there is a tendency to move away from each other reducing the possibility of interaction which may further reduce cohesive forces and leads to decrease in internal pressure and increase in free volume.

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