Ultrasonic analysis of intermolecular interaction in the mixtures of benzene with N, N-dimethylformamide and cyclohexane at different temperatures

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ABSTRACT

The ultrasonic velocity, density and viscosity values have been measured at 288 K, 298 K, 308 K and 318 K in the ternary system of N,N-dimethylformamide, cyclohexane and benzene. From these experimental data, acoustical parameters such as adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (Π_i), relaxation time (τ), Gibb's free energy (ΔG), acoustic impedance (Z) and their excess values have been estimated using the standard relations. The results are interpreted in terms of molecular interaction between the components of the mixtures.

Key Words: Sound velocity, adiabatic compressibility, free length, free volume, internal pressure, molecular interaction.
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INTRODUCTION

Ultrasonic investigations of liquid mixtures consisting of polar and non-polar components are of considerable importance in understanding the intermolecular interactions between the component molecules and find applications in several industrial and technological processes [1-4]. The ultrasonic velocity in a liquid is fundamentally related to the binding forces between the atoms or molecules and has been successfully employed in understanding the nature of molecular interactions in pure liquids and binary and ternary mixtures [5-7]. The variation of ultrasonic velocity and related parameters throw much light upon the structural changes associated with the liquid mixtures having strongly interacting components [8] as well as weakly interacting components [9].

In order to have a clear understanding of the intermolecular interactions between the component molecules, the author's have performed a thorough study on the liquid mixtures using ultrasonic velocity data.

The present work deals with the ultrasonic velocity and computation of related parameters with their excess values in ternary system of N,N-Dimethylformamide + Cyclohexane + Benzene at 288k, 298K, 308k & 318K (at f=6MHz). For preparing various concentration mixtures, mole fractions of component liquids were varied from 0.0 to 0.6.

N-N-Dimethyl formamide (DMF), as a polar solvent, is certainly to some extent associated by dipole-dipole interactions, and is of particular interest because of the absence of any significant structural effects due to the lack of hydrogen bonds; therefore, it may work as an aprotic, protophilic solvent with a large dipole moment and high dielectric constant (μ=3.24D and ε=36.71). It is used in the separation of saturated and unsaturated hydrocarbons and serves as a solvent for many polymers. Cyclohexane (ε=2.02) belongs to alicyclic hydrocarbon (closed chain). It is non-polar, unassociated, inert hydrocarbons and has globular structure [10]. Hence it is not involved in any interaction with DMF or benzene. However dispersion forces caused by correlated movements of electrons in interactive molecules are possible between cyclohexane and the other components. Benzene is a non-polar solvent,

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which is freely miscible with many organic solvents [11]. It has slightly polar nature due to the delocalized electron cloud, which results in the solute-solvent molecular associates.

EXPERIMENTAL SECTION

N, N-Dimethylformamide, Cyclohexane, Benzene (AR grade) were purified by the standard methods [12]. Various concentrations of the ternary liquid mixtures were prepared in terms of mole fraction, out of which the mole fraction of the second component, Cyclohexane ($X_2 = 0.4$) was kept fixed while the mole fractions of remaining two (X_1 and X_3) were varied from 0.0 to 0.6. There is nothing significant in fixing the mole fraction of second component at 0.4. Ultrasonic velocity measurements were made using ultrasonic interferometer (Model M-84, Mittal enterprises, New Delhi) at 6 MHz with accuracy of $\pm 0.1 ms^{-1}$. Density and viscosity was determined using a specific gravity bottle and Ostwald's viscometer. All the measurements were made at 288 K, 298 K, 308 K, and 318K with the help of an electronically operated digital constant temperature bath (Model SSI-03spl, Mittal Enterprises, New Delhi), operating in the temperature range -10°c to 85°c with an accuracy of $\pm$ 0.1K.

THEORY

The ultrasonic velocity (U), density (ρ) and viscosity (η) in pure liquids and liquid mixture of various concentrations have been measured at 288 K, 298 K, 308 K and 318 K. Thermodynamic and acoustical parameters such as adiabatic compressibility (β), inter molecular free length (L_f), free volume (V_f), viscous relaxation time (τ), internal pressure (π_i), Gibbs free energy (ΔG) and acoustic impedance (Z), were determined using the observed values of velocity, density and viscosity using respective equations and the Excess values of these parameters were evaluated using the equations given below .

Intermolecular free length (L_f), is calculated using the standard expression

$$L_f = K. \beta^{1/2} \text{ ----------------------------- (1)}$$

Where K is a temperature dependent constant known as Jacobson constant and ß is the adiabatic compressibility that can be calculated from the speed of sound (U) and the density of the medium (ρ) as

$$\beta = (u^2 \cdot \rho)^{-1} \text{ ----------------------------- (2)}$$

The relation for free volume in terms of ultrasonic velocity and the viscosity (η) of liquid as

$$V_f = (M_{eff}.U / k.\eta)^{3/2} \text{ -------------------- (3)}$$

Expression for the determination of internal pressure Π_i is

$$\Pi_i = b.R.T.(K.\eta/U)^{½} \cdot (\rho^{2/3}/M_{eff}^{7/6}) \text{ ---- (4)}$$

Where b stands for cubic packing which is assumed to be '2' for liquids and 'K' is a dimensionless constant independent of temperature and nature of liquids and its value is 4.281×10^9, 'T' is the absolute temperature and " " M_{eff} " is the effective molecular weight.

The viscous relaxation time is obtained using the relation

$$\tau = (4/3) \beta \eta \text{ ----------------------------(5)}$$

Gibbs free energy is calculated from the relation

$$\Delta G = K.T.\ln (K.T.\tau / h) \text{ ----------------(6)}$$

Where 'τ' is the viscous relaxation time, 'K' is the Boltzmann's constant, 'T' is the absolute temperature and h is the Planck's constant.

The specific acoustic impendence is given by,

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$$Z = U.\rho \text{ -------------------------------- (7)}$$

Where, 'U' and 'ρ' are the velocity and density of liquid respectively.

In order to understand the nature of the molecular interactions between the components of the liquid mixtures, it is of interest to discuss the same in term of excess parameters rather than actual values.

Excess parameters (A^E) of all the parameters are computed by the relation

$$A^E = A_{exp} - A_{id} \text{ ----------------------- (8)}$$

Where $A_{id} = \sum_i^n A_i X_i$, '$A_i$' is any parameters and 'X_i' the mole fraction of the liquid components of 'i'.

TABLE – I: Values of Density (ρ), Viscosity (η) and velocity (U) at 288k, 298k, 308k and 318k.

Mole fraction		Density (ρ) Kg.m^{-3}				Viscosity (η) (10^{-3} N.s.m^{-2})				Velocity (U) m.s^{-2}			
X$_1$	X$_2$	288K	298K	308K	318K	288K	298K	308K	318K	288K	298K	308K	318K
0.0000	0.6000	835.26	830.94	824.87	818.23	0.9123	0.6798	0.5364	0.4585	1280.4	1247.7	1220.1	1165.1
0.0999	0.4999	842.89	837.12	831.16	824.30	0.9265	0.6852	0.543	0.4662	1286.2	1252.8	1226.1	1175.4
0.1998	0.4001	850.26	843.41	837.55	830.47	0.9345	0.6935	0.5531	0.4765	1294.4	1258.2	1233.3	1185.3
0.3001	0.3000	855.45	849.81	844.06	836.76	0.9425	0.7015	0.5635	0.4868	1302.3	1267.4	1241.4	1196.4
0.4000	0.1999	862.86	856.25	850.61	843.09	0.9585	0.7189	0.5741	0.4975	1312.7	1280.9	1250.8	1208.5
0.4998	0.1001	869.85	862.77	857.24	849.49	0.9627	0.7301	0.5845	0.5077	1323.5	1287.7	1259.5	1218.5
0.5997	0.0000	875.45	869.38	863.96	855.98	0.9729	0.7465	0.5951	0.5181	1334.5	1298.8	1270.2	1230.9

TABLE – II: Values of Adiabatic compressibility (β) and free length (L$_f$) at 288k, 298k, 308k and 318k.

Mole fraction		Adiabatic compressibility (β) (10^{-10}N^{-1}.m^2)				Free length (L$_f$) (10^{-10} m)			
X$_1$	X$_2$	288K	298K	308K	318K	288K	298K	308K	318K
0.0000	0.6000	7.3028	7.7306	8.1437	9.0033	0.5297	0.5506	0.5768	0.6094
0.0999	0.4999	7.1715	7.6111	8.0032	8.7810	0.525	0.5463	0.5718	0.6018
0.1998	0.4001	7.0196	7.4897	7.8497	8.5707	0.5194	0.5420	0.5663	0.5946
0.3001	0.3000	6.8926	7.3258	7.6878	8.3492	0.5147	0.5360	0.5604	0.5869
0.4000	0.1999	6.7256	7.1182	7.5144	8.1215	0.5084	0.5283	0.5541	0.5788
0.4998	0.1001	6.5631	6.9900	7.3536	7.9285	0.5022	0.5236	0.5481	0.5719
0.5997	0.0000	6.4140	6.8188	7.1740	7.7106	0.4965	0.5171	0.5414	0.564

TABLE – III: Values of Viscous relaxation time (τ) & Gibb's free energy (ΔG) at 288k, 298k, 308k and 318k.

Mole fraction		Viscous relaxation time(τ) (x 10^{-12} s)				Gibb's free energy (ΔG) (x 10^{-20} k.J.mol^{-1})			
X$_1$	X$_2$	288K	298K	308K	318K	288K	298K	308K	318K
0.0000	0.6000	0.8883	0.7007	0.5824	0.5504	0.6654	0.6050	0.5607	0.5681
0.0999	0.4999	0.8859	0.6953	0.5794	0.5458	0.6643	0.6018	0.5585	0.5644
0.1998	0.4001	0.8746	0.6925	0.5789	0.5445	0.6592	0.6001	0.5581	0.5634
0.3001	0.3000	0.8661	0.6852	0.5776	0.5419	0.6554	0.5958	0.5571	0.5613
0.4000	0.1999	0.8595	0.6823	0.5752	0.5387	0.6523	0.5940	0.5554	0.5587
0.4998	0.1001	0.8424	0.6804	0.5731	0.5367	0.6443	0.5929	0.5538	0.5570
0.5997	0.0000	0.8320	0.6787	0.5692	0.5326	0.6394	0.5918	0.5509	0.5537

TABLE – IV: Values of Free volume (V$_f$) & Internal pressure (Π$_i$) at 288k, 298k, 308k and 318k.

Mole fraction		Free volume (V$_f$) (10^{-7} m^3.mol^{-1})				Internal pressure(Π$_i$) (x 10^6 N.m^{-2})			
X$_1$	X$_2$	288K	298K	308K	318K	288K	298K	308K	318K
0.0000	0.6000	1.3565	2.0287	2.7988	3.3049	443.29	399.71	369.29	358.80
0.0999	0.4999	1.3217	1.9976	2.7416	3.2348	451.81	405.50	375.34	364.72
0.1998	0.4001	1.3050	1.9563	2.6656	3.1408	458.25	412.07	382.39	371.69
0.3001	0.3000	1.2883	1.9262	2.5936	3.0561	463.99	418.01	389.49	378.53
0.4000	0.1999	1.2588	1.8680	2.5258	2.9736	472.35	426.30	396.70	385.60
0.4998	0.1001	1.2540	1.8221	2.4607	2.8924	477.54	433.88	403.97	392.82
0.5997	0.0000	1.2373	1.7675	2.4017	2.8204	483.87	442.49	411.19	399.92

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TABLE – V: Values of Acoustic impedance (Z) at 288k, 298k, 308k and 318k.

Mole fraction		Acoustic impedance (Z) (x 10^6 Kg.m^2.s^{-1})			
X$_1$	X$_2$	288K	298K	308K	318K
0.0000	0.6000	1.0695	1.0368	1.0064	0.9533
0.0999	0.4999	1.0841	1.0487	1.0191	0.9689
0.1998	0.4001	1.1006	1.0612	1.033	0.9844
0.3001	0.3000	1.1141	1.077	1.0478	1.0011
0.4000	0.1999	1.1327	1.0968	1.0639	1.0189
0.4998	0.1001	1.1512	1.111	1.0797	1.0351
0.5997	0.0000	1.1683	1.1291	1.0974	1.0536

TABLE – VI: Excess values of adiabatic compressibility (β), Free length (L$_f$) and free volume (V$_f$) at 288k, 298k, 308k and 318k.

Mole fraction		Adiabatic comp. (β^E) (10^{-10}N^{-1}.m^2)				Free length (L$_f^E$) (10^{-10} m)				Free volume (V$_f^E$) (10^{-7} m^3.mol^{-1})			
X$_1$	X$_2$	288K	298K	308K	318K	288K	298K	308K	318K	288K	298K	308K	318K
0.0000	0.6000	0.521	0.350	0.138	0.324	0.020	0.013	0.006	0.012	0.298	0.551	0.828	0.894
0.0999	0.4999	0.563	0.427	0.216	0.345	0.022	0.017	0.010	0.014	0.231	0.489	0.737	0.790
0.1998	0.4001	0.582	0.501	0.278	0.376	0.024	0.021	0.013	0.016	0.183	0.417	0.628	0.662
0.3001	0.3000	0.626	0.532	0.331	0.395	0.026	0.023	0.016	0.018	0.134	0.356	0.522	0.542
0.4000	0.1999	0.633	0.521	0.376	0.411	0.028	0.023	0.018	0.019	0.073	0.267	0.421	0.425
0.4998	0.1001	0.642	0.588	0.431	0.459	0.029	0.026	0.021	0.022	0.036	0.190	0.322	0.310
0.5997	0.0000	0.666	0.613	0.469	0.485	0.030	0.028	0.023	0.024	0.012	0.105	0.230	0.204

TABLE – VII: Excess values of Internal pressure (π$_i$), Acoustic impedance (Z) and Gibb's free energy (ΔG) at 288k, 298k, 308k & 318k.

Mole fraction		Internal pressure(π$_i^E$) (x 10^6 N.m^{-2})				Acoustic impedance (Z^E) (x 10^6 Kg.m^2.s^{-1})				Gibb's free energy (ΔG^E) (x 10^{-20} k.J.mol^{-1})			
X$_1$	X$_2$	288K	298K	308K	318K	288K	298K	308K	318K	288K	298K	308K	318K
0.0000	0.6000	-41.91	-47.81	-50.59	-46.24	-0.05	-0.03	-0.02	-0.03	-0.05	-0.08	-0.10	-0.09
0.0999	0.4999	-33.38	-43.22	-46.16	-42.12	-0.06	-0.05	-0.03	-0.04	-0.03	-0.06	-0.08	-0.07
0.1998	0.4001	-27.10	-37.99	-40.86	-37.10	-0.07	-0.06	-0.04	-0.05	-0.02	-0.05	-0.07	-0.06
0.3001	0.3000	-21.55	-33.45	-35.58	-32.25	-0.08	-0.07	-0.05	-0.05	-0.01	-0.04	-0.05	-0.04
0.4000	0.1999	-13.19	-26.36	-29.98	-26.98	-0.09	-0.08	-0.06	-0.06	0.01	-0.02	-0.03	-0.03
0.4998	0.1001	-8.09	-20.08	-24.42	-21.66	-0.10	-0.09	-0.07	-0.07	0.02	-0.01	-0.02	-0.01
0.5997	0.0000	-1.76	-12.67	-18.81	-16.37	-0.11	-0.10	-0.08	-0.08	0.03	0.01	-0.01	0.00

TABLE – VIII: Excess values of Acoustic impedance (Z) at 288k, 298k, 308k and 318k.

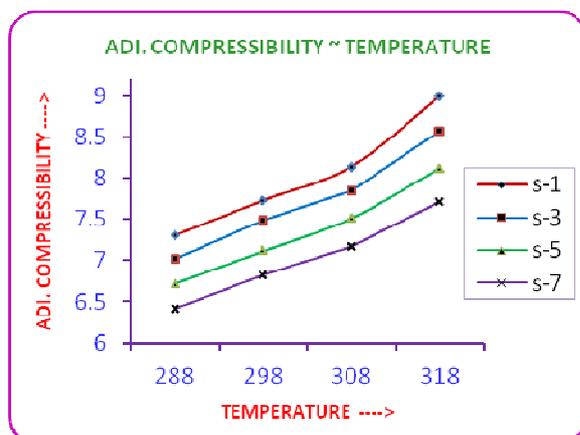| Mole fraction		Viscous relaxation time (τ^E) (x 10^{-12} s)			
X$_1$	X$_2$	288K	298K	308K	318K
0.0000	0.6000	-0.1205	-0.1447	-0.1487	-0.1213
0.0999	0.4999	-0.0881	-0.1231	-0.1282	-0.104
0.1998	0.4001	-0.0649	-0.0991	-0.1054	-0.0836
0.3001	0.3000	-0.0389	-0.0796	-0.0833	-0.0645
0.4000	0.1999	-0.0107	-0.0555	-0.0621	-0.0458
0.4998	0.1001	0.0067	-0.0305	-0.0408	-0.0261
0.5997	0.0000	0.0311	-0.0052	-0.0211	-0.0083

Fig.-1: Variation of adiabatic Compressibility with temperature
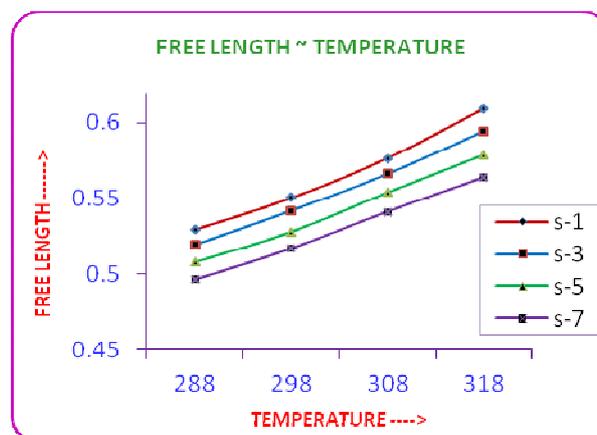

Fig.-2: Variation of free length with temperature
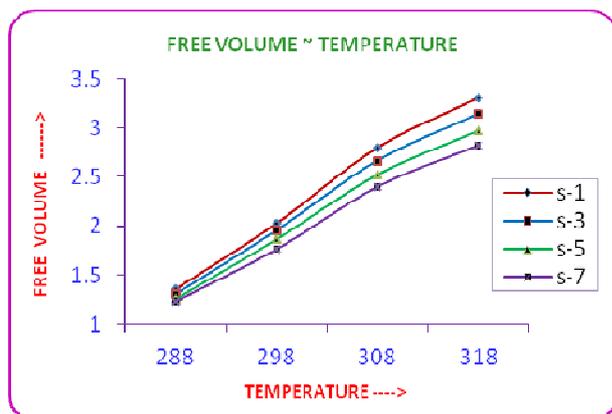
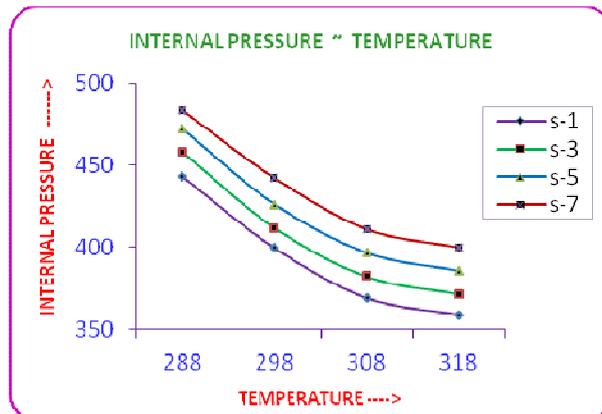**Fig.-3: Variation of free volume with temperature**

Fig.-4: Variation of Internal Pressure with temperature
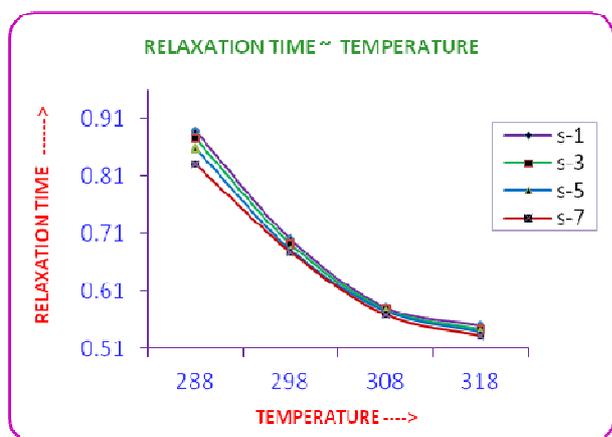

Fig.-5: Variation of Viscosity relaxation time with temperature
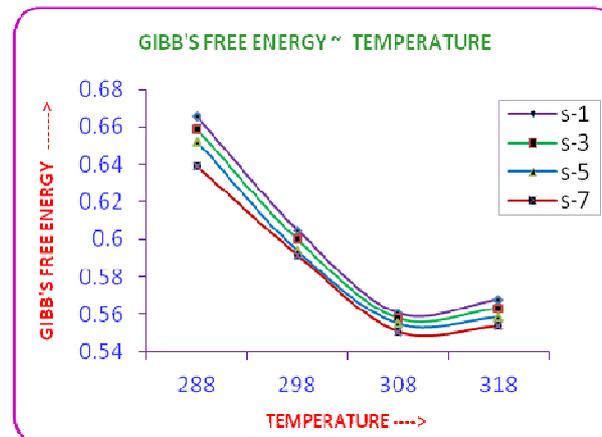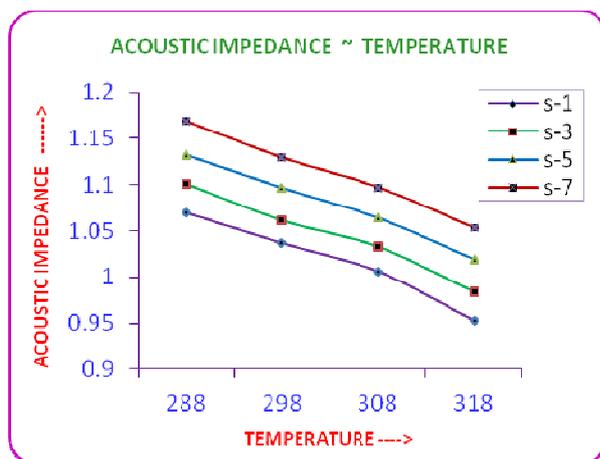

Fig.-6: Variation of Gibb's free energy with temperature
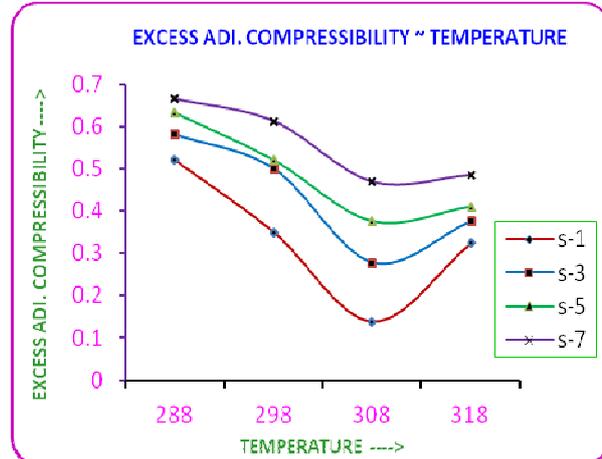

Fig.-7: Variation of Acoustic impedance with temperature.

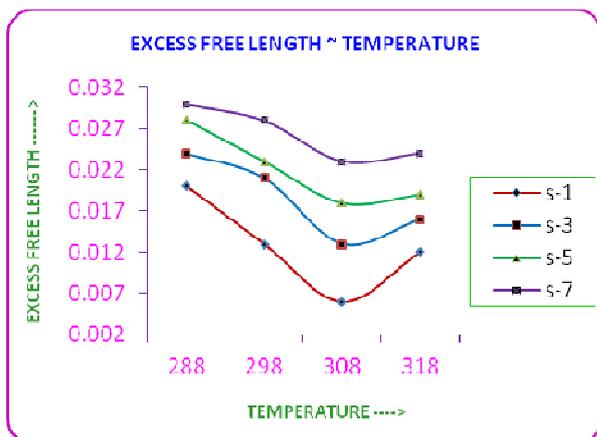**Fig.-8: Variation of Excess adiabatic compressibility with temperature**

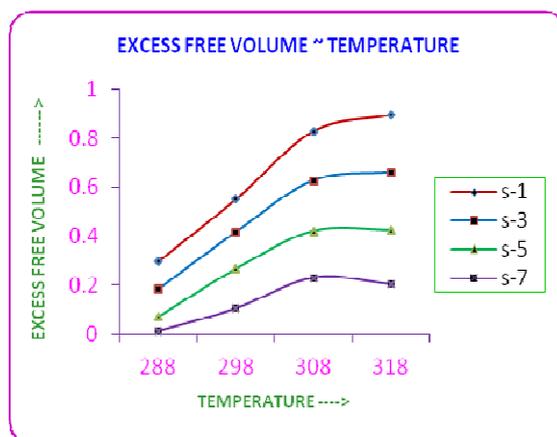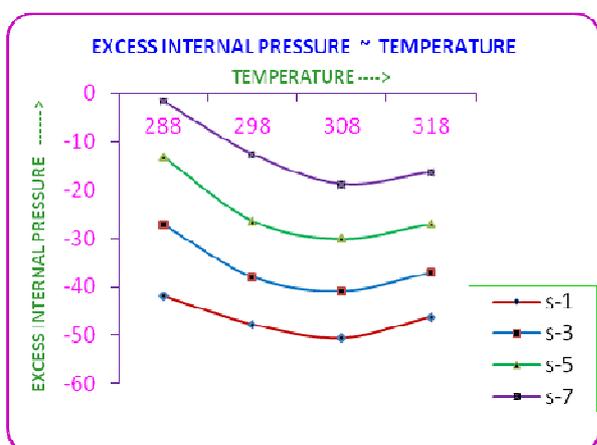_____

Fig.-9: Variation of Excess free length with temperature

Fig.-10: Variation of Excess free volume with temperature

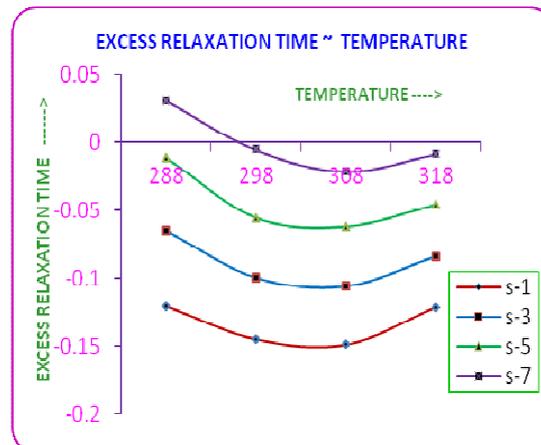**Fig.-11: Variation of Excess internal pressure with temperature**

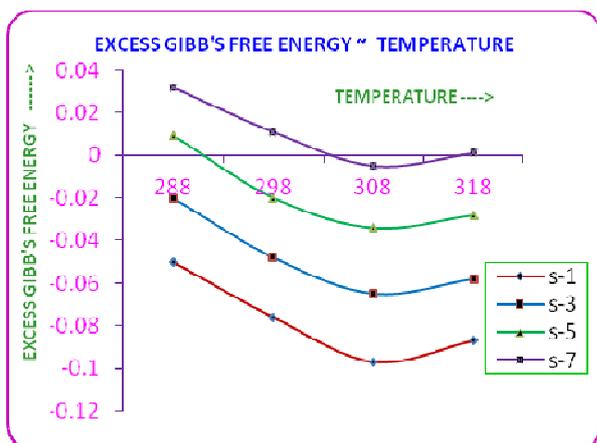**Fig.-12: Variation of Excess relaxation time with temperature**

Fig.-13: Variation of Excess Gibbs' free energy with temperature
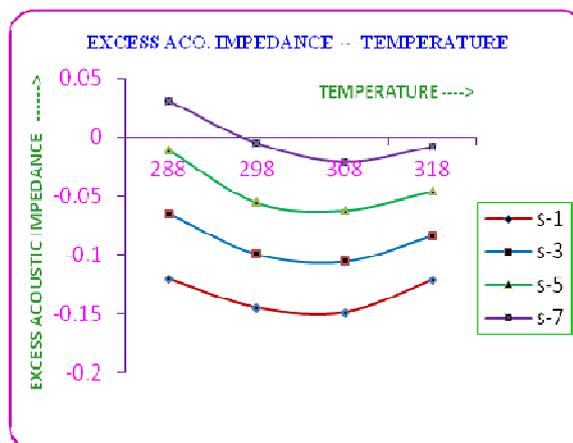

Fig.-14: Variation of Excess acoustic impedance with temperature

RESULTS AND DISCUSSION

It is evident from table-I that density, viscosity and ultrasonic velocity decreases with increase of temperature for a particular mole fraction of the components in the ternary mixture, whereas the same parameters increases as the mole fraction of DMF is increased relative to the other components.

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Benzene and cyclohexane are both non-polar. However benzene has a relatively higher dielectric constant and is an electron donor. Hence dispersive types of interactions are expected between benzene and cyclohexane.

DMF is a polar molecule, when it is in association with benzene and cyclohexane, the DMF-DMF dipolar association tends to breakdown releasing several DMF dipoles. These free dipoles of DMF induce moments in the neighboring cyclohexane and benzene molecules resulting in induced dipolar interaction.

Increase in concentration of DMF thus results in decrease in free length and adiabatic compressibility. The regular fall in free length with increase in concentration of DMF causes a rise in sound velocity [13]. This trend is an indication of clustering together of the molecules as the associative effect of the polar group dominates over the other type of interaction [14].

Velocity shows a reverse trend as temperature is increased. This happens as the spacing between the molecules increases leading to a less ordered structure.

Relaxation time decreases very slowly with increase in mole fraction of DMF, but decreases rapidly as temperature increases. The former indicates lack of strong molecular interaction between the components of the mixture, and the latter is true because of instantaneous conversion of excitation energy to translational energy.

Acoustic impedance (Z) is the ratio of the effective sound pressure at a point to the effective particular velocity at that point. The pressure is measured by the totality of the force of dispersion, repulsion, ionic and dipolar. In our present investigation, acoustic impedance increases slowly with increase in concentration of DMF, showing weak molecular interaction (as both benzene and cyclohexane are non-polar). Since $Z = U.\rho$, as temperature increases, Z decreases. Acoustic impedance is also used for assessing the absorption of sound in the medium.

Gibbs' free energy (ΔG) decreases slowly with increase of concentration of DMF, where as it decreases rapidly when temperature increases. Decrease in ΔG suggests longer time for rearrangement of molecules in the mixture. Since in the present case, two of the components in the mixture are non-polar the intermolecular interaction is weak and becomes weaker with increase in temperature.

Increase in internal pressure (Π_i) may be due to strengthening of cohesive force. Since the interaction in our case is weak, 'Π_i' increases slowly with concentration of DMF, but decreases rapidly with increase of temperature.

The nature of molecular interaction may also be analysed in terms of the excess parameters. Excess adiabatic compressibility (β^E) and excess free length (L_f^E) are positive, indicating weak molecular interaction between the components of the mixture. Positive excess value of free volume predicts breaking of liquid order on mixing and presence of non-specific physical interaction between unlike molecules. This leads to expansion of volume during mixing.

Excess value of internal pressure (Π_i^E) is negative and it decreases as temperature increases. Negative value of Π_i^E indicates absence of complex formation and weak interaction between component molecules. It is also seen that the excess free volume and excess internal pressure are of opposite nature. Excess acoustic impedance Z^E and excess Gibbs' free energy ΔG^E are both negative. This indicates dominance of dispersion forces.

CONCLUSION

Density, viscosity and ultrasonic velocity increases with increase in mole fraction of DMF. This is due to the dipole-induced dipole interaction between DMF and the other two non-polar components. They shows a reverse trend when the temperature increases. Parameters like Gibbs' free energy, acoustic impedance, relaxation time also indicate a weak dipole-induced dipole interaction between the components, which is also confirmed by the nature of their excess values.

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