Molecular interactions in ternary liquid mixture involving toluene at different frequencies

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ABSTRACT

The ultrasonic velocity(U), density(ρ), and viscosity(η) have been measured for ternary mixtures of toluene, N,N-dimethylformamide, and cyclohexane at temperature T = 318 K at different frequencies such as 1 MHz, 4 MHz, 6 MHz, and 8 MHz. These experimental data's have been used to estimate the parameters such as adiabatic compressibility (β), intermolecular free length (L_f), internal pressure (Π_i), free volume (V_f), acoustic impedance (Z), surface tension (S) and their excess values. In particular, it is seen that their exist some molecular interaction between the components of the mixture.

Key words: Ultrasonic velocity, thermodynamic parameters, excess values.
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INTRODUCTION

The ultrasonic study of liquids plays an important role in understanding the nature and strength of molecular interactions [1,2]. A large number of studies have been made on the molecular interaction in liquid systems by various physical methods like, Raman effect[3], Nuclear Magnetic Resonance, ultra violet and ultrasonic method [4-9]. Velocity of sound waves in a medium is fundamentally related to the binding forces between the atoms or the molecules. The variations of ultrasonic velocity and related parameters throw some light on the intermolecular interactions and the structural changes associated with the liquid mixtures having weakly interacting components [10-14] as well as strongly interacting components [15-17]. The variation of ultrasonic velocity and other acoustic parameters along with their excess values in binary and ternary liquid mixtures has been investigated by different authors [18-21].

In the present study, molecules of Cyclohexane are non-polar, molecules of toluene is polar in nature due to presence of electron releasing methyl group [22], where as that of N,N-dimethylformamide (DMF) is highly polar. Molecular interactions are studied through different excess parameters as they play a vital role in assessing the same.

N-N-Dimethyl formamide (DMF), as a polar solvent, is certainly to some extent associated by dipole-dipole interactions. Cyclohexane belongs to alicyclic hydrocarbon (closed chain). It is non-polar, unassociated, inert hydrocarbons and has globular structure. Toluene is aprotic in nature. It is used as an octane booster in fuel, as a solvent for many organic compounds, paints, cleaning of polymer surface and electronic materials.

EXPERIMENTAL SECTION

The mixtures of various concentrations in mole fraction were prepared by taking analytical reagent grade and spectroscopic reagent grade chemicals with minimum assay of 99.9% and obtained from E.Merck Ltd (India). All the component liquids were purified by the standard methods [23]. The density, viscosity, and ultrasonic velocity were measured as a function of concentration of the ternary liquid mixture at 1 MHz, 4MHz, 6 MHz and 8 MHz and

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at temperature T = 318K.

Ultrasonic velocity measurements were made using an ultrasonic interferometer (Model M-84, supplied by M/S Mittal Enterprises, New Delhi) with the accuracy of $\pm 0.1 m \cdot s^{-1}$. An electronically operated digital constant temperature bath (Model SSI-03 Spl, supplied by M/S Mittal Enterprises, New Delhi), operating in the temperature range of $-10°C$ to $85°C$ with an accuracy of $\pm 0.1°C$ has been used to circulate water through the outer jacket of the double-walled measuring cell containing the experimental liquid. The densities of the mixture were measured using a 10-ml specific gravity bottle by relative measurement method with an accuracy of ± 0.01 kg·m^{-3}. An Oswald viscometer (10 ml) with an accuracy of ± 0.001 Ns·m^{-2} was used for the viscosity measurement. The flow time was determined using a digital racer stopwatch with an accuracy of $\pm 0.1 s$.

Using the experimental values, the following thermodynamic parameters were calculated:
(i) Adiabatic Compressibility   : $\beta = 1/U^2 \cdot \rho$
(ii) Intermolecular free length   : $L_f = K_T \beta^{1/2}$

Where K_T is the temperature dependent constant and 'β' is the adiabatic compressibility.
(iii) Free Volume   : $V^f = (M_{eff} \cdot U/K \cdot \eta)^{3/2}$

Where 'M_{eff}' 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 (π_i)   : $\pi_i = bRT (k\eta/U)^{1/2} (\rho^{2/3}/M^{7/6})$

Where, 'b' stands for cubic packing, which is assumed to be '2' for all liquids, ' k' is a dimensionless constant independent of temperature and nature of liquids. Its value is 4.281 x 10^9. ' T' is the absolute temperature, 'M_{eff}' is the effective molecular weight, 'R' is the Universal gas constant.
(v) Acoustic impedance (Z)   : $Z = U \cdot \rho$
(vi) Surface tension   : $S = 6.3 \times 10^{-4} \cdot (\rho \cdot U^{3/2})$
(vii) The excess values of parameters has been calculated by using the relation
$$A^E = A_{exp} - A_{id}$$
Where $A_{id} = \Sigma^n A_i X_i$, A_i is any parameters and 'X_i, the mole fraction of the liquid components of 'i'.

RESULTS AND DISCUSSION

The experimental data relating to density, viscosity and velocity of pure liquids at 318 K for frequencies 1 MHz, 4 MHz, 6 MHz and 8 MHz are given in table-1..The calculated excess values of adiabatic compressibility(β^E), free length(L_f^E), free volume(V_f^E), internal pressure(π_i^E), acoustic impedance(Z^E)and surface tension(S^E) are reported in table-2-4 and their variation with molefraction of DMF are shown in Figs.1-3.

Excess parameters play a vital role in assessing the compactness due to molecular arrangement and the extent of molecular interactions in the liquid mixtures through charge transfer, dipole-dipole and dipole-induced dipole interactions. The sign and the extent of deviation of these functions from ideality depend on the strength of interactions between unlike molecules. Excess values are affected by three factors

1. The specific force between molecules such as hydrogen bonds, charge transfer complexes, breaking of hydrogen bonds and complexes bringing negative excess values

2. Physical intermolecular forces (electrostatic forces between charged particles of a permanent dipole and an induced dipole or force of attraction or repulsion between non-polar molecules). These forces are weak.

3. Structural characteristics of the components arising from geometrical fitting of one component in to another due to the difference in shape and size of the components and free volume.

It is learn that the dispersion forces are responsible for possessing positive excess values, while dipole-dipole, dipole-induced dipole, charge transfer interaction and hydrogen bonding between unlike molecules are responsible for possessing negative excess values [24].

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TABLE – 1: Measured Values of Density (ρ), Viscosity (η) and velocity (U) of ternary mixture for different frequencies at 318k

Mole fraction		Density(ρ) Kg.m^{-3}	Viscosity (η) 10^{-3} N.s.m^{-2}	Velocity (U) m.s^{-1}			
X$_1$	X$_3$			1 MHz	4 MHz	6 MHz	8 MHz
0.0000	0.6000	798.41	0.468	1190.35	1178.41	1175.23	1171.62
0.0999	0.4999	808.95	0.486	1192.65	1187.26	1184.84	1182.36
0.1998	0.4001	819.16	0.520	1209.35	119.46	1196.12	1194.35
0.3001	0.3000	829.44	0.548	1211.55	1203.63	1200.45	1198.42
0.4000	0.1999	841.02	0.574	1189.8	1183.2	1182.42	1179.52
0.4998	0.1001	851.86	0.636	1182.54	1176.45	1174.38	1172.24
0.5997	0.0000	861.98	0.701	1170.23	1168.56	1166.14	1164.51

TABLE – 2: Calculated excess values of Density (ρ^E), Viscosity (η^E) and velocity (U^E) of ternary mixture for different frequencies

Mole fraction		Excess Density(ρ^E) Kg.m^{-3}	Excess Viscosity (η^E) 10^{-3} N.s.m^{-2}	Excess Velocity (U^E) m.s^{-1}			
X$_1$	X$_3$			1 MHz	4 MHz	6 MHz	8 MHz
0.0000	0.6000	-6.5560	0.0323	-31.51	-41.59	-42.92	-44.78
0.0999	0.4999	-5.3057	0.0267	-42.86	-46.29	-46.96	-47.65
0.1998	0.4001	-4.6356	0.0371	-40.20	-49.03	-49.71	-49.66
0.3001	0.3000	-4.0169	0.0417	-52.21	-57.97	-59.58	-59.76
0.4000	0.1999	-1.7266	0.0440	-87.61	-91.95	-91.26	-92.27
0.4998	0.1001	-0.3336	0.0822	-108.77	-112.50	-113.19	-113.41
0.5997	0.0000	0.4967	0.1239	-134.73	-133.94	-135.08	-134.75

TABLE–3: Calculated Excess values of adiabatic compressibility (β^E), Free length (L$_f^E$) and free volume (V$_f^E$)

Mole fraction		Excess Adia. Comp. (β^E) (10^{-10} N^{-1}.m^2)				Excess Free length (L$_f^E$) (10^{-10} m)				Excess Free volume (V$_f^E$) (10^{-7} m^3.mol^{-1})			
X$_1$	X$_3$	1MHz	4MHz	6MHz	8MHz	1MHz	4MHz	6MHz	8MHz	1MHz	4MHz	6MHz	8MHz
0.0000	0.6000	0.427	0.582	0.606	0.638	0.012	0.017	0.018	0.019	-0.02	-0.07	-0.08	-0.09
0.0999	0.4999	0.484	0.538	0.550	0.564	0.018	0.019	0.020	0.020	-0.29	-0.30	-0.31	-0.31
0.1998	0.4001	0.343	0.471	0.482	0.484	0.014	0.018	0.019	0.019	0.07	0.03	0.03	0.03
0.3001	0.3000	0.413	0.497	0.521	0.526	0.022	0.025	0.026	0.026	-0.12	-0.14	-0.14	-0.15
0.4000	0.1999	0.804	0.873	0.866	0.886	0.036	0.039	0.039	0.039	-0.33	-0.35	-0.34	-0.35
0.4998	0.1001	1.003	1.066	1.079	1.088	0.044	0.046	0.047	0.047	-0.48	-0.49	-0.49	-0.49
0.5997	0.0000	1.285	1.285	1.305	1.308	0.054	0.054	0.055	0.055	-0.28	-0.27	-0.28	-0.28

Excess value of density is negative, which indicates dense packing of molecules in the mixture. Excess velocity is found to be negative, which indicates weak interaction between components of the mixture. Excess values of adiabatic compressibility, is positive, indicates weak interaction between molecules due to dispersive forces. Excess free length is positive indicating the presence of weak dipolar and dispersive interactions between the component molecules in the mixtures. Excess free length increases with increase in frequency indicating weakening of interaction.
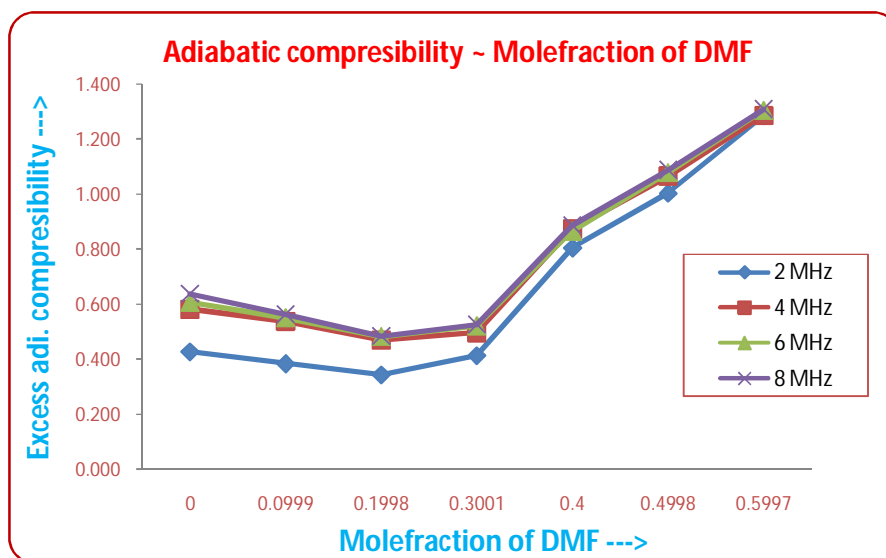

Fig. 1: Variation of excess adiabatic compressibility with mole fraction of DMF

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Negative excess free volume leads to reduction in volume. This may be due to the formation of new bonds. The relatively small size of N,N-DMF and its linear aliphatic configuration may be the factor contributing to the volume contraction of the mixture.
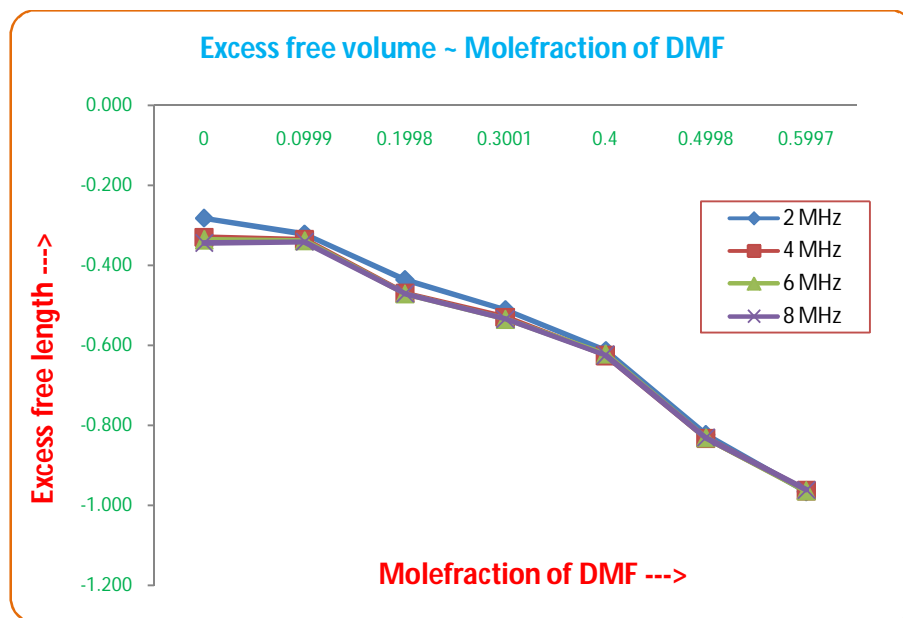
Excess free volume ~ Molefraction of DMF

Fig. 2: Variation of excess free volume with molefraction of DMF

TABLE-4: Calculated Excess values of Internal pressure (π_i), Acoustic impedance (Z^E) and Surface tension (S^E)

Mole fraction		Excess Int. pressure (π_i) (x 10^6 N.m-^{2})				Excess Acou.Imp.(Z^E) (x 10^6 Kg.m^2.s^{-1})				Excess Surface tension (S^E) (N.m^{-1})			
X_1	X_3	1MHz	4MHz	6MHz	8MHz	1MHz	4MHz	6MHz	8MHz	1MHz	4MHz	6MHz	8MHz
0.0000	0.6000	-17.94	-16.62	-16.45	-16.20	-0.023	-0.031	-0.032	-0.034	-1002	-1263	-1296	-1343
0.0999	0.4999	-12.85	-12.37	-12.27	-12.17	-0.040	-0.043	-0.044	-0.044	-1287	-1376	-1392	-1409
0.1998	0.4001	-23.59	-22.37	-22.27	-22.29	-0.039	-0.047	-0.047	-0.047	-1220	-1456	-1473	-1470
0.3001	0.3000	-19.76	-18.92	-18.67	-18.65	-0.067	-0.072	-0.073	-0.073	-1553	-1709	-1751	-1755
0.4000	0.1999	-5.49	-4.77	-4.86	-4.68	-0.094	-0.098	-0.097	-0.098	-2495	-2612	-2591	-2617
0.4998	0.1001	10.34	11.03	11.19	11.26	-0.112	-0.115	-0.116	-0.116	-3089	-3189	-3206	-3210
0.5997	0.0000	9.21	9.11	9.35	9.33	-0.133	-0.132	-0.133	-0.132	-3846	-3820	-3850	-3837

The negative values of excess internal pressure, confirms the existence of molecular association between unlike molecules. This also indicates the absence of complex formation in the mixture and hence weak molecular interaction. [25-26].
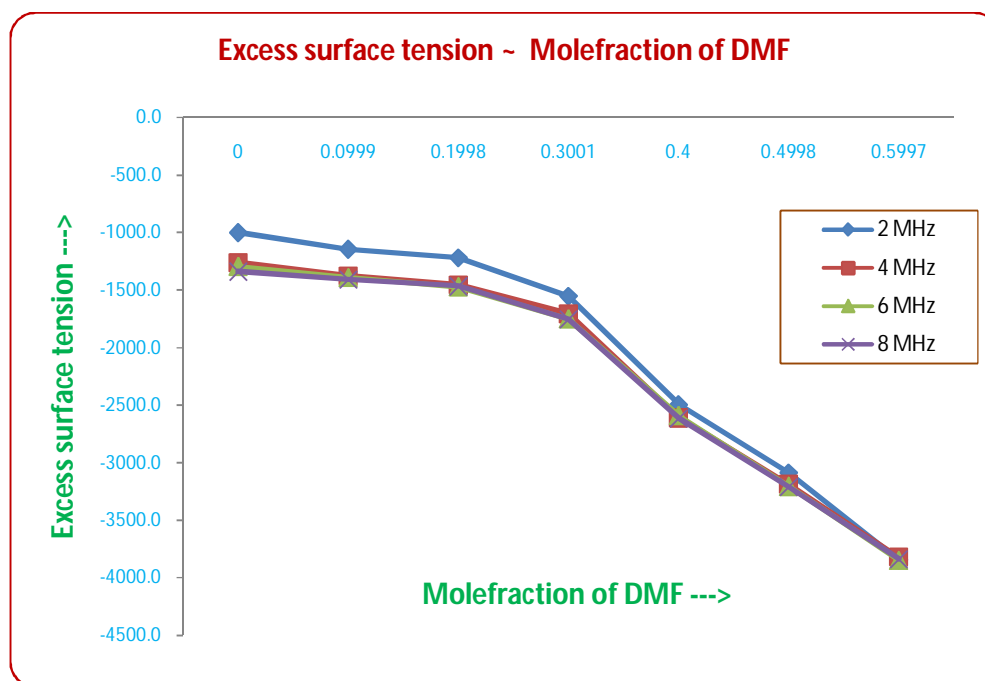
Fig. 3: Variation of excess surface tension with mole fraction of DMF

The deviations of surface tension of a liquid mixture from linearity, reflects changes of structure and cohesive forces during the mixing process. Excess values of surface tension are negative, indicating weak interaction between the components of the mixture.

CONCLUSION

It is obvious that, there exist a molecular interaction between the components of the mixture. In specific weak molecular interaction (like dipole-dipole, dipole-induced dipole and dispersive forces) are found to exist between components of the mixtures.

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