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Comparative Study of Molecular Interaction in Ternary Liquid Mixtures of Polar and Non-Polar Solvents by Ultrasonic Velocity Measurements

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Abstract: ***The ultrasonic velocity (U), density (ρ) and viscosity (η) have been measured for the ternary mixture of benzene, chlorobenzene, nitrobenzene and pyridine successively with N, N-dimethylformamide in cyclohexane at different frequencies and at temperature 308 K for different concentrations of component liquids. The experimental data of velocity, density and viscosity have been used for a comparative study of the molecular interaction in the different mixtures using the excess values of parameters such as excess adiabatic compressibility (β^E), excess free length (L_f^E), excess free volume (V_f^E) and excess surface tension (S^E). Variation in the above parameters for the different mixtures is indicative of the nature of interaction between them.***

Keywords: Ternary mixture, ultrasonic velocity, adiabatic compressibility, surface tension and excess values

1. Introduction

Ultrasonic investigations of liquid mixtures consisting of polar and non-polar components enable to understand the molecular interactions and structural behavior of molecules in the mixture **[1-5]**.

The ternary liquid systems taken up for study are

System- I**:** DMF + cyclohexane + benzene
System-II: DMF + cyclohexane + chlorobenzene
System-III: DMF + cyclohexane + nitrobenzene
System- IV: DMF + cyclohexane + Pyridine

N, N-Dimethlformamide (C_3H_7NO) is a non-aqueous solvent which has no hydrogen bonding in pure state. Therefore it acts as an aprotic, protophilic medium with high dielectric constant. Cyclohexane (C_6H_{12}) is a non polar unassociated, inert hydrocarbon possessing globular structure. The packing of carbon atoms in the even numbered alkane groups allows the maximum intermolecular attractions **[6]**. It is highly inert towards an electrophille or a nucleophille at ordinary temperature. Due to the non-polar nature of cyclohexane and its inertness towards electron donors **[7]**, dispersive types of interaction are expected between it and other components.

Benzene (C_6H_6) is a non-polar solvent, which is freely miscible with many organic solvents **[8]**. It has slightly polar nature due to the delocalized electron cloud, which results in the solute-solvent molecular associates. Chlorobenzene (C_6H_5Cl) is a poor electron donor towards the electron seeking proton of any group. It is neither acidic nor basic and is more reactive. Nitrobenzene ($C_6H_5NO_2$) is relatively a complex molecule and its non-ideality in all probabilities may be due to the polarity arising out of C-N and N-O bonds. Pyridine (C_5H_5N) is a polar aprotic solvent. Pyridine (C_5H_5N) is a polar aprotic solvent. It is used in wide variety of reaction including electrophilic substitution, nucleophilic substitution, oxidation and reduction as it has the property to form complexes with many salts. Chlorobenzene is more reactive because the chlorine atom is bonded with SP^3 hybridized carbon atom and consequently can be removed easily. Nitrobenzene has higher dipole moment and dielectric constant compared to chlorobenzene. It rotates freely along the CN axis where it is likely to give more flexibility to the interaction arising due to the two highly polar N-O bonds.

2. Materials and Methods

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 **[9].** In all the mixtures, the mole fraction of the second component, cyclohexane (X_2 = 0.4), was kept fixed while the mole fractions of the remaining two (X_1 and X_3) were varied from 0.0 to 0.6, so as to have the mixture of different concentration. There is nothing significant in fixing the mole fraction of the second component at 0.4. The density, viscosity, and ultrasonic velocity were measured as a function of concentration of the ternary liquid mixture at 2, 4, 6 and 8 MHz and at temperature T = 318 K.

Ultrasonic velocity measurements were made using an ultrasonic interferometer (Model M-84, supplied by M/S Mittal Enterprises, New Delhi) with the accuracy of $\pm 0.1 m\cdot s^{-1}$. The measuring cell of interferometer is a specially designed double-walled vessel with provision for temperature constancy. 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 ±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 $\pm 0.01\ kg\cdot m^{-3}$. The specific gravity bottle with the experimental mixture was immersed in the temperature-controlled water bath. An Oswald viscometer (10 ml) with an accuracy of $\pm 0.001\ Ns\cdot m^{-2}$ was used for the viscosity measurement. The flow time was determined using a digital racer stopwatch with an accuracy of ±0.1s.

3. Theory

The various acoustical parameters such as adiabatic compressibility (β), **i**ntermolecular free length (L_f), Free volume (V_f), surface tension (S) has been calculated from the measured values of ultrasonic velocity (U) ,the density (ρ) and viscosity(η) of the system using the following standard equations as:

a) Adiabatic Compressibility (β): The adiabatic compressibility is the fractional decrease of volume per unit increase of pressure, when no heat flows in or out. It is calculated from the speed of sound (U) and the density (ρ) of the medium by using the equation of Newton Laplace as **[10]**,

$$\beta = \frac{1}{U^2 . \rho} \qquad (1)$$

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

$$L_f = K_T . \beta^{1/2} \qquad (2)$$

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

c) Free Volume (V_f): Free volume is a free space in which the core molecules move inside the solution due to the repulsion of the neighboring molecules. Suryanarayana et al. **[12]** obtained a formula for free volume in terms of the ultrasonic velocity (U) and the viscosity of the liquid (η) as

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

Where 'M_{eff}' is the effective mass of the mixture, 'K' is a dimensionless constant independent of temperature and liquid. Its value is 4.281×10^9.

d) Surface tension: According to Aurebach relation **[13]**, Surface tension of liquid is

$$S = 6.4 \times 10^{-3} . \rho . U^{3/2} \qquad (4)$$

Excess Parameters (A^E)

In order to study the non-ideality of the liquid mixtures, the difference between the values of the real mixture (A_{exp}) and those corresponding to an ideal mixture (A_{id}) , namely the excess parameters (A^E) of some of the acoustic parameters, were computed using the equation

$$A^E = A_{exp} - A_{id} \qquad (5)$$

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'.

4. Result and Disscusion:

The experimental data relating to density, viscosity and velocity of pure liquids at 318 K for frequencies 2MHz, 4MHz, 6MHz, 8MHz are given in table-I..The calculated excess values of adiabatic compressibility (β^E), free length (L_f^E), free volume (V_f^E) and surface tension (S^E) are reported in table-II and table-III.

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 **[14]**. The sign and the extent of deviation of these functions from ideality depend on the strength of interactions between unlike molecules.

Excess value of density is negative for system-I & III and is more negative in system-III. The same is positive in system-II. When liquids are mixed together, there may either be contraction (increase in density by association) as is observed in system-II or expansion in volume from additivity (decrease in density by decrease in association) as observed in system-I & III. In system-III it is more negative because of steric hindrance. Free volume in case of chlorobenzene is more than that of Nitrobenzene as the vibrations are transmitted to effectively large distance due to close association of molecule in system-II.

Excess value of viscosity is negative for all systems. Negative values of excess viscosity predict easier flow of liquid mixture as compared to those of pure liquids. Hence it indicates weakening of intermolecular interaction between component molecules that is existence of dispersion and dipolar forces with complete absence of specific interactions. Mixtures for which excess free volume is positive, excess viscosity will be negative, which is evident from our results. Negative excess viscosity is the least for system-II, indicating strong molecular association compared to the other mixtures. In all the system, the excess velocity is found to be negative, which indicates weak interaction between components of the mixture. Negative excess viscosity and negative excess velocity support each other. Excess velocity of system-II is least negative and maximum negative in case of system-III. Excess values of adiabatic compressibility, is positive for all systems (Fig.-1 to 4). Positive value of 'β^E' indicates weak interaction between molecules due to dispersive forces.

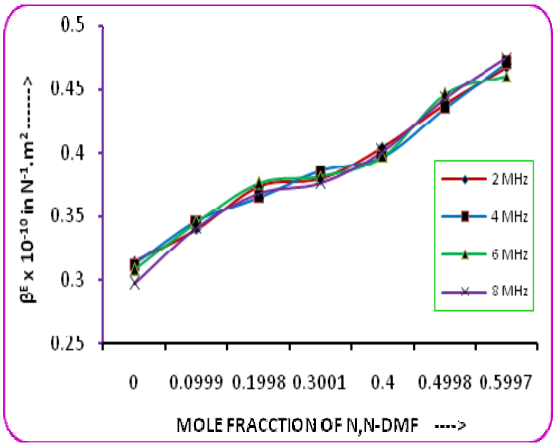

Figure 1: Variation of excess adiabatic compressibility with mole fraction of DMF for system-I mixture

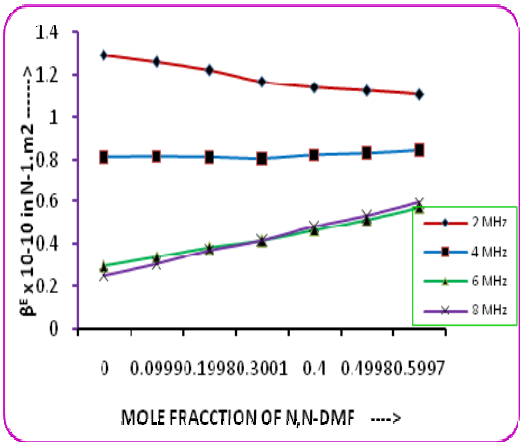

Figure 2: Variation of excess adiabatic compressibility with mole fraction of DMF for system-II mixture

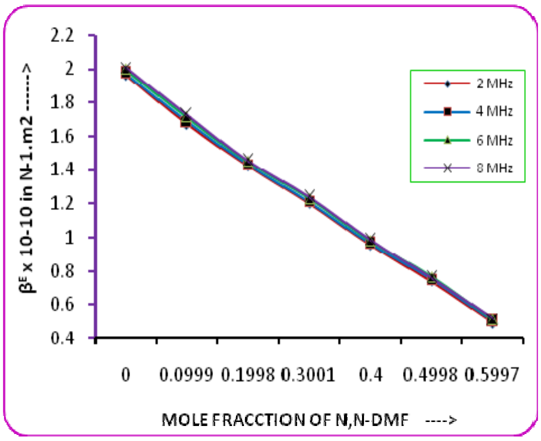

Figure 3: Variation of excess adiabatic compressibility mole fraction of DMF for system-I mixture

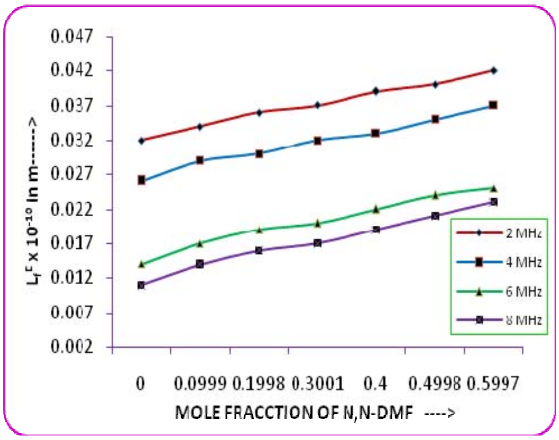

Figure 4: Variation of excess free length with mole with fraction of DMF for system-I mixture

In all the systems excess free length is positive indicating the presence of weak dipolar and dispersive interactions between the component molecules in the mixtures. In case of system-I and system-II, excess free length decreases with increase in frequency (fig.-5 &6), showing that the interaction becomes stronger. In case of system-III, excess free length increases with increase in frequency (fig.-6) indicating weakening of interaction.

Positive value of excess free volume predicts breaking of liquid order (dissociation) on mixing. Hence it leads to expansion. This may be also due to dispersion forces, steric hindrance in component molecules, unfavorable geometric fitting and electrostatic repulsion. Negative excess free volume leads to reduction in volume. This may be due to the formation of new bonds. Excess free volume is positive in system-I, system-II and system-III (fig.- 7 to 9).

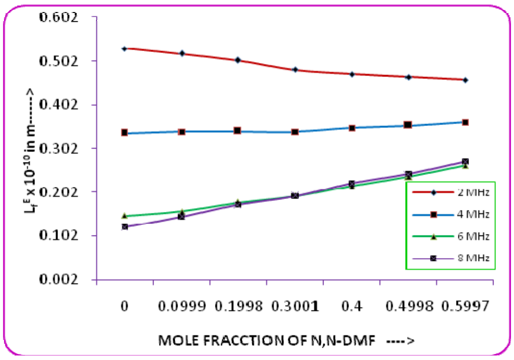

Figure 5: Variation of excess free length with mole fraction of DMF for system-II mixture

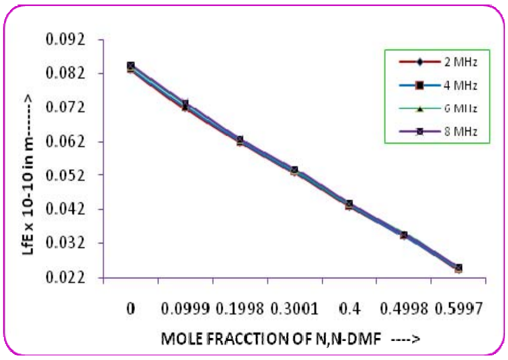

Figure 6: Variation of excess free length fraction of DMF for system-III mixture

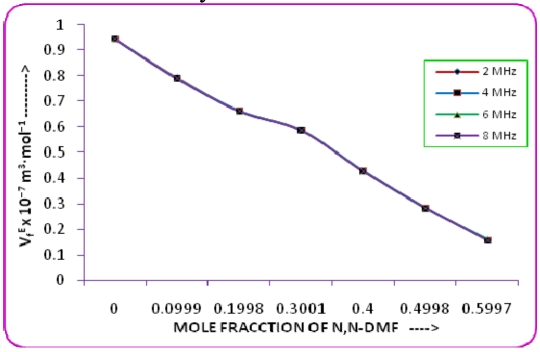

Figure 7: Variation of excess free volume with mole fraction of DMF for system-I mixture

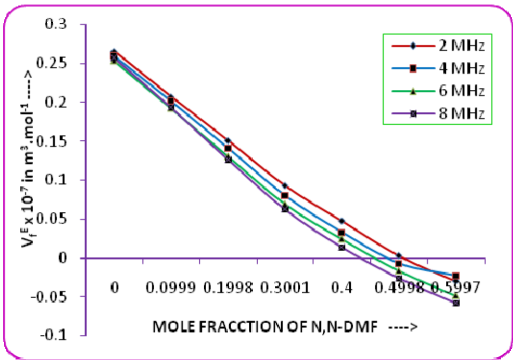

Figure 8: Variation of excess free volume with mole fraction of DMF for system-II mixture

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 over the entire composition range and for all frequencies, indicating weak interaction between the components of the mixture. It is the least negative in case of chlorobenzene mixture and maximum negative in case of Nitrobenzene mixture indicating difference in degree of interaction between the component molecules in the different mixtures. In all the cases surface tension decreases with increase in frequency, which indicate reduction in the intermolecular interaction.

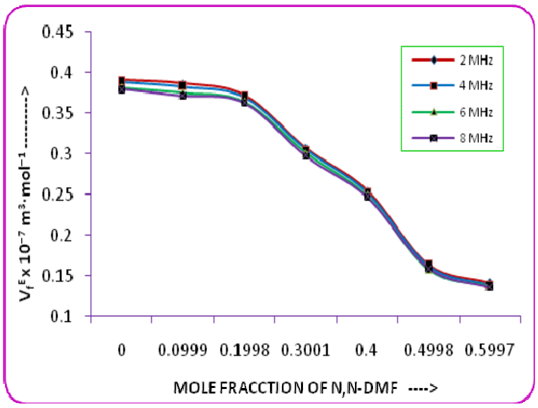

Figure 9: Variation of excess free volume with mole fraction of DMF for system-III mixture

5. 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 individual mixtures. Molecular interactions are studied through different excess parameters as they play a vital role in assessing the same.

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Table 1: Experimental values of density (ρ), Viscosity (η) and velocity (U) of pure liquids for different frequencies at temperature 318 K.

Pure Liquid	**ρ Kg.m^{-3}**	**η x 10^{-3} N.s.m^{-2}**	**Velocity (U) m.s^{-1}**			
			2MHz	4MHz	6MHz	8MHz
DMF	928.95	0.622	1401.7	1398.6	1397.4	1395.2
C.H	761.0	0.511	1160.9	1159.4	1158	1156.4
Ben.	862.4	0.638	1212.1	1210.4	1209	1207.6
C.Ben.	1082.1	0.628	1997.3	1195.2	1193.7	1192.4
N. Ben	1179.5	1.010	1383.1	1382.0	1381.5	1380.8
Pyr.	964.2	0.530	1341.4	1338.6	1336.5	1332.2

Table 2: Calculated excess values of adiabatic comp. (β^E), and free length (L_f^E) in ternary mixtures for different frequencies at temperature 318 K.

Mole fraction		**Excess adiabatic comp. (β^E) (10^{-10} $N^{-1}.m^2$)**				**Excess free length (L_f^E) (10^{-10} m)**			
X_1	**X_2**	**2 MHz**	**4 MHz**	**6 MHz**	**8 MHz**	**2 MHz**	**4 MHz**	**6 MHz**	**8 MHz**
SYSTEM – I (DMF + Cyclohexane + benzene)									
0.0000	0.6000	0.314	0.312	0.308	0.297	0.032	0.026	0.014	0.011
0.0999	0.4999	0.340	0.346	0.345	0.341	0.034	0.029	0.017	0.014
0.1998	0.4001	0.373	0.365	0.376	0.368	0.036	0.030	0.019	0.016
0.3001	0.3000	0.379	0.385	0.381	0.376	0.037	0.032	0.020	0.017
0.4000	0.1999	0.404	0.397	0.397	0.401	0.039	0.033	0.022	0.019
0.4998	0.1001	0.438	0.435	0.446	0.443	0.040	0.035	0.024	0.021
0.5997	0.0000	0.467	0.470	0.460	0.474	0.042	0.037	0.025	0.023
SYSTEM – II (DMF + Cyclohexane + Chlorobenzene)									

0.0000	0.6000	1.2901	0.8123	0.2989	0.2562	0.5305	0.3369	0.1488	0.1223
0.0999	0.4999	1.2582	0.8141	0.3410	0.3097	0.5187	0.3402	0.1587	0.1465
0.1998	0.4001	1.2200	0.8120	0.3853	0.3726	0.5039	0.3411	0.1785	0.1733
0.3001	0.3000	1.1655	0.8043	0.4175	0.4179	0.4826	0.3397	0.1936	0.1933
0.4000	0.1999	1.1389	0.8221	0.4667	0.4837	0.4727	0.3488	0.2161	0.2220
0.4998	0.1001	1.1238	0.8297	0.5153	0.5338	0.4667	0.3536	0.2378	0.2443
0.5997	0.0000	1.1061	0.8443	0.5720	0.5956	0.4602	0.3615	0.2630	0.2714
SYSTEM – III (DMF + Cyclohexane + Nitrobenzene)									
0.0000	0.6000	1.965	1.975	1.999	2.009	0.0828	0.0831	0.0839	0.0842
0.0999	0.4999	1.672	1.687	1.714	1.727	0.0715	0.0719	0.0729	0.0733
0.1998	0.4001	1.424	1.433	1.452	1.458	0.0616	0.0618	0.0625	0.0627
0.3001	0.3000	1.203	1.212	1.228	1.240	0.0526	0.0529	0.0534	0.0538
0.4000	0.1999	0.956	0.964	0.980	0.986	0.0428	0.0430	0.0436	0.0438
0.4998	0.1001	0.740	0.749	0.767	0.761	0.0340	0.0342	0.0349	0.0346
0.5997	0.0000	0.496	0.507	0.515	0.519	0.0242	0.0245	0.0248	0.0249

Table 3: Calculated excess values of free volume (V_f^E), and surface tension (S^E) in ternary mixtures for different frequencies at temperature 318 K.

Mole fraction		**Excess free volume (10^{-7} $m^3 \cdot mol^{-1}$)**				**Excess surface tension (S^E) ($N.m^{-1}$)**			
X_1	X_2	2 MHz	4 MHz	6 MHz	8 MHz	2 MHz	4 MHz	6 MHz	8 MHz
SYSTEM – I (DMF + Cyclohexane + benzene)									
0.0000	0.6000	0.944	0.943	0.942	0.944	-0.75	-0.74	-0.76	-0.74
0.0999	0.4999	0.794	0.791	0.79	0.79	-1.10	-1.11	-1.10	-1.09
0.1998	0.4001	0.664	0.665	0.662	0.663	-1.46	-1.44	-1.45	-1.43
0.3001	0.3000	0.589	0.587	0.587	0.587	-1.75	-1.75	-1.77	-1.74
0.4000	0.1999	0.428	0.43	0.429	0.428	-2.04	-2.01	-2.04	-2.01
0.4998	0.1001	0.286	0.286	0.283	0.284	-2.33	-2.31	-2.36	-2.32
0.5997	0.0000	0.159	0.159	0.162	0.158	-2.58	-2.57	-2.60	-2.57
SYSTEM – II (DMF + Cyclohexane + Chlorobenzene)									
0.0000	0.6000	0.266	0.260	0.253	0.257	0.128	0.092	0.050	0.077
0.0999	0.4999	0.207	0.202	0.192	0.193	-0.125	-0.160	-0.225	-0.216
0.1998	0.4001	0.151	0.141	0.130	0.126	-0.379	-0.447	-0.527	-0.555
0.3001	0.3000	0.093	0.080	0.069	0.062	-0.634	-0.730	-0.816	-0.868
0.4000	0.1999	0.048	0.033	0.024	0.014	-0.955	-1.070	-1.144	-1.227
0.4998	0.1001	0.003	-0.007	-0.016	-0.026	-1.330	-1.409	-1.494	-1.572
0.5997	0.0000	-0.030	-0.023	-0.048	-0.058	-1.709	-1.633	-1.875	-1.956
SYSTEM – III (DMF + Cyclohexane + Nitrobenzene)									
0.0000	0.6000	0.391	0.388	0.382	0.379	-8.9	-8.9	-8.96	-8.97
0.0999	0.4999	0.387	0.383	0.376	0.372	-7.8	-7.8	-7.87	-7.89
0.1998	0.4001	0.372	0.370	0.365	0.363	-6.8	-6.8	-6.84	-6.85
0.3001	0.3000	0.307	0.305	0.301	0.297	-5.9	-5.9	-5.88	-5.90
0.4000	0.1999	0.255	0.253	0.249	0.247	-4.9	-4.9	-4.89	-4.89
0.4998	0.1001	0.165	0.163	0.158	0.160	-3.9	-3.9	-3.95	-3.92
0.5997	0.0000	0.142	0.139	0.137	0.136	-2.9	-2.9	-2.94	-2.93