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Intermolecular Interaction Studies in Organic Ternary Liquid Mixtures by Ultrasonic Velocity Measurements

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Abstract

The ultrasonic velocity, density and viscosity have been measured for the ternary mixtures of benzene, chlorobenzene and nitrobenzene with N-N dimethylformamide (DMF) in cyclohexane at 303K. The experimental data have been used to calculate the acoustical parameters namely adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π_i), viscous relaxation time (τ), Gibbs' Free Energy (ΔG^*) and acoustic impedance (Z). The excess values of some the above parameters are also evaluated and discussed in the light of molecular interaction in the mixtures. It is observed that a weak molecular interaction prevailing in the present systems of the mixtures. Such interactions are primarily due to weak dipole-dipole and dipole- induced dipole types. Dispersive forces are also found to exist between the components of the mixtures.

Key Words: intermolecular free length, aprotic, internal pressure, Gibb's free energy

Introduction

Investigations on being binary and ternary mixtures of non-electrolytes by calculating excess thermodynamic parameters are found to be highly useful in understanding the solute-solvent interactions in these mixtures. Ultrasonic wave propagation affects the physical properties of the medium and hence, can furnish information on the physics of the liquid and liquid mixtures. The measured ultrasonic parameters are being extensively useful to study intermolecular processes in liquid systems.[1-3] The sign and magnitude of the non-linear deviations from ideal values of velocities and adiabatic compressibilities of liquid mixtures with composition are attributed to the difference in molecular size and strength of interaction between unlike molecules.[4]· The present investigation related on thermodynamic properties of binary as well as ternary liquid mixtures of containing N-N dimethylformamide (DMF). DMF is a versatile compound. It is a non-aqueous solvent which has no hydrogen bonding in pure state. Therefore, it acts as an aprotic protophylic medium with high dielectric constant and it is considered as dissociating solvent.[5] Binary and ternary mixtures of DMF with aromatic solvents are of interest in studies of polymer miscibility, polymer phase diagrams and preferential interactions of polymers in mixed solvents.[6-8] Therefore, a better understanding of the physico-chemical properties of mixed solvent systems I-DMF + cyclohexane + benzene, II-DMF + cyclohexane + chlorobenznene, and III-DMF + cyclohexane + nitrobenznene may help in the study of chemical and biological processes in these media. Moreover, no ultrasonic or volumetric behaviour of these mixtures are reported so far.

Hence, the authors had gone to investigate the present study with aid of ultrasonic parameters and some of its related excess values with a view to throw light on intermolecular interaction between the component molecules of the mixtures.

The present ternary liquid systems taken up study at 303K are

System-I	DMF	+ cyclohexane	+ benzene
System-II	DMF	+ cyclohexane	+ chlorobenzene
System-III	DMF	+ cyclohexane	+ nitrobenzene

Materials and Methods

Experimental Section

The chemicals used in the present work were analytical reagent (AR) and spectroscopic reagent (SR) grades with minimum assay of 99.9% were obtained from Sd fine chemicals India and E-merck, Germany. In all systems, the 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 the remaining two (X_1 and X_3) were varied from 0.0 to 0.6. There is nothing significant in fixing the second component at 0.4. The density of pure liquids and liquid mixtures are determined using a specific gravity bottle by relative measurement method with a reproducibility of ± 0.01 $kg.m^{-3}$ (Model: SHIMADZU AX-200).An Ostwald's viscometer of 10ml capacity is used for the viscosity measurement of pure liquids and liquid mixtures and efflux time was determined using a digital chronometer to within ±0.01sec. An ultrasonic interferometer (Model: F81) supplied by M/s. Mittal Enterprises, New Delhi, working at a frequency 3MHz with an overall accuracy of ± 2 ms^{-1} has been used for velocity measurement. An electronically digital constant temperature bath (RAAGA Industries, Chennai) has been used to circulate water through the double walled measuring cell made up of steel containing experimental mixtures at the desired temperature. The accuracy in the temperature measurement is ± 0.1K.

Results and Discussion

The experimentally determined values of density (ρ), viscosity (η) and ultrasonic velocity (U) of three liquid ternary systems at 303K are presented in Table 1. The values of adiabatic compressibility (β), free length (L_f), free volume (V_f), internal pressure (π_i) for the three liquid systems are reported in Table2. Further relaxation time (τ), Gibb's free energy (ΔG*) and acoustic impedance (Z) for all the ternary mixtures have been computed and reported in Table 3. The excess values of adiabatic compressibility (β^E), excess free length(L_f^E), excess free volume (V_f^E), and excess internal pressure (π_i^E) are furnished in Table 4.

Table 1 Density (ρ), viscosity (η) and velocity (U) at 303 K

Mole Fraction		DENSITY $\rho/(kg/m^3)$	VISCOSITY $\eta/(\times 10^{-3} NSm^{-2})$	VELOCITY U/(m/s)
X_1	X_3			
FOR SYSTEM-I				
0.0000	0.5999	824.93	0.6530	1225
0.1060	0.9960	832.03	0.6644	1228
0.1177	0.4712	888.99	0.6920	1231
0.3146	0.2937	943.24	0.8248	1234
0.4150	0.1942	949.13	0.9417	1236
0.5259	0.0609	954.56	1.0320	1244
0.6001	0.0000	959.45	1.0695	1246
FOR SYSTEM-II				
0.0000	0.6000	926.60	0.7676	1224.0
0.0999	0.4994	941.28	0.8318	1229.0
0.2999	0.4000	954.00	0.8606	1233.0
0.2999	0.2999	960.05	0.8941	1238.0

0.4000	0.1999	966.70	0.9729	1241.0
0.5001	0.0998	972.40	1.0473	1244.7
0.6001	0.0000	977.14	1.0830	1246.2
FOR SYTEM-III				
0.0000	0.4342	1002.55	1.1015	1282.0
0.0999	0.5000	1006.86	1.1376	1294.0
0.1999	0.4000	1009.50	1.1754	1309.3
0.2999	0.2999	1012.10	1.2368	1324.2
0.4000	0.2000	1016.60	1.2736	1332.0
0.5000	0.1000	1021.60	1.3170	1341.1
0.6000	0.0000	1024.50	1.3384	1347.6

It is evident from the Table 1 that the density (ρ), viscosity (η) and ultrasonic velocity (U) increases with increasing molar concentration of DMF in all the three liquid systems. The pronounced increase or decrease in these parameters with composition of mixtures indicates the presence of interactions between the component molecules in the ternary mixtures. DMF, the widely organic solvent is an aprotic, protophylic, potentially basic medium. Additionally, DMF can serve as a model compound of peptides to obtain information on protein systems.[9]

DMF itself being a polar molecule. When it is associated with substituted benzenes such as benznene, chlorobenzene and nitrobenzene and the mixtures formed by these combinations have not only dipolar-dipolar interaction between DMF molecules, but also the interaction of dipolar-induced dipolar between DMF molecules and the substituted benzene molecules. The interaction between unlike molecules seems to be stronger than the intra-molecular interactions and it leads to decrease of interaction of molecule. In addition, the relatively small size of DMF as well as its linear aliphatic configuration may be another factor contributing to the volume contraction of the mixtures.

When DMF is in association with benzene, DMF being a polar one where both benzene and the cyclohexane are non-polar. Mixing of benzene/cyclohexane with DMF tends to break DMF-DMF dipolar association releasing several DMF dipoles. Consequently, the free dipoles of DMF would induce moments in the neighboring molecules (cyclohexane/benzene), resulting in dipolar-induced dipole interaction leading to contraction in volume. This leads to subsequent decrease in adiabatic compressibility (β), and as well as in intermolecular free length (L_f) is observed in all the three liquid systems, with the increasing molar concentration of DMF, which is evident from the Table 2.

Table 2 Adiabatic compressibility (β), Free length (L_f) Free volume (V_f) and Internal pressure (π_i) at 303 K

Mole Fraction		Adiabatic compressibility $\beta/(\times10^{-10}\ m^2 N^{-1})$	Free length $L_f/(\times10^{-10}\ m)$	Free volume $V_f/(\times10^{-7} m^3\ mol^{-1})$	Internal pressure $\pi_i/(\times10^6\ Nm^{-2})$
X_1	X_3				
FOR SYSTEM-I					
0.0000	0.5999	8.0780	0.5671	2.0893	364.30
0.1060	0.9960	7.9710	0.5587	2.0222	409.68
0.1177	0.4712	7.4231	0.5436	1.6983	421.85
0.3146	0.2937	6.9620	0.5264	1.4430	503.67
0.4150	0.1942	6.8960	0.5239	1.1714	544.00
0.5259	0.0609	6.7690	0.5191	1.0085	554.34
0.6001	0.0000	6.7130	0.5169	0.9653	587.98
FOR SYSTEM-II					
0.0000	0.6000	7.2035	0.5355	2.3070	284.79
0.0999	0.4994	7.0335	0.5291	1.9381	396.15
0.2999	0.4000	6.8948	0.5239	1.7398	425.78
0.2999	0.2999	6.7961	0.5201	1.5487	454.86
0.4000	0.1999	6.7168	0.5171	1.2796	504.80
0.5001	0.0998	6.6378	0.5140	1.0170	554.80

0.6001	0.0000	6.5897	0.5122	0.9447	599.53
FOR SYTEM-III					
0.0000	0.4342	6.069	0.4915	1.575	413.76
0.0999	0.5000	5.9314	0.4859	1.4185	443.90
0.1999	0.4000	5.7785	0.4796	1.2742	476.27
0.2999	0.2999	5.6363	0.4737	1.1730	513.12
0.4000	0.2000	5.5442	0.4698	0.9856	560.21
0.5000	0.1000	5.4424	0.4654	0.8662	610.29
0.6000	0.0000	5.3748	0.4625	0.7761	661.45

Also, in particular, in the DMF + cyclohexane + chlorobenzne system, the chlorobenzene molecules which are quite polar (μ = 1.54 D)[10] The chlorine atom being an electron withdrawing atom, attracts the π-electrons of the benzene ring in C_6H_5Cl molecules and thus decrease of electron density of the ring. This makes the benzene ring a relatively poor electron donor towards the cyclohexane molecules, thereby a weak interaction between chlorobenzne and cyclohexane is expected.

On the other hand, a dipole-dipole interaction between DMF and chlorobenzene seems to be significant, which suggest that dipole-dipole interaction between them predominates in these systems. Similar observations were noticed by earlier workers supports the present study.[11]

Similarly in the system-III, it is noticed that DMF and nitrobenzene mixtures are characterised by the interactions between the π-electrons cloud of benzene ring with the delocalised π-electron cloud over the nitrogen and oxygen atoms of the nitro group of nitrobenzene resulting in the formation of weak interactions between them.[12]

Further, Cyclohexane belongs to alicyclic hydrocarbon (closed chain). The packing of carbon atoms in this even numbered alkane group allows the maximum intermolecular attractions[13] and therefore these molecules are highly inert towards an electrophile or nucleophile at ordinary temperature. In the present study, among the three components, Cyclohexane is not expected to involve in any interactions either with DMF or with other components due to its non-polar nature. Further. Dispersive types of interactions are expected between the other components and cyclohexane due to the non-polar nature of the cyclohexane and its inertness towards the electron donors.[14]

Further, a decrease in free volume and an increase in internal pressure with increase in concentrations of DMF is observed, which may be attributed to increasing magnitude of interactions[27] which are evident from the Table 2.

Table 3 **Viscous relaxation time (V_τ), Gibb's free Energy (ΔG) and Acoustic impedance (Z) at 303 K**

Mole Fraction		**Viscous relaxation time $\tau/(\times 10^{-12}$ S)**	**Gibb's free energy $\Delta G^*/(\times 10^{-20}$ KJ mol^{-1})**	**Acoustic impedance $Z/(\times 10^{6}$ kg m^{2} s^{-1})**
X_1	**X_3**			
FOR SYTEM-I				
0.0000	0.5999	0.7031	0.6235	1.0105
0.1060	0.9960	0.7124	0.6231	1.0217
0.1177	0.4712	0.7255	0.6358	1.0943
0.3146	0.2937	0.7644	0.6582	1.1639
0.4150	0.1942	0.8656	0.7105	1.1731
0.5259	0.0609	0.9312	0.7411	1.1874
0.6001	0.0000	0.9571	1.2330	1.1954
FOR SYTEM-II				
0.0000	0.6000	0.7370	0.40260	1.1342
0.0999	0.4994	0.7798	0.66684	1.1568
0.2999	0.4000	0.7908	0.6727	1.1763
0.2999	0.2999	0.8100	0.7179	1.1885
0.4000	0.1999	0.8710	0.7132	1.1997
0.5001	0.0998	0.9266	0.7390	1.2104

0.6001	0.0000	0.9513	0.7506	1.2115
FOR SYSTEM -III				
0.0000	0.4342	0.8911	0.7227	1.2852
0.0999	0.5000	0.8994	0.7265	1.3029
0.1999	0.4000	0.9054	0.7293	1.3217
0.2999	0.2999	0.9118	0.7323	1.3402
0.4000	0.2000	0.9412	0.7456	1.3541
0.5000	0.1000	0.9554	0.7518	1.3701
0.6000	0.0000	0.9589	0.7534	1.3806

From Table 3, it is observed that the relaxation time (τ) increases continuously with increase in mole fraction of DMF. The relaxation time, which is of the order of 10^{-12} seconds, is due to structural relaxation process [15] and such situation suggests that the molecules get rearranged due to co-operation process[16]. The Gibb's free energy (ΔG^*) (Table 3) increases with increase in composition of DMF in all the three systems. The increasing values of Gibb's function suggest that the closer approach of unlike molecules is due to hydrogen bonding [17-18]. The increase in ΔG^* in all the mixtures indicates the need for shorter time for the co-operative process or the rearrangement of the molecules in the mixtures.[19]

Further, in all three liquid systems, the values of acoustic impedance (Z) is found to be increased, which are listed in Table 3. when an acoustic wave travels in a medium, there is a variation of pressure from particle to particle. The ratio of the instantaneous pressure excess at any particle of the medium to the instantaneous velocity of that particle is known as 'specific acoustic impedance' of the medium. This factor is governed by the inertial and elastic properties of the medium. It is important to examine specific acoustic impedance in relation to concentration and temperature. When a plane ultrasonic wave is set up in a liquid, the pressure and hence density and refractive index show specific variations with distance from the source along the direction of propagation. In the present investigation, it is observed that these acoustic impedance (Z) values increase with increasing concentration of DMF. Such an increasing values of acoustic impedance (Z), further supports the possibility of molecular interactions between the unlike molecules.

In order to understand the nature of molecular interactions between the components of the liquid mixtures, it is of interest to discuss the same in term of excess parameter rather than actual values. Non-ideal liquid mixtures show considerable deviation from linearity in their physical behaviour with respect to concentration and these have been interpreted as arising from the presence of strong or weak interactions. The extent of deviation depends upon the nature of the constituents and composition of the mixtures. The excess values of adiabatic compressibility (β^E), free length (L_f^E), free volume (V_f^E) and internal pressure (π_i^E) for all the three liquid systems are furnished in Table 4.

Table 4 Excess values of Adiabatic compressibility (β^E), Free length (L_f^E) Free volume (V_f^E) and Internal pressure (π_i^E) at 303 K

Mole Fraction		Excess adiabatic compressibility $\beta^E/(\times10^{-10}\,m^2\,N^{-1})$	Excess free length $L_f^E/(\times10^{-10}\,m)$	Excess free volume $V_f^E/(\times10^{-7}m^3\,mol^{-1})$	Excess internal pressure $\pi_i^E/(\times10^6\,Nm^{-2})$
X_1	X_3				
FOR SYSTEM-I					
0.0000	0.6000	0.3125	0.0117	0.5385	14.63
0.1004	0.4988	0.4098	0.0115	0.473	1.23
0.1998	0.4001	0.0654	0.0048	0.1497	1.66
0.3000	0.3000	0.1527	0.0544	0.1644	37.69
0.4000	0.3000	0.0859	0.064	0.0473	78.02
0.5000	0.0999	0.0231	0.0965	0.0288	80.79
0.6002	0.0000	0.1781	0.0103	0.1154	109.64
FOR SYSTEM-II					
0.0000	0.6000	0.1655	0.0085	0.2971	3.80
0.1000	0.5000	0.0765	0.0556	0.0068	3.18
0.1991	0.4001	0.0244	0.0042	0.0399	0.94
0.3000	0.3001	0.2025	0.0035	0.0708	24.28

0.4000	0.2000	0.0009	0.0041	0.4326	74.22
0.5001	0.1998	0.6207	0.024	0.0008	89.36
0.6001	0.0000	0.0479	0.0062	0.0220	121.19
FOR SYSTEM-III					
0.0000	0.5657	0.1679	0.0100	-0.5488	16.45
0.0999	0.5001	1.0430	0.0056	-0.6613	36.58
0.2998	0.4000	0.7937	0.0074	-0.7745	52.86
0.3999	0.3999	0.584	0.0147	-2.7025	87.68
0.3999	0.4000	0.3954	0.0108	-1.1393	134.90
0.5000	0.1000	0.2052	0.0012	-0.7859	146.17
0.6000	0.0000	0.0475	0.0006	-0.7689	183.72

It is learnt 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.[20].In the present study, the excess values of adiabatic compressibility (β^E) and intermolecular free length (L_f^E) which are given in Table 4 whose values exhibit positive deviations over the entire range of composition in all the three liquid systems. This suggests that in addition to dipole-dipole and dipole-induced dipole interactions, dispersive forces are also operative in all these systems. It has been reported that dispersive forces tend to make a positive contribution to the excess functions is obvious.[1-3] The positive values further attribute that apart from dispersion forces, weak dipolar forces are also operating with some specific interaction between molecules of the mixtures. Since dispersive interactions [21-23] are dominant between benzene and cyclohexane, same types of interaction may also play between chlorobenzene, nitrobenzene and cyclohexane and its inertness towards the electron donors.

The excess values of internal pressure (πi^E) which are furnished in the Table 4. The positive values of this parameter over the entire range of composition in all the three liquid systems clearly supporting this.

Conclusion

From the present investigation, it is obvious that there exists a molecular association between the components of the mixtures. In specific, a weak molecular interaction prevailing in the present systems of the mixtures. Such interactions are primarily due to weak dipole-dipole and dipole- induced dipole types. Dispersive forces are also found to exist between the components of the mixtures.

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