Ultrasonic Studies in Ternary Mixtures of Alcohols With NN DMA in N-Hexane at 303K

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Abstract

The ultrasonic velocity, density and viscosity have been measured at 303 K by the ternary mixtures of alcohols (ethanol, propanol, butanol, pentanol and hexanol) with NN Dimethyl aniline in n hexane systems. The adiabatic compressibility (β), acoustic impedance (z), intermolecular free length (Lf), and their excess values have been calculated from the experimental data. These parameters are used to discuss the molecular interactions between the component molecules and the excess functions are found to be sensitive to the nature and extent of the interactions taking place in these ternary mixtures.

Key words: Ternary systems, Ultrasonic velocity, Acoustical parameters, Excess parameters, Molecular interactions.

Introduction

Ultrasonic velocities, densities, viscosities and derived thermodynamic and acoustical parameters are of considerable interest in understanding the intermolecular interactions in binary as well as ternary liquid mixtures. Ultrasonic studies in recent years are adequately employed in understanding the behaviour of molecular interactions in pure liquids and liquid mixtures. Ultrasonic studies are of great importance in various fields like leather industries, automobile industries, textile industries, pharmaceutical industries, constructional industries, etc… The study of molecular interactions in binary mixtures containing of alcohols on density, velocity, viscosity and acoustic properties of binary mixtures containing acetonitrile, dimethyl sulfoxide, ethyl acetate and chloroform have been reported[1-4]. Excess molar volumes and viscosities of binary mixtures of N, N-dimethylformamide with methanol, ethanol and 2-propanol at different temperatures have been reported. [5]. The ultrasonic technique is used to study the properties and structures of liquids, the nature and strength of molecular interactions between the components of liquids of pentanol, hexanol, heptanol, octanol and decanol with dimethylketone in carbon tetrachloride / benzene systems. [6].Thermodynamic properties of ternary mixtures of N, N-dimethylformamide + benzene + chlorobenzene have been reported. [9]. However no attempts have been made to study for ternary system of NN Dimethyl Aniline, n-hexane with aliphatic alcohols. The main aim of the present attempt to characterize the nature of molecular interaction in the system and measurement of ultrasonic velocity enable us to the measurement of thermodynamic and acoustic parameters and their related excess values of adiabatic compressibility, acoustic impedance and intermolecular free length in ternary mixture are useful to study molecular interactions in the system.

Material and Methods

Chemicals

The chemicals alcohols, N N Dimethyl Aniline and n hexane used were of analytical grade and purchased from Loba Chemie Private limited, Mumbai, Ranbaxy Fine Chemicals Limited, New Delhi and

Quligens fine Chemicals, Mumbai. These chemicals were purified by standard procedures [18& 19] and redistilled before use. The double distilled water used for preparation of liquid mixtures.

Ultrasonic velocity, density and viscosity measurement

Ultrasonic velocity of the ternary system has been measured with help of ultrasonic single crystal interferometer (Mittal Enterprises, Rearch model F81) at a frequency of 2MHz.The densities of the solutions were measured using specific gravity bottle. Viscosities of the mixtures were determined using Oswald's viscometer with accuracy of ±0.002% calibrated with double distilled water. All the experimental are carried at 303.15K by using digital thermostat.

Table-1 Ultrasonic velocities(U), densities(ρ), viscosities(η), adiabatic compressibility's(β)**,** acoustic impedance(Z) and intermolecular free length(Lf) in various concentration of Ethanol+ N, N Dimethyl aniline +n hexane at 303K

Concentration	**Velocity(U) ms^{-1}**	**Density (ρ) kgm^{-3}**	**Viscosity (η) x10^{-3} ($Nm^{-2}s$)**	**Adiabatic compressibility (β)/$10^{-10}Kg^{-1}ms^{-2}$**	**Acoustic impedance (Z) /10^6 $Kgm^{-2}S^{-1}$**	**Int. mole. free length (Lf)/10^{-11}m**
0.0004	1044.0	650	2.9072	1.4104	6.7912	7.4511
0.0006	1046.0	650	2.8968	1.4053	6.8032	7.4374
0.001	1049.0	650	2.8846	1.3977	6.8206	7.4172
0.0014	1035.0	648	2.871	1.4359	6.7285	7.5182
0.0018	1038.0	648	2.8496	1.4305	6.7345	7.5039
0.002	1040.0	648	2.8440	1.4255	6.7454	7.4907
0.004	1042.0	648	2.840	1.4202	6.7574	7.4769
0.008	1044.0	648	2.8312	1.4152	6.7683	7.4637
0.01	1045.0	648	2.8224	1.4134	6.7706	7.4588

Table-2 Ultrasonic velocities(U), densities(ρ), viscosities(η), adiabatic compressibility's(β)**,** acoustic impedance(Z) and intermolecular free length(Lf) in various concentration of propanol+ N, N Dimethyl aniline +n hexane at 303K

Concentration	**Velocity(U) ms^{-1}**	**Density (ρ) kgm^{-3}**	**Viscosity (η) x10^{-3} ($Nm^{-2}s$)**	**Adiabatic compressibility (β)/$10^{-10}Kg^{-1}ms^{-2}$**	**Acoustic impedance (Z) /10^6 $Kgm^{-2}S^{-1}$**	**Int. mole. free length (Lf)/10^{-11}m**
0.0004	1039	652	2.8984	1.4208	6.7743	7.4783
0.0006	1041	651	2.8936	1.4175	6.7769	7.4697
0.001	1043	650	2.8848	1.4142	6.7795	7.4611
0.0014	1045	648	2.8632	1.4132	6.7716	7.4583
0.0018	1040	651	2.8712	1.4202	6.7704	7.4768
0.002	1041	650	2.8616	1.4197	6.7665	7.4754
0.004	1042	650	2.856	1.4169	6.773	7.4682
0.008	1046	650	2.852	1.4061	6.799	7.4397
0.01	1047	651	2.848	1.4013	6.816	7.4268

The acoustical parameters are used for the study of the molecular interactions using standard relations
Acoustical impedance (Z) = U ρ ------------ (1)
Adiabatic Compressibility (β) = $1/u^2\rho$---------- (2)
Intermolecular free length (Lf) = K √β----------- (3)
An excess value of ultrasonic related parameters has been calculated by using the relation.
$Y^E = Y_{MIX} - [X_1Y_1+X_2Y_2+X_3Y_3]$ --------------- (4)
Where, Y^E is excess values of parameters , X_1, X_2, X_3 and Y_1, Y_2, Y_3 are mole fraction and parameters of components of 1, 2 and 3 respectively.

Table-3 Ultrasonic velocities(U), densities(ρ), viscosities(η), adiabatic compressibility's(β)**,** acoustic impedance(Z) and intermolecular free length(Lf) in various concentration of butanol + N, N Dimethyl aniline +n hexane at 303K

Concentration	Velocity(U) ms^{-1}	Density (ρ) kgm^{-3}	Viscosity (η) $x10^{-3}$ ($Nm^{-2}s$)	Adiabatic compressibility $(\beta)/10^{-10}Kg^{-1}ms^{-2}$	Acoustic impedance (Z) $/10^6$ $Kgm^{-2}S^{-1}$	Int. mole. free length $(Lf)/10^{-11}m$
0.0004	1048.0	651	2.8424	1.3986	6.8225	7.4198
0.0006	1050.0	652	2.8432	1.3911	6.846	7.3999
0.001	1053.0	653	2.844	1.3811	6.8761	7.3732
0.0014	1039.0	651	2.8304	1.4229	6.7639	7.484
0.0018	1041.0	651	2.8232	1.4175	6.7769	7.4697
0.002	1043.0	651	2.82	1.4121	6.7899	7.4553
0.004	1045.0	652	2.8248	1.4045	6.8134	7.4354
0.008	1046.0	652	2.8152	1.4018	6.8199	7.4282
0.01	1048.0	652	2.8056	1.3965	6.833	7.4141

Table-4 Ultrasonic velocities(U), densities(ρ), viscosities(η), adiabatic compressibility's(β)**,** acoustic impedance(Z) and intermolecular free length(Lf) in various concentration of pentanol + N, N Dimethyl aniline +n hexane at 303K

Concentration	Velocity(U) ms^{-1}	Density (ρ) kgm^{-3}	Viscosity (η) $x10^{-3}$ ($Nm^{-2}s$)	Adiabatic compressibility $(\beta)/10^{-10}Kg^{-1}ms^{-2}$	Acoustic impedance (Z) $/10^6$ $Kgm^{-2}S^{-1}$	Int. mole. free length $(Lf)/10^{-11}m$
0.0004	1043	650	2.8824	1.4142	6.7795	7.4611
0.0006	1045	651	2.8744	1.4088	6.7925	7.4468
0.001	1047	652	2.8704	1.4034	6.8055	7.4326
0.0014	1038	650	2.8552	1.4301	6.7366	7.5028
0.0018	1040	651	2.8552	1.4202	6.7704	7.4768
0.002	1042	649	2.8416	1.4169	6.773	7.4682
0.004	1044	650	2.8432	1.4072	6.8069	7.4425
0.008	1046	650	2.8376	1.404	6.8095	7.4339
0.01	1049	650	2.8336	1.3981	6.8185	7.4184

Table-5 Ultrasonic velocities(U), densities(ρ), viscosities(η), adiabatic compressibility's(β), acoustic impedance(Z) and intermolecular free length(Lf) in various concentration of hexanol+ N, N Dimethyl aniline +n hexane at 303K

Concentration	Velocity(U) ms^{-1}	Density (ρ) kgm^{-3}	Viscosity (η) $x10^{-3}$ ($Nm^{-2}s$)	Adiabatic compressibility $(\beta)/10^{-10}Kg^{-1}ms^{-2}$	Acoustic impedance (Z) $/10^{6}$ $Kgm^{-2}S^{-1}$	Int. mole. free length $(Lf)/10^{-11}m$
0.0004	1045	652	2.8688	1.4045	6.8134	7.4354
0.0006	1047	651	2.8584	1.4013	6.816	7.4268
0.001	1049	651	2.8544	1.3959	6.829	7.4127
0.0014	1036	651	2.8496	1.4312	6.7444	7.5057
0.0018	1038	650	2.8384	1.4279	6.747	7.497
0.002	1040	651	2.8392	1.4202	6.7704	7.4768
0.004	1043	649	2.8248	1.4164	6.7691	7.4668
0.008	1046	651	2.8272	1.404	6.8095	7.4339
0.01	1050	650	2.8168	1.3954	6.825	7.4113

Table-6 Excess parameters of Excess Adiabatic compressibility (β^E), Excess acoustic impedance (Z^E), Excess free length (Lf^E) ternary mixtures of Ethanol + N N Dimethyl aniline + n Hexane at 303K

Mole fraction	Excess Adiabatic compressibility, (β^E $x10^{-08}$, $Kg^{-1}ms^{-2}$)	Excess aq. impedance, Z^E $/10^6$ Kg $m^{-2}S^{-1}$	Excess free length, Lf^E $x10^{-11}$$_m$
0.001	-3.9399	4.19075	-3.2534
0.0016	-4.4351	4.83624	-3.6399
0.0032	-5.0032	5.22047	-4.0775
0.0046	-1.2213	-5.31692	-0.7223
0.0059	-1.1871	-6.64776	-0.8289
0.0067	-1.6054	-6.06729	-1.144
0.0138	-1.1245	-11.787	-0.5791
0.0293	0.6077	-25.659	1.2462
0.0378	1.7989	-36.464	2.8177

Table-7 Excess parameters of Excess Adiabatic compressibility (β^E), Excess acoustic impedance (Z^E), Excess free length (Lf^E) ternary mixtures of propanol + N N Dimethyl aniline + n Hexane at 303K

Mole fraction	Excess Adiabatic compressibility, (β^E $x10^{-08}$, $Kg^{-1}ms^{-2}$)	Excess aq. impedance, Z^E $/10^6$ Kg $m^{-2}S^{-1}$	Excess free length, Lf^E $x10^{-11}$$_m$
0.001	-3.0361	2.96655	-2.4736
0.0016	-3.2853	2.54373	-2.6771
0.0032	-3.3622	1.15345	-2.6992
0.0046	-3.265	-1.14701	-2.5931
0.0059	-2.3437	-2.5397	-1.7792
0.0067	-2.2594	-3.68698	-1.676
0.0138	-1.4418	-11.423	-0.8192
0.0293	-0.1124	-23.8	0.6954
0.0378	0.71143	-30.865	1.6161

Table-8 Excess parameters of Excess Adiabatic compressibility (β^E), Excess acoustic impedance (Z^E), Excess free length (Lf^E) ternary mixtures of butanol + N N Dimethyl aniline + n Hexane at 303K

Mole fraction	Excess Adiabatic compressibility, (β^E x10^{-08}, $Kg^{-1}ms^{-2}$)	Excess aq. impedance, Z^E /10^6 Kg $m^{-2}S^{-1}$	Excess free length, Lf^E x$10^{-11}$$_m$
0.001	-5.2457	7.77563	-4.3185
0.0016	-5.9095	9.43524	-4.8718
0.0032	-6.6549	10.777	-5.458
0.0046	-2.2609	-1.96828	-1.7504
0.0059	-2.5831	-1.95317	-1.9705
0.0067	-2.9827	-1.41719	-2.2699
0.0138	-2.6085	-6.53378	-1.7748
0.0293	-0.3784	-22.028	0.5125
0.0378	0.4517	-29.579	1.4418

Table-9 Excess parameters of Excess Adiabatic compressibility (β^E), Excess acoustic impedance (Z^E), Excess free length (Lf^E) ternary mixtures of pentanol + N N Dimethyl aniline + n Hexane at 303K

Mole fraction	Excess Adiabatic compressibility, (β^E x10^{-08}, $Kg^{-1}ms^{-2}$)	Excess aq. impedance, Z^E /10^6 Kg $m^{-2}S^{-1}$	Excess free length, Lf^E x$10^{-11}$$_m$
0.001	-3.6802	3.42549	-3.0078
0.0016	-4.1364	4.00183	-3.3834
0.0032	-4.4096	3.55165	-3.5667
0.0046	-1.5285	-4.9351	-1.1367
0.0059	-2.2863	-2.91176	-1.7166
0.0067	-2.4665	-3.4595	-1.8317
0.0138	-2.2829	-7.90524	-1.487
0.0293	-0.2396	-23.556	0.8257
0.0378	0.7744	-32.996	1.7498

Table-10 Excess parameters of Excess Adiabatic compressibility (β^E), Excess acoustic impedance (Z^E), Excess free length (Lf^E) ternary mixtures of hexanol + N N Dimethyl aniline + n Hexane at 303K

Mole fraction	Excess Adiabatic compressibility, (β^E x10^{-08}, $Kg^{-1}ms^{-2}$)	Excess aq. impedance, Z^E /10^6 Kg $m^{-2}S^{-1}$	Excess free length, Lf^E x$10^{-11}$$_m$
0.001	-4.64951	6.78893	-3.8168
0.0016	-4.88384	6.30632	-4.0072
0.0032	-5.1474	5.81564	-4.1818
0.0046	-1.40014	-4.2833	-1.0251
0.0059	-1.49768	-5.4085	-1.0544
0.0067	-2.11517	-3.89749	-1.5317
0.0138	-1.31111	-12.053	-0.6605
0.0293	0.06305	-25.38	-0.9467
0.0378	0.64549	-33.35	1.6825

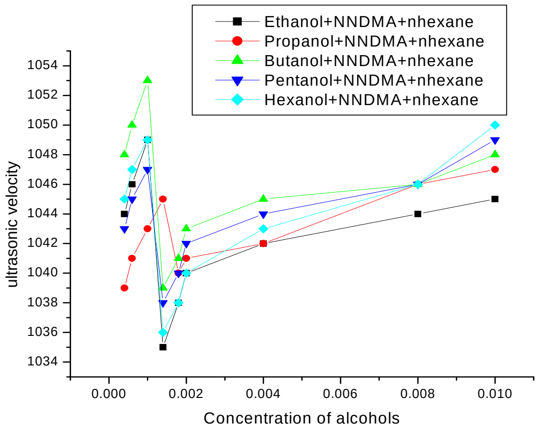

Figure -1 Variation of ultrasonic velocity with Concentration

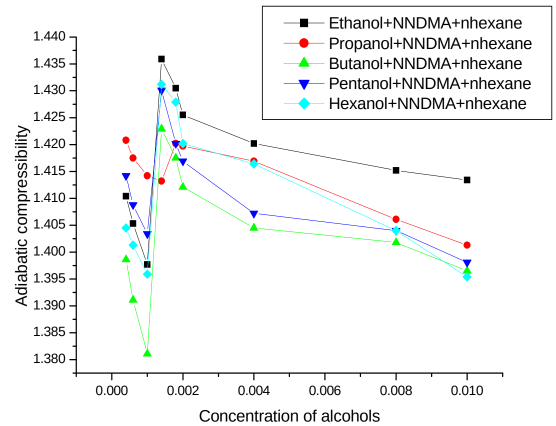

Figure-2 Variation of adiabatic compressibility with Concentration

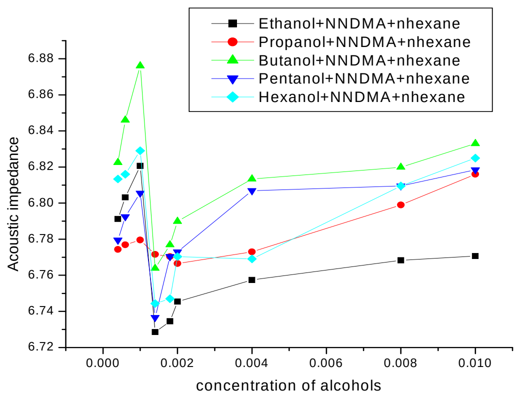

Figure-3 Variation of acoustic impedance with Concentration

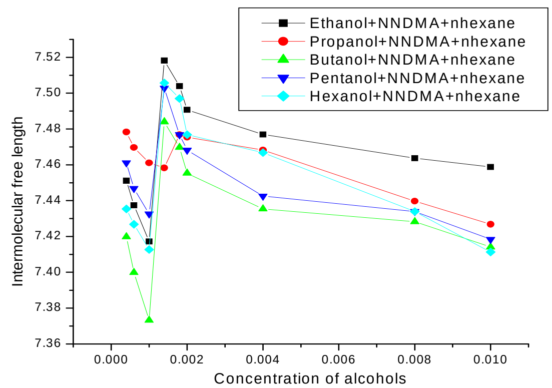

Figure- 4 Variation of intermolecular free length with Concentration

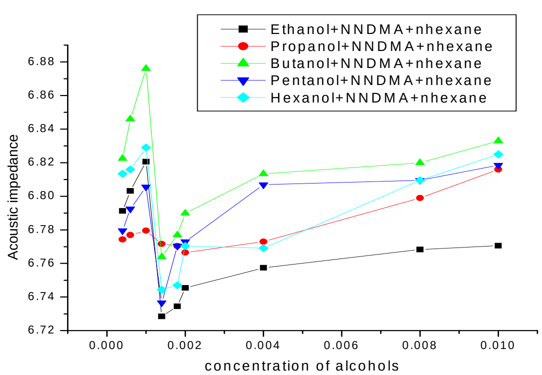

Figure-5 Variation of Excess acoustic impedance with Mole fraction

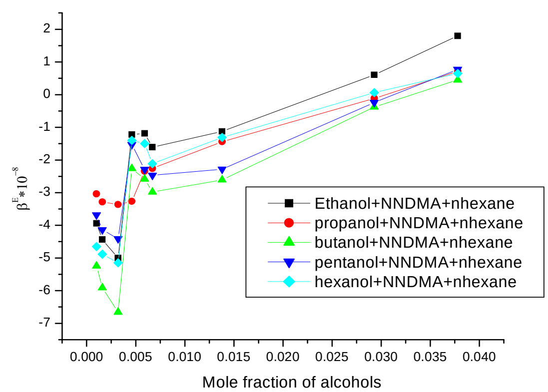

Figure- 6 Variation of Excess adiabatic compressibility with Mole fraction

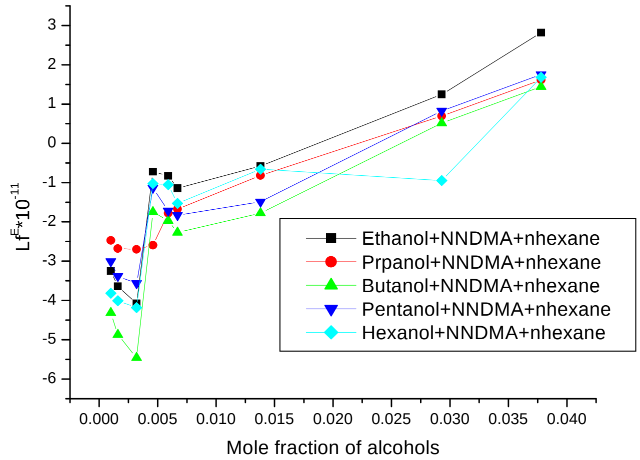

Figure-7 Variation of Excess free length with Mole fraction

Result and Discussion

The ultrasonic velocities and densities at various composition of the ternary system are tabulated in Table1, 2, 3, 4 and5.The variation of ultrasonic velocity with respect to the composition of alcohols is represented in the fig.1.The nonlinear variation in velocity values with the change in composition of the mixture in each system shows the presence of molecular interaction between the molecules in liquid mixture. In all the systems initially increases in velocity the sudden decrease occur at concentration 0.0014N. Then the gradual increases in velocity. A sudden decrease in velocity is due to the molecular interaction between the molecules in ternary liquid mixture. The increase in velocity is also due to the decrease in intermolecular free length. The variation of ultrasonic velocity in solution depends upon increase or decrease of intermolecular free length. Inter molecular free length is one of the predominating factor in deciding the nature of change in ultrasonic parameter. The density values and viscosity decrease in all the systems indicates more attraction between the molecules in liquid mixture.

Adiabatic compressibility (β)

Adiabatic compressibility is calculated using equ.2. These values are presented in table 1, 2, 3, 4 &5; the corresponding plot is given in fig.2. In the present case adiabatic compressibility (β) decreases with increase the concentration. A sudden increase in compressibility occurs at concentration 0.0014N. Then the gradual decrease occurs in adiabatic compressibility. A sudden decrease in compressibility is due to molecular interaction in ternary liquid mixtures.

Acoustic impedance (Z)

The acoustic impedance is the product of density and ultrasonic velocity of solvent /solution. The values of acoustic impedance (z) are shown in table 1, 2, 3, 4&5 for all the systems and corresponding plot is given in fig.3. It is noted that for a given concentration the adiabatic compressibility (β) decreases with increase in concentration, whereas, acoustic impedance increases for the same concentration. However a sudden decreases the acoustic impedance at concentration 0.0014N. Then there is a regular increase in z. A sudden decrease in acoustic impedance is due to interaction between alcohols+ NN DMA +n hexane mixture.

Intermolecular free length (Lf)

Increase in concentration leads to decrease in gap between two species which is referred by intermolecular free length. When increase in concentration the intermolecular free length will decrease. The values of intermolecular free length for the ternary system have been calculated using equ.3. From the table1, 2, 3, 4 &5, the corresponding plot is given in fig.4. It has been observed that, in present investigation, intermolecular free length decrease nonlinearly in increasing the concentration of the ternary liquid mixture. A sudden increasing in Lf observed at concentration 0.0014N. Then the regular decreases in Lf. A sudden increase and decrease in Lf is indicating that there is significant interaction between the molecules of ternary liquid mixture.

Excess parameters

From the table 6, 7, 8, 9&10 and the corresponding plots are given in fig. 5, 6 & 7. The excess acoustical parameters can be used to find out the extent of deviation from ideal behaviour in ternary liquid mixture. These values are calculated for all the five ternary systems for different mole fraction at 303K. From the table 6, 7, 8, 9&10 the excess adiabatic compressibility (β^E), excess acoustic impedance (Z^E) and excess intermolecular free length (Lf^E) are almost negative values for all the ternary systems. This is clearly shows that the attractive forces between the molecules of components are stronger. As given in the table 6, 7, 8, 9&10 the β^E value are negative which suggest the presence of hydrogen bonding between the components of the liquid mixture. Some of the β^E, Z^E, and Lf^E values are positive which suggest that absence of hydrogen binding. Also indicate less interaction in the alcohol+ NN DMA + n hexane system.

Conclusion

Ultrasonic velocity, density, viscosity and other parameters were calculated. The nonlinear increase in velocity and acoustic impedance and decrease in adiabatic compressibility and intermolecular free length indicate the molecular interaction among molecules. The negative values of excess parameters due to hydrogen bond and some positive values indicate the absence of hydrogen bond. Also shows the less interaction between the molecules in liquid mixtures.

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