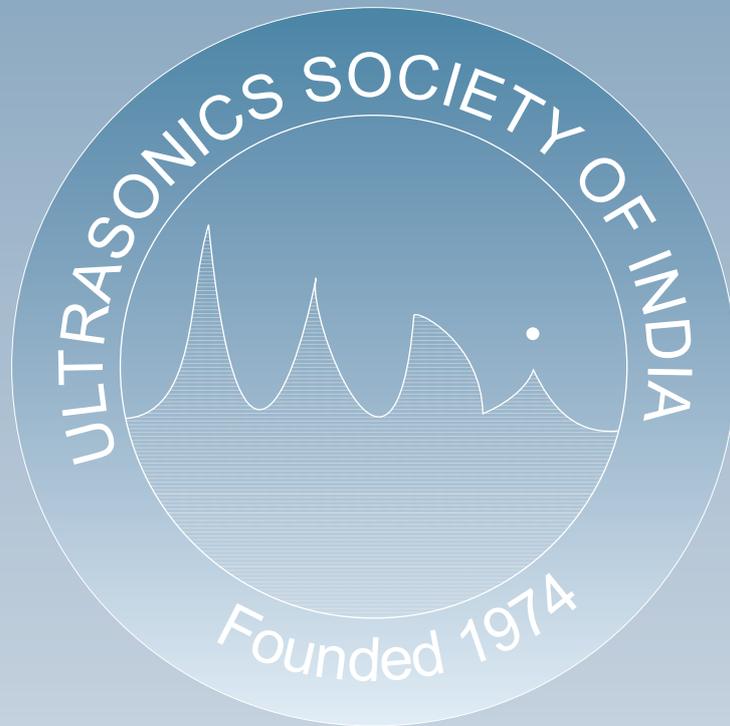


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Solvation number and optical absorbance studies in polyaniline derivatives

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Over the past two decades the polyaniline has received the greatest attention due to its stability, easy synthesis and the potential as a material for numerous applications. This makes PANI an attractive material for researchers. The solvation number in the polyaniline solution has been found to be of great interest during the recent years. Solvation number has effects of both physical and chemical. In the present work the solvation number on some polyaniline derivatives is analysed. The solutions of some polyaniline derivative are prepared for different molalities and measured at various temperatures. Solvation number of solutions depends on the number of moles of the solute and the solvent molecules present in the solution. The optical absorption spectra suggests that the presence of molecular interaction between the PANI and the solvent through enolic form. This analysis also confirms the dual nature of the solvent.

Keywords: Polyaniline, solvation number, optical absorption.

Introduction

Polyaniline is a conducting polymer of the semi-flexible rod polymer family¹. It has captured the attention of the scientific community due to the discovery of its electrical conductivity. It has unlimited worldwide commercial availability. PANI is an organic metal and its specific conductivity is semi-metallic. In electrostatic dissipation, anticorrosion coatings in various optoelectronic devices and as an antistatic material, polyaniline salts are used. Polyaniline can be configured to conduct across a wide range, from being utterly non-conductive for insulation use to highly conductive for other electrical purposes. Depending on the desired conductivity of the polyaniline, the resulting polymer will be exposed to other chemicals in a process called doping. Doping polyaniline leads to a more stable polymer, and also allow it to conduct current evenly².

Synthesis of polyaniline salts with various dopants is of fundamental importance in exploiting its solubility in common organic solvents for improved processibility³. Various types of acids have been used in the protonation of polyaniline. The efficient

polymerization of aniline is achieved only in an acidic medium, where aniline exists as an anilinium cation. A variety of inorganic and organic acids of different concentration have been used in the synthesis of PANI⁴. Electrically conducting organic polymers with π -conjugated systems have been studied extensively for a variety of application including electrochromic displays, batteries, solar energy conversion etc. Among the polymers studied, polyaniline is considered to be a unique one that can be synthesized either chemically or electrochemically as a bulk powder or films. In order to understand the effect of the substituents on polyaniline, solvation number is an interesting aspect posed by the conducting polymer family⁵. So in the present investigation an attempt is made to investigate the solvation number of the polyaniline samples. Optical absorbance study also carried out for the samples in order to define the nature of the polymer interactions.

Material and Method

For the present work, polyaniline salts have been prepared by tri, di and mono chloro acetic acid as doping acid. Polyaniline (III) is synthesized by oxidative

polymerization of aniline using ammonium per sulphate as an oxidant in the presence of chloro acids at room temperature washed by ethanol, acetone and ether respectively. Solvent here used is the formamide a polar a protic solvent. The present work dealt with the solvation number and spectroscopic study of polyaniline derivatives, PANI trichloroacetate (tri), PANI dichloroacetate (di) PANI mono chloro acetate (mono) in formamide. The basic parameters like density, viscosity and ultrasonic velocity are determined for various concentrations from 5°C to 55°C in order to compute the solvation effect of the PANI solutions. Similarly the optical absorbance spectra have been recorded and they are analysed. Solvation number is computed by passing the ultrasonic waves with the frequency of 2 MHz using the following formulae.

$$\eta_h = \frac{n_s}{n_l} [1 - (\beta / \beta_0)] \quad (1)$$

$$\beta = \frac{1}{u^2 \rho} \text{ cm}^2/\text{dyne} \quad (2)$$

Where,

η_h → solvation number

β → adiabatic compressibility

u → ultrasonic velocity

Results and Discussion

Solvation Number

The solvation numbers are tabulated and shown in

Table I and the variations are shown in Fig. 1-6. The effect of solvation is appropriate only at lower concentrations for all temperatures. At very low temperature & room temperature positive solvation number is found and at all other temperatures both positive and negative values are found (Fig 1-6). The solutions are found to be more compressible above the room temperature due to the passage of ultrasonic/pressure waves through the solution. Negative values of solvation number indicate that the solutions are more compressible than the solvent. Many authors in literature report negative solvation number⁶⁻⁸. The positive values are an indication of stronger interaction between the molecules⁹.

The ion solvent interaction may be equal to intermolecular interaction energy¹⁰ which results in zero values. In general one can consider two types of interactions between the component molecules such as physical and chemical interactions which are arising from dispersion forces or weak dipole-dipole interactions making a positive contribution and the chemical or specific interactions due to the charge transfer, hydrogen bond formation and other complex forming interaction results in negative values^{11, 12}. Comparing to the three PANI solutions the solvation effect is found to be very low in mono and high in tri chloro acetate solutions. This implies that tri chloro acetate solution is more compressible than the other two solutions. These results indicate that strong solute-solvent interaction takes place in the solution. The solvation effect is found to be in the order as given below.

Table 1 – Solvation Number

MOLALITY	5°C	15°C	25°C	35°C	45°C	55°C
0.001(MONO)	-18	-9	-1	-2	12	21
0.001(DI)	319	-234	33	-13	124	85
0.001(TRI)	519	-325	303	-647	-101	-709
0.005 (MONO)	-5	-3	-1	-2	-2	0
0.005 (DI)	49	-12	-4	54	33	33
0.005 (TRI)	-58	-34	168	75	53	108
0.01(MONO)	-1	-1	-1	1	-1	2
0.01 (DI)	27	-14	-18	-6	10	16
0.01 (TRI)	-25	12	7	-13	17	19
0.015 (MONO)	0	0	1	0	0	0
0.015 (DI)	-3	2	-8	-1	21	25
0.015 (TRI)	-3	-2	45	3	-96	51
0.02 (MONO)	0	0	0	0	0	0
0.02 (DI)	3	4	-8	12	6	13

MONO<DI<TRI

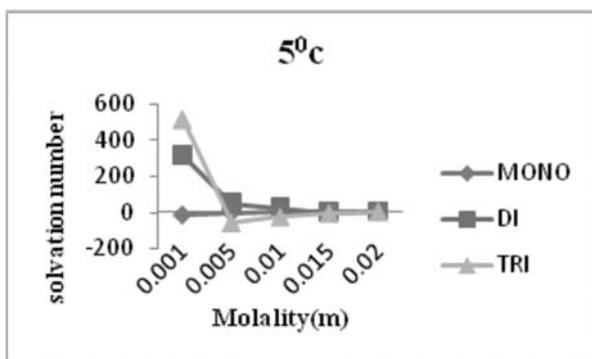


Fig. 1 Solvation number-5°C

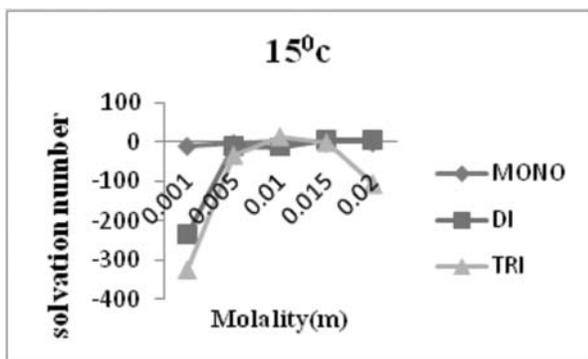


Fig. 2 Solvation number-15°C

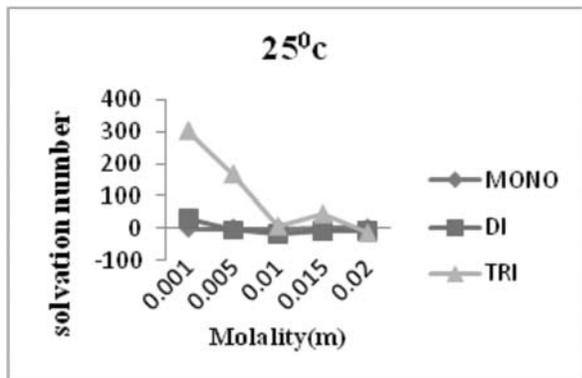


Fig. 3 Solvation number-25°C

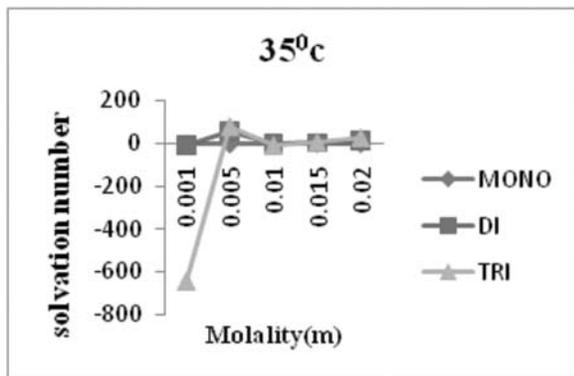


Fig. 4 Solvation number-35°C

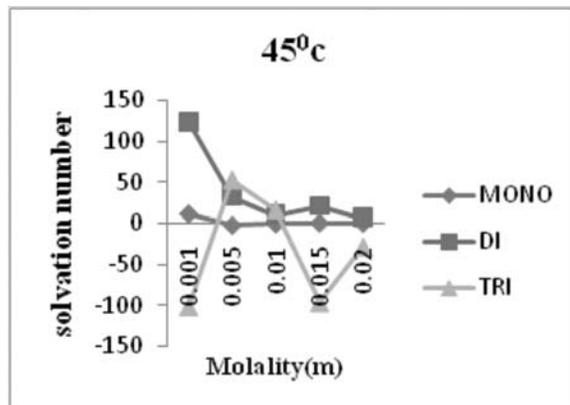


Fig. 5 Solvation number-45°C

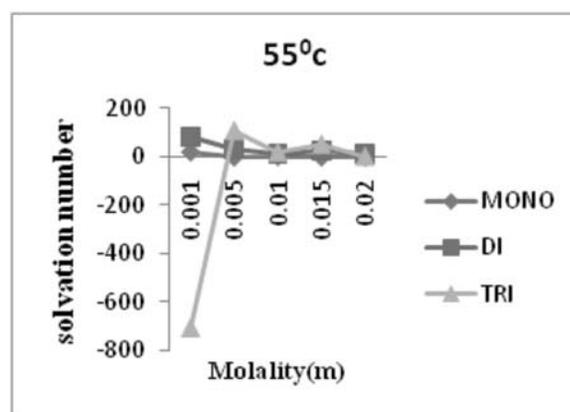


Fig. 6 Solvation number-55°C

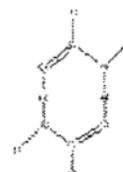


Fig. 7 Dimer form of formamide

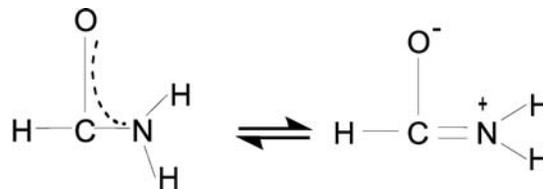


Fig. 8 Enolic form of formamide

Optical Analysis

The presence of two very close peaks at 210 nm and 213 nm in the visible spectrum of the solvent (Fig. 9) are attributed to the dimer (Fig. 7) and the enolic form (Fig. 8).

i. Tri Chloro Acetate

In the visible spectra (Fig.10) peaks are observed at

262 nm, 271 nm and 380 nm. These absorptions are due to formamide and solute. The peak at 380 nm is due to the solute particle while peaks at 262 nm and 271 nm have shifted bathochromically by ~50nm from the solvent. This indicates the strong solute- solvent interaction.

ii. Di Chloro Acetate

In the visible spectra (Fig.11) peaks are observed at 262 nm, 270 nm, 375 nm and 571 nm. The solvent peaks are bathochromically shifted by ~50 nm while solute peaks are found at 370 nm and 571 nm. Bathochromic shift of solvent peak are indicative of solute- solvent interaction.

iii. Mono Chloro Acetate

In the UV spectra (Fig.12) broad absorptions at 328 nm and 644 nm are indicative of very strong absorption due to solute particle. Strong solute - solvent interaction may be inferred from intense absorption at 328 nm.

Table 2 – Optical Absorbance for Pani Solutions

Formamide λ_{nm}	PANI tri λ_{nm}	PANI di λ_{nm}	PANI mono λ_{nm}
210.27	260.04	262.75	261.12
213.12	271.57	270.21	276.06
--	380.28	374.93, 571.02	607.05

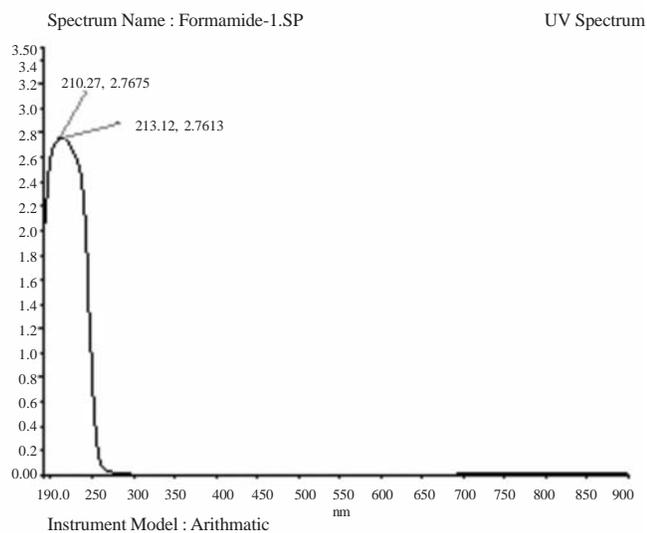


Fig. 9 Optical absorbance spectra of solvent

In all the above three PANI solution the presence of quinoid and benzenoid are identified. By comparing the solvent spectrum with the solutions it is observed that

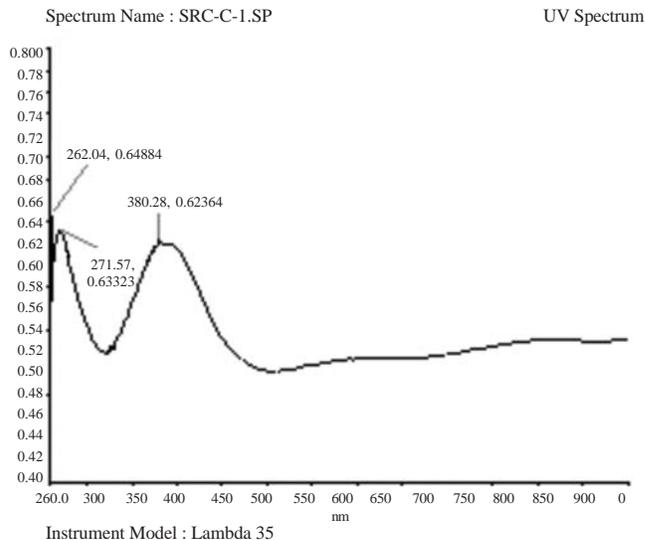


Fig. 10 Optical absorbance spectra of PANI tri

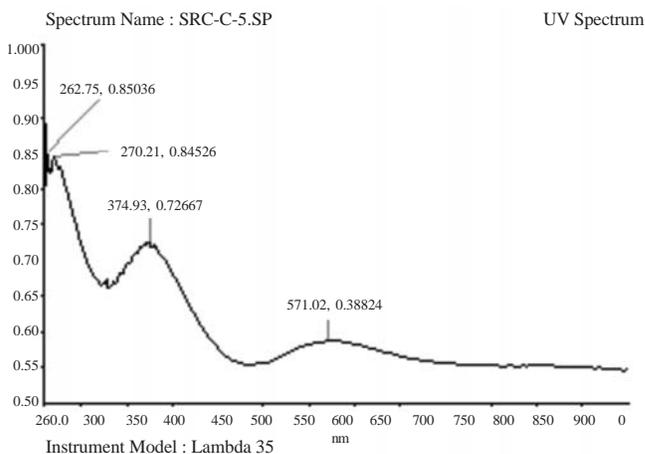


Fig. 11 Optical absorbance spectra of PANI di

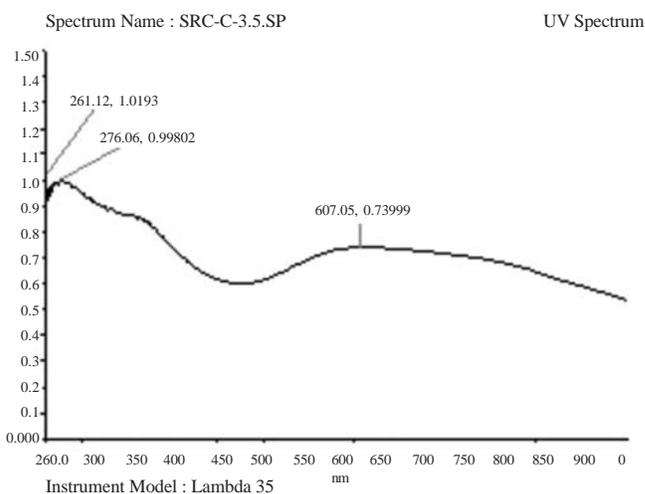


Fig. 12 Optical absorbance spectra of PANI mono

the absorption peaks are shifted towards the longer wavelength region. This may be due to the solvent effect. It has been found that there is a bathochromic shift which results from a reduction in the energy level of the excited state accompanying the dipole-dipole interaction which in turn results in intermolecular hydrogen bonding¹³.

When a transition ($n \rightarrow \pi^*$) appears in the spectrum of an aromatic compound that contains ($\pi \rightarrow \pi^*$) transitions the shift occur at longer wavelengths. From this analysis, it is inferred that solutions of PANI are enhancing the structure of the solvent. The spectroscopic studies obtained are found to be in good agreement with the acoustic study.

Conclusion

The present investigation confirms that the solvent effect enhances the compressibility of the Tri chloro acetate solution compare to Di and Mono chloro acetate solutions. This result is found to be in good agreement with optical absorbance study which reveals that the solute is bound to the solvent through the enolic form of the solvent.

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Comparative study of molecular interaction in ternary liquid mixtures of Polar and non-polar solvents

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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 over the whole range of composition 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.

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.

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-dimethylformamide (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 attractions¹. It is highly inert towards an electrophile or a nucleophile at ordinary temperature. Due to the non-polar nature of cyclohexane and its inertness towards electron donors², 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 solvent³. 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. However the interaction between molecules appears to be weaker in Nitrobenzene which may be attributed to steric hindrance. Since pyridine molecules are spherical in

shape and monomers, they have weak interaction with their neighbors.

Material and Method

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 methods⁴ 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 with the accuracy of $\pm 0.1 \text{ m}\cdot\text{s}^{-1}$. The measuring cell of interferometer is a specially designed double-walled vessel with provision for temperature constancy. An electronically operated digital constant temperature bath operating in the temperature range of -10°C to 85°C with an accuracy of $\pm 0.1^\circ\text{C}$ 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 $\pm 0.01 \text{ kg}\cdot\text{m}^{-3}$. 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 $\pm 0.001 \text{ Ns}\cdot\text{m}^{-2}$ was used for the viscosity measurement. The flow time was determined using a digital racer stopwatch with an accuracy of ± 0.1 s.

Theory

The various acoustical parameters such as adiabatic compressibility (β), intermolecular 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 as⁵,

$$\beta = \frac{1}{U^2 \cdot \rho} \quad (1)$$

(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 relation⁶

$$L_f = K_T \cdot \beta^{1/2} \quad (2)$$

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.⁷ obtained a formula for free volume in terms of the ultrasonic velocity (U) and the viscosity of the liquid (η) as :

$$V_f = \left(\frac{M_{eff} \cdot U}{K \cdot \eta} \right)^{1/2} \quad (3)$$

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 .

(a) Surface tension

According to Aurebach relation⁸, Surface tension of liquid is

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

Excess Parameters (AE)

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

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

where $A_{id} = \sum^i A_i X_i$, ' 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

Table 1 – Experimental data relating to density, viscosity and velocity of pure liquids at 318 K for different frequencies

Pure Liquid	ρ Kg.m ⁻³	$\eta \times 10^{-3}$ N.s.m ⁻²	Velocity (<i>U</i>) 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 – Experimental values of density (ρ), Viscosity (η) and velocity (*U*) in ternary mixtures for different frequencies at temperature 318 K.

Mole fraction		Density (ρ) Kg. m ⁻³	Viscosity (η) (10 ⁻³ N.s.m ⁻²)	Velocity (<i>U</i>) m.s ⁻¹			
X ₁	X ₂			2 MHz	4 MHz	6 MHz	8 MHz
SYSTEM - I (DMF + Cyclohexane + benzene)							
0.0000	0.6000	818.23	0.4545	1168.6	1167.2	1166.1	1165.4
0.0999	0.4999	824.30	0.4662	1178.6	1176.6	1175.4	1174.2
0.1998	0.4001	830.47	0.4765	1188.4	1187.3	1185.3	1184.3
0.3001	0.3000	836.76	0.4825	1200.6	1198.4	1197.4	1196.2
0.4000	0.1999	843.09	0.4975	1212.1	1210.8	1209.5	1207.6
0.4998	0.1001	849.49	0.5113	1223.3	1221.6	1219.5	1218.1
0.5997	0.0000	855.98	0.5242	1235.5	1233.3	1232.9	1230.1
SYSTEM - II (DMF + Cyclohexane + Chlorobenzene)							
0.0000	0.6000	975.25	0.5486	1172.2	1169.2	1166.4	1165.9
0.0999	0.4999	959.40	0.5509	1184.7	1181.6	1178.1	1176.9
0.1998	0.4001	942.24	0.5536	1198.9	1194.6	1190.6	1188.1
0.3001	0.3000	923.52	0.5573	1215	1209.6	1205.4	1202.0
0.4000	0.1999	903.07	0.5594	1230.6	1224.4	1220.6	1216.0
0.4998	0.1001	880.71	0.5615	1247	1241.8	1237.6	1233.0
0.5997	0.0000	855.98	0.5631	1266.1	1261.6	1256.4	1251.5
SYSTEM - III (DMF + Cyclohexane + Nitrobenzene)							
0.0000	0.6000	856.69	0.6459	1170.2	1168.5	1166.1	1164.5
0.0999	0.4999	853.91	0.6255	1185.3	1183.1	1180.4	1178.4
0.1998	0.4001	848.35	0.6052	1199.5	1197.6	1195.3	1193.7
0.3001	0.3000	844.64	0.5890	1210.7	1208.6	1206.4	1204.2
0.4000	0.1999	834.44	0.5734	1229	1226.8	1224.5	1222.6
0.4998	0.1001	827.95	0.5595	1242.6	1240.1	1237.5	1236.4
0.5997	0.0000	817.70	0.5376	1261.7	1258.8	1256.9	1254.9
SYSTEM - IV (DMF + Cyclohexane + Pyridine)							
0.0000	0.6000	869.56	0.571	1247.2	1238.4	1224.6	1209.7
0.0999	0.4999	864.92	0.599	1251.3	1242.6	1228.6	1213.8
0.1998	0.4001	861.20	0.612	1255.0	1246.1	1232.9	1216.3
0.3001	0.3000	858.42	0.630	1258.9	1248.8	1235.5	1221.1
0.4000	0.1999	854.71	0.643	1263.6	1252.1	1238.8	1224.6
0.4998	0.1001	851.00	0.660	1268.5	1255.4	1242.1	1228.2
0.5997	0.0000	846.23	0.670	1274.5	1260.6	1247.2	1231.4

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

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 interactions⁹. 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

Table 3 – Calculated excess values of density (ρ^E), Viscosity (η^E) and velocity (U^E) in ternary mixtures for different frequencies at temperature 318 K.

Mole fraction		ρ^E (Kg.m ⁻³)	η^E (10 ⁻³ N.s.m ⁻²)	U^E m.s ⁻¹			
X_1	X_2			2 MHz	4 MHz	6 MHz	8 MHz
SYSTEM - I (DMF + Cyclohexane + benzene)							
0.0000	0.6000	-3.62	-0.133	-23.02	-22.80	-23.50	-22.72
0.0999	0.4999	-4.02	-0.119	-31.72	-31.96	-31.78	-31.42
0.1998	0.4001	-4.58	-0.107	-40.98	-40.18	-40.82	-40.18
0.3001	0.3000	-5.14	-0.100	-48.04	-48.20	-48.86	-48.04
0.4000	0.1999	-5.28	-0.083	-55.24	-54.36	-55.34	-54.44
0.4998	0.1001	-5.52	-0.068	-62.96	-62.34	-64.14	-62.96
0.5997	0.0000	-5.50	-0.053	-69.46	-69.20	-70.32	-69.16
SYSTEM - II (DMF + Cyclohexane + Chlorobenzene)							
0.0000	0.6000	21.62	-0.033	-10.54	-11.68	-13.02	-12.10
0.0999	0.4999	21.28	-0.029	-18.22	-19.36	-21.43	-21.12
0.1998	0.4001	19.31	-0.026	-24.56	-26.80	-29.40	-30.30
0.3001	0.3000	15.74	-0.022	-29.20	-32.44	-35.27	-36.98
0.4000	0.1999	10.80	-0.019	-33.78	-37.72	-40.18	-43.00
0.4998	0.1001	3.72	-0.016	-37.78	-40.62	-43.51	-46.24
0.5997	0.0000	-5.50	-0.014	-38.86	-36.40	-44.82	-47.76
SYSTEM - III (DMF + Cyclohexane + Nitrobenzene)							
0.0000	0.6000	-155.4	-0.164	-124.0	-124.5	-126.0	-126.5
0.0999	0.4999	-132.9	-0.146	-110.5	-111.2	-113.0	-113.8
0.1998	0.4001	-113.6	-0.127	-98.3	-98.5	-99.8	-100.1
0.3001	0.3000	-92.4	-0.105	-89.2	-89.5	-90.6	-91.3
0.4000	0.1999	-77.3	-0.081	-72.5	-72.7	-73.8	-74.1
0.4998	0.1001	-58.8	-0.057	-60.8	-61.0	-62.4	-61.7
0.5997	0.0000	-43.8	-0.039	-43.3	-43.7	-44.3	-44.4
SYSTEM - IV (DMF + Cyclohexane + Pyridine)							
0.0000	0.6000	-12.25	-0.239	-22.00	-28.52	-40.50	-52.18
0.0999	0.4999	-13.36	-0.172	-23.66	-30.05	-42.32	-54.11
0.1998	0.4001	-13.83	-0.120	-26.11	-32.67	-44.23	-58.03
0.3001	0.3000	-13.46	-0.064	-28.53	-36.26	-48.01	-59.82
0.4000	0.1999	-13.64	-0.012	-29.59	-38.69	-50.53	-62.35
0.4998	0.1001	-14.02	0.044	-30.70	-41.37	-53.30	-65.03
0.5997	0.0000	-20.25	0.093	-30.46	-41.90	-54.02	-67.86

- hydrogen bonds, charge transfer complexes, breaking of hydrogen bonds and complexes bringing negative excess values
- 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 and the sign of excess value may be positive or negative.
 - 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.
- Excess value of density is negative for all systems (except system-II), which indicates dense packing of molecules. The negative value is more in system-III, indicating densely packed molecules. Excess value of density is positive in system-II indicating loosely packed

Table 4 – 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
SYSTEM - IV (DMF + Cyclohexane + Pyridine)									
0.0000	0.6000	0.035	0.115	0.265	0.422	0.0060	0.0090	0.0145	0.0201
0.0999	0.4999	0.055	0.134	0.287	0.443	0.0070	0.0099	0.0155	0.0211
0.1998	0.4001	0.071	0.152	0.295	0.475	0.0077	0.0107	0.0159	0.0225
0.3001	0.3000	0.077	0.172	0.316	0.469	0.0080	0.0115	0.0168	0.0224
0.4000	0.1999	0.084	0.194	0.338	0.491	0.0085	0.0126	0.0179	0.0234
0.4998	0.1001	0.087	0.216	0.360	0.510	0.0088	0.0135	0.0189	0.0243
0.5997	0.0000	0.132	0.270	0.416	0.592	0.0090	0.0141	0.0195	0.0252

molecules. This is also confirmed by the fact that the free volume in case of chlorobenzene is more than that of Nitrobenzene.

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. System-II mixtures have least negative excess viscosity, indicating strong intermolecular interaction as compared to the other mixtures.

In all the system, the excess velocity is found to be

Table 5 – 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 ($10^{-7} \text{ m}^3 \cdot \text{mol}^{-1}$)				Excess surface tension (S^E) ($N \cdot m^{-1}$)			
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
SYSTEM - IV (DMF + Cyclohexane + Pyridine)									
0.0000	0.6000	-0.45	-0.47	-0.508	-0.544	-1.36	-1.55	-1.89	-2.21
0.0999	0.4999	-0.57	-0.588	-0.623	-0.655	-1.45	-1.63	-1.98	-2.31
0.1998	0.4001	-0.585	-0.602	-0.633	-0.669	-1.54	-1.72	-2.05	-2.44
0.3001	0.3000	-0.616	-0.635	-0.666	-0.697	-1.60	-1.82	-2.15	-2.48
0.4000	0.1999	-0.618	-0.64	-0.67	-0.698	-1.65	-1.90	-2.24	-2.57
0.4998	0.1001	-0.631	-0.655	-0.683	-0.712	-1.70	-2.00	-2.34	-2.66
0.5997	0.0000	-0.608	-0.634	-0.661	-0.69	-1.89	-2.21	-2.55	-2.93

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- 4). Positive value of ' β^E ' indicates weak interaction between molecules due to dispersive forces. However β^E has the lowest value for the mixture containing pyridine. This may be due to the relatively small size of DMF and its linearly aliphatic structure and also because of the spherical shape of pyridine molecules, which are tightly packed.

In all 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 and system-IV, excess free length increases

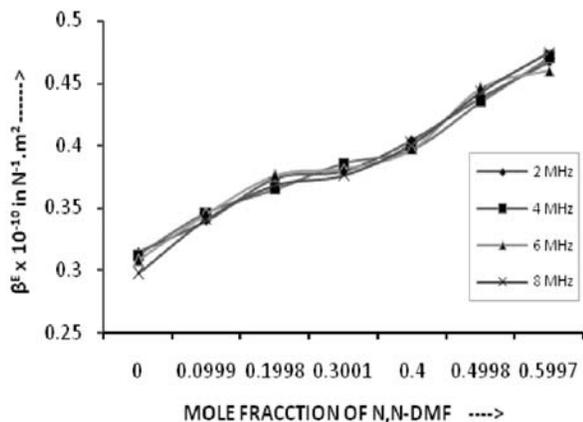


Fig. 1 Variation of excess adiabatic compressibility with mole fraction of DMF for system-I mixture.

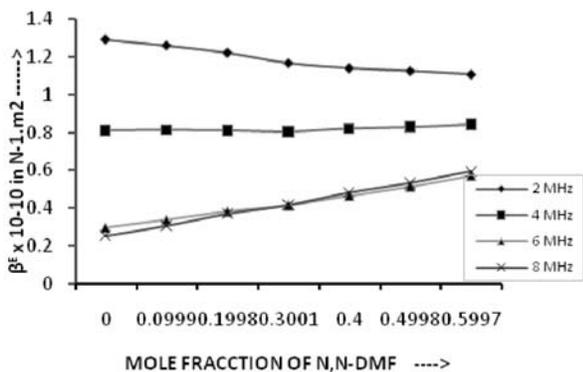


Fig. 2 Variation of excess adiabatic compressibility with mole fraction of DMF for system-II mixture.

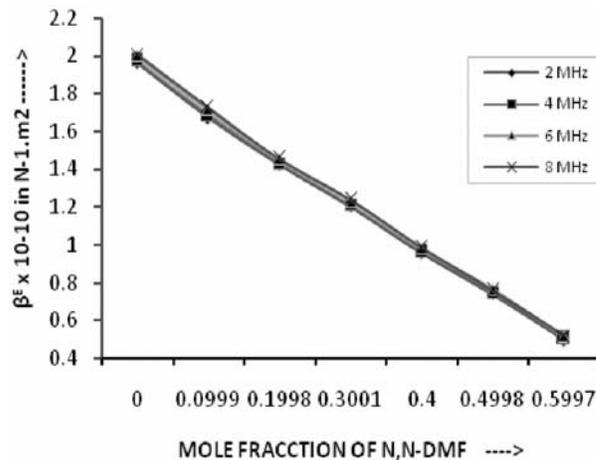


Fig. 3 Variation of excess adiabatic compressibility with mole fraction of DMF for system-III mixture.

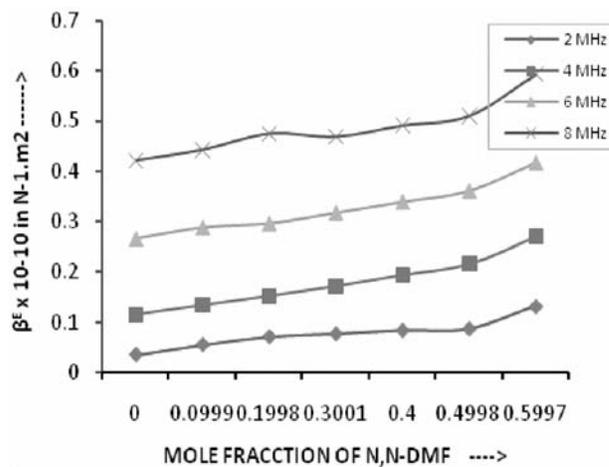


Fig. 4 Variation of excess adiabatic compressibility with mole fraction of DMF for system-IV mixture.

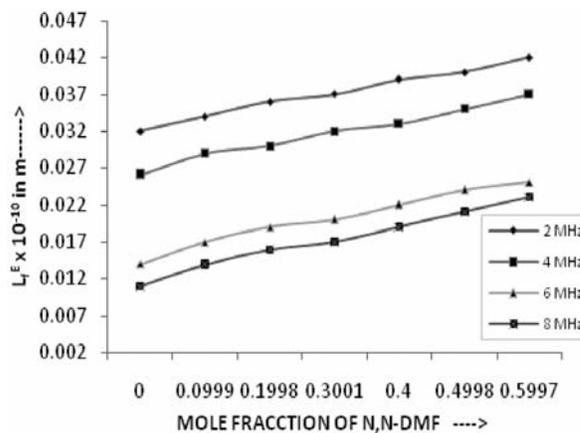


Fig. 5 Variation of excess free length with mole fraction of DMF for system-I mixture.

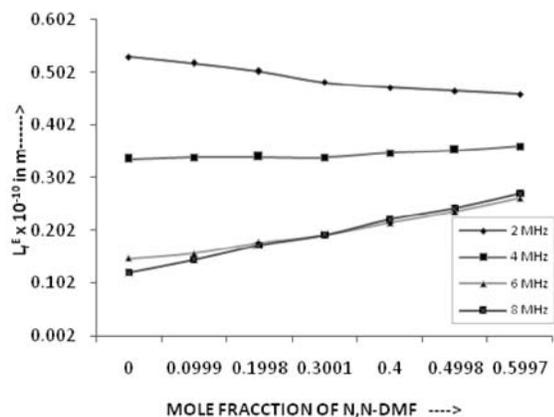


Fig. 6 Variation of excess free length with mole fraction of DMF for system-II mixture.

with increase in frequency (Fig. 7 - 8) indicating weakening of interaction. In case of system-III, this may be due to steric hindrance and in system-IV, this is extremely small, which may be due to the spherical shape of the molecules, which are tightly packed.

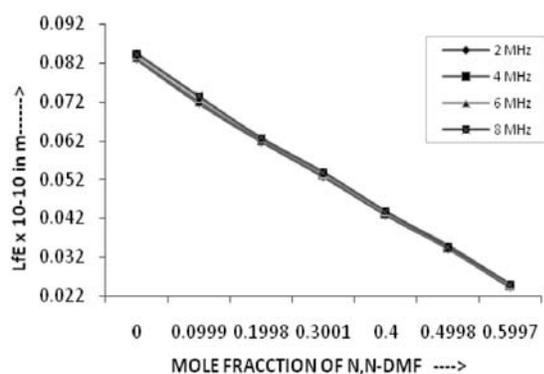


Fig. 7 Variation of excess free length with mole fraction of DMF for system-III mixture.

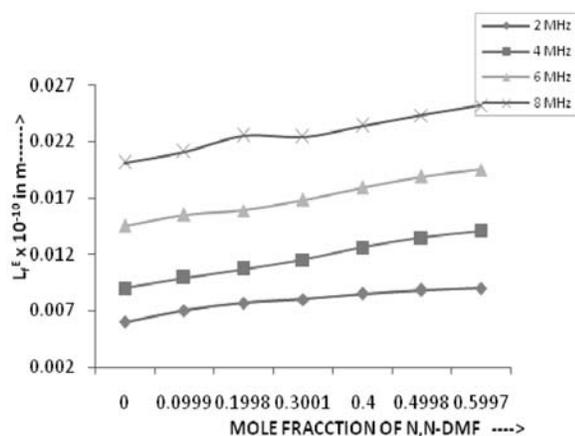


Fig. 8 Variation of excess free length with mole fraction of DMF for system-IV mixture.

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

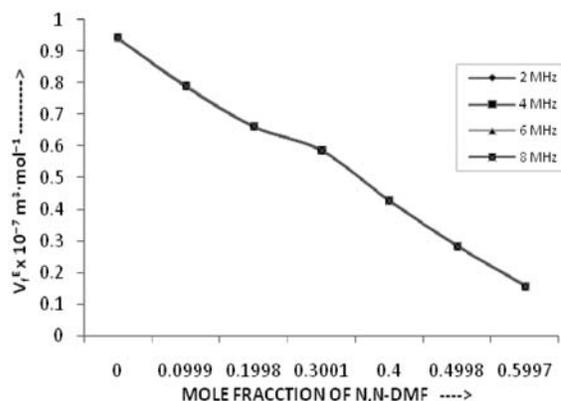


Fig. 9 Variation of excess free volume with mole fraction of DMF for system-I mixture.

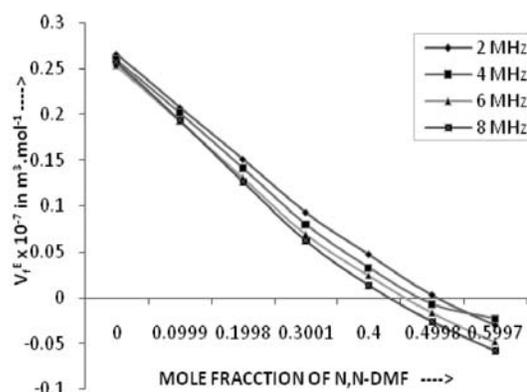


Fig. 10 Variation of excess free volume with mole fraction of DMF for system-II mixture.

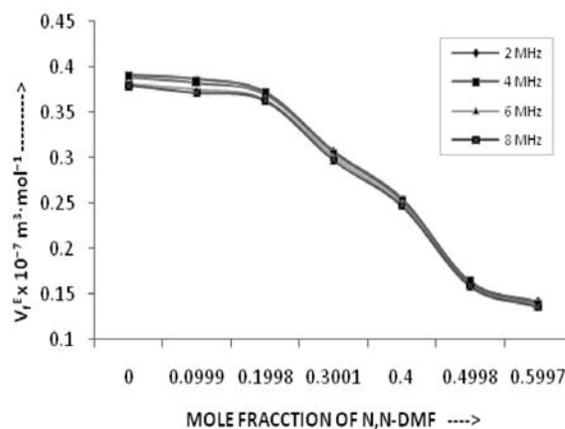


Fig. 11 Variation of excess free volume with mole fraction of DMF for system-III mixture.

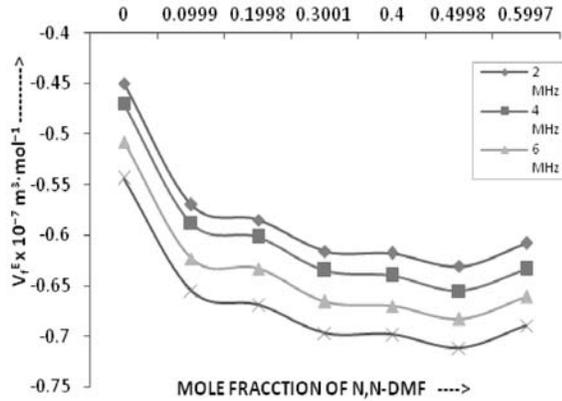


Fig. 12 Variation of excess free volume with mole fraction of DMF for system-IV mixture.

may be due to the formation of new bonds. Excess free volume is positive in system-I, system-II and system-III (Fig. 9 - 11), whereas in system-IV (Fig. 12) it comes out to be negative. This negative excess free volume in pyridine may be due to the presence of moisture which leads to hydrogen bonding.

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 (Fig. 13 - 16), 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 indicates reduction in the intermolecular interactions.

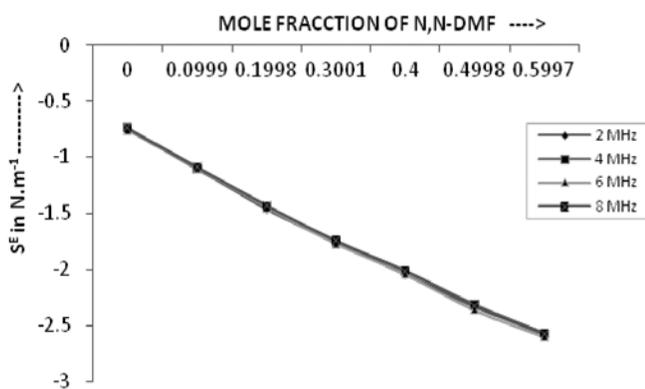


Fig. 13 Variation of excess surface tension with mole fraction of DMF for system-I mixture.

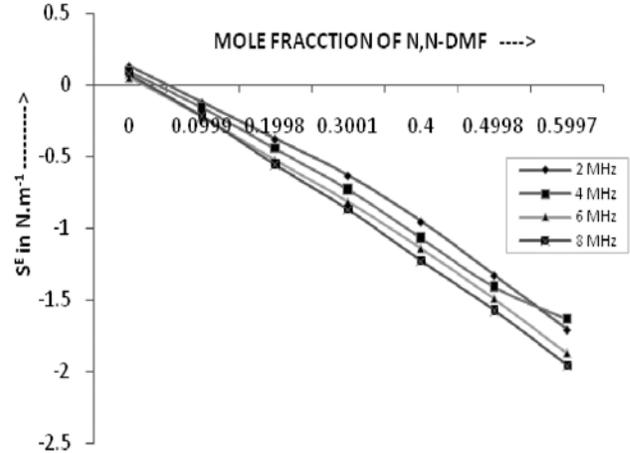


Fig. 14 Variation of excess surface tension with mole fraction of DMF for system-II mixture.

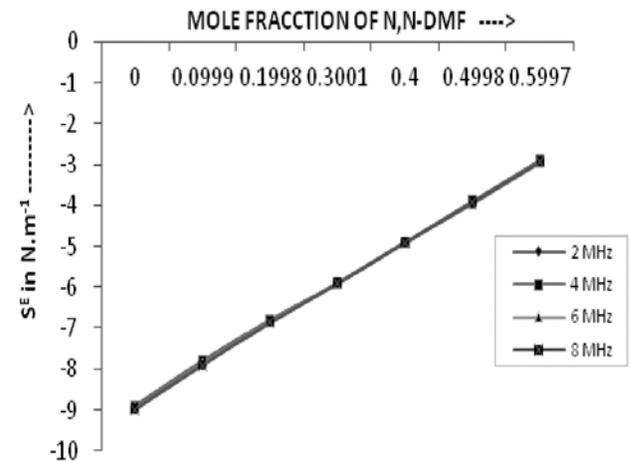


Fig. 15 Variation of excess surface tension with mole fraction of DMF for system-III mixture.

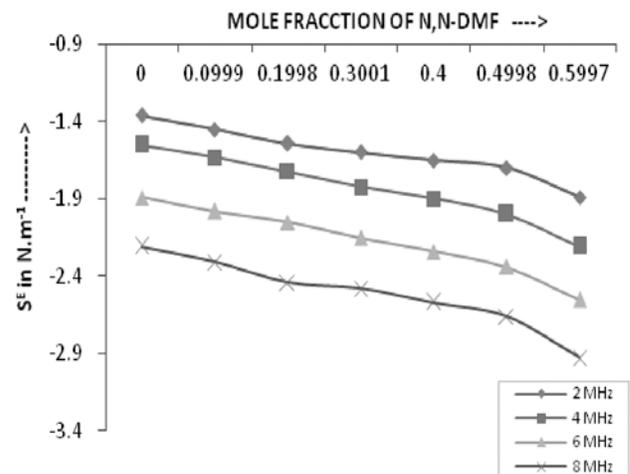


Fig. 16 Variation of excess surface tension with mole fraction of DMF for system-IV mixture.

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

Acknowledgements

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Acoustic wave propagation in some rock-forming oxides at high temperatures

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The acoustic wave velocities have been calculated using the values of second order elastic constants (SOECs) and density ρ . In this study first the second order elastic constants for some oxides CdO, CoO and FeO which possess face centered cubic crystal structure are computed and then acoustic wave velocities has been obtained along different crystallographic directions starting from 100K to an elevated temperature 1000K. The results thus obtained are presented graphically, compared and discussed. The relations presented can be applied to all materials likely to exist in the earth's mantle and crust with rock-salt structure and therefore provide a useful means of considering the properties of rock-forming compounds.

Keywords: Elastic constants, ultrasonic velocity, face centered cubic

Introduction

Oxides and silicates make up the bulk of the Earth's mantle and crust, and thus it is important to predict their behaviour for the study of seismic and volcanic activities. Ultrasonics offer the possibility to detect and characterize microstructural properties as well as flaws in material behaviour based on the physical mechanism to predict future performance of the materials^{1, 2} and aqueous solutions³. There are three types of ultrasonic velocities one longitudinal (V_l) and two shear (V_{s1} and V_{s2}) for each direction of propagation in cubic crystals. The study of propagation of ultrasonic wave through crystal reveals many important features of the crystal. These values are used to calculate Debye average velocity from which the thermal relaxation time can be calculated. Using thermal relaxation time, longitudinal wave velocity and shear wave velocity the ultrasonic attenuation can be calculated which is used as a basic parameter for the characterization of the materials. In this paper the study is done for some oxides CdO, CoO and FeO crystals which are of geographical importance. The present study will also be helpful in making qualitative understanding of elastic behaviour of other rock-forming oxides. In the absence of any experimental

data on the properties studied at higher temperature, comparison could not be made.

Theory

The temperature variation of second order elastic constant and ultrasonic velocities have been discussed in two parts. The whole evaluation is based on the assumption that the basic structure of the crystal does not change in the range of temperature under investigation.

(a) Temperature Variation of Second Order Elastic Constants

The crystals under investigation possess face centered cubic crystal structure. The potential used for evaluation of second elastic constants (SOECs) is taken as the sum of Coulomb and Börn-Mayer potentials.

$$Q(r) = Q(C) + Q(B) \quad (1)$$

where $Q(C)$ is the Coulomb potential and $Q(B)$ is the Börn-Mayer potential, given as :

$$Q(r) = Q(C) + Q(B) \quad (1)$$

$$Q(C) = \{\pm (e^2/r)\} \text{ and } Q(B) = A \exp (-r/q) \quad (2)$$

Table 1 – Coefficients of Best Fit Polynomial for Linear Thermal Expansion Coefficient α_T

Crystal	A_0	A_1	A_2	A_3	A_4
CdO	11.82	7.11e-03	-1.18e-05	1.41e-08	-5.70e-12
CoO	11.82	7.11e-03	-1.18e-05	1.41e-08	-5.70e-12
FeO	10.92	8.94e-03	-2.67e-05	3.13e-08	-8.29e-12

where e is the electronic charge, r is the nearest-neighbour distance, q is the hardness parameter and A is the strength parameter. The elastic energy density for a crystal of a cubic symmetry can be expanded up to quartic terms as shown below :

$$\begin{aligned}
 U_0 &= U_2 + U_3 + U_4 \\
 &= [1/2!] C_{ijkl} \alpha_{ij} \alpha_{kl} + [1/3!] C_{ijklmn} \alpha_{ij} \alpha_{kl} \alpha_{mn} + \\
 &\quad [1/4!] C_{ijklmnpq} \alpha_{ij} \alpha_{kl} \alpha_{mn} \alpha_{pq} \quad (3)
 \end{aligned}$$

where C_{ijkl} , C_{ijklmn} and $C_{ijklmnpq}$ are the SOECs, TOECs and FOECs in tensorial form; α_{ij} are the Lagrangian strain components; C_{IJ} , C_{IJK} and C_{IJKL} are the SOECs, TOECs and FOECs in Brügger's definition and Voigt notations.

Following Brügger's⁴ definition of elastic constants at absolute zero, second and third order elastic constants (SOECs and TOECs) are obtained. According to lattice dynamics developed by Leibfried and Ludwig^{5, 6} lattice energy changes with temperatures. Hence adding vibrational energy contribution to the static elastic constants, one gets second order elastic constants (C_{ij}) at the required temperature.

$$C_{ij} = C_{ij}^0 + C_{ij}^{vib} \quad \text{and} \quad C_{ijk} = C_{ijk}^0 + C_{ijk}^{vib} \quad (4)$$

The variation of nearest neighbour distance and linear thermal expansion coefficient (α_T) with temperature is also taken in to account.

$$\alpha_T = A_0 + A_1 T + A_2 T^2 + A_3 T^3 + A_4 T^4 \quad (5)$$

(b) Temperature Variation of Acoustic Wave Velocities

There are three types of acoustic wave velocities one longitudinal (V_l) and two shear (V_{s1} and V_{s2}) for each direction of propagation in cubic crystals^{7, 8}. The ultrasonic velocities can be calculated using calculated values of second order elastic constants C_{ij} 's and density ρ . The expressions for velocities are as follows.

Along the $\langle 100 \rangle$ crystallographic direction

$$V_l = \sqrt{\frac{C_{11}}{\rho}} \quad V_{s1} = V_{s2} = \sqrt{\frac{C_{44}}{\rho}} \quad (6)$$

 Table 2 – The Second Order Elastic Constants (SOECs) in 10^{10} N/m².

Crystal	Temp	C_{11}	C_{12}	C_{44}
CdO	100	20.2	18.3	18.5
	200	20.5	18.2	18.4
	300	21.1	18.0	18.3
	400	21.7	17.9	18.2
	500	22.4	17.7	18.1
	600	23.2	17.5	18.0
	700	23.9	17.4	17.8
	800	24.6	17.2	17.7
	900	25.4	17.0	17.6
	1000	26.1	16.8	17.5
CoO	100	18.8	27.0	27.2
	200	19.1	26.8	27.0
	300	19.7	26.6	26.9
	400	20.4	26.4	26.7
	500	21.2	26.2	26.6
	600	22.0	25.9	26.4
	700	22.8	25.7	26.3
	800	23.6	25.5	26.1
	900	24.5	25.2	25.9
	1000	25.3	25.0	25.7
FeO	100	18.7	27.4	27.5
	200	19.0	27.2	27.4
	300	19.6	27.0	27.3
	400	20.3	26.8	27.1
	500	21.1	26.6	27.0
	600	21.9	26.4	26.9
	700	22.7	26.2	26.7
	800	23.5	25.9	26.5
	900	24.4	25.6	26.3
	1000	25.3	25.2	26.0

Along the $\langle 110 \rangle$ crystallographic direction

$$V_l = \sqrt{\frac{C_{11} + C_{12} + 2C_{44}}{2\rho}} \quad V_{s1} = \sqrt{\frac{C_{44}}{\rho}} \quad V_{s2} = \sqrt{\frac{C_{11} - C_{12}}{\rho}} \quad (7)$$

Along the $\langle 111 \rangle$ crystallographic direction

$$V_l = \sqrt{\frac{C_{11} + 2C_{12} + 4C_{44}}{3\rho}} \quad V_{s1} = V_{s2} = \sqrt{\frac{C_{11} + C_{12} + C_{44}}{3\rho}} \quad (8)$$

Results and Discussion

Second and third order elastic constants (SOECs and TOECs) for CdO, CoO and FeO crystals are calculated at different temperatures (100-1000 K) at an interval of 100 K using taking nearest neighbor distance and hardness parameter as basic input data and is given in Table 1.

Also the ultrasonic velocities along different crystallographic directions are calculated from 100 K - 1000 K. The temperature variation of thermal expansion coefficients for these crystals is also taken in to the consideration and the coefficients for best fit polynomials are given in Table 2. The values of ultrasonic wave velocities in 10^3 m/s at different temperatures for these oxides are given in Table 3. The graphical representations of these parameters are given

in Figs. 1-6.

Looking on the Table 2 it is clear that the values of all the second order elastic constants are positive in nature which is also exhibited by other divalent solids like MgO, MgS, CaO, SrO etc. under some exemptions [reference]. As we approach to higher temperature the magnitude of C_{11} increases while the magnitude of C_{12} and C_{44} decreases.

It is clear from Figs. 1 and 2 that the longitudinal wave velocity for all the oxides taken varies linearly with temperature and follows the same nature above room temperature while the shear wave velocity decreases with temperature along $\langle 100 \rangle$ direction. Figs. 3 and 4 represents the longitudinal and shear wave velocities for these oxides along $\langle 110 \rangle$ crystallographic direction. The longitudinal wave velocity along $\langle 110 \rangle$ direction is not

Table 3 – The longitudinal and shear wave velocities in 10^3 m/s along different crystallographic directions.

Crystal	Temp. (K)	$\langle 100 \rangle$		$\langle 110 \rangle$		$\langle 111 \rangle$	
		V_L	$V_{s1} = V_{s2}$	V_L	V_{s1}	V_L	$V_{s1} = V_{s2}$
CdO	100	4.98	4.76	6.81	4.76	7.31	2.89
	200	5.02	4.75	6.81	4.75	7.31	2.91
	300	5.09	4.74	6.81	4.74	7.30	2.96
	400	5.16	4.73	6.83	4.73	7.30	3.00
	500	5.24	4.71	6.84	4.71	7.30	3.05
	600	5.34	4.70	6.86	4.70	7.30	3.11
	700	5.42	4.69	6.88	4.69	7.30	3.16
	800	5.51	4.67	6.90	4.67	7.30	3.22
	900	5.58	4.66	6.91	4.66	7.30	3.26
	1000	5.66	4.63	6.92	4.63	7.29	3.30
CoO	100	5.55	6.67	9.06	6.67	9.95	3.22
	200	5.59	6.65	9.04	6.65	9.93	3.24
	300	5.68	6.64	9.05	6.64	9.92	3.30
	400	5.78	6.61	9.06	6.61	9.91	3.36
	500	5.89	6.60	9.07	6.60	9.91	3.43
	600	6.00	6.59	9.09	6.59	9.91	3.50
	700	6.11	6.56	9.10	6.56	9.90	3.57
	800	6.23	6.55	9.12	6.55	9.90	3.65
	900	6.33	6.52	9.13	6.52	9.88	3.71
	1000	6.45	6.50	9.14	6.50	9.87	3.78
FeO	100	5.71	6.92	9.38	6.92	1.03	3.30
	200	5.75	6.91	9.38	6.91	1.03	3.34
	300	5.84	6.90	9.39	6.90	1.03	3.40
	400	5.95	6.87	9.39	6.87	1.03	3.46
	500	6.06	6.86	9.41	6.86	1.03	3.53
	600	6.18	6.85	9.43	6.85	1.03	3.61
	700	6.29	6.82	9.44	6.82	1.03	3.67
	800	6.41	6.81	9.46	6.81	1.03	3.76
	900	6.52	6.77	9.45	6.77	1.02	3.82
	1000	6.64	6.73	9.45	6.73	1.02	3.89

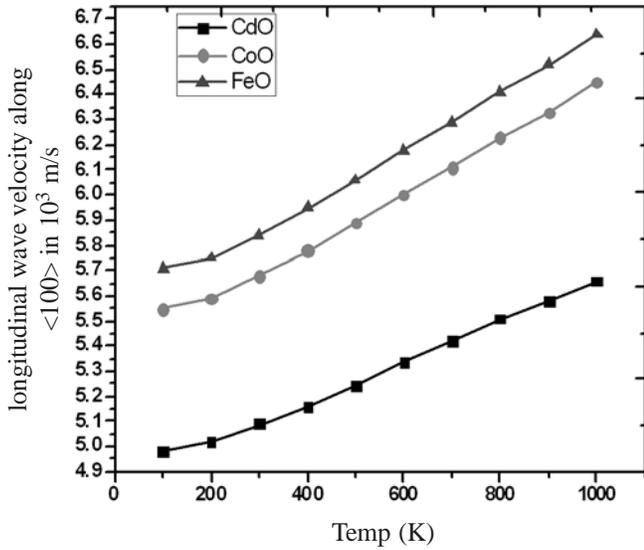


Fig. 1 Variation longitudinal wave velocity with temperature along <100> direction

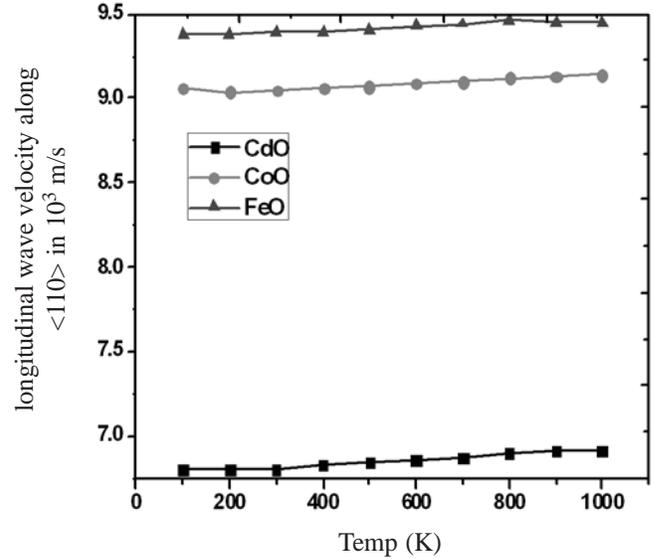


Fig. 3 Variation longitudinal wave velocity with temperature along <110> direction

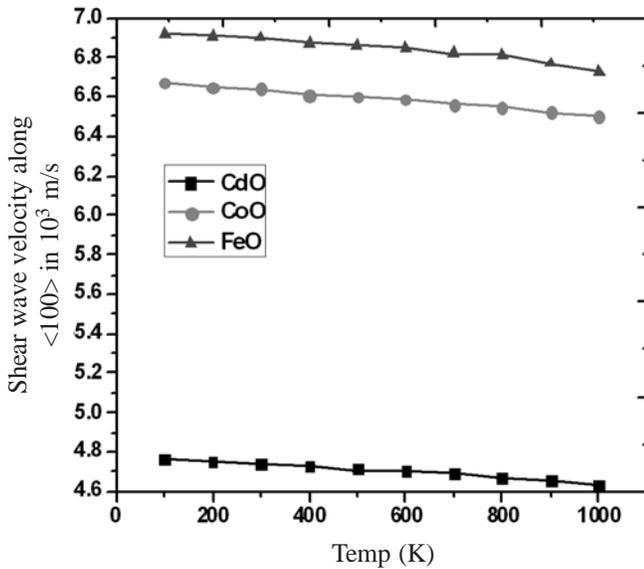


Fig. 2 Variation shear wave velocity with temperature along <100> direction

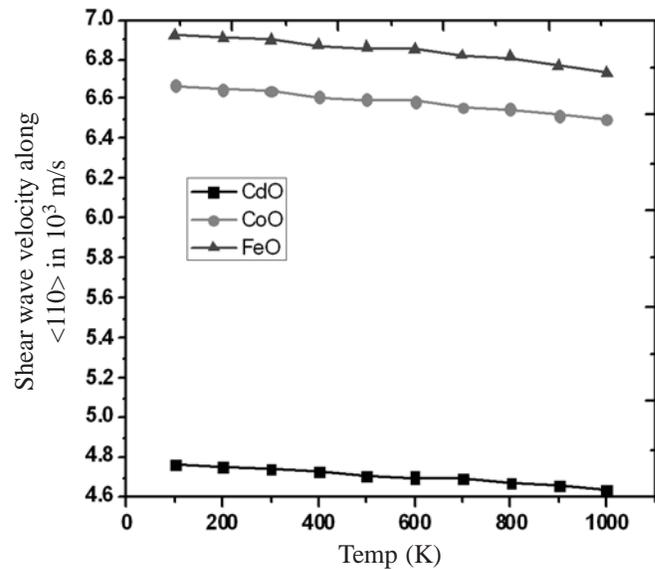


Fig. 4 Variation shear wave velocity with temperature along <110> direction

very much affected by temperature. From Fig. 5 it is clear that the longitudinal wave velocity along <111> direction remains almost constant with rise in temperature while in shear wave velocity a very sharp increment is observed with rise in temperature.

Conclusion

From the acoustic velocity components and their magnitudes along different directions it is evident that the acoustic wave velocity is different along different

directions *i.e.* varies with the orientation of the crystal, similar behavior has been observed by some investigators in other divalent crystals.

The longitudinal wave velocity for CdO and CoO is higher along <111> direction while for FeO it is higher along <110> direction and almost independent of temperature, hence these crystallographic directions are more suitable for acoustic purpose where effect of temperature is need to be reduced for the particular crystals. All these discussions are sufficient to conclude

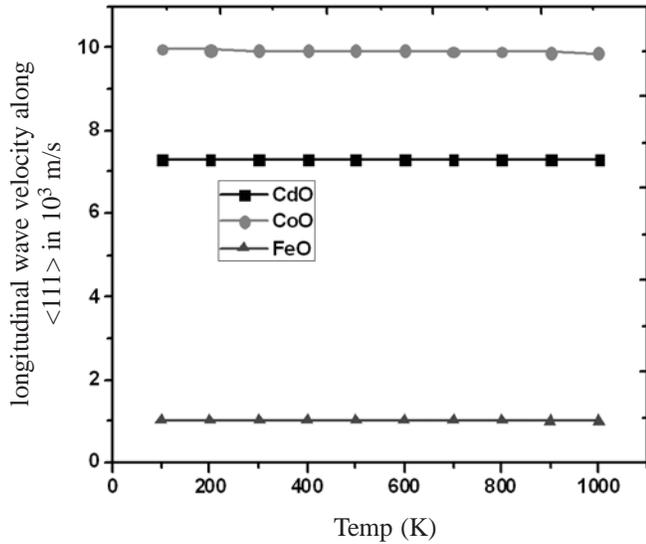


Fig. 5 Variation longitudinal wave velocity with temperature along <111> direction

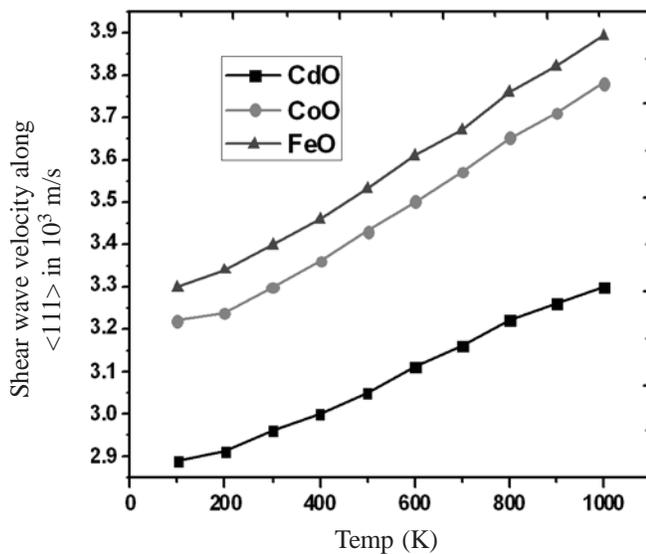


Fig. 6 Variation shear wave velocity with temperature along <111> direction

that the acoustic wave velocity is an important property of any crystal.

This work presents a method for determining various properties⁹⁻¹¹ of a solid as its internal structure and nature

and also be helpful in designing acoustic metamaterials which can control, direct and manipulate acoustic waves.

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Ultrasonic absorption and excess absorption study of polar and non-polar binary liquid mixtures

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Ultrasonic absorption & excess absorption study of binary liquid mixtures of polar solute acrylonitrile with non polar solvent cyclohexane and their binary liquid mixtures were carried out at 298 K in the frequency range 1MHz-10MHz and at different temperatures for 7 MHz over the entire range of composition. The observed ultrasonic absorption (αf^2_{obs}), classical absorption (αf^2_{class}), excess absorption (αf^2_{excess}) and the ratio of the observed ultrasonic absorption (αf^2_{obs}) and classical absorption (αf^2_{class}) at different temperatures and at 7 MHz over the entire range of composition were studied. In this binary liquid mixture ultrasonic absorption is higher than the classical absorption. The thermo acoustical parameters acoustic impedance (Z), molecular weight (M), molar volume (V), molar sound velocity (R), molar compressibility (W), Vander Waal's constant (b), internal pressure (π_i), viscosity (η), intermolecular radius (r_o), relaxation time (τ), adiabatic compressibility (π_a), free volume (V_f), isothermal compressibility (β_i), intermolecular free length (L_p), etc were computed from ultrasonic velocities, densities and viscosities at 303 K and at frequency 7 MHz. Comparison of experimental ultrasonic velocity and its theoretically calculated values by Junjie's relation, Impedance dependence relation and Nomoto's relation were studied. The increase in ultrasonic absorption with molar concentration is due to the possible structural relaxation process in the constituents. These structural relaxation processes play very important role in the study of molecular and structural properties of the constituent molecules in binary liquid mixture.

Keywords: Ultrasonic absorption; excess absorption; relaxation time; thermo acoustic parameters; cyclohexane; acrylonitrile.

Introduction

Ultrasonic absorption & excess absorption study of binary liquid mixtures is one of the most important method of investigation of properties of matter in all the three states. It is well known that ultrasonic absorption & excess absorption study provides valuable information about the physical properties of the medium & provides important information about various inter and intra-molecular processes such as relaxation of the medium, existence of isomeric states, exchange of energy between various molecular degrees of freedom, etc. Ultrasonic absorption & excess absorption measurement provides qualitative information regarding the nature and strength of interaction between the constituents¹⁻³.

Thermo-acoustic parameters are extensively being used to study molecular interactions in pure liquids,

binary liquid mixtures⁴⁻⁵ and ionic interactions in single and mixed salt solutions of binary liquid mixtures⁶⁻⁷.

Materials and Method

The liquids used were of BDH analar grade and were redistilled in the laboratory. In this study the measurements have been made in the temperature range 293 K-313 K. The temperature of the liquid mixture was kept constant by the use of thermostat U-10 with ± 0.01 K accuracy. Density measurement was carried out by using hydrostatic sinker method with an accuracy $\pm 0.01\%$. A monopan electrical balance of least count as 0.0001 gm was used to record change in plunger weight dipped in the solutions correct to fourth place of decimal. Ultrasonic velocity and absorption measurements were made with an ultrasonic multifrequency interferometer

in the frequency range 1 MHz to 10 MHz with an accuracy of $\pm 0.1\%$. The time of descent of the liquid between the viscometer marks was measured using electronic timer. The time of descent of the liquids between the viscometer marks was measured using an electronic digital timer with least count 0.01 sec. The viscosity was measured in Ostwald's viscometer with an accuracy 0.001 cP.

Experimental Details

The ultrasonic velocity of the above liquids and their mixtures were measured using multi-frequency ultrasonic interferometer operating at different frequencies like 1 MHz, 3 MHz and 5 MHz. The accuracy in the measurement of ultrasonic velocity was within $\pm 0.01 \text{ ms}^{-1}$. The working principle used in the measurement of velocity of sound through medium was based on the accurate determination of the wave length of ultrasonic waves of known frequency produced by quartz crystal in the measuring cell⁸⁻¹⁰. The temperature of the solution was controlled by circulating water at a desired temperature through the jacket of double walled cell within $\pm 0.01 \text{ K}$ using a constant temperature bath and the temperature was monitored with a platinum resistance thermometer with an accuracy of $\pm 0.001 \text{ K}$.

Results and Discussion

In present work molecules of acrylonitrile are polar with dipole moment 1.68 D and cyclohexane molecules are non-polar with zero dipole moment. The nature and the strength of heteromolecular cyclohexane-acrylonitrile or acrylonitrile- cyclohexane interaction is determined by the interacting molecules. So the nature of the forces responsible for the observed heteromolecular interactions in this binary liquid mixture are dipole-induced dipole.

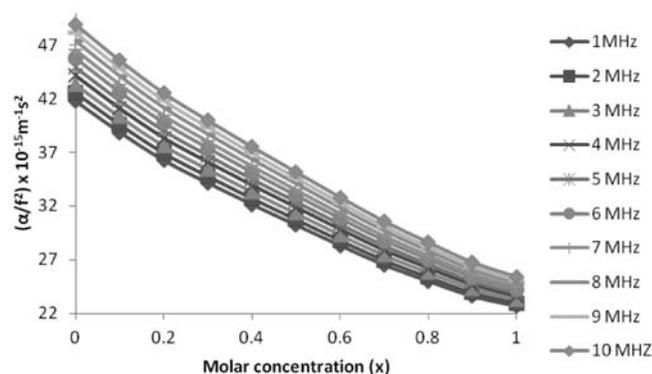


Fig. 1 Variation of (α/f^2) versus x

Fig.1 contains the plot of experimental ultrasonic absorption (α/f^2) versus molar concentration at different frequencies. Ultrasonic absorption (α/f^2) slightly decreases with increase in the molar concentration due to less stability of acrylonitrile molecules. Acrylonitrile molecule has single resonating structure (Fig. 2) which decreases the relaxation time. Decrease in relaxation time decreases the ultrasonic absorption in this binary mixture.

In this binary liquid mixture structural relaxation plays a predominant role over thermal relaxation process. The

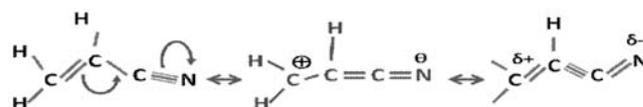


Fig. 2 Resonating structure of acrylonitrile

decrease in ultrasonic absorption with increase in molar concentration is due to the possible structural relaxation process. These structural relaxation processes play very important role in the study of molecular and structural properties of the constituent.

The curve obtained for 10 MHz is steeper than the other which indicates that slightly stronger dipole-induced dipole interaction exists in the former while weak dipole- induced dipole interactions exist in the latter. Intermolecular dipole-induced dipole interaction or London forces decreases the ultrasonic absorption of binary liquid mixture with increase in molar concentration. The maximum absorption occurs at 10 MHz, this shows that binary liquid mixture is more structured at higher frequencies. This higher structured solution generally absorbs more ultrasonic energy.

Figure 3 contains the plot of observed experimental ultrasonic absorption $(\alpha/f^2)_{\text{obs}}$ versus molar concentration at different temperature for 7MHz. Ultrasonic absorption (α/f^2) slightly decreases with

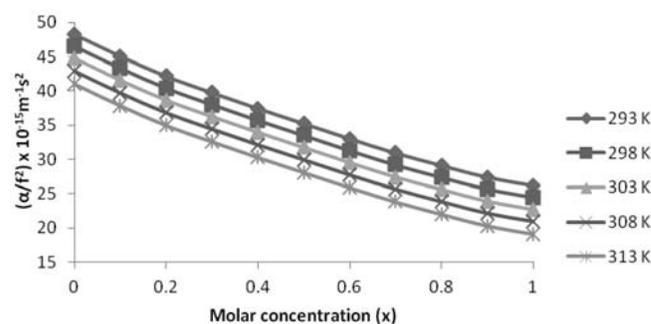


Fig. 3 Variation of (α/f^2) versus x

increase in the molar concentration of acrylonitrile in cyclohexane and decreases with increase in the temperature.

The maximum absorption occurs at 293 K, this shows that binary liquid mixture is more structured at lower temperature. This higher structured solution generally absorbs more ultrasonic energy.

Figure 4 contains the plot of ultrasonic velocity versus molar concentration. It is observed that ultrasonic velocity increases with increase in molar concentration indicating association in the the constituent. The electrons surrounding the nucleus in the atom of each cyclohexane molecule are symmetrical, distributed round the nucleus. According to London these electrons are in continuous and rapid motion with respect to the nucleus and hence it is possible that at any instant, the electron density round the nucleus may be concentrated in the other region of the same molecule. This results in an unsymmetrical distribution of the electron density round the nucleus and hence the non-polar molecule becomes an instantaneous or temporary dipole. The permanent dipoles are present in the molecules of the acrylonitrile. Thus there is dipole-induced dipole interaction between constituents^{8, 11-13}. The stronger heteromolecular dipole-induced dipole interaction between the unlike molecules (Fig. 5) are responsible for the association. Interstitial accommodation, induction and London dispersion forces in cyclohexane molecules may leads association in the constituents.

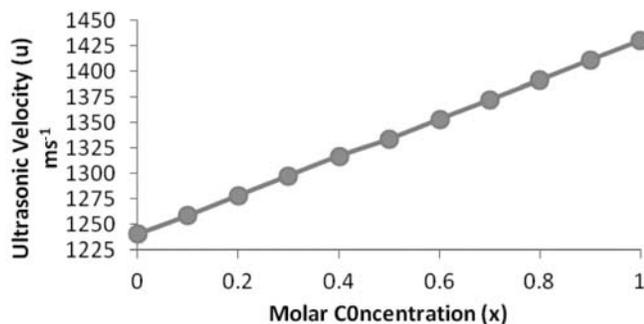


Fig. 4 Variation of u versus x

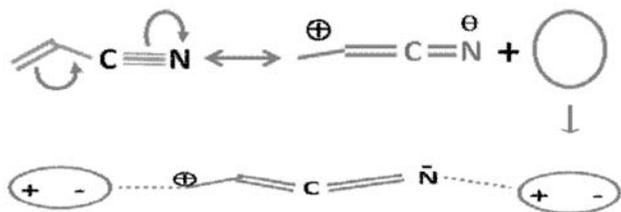


Fig. 5 Intermolecular Interactions between cyclohexane and acrylonitrile

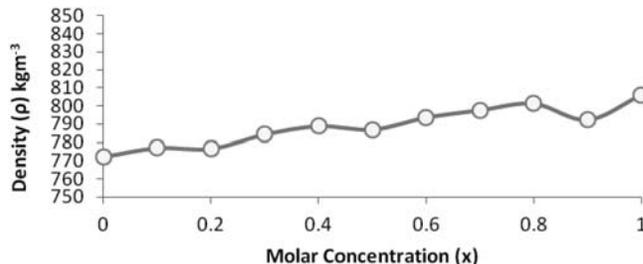


Fig. 6 Variation of ρ versus x

Figure 6 contains the plot of density versus molar concentration. Density increases with increase in molar concentration. It may be increase due to structural reorganization indicating increase in closed packed structure of molecular cluster. This makes the liquid medium less compressive.

Figure 7 contains the plots of adiabatic compressibility (β_a) versus molar concentration. Adiabatic compressibility decreases with increase in molar concentration indicating strong intermolecular interaction between the constituent which shows associating tendency of the constituents.

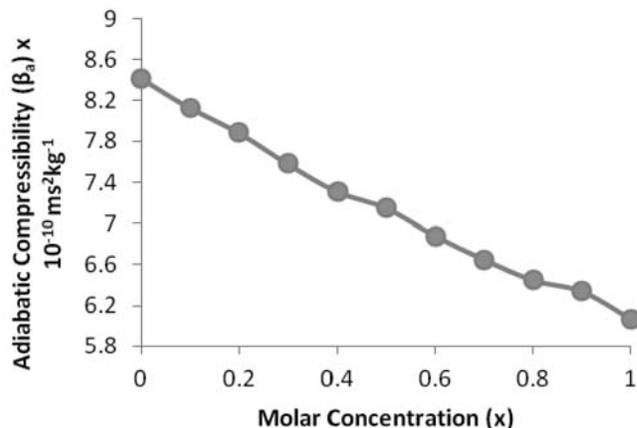


Fig. 7 Variation of β_a versus x

A strong molecular interaction through dipole-induced dipole interaction, induction in cyclohexane molecules and interstitial accommodation lead to a more compact structure which decreases adiabatic compressibility^{9,10,14,15}.

The observed decrease of adiabatic compressibility indicates the enhancement of degree of association in the constituent molecules. Hence the intermolecular distance decreases with increase in molar concentration. Decrease in adiabatic compressibility indicated there is definite contraction in the constituent molecules. The decrease in adiabatic compressibility brings the

molecules to a closer packing resulting into a decrease of intermolecular free length. The decrease in the values of adiabatic compressibility strengthens the strong molecular association between the unlike molecules.

Figure 8 contains the plot of viscosity (η) versus molar concentration. It is observed that viscosity decreases with increase in molar concentration. Viscosity of a mixture strongly depends on the liquid's structure and molecular interactions between the components of the mixtures.

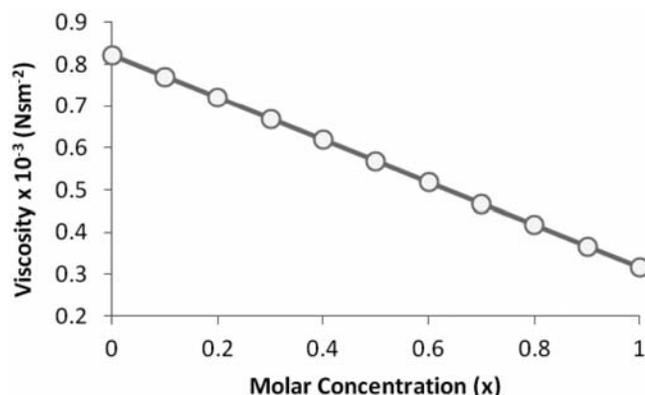


Fig. 8 Variation of η versus x

Measurements of viscosity in binary mixture yield some reliable information in the study of molecular interaction. The viscosity gives the strength of molecular interaction between the interacting molecules. Dispersion, induction and dipolar forces which are operated by the viscosity, these forces are responsible for the existence of specific interactions in the interacting molecules leading to the decrease in viscosity in binary liquid mixture.

Figure 9 contains the plot of relaxation time (τ) versus molar concentration. Relaxation time decreases with increase in molar concentration, indicating less stability of methyl methacrylate molecules. Acrylonitrile molecule has single resonating structure which decreases

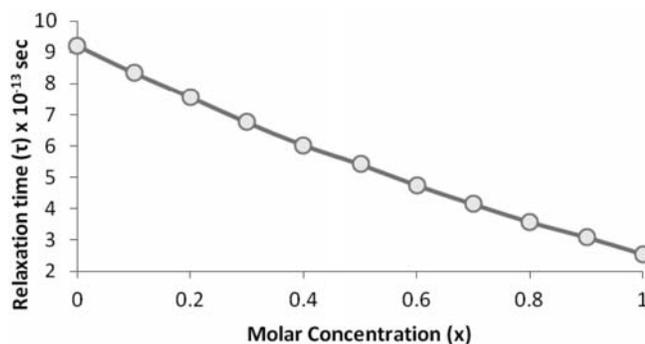


Fig. 9 Variation of τ versus x

the relaxation time. More the resonating structure more stable will be the molecules. The relaxation is caused by the energy transfer between translational and vibrational degrees of freedom and all these degrees take part in the process observed. Decrease in viscosity and adiabatic compressibility with molar concentration also decreases the relaxation time (τ).

Figure 10 contains the plot of free length versus molar concentration. Free length decreases with increase in molar concentration. Decrease in free length shows association in the constituents. It is a result of dipole-induced dipole heteromolecular interactions or interstitial accommodation of unlike molecules or due to lack of perfect symmetry and decrease in available space between the constituents. The decrease in free length with increase in molar concentration indicates the enhancement in the closed structure of the constituents.

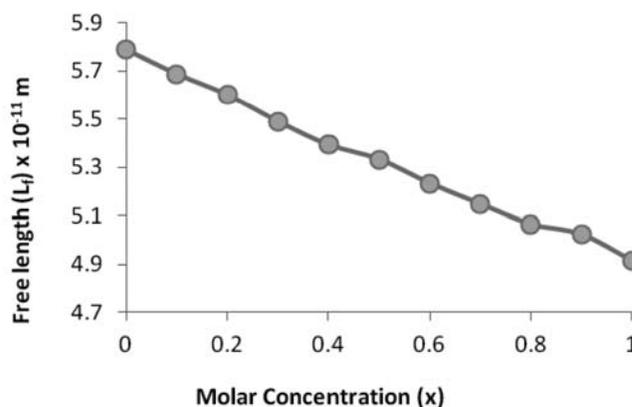


Fig. 10 Variation of L_f versus x

Figure 11 and 12 respectively contain the plots of internal pressure (π_i) and free volume (V_f) versus molar concentration. It is observed that internal pressure slightly increases and free volume (V_f) increases in large extent with increase in molar concentration. It is a characteristic property of this binary liquid system. This odd behavior of internal pressure and free volume is may be due to weakening of heteromolecular interaction than the homomolecular interactions in the constituent molecules of the binary mixture or due to London forces or due to geometry of the molecules, because it play vital role in deciding the volume of a liquid mixture. Increase in free volume enhancement the disorder in the liquid mixture due to increase in the mobility of the molecules in the binary liquid mixture is also one of the reason for such behavior of this binary liquid mixture.

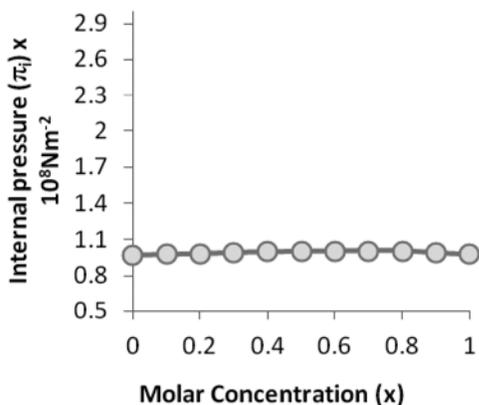
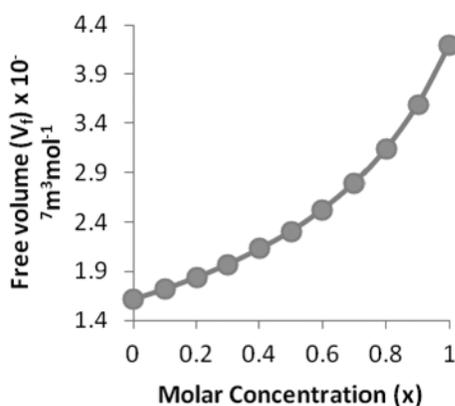
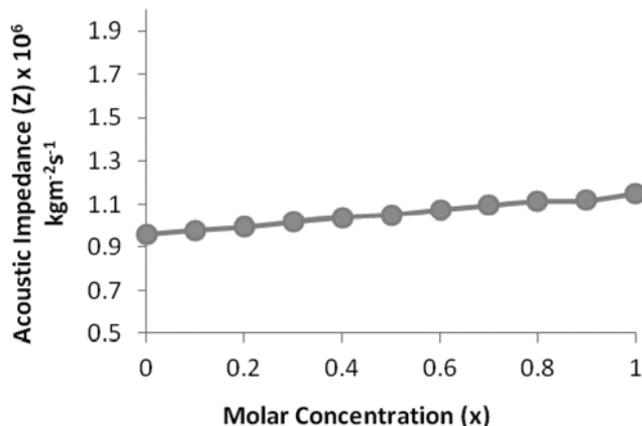
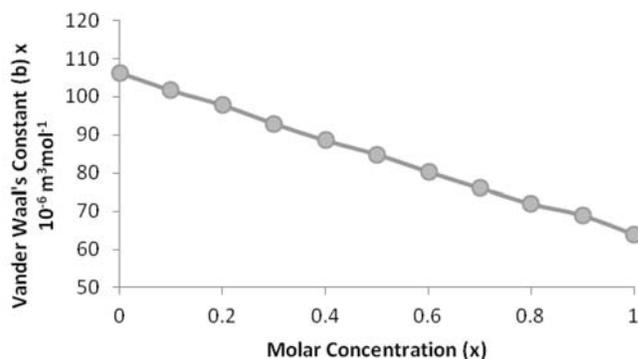
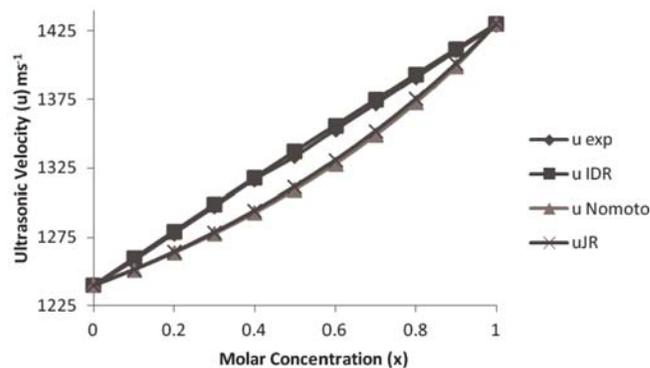
Fig. 11 Variation π_i of versus x Fig. 12 Variation of V_f versus x

Figure 13 contains the plot of acoustic impedance (Z) versus molar concentration. Acoustic impedance increases with increase in the molar concentration. Increase in acoustic impedance in this binary liquid mixture with molar concentration is mainly due to large values of densities of molecules of the constituent in

Fig. 13 Variation of Z versus x

this binary liquid mixture, indicating close pack structure of the constituents.

Figure 14 contains the plot of Vander Waal's constant (b) versus molar concentration. It is observed that Vander Waal's constant decreases with increase in molar concentration. This is because due change in intermolecular geometry of liquid molecules in the binary liquid mixture.

Fig. 14 Variation of b versus x Fig. 15 Comparison of u versus theoretical values at different x

The ultrasonic velocity produced by IDR empirical relation are in good agreement with the experimental data as compare to Nomoto's relation and Junjie's relation (Fig. 15).

The observed ultrasonic absorption (αf^2_{obs}), classical absorption ($\alpha f^2_{\text{class}}$), excess absorption ($\alpha f^2_{\text{excess}}$) and the ratio of observed ultrasonic absorption and classical absorption at 293 K, 298 K, 303 K, 308 K and 313 K are represented in Tables 1-5. Decrease in observed ultrasonic absorption, classical absorption, excess absorption and increase in the ratio of observed ultrasonic absorption and classical absorption with molar concentration may be attributed strong intermolecular

Table 1 – Ultrasonic velocity (u), density (ρ), viscosity (η) and absorption coefficient (α/f^2) classical, observed, excess, and ratio of observed and classical absorption coefficient at 293 K for Cyclohexane + Acrylonitrile.

X	$u(\text{m/s})$	$P(\text{kg/m}^3)$	$\eta(\text{cP})$	(α/f^2) Observed $\times 10^{17} \text{ s}^2/\text{cm}$	(α/f^2) Classical $\times 10^{17} \text{ s}^2/\text{cm}$	(α/f^2) Excess $\times 10^{17} \text{ s}^2/\text{cm}$	(α/f^2) Observed (α/f^2) Classical
0	1284	780.8	0.9617	48.3234	15.298	33.0254	3.1588
0.1	1303.16	787	0.9019	45.1146	13.615	31.4996	3.3136
0.2	1383.4	790.4	0.8422	42.2053	10.582	31.6233	3.9884
0.3	1341.24	798.2	0.7824	39.7962	10.681	29.1152	3.7259
0.4	1360.28	805.6	0.7227	37.4873	9.3709	28.1164	4.0004
0.5	1376.36	805	0.6629	35.2779	8.3039	26.974	4.2483
0.6	1395.44	814.4	0.6031	33.0687	7.1655	25.9032	4.6149
0.7	1414.48	820.4	0.5434	30.9598	6.1536	24.8062	5.0312
0.8	1432.52	826.2	0.4836	29.1507	5.2351	23.9156	5.5683
0.9	1478.92	828.2	0.4238	27.4417	4.1593	23.2824	6.5977
1.0	1469.9	835	0.3641	26.2334	3.60993	22.6235	7.2671

Table 2 – Ultrasonic velocity (u), density (ρ), viscosity (η) and absorption coefficient (α/f^2) classical, observed, excess, and ratio of observed and classical absorption coefficient at 298 K for Cyclohexane + Acrylonitrile.

X	$u(\text{m/s})$	$P(\text{kg/m}^3)$	$\eta(\text{cP})$	(α/f^2) Observed $\times 10^{17} \text{ s}^2/\text{cm}$	(α/f^2) Classical $\times 10^{17} \text{ s}^2/\text{cm}$	(α/f^2) Excess $\times 10^{17} \text{ s}^2/\text{cm}$	(α/f^2) Observed (α/f^2) Classical
0	1262	776.5	0.8912	46.5434	15.014	31.5294	3.1
0.1	1280.7	782	0.8361	43.3385	13.383	29.9555	3.2383
0.2	1376.5	783.5	0.7809	40.4332	10.047	30.3862	4.0244
0.3	1319.3	791.25	0.7258	38.0281	10.503	27.5251	3.6207
0.4	1338.6	797.25	0.6707	35.7231	9.2217	26.5014	3.8738
0.5	1354.95	796	0.6156	33.5179	8.1742	25.3437	4.1005
0.6	1374.3	804	0.5605	31.3128	7.0616	24.2512	4.4342
0.7	1393.6	809	0.5054	29.2077	6.0688	23.1389	4.8127
0.8	1411.9	813.75	0.4502	27.4026	5.1681	22.2345	5.3023
0.9	1465.4	817	0.3954	25.6975	4.0406	21.6569	6.3598
1.0	1449.875	820.5	0.34	24.4923	3.57468	20.9176	6.851

Table 3 – Ultrasonic velocity (u), density (ρ), viscosity (η) and absorption coefficient (α/f^2) classical, observed, excess, and ratio of observed and classical absorption coefficient at 308 K for Cyclohexane + Acrylonitrile.

X	$u(\text{m/s})$	$P(\text{kg/m}^3)$	$\eta(\text{cP})$	(α/f^2) Observed $\times 10^{17} \text{ s}^2/\text{cm}$	(α/f^2) Classical $\times 10^{17} \text{ s}^2/\text{cm}$	(α/f^2) Excess $\times 10^{17} \text{ s}^2/\text{cm}$	(α/f^2) Observed (α/f^2) Classical
0	1240	772.2	0.8213	44.7433	14.6668	30.0765	3.0506
0.1	1258.2	777	0.7707	41.5425	13.1985	28.4506	3.1731
0.2	1278	776.6	0.7201	38.6412	11.897	26.9615	3.3084
0.3	1297.4	784.3	0.6696	36.2401	10.5934	25.9604	3.5254
0.4	1316.9	788.9	0.6191	33.9392	0.94359	24.905	3.7567
0.5	1333.5	787	0.5686	31.7378	0.84983	23.7276	3.9622
0.6	1353.2	793.6	0.5181	29.5369	0.748468	22.6091	4.2635
0.7	1372	797.6	0.4676	27.4357	0.6596	21.4674	4.5969
0.8	1391.3	801.3	0.4169	25.6346	0.57664	20.5551	5.0467
0.9	1410.8	792.3	0.3664	23.9335	0.508054	19.6038	5.5277
1.0	1429.9	806	0.3163	22.7324	0.43169	19.2029	6.4407

Table 4 – Ultrasonic velocity (u), density (ρ), viscosity (η) and absorption coefficient (α/f^2) classical, observed, excess, and ratio of observed and classical absorption coefficient at 308 K for Cyclohexane + Acrylonitrile.

X	$u(\text{m/s})$	$P(\text{kg/m}^3)$	$\eta(\text{cP})$	(α/f^2) Observed $\times 10^{17} \text{ s}^2/\text{cm}$	(α/f^2) Classical $\times 10^{17} \text{ s}^2/\text{cm}$	(α/f^2) Excess $\times 10^{17} \text{ s}^2/\text{cm}$	$\frac{(\alpha/f^2) \text{ Observed}}{(\alpha/f^2) \text{ Classical}}$
0	1218	769.9	0.7512	42.9232	14.197	28.7262	3.0234
0.1	1235.78	772	0.7053	39.7264	12.728	26.9984	3.1212
0.2	1362.7	769.7	0.6593	36.8291	8.9	27.9291	4.1381
0.3	1275.42	777.35	0.6134	34.4322	9.9999	24.4323	3.4433
0.4	1295.24	780.55	0.5675	32.1352	8.7972	23.338	3.6528
0.5	1312.13	778	0.5216	29.9368	7.8029	22.1339	3.8366
0.6	1332.02	783.2	0.4756	27.7407	6.7556	20.9851	4.1063
0.7	1351.84	786.2	0.4297	25.6537	5.8168	19.8369	4.4103
0.8	1370.66	788.85	0.3838	23.8466	4.9676	18.879	4.8004
0.9	1438.36	794.6	0.3378	22.1495	3.7561	18.3934	5.8969
1.0	14.9.825	791.5	0.2919	20.9514	3.4603	17.4911	6.0547

Table 5 – Ultrasonic velocity (u), density (ρ), viscosity (η) and absorption coefficient (α/f^2) classical, observed, excess, and ratio of observed and classical absorption coefficient at 313 K for Cyclohexane + Acrylonitrile.

X	$u(\text{m/s})$	$P(\text{kg/m}^3)$	$\eta(\text{cP})$	(α/f^2) Observed $\times 10^{17} \text{ s}^2/\text{cm}$	(α/f^2) Classical $\times 10^{17} \text{ s}^2/\text{cm}$	(α/f^2) Excess $\times 10^{17} \text{ s}^2/\text{cm}$	$\frac{(\alpha/f^2) \text{ Observed}}{(\alpha/f^2) \text{ Classical}}$
0	1196	763.6	0.6715	41.0821	13.716	27.3661	2.9952
0.1	1213.32	767	0.6401	37.8904	12.284	25.6064	3.0845
0.2	1355.8	762.8	0.5987	34.9969	8.2802	26.7167	4.2265
0.3	1253.48	770.4	0.5573	32.6042	9.6571	22.9471	3.3761
0.4	1273.56	772.2	0.5159	30.3111	8.5037	21.8074	3.5644
0.5	1290.72	769	0.4745	28.1159	7.5447	20.5712	3.7265
0.6	1310.88	772.8	0.4271	25.9248	6.4506	19.4742	4.0189
0.7	1330.96	774.8	0.3857	23.8417	5.5513	18.2904	4.2947
0.8	1350.04	776.4	0.3443	22.0385	4.7385	17.3	4.6509
0.9	1424.84	783.4	0.3029	20.3454	3.5144	16.831	5.7891
1.0	1389.8	777	0.2674	19.1401	3.5204	15.6197	5.4369

interaction in the constituent molecules. It is observed that the observed absorption is higher than the classical absorption. It is a characteristic feature of the solution. The excess absorption arises due to structural relaxation in this binary liquid mixture.

Conclusion

1. The nonlinear variation of absorption coefficient with molar concentration provides useful information about nature of intermolecular forces existing in binary liquid mixtures.
2. In this work absorption process is due to structural relaxation. These structural relaxation processes play very important role in the study of molecular

and structural properties of the constituents.

3. Weakening of the intermolecular forces is indicated by the observed decrease in ultrasonic absorption in the binary liquid mixtures.
4. The observed molecular association due to the formation hydrogen bond or due to interstitial accommodation or due to induction or due to London dispersion forces in the constituents molecules.
5. Decrease in adiabatic compressibility and free length with increase in molar concentration is due to association.
6. Thermo-acoustic parameters such as adiabatic compressibility, density, viscosity, relaxation time,

free length, molar volume, acoustic impedance, internal pressure, molecular radius, etc indicates the strength of molecular interactions in the binary liquid mixtures.

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