ULTRASONIC STUDIES ON NON-AQUEOUS SOLUTIONS OF TOLUENE IN NITROBENZENE

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ABSTRACT

Ultrasonic studies are extensively used in the conformational analysis of organic molecules. The ultrasonic study can give the indication of complex formation through hydrogen bonding in the system. Recently researchers suggested that adiabatic compressibility also used for detecting hydrogen bond formation in solutions. The ultrasonic velocity measurement is a unique tool in characterizing the structure and properties of the system and provides significant information on the arrangement of matter in solutions and also finds an extensive application in studying the nature of intermolecular forces. In the present work, attempts have been made to investigate the behavior of Toluene and Nitrobenzene at various concentrations also at different temperatures. The Ultrasonic velocity, viscosity and density are measured experimentally. In order to get more information on the nature and strength of molecular interaction, we have calculated the other related acoustical parameter such as adiabatic compressibility, intermolecular free length, Rao's constant, internal pressure, and free volume. The non-linear variations of these derived acoustical parameters with different concentration of the solute explained on the basis of structural changes occurring in a solution.

Author Keywords:

Toluene, Nitrobenzene, Velocity, Rao's Constant, adiabatic compressibility etc.,

Introduction

Ultrasonic investigation of liquid mixtures consisting of polar and non-polar components is of considerable importance in understanding intermolecular interaction between the component molecules and they find applications in several industrial and technological processes [1-3]. Moreover, the behaviour of a non-polar molecule in a different polar environment can also be discussed with the ternary system. These liquid mixtures are of interest to organic chemists who want to know about the types of bonds, type of molecular interactions, etc. The values of ultrasonic velocity, density, viscosity and adiabatic compressibility as a function of concentration will be of much help in providing such information. Further, such studies as a function of concentration are useful in gaining insight into the structure and bonding of associated molecular complexes and other molecular processes. The ultrasonic study can give the indication of complex formation through hydrogen bonding in the system. Recently researchers suggested that adiabatic compressibility also used for detecting hydrogen bond formation in solutions. The ultrasonic velocity measurement is a unique tool in characterizing the structure and properties of the system and provides significant information on the arrangement of matter in solutions and also finds an extensive application in studying the

nature of intermolecular forces. Accurate knowledge of thermodynamic mixing properties such as adiabatic compressibility, intermolecular free length, free volume, internal pressure and molar volume and their excess values for mixtures of protic, non-protic and associated liquids has a great importance in theoretical and applied areas of research.

Toluene is mono-substituted benzene derivative, i.e. one in which a single hydrogen atom from the benzene molecule has been replaced by a univalent group, in this case CH_3. Toluene is an important organic solvent, but is also capable of dissolving a number of notable inorganic chemicals such as sulfur.

Nitrobenzene is an organic compound with the chemical formula $C_6H_5NO_2$. It is highly toxic. Nitrobenzene is a nitro aromatic hydrocarbon used to produce aniline. Nitrobenzene is produced in a continuous process by the direct nitration of benzene. Nitrobenzene also is used in the manufacture of compounds including benzidine and quinoline, in the production of isocyanates, pesticides, and pharmaceuticals, and as a solvent in petroleum refining. Nitrobenzene has been detected in air and appears to volatilize from water and soil

MATERIALS AND METHODS

The pure chemicals Toluene and Nitrobenzene were used as such without any purification. Measurement of Ultrasonic Velocity is generally made either by continuous wave method or by pulse methods. In the present study, continuous wave variable path interferometer is used. The ultrasonic velocity was measured using a multi variable frequency interferometer working at 1,3,5 MHz by standard procedure .The accuracy of ultrasonic velocity determination in non–aqueous solutions is 0.001%

The constant temperature was maintained by circulating water from the thermostatically controlled ($\pm$ 0.1^{o}C) water bath. The density at room temperature was measured using specific gravity bottle and single pan microbalance. The viscosity at different temperature was measured using Oswald's Viscometer and stop clock. Acoustical parameters were calculated using the measure values of velocity, viscosity and density. The values of ultrasonic velocity, viscosity, Adiabatic compressibility, Free volume, intermolecular free length, Rao's Constant, Internal pressure of Toluene in Nitrobenzene for various concentration (0.0 to 1.0) at different temperatures (303K, 308K, 313K, 318K and 323K) are given in Table 1 to Table 2.

TABLE: 1

Concentration	Temperature In K	Density In Kgm^{-3}	Viscosity $\eta \times 10^{-3} Nsm^{-2}$	Velocity In Ms^{-1}	Adiabatic Compressibility $\times 10^{-10}$m
0	303	1228	1.66	1680	2.1089
	308	1228	1.42	1650	2.9911
	313	1228	1.19	1635	3.0462
	318	1228	0.95	1605	3.1611

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	323	1228	0.82	1560	3.3462
0.2	303	1129	1.58	1635	3.3133
	308	1129	1.37	1590	3.5035
	313	1129	1.33	1545	3.7106
	318	1129	0.90	1485	4.0166
	323	1129	0.78	1455	4.1838
0.4	303	1092	1.52	1605	3.5549
	308	1092	1.30	1545	3.8364
	313	1092	1.09	1500	4.0700
	318	1092	0.87	1455	4.3257
	323	1092	0.75	1425	4.5097
0.6	303	1030	1.44	1575	3.9138
	308	1030	1.23	1515	4.2299
	313	1030	1.03	1470	4.4929
	318	1030	0.82	1440	4.6821
	323	1030	0.71	1410	4.8834
0.8	303	945.15	1.33	1530	4.5197
	308	945.15	1.14	1485	4.7978
	313	945.15	0.95	1440	5.1024
	318	945.15	0.76	1410	5.3218
	323	945.15	0.65	1380	5.5557
1.0	303	913.14	1.27	1485	4.9660
	308	913.14	1.09	1425	5.3930
	313	913.14	0.91	1380	5.7505
	318	913.14	0.73	1365	5.8778
	323	913.14	0.62	1350	6.0089

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TABLE: 2

Concentration	Temperature In K	Inter molecular Free length $L_F \times 10^{-10}$ m	Free Volume $V_F \times 10^{-9}$ m^{3}mol^{-1}	Internal Pressure $\pi_i \times 10^{-6}$ pa	Rao's Constant
0	303	0.3124	4.9644	784.951	**116.956**
	308	0.3481	6.1074	604.182	**115.538**
	313	0.3543	7.8527	564.646	**115.189**
	318	0.3638	10.7075	517.328	**114.488**
	323	0.3774	12.7946	495.178	**113.418**
0.2	303	0.3633	5.1289	595.845	**125.227**
	308	0.3768	5.8640	571.918	**124.079**
	313	0.3910	7.7895	535.476	**122.909**
	318	0.4100	10.3266	495.229	**121.313**
	323	0.4219	12.4133	473.085	**120.499**
0.4	303	0.3763	5.2827	586.758	**128.617**
	308	0.3942	6.3079	553.072	**128.010**
	313	0.2199	7.8597	522.319	**125.777**
	318	0.4255	11.5074	467.333	**124.519**
	323	0.4381	13.8434	446.322	**123.666**
0.6	303	0.3948	5.5648	545.796	**135.444**
	308	0.4140	6.6503	522.810	**133.720**
	313	0.4302	8.2947	493.573	**132.400**
	318	0.4427	11.3215	452.064	**131.498**
	323	0.4558	13.6151	431.787	**130.588**
0.8	303	0.4243	5.9981	502.830	**146.125**
	308	0.4409	7.2274	480.328	**144.692**
	313	0.4585	9.0721	452.505	**143.230**
	318	0.4719	12.2842	415.559	**142.236**

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	323	0.4863	15.0383	394.564	**141.233**
	303	**0.4448**	**6.1652**	**486.272**	**150.070**
	308	**0.4675**	**7.2886**	**467.470**	**148.038**
1.0	**313**	**0.4868**	**9.1058**	**441.086**	**146.479**
	318	**0.4960**	**12.4674**	**403.571**	**145.951**
	323	**0.5057**	**15.6666**	**379.865**	**145.420**

Theory and Calculations

Using the measured data, the acoustical parameters have been calculated

Adiabatic Compressibility $\beta = 1 / U^2\rho$ --- (1)

Intermolecular free length (L_f) has been calculated from relation,

$LT_f = K_T\sqrt{B}$ --- (2)

Where, K_T is a temperature dependent constant.

Free volume (V_f) has been calculated from relation,

$V_f = (M_{eff}U / K\eta)$ -------------------------------- (3)

Where M_{eff} is the effective molecular weight ($M_{eff} = \Sigma m_i f_i x_i$, in which m_i and x_i are the molecular weight and the mole fraction of the individual constituents respectively). K is a temperature independent constant which is equal to 4.28×10^9 for all liquids.

The internal pressure (π_i) can be found out as

$\Pi = bRT (K\eta/U)^{1/2} (\rho^{2/3}/M_{eff}^{7/6})$ -------------(4)

K is a constant, T the absolute temperature, η the viscosity in Nsm^{-2}, U the ultrasonic velocity in ms^{-1}, ρ the density in Kgm^{-3}, M_{eff} the effective molecular weight.

RESULTS AND DISCUSSION:

Ultrasonic velocity measurements in liquids and liquid mixtures were carried out by many researchers [1-24]. In our present work, ultrasonic velocity on non-aqueous solutions of Toluene in Nitrobenzene at different concentration and temperature were studied. The concentration ranges from 0.0 to 1.0 were prepared by adding known weight of the Toluene in Nitrobenzene.

From **figure 1** we have concluded that the value of density decreases with the increasing value of concentration that means the morality of Toluene in Nitrobenzene decreases with the increasing value of density. [5,6]

Figure 2 shows the variation of viscosity with concentration and temperature. It is almost reflected the behavior of the variation of velocities as discussed [15-19] it is observed that the increase of absorption and viscosity with concentration and their decrease with increase in temperature.

Figure 3 has been drawn for various velocities, which are varying with different concentration and temperature. From the graph it is observed that the velocities are decreases with the increasing value of concentration.[9,23,24] found that the increase in Ultrasonic velocity at higher concentrations may be due to polymer-polymer interaction and decrease in velocity with increase in temperature may be due to the weakening of intermolecular forces

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between the molecules. It was concluded that the non-linear variations of Rao's constant with concentration of one of the components generally indicates strong association between the molecules. [11,12,13]

Figure 4 describes the variation of adiabatic Compressibility with different values of temperature as well as concentration. It was found that adiabatic compressibility increases with the increasing value of concentration [6,10,14] **S.K.Kor**[14] et al was concluded that the velocity in general decreases with increase of temperature irrespective of its molecular weight and concentration.

From **figure 5** describes the variation of Rao's Constant with various temperature and concentration. Since Rao's Constant is independent of temperature there is no appreciable variation of Rao's Contant with the effect of temperature. However it slowly increases with the increasing value of concentration.[1,2,3,4,7]

From **figure 6** describes the variation if free length for different value of temperature and concentration. Since the free length L_f is proportional to the adiabatic compressibility β_{ad} the same trend of variation similar to the variation of adiabatic compressibility has repeated in this graph.

Figure 7 the graph has been plotted for the variation of free volume at the various values of concentration and temperature. It is also that the free volume increases with increasing the value of concentration.[11] The absorption decreases almost linearly with increasing temperature at a given concentration and increases with concentration at a given temperatures. The velocity is a linearly increasing function of the temperature and also increases with concentration at a given temperature. In addition, the viscosity decreases linearly with temperature and increase with concentration. **[20-22]**

Figure 8 describes the variation of internal pressure with various temperature and concentration. It is observed that internal pressure is decreases with the increasing value of concentration.
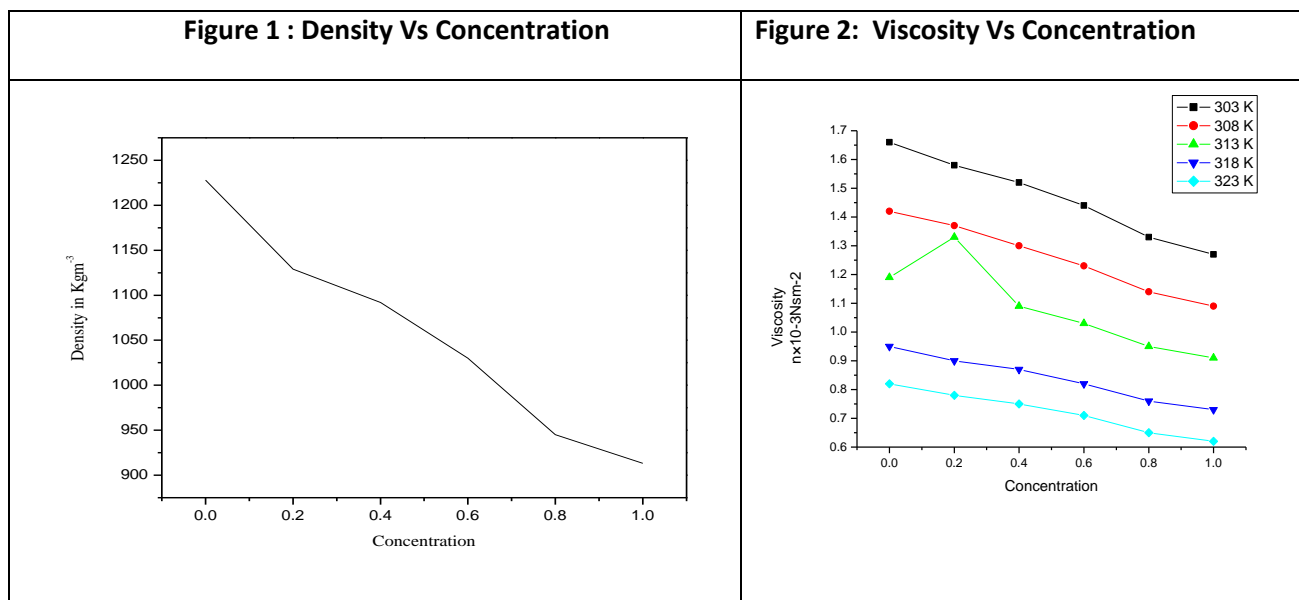
Figure 1 : Density Vs Concentration	Figure 2: Viscosity Vs Concentration

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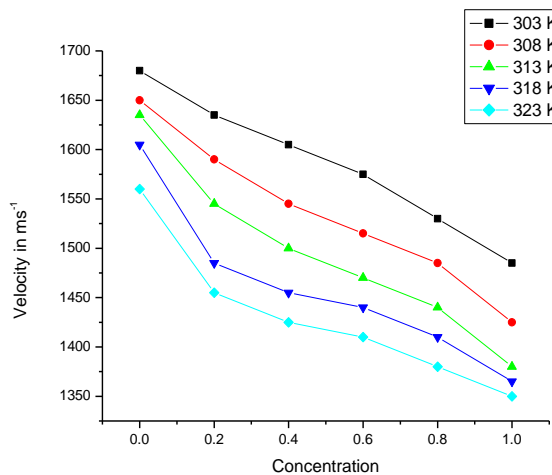
Figure 3: Velocity Vs Concentration

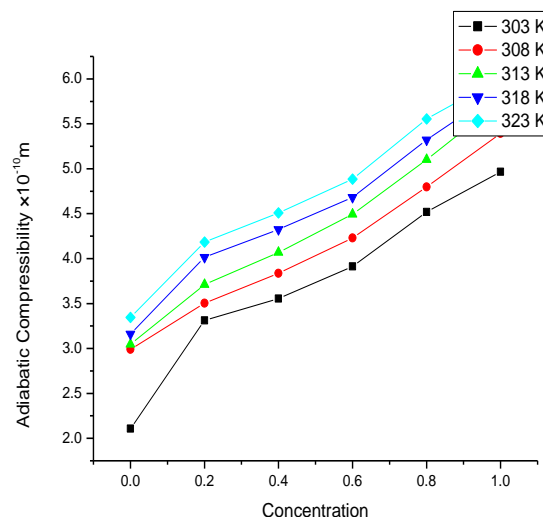## Figure 4 : Adiabatic compressibility Vs Concentration

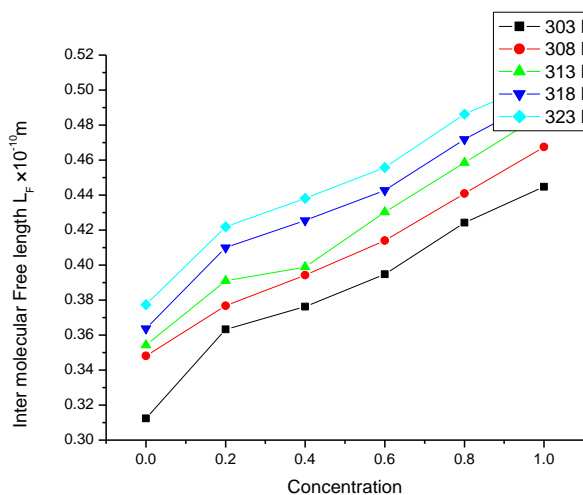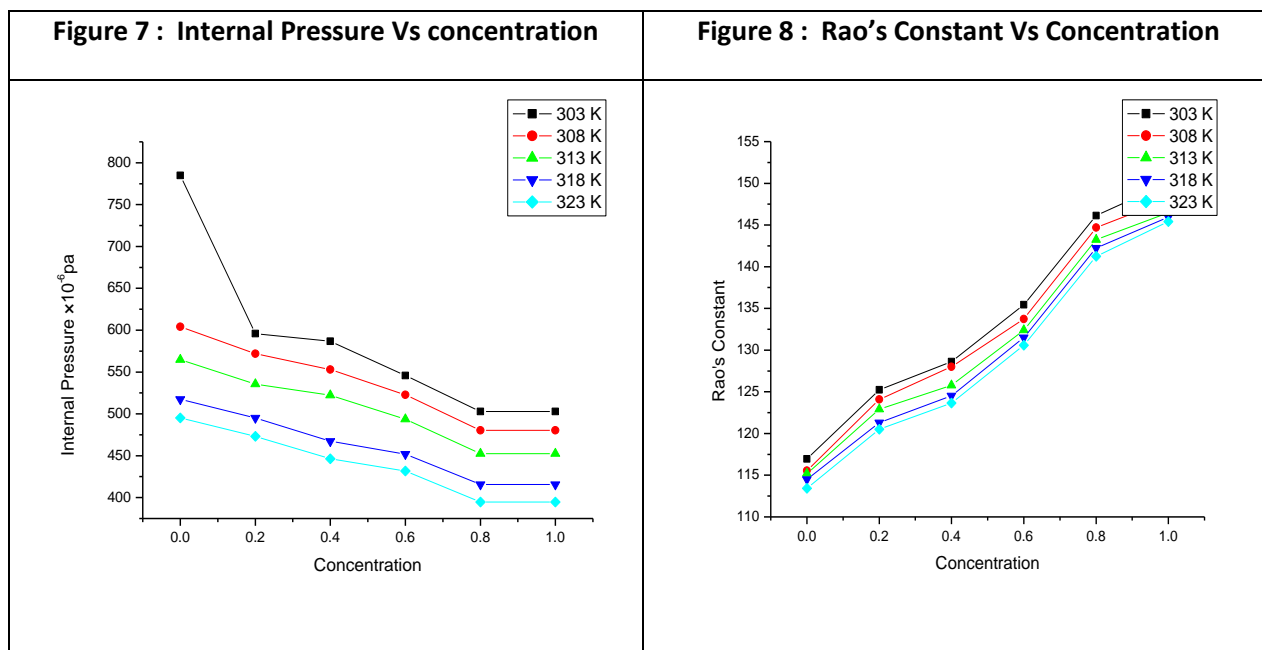## Figure 5 : Internal Molecular Free length Vs Concentration

Figure 6: Free volume Vs Concentration

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Figure 7 : Internal Pressure Vs concentration	Figure 8 : Rao's Constant Vs Concentration

Figure 7 : Internal Pressure Vs concentration

Figure 8 : Rao's Constant Vs Concentration
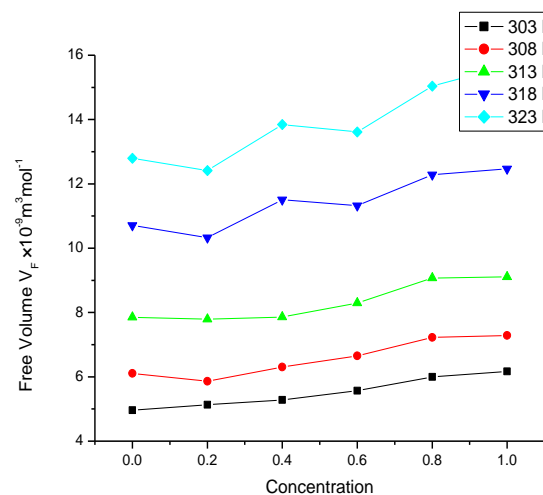
CONCLUSION:

Ultrasonic studies have been carried out in the solutions of Toluene in Nitrobenzene at five different temperatures (namely 303k, 308k, 313k, 318 and 323k) for the concentration ranging from 0.0 to 1.0 in temperature of 0.2. There is an interaction between the solute (Toluene) and solvent (Nitro Benzene) molecules. At lower concentrations in the interaction are very less and the interaction is mostly between the solute and the solvent molecules. At higher concentration, the solute molecules are pushed closer to the solvent molecules, there by producing hydrogen bonds. The trend of increase in adiabatic compressibility and free length with increase of solute concentration further concludes the possibility of molecular interaction. This interaction indicates that there is a possibility of some complex formation such as hydrogen bond in the present system. As the temperature increases, the hydrogen bonds are broken up due to thermal agitations and hence the ultrasonic velocity decreases.

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