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Research Article

ULTRASONIC STUDIES ON NON-AQUEOUS SOLUTIONS OF CARBON TETRA CHLORIDE IN TOLUENE

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ABSTRACT

Ultrasonic studies are extensively used in the conformational analysis of organic molecules. In the present work, attempts have been made to investigate the behaviour of Carbon Tetra Chloride and Toluene 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, relaxation time, acoustical impedance and Gibb's energy. 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.

Keywords: Carbon Tetra Chloride, Toluene, Ultrasonic 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.

Carbon tetra chloride is a non polar organic compound because of its symmetrical geometry ie four chlorine atoms are positioned symmetrically as corners in a tetrahedral configuration joined to a central carbon atom by single covalent bonds. Toluene is an aromatic hydro carbon and it is a mono-substituted benzene derivative ie one in which a single hydrogen atom from the benzene molecule has been replaced by a univalent group (CH_3). The present study deals with the mono substituted benzene derivative with CCl_4 at different concentrations and temperatures.

MATERIALS AND METHODS

The liquid mixtures of various concentrations in mole fraction were prepared by taking AR grade chemicals of Carbon Tetra Chloride and Toluene and 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 mole fraction of the component varied form 0.0 to 1.0 with a difference of 0.2.The constant temperature was maintained by circulating water from the thermostatically controlled (+ 0.1°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 measured values of velocity, viscosity and density. The values of ultrasonic velocity, viscosity, Adiabatic compressibility, Free volume, intermolecular free length, Rao's Constant, Acoustical Impedance, Relaxation time, Gibb's energy, Internal pressure of Toluene in Carbon Tetra Chloride 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. The values obtained are compared with literature and found that they make very with each other.

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,

$Lf = K_T\sqrt{B}$ ---------- (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.

The relaxation time is estimated from the following relation,

$\tau = 4/3\ \eta\beta$ ---------- (5)

Knowing the viscosity of the liquid (η) and adiabatic compressibility (β), then τ can be calculated.

The Gibb's free energy can be related as

$\Delta G^{*} = -2.303\ KT \log (h/KT\tau)$ ---------- (6)

Where K is Boltzmann's constant and h, the Planck's constant.

The acoustic impedance can be related as

$Z = U\rho$ ---------- (7)

Where U is a velocity of ultrasound in medium and ρ is density.

Table 1:

Concentration	Temperature In K	Density In Kgm^{-3}	Viscosity $\eta \times 10^{-3} Nsm^{-2}$	Velocity In Ms^{-1}	Adiabatic Compressibility $\times 10^{-10} m$	Relaxation time $\tau * 10^{-12}$ s
0	303	913.14	1.27	1455	5.1729	8.738
	308	913.14	1.09	1425	5.3930	7.818
	313	913.14	0.91	1395	5.6275	6.868
	318	913.14	0.73	1365	5.8776	5.706
	323	913.14	0.62	1350	6.0089	4.955
	303	984.92	1.38	1485	4.6041	8.450
	308	984.92	1.18	1455	4.7959	7.526
0.2	313	984.92	0.99	1425	4.9999	6.583
	318	984.92	0.79	1410	5.1069	5.365
	323	984.92	0.68	1365	5.4492	4.928
	303	1117	1.56	1515	3.9005	8.093
	308	1117	1.34	1485	4.0597	7.235
0.4	313	1117	1.12	1440	4.3174	6.431
	318	1117	0.89	1425	4.4088	5.218
	323	1117	0.77	1380	4.7069	4.820
	303	1365	1.91	1545	3.0691	7.796
	308	1365	1.64	1515	3.1918	6.962
0.6	313	1365	1.37	1470	3.3903	6.177
	318	1365	1.09	1440	3.5329	5.121
	323	1365	0.94	1410	3.6849	4.606
	303	1435	2.00	1575	2.8092	7.472
	308	1435	1.72	1545	2.9194	6.678
0.8	313	1435	1.44	1500	3.0972	5.932
	318	1435	1.15	1455	3.2917	5.005
	323	1435	0.99	1425	3.4318	4.518
	303	1542	2.16	1590	2.5652	7.369
1.0	308	1542	1.85	1560	2.6648	6.556
	313	1542	1.55	1515	2.8255	5.825
	318	1542	1.24	1470	3.0011	4.949
	323	1542	1.06	1440	3.1275	4.409

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 $\pi_i \times 10^{-6} pa$	Acoustical Impedance $Z(10^6 Kgm^2 s^{-1})$	Rao's Constant
	303	0.4539	3.8734	688.599	1.328	111.590
	308	0.4675	4.7216	655.254	1.301	110.830
0	313	0.4816	5.9952	614.938	1.273	110.050
	318	0.4960	8.0765	565.686	1.246	109.270
	323	0.5057	10.0149	532.457	1.232	108.870
	303	0.4282	3.5151	749.096	1.462	103.950
	308	0.4408	4.3116	711.343	1.433	103.250
0.2	313	0.4539	5.4379	669.073	1.404	102.540
	318	0.4624	7.5084	610.450	1.389	102.180
	323	0.4816	8.9556	584.686	1.344	101.090
	303	0.3942	3.0305	853.842	1.692	92.609
	308	0.4056	3.6943	812.491	1.658	92.001
0.4	313	0.4218	4.6164	766.569	1.608	91.070
	318	0.4295	6.4155	697.901	1.592	90.757
	323	0.4472	7.5976	670.019	1.541	89.801
	303	0.3496	2.3066	1068.401	2.109	76.339
	308	0.3596	2.8151	999.764	2.068	75.847
0.6	313	0.3738	3.5239	942.956	2.006	75.096
	318	0.3846	4.8143	877.413	1.966	74.586
	323	0.3960	5.8247	836.365	1.925	74.071
	303	0.3345	2.2251	1115.850	2.260	73.286
	308	0.3439	2.7107	1062.036	2.217	72.822
0.8	313	0.3573	3.3852	1002.233	2.153	72.115
	318	0.3712	4.5314	923.918	2.088	71.394
	323	0.3822	5.4986	879.836	2.045	70.905
	303	0.3196	2.0139	1209.441	2.452	68.482
	308	0.3302	2.4705	1148.220	2.406	68.075
1.0	313	0.3412	3.0829	1083.814	2.336	67.421
	318	0.3544	4.1180	999.839	2.267	66.753
	323	0.3648	5.0516	948.692	2.220	66.301

RESULTS AND DISCUSSION

Ultrasonic velocity measurements in liquids and liquid mixtures were carried out by many researchers [1-15]. In our present work, ultrasonic velocity on non-aqueous solutions of Toluene in Carbon Tetra Chloride at different concentration and temperature were studied. The concentration ranges from 0.0 to 1.0 were prepared by adding known weight of the Carbon Tetra Chloride in Toluene.

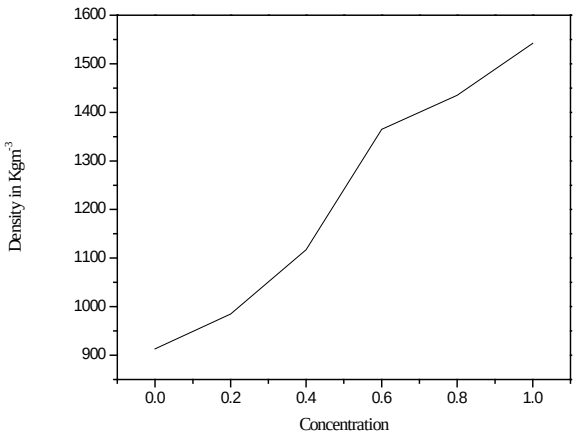

Fig. 1:

From figure 1 we have concluded that the value of density increases with the increasing value of concentration that means the morality of Carbon Tetra Chloride in Toluene increases with the decreasing value of density[1,2].

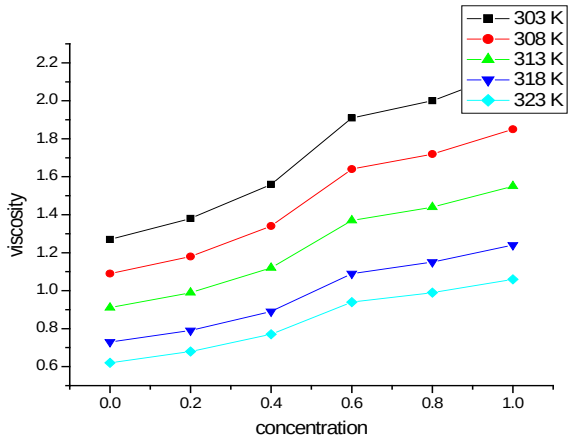

Fig. 2:

Figure 2 shows the variation of viscosity with concentration and temperature. It is almost reflected the behavior of the variation of velocities as discussed [3,4] 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[6,8,9] .S.Thirumaran [6]et al., 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 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]

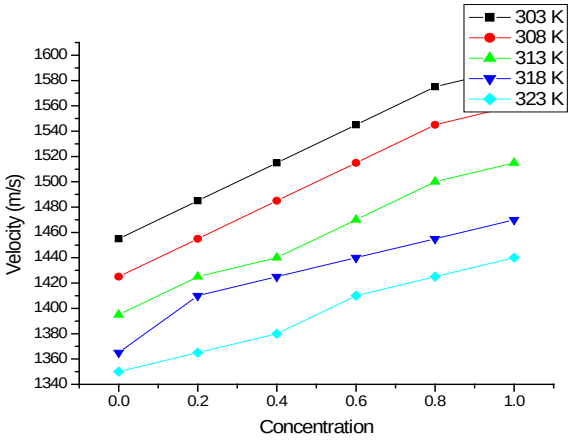

Fig. 3:

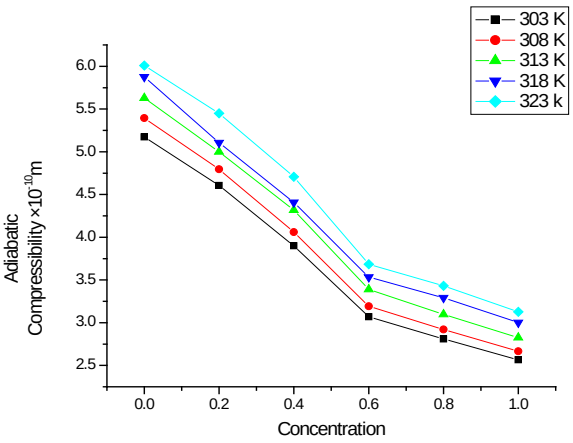

Fig. 4:

Figure 4 describes the variation of adiabatic Compressibility with different values of temperature as well as concentration. It was found that adiabatic compressibility decreases with the increasing value of concentration which clearly indicates that the molecules are forming a more tightly bounded system[4-7]. It was concluded that the velocity in general decreases with increase of temperature irrespective of its molecular weight and concentration.

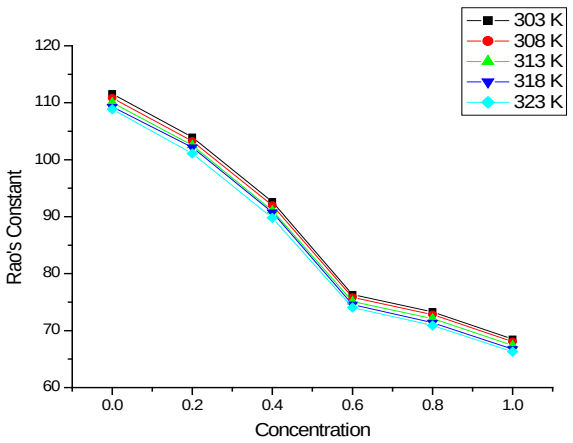

Fig. 5:

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 decreases with the increasing value of concentration[13,15]

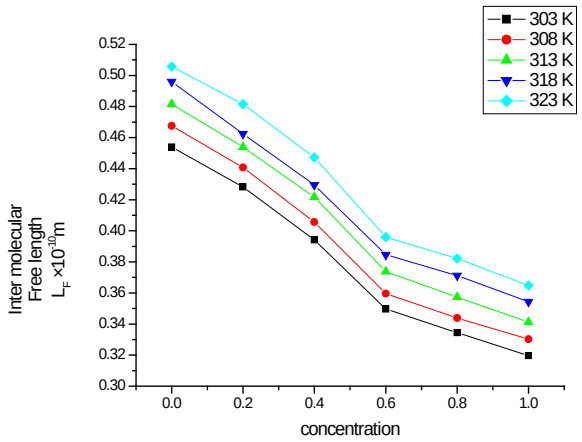

Fig. 6:

The variation of ultrasonic velocity in a mixture depends upon the increase or decrease of intermolecular free length[3, 7]. Figure 6 describes the variation of 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. However, the decrease in β_{ad} and L_f mat also be attributed to the internal interaction between the π electrons of C=O bond and π electrons of benzene ring[11].

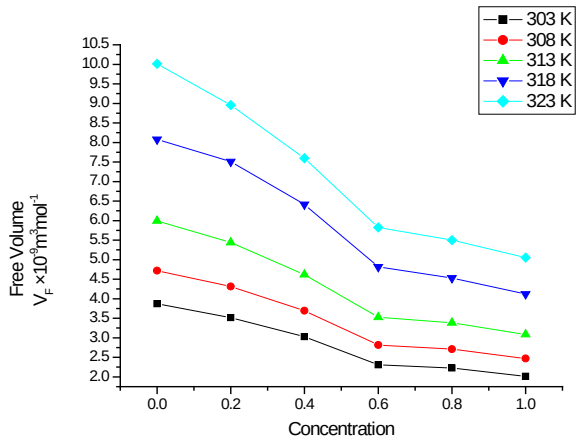

Fig. 7:

From figure 7, it is concluded that the free volume decreases with increasing the value of concentration which clearly indicates the increasing magnitude of interactions[11,14]. 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.

Figure 8 describes the variation of internal pressure with various temperature and concentration. It is observed that internal pressure is increases with the increasing value of concentration which clearly indicates the increasing magnitude of interactions[5,9].

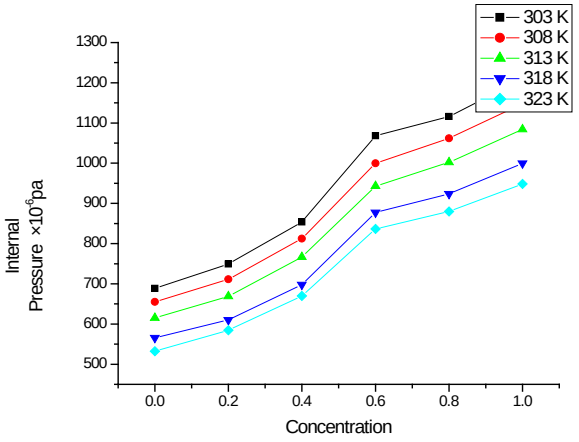

Fig. 8:

From Equation (6) Gibb's Free Energy is calculated and it is listed in the Table 3.

Table 3:

Temperature in Kelvin	Gibb's Free Energy $\Delta G^* 10^{-20}$KJ mol^{-1}
303	1.638
308	1.625
313	1.605
318	1.558
323	1.540

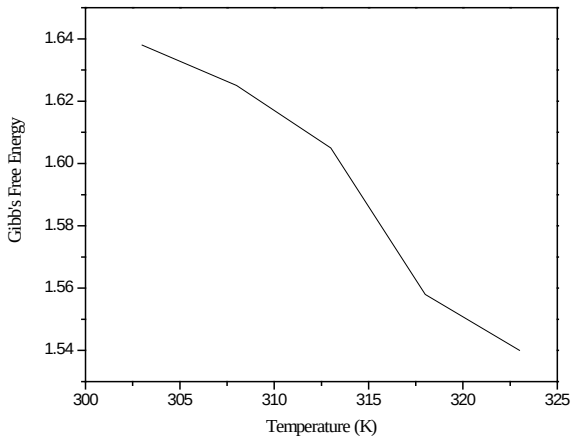

Fig. 9:

From figure 9 it is concluded that Gibb's free energy decreases with increase in temperature indicates the need for shorter time for the co-operative process or the rearrangement of the molecules in the mixtures. The increasing positive values of Gibb's function suggest that the closer approach of unlike molecules is due to hydrogen bonding.[10]

CONCLUSION

Ultrasonic studies have been carried out in the solutions of Toluene in Carbon Tetra Chloride at five different temperatures (namely 303K, 308K, 313K, 318K and 323K) for the concentration ranging from 0.0 to 1.0 with a difference of 0.2 . It is concluded that there exist a weak molecular interactions in the liquid mixtures. 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. The increasing value of acoustical impedance supports the possibility of molecular interactions between the unlike molecules.

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