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Ultrasonic Behaviour of Thiophenol in Carbon Tetrachloride

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Abstract: ***Ultrasonic velocity (U) and density (ρ) for the binary liquid mixtures of thiophenol with Carbon tetrachloride, have been measured for 2MHz ultrasonic frequency at 30^{0}C.The experimental data have been used to calculate acoustic parameters such as Adiabatic compressibility (β_{ad}), Intermolecular free length (L_f), Acoustic impedance (Z) and Relative association (R_A).The results are interpreted in terms of molecular interaction between the components of the mixture***

Keywords: Thiophenol, ultrasonic velocity, adiabatic compressibility, intermolecular free length, acoustic impedance, relative association.

1. Introduction

Determination of Ultrasonic velocity and absorption coefficient in liquid mixture helps us to reveal the intermolecular interaction due to its useful wave length range. Study of intermolecular interaction in liquid mixture provides valuable information regarding internal structure, molecular association, complex formation, internal pressure etc[1].

Thiophenol (Phenyl Mercaptan (C_6H_5SH)) is used as an intermediate in the manufacture of pesticides, pharmaceuticals and amber dyes and is also used as mosquito larvicides. It is an odorous, colorless liquid. The disagreeable odor has been described as penetrating, repulsive and garlic like. Phenyl Mercaptan depresses the central nervous system and affects the respiratory centre, similar to hydrogen sulfide, producing death by respiratory paralysis. Clinical signs of exposure are eye and mucous membrane irritation, headache, dizziness, staggering gait, nausea and vomiting. Paralysis of the locomotors muscles has also been observed.

Experimental investigation of dielectric properties of organic compounds is of great value in understanding the nature of complex formation between the molecules. The knowledge of dielectric properties of organic compounds and their mixtures at microwave frequencies helps in their characterization and applications (Kalamse et al., 2002). During literature review, the author came to know that thiophenol (Phenyl Mercaptan) due to its toxicity remains untouched. Therefore this is an attempt to throw light on thiophenol and its mixture with Carbon tetrachloride.

2. Experiment

In the present work, chemicals used are obtained from E-Merk, Germany and S.D. Fine Chemicals, India. A pyknometer employed to determine the density of mixture and Ultrasonic sound velocities were measured using multi frequency ultrasonic interferometer (Mittal M-83) at 2MHz for the system Thiophenol with Carbon tetrachloride [2].

From the measured values of density (ρ) and ultrasonic velocity (U), acoustic parameters like adiabatic compressibility (β_{ad}), intermolecular free length (L_f), Acoustic impedance (Z) and relative association (R_A) were calculated using the following relations.

$$\beta_{ad} = \frac{1}{\rho U^2} \ldots (1)$$

$$L_f = K\,(\beta_{ad})^{1/2} \ldots (2)$$

$$Z = U\rho \ldots (3)$$

$$R_A = \frac{\rho_s}{\rho_0}\left(\frac{U_0}{U_s}\right)^{1/3} \ldots (4)$$

Where, K is temperature dependent constant.

3. Results and Discussions

The observed values of ρ and U and calculated values of (β_{ad}), L_f, Z and R_A along with mole fraction (X) of thiophenol in carbon tetrachloride are listed in table 1. Also the graphical representations for above said parameters are depicted in fig. 1, 2, 3, 4 & 5.

Ultrasonic velocity of sound waves in a medium is fundamentally related to the binding forces between the molecules[3].

It has been observed that ultrasonic velocity increases with mole fraction of thiophenol in the system. The velocity increases non-linearly with concentration indicates that there is intermolecular interaction exists within the mixture. On the basis of the model for the sound propogation proposed by Eyring and Kincaid, ultrasonic velocity increases on decrease of intermolecular free length and vice-versa[4] as shown in fig. (1).

Adiabatic compressibility decreases with increase in concentration of thiophenol in the system as shown in fig (2) indicates that the free dipoles of thiophenol molecules would

induce moments in the neighbouring molecules of carbon tetrachloride resulting in dipolar – induced dipolar interaction leading to contraction in volume. This leads to subsequent decrease in adiabatic compressibility (β_{ad}) as well as intermolecular free length (L_f)[5] In fig. (3), the intermolecular free length decreases with concentration of thiophenol in the system. This is an indication that the structural readjustment in the liquid binary mixture proceeds in the direction of less compressible phase as closer packing of molecules[6]. When an acoustic wave travels in a medium, there is a variation of pressure from particle to particle. The ratio of the instantaneous pressure excess at any particle of the medium to the instantaneous velocity of that particle is known as specific acoustic impedance of the medium. This factor is governed by the inertial and elastic properties of the medium[7]. From Fig. (4), it is observed that the acoustic impedance (z) value increases with increase in concentration of thiophenol in the system. The linear variation in acoustic impedance with concentration of thiophenol confirms the presence of molecular association between solute – solvent molecules. Such increasing trends of impedance further support the possibility of molecular interaction between the solute – solvent molecules[8].

Relative association R_A is an acoustic property of understanding interaction, which is influenced by two opposing factors:
i) Breaking of solvent structure on addition of solute to it and
ii) Solvation of the solutes, those are simultaneously present, by the free solvent molecules.
The former effect results in the decrease in R_A values while the later resulting in increase of R_A values.

In fig (5), the R_A decreases with increase in concentration of thiophenol this means we can say that the thiophenol is breaking the solvent structure on addition to it to the carbon tetra chloride[9].

4. Excess Parameters

In order to understand the nature of molecular interactions between the components of the liquid mixtures, it is of interest to discuss the same in term of excess parameters rather than actual values. Non-ideal liquid mixtures show considerable deviation from linearity in their physical behaviour with respect to concentration and these have been interpreted as arising from the presence of strong or weak interactions. The extent of deviation depends upon the nature of the constituents and composition of the mixtures[5].
The values of excess adiabatic compressibility (($\Delta\beta_{ad}$), excess intermolecular free length (ΔL_f), and excess acoustic impedance (ΔZ) are enlisted in table No. 2 for the system and calculated using following relation[9].

$$\Delta Y = Y_m - (X_1Y_1 + X_2Y_2) \text{ --- } 5$$

Where, ΔY is any excess parameter. Y_m is the value of corresponding parameter of binary mixture. X_1 & X_2 are the mole fraction of liquid 1 and liquid 2 of the binary mixture. Y_1 and Y_2 are the corresponding parameters of pure liquid 1 and pure liquid 2 of the binary mixture.

Fig. 6 shows the graph of mole fraction of thiophenol (X) against excess adiabatic compressibility of carbon tetrachloride. In the system, $\Delta\beta$ shows negative values. The negative values of $\Delta\beta$ are attributed to intermolecular interactions due to charge transfer, dipole-dipole, dipole-induced dipole interactions, interstitial accommodation and orientational ordering.

Fig. 7 shows the graph of mole fractions of thiophenol (X) against excess intermolecular free length (ΔL_f) for the system carbon tetrachloride the values are negative. According to Kanappan et al.[6] , the negative values of ΔL_f indicates that sound waves cover long distances due to decrease in intermolecular free length describing the dominant nature of hydrogen bond interaction between unlike molecules. In the present study, the negative excess values of free length predict the existence of much more influenced molecular interactions,

Fig. (8) Shows the graph of mole fraction (X) of thiophenol against excess acoustic impedance (ΔZ) of carbon tetrachloride. Carbon tetrachloride shows positive values. The positive values of ΔZ clearly suggest that there is a strong molecular interaction existing between unlike molecules[7].

5. Conclusions

1) Intermolecular interaction exists between the components of mixture.
2) The result of excess properties reveals that, the molecular interaction exists in the mixtures which may be due to the dominance of hydrogen bonding between the mixing components.

Table 1: The values of ρ and U and calculated values of (β_{ad}), L_f, Z and R_A along with mole fraction (X) of thiophenol in carbon tetrachloride

X	ρ	v	$ß_{ad}$	z	R_A	L_f
0.0000	1592	914.4	7.5125	1.455725	1	5.67708
0.11886	1527.62	1010.4	6.41207	1.543507	0.92815	5.24483
0.23942	1463.25	1060.8	6.07316	1.552216	0.87473	5.10434
0.36167	1398.87	1115.2	5.748	1.560020	0.82242	4.96582
0.48571	1334.5	1183.2	5.3526	1.578980	0.76925	4.79198
0.61152	1270.12	1252.8	5.0164	1.591206	0.71832	4.63904
0.73918	1205.75	1298.4	4.91955	1.565546	0.67383	4.59405
0.86864	1141.37	1360.8	4.73135	1.553176	0.62795	4.50531
1.0000	1077	1455.2	4.38469	1.567250	-	4.33713

Table 2: The values of excess adiabatic compressibility (($\Delta\beta_{ad}$), excess intermolecular free length (ΔL_f), and excess acoustic impedance (ΔZ) along with mole fraction (X) of thiophenol in carbon tetrachloride

X	$\Delta ß_{ad}$	ΔL_f	ΔZ
0.000	0	0	0
0.119	-0.729	-0.273	0.075
0.239	-0.69	-0.252	0.07
0.362	-0.633	-0.227	0.064
0.486	-0.641	-0.234	0.069
0.612	-0.583	-0.219	0.067
0.739	-0.281	-0.093	0.027
0.869	-0.064	-0.008	6E-04
1.000	0	0	0

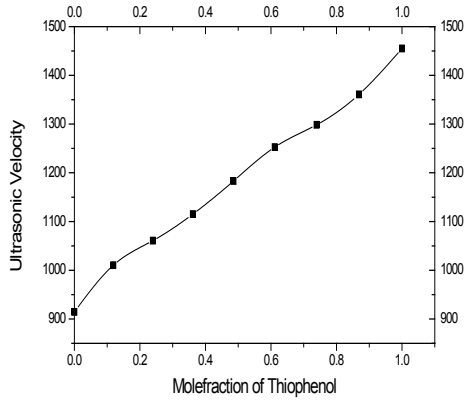

Figure 1: The Ultrasonic velocity for binary mixtures of thiophenol with carbon tetrachloride

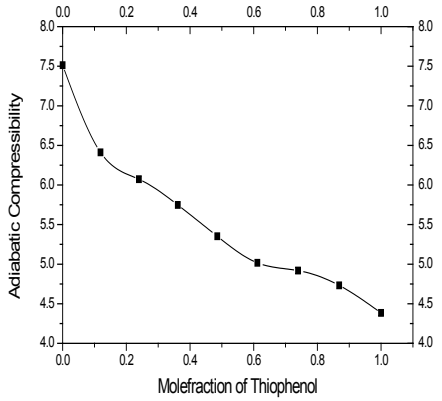

Figure 2: The Adiabatic Compressibility for binary mixtures of thiophenol with carbon tetrachloride

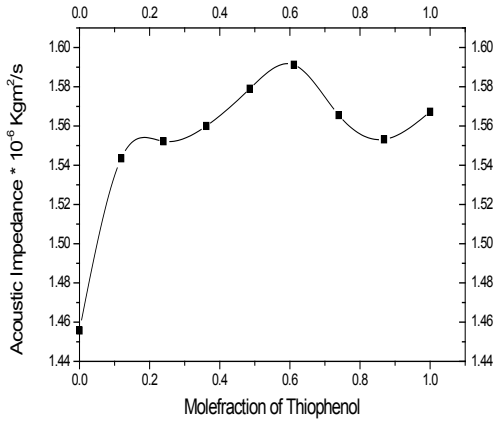

Figure 4: The Acoustic impendance for binary mixtures of thiophenol with carbon tetrachloride

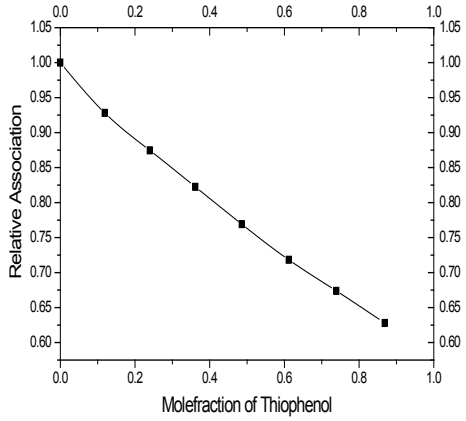

Figure 5: The Relative association for binary mixtures of thiophenol with carbon tetrachloride

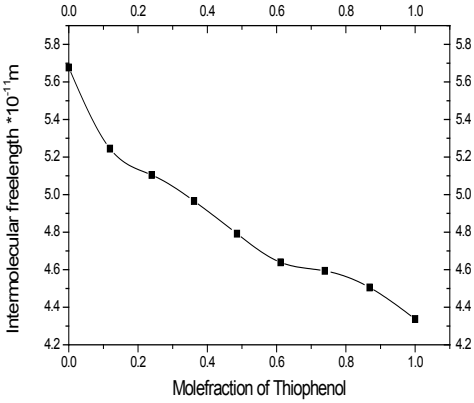

Figure 3: The Intermolecular free length for binary mixtures of thiophenol with carbon tetrachloride, cyclohexane and n-hexane

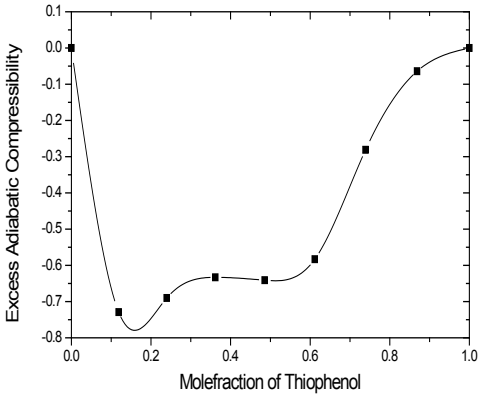

Figure 6: The Excess adiabatic compressibility for binary mixtures of thiophenol with carbon tetrachloride

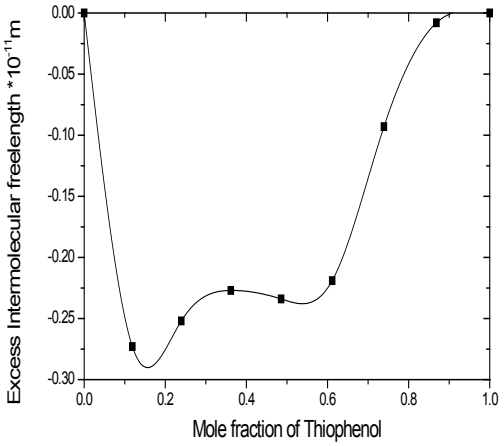

Figure7: The Excess intermolecular free length for binary mixtures of thiophenol with carbon tetrachloride

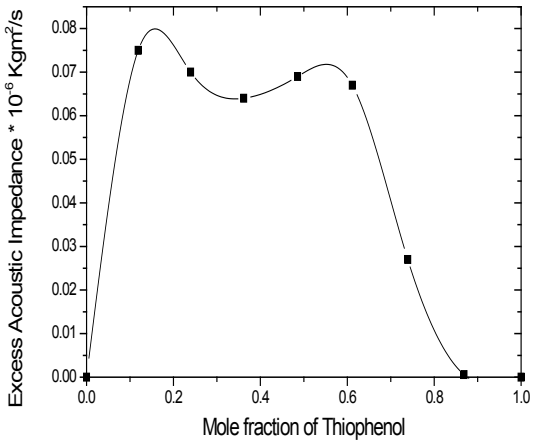

Figure 8: The Excess Impendence for binary mixtures of thiophenol with carbon tetrachloride

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