

Ultrasonic Studies of Substituted Aryl Bisthiourea in Binary Solution at 298K Temperature

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Abstract: *The ultrasonic velocity (u), density (ρ) and viscosity (η) have been measured for substituted aryl Bisthiourea in binary solution at 298K temperature by using ultrasonic interferometric technique. The observed experimental data have been used to study molecular interactions in different percent composition of 1,4 dioxane and water binary solution for different parameters such as adiabatic compressibility, apparent molar volume, apparent molar compressibility, relative association, acoustic impedance, free length, and relaxation time.*

Keywords: Substituted aryl bisthiourea, Binary solution, Ultrasonic velocity, Viscosity, Density, Acoustic parameters.

I. INTRODUCTION

Thiourea and its derivatives display a wide applications in industries, chemistry, medicine and others. It is a unique compound having three different functional groups which are amino, imino and thiol and it can occur in tautomeric forms. There are many possible reactions that can lead to synthesis of new derivatives. Thiourea derivatives are widely used in many fields including pharmaceutical industry due to their biological properties such as antiparasitic[1], anticancer[2], antimicrobial[3], antibacterial[4-5], antifungal[6] and antimalarial[7]. Thiourea derivative has been reported to have anti-oxidant[8-9], anti-HIV[10-11], anti-tuberculosis agent[12] and many other properties.

Due to numerous properties, thiourea becomes an important compound that has the ability to become a precursor in organic synthesis. In addition, bis-thiourea derivatives are used as powerful organocatalysts in asymmetric organic reactions. The synthesis and antibacterial studies of monothiourea derivative are progressing at the considerable rate while bisthiourea compounds are relatively less reported. In present study, ultrasonic parameters investigated for substituted aryl bisthiourea in 1,4dioxane and water binary solution.

In recent years, the measurement of ultrasonic velocity have been extensively applied in understanding the nature of molecular systems, physicochemical behaviour and molecular interactions in liquid mixtures. The ultrasonic velocity measurements are highly sensitive to weak and strong molecular interaction and find extensive applications in physico-chemical study of binary and ternary liquid mixtures. Mahajan M.M. et al [13] studied molecular interactions of N-(2-hydroxybenzylidene)-3-substituted pyridine-2-amine Schiff bases in ethanol-water mixture by interferometric measurement. Rode S. Et al [14] studied theoretical velocities of binary liquid mixtures of 1,4-dioxane with ethylamine, diethylamine and triethylamine at 7MHz at temperatures 308.15K and evaluated as a function of mole concentration and showed that there is a deviation between experimental and theoretical values which confirms the existence of molecular interaction. Ganjare P.J. et al [15] have been measured ultrasonic speed, density and viscosity of sodium salicylate solution using ethanol and water in 1:1 ratio as a solvent at 298K, 303K and 308K and ultrasonic speed at 4MHz frequency and observed that molecular interactions are due to heteromolecular interactions in the solutions by the formation of hydrogen bonds. This gives valuable information about the existence of intermolecular and intramolecular interactions in the liquid mixtures.

Due to non-destructive nature, ultrasonic investigation has wide range of application in material science, polymer, surface profiling, astronomy, agriculture, medicine, biology, industry, oceanography and sonochemistry research.

II. MATERIAL AND METHODS

In the present study, the chemicals used were of A.R. grade. They were purified by recommended methods. All the weighing in the present study was made on MechanikiZakatasyPrecyzynej Gdansk balance made in Poland. The densities of the solution were determined by standardize capillary pyknometer containing a bulb of volume of about 10 cm³ and capillary having an internal diameter of 1 mm. An Ostwald's viscometer was used for the viscosity determination of pure liquid and liquid mixtures. The flow of time of pure liquid and liquid mixtures was measured using an accurate stop watch with a precision of ±0.1. The velocity of sound waves was found using an ultrasonic interferometer (Mittal Enterprises, New Delhi) at a fixed frequency of 1MHz with an accuracy of ±2ms⁻¹. All the solutions for investigation were freshly prepared from the deionized water to avoid any ionic contamination. The 0.01M solution of each ligand was prepared in different percentage (75%, 80%, 85% and 90%) of 1,4-dioxane-water mixture. The density, viscosity and the ultrasonic velocity measurements of the ligand solutions were done at different temperature. In present study, results were discussed for 298K temperature.

III. RESULTS AND DISCUSSION

These experimental values are used in computing various thermodynamic parameters such as Adiabatic compressibility (β_s), Apparent Molar compressibility (Φ_k), Specific acoustic impedance (Z), Intermolecular free length (L_f), Relative association (R_A) measurements are presented in Tables 1,2 & 3. The variation of ultrasonic velocity (u) and densities (ρ) and viscosities (ν) with volume component percentage of the systems of 1,4dioxane are shown in Fig. 1,2 & 3.

The following formulae were used to calculate the acoustical parameters.

1. Adiabatic Compressibility (β_s) = 1/u²ρ_s
2. Free Length (L_f) = K√β_s
3. Specific acoustic impedance (Z)=u_sρ_s
4. Apparent Molar compressibility (Φ_k)=[1000(β_sρ₀-β₀ρ_s)/mρ_sρ₀] + [β_sM/ρ_s]
5. Relative association (R_A)= ρ_s/ρ₀[u₀/u_s]^{-1/3}
6. Relaxation time (τ) = 4/3 β x η

The experimental data relating to viscosity, density and ultrasonic velocity at 298K for the mixture.

Table 1: Ligand L₁: 1-phenyl Bisthiourea

Temp. = 298K, Conc.= 0.01M, Ultrasonic Frequency: 1MHz

% Dioxane	U (m/sec)	ds x 10 ³ (Kg.m ⁻³)	η (Kgm ⁻¹ s ⁻¹)	βs x 10 ⁻¹⁰ (pa ⁻¹)	τx 10 ⁻¹⁰ (S)
75	1491.888	0.9729	1.0132	4.6180	6.2386
80	1447.208	0.9711	1.0149	4.9167	6.6533
85	1442.376	0.9723	1.0293	4.9435	6.7845
90	1446.392	0.9694	1.0397	4.9308	6.8354
% Dioxane	Φ _k x 10 ⁻⁶ (m ³ mol ⁻¹ pa ⁻¹)	Φ _v x 10 ⁻⁵ (m ³ mol ⁻¹)	R _A	L _f x 10 ⁻¹¹ (m ⁻¹)	Z x 10 ³ (kg m ⁻² sec ⁻¹)
75	-10.8101	1.0267	0.9788	4.4188	1451.457
80	-7.7181	1.0288	0.9869	4.5594	1405.383
85	-7.5195	1.0274	0.9892	4.5719	1402.422
90	-7.4767	1.0308	0.9854	4.5660	1402.132

Table 2: Ligand L₂: p-tolylBisthiourea

Temp. = 298K, Conc.= 0.01M, Ultrasonic Frequency: 1MHz

% Dioxane	U (m/sec)	ds x 10 ³ (Kg.m ⁻³)	η (Kgm ⁻¹ s ⁻¹)	βs x 10 ⁻¹⁰ (pa ⁻¹)	τx 10 ⁻¹⁰ (S)
75	1484.008	0.9770	1.0985	4.6476	6.8072
80	1463.192	0.9758	1.1378	4.7867	7.2617
85	1458.448	0.9752	1.1986	4.8208	7.7043
90	1444.808	0.9688	1.3173	4.9447	8.6849
% Dioxane	Φ _k x 10 ⁻⁶ (m ³ mol ⁻¹ pa ⁻¹)	Φ _v x 10 ⁻⁵ (m ³ mol ⁻¹)	R _A	L _f x 10 ⁻¹¹ (m ⁻¹)	Z x 10 ³ (kg m ⁻² sec ⁻¹)

75	-10.7543	1.0220	0.9846	4.4329	1449.875
80	-9.2934	1.0234	0.9881	4.4987	1427.782
85	-8.9167	1.0241	0.9885	4.5148	1422.278
90	-7.3028	1.0315	0.9851	4.5724	1399.729

Table 3: Ligand L₃: p-chlorophenylBisthiourea

Temp. = 298K, Conc.= 0.01M, Ultrasonic Frequency: 1MHz

% Dioxane	U (m/sec)	ds x 10 ³ (Kg.m ⁻³)	η (Kg.m ⁻¹ .s ⁻¹)	βs x 10 ⁻¹⁰ (pa ⁻¹)	τx 10 ⁻¹⁰ (S)
75	1481.656	0.9747	1.1767	4.6734	7.3323
80	1476.800	0.9723	1.1962	4.7158	7.5214
85	1450.472	0.9735	1.2028	4.8825	7.8302
90	1452.784	0.9717	1.2818	4.8760	8.3334
% Dioxane	Φ _k x 10 ⁻⁶ (m ³ mol ⁻¹ pa ⁻¹)	Φ _v x 10 ⁻⁵ (m ³ mol ⁻¹)	R _A	L _r x 10 ⁻¹¹ (m ⁻¹)	Z x 10 ³ (kg m ⁻² sec ⁻¹)
75	-10.3619	1.0246	0.9828	4.4452	1444.170
80	-9.7973	1.0274	0.9815	4.4653	1435.892
85	-8.2004	1.0260	0.9886	4.5435	1412.034
90	-8.1600	1.0281	0.9862	4.5405	1411.670

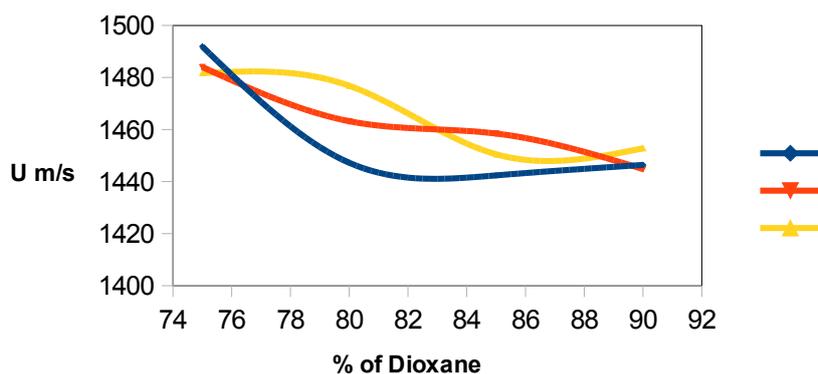


Figure [1]: Variation of ultrasonic velocity with concentration of substituted bisthiourea in 1,4dioxane and water binary solution at 298K.

It was found that the ultrasonic velocity (U) decreased with the increase in concentration of 1,4Dioxane and water mixture. It happened because there was significant interaction between ions and solvent molecules suggesting a structure promoting behaviour of the added solvent mixture. The changes in ultrasonic velocity for solution depends upon the increase or decrease of molecular free length after mixing the component.

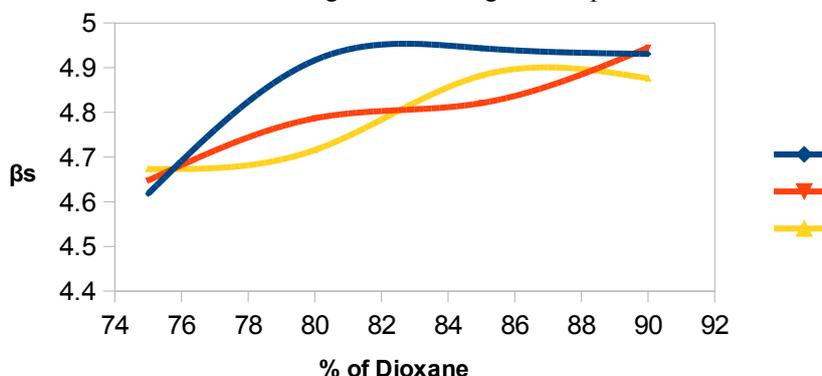


Figure [2]: Variation of Adiabatic compressibility with concentration of substituted bisthiourea in 1,4dioxane and water binary solution at 298K.



The adiabatic compressibility (β_s) increased with the increase in concentration of solution. It mainly due to collection of solvent molecule around ions, this supporting weak ion-solvent interaction. This indicates that there is significant solute- solvent interaction.

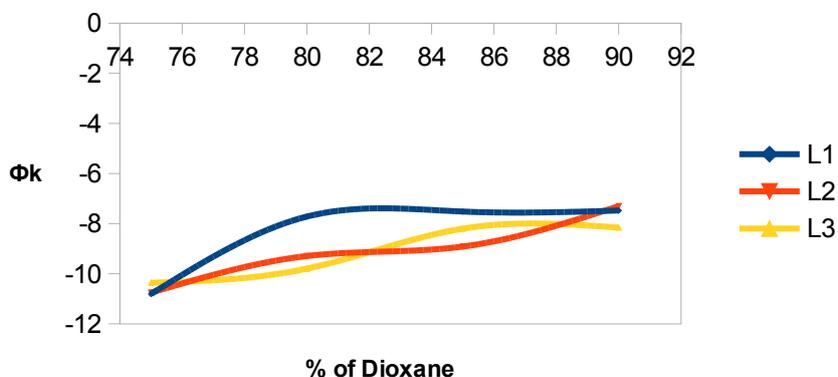


Figure [3]: Variation of Apparent molar compressibility with concentration of substituted bithiourea in 1,4 dioxane and water binary solution at 298K.

It was found that the value of apparent (molar) adiabatic compressibility (Φ_k) was increased with increase in concentration of ligands in dioxane. It has showed strong electrostatic attractive force in the vicinity of ions.

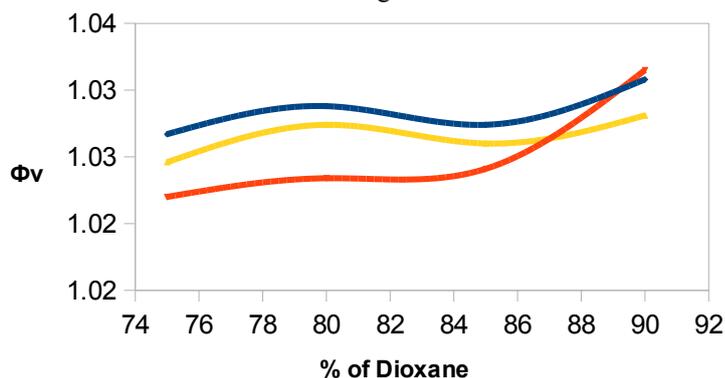


Figure [4]: Variation of Apparent molar volume with concentration of substituted bithiourea in 1,4 dioxane and water binary solution at 298K.

It was observed that apparent molar volume (Φ_v) increased with concentration in both systems. It indicates the existence of strong ion-solvent interaction.

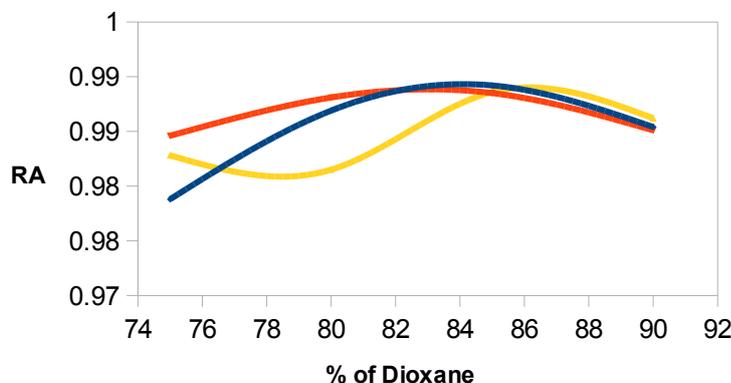


Figure [5]: Variation of Relative association with concentration of substituted bithiourea in 1,4 dioxane and water binary solution at 298K.



Relative association (R_A) is influenced by two factors (i) the breaking up of the solvent molecules on addition of electrolyte to it resulting in decrease in value of R_A and (ii) the solvation of ions that are simultaneously present, resulting in increase in the value of R_A . It was observed that the value of relative association (R_A) increased with the increased in concentration. It has found that there was strong interaction between solute and solvent. The increase of R_A with concentration suggests that solvation of ions predominates over the breaking up of the solvent aggregate (1,4Dioxane-water) on addition of substituted Bisthioureas.

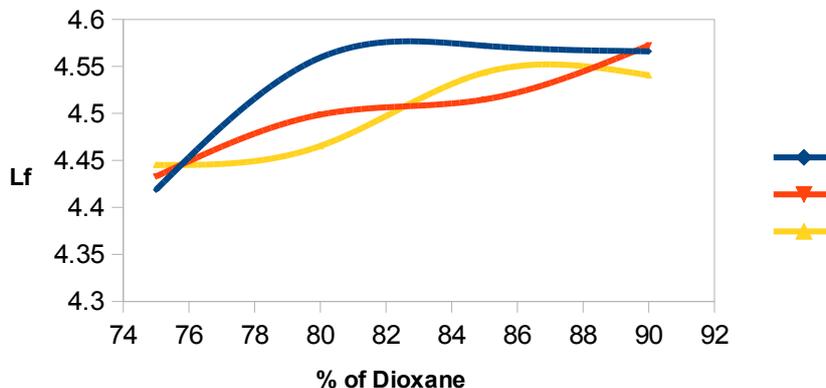


Figure [6]: Variation of Intermolecular Free length with concentration of substituted bisthiourea in 1,4 dioxane and water binary solution at 298K.

Intermolecular free length (L_f) is an important parameter that has association with adiabatic compressibility (β_s). It is clear that the intermolecular free length shows a similar behavior as reflected by ' β_s '. Thus the free length is a predominant factor in determining the variation of ultrasonic velocity in solutions. The inter dependence of ' L_f ' and ' U ' has been evolved from a model for sound propagation proposed by Eyring and Kincaid. According to the proposed theory, the increase in the value of ' β_s ' and ' L_f ' with decrease in ultrasonic velocity further strengthens the process of complex formation between the solute molecules due to which structural arrangement is considerably altered. In the present study also, there is a possibility of complex formation due to interactions as revealed by the nonlinear variation of ultrasonic velocity and their related parameters due to strong interaction of forces.

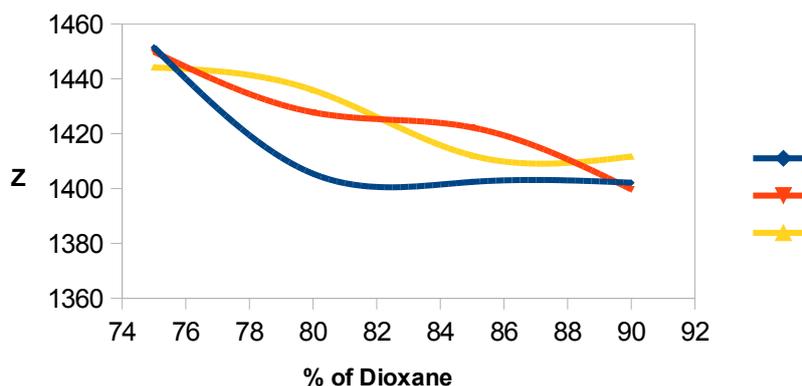


Figure [7]: Variation of Acoustic impedance (Z) with concentration of substituted bisthiourea in 1,4 dioxane and water binary solution at 298K.

From data, it shows the variation of acoustic impedance with concentration and it is important to examine specific acoustic impedance in relation to concentration and temperature. In the present study, the specific acoustic impedance (Z) decreased with the increase in concentration in dioxane and water mixture. When concentration of solution was increased, the thickness of oppositely charged ionic atmosphere increases due to decrease in ionic strength. This is suggested by decrease in acoustic impedance with increase concentration.

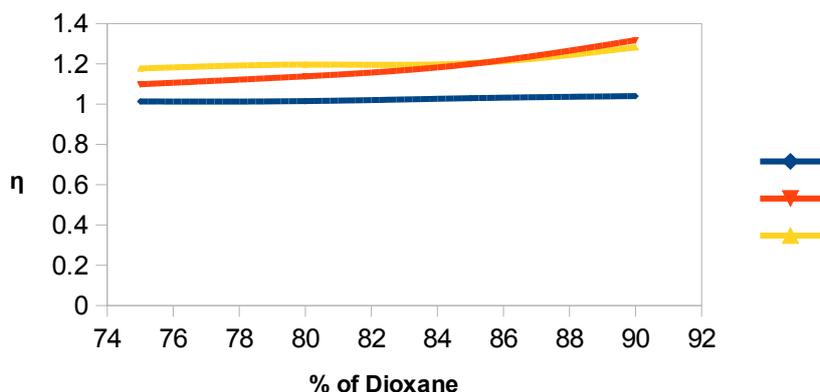


Figure [8]: Variation of viscosity with concentration of substituted bithiourea in 1,4 dioxane and water binary solution at 298K.

The relative viscosity increases with increase in the concentration of solute that may be attributed to increasing solute-solvent interactions.

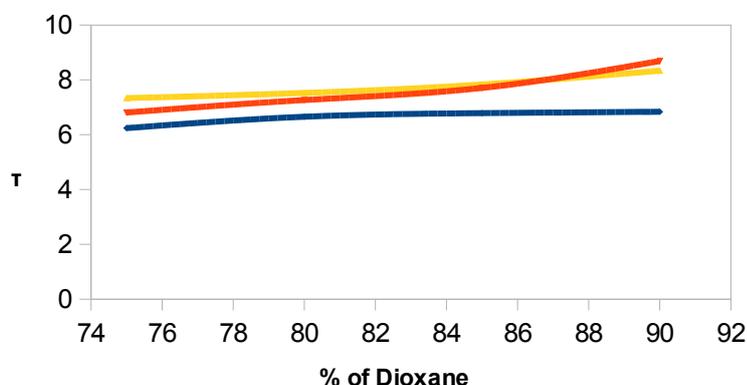


Figure [9]: Variation of Relaxation Time with concentration of substituted bithiourea in 1,4 dioxane and water binary solution at 298K.

Acoustical relaxation time varies mainly due to the variations in the viscosity of the solutions due to both concentration and temperature. In present study it increases with increase in concentration.

IV. CONCLUSION

The present study shows the experimental data for ultrasonic velocity, density and viscosity at 298K for substituted Bithiourea in 1,4dioxane . From observed experimental data, the acoustical properties were calculated for present system. The solute-solvent interaction and ion-ion / solute-solute interaction existing between solute and 1,4dioxane were also studied with the help of experimental data. Lastly it has been concluded from the experimental data, that the solute-solvent interaction in aryl substituted bithiourea and binary solution systems are weak.

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