

STUDIES OF SOME ACOUSTIC PROPERTIES OF SUBSTITUTED THIAZOLYL SCHIFF'S BASES IN BINARY SOLVENT MIXTURES AT $30 \pm 0.1^\circ\text{C}$

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ABSTRACT

Density (ρ), and Ultrasonic velocity (U) in binary mixtures of thiazolyl substituted schiff's bases with dioxane-water, acetone-water and ethanol-water mixture were measured at 30°C by using a Ultrasonic Interferometer at a frequency of 1 MHz. The study was carried out with change in concentrations & were used to calculate various thermodynamic parameters such as adiabatic compressibility (β_s), Apparent molar compressibility (ϕ_{β}), Apparent molar volume (ϕ_V), intermolecular free length (L_f), specific acoustic impedance (Z) and relative association (R_A). The results were used to discuss the interaction between solute and solvent.

Keywords: Ultrasonic velocity, Density, Thiazolyl substituted schiff's bases.

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INTRODUCTION

The study of propagation of ultrasonic waves in liquid systems and solids is now well established as an effective means of examining certain physical properties of the materials. It is particularly well adapted to examine changes in such physical properties at the micro level. Also the ultrasonic measurements provide useful information regarding the molecular interactions in pure liquids, liquid mixtures and ionic interactions in pure liquids, liquid mixtures and ionic interactions in solutions comprising of either single or mixed solutes¹⁻⁴. The study of the solution properties of liquid mixtures consisting of polar as well as non-polar components finds applications in industrial and technological processes⁵. Most of the work on binary mixtures is channelized towards the estimation of thermodynamic parameters like adiabatic compressibility, free length, etc., and their excess values so as to relate them towards explaining the molecular interactions taking place between these components of the binary mixtures⁶⁻¹². The data obtained from ultrasonic propagation parameters in liquid mixtures and solutions viz., ultrasonic velocity and attenuation, and their variation with concentration of one of the components, helps to understand the nature of molecular interactions in the mixtures. Owing to high sensitivity to very low population densities at high energy states, ultrasonic methods have been preferred, and are reported to be complementary to the other techniques, like dielectric relaxation, infrared spectroscopy, nuclear magnetic resonance, etc. Thiazoles are the important class of heterocyclic compounds found potent biologically active¹³⁻¹⁴. We have synthesized some new thiazole derivatives. In continuation of our work we intended to investigate the solute-solute, solute-solvent molecular interactions of these newly synthesized thiazole derivatives in the polar acetone, ethanol and non-polar dioxane solvents. Adiabatic compressibility β_s , Apparent molar compressibility ϕ_{β} , Apparent molar volume ϕ_V , intermolecular free length L_f , specific acoustic impedance Z and relative association R_A are determined from the ultrasonic velocity and density measurements of the solutions at 30°C . From the observations of these properties the molecular interactions are predicted.

EXPERIMENTAL

All the chemicals used were of AR grade. 2-[3-(4-methoxy phenyl)-1-(4-phenyl-thiazol-2-ylimino)-allyl]-4-methyl phenol (MPPTMP-I), 2-[3-phenyl-1-(4-phenyl-thiazol-2-ylimino)-allyl]-4-methoxy phenol (PPTMP-I), 2-[3-(4-chlorophenyl)-1-(4-phenyl-thiazol-2-ylimino)-allyl]-4-methyl-phenol (CPTMP-I).

These compounds are recrystallized. The double distilled water was used for preparation of solutions. Densities were measured with the help of bicapillary pycnometer. Weighing was done on Contech CB-Series Balance, (± 0.001 g). Interferometer (Mittal Enterprises, Model F-80 D) with accuracy of $\pm 0.03\%$ and frequency 1 MHz was used in the present work. The working of the ultrasonic interferometer was checked by measuring ultrasonic velocity of pure water at 303.15 K. The measured value 1489 ms^{-1} is in good agreement with literature¹⁵ value. The densities and ultrasonic velocities of all compounds in acetone solvent were measured at 303.15 K.

In the present investigation, different thermodynamic parameters such as adiabatic compressibility β_s , Apparent molar compressibility ϕ_k , Apparent molar volume ϕ_v , intermolecular free length (L_f), specific acoustic impedance (Z) and relative association (R_A) have been calculated at 30°C in dioxane-water, acetone-water and ethanol-water mixture with the help of following equations-

$$\beta_s = \frac{1}{U_s^2 \cdot ds} \quad (1)$$

$$\phi_v = \left(\frac{M}{ds} \right) + \left[\frac{(d_0 - ds) \times 10^3}{m \times ds \times d_0} \right] \quad (2)$$

$$\phi_k = \frac{\beta_s \cdot M}{ds} + \left[\frac{1000(\beta_s d_0 - \beta_0 ds)}{m \times ds \times d_0} \right] \quad (3)$$

$$L_f = K \sqrt{\beta_s} \quad (4)$$

$$Z = U_s \cdot ds \quad (5)$$

$$R_A = \frac{ds}{d_0} \left(\frac{U_0}{U_s} \right)^{1/2} \quad (6)$$

Where, d_s , d_0 and U_s , U_0 are the densities and ultrasonic velocities of solution and pure solvent respectively. M is the molecular weight of substituted thiazoles. β_s and β_0 are the adiabatic compressibilities of solution and solvent respectively. K is Jacobson's constant and m is the molality of solution.

Table-1: Ultrasonic velocity (U_s), density(d_s), Adiabatic compressibility (β_s), Intermolecular free length (L_f), Apparent molal volume (ϕ_v), Apparent molal compressibility (ϕ_k), Relative Association (R_A) and Specific Acoustic Impedance (z) at different concentrations.
[Temperature: $30 \pm 0.1^\circ \text{C}$; Ultrasonic freq: 1 MHz; Medium : 70% Acetone –Water mixture]

Conc. M	Density (d_s) gm^{-1}	Ultrasonic Velocity (U_s) ms^{-1}	Adiabatic compressibility (β_s) $\times 10^{-6} \text{ m}^2 \text{ n}^{-1}$	Inter molecular free length (L_f)	Apparent molal volume (ϕ_v) $\times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$	Apparent molal compressibility (ϕ_k) $\text{m}^2 \text{ n}^{-1}$	Relative Association (R_A)	Specific Acoustic Impedance (z) $\times 10^2 \text{ v kg m}^2 \text{ s}^{-1}$
System-MPPTMP-I								
0.01	0.8861	941.8	1.27	67888	12.3418	4.8891	0.4625	8.3452
0.02	0.8870	944.6	1.26	6.7652	6.0124	2.4423	0.4616	8.3786
0.03	0.8878	947.9	1.25	6.7386	3.8986	1.6269	0.4604	8.4154
0.04	0.8890	948.9	1.25	6.7270	2.2182	1.2185	0.4604	8.4357
0.05	0.8898	951.3	1.24	6.7070	1.4060	0.9740	0.4598	8.4646

System-PPTMP-I								
0.01	0.9001	950.6	1.23	6.6738	8.3156	4.8183	0.4654	8.5554
0.02	0.9250	953.7	1.19	6.5616	5.4193	2.3460	0.4768	8.8217
0.03	0.9256	956.8	1.18	6.5382	3.9653	1.5631	0.4755	8.8561
0.04	0.9260	959.2	1.17	6.5204	3.1072	1.1718	0.4746	8.8821
0.05	0.9270	961.5	1.17	6.5013	1.8301	0.9365	0.4739	8.9131
System-CPTMP-I								
0.01	0.9357	961.5	1.16	6.4710	8.9516	4.6424	0.4784	8.9967
0.02	0.9362	963.0	1.15	6.4592	5.8353	2.3199	0.4779	9.0156
0.03	0.9367	965.8	1.14	6.4388	4.2714	1.5458	0.4768	9.0466
0.04	0.9370	969.6	1.14	6.4125	3.3495	1.1591	0.4750	9.0851
0.05	0.9380	971.4	1.13	6.3972	1.8828	0.9263	0.4747	9.1117

Table-2: Ultrasonic velocity (Us), density(ds), Adiabatic compressibility (β_s), Intermolecular free length (L_F), Apparent molal volume (v_ϕ), Apparent molal compressibility (k_ϕ), Relative Association (R_A) and Specific Acoustic Impedance (z) at different concentrations.
[Temperature: 30 ± 0.1 °C; Ultrasonic freq: 1 MHz; Medium : 70% Dioxane – water mixture]

Conc. M	Density (ds) gm^{-3}	Ultrasonic velocity (Us) ms^{-1}	Adiabatic compressibility (β_s) $\times 10^{-6} \text{m}^2 \text{n}^{-1}$	Inter molecular free length (L_F)	Apparent molal volume (v_ϕ) $\times 10^{-3} \text{m}^3 \text{mol}^{-1}$	Apparent molal compressibility (k_ϕ) $\text{m}^2 \text{n}^{-1}$	Relative Association (R_A)	Specific Acoustic Impedance (z) $\times 10^2 \text{v kg m}^2 \text{s}^{-1}$
System-MPPTMP-I								
0.01	0.8501	841.8	1.66	7.7549	7.5304	5.0509	0.5750	7.1553
0.02	0.8510	837.9	1.67	7.7864	3.6096	2.5213	0.5784	7.1305
0.03	0.8529	834.8	1.68	7.8066	2.3446	1.6765	0.5818	7.1200
0.04	0.8432	831.0	1.72	7.8873	1.3038	1.2706	0.5778	7.0069
0.05	0.8350	827.2	1.75	7.9623	7.1484	1.0255	0.5748	6.9071
System-PPTMP-I								
0.01	0.9620	924.8	1.22	6.6352	7.2896	4.5093	0.4578	8.8965
0.02	0.9631	922.6	1.22	6.6470	3.7987	2.2510	0.4594	8.8855
0.03	0.9642	920.7	1.22	6.6572	2.6347	1.4990	0.4609	8.8773
0.04	0.9648	918.7	1.23	6.6696	2.0662	1.1233	0.4622	8.8636
0.05	0.9656	915.4	1.24	6.6909	1.7206	0.8976	0.4642	8.8391
System-CPTMP-I								
0.01	0.9781	948.4	1.14	6.4170	5.5976	4.4435	0.4538	9.2753
0.02	0.9790	944.2	1.15	6.4422	2.9639	-2.218	0.4563	9.2457
0.03	0.9801	941.4	1.15	6.1518	2.0858	1.4773	0.4581	9.2257
0.04	0.9810	938.9	1.16	6.4720	1.6466	1.1066	0.4598	9.2106
0.05	0.9830	932.8	1.17	6.5077	1.3617	0.8831	0.4638	9.1694

The ultrasonic velocity of the liquids and liquid mixtures can be calculated using the relation-

$$\lambda = 2d/n \quad (7)$$

The sound velocities of thiazoles were measured in 0.01 M to 0.05 M range in dioxane - water mixture, acetone - water mixture and ethanol- water mixture.

From the measured value of wavelength (λ), the ultrasonic velocity (U) can be calculated using the relation-

$$U = v\lambda \text{ ms}^{-1} \quad (8)$$

Where, v is the frequency of the generator which is used to excite the crystal whose value is 2×10^6 hertz.

Table-3: Ultrasonic velocity (Us), density(ds), Adiabatic compressibility (β_s), Intermolecular free length (L_f), Apparent molal volume (ϕv), Apparent molal compressibility (ϕk), Relative Association (R_A) and Specific Acoustic Impedance (Z) at different concentrations.
 [Temperature: 30 ± 0.1 °C; Ultrasonic freq: 1 MHz; Medium : 70% Ethanol – water mixture]

Conc. M	Density (ds) gm^{-3}	Ultrasonic velocity (Us) ms^{-1}	Adiabatic compressibility (β_s) $\times 10^{-6} \text{m}^2 \text{n}^{-1}$	Inter molecular free length (L_f)	Apparent molal volume (ϕv) $\times 10^{-3} \text{m}^3 \text{mol}^{-1}$	Apparent molal compressibility (ϕk) $\text{m}^2 \text{n}^{-1}$	Relative Association (R_A)	Specific Acoustic Impedance (Z) $\times 10^2 \text{v kg m}^2 \text{s}^{-1}$
System-MPPTMP-I								
0.01	0.9480	935.3	1.21	6.6090	20.7571	4.5769	0.4850	8.8664
0.02	0.9521	938.8	1.19	6.5719	10.3998	2.2793	0.4898	8.9354
0.03	0.9581	940.8	1.18	6.5360	7.0209	1.5103	0.4917	9.0128
0.04	0.9640	943.6	1.17	6.4963	5.3306	1.1259	0.4933	9.0963
0.05	0.9740	945.3	1.15	6.4512	4.4021	0.8917	0.4976	9.2072
System-PPTMP-I								
0.01	0.9520	941.3	1.19	6.5531	21.1726	4.5598	0.4884	8.9611
0.02	0.9561	945.7	1.17	6.5089	10.5920	2.2709	0.4882	8.0408
0.03	0.9620	948.6	1.16	6.4688	7.1381	1.5040	0.4897	9.1255
0.04	0.9680	951.8	1.14	6.4270	5.4105	1.1219	0.4911	9.2134
0.05	0.9741	954.6	1.13	6.3884	4.3734	0.8922	0.492	9.2978
System-CPTMP-I								
0.01	0.9401	950.9	1.19	6.5282	19.8102	4.6189	0.4774	8.9384
0.02	0.9480	954.6	1.16	6.4754	10.1312	2.2907	0.4796	9.0496
0.03	0.9561	957.8	1.14	6.4267	6.9023	1.5148	0.4820	9.1565
0.04	0.9641	959.8	1.13	6.3866	5.2860	1.1269	0.4850	9.2524
0.05	0.9720	960.7	1.11	6.3544	4.3148	0.8942	0.4886	9.3380

RESULTS AND DISCUSSION

The experimental values of density (ρ), viscosity (η) and ultrasonic velocity (U), adiabatic compressibility, acoustic impedance, apparent molal compressibility, apparent molal volume and relative association at different concentration at temperature 303°K are shown in Table 1, 2 & 3. The ultrasonic velocity values found to be increasing with increase in concentration of thiazoles (table no.1-3). Molecular association is thus responsible for the observed increase of ultrasonic velocities. This may be due to the cohesion brought about by the ionic hydration. The increased β_s values with the increase of concentration of solute in dioxane-water mixture may be due to departure of solvent molecules around the ions. The variations in results of β_s values for acetone-water mixture may be due to variations in solute-solvent interactions. It is observed that there is linear variation of R_A and Z with concentration in dioxane-water mixture & non-linear variation in acetone-water and alcohol-water mixture. The values of R_A & Z increases with increase in concentration of solute in Acetone-water and Ethanol-water mixture.

The values of intermolecular free length (L_f) decreases in acetone-water and ethanol-water mixture with increase in concentration of solutes and it found to be increases with increases in concentration in dioxane-water mixture. This indicates that there is weak solute-solvent interaction. This may also imply the increase in number of free ions, showing the occurrence of ionic dissociation due to weak ion- interactions. Three types of Vander wall's forces interacting exists between liquid molecules as London forces, dipole-dipole interaction and hydrogen bonding. Water is polar solvent and exhibit hydrogen bonding but has weak London forces. With the addition of other solvent intermolecular forces are interrupted and new force developed which again changes on addition of other solvent.

ACKNOWLEDGEMENTS

The authors are thankful to the Principal, Shri Shivaji Science College Amravati for providing necessary facilities during this work.

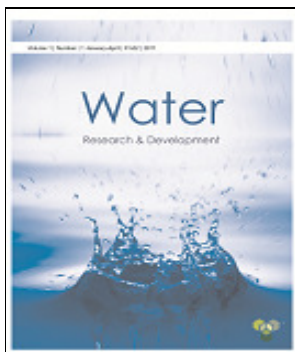
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[RJC-986/2013]

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ISSN: 2249-2003
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[April, August and December]

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