Ultrasonic study of substituted Thiazoles at different temperatures

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ABSTRACT. Density, ultrasonic velocity of pure solvent, dimethylformamide (DMF) and ligand solutions of substituted thiazoles in DMF-water mixture were measured at different temperatures (303.15, 308.15, 313.15 and 318.15) K. Acoustical parameters such as adiabatic compressibility, intermolecular free length, acoustical impedance and relative association were determined from experimental data of density and ultrasonic velocity. The effect of temperature variations on the strength of molecular interaction has also been studied. An excellent correlation represents in terms of solute-solvent and solvent-solvent interaction at all temperatures.

INTRODUCTION

The measurement of physico-chemical properties of pure components and their mixtures are being used as a tool for investigations of molecular interactions. Among these density, viscosity and ultrasonic velocity plays an important role in many industrial process[1]. Ultrasonic method have established a permanent place in science and technology and found the solution of many theoretical and practical problems[2]. Most important features of ultrasonic systems are rapidity, robustness, non-invasiveness and high precession. The concentration and temperature dependance of acoustical and thermodynamical properties like adiabatic compressibility, linear free length, acoustic impedance and relative association etc. have proven immense value in predicting nature and strength of molecular interaction in liquid medium[3-5].

Heterocyclic compounds provide a great variability due to their having number of potential substitution and possibility of formation complexes with metal ions[6-8]. In the recent years thiazole derivatives have attracted immense attention because of their broad range of biological and medicinal applications[9,10]. The applications of these thiazoles in different field of science developed our interest in the measurement of their velocities and densities and compute the acoustical properties to understand their interaction with non aqueous solvent mixture at different temperature.

Dimethylformamide (DMF), a simplest amide containing a peptide linkage is molecules are highly polar and strongly self-associated through extensive three-dimensional network of hydrogen bonds, through its three hydrogen bond donors (3H atoms) and three acceptors (two lone pairs of electrons at oxygen and one at nitrogen atom). The study of their hydrogen bonding yields into the nature of protein structure[11]. It is mainly used as a reagent in various organic synthesis with some applications as a highly polar solvent.

The present work is the continuation of our earlier studies on thermodynamical and acoustical properties of binary and ternary mixtures[12-14]. The ultrasonic velocities, densities and relative association of substituted thiazoles used in this investigation in polar aprotic-polar protic mixed media at different temperature was lacking and therefore the present work is undertaken to study sound velocities and densities of these thiazoles of 0.01 mol/dm³ concentrations in 70:30 (v/v) DMF-water mixture at different temperature (303.15, 308.15, 313.15 and 318.15) K in order to know effect of temperatures on various acoustical properties.
2. MATERIALS AND METHOD:
The solvent Dimethylformamide (DMF) of Anal grade used without purification. The ligands 2-Mercaptobenzothiazole \( L_1 \), 2-Amino-5-methylthiazole \( L_2 \), 2-Amino-5-nitrothiazole \( L_3 \), 2-Chlorobenzothiazole \( L_4 \) and Benzoylthiazole \( L_5 \) used were of Anal grade (Hi-MEDIA, India). The ligand solutions were prepared by dissolving an accurate amount in an organic-aqueous mixture in standard flask with airtight caps and the mass measurement were performed using high precision digital balance (Shimadzu, Japan accuracy ± 0.1 mg). The ultrasonic velocities of pure component and their mixtures were measured by ultrasonic interferometer (Mittal enterprises, model F-18s) at 2 MHz with frequency tolerance ± 0.03 %. It consists of high frequency generator and a measuring cell. The densities of DMF and ligand solutions were measured by digital density meter (Anton Paar DMA 35).

3. THEORY
Numerous methods are available in the literature for measuring ultrasonic velocity in solid and liquids. The ultrasonic interferometer is considered as more reliable and precise instrument. The expression used to determine ultrasonic velocity using ultrasonic interferometer is;

\[ u = \frac{v}{\lambda} \]  

Where \( u \) is ultrasonic velocity and \( \lambda \) is wavelength.

The adiabatic compressibility \( (\beta_s) \) was calculated from following equation;

\[ \beta_s = \frac{1}{\rho_s u^2} \]  

Where \( \rho_s \) is density of solution and \( u \) is speed of ultrasonic velocity.

Intermolecular force is one way or another way to determine the properties of liquids of attractive and repulsive forces \[15\]. The intermolecular free length \( (L_f) \) is calculated by using the standard expression;

\[ L_f = K \beta_s^{1/2} \]  

Where \( K \) is temperature dependent constant known as a Jacobson constant.

The acoustic impedance \( (Z) \) are obtained by equation;

\[ Z = u \rho \]  

The relative association \( (R_A) \) was calculated by the following equation;

\[ R_A = \frac{(\rho_s/\rho_o)}{u_o/u_s}^{1/3} \]  

Where \( \rho_o \) is density of solvent and \( u_o \) is velocity of solvent.

4. RESULTS AND DISCUSSION
The calibration of the ultrasonic interferometer was done by measuring the ultrasonic velocities and densities of the pure DMF and distilled water presented in Table 1. The measured value is found to be good concordance with literature values. Small difference may occur due to difference in purity of chemicals, measurements, techniques and calibrations.

Table 1: Density [kg m\(^{-3}\)] and ultrasonic velocity [ms\(^{-1}\)] of Distilled water and DMF

| Solvent   | T[K]   | Exptl. | Literature |
|-----------|--------|--------|------------|
|           | \( \rho \) | \( u \) | \( \rho \) | \( u \) |
| Dist. Water (DW) | 303.15 | 996.5 | 1513 | ----- | 1510\[18\] |
| DMF       | 303.15 | 949.6 | 1472 | 939.59\[17\] | 1476.2\[16\] |
|           | 308.15 | 934.2 | 1463 | 935.5\[16\] | 1464.6\[16\] |
|           | 313.15 | 930.8 | 1454 | 930.9\[16\] | 1453.5\[16\] |
|           | 318.15 | 924.8 | 1399 | 925.89\[19\] | 1385.74\[19\] |
Table 2. Experimental density [kg. m⁻³] and ultrasonic velocities [m.s⁻¹] of L₁, L₂, L₃, L₄ and L₅ in DMF-water at different temperatures with solute concentration 1×10⁻² M

| T [K]  | L₁   | L₂   | L₃   | L₄   | L₅   |
|--------|------|------|------|------|------|
|        | ρ    | u    | ρ    | u    | ρ    | u    | ρ    | u    | ρ    | u    |
| 303.15 | 996.3 | 1666 | 995.8 | 1660 | 999.1 | 1652 | 998.5 | 1652 | 995.6 | 1660 |
| 308.15 | 994.5 | 1656 | 992.4 | 1642 | 997.7 | 1648 | 995.4 | 1640 | 992.2 | 1635 |
| 313.15 | 991.7 | 1635 | 989.2 | 1635 | 994.3 | 1628 | 992.1 | 1624 | 989.5 | 1614 |
| 318.15 | 987.4 | 1613 | 986.2 | 1617 | 991.4 | 1615 | 989.1 | 1608 | 985.8 | 1602 |

The values of densities and ultrasonic velocities of L₁, L₂, L₃, L₄ and L₅ listed in Table 2, show that decreases with increase of temperature due to the breaking of hetero and homomolecular clusters at high temperatures[20] (Fig.1 and Fig. 2) indicates that cohesive forces decreased. The increasing temperature has two opposite effects namely increase of molecular interaction (structure formation) and destruction of structure formed previously. When the thermal energy is greater than the interaction energy, it causes the destruction of previously formed structure [21]. Thus, the increase of temperature favors the increase of kinetic energy and volume expansion and hence, results in the decrease of density and ultrasonic velocity.

![Fig. 1] Density of subs. thiazoles at diff. temp.  ![Fig. 2] Ultrasonic velocity of subs. thiazoles at diff. Temp.

Table 3. The adiabatic compressibility, linear free length, acoustic impedance and relative association of L₁, L₂, L₃, L₄ and L₅ at different temperature.

| T [K]  | β × 10⁻¹⁰ (kg⁻¹.m².s⁻¹) | L₉ × 10¹⁰ m | Z(kg.m².s⁻¹) | R_A  |
|--------|-------------------------|--------------|--------------|------|
|        | L₁                      |              |              |      |
| 303.15 | 3.616                   | 5.16759      | 1.6598       | 0.9927 |
| 308.15 | 3.667                   | 5.23295      | 1.6468       | 0.9945 |
| 313.15 | 3.772                   | 5.31933      | 1.6214       | 0.9970 |
| 318.15 | 3.893                   | 5.41298      | 1.5926       | 0.9994 |
|        | L₂                      |              |              |      |
| 303.15 | 3.644                   | 5.17822      | 1.6530       | 0.9940 |
| 308.15 | 3.737                   | 5.26077      | 1.6295       | 0.9951 |
| 313.15 | 3.782                   | 5.32604      | 1.6173       | 0.9964 |
| 318.15 | 3.878                   | 5.40957      | 1.5946       | 0.9987 |
|        | L₃                      |              |              |      |
| 303.15 | 3.668                   | 5.18217      | 1.6505       | 0.9930 |
| 308.15 | 3.691                   | 5.23722      | 1.6442       | 0.9945 |
| 313.15 | 3.795                   | 5.32378      | 1.6187       | 0.9957 |
| 318.15 | 3.867                   | 5.3987       | 1.6011       | 0.9978 |
| L<sub>4</sub> |   |   |   |   |
|---|---|---|---|---|
| 303.15 | 3.67 | 5.18372 | 1.6495 | 0.9935 |
| 308.15 | 3.735 | 5.25604 | 1.6324 | 0.9950 |
| 313.15 | 3.822 | 5.33624 | 1.6111 | 0.9964 |
| 318.15 | 3.91 | 5.41673 | 1.5904 | 0.9972 |

| L<sub>5</sub> |   |   |   |   |
|---|---|---|---|---|
| 303.15 | 3.645 | 5.17874 | 1.6526 | 0.9946 |
| 308.15 | 3.77 | 5.27255 | 1.6222 | 0.9960 |
| 313.15 | 3.88 | 5.35977 | 1.5970 | 0.9971 |
| 318.15 | 3.953 | 5.43594 | 1.5792 | 0.9988 |

When ultrasonic waves incident on the solution, the molecules get perturbed. The reason is medium has some elasticity and due to this perturbed molecules regain their equilibrium positions\textsuperscript{[22]}. When a solute is added to a solvent, its molecules attract certain solvent molecules toward them, this phenomenon is known as compression. Every solvent has a limit for compression and is known as limiting compressibility. The increase of adiabatic compressibility (\(\beta\)) with increase in temperature might be due to molecular interaction in solution which supports solvent–solute interactions. The increase of adiabatic compressibility and linear free length for all system suggest breaking of hetero and homo association of molecules\textsuperscript{[23]}.

The variation of ultrasonic velocity in a solution depends on the intermolecular free length on mixing. On the basis of a model for sound propagation given by Erying and Kincaid\textsuperscript{[24]}, ultrasonic velocity increases with decrease of free length (\(L_f\)) and vice versa. Intermolecular free length is a predominant factor for determining the variation of ultrasonic velocity, in liquids and their solutions. Intermolecular free length is the distance between the surfaces of the neighboring molecules and indicates a significant interaction between solute-solvent as well as solvent-solvent molecules. Hence, it is also a good tool to investigate the molecular interactions in the binary solvent mixture.

When the ultrasonic wave travels through a solution, some part of it travels through the medium and remaining part of ultrasonic wave gets reflected by the ion it means ions restricts free flow of sound wave. The character that decreases this restriction or backward movement of sound waves is known as acoustic impedance. If the temperature increases, ultrasonic velocity decreases and value of acoustic impedance (\(z\)) decreases\textsuperscript{[25]} as acoustic impedance (\(Z\)) is the product of ultrasonic velocity (\(u\)) and density (\(\rho\)). From the observation Table 3, seen that value of relative association (\(R_A\)) influence by two factors; 1) breaking up of the solvent molecules on addition of solute and 2) the solvation of ions that are simultaneous present. The result shows relative association increases along with temperature. the value of \(R_A\) depend on breaking of bonds of solvents molecule due to the addition of solute and salvation of the solute\textsuperscript{[26]}.

5. CONCLUSION
The ultrasonic method is powerful tool for characterizing physicochemical properties and existence of molecular interaction in the mixture. The result reveals that the density and ultrasonic velocity of pure DMF and ligand solutions decreases with increase in temperature. It is also seen that the formation of linear plot between and respective parameters indicated that the stronger solute-solvent interaction.

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