



ULTRASONIC STUDY OF MOLECULAR INTERACTION IN AQUEOUS SODIUM LIGNOSULFONATE

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ABSTRACT

The ultrasonic study of liquid mixtures helps in understanding the intermolecular interaction of solute-solvent mixtures. The study involves the measurement of the ultrasonic velocity, density, and viscosity of a binary system consisting of sodium lignosulfonate in an aqueous medium at 298.15 K. Sodium lignosulfonate is commonly used as a dispersing agent in industries such as agriculture, ceramics, and construction. It helps to disperse cement particles, improving the work ability of the mixture and reducing water content. The Various thermo-acoustical parameters, such as adiabatic compressibility (  $\beta_{ad}$  ), free length (L<sub>f</sub>), free volume (V<sub>f</sub>), acoustic impedance (Z), relaxation time (  $\tau$  ), etc., have been computed. The variations of these parameters with concentration are analysed to gain insights into the molecular interactions between the components of the mixtures.

**KEYWORDS :** Ultrasonic velocity (u), density (  $\rho$  ) and viscosity (  $\eta$  ), free length (L<sub>f</sub>), adiabatic compressibility (  $\beta_{ad}$  )

INTRODUCTION

Sodium lignosulfonate (C<sub>20</sub>H<sub>24</sub>Nα<sub>2</sub>O<sub>10</sub>S<sub>2</sub>) is a water-soluble compound derived from lignin. The lignin is generally found in the cell walls of plants. Sodium lignosulfonate is a naturally occurring anionic surfactant with a high molecular polymer structure, abundant in sulfo and carboxyl groups. It exhibits superior surfactant properties and excellent dispersion capabilities [1-2]. On the basis of its water-soluble property determined by the sulfonic acid group, lignosulfonate can be widely used in building, agriculture, and light industry [3-5]. It can also be used in animal feed additives due to its antimicrobial and preservative properties [6].

Ultrasonic investigations reveal insights into solvation dynamics, association phenomena, and intermolecular interactions in liquid mixtures [7-8]. This study investigates the ultrasonic properties of a sodium lignosulfonate solution, specifically its ultrasonic velocity, density, and viscosity and calculating its derived parameters at 298.15 K to gain inside the molecular structure and interactions in the liquid medium [9-11].

MATERIAL & METHODS

In the reported study, sodium lignosulfonate with 99.5% purity of analytical grade was obtained from Vedayukt India Private Ltd. Initially, a standard solution of 1-6 % concentration of sodium lignosulfonate in double-distilled water in steps of 1% was prepared. The ultrasonic velocities (U) in the liquid mixtures have been measured by a digital ultrasonic velocity meter supplied by Vi Microsystem Pvt. Ltd., Chennai, at a central frequency of 2 MHz with an accuracy of ± 0.01 m/s. The viscosity (η) of the solution is measured by an Ostwald's viscometer with accuracy ± 0.001Nm<sup>-2</sup>s. The density (ρ) is measured using a Pycnometer Specific Density Gravity Bottle with an accuracy of ±0.1 kg/m<sup>3</sup>. The temperature of the solution is maintained constant at 298.15 K using a temperature-controlled water bath with an accuracy of ± 0.01K.

The data measured are used to calculate derived acoustical parameters such as adiabatic compressibility (β<sub>ad</sub>), intermolecular free length (L<sub>f</sub>), free volume (V<sub>f</sub>), acoustical impedance (Z) and relaxation time (τ) etc.

Theory

The Density of experimental liquid was measured using the formula

$$\rho_2 = \left(\frac{w_2}{w_1}\right) \rho_1 \text{ ----- (1)}$$

Where, w<sub>1</sub> & ρ<sub>1</sub> = weight & density of distilled water.

w<sub>2</sub> & ρ<sub>2</sub> = weight & density of experimental liquid. Viscosity of the experimental liquid was determined using relation.

$$\eta_2 = \left(\frac{t_2}{t_1}\right) \left(\frac{\rho_2}{\rho_1}\right) \eta_1 \text{ ----- (2)}$$

Where, η<sub>1</sub>, ρ<sub>1</sub> & t<sub>1</sub> is viscosity, density & time flow of water. η<sub>2</sub>, ρ<sub>2</sub> & t<sub>2</sub> is viscosity, density & time flow of mixture.

Adiabatic Compressibility (β<sub>ad</sub>) has been calculated using the relation

$$\beta_{ad} = \frac{1}{\rho u^2} \text{ ----- (3)}$$

Intermolecular free length (L<sub>f</sub>) has been determined by the equation:

$$L_f = K_T \sqrt{\beta_{ad}} \text{ ----- (4)}$$

Where K<sub>T</sub> is a Jacobsen's constant (93.875 + 0.375 T) X 10<sup>-8</sup> and T being the absolute temperature.

Free Volume (V<sub>f</sub>) is determined using the equation:

$$V_f = \left(\frac{M_{eff} u}{K \eta}\right)^{3/2} \text{ ----- (5)}$$

Where, M<sub>eff</sub> = Σ m<sub>i</sub> x<sub>i</sub> and K = 4.28 × 10<sup>9</sup> for all liquids in MKS system.

Specific Acoustic Impedance is calculated using relation:

$$Z = U \cdot \rho \text{ ----- (6)}$$

Relaxation Time is calculated from the relation.

$$\tau = 4/3 \cdot (\beta_{ad} \cdot \eta) \text{ ----- (7)}$$

RESULTS AND DISCUSSIONS

The ultrasonic velocity, density, viscosity, and other relevant thermodynamic parameters i.e adiabatic compressibility (β<sub>ad</sub>), intermolecular free length (L<sub>f</sub>), acoustic Impedance (Z), free volume (V<sub>f</sub>) and relaxation time (τ) of aqueous sodium lignosulphonate were tabulated in Table-1. These parameters

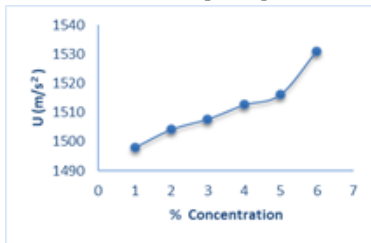
were evaluated and analyzed at various concentration percentages, at a fixed temperature of 298.15 K.

**Table-1**

Measured parameters of ultrasonic Velocity(U), density( $\rho$ ), viscosity( $\eta$ ), adiabatic compressibility ( $\beta_{ad}$ ), intermolecular free length (L<sub>f</sub>), acoustic Impedance (Z), free volume (V<sub>f</sub>) and relaxation time ( $\tau$ ) of sodium lignosulphonate in Double Distilled water at 298.15 K

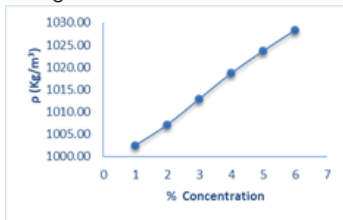
| % Concentration | (U) (m/s) | ( $\rho$ ) (Kg/m <sup>3</sup> ) | ( $\eta$ ) (mP) | $\beta_{ad} \times 10^{10}$ (m <sup>2</sup> N <sup>-1</sup> ) | L <sub>f</sub> X 10 <sup>11</sup> (m) | Zx10 <sup>6</sup> (Kg m <sup>2</sup> s <sup>-1</sup> ) | V <sub>f</sub> x10 <sup>8</sup> (m <sup>3</sup> ) | $\tau$ x 10 <sup>-13</sup> (s) |
|-----------------|-----------|---------------------------------|-----------------|---|---------------------------------------|--|---|--------------------------------|
| 1%              | 1498.073  | 1002.51                         | 0.9065          | 4.4447  | 4.3363                                | 1.5018   | 1.8613  | 5.3721                         |
| 2%              | 1504.2567 | 1007.17                         | 0.9259          | 4.3878  | 4.3084                                | 1.5150   | 1.8402  | 5.4170                         |
| 3%              | 1507.7960 | 1012.90                         | 0.9425          | 4.3425  | 4.2861                                | 1.5273   | 1.8237  | 5.4573                         |
| 4%              | 1512.6784 | 1018.64                         | 0.9573          | 4.2902  | 4.2602                                | 1.5409   | 1.8155  | 5.4760                         |
| 5%              | 1516.1846 | 1023.66                         | 0.9785          | 4.2495  | 4.2400                                | 1.5521   | 1.7876  | 5.5440                         |
| 6%              | 1531.1282 | 1028.32                         | 0.9944          | 4.1481  | 4.1891                                | 1.5745   | 1.7950  | 5.5001                         |

The increase variation of ultrasonic velocity with % concentration (fig.1) at constant temperature 298.15 K indicates that the solution becomes less compressible and more rigid, primarily due to strong dipole-dipole interactions and hydrogen bonding in between sulfonate and hydroxyl functional groups of sodium lignosulfonate and hydroxide group of water. Similar observations were made by S. V. Khangar et al. [12] in the investigation of temperature dependence of ultrasonic velocity in Aqueous PVA solutions.

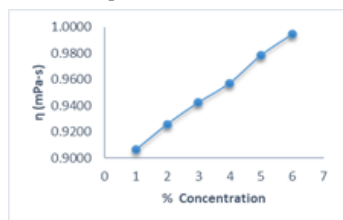


**Fig.1** Variation of Ultrasonic Velocity with % concentration at 298.15 K

The increase in density and viscosity with the increase of SLS concentration (fig.2 & fig.3) indicates that SLS are integrating well into the water due to strong hydrogen bonds form between -OH group of water molecules and -SO<sub>3</sub> groups of sodium lignosulfonate. At higher SLS concentrations, the solution becomes more compact and dense due to enhanced molecular bonding.

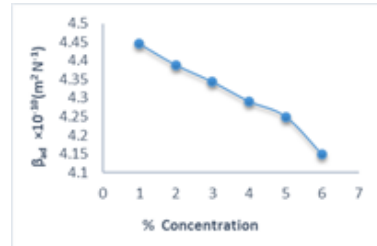


**Fig.2** Variation of density with % concentration at 298.15 K



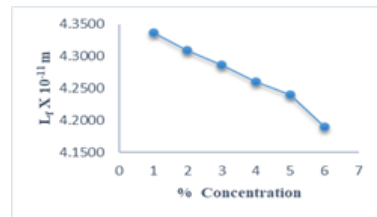
**Fig.3** Variation of Viscosity at with % concentration at 298.15 K

A decrease in adiabatic compressibility (fig.4) with increase in concentration corresponds to a decrease in compressibility of the liquid and hence the decrease in intermolecular distance. This indicates the enhancement of degree of association in the component molecules. This decrease also implies that the solution becomes less compressible due to the stronger dipole interactions and hydrogen bonding, which make the solution more resistant to volume changes under pressure. Similar observations were made by S. P Dange et al. [13] and R. Palani, A. Geetha [14].



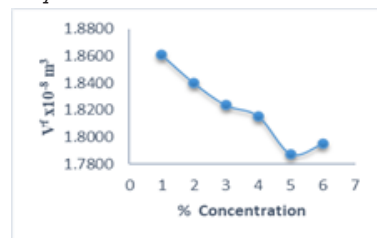
**Fig.4** Variation of Adiabatic Compressibility with % concentration at 298.15 K

The reduction in intermolecular free length with increase in concentration (fig.5) points to decreased distances between molecules, confirming the close packing facilitated by strong intermolecular forces. Increased SLS concentration enhancing hydrogen bonding and solvation interactions between SLS and water molecules.

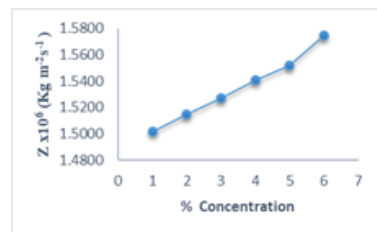


**Fig.5** Variation of Free length with % concentration at 298.15 K

The interactions further reduce the free volume(fig.6) available for molecular motion by restricting the movement of water molecules and other solutes in the solution that leads to an increase in acoustic impedance (fig.7), indicating Micelle formation, altered molecular packing, and changes in solution density.



**Fig.6** Variation of Free Volume at different % concentration at 298.15 K



**Fig. 7** Variation of Acoustic Impedance with % concentration at 298.15 K

The increase in relaxation time with concentration (fig.8)

indicates that the time required for the molecules to return to equilibrium after a disturbance increases, which may be due to the increased interaction between the molecules. The slight decrease at the highest concentration might indicate the onset of a different interaction mechanism or saturation point.

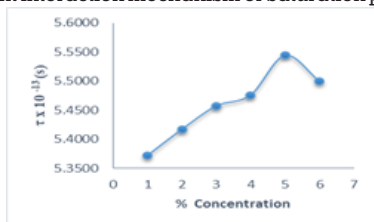


Fig.8 Variation of Relaxation Time with % concentration at 298.15 K

## CONCLUSION

These findings highlight the crucial role of hydrogen bonding and dipole-dipole interactions influencing the physical properties of sodium lignosulfonate solutions. As concentration increases, these interactions become more pronounced, leading to changes in ultrasonic velocity, density, viscosity, compressibility, intermolecular free length, acoustic impedance, free volume, and relaxation time. Understanding these interactions is essential for optimizing the use of sodium lignosulfonate in various industrial applications, such as dispersants, binders, and surfactants, where its concentration-dependent properties can be strategically utilized to achieve desired outcomes.

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