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Molecular Interaction of Dextran and Sodium Hydroxide through Ultrasonic Investigation

Subhraraj Panda[1]

[1]Centurion University of Technology and Management, Odisha, India.

Abstract: Studies were conducted to analyze the intermolecular interactions between dextran solute and 1M sodium hydroxide solvent in aqueous solutions at different temperatures and concentrations. This involved measuring ultrasonic speed (U), density (ρ), and viscosity (η). Various acoustic parameters such as free volume (V_f), internal pressure (Πi), Rao's constant (R), and Wada's constant (W) were calculated at a constant frequency using the experimentally obtained values of density (ρ), viscosity (η), and ultrasonic speed (U) of the solutions. The results provide insight into the temperature and concentration dependence of these parameters and the intermolecular interactions within the system. This investigation offers valuable information about the interaction type between solute and solvent, structural rearrangement, and the extent of molecular interaction in liquid solutions.

Keywords: Aqueous dextran, Ultrasonic speed, Density, Viscosity, Molecular interactions.

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***Corresponding author's E-mail:** subhraraj4u@gmail.com

1. INTRODUCTION

The study of molecular interactions is crucial to comprehending the composition and properties of liquids. Several studies have been carried out on the interaction in liquid mixtures Using various techniques, including infrared spectroscopy, nuclear magnetic resonance spectroscopy, and ultrasonic research. These methods have proven to be practical tools for obtaining information about liquid systems' physical and chemical properties (1). The approach of researching molecular interactions using knowledge of thermodynamic parameter fluctuation with composition and temperature provides insight into the molecular process. Industry demands a broad spectrum of chemical and physical properties of liquid solutions.

Researchers have used ultrasonic methods to study polymer structures from various perspectives (2-4). Researching acoustic characteristics is a convenient approach for investigating liquid structures, particularly dilute polymer solutions. Using basic procedures, it provides a strong understanding of the potential structure of the polymer and solvent molecules at various concentrations and some information about the amount of connection (5). In previous years, the most popular and cost-effective technique for determining density (ρ), viscosity (η), and ultrasonic speed (U) was to use a specific gravity bottle, a capillary viscometer, and an ultrasonic interferometer (6-10). To anticipate the solute-solvent, ion-solvent, and solvent-solvent interactions in aqueous solutions, including electrolytes, ultrasonic speed measurements are beneficial in the field of study.

Since ultrasonic speed is essentially connected to the binding forces between the medium's constituents, it is very sensitive to the structure and interactions seen in liquid systems. The intermolecular free path length in a solution determines the ultrasonic speed. The presence of ultrasonic waves stirs the molecules in the solution. The medium is flexible, allowing disrupted molecules to return to their equilibrium positions. The molecules of a solute attract the molecules of a solvent when they are introduced together. This phenomenon is referred to as restricted compressibility and compression. Aggregation of solvent molecules around solute molecules strengthens solvent-solute interactions. Solvent-solute interactions result in a considerable alteration of the solute's structure (11).

Utilizing a through transmission approach at a frequency of 5 MHz, ultrasonic investigations were

carried out to measure longitudinal and shear wave velocities and attenuation across a temperature range of 300 to 700 K (12). Using the through transmission technique, ultrasonic velocities and attenuation for $La_{1-x}Ca_xMnO_3$ samples were evaluated using a high-power ultrasonic pulser receiver and recorded via a 1 GHz digital storage oscilloscope. 5 MHz X- and Y-cut transducers produced longitudinal and shear waves, and a programmable temperature controller was used to regulate the heating rate, which allowed for measurements to be made between 300 and 600 K at a rate of 0.5 K/min. The recorded ultrasonic velocities and densities were used to determine elastic constants that took temperature variations into account, such as bulk, longitudinal, shear, and Poisson's moduli and Young's modulus (13). According to in situ ultrasonic experiments, NLSMO's Curie temperature was lower than BLSMO's and continued to drop as the Sr concentration increased. Furthermore, the extensive transitions seen in the NLSMO samples indicated that the usual phase transition from ferromagnetic to paramagnetic (FM to PM) was absent (14).

If ionic solvents are present in solutions, then the interaction is purely ion-dipole interaction, which depends on the ion size and polarity of the solute (15-17). After adding the solute to the solvent, the ion and solute molecule interact, which causes volume contraction (18,19). Several researchers have determined the ultrasonic speed and related parameters (20-23). From the literature review, it is found that studies have been made for various univalent and bivalent electrolytes, biomolecules, heterocyclic compounds, drugs, and different solvent systems like CH_3OH, ethylene glycol propanol, and other proteins.

The values of the relevant thermodynamic and acoustic parameters, as well as ρ,η, and U, have been determined in this article at temperatures of "303K, 308K, 313K, 318K, and 323K" in 1MHz frequency, of dextran 0.1, 0.25, 0.50, 0.75, and 1 percent concentrations in 1(M) sodium hydroxide solution. The various acoustic parameters like free volume (V_f), internal pressure (Πi), Rao's constant (R), and Wada's constant (W) have been calculated at constant frequency in different temperatures and concentrations (24-26). Dextran has broad industrial applicability, particularly in the pharmaceutical industry, so we chose it for our study. Dextran is water soluble. Dextran, initially utilized to convert human red blood cells into synthetic blood-volume expanders to enhance the degree of polymerization, is now being employed in clinical applications and pharmaceutical industry tablet studies (27-29).

Ultrasonic techniques are widely utilized in engineering and many other fields to study molecular interactions in liquids. These techniques use the propagation of ultrasonic waves through liquids to gather information on the properties, compositions, and behaviors of molecules. It is possible to use ultrasonic interferometry to determine conformational changes in the molecules. Understanding the underlying chemical mechanisms and how the structure of molecules changes during binding may be gained from this. Using ultrasonic techniques, phase shifts and the solidification of liquids are detected. Changes in ultrasonic wave properties, which can be utilized to detect changes in molecular interactions during cooling or heating, aid in the understanding of the freezing and melting processes.

2. EXPERIMENTAL MATERIALS & METHODS

For studies, 1(M) sodium hydroxide AR (analytical reagent) grade with a minimum assay of 99.9% and the polymer dextran with a molecular weight of 70,000 Da manufactured by HI Media Laboratories Private Limited, India. The NaOH solution was made from freshly distilled water. The solute, dextran 70,000 Da, was utilized, and its concentrations varied throughout distinct (w/v) percentage ranges (30,31).

2.1. Measurements

The mass of a known volume of the solution was measured, and density was calculated using a Pycnometer (specific gravity bottle). Using a conventional equation and a 25mL specific gravity bottle (Figure 1), the density (32-34) of the solution is calculated with an accuracy of 0.1 $kg.m^{-3}$. Utilizing a specific gravity bottle, the thickness was measured with an error of 0.04%.

Figure 1: Specific gravity bottle.

$$\rho_2 = \frac{w_2}{w_1}\rho_1 \quad (1)$$

Where w_1 and w_2 denote the weight, ρ_1 and ρ_2 denote the density of distilled water and the experimental solution, respectively

Viscosity was measured by timing the flow of the solution through the viscometer capillary at controlled temperature conditions. The viscosity (32-34) of the polymer solution was assessed using a pre-calibrated Ostwald's viscometer (Figure 2) with an error range of 0.067% (Figure 2). The flow time of the solutions used for the inquiry is used to calculate the viscosity, with an inaccuracy of up to 0.01 seconds. The equation was used to calculate the values at the specified temperatures.

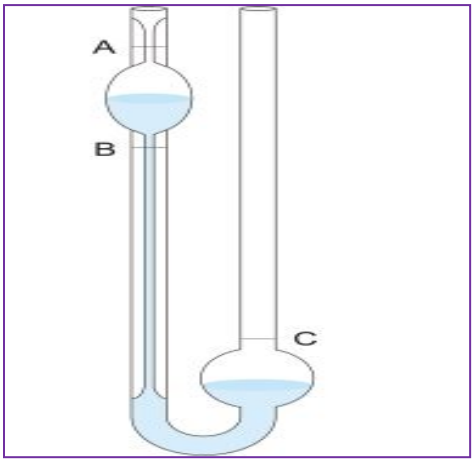

Figure 2: Ostwald's viscometer.

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

where η1 and η2 are the viscosities, and t1 and t2 are the times of flow of distilled water and the experimental solution, respectively.

Using an ultrasonic interferometer (Figure 3) having uncertainty within the order of ±0.056, The ultrasonic wave's speed in solution was measured using 11 distinct frequency bands (35). The interferometer measuring cell is a specially created double-walled vessel with a temperature constant configuration. Water was circulated through the outer jacket of the double-walled estimation cell containing the test solution using an electronically controlled advanced steady temperature shower that functioned in the temperature range of -10 °C to 85 °C with an accuracy of 0.1 K. All measurements were made in a water bath with a flowing medium that had a 0.10°C uncertainty. Measurements were taken at multiple frequencies (1 MHz, 5 MHz, 9 MHz, and 12 MHz). The sample was placed in the interferometer, and ultrasonic velocity was recorded at each frequency.

Figure 3: Ultrasonic interferometer.

3. THEORETICAL ASPECT

The calculated thermodynamic and acoustic parameters (36)

Free volume:
"Free volume (V_f) in terms of ultrasonic velocity (U) and the viscosity (η)" of the liquid is as follows:

$$V_f = \left(\frac{M_{eff}U}{K\eta}\right)^{\frac{3}{2}} \quad (3)$$

Where Meff is the solution's effective molecular weight, and K is the temperature-independent constant, which is 4.281 x 10^9 for all liquids.

Internal pressure:
It can be calculated using the relation given below

$$\pi_i = bRT\left(\frac{k\eta}{U}\right)^{3/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right) \quad (4)$$

Where b stands for cubic packing, which is assumed to be 2 for all liquids, T is the absolute temperature in Kelvin, and R is the universal gas constant.

Rao's constant:
Rao has demonstrated the empirical relationship between molecular weight, density, and ultrasonic velocity of liquids.

$$R = \frac{M_{eff}}{\rho}U^{1/3} \quad (5)$$

This equation is called Rao's rule, and R is also called the molar sound velocity. Rao provided a theoretical explanation of his formula based on the phase rule and kinetic theory of liquids.

Wada's constant:
Wada explored how molar compressibility changed with a concentration in a variety of liquid systems. He came up with the empirical relationship,

$$W = \frac{M_{eff}}{\rho}\ \beta^{-1/7} \quad (6)$$

4. RESULTS AND DISCUSSION

The experimental values of density (ρ), viscosity (η), and ultrasonic speed (U), the derived parameters free volume (Vf), internal pressure (Πi), Rao's constant (R), and Wada's constant (W) of dextran in H_2O-NaOH are given in Table 1-3.and displayed in Figure 4 to 10.

Table 1: Ultrasonic speed (U) and free volume (V_f).

T (K)	(U) m/s					(V_f) (x10^{-3}m^3·mol^{-1})				
	0.10%	0.25%	0.50%	0.75%	1%	0.10%	0.25%	0.50%	0.75%	1%
303	1587.0	1589.0	1590.0	1591.0	1593.0	7.437	7.348	7.156	6.887	6.671
308	1594.0	1596.0	1597.0	1598.0	1599.0	8.870	8.621	8.381	8.157	7.784
313	1600.0	1601.0	1603.0	1604.0	1606.0	10.759	10.098	9.946	9.509	9.032
318	1606.0	1607.0	1608.0	1610.0	1612.0	11.641	11.054	10.882	10.712	10.212
323	1611.0	1613.0	1614.0	1615.0	1618.0	13.232	12.988	12.545	11.914	11.312

Table 2: Internal pressure (Π_i).

T (K)	$\Pi_i(\times 10^3\ N{\cdot}m^{-2})$				
	0.10%	0.25%	0.50%	0.75%	1%
303	122.65	123.17	124.33	125.96	127.44
308	117.41	118.62	119.80	120.92	122.99
313	111.74	114.19	114.86	116.62	118.83
318	110.40	112.42	113.04	113.72	115.74
323	107.24	107.97	109.29	111.30	113.40

Table 3: Rao's constant (R) and Wada's constant(W).

T (K)	(R) $(m^3/mole)(m/s)^{1/3}(\ 10^{-3})$					(W) $(m^3/mole)(N/m^2)^{1/7}(\ 10^{-3})$				
	0.10%	0.25%	0.50%	0.75%	1%	0.10%	0.25%	0.50%	0.75%	1%
303	1.126	1.126	1.126	1.125	1.124	0.0797	0.0797	0.0797	0.0796	0.0796
308	1.130	1.129	1.129	1.128	1.126	0.0799	0.0799	0.0798	0.0798	0.0797
313	1.134	1.133	1.132	1.132	1.130	0.0801	0.0801	0.0800	0.0800	0.0799
318	1.138	1.137	1.136	1.135	1.133	0.0804	0.0803	0.0803	0.0802	0.0801
323	1.142	1.142	1.141	1.140	1.138	0.0807	0.0806	0.0806	0.0805	0.0804

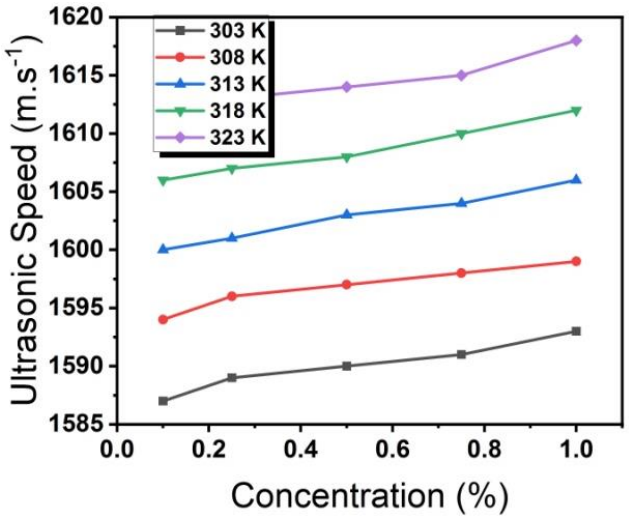

Figure 4: Ultrasonic speed vs concentration.

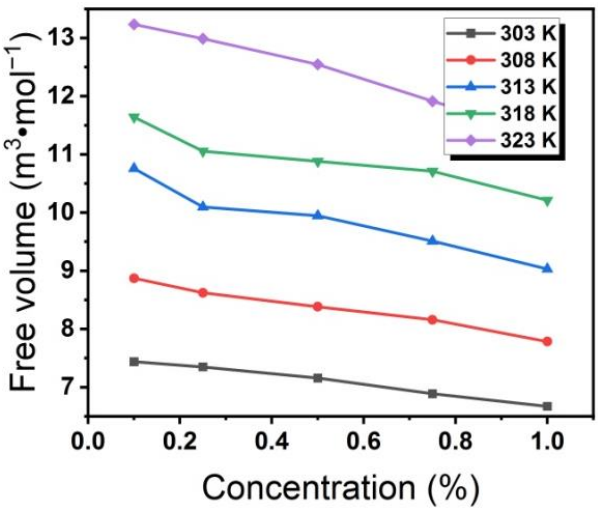

Figure 6: Free volume vs concentration.

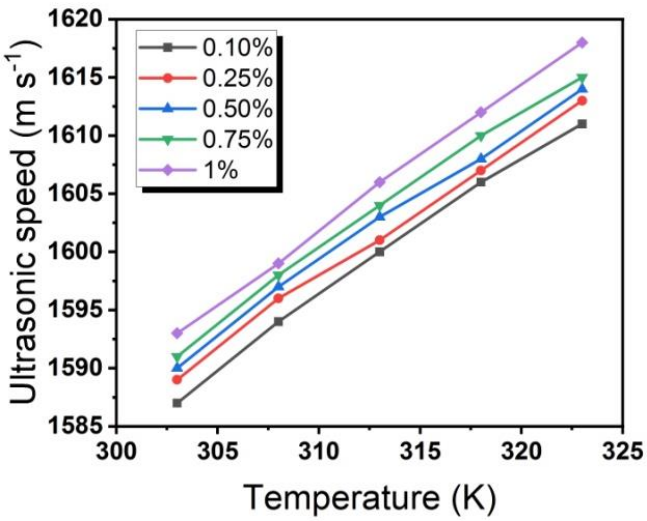

Figure 5: Ultrasonic speed vs temperature.

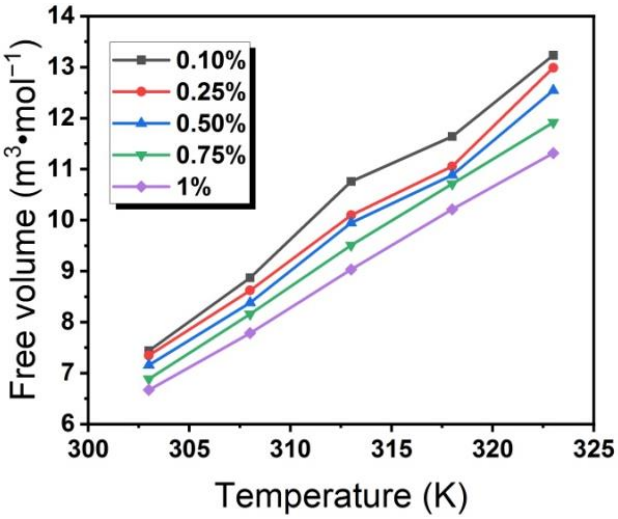

Figure 7: Free volume vs temperature.

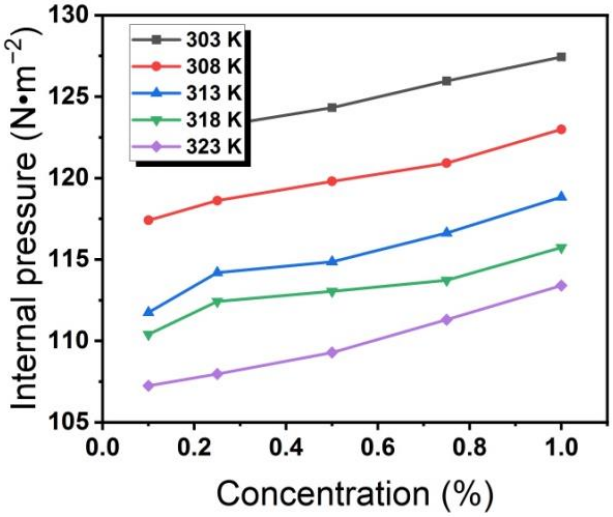

Figure 8: Internal pressure vs concentration.

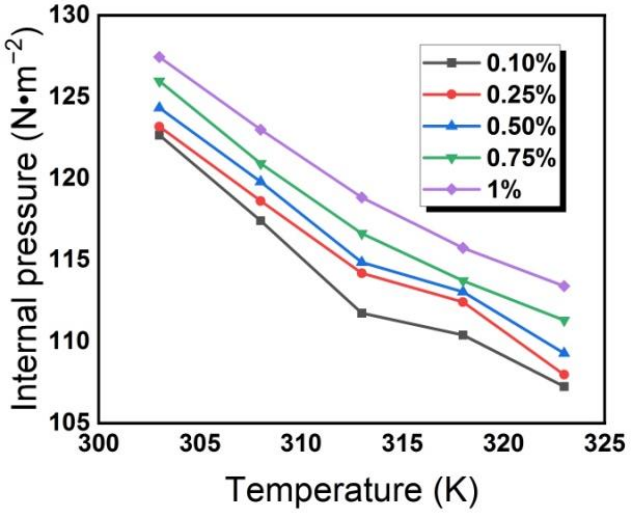

Figure 9: Internal pressure vs temperature.

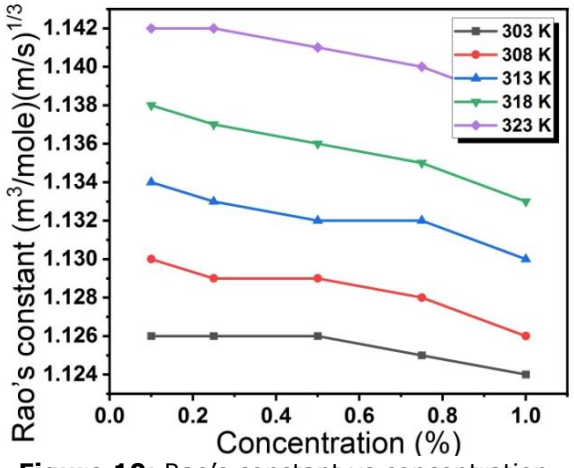

Figure 10: Rao's constant vs concentration.

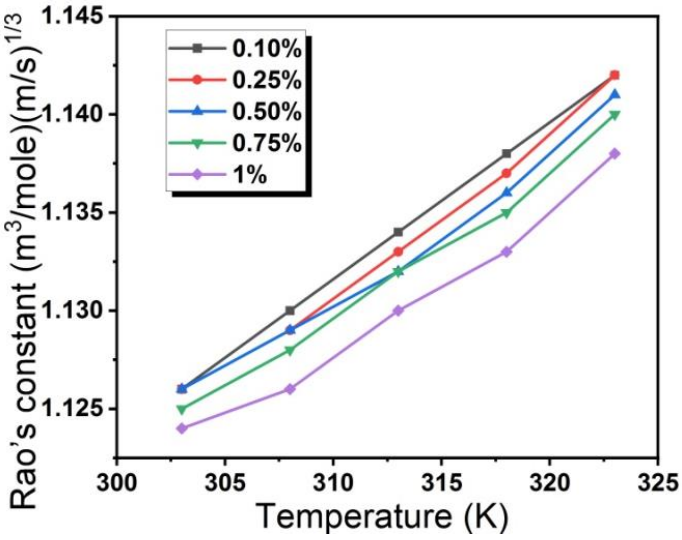

Figure 11: Rao's constant vs temperature.

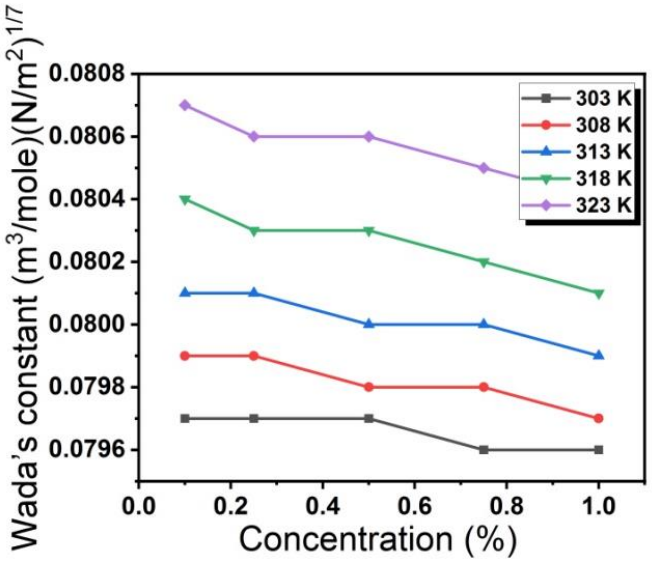

Figure 12: Wada's constant vs with concentration.

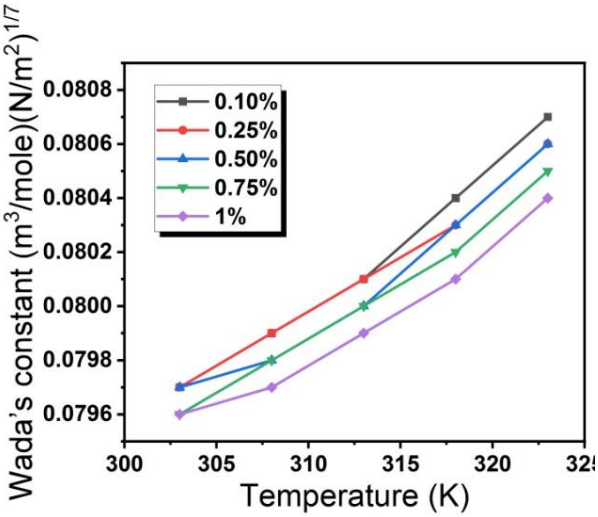

Figure 13: Wada's constant vs temperature.

5. DISCUSSION

The number of molecules in the medium rises as the concentration of dextran increases, making the medium denser and increasing sound speed. The rise in speed (Figure 4) might be owing to cohesive forces, implying that the observed values are due to molecular attachment (37,38). This suggests a molecular connection, which may be brought about by hydrogen or dipole-hydrogen bonds between NaOH and water. The relationship between sodium hydroxide (Na^+) and water molecules rather than between sodium hydroxide (Na^+) and dextran molecules is caused by ion-dipole interaction. The variation in speed may be caused by the solvent particles' self-relationship and concentration-dependent dipole-induced dipole cooperation between the segment atoms. At the mixture's saturation area, there is a slight shift in speed, indicating that the dispersive force outweighs the dipole-induced dipole force, and the molecular association comes to an end. This is so because the dextran molecule is larger than the water molecule. Therefore, the polarizability will increase with size and may result in substantial contact forces. With increased temperature, ultrasonic speed increases (Figure 5), indicating that molecular association takes place in the solution (39-42).

The free volume is a practical volume in which the core molecules can move within the solution due to the attraction of nearby molecules. The reduction in free volume (Figure 6) and temperature increase (Figure 7) with increasing concentration and temperature validate the ion–solvent interactions. As the concentration (vol.%) of dextran in NaOH increases, it is seen that the free volume (V_f) falls and the internal pressure (π_i) rises, indicating interaction in the molecules of the component liquids. The fact that the free volume reduces as the concentration increases shows that the molecules have arranged themselves so that less vacant space is accessible, indicating a reduction in compressibility (43,44).

The internal pressure is observed in the opposite trend, which is accepted. It is seen from Figure 8 that internal pressure increases with an increase in concentration because, with the addition of more solute, ion-solvent interaction increases. The internal pressure (45) drops as the temperature rises because increased thermal energy causes thermal agitation of ions, which limits the likelihood of contacts and lessens cohesive forces, resulting in a decrease in the internal pressure (Figure 9). The space a molecule has to travel in a hypothetical unit cell is called the free volume. The system's increased free volume demonstrates how the intensity of the interaction steadily grows as the solute concentration rises. It suggests that there is just minimal contact between the solvent molecules and the solute. Internal pressure is a more general term and a measurement of all the forces (dispersion, ionic, and dipolar) at work in the liquid system, contributing to its overall cohesion and adhesion. Figures 11 and 13 illustrate Rao's and Wada's constant rise as the temperature rises. The increasing trends of Rao's constant and Wada's constant (46,47) with concentration imply that more components are available in a given location, resulting in a close packing of the medium and increasing interactions.

6. CONCLUSION

The impact of temperatures and concentrations on thermoacoustic parameters has been researched. The investigations above have revealed the characteristics of molecular forces, such as hydrogen bonds, charge transfer complexes, hydrogen bond breaking, and complexes. Intermolecular forces, also referred to as electrostatic forces, are weak between charged particles of a permanent dipole and an induced dipole molecule. Due to the different sizes and shapes of the molecules, the geometric fitting of one molecule into another results in the components' structural features. Depending on the chemical makeup of the polymer fragment, its polarity, and its solubility parameter, forces of attraction or dispersion start to develop between them when introduced to a solvent. When the solvent-solute interaction outweighs the solute-solute attraction, the troops holding the polymer coil in place weaken. As a result, the solvent molecules penetrate the spaces between the segments and disrupt their interaction. They encircle and make contact with each piece individually. The segments release or unfurl from their tightly coiled structure during this process. To put it another way, the combined segments without a solvent are now solvated.

7. CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this paper.

8. ACKNOWLEDGMENTS

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