ACOUSTIC AND THERMODYNAMICS STUDY OF AQUEOUS DEXTRAN: AN ULTRASONIC ANALYSIS

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Abstract. The acoustical investigation of molecular interaction has been performed from the measurement parameters of ultrasonic velocity (U), density (ρ) and viscosity (η) of aqueous dextran solution at different temperatures. The thermodynamic and other allied parameters like internal pressure (π_i), free volume (π), absorption coefficient or attenuation coefficient (α), Rao's constant (Ro) and Wada's constant (W) have been computed. To understand the structural reorganization of the solute (dextran) and solvent (distilled water) in aqueous solution, concentration and temperature changes of these parameters have been investigated. Differences in ultrasonic velocity and other factors are crucial to comprehending the solute-solvent intra and intermolecular interactions between the constituent molecules.

Key words: Dextran, acoustical parameters, molecular interactions, ultrasonic velocity.

INTRODUCTION

Due to their widespread commercial use in the fields of medicine, industry, and research, many solvent extractants and diluents from acoustic measurements were found to exhibit molecular interactions that are of increasing interest. Thermodynamic characteristics relating to ultrasonic velocity (U), density (ρ), and viscosity (η) are crucial for determining the type and degree of molecular interaction among solution's constituents [9, 15, 16, 17]. The molecular environments can be learned a lot from ultrasonic velocity and the derived acoustical characteristics like internal pressure (π_i), free volume (V_f), absorption coefficient or attenuation coefficient (α), Rao's constant (Ro), and Wada's constant (W). Regarding changes in temperature and solution concentration, this has been researched in [1, 8, 22, 23].

In understanding the nature and power of molecular interactions, liquid ultrasonic research is of tremendous significance. Basically, the biological activity of drug molecules and the metabolic process activation energy depend on the form and strength of intermolecular interactions. Thermodynamic and transport aspects of

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liquid mixtures have frequently been utilized to study how real liquid mixture behavior deviates from ideality. According to the literature [13, 14, 21], the kind of solvent, the solvent's molecule composition, and the amount of solutes present in the solution all influence the existence and strength of molecular interactions in different solutions [2, 5, 10, 20].

In this paper, values of ultrasonic velocity (U), density (ρ) and viscosity (η), and some important ultrasonic parameters like: internal pressure (π_i), free volume (V_f), absorption or attenuation coefficient (α), Rao's constant (Ro), and Wada's constant (W) of dextran solutions were evaluated in the following experimental conditions: at four different concentrations (0.25 %, 0.50 %, 0.75 % and 1 %), at five different temperatures, *i.e*. 303 K, 308 K, 313 K, 318 K and 323 K, and at 12 MHz frequency. The interactions between dextran and water as well as the structural changes in dextran in aqueous solution have been examined in relation to the results.

Dextran is a complex, branched polysaccharide consisting of several glucose molecules consisting of chains of various lengths. Dextran is used in the manufacture of blood plasma expanders, heparin replacements, cosmetics and other products for the treatment of anticoagulants. The processing of Sephadex gel breads, which are commonly used for industrial and laboratory protein separations, is another application of dextran. It is crucial to comprehend the structure and molecular interactions of dextran because of its many uses in the pharmaceutical, medical, and food industries. This inspired the use of an ultrasonic approach to investigate the thermoacoustic parameter of dextran.

MATERIALS AND METHODS

70,000 Da dextran was utilized as the solute. Dextran solution has been prepared using distilled water as a solvent [13]. The conventional method [18, 19] has been used to measure velocity, density, and viscosity using an ultrasonic interferometer, a 10 mL specific gravity bottle, and an Ostwald viscometer, respectively.

THEORETICAL ASPECT

The thermodynamic and acoustic parameters listed below have been computed as in [7]. At various concentrations and temperatures, the fundamental parameters ultrasonic velocity, density, and viscosity, were measured. With the aid of standard formulae, the various acoustical parameters, such as internal pressure (π_i) free volume (V_f), absorption coefficient or attenuation coefficient (α), Rao's constant, and Wada's constant, were determined from the values of ultrasonic velocity, density, and viscosity.

MEASUREMENTS

The density of the solution was measured using a standard equation and a 25 mL specific gravity bottle with an accuracy of 0.1 kg·m^{-3} [18], according to the following equation:

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

where w_1 and w_2 denote the weight, ρ_1 and ρ_2 are the densities of water and solution, respectively.

The viscosity of the polymer solution was measured with viscometer accuracy of 0.001 Nsm^{-2}. The flow time was measured with a digital racing stopwatch with an accuracy of 0.01 s at the temperature stated, and the equation was used to calculate it [18].

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

where η_1 and η_2 are the viscosities, t_1 and t_2 are the times of flow of water and solution, respectively.

The velocity of ultrasonic waves in the solution was measured using a multi-frequency ultrasonic interferometer working in the temperature range of –10 °C to 85 °C [18], with an accuracy of 0.1 K. The expression used to determine the ultrasonic velocity is:

$$U = \frac{2d}{t} = 2d \times \nu = \lambda \times \nu \quad (3)$$

where λ is the wavelength, ν is the frequency of the generator used to stimulate the crystal, d is the distance between the reflector and the crystal (λ equals 2×d) and t is the ultrasonic wave time period.

All the measurements have been carried out in a water bath with circulating medium having an uncertainty of ± 0.10 °C. The viscosity of the solution was determined using pre-calibrated Ostwald's viscometer having uncertainty within the order of ± 0.067 %. The viscosity measurements were based on the measurement of flow time of the solutions taken for the investigation with an uncertainty up to ±0.01 s. The density measurement has been done using a pycnometer with an uncertainty of ±0.06 %. Sound speeds in solutions were measured using an ultrasonic interferometer having uncertainty within the order of ±0.056 %.

COMPUTATIONS

[11]

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

$$V_f = \left(\frac{M_{eff}U}{K\eta}\right)^{\frac{3}{2}} \quad (4)$$

where M_{eff} is the solutions effective molecular weight, and K is the temperature independent constant, which is 4.281 × 109 for all liquids.

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Internal pressure was calculated using the relation as given below:

$$\pi_i = bRT\left(\frac{k\eta}{U}\right)^{3/2}\left(\frac{\rho^{2/3}}{M_{eff}{}^{7/6}}\right) \quad (5)$$

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

Absorption coefficient or attenuation coefficient is a defining feature of the medium. It is determined by external factors such as temperature, pressure, and measurement frequency. The following relationship explains it:

$$\propto = \frac{8\pi^2\eta f^2}{3\rho U^3} \quad (6)$$

where f is the frequency of ultrasonic wave.

The empirical relationship between molecular weight, density, and ultrasonic velocity of liquids has been demonstrated by Rao:

$$Ro = \frac{M_{eff}}{\rho}U^{1/3} \quad (7)$$

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

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

$$W = \frac{M_{eff}}{\rho}\ \beta^{-1/7} \quad (8)$$

RESULTS AND DISCUSSION

Some thermodynamic and acoustic parameters have been calculated using the ultrasonic velocity, density, and viscosity of an aqueous solution of dextran at different concentrations and temperatures.

Table 1

Values of internal pressure (π_i) and free volume (V_f)

T (K)	π_i ($\times 10^3$ N·m^{-2})				V_f ($\times 10^{-3}$ m^3·mol^{-1})			
	0.25 %	0.50 %	0.75 %	1 %	0.25 %	0.50 %	0.75 %	1 %
303	846.83	864.44	872.11	903.61	0.642	0.602	0.583	0.526
308	805.30	825.70	836.90	866.98	0.782	0.719	0.692	0.621
313	784.50	803.30	819.96	835.78	0.881	0.818	0.770	0.724
318	763.53	785.85	794.30	813.51	0.998	0.913	0.883	0.819
323	741.55	756.46	765.09	803.49	1.142	1.069	1.028	0.890

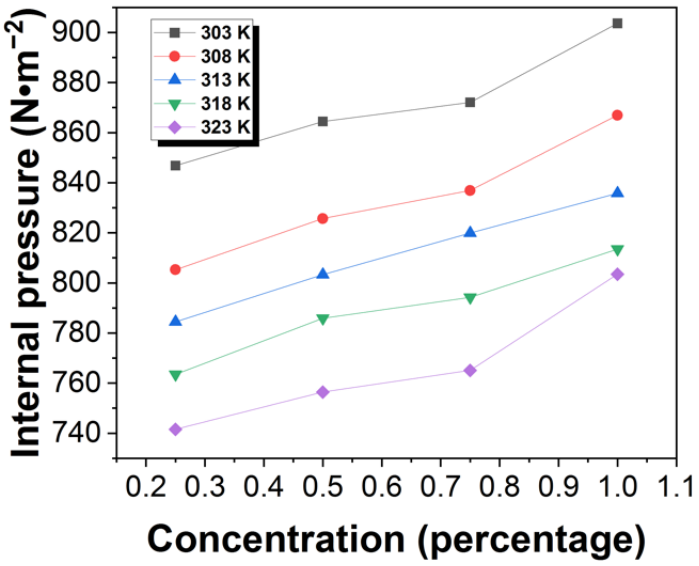

Fig. 1. Internal pressure *vs* concentration.

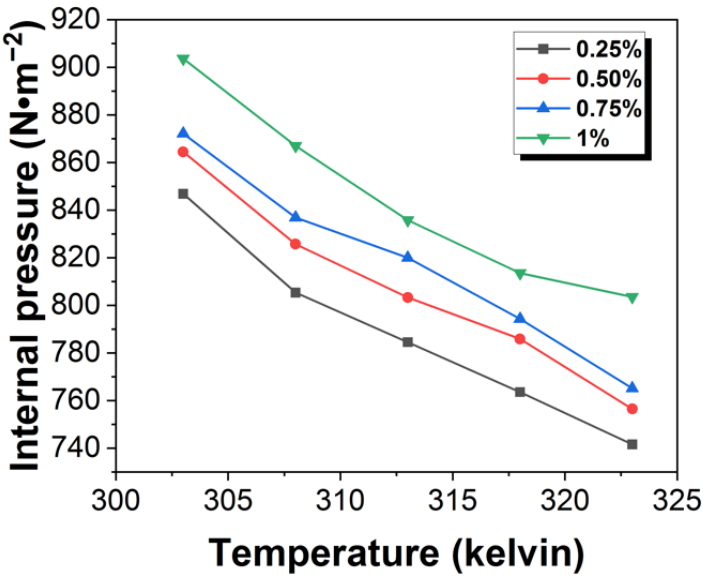

Fig. 2. Internal pressure *vs* temperature.

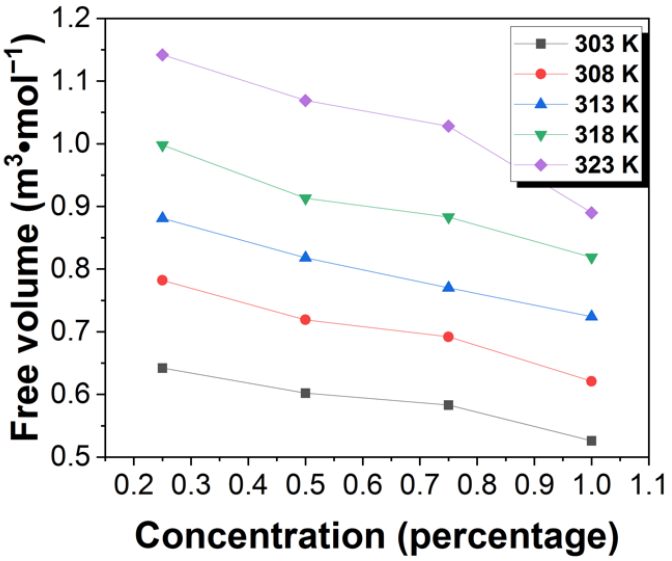

Fig. 3. Free volume *vs* concentration.

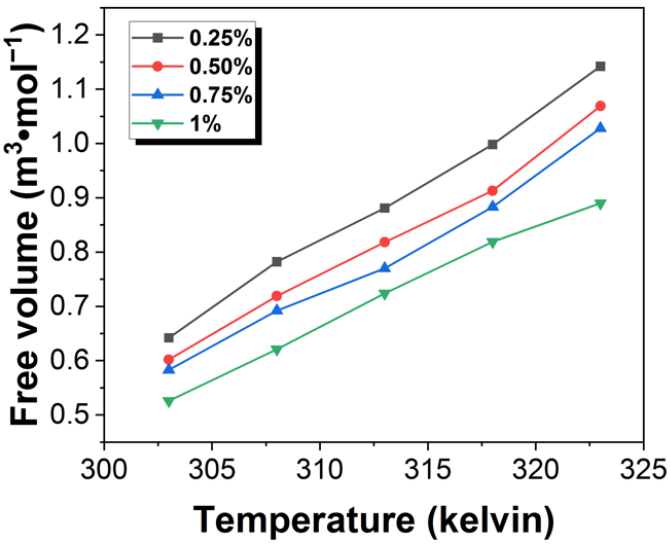

Fig. 4. Free volume *vs* temperature.

Table 2

Values of attenuation coefficient (α)

T (K)	α ($\times 10^6$ np·m^{-1})			
	0.25%	0.50%	0.75%	1%
303	142.28	148.91	152.26	162.70
308	124.09	131.75	134.87	145.12
313	114.27	120.38	125.32	130.57
318	104.84	111.72	113.94	119.98
323	95.54	100.25	102.96	113.16

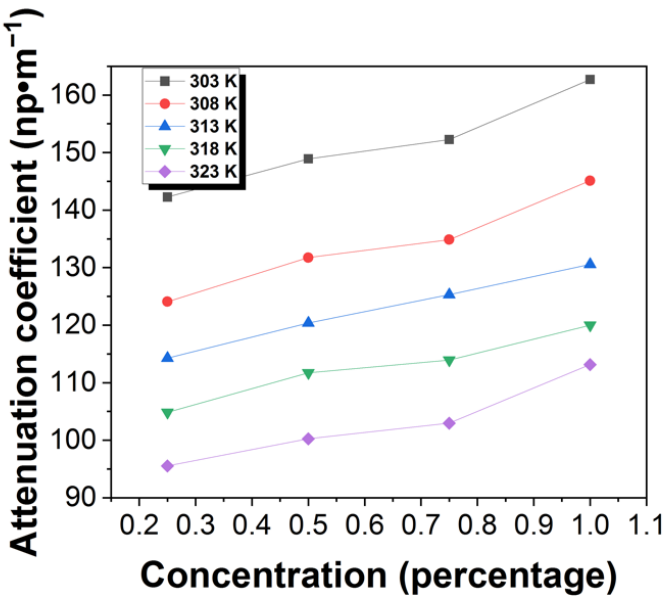

Fig. 5. Attenuation coefficient *vs* concentration.

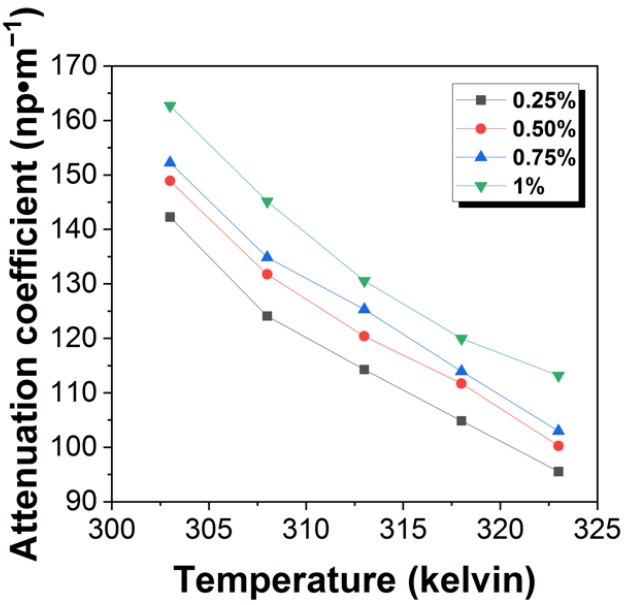

Fig. 6. Attenuation coefficient *vs* temperature.

Table 3

Values of Rao's constant (*Ro*) and Wada's constant (*W*)

T (K)	*Ro* (m^3/mole)(m/s)$^{1/3}$($\times10^{-3}$)				*W* (m^3/mole)(N/m^2)$^{1/7}$($\times10^{-3}$)			
	0.25 %	0.50 %	0.75 %	1 %	0.25 %	0.50 %	0.75 %	1 %
303	0.2076	0.2075	0.2078	0.2082	0.0146	0.0146	0.0146	0.0147
308	0.2082	0.2084	0.2085	0.2090	0.0146	0.0147	0.0147	0.0147
313	0.2089	0.2091	0.2095	0.2099	0.0147	0.0147	0.0148	0.0148
318	0.2101	0.2101	0.2103	0.2109	0.0148	0.0148	0.0148	0.0148
323	0.2108	0.2110	0.2113	0.2117	0.0148	0.0148	0.0149	0.0149

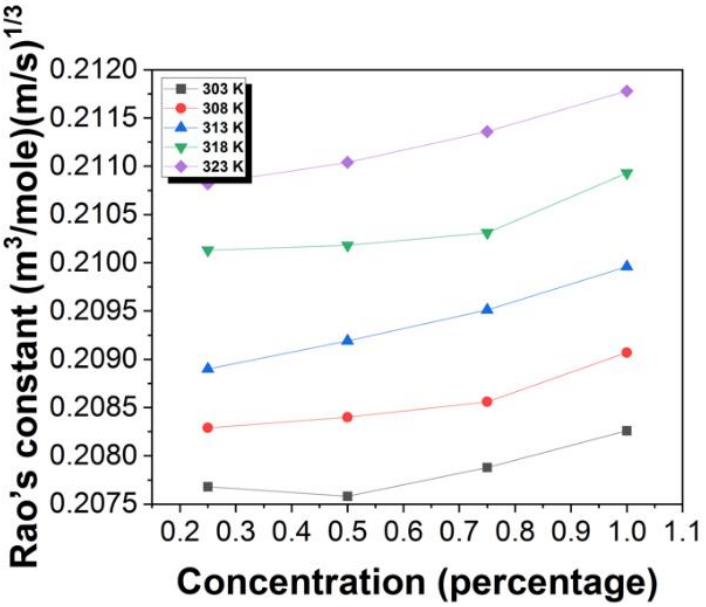

Fig. 7. Rao's constant *vs* concentration.

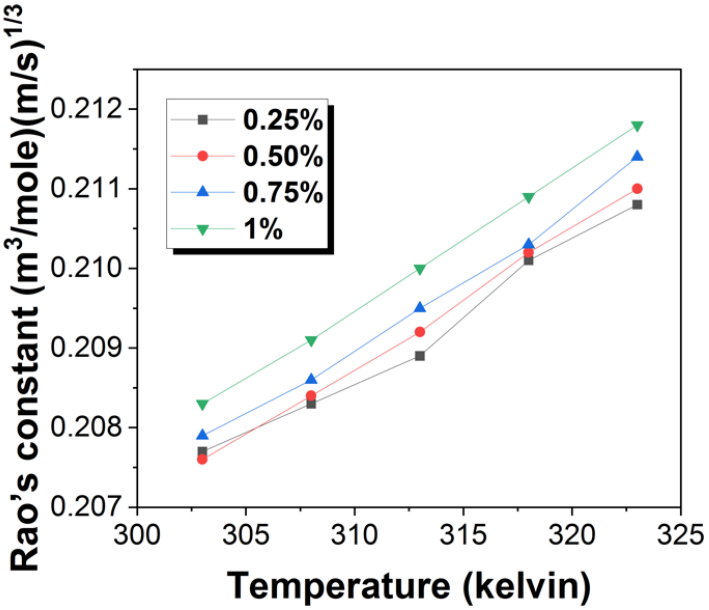

Fig. 8. Rao's constant *vs* temperature.

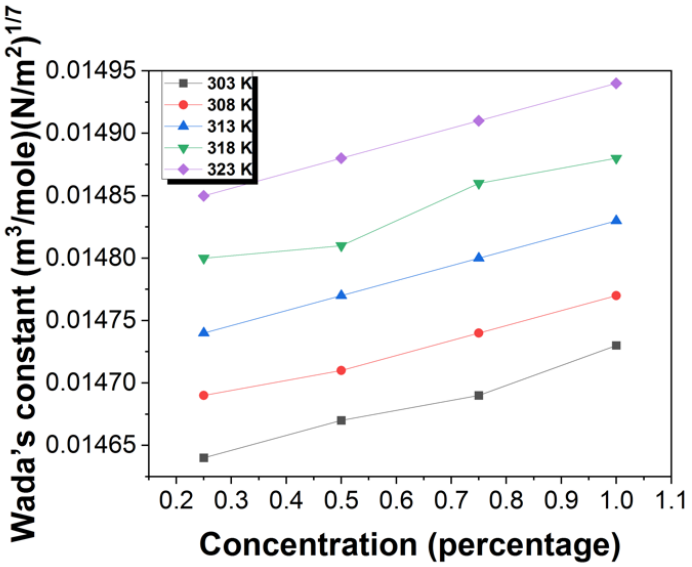

Fig. 9. Wada's constant *vs* concentration.

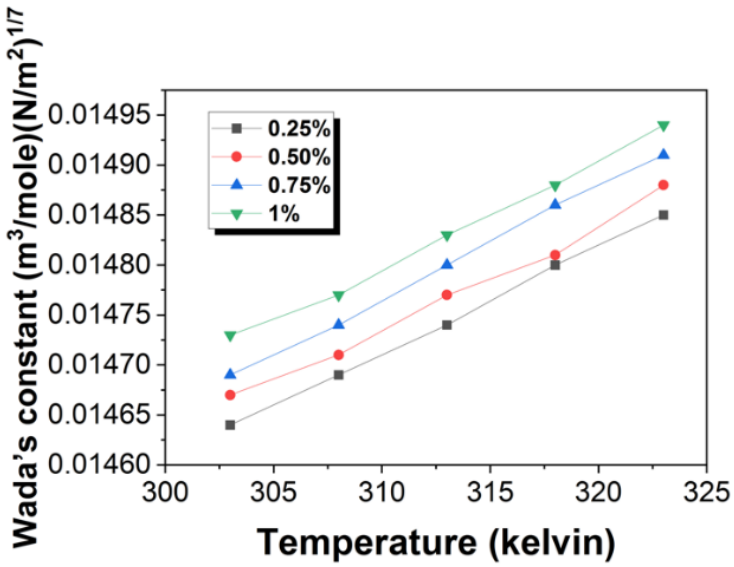

Fig. 10. Wada's constant *vs* temperature.

The greater association of the dextran molecules in distilled water is indicated by the fact that free volume declines (Fig. 3) and internal pressure increases (Fig. 1) with an increase in dextran concentration (volume in %). The fall in free volume with increasing concentration focus indicates that the particles have organized themselves to make the empty space less accessible [7, 6, 24]. Fig. 1 shows that as dextran concentration rises, internal pressure also does (as expected), while Fig. 3 shows that free volume exhibits the exact opposite trend with respect to internal pressure concentration. The nearby association between solute and dissolvable particles is the cause of the monitored increment estimations of internal pressure in the framework [13]. Atoms cooperate less when they distance themselves from one another at higher temperatures. As a result, the cohesive force is reduced, which lowers the value of πi in Fig. 2 [18, 24].

A measurement of the spatial rate of reduction in the sound wave's intensity level is the variation in the attenuation coefficient. The increases as the dextran concentration increases (Fig. 5). Furthermore, it gets smaller as the temperature rises (Fig. 6). With an increase in temperature, Rao's constant and Wada's constant exhibit an increasing tendency (Fig. 8 and Fig. 10). The rising trends with temperature suggest that there are more components available in a given region, which causes the medium to pack tightly and strengthen interactions between dextran and distilled water. Additionally, Rao's constant and Wada's constant both exhibit a rising trend with concentration (Fig. 7 and Fig. 9), indicating that mass is gradually accumulating in the solution's constituent parts as opposed to size expansion [3, 4, 11, 12].

CONCLUSIONS

The ultrasonic speed, itself, is highly sensitive to the structure and interactions present in the liquid systems as it is fundamentally related to the binding forces between the constituents of the medium. The ultrasonic speed in solutions is determined by the intermolecular free path length. The molecules in the solution are agitated when ultrasonic waves are present. Because of the medium's flexibility, disturbed molecules restore their equilibrium locations. When a solute is introduced to a solvent, the molecules of the solute attract the molecules of the solvent. Compression and limited compressibility are terms used to describe this phenomenon. Solvent-solute interactions are strengthened by the aggregation of solvent molecules around solute molecules. The structure of the solute is significantly altered because of solvent-solute interactions. Our findings show that particular solvent-solute interactions play an important role in understanding the parameters of thermo-acoustics. Because of the hydrogen bonds formed by the dextran and distilled water, this is a certain sign of intermolecular interactions.

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