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Research Article

MOLECULAR INTERACTION OF A NOVEL POLYMER DEXTRAN WITH 2(M) GLYCINE –FREE VOLUME, INTERNAL PRESSURE, ABSORPTION COEFFICIENT, RAO'S CONSTANT AND WADA'S CONSTANT

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ABSTRACT
Ultrasonic studies have been found to be useful in describing the theory of liquid state of matter. Molecular interaction of polymer dextran with 2(M) glycine leads to some changes in their physical and thermodynamic properties because of free volume change, change in energy and change in molecular orientations. The thermo-physical parameters density (ρ), ultrasonic velocity (U) and viscosity (η) have been measured for dextran solution with 2(M) glycine at 303K, 308K, 313K, 318K & 323K at 5MHz frequency in different concentration of dextran. Using the experimental values of density (ρ), viscosity (η) and ultrasonic velocity (U), some of the acoustical parameters like free volume (V_f), internal pressure (Π_i), absorption coefficient or attenuation coefficient (α), Rao's constant (R) and Wada's constant (W) have been calculated at constant frequency. The variation of these parameters with respect to concentration and temperature has also been studied which throws light into the structural rearrangement of solute and solvent in aqueous solution.

Keywords: *Ultrasonicvelocity, Free Volume (V_f), Internal Pressure (Π_i), Absorption Coefficient or Attenuation Coefficient (α), Rao's Constant (R), Wada's Constant (W)*

INTRODUCTION
Measurement of ultrasonic velocity (U), viscosity (η) through ultrasonic interferometer and capillary viscometer (Mahapatra *et al.,* 2001) respectively had been the most common and economical method adpotedin the past years. In this paper, values of η, ρ, U and related thermodynamic and acoustic parameters have been determined. The ultrasonic velocity, viscosity and density of novel polymer dextran of molecular weight 70,000 at five different concentrations i.e. 0.1%, 0.25%, 0.50%, 0.75% and 1% in solvent aqueous 2(M) glycine have been studied at temperature 303K, 308K, 313K, 318K & 323K in 5MHz frequency. The interactions between solute-solvent molecules are responsible for change in physical–chemical properties (Mahapatra *et al.*, 2001). Dextran is the collective name of a large class of extracellular bacterial polysaccharide composed of exclusively of the monomeric unit α- D-glucopyranose linked mainly by 1, 6 bonds. Dextran is synthesised from sucrose by certain species of the family such as streptococcus and lactobacillus. Dextran develops naturally in sucrose containing solutions that have been included with dextran producing bacteria from air, plants or soil. It is the only polysaccharide that is water soluble. Dextran and their derivatives find wide applications in various industries particularly in pharmaceutical sector (Castellanos Gil *et al.,* 2008). The fast increasing of these polyglucosans for medical (Jeanes *et al.,* 1954; Arond and Fran, 1954), industrial and research purposes motivate to carry out investigation of thermo acoustic parameter of dextran by ultrasonic technique (Dash *et al.,* 2010).

MATERIALS AND METHODS
Experimental Section
Materials
Polymer dextran of molecular weight 70,000 has been used as solute is of analytical reagent (AR) grade, manufactured by HI Media Laboratories Private Limited, India. Solvent glycine is also of AR grade, manufactured by Merck Specialties Private Limited and is used as such throughout the experiments.

Methods

Velocity, density and viscosity have been measured following the standard procedure using an ultrasonic interferometer (Model M-84, supplied by M/S Mittal Enterprises, New Delhi), a 25-ml specific gravity bottle and an Oswald viscometer respectively (Panda and Mahapatra, 2015; Panda and Mahapatra, 2013).

Theoretical Aspect

The following thermodynamic and acoustic parameters have been calculated:

1. *Internal Pressure* (π_i): It can be calculated using the relation as given below

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

Where, b stands for cubic packing, which is assumed to be 2 for all liquids, k is a dimensionless constant independent of temperature and nature of liquids. Its value is 4.281×10^9. T is the absolute temperature in Kelvin, M_{eff} is the effective molecular weight, R is the universal gas constant, η is the viscosity of solution in $Ns \cdot m^{-2}$, U is the ultrasonic velocity in $m \cdot s^{-1}$, and ρ is the density in $kg \cdot m^{-3}$ of solution.

2. *Absorption Coefficient or Attenuation Coefficient*: It is a characteristic of the medium. It depends on the external condition like temperature, pressure and frequency of measurement. It is given by the following relation

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

Where, f is the frequency of ultrasonic wave

3. *Free Volume* (V_f): The free volume is broadly defined as the average volume in which the molecules can move inside the hypothetical cell due to the repulsion of the surrounding molecules. The free volumes can be calculated using the relation as given below

$$V_\mathrm{f} = \left(\frac{\mathrm{M_{eff}U}}{\mathrm{K}\eta}\right)^{\frac{3}{2}}$$

Where, M_{eff} is the effective molecular weight of the solution ($M_{eff} = \Sigma m_i X_i$, where mi and Xi are the molecular weight and mole fraction of solute and solvent), K is the temperature independent constant which is equal to 4.281×10^9 for all liquids

4. *Rao's Constant:* Rao has established the empirical relation between molecular weight, density and ultrasonic velocity of liquids as

$$\mathrm{R} = \frac{\mathrm{M_{eff}}}{\rho}\mathrm{U}^{1/3}$$

This equation is called Rao's rule and R is also called as the molar sound velocity. A number of authors have provided a theoretical explanation of Rao's formula on the basis of phase rule and kinetic theory of liquids.

5. *Wada's Constant:* Wada had analyzed the variation of molar compressibility with concentration for many liquid systems. He derived the empirical relation,

$$\mathrm{W} = \frac{\mathrm{M_{eff}}}{\rho}\beta^{-1/7}$$

RESULTS AND DISCUSSION

The density, viscosity, ultrasonic velocity and free volume of aqueous solution of dextran of different concentration with (2M) Glycine are represented in Table 1 and Table 2 at different temperatures i.e. 303K, 308K, 313K, 318K and323K.

It is observed that ultrasonic velocity increases with increase in concentration (vol. %) of dextran in glycine, indicating their association. The increase suggests a structure-making capacity of polymers in solution. With increase in the temperature there occurs a structural rearrangement as a result of solvation leading to a comparatively more ordered state.

Free volume is one of the significant factors in explaining the free space and has close connection with molecular structure and it may show interesting features about interactions between solute and solvent. It

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is observed that free volume decreases (Figure 3) and internal pressure increases (Figure 5) with increase in concentration (vol.%) of dextran in glycine, indicating association of the molecules of solute and solvent. The decrease in free volume with increase in concentration suggests that the molecules arrange themselves in such a way that the void space is less available showing that compressibility decreases.

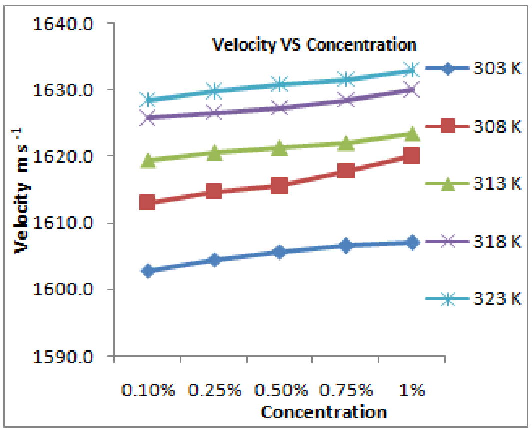

Figure 1: Variation of Ultrasonic Velocity with Concentration

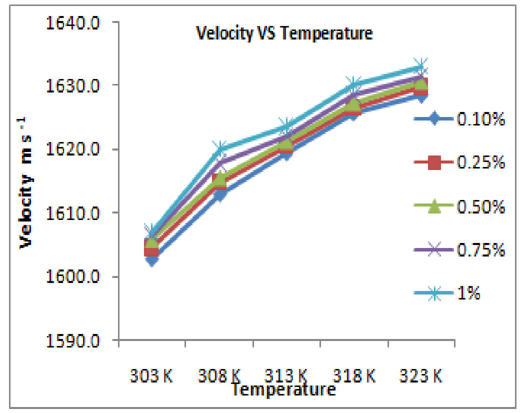

Figure 2: Variation of Ultrasonic Velocity with Temperature

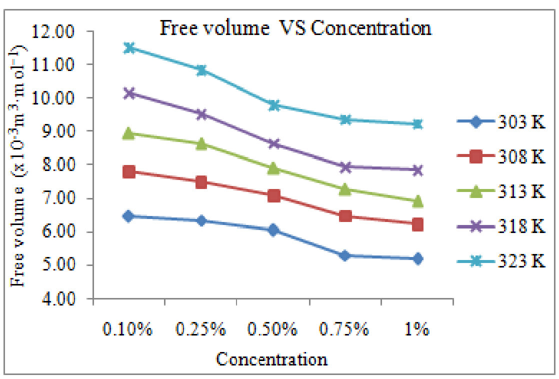

Figure 3: Variation of Free Volume (V_f) with Concentration

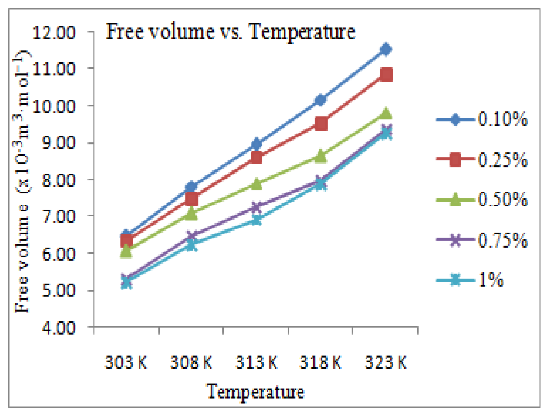

Figure 4: Variation of Free Volume (V_f) with Temperature

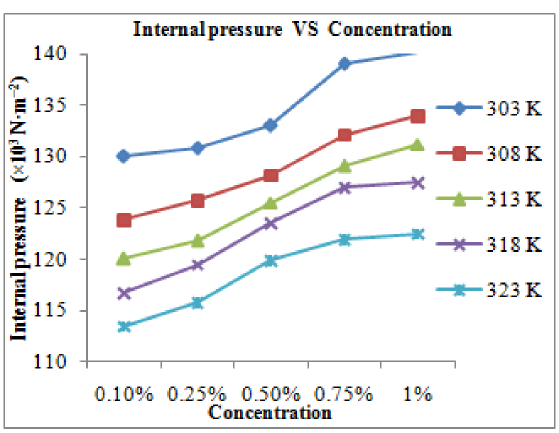

Figure 5: Variation of Internal Pressure with Concentration

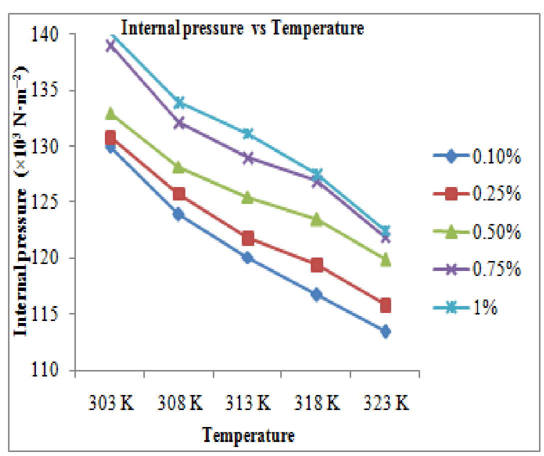

Figure 6: Variation of Internal Pressure with Temperature

Table 1: Values of Density (ρ) and Viscosity (η) of Dextran with 2(M) Glycine at Different Concentrations and Temperatures

T (Kelvin)	Concentration									
	0.10%		0.25%		0.50%		0.75%		1%	
	ρ kg m^{-3}	η 10^{-3}N s m^{-2}	ρ kg m^{-3}	η 10^{-3}N s m^{-2}	ρ kg m^{-3}	η 10^{-3}N s m^{-2}	ρ kg m^{-3}	η 10^{-3}N s m^{-2}	ρ kg m^{-3}	η 10^{-3}N s m^{-2}
303	1053.502	1.079	1054.690	1.093	1055.482	1.129	1056.274	1.233	1057.858	1.251
308	1051.885	0.957	1053.469	0.985	1054.261	1.023	1055.053	1.087	1055.845	1.118
313	1049.660	0.877	1051.243	0.900	1052.431	0.955	1052.827	1.010	1053.223	1.044
318	1047.235	0.808	1049.214	0.845	1050.006	0.902	1050.402	0.953	1050.797	0.962
323	1043.417	0.745	1044.207	0.776	1044.998	0.831	1047.371	0.857	1047.766	0.865

Table 2: Values of Ultrasonic Velocity (U) and Free Volume (V_f) of Dextran with (2M) Glycineat 5MHz Frequency at Different Temperatures and Concentrations

T (Kelvin)	Ultrasonic Velocity (U) m/s^2					Free Volume(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	1602.8	1604.5	1605.8	1606.5	1607.0	6.464	6.354	6.057	5.308	5.197
308	1613.0	1614.8	1615.5	1617.8	1620.0	7.818	7.491	7.089	6.479	6.227
313	1619.5	1620.5	1621.3	1622.0	1623.5	8.965	8.623	7.902	7.270	6.926
318	1625.8	1626.5	1627.3	1628.5	1630.0	10.183	9.540	8.656	7.970	7.874
323	1628.5	1629.8	1630.8	1631.5	1633.0	11.538	10.870	9.817	9.378	9.254

Table 3: Values of Internal Pressure and Attenuation Coefficient of Dextran with 2(M) Glycine at Different Temperatures and Concentrations at 5MHz Frequency

T (Kelvin)	Internal Pressure((×10^3 N·m^{-2})					Attenuation Coefficient(x10^6(np·m^{-1})				
	0.10%	0.25%	0.50%	0.75%	1%	0.10%	0.25%	0.50%	0.75%	1%
303	129.989	130.832	132.999	139.057	140.176	262.540	264.971	273.128	297.913	301.577
308	123.890	125.793	128.191	132.161	133.987	230.161	236.195	244.745	259.319	265.698
313	120.112	121.802	125.496	129.066	131.196	209.673	214.725	227.239	240.031	247.574
318	116.778	119.495	123.494	126.971	127.519	192.308	200.382	213.543	225.366	226.907
323	113.501	115.836	119.899	121.926	122.498	177.291	184.196	196.872	202.419	203.954

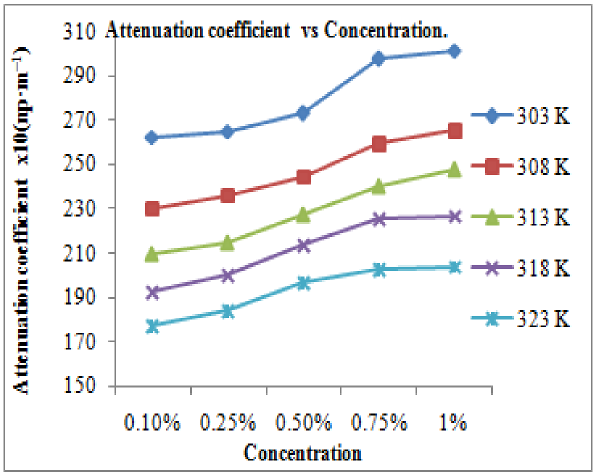

Figure 7: Variation of Attenuation Coefficient with Concentration

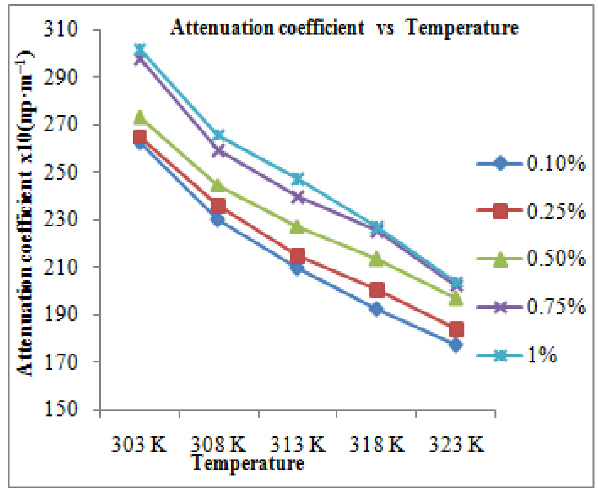

Figure 8: Variation of Attenuation Coefficient with Temperature

Internal pressure is the forces of interaction that contribute to the overall cohesion or adhesion of the liquid system. When concentration of dextran increases, internal pressure increases as the force of cohesion increases as in Figure 5.

Free volume as in figure 3 has shown exactly the opposite trend with concentration to that of internal pressure as expected. The observed increase values of internal pressure in system are due to close association between solute and solvent molecules. When the temperature increases there is reduction in molecular interaction as they move away from each other.

This reduces the cohesive force thus decrease in internal pressure as shown in Figure 6. i.e. it also represents that there is weak interaction between the solute and solvent molecules (Panda and Mahapatra, 2015; Palani and Balakrishnan, 2010).

Attenuation coefficient is the measure of rate of decrease in the intensity level of ultrasonic wave. When concentration of dextran increases, the attenuation coefficient increases i.e. the wave is more and more attenuated and it decreases with the increase in temperature.

The effect of temperature on attenuation is more appreciable than that of concentration. This confirms that the intermolecular interactions are progressively increases with increase in concentration of dextran (Das *et al.*, 1999).

Table 4: Values of Rao's Constant (R) and Wada's Constant (W) of Dextran with 2(M) Glycine at Different Temperatures and Concentrations at 5MHz Frequency

T (Kelvin)	**Rao's Constant R (m^3/mole)(m/s)$^{1/3}$(10^{-3})**					**Wada's Constant 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	1.111	1.110	1.109	1.109	1.107	2.113	2.111	2.110	2.109	2.107
308	1.115	1.114	1.113	1.113	1.112	2.119	2.117	2.116	2.116	2.115
313	1.119	1.117	1.116	1.116	1.116	2.126	2.123	2.122	2.121	2.121
318	1.123	1.121	1.120	1.120	1.120	2.132	2.129	2.128	2.128	2.128
323	1.128	1.127	1.126	1.124	1.124	2.140	2.139	2.138	2.134	2.134

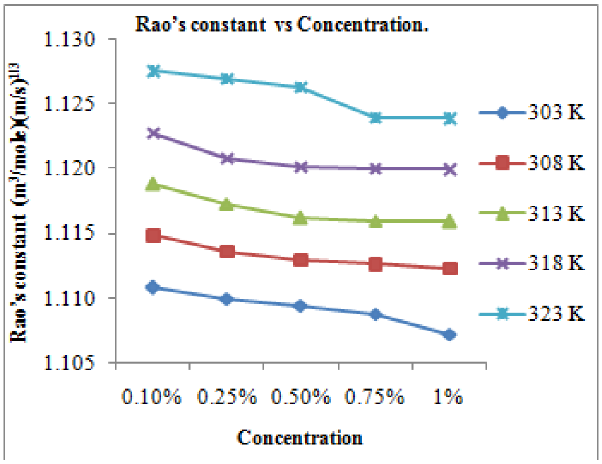

Figure 9: Variation of Rao's Constant (R) with Concentration

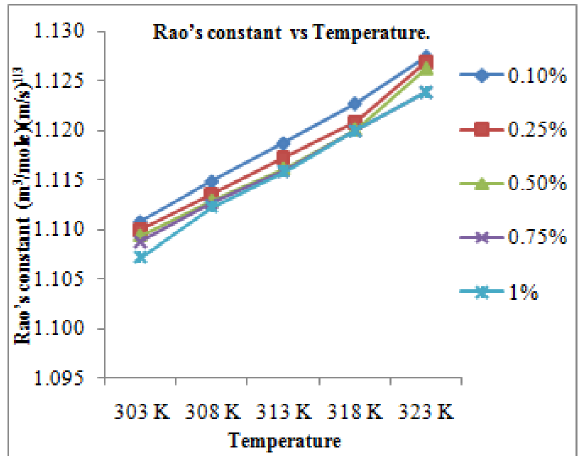

Figure 10: Variation of Rao's Constant (R) with Temperature

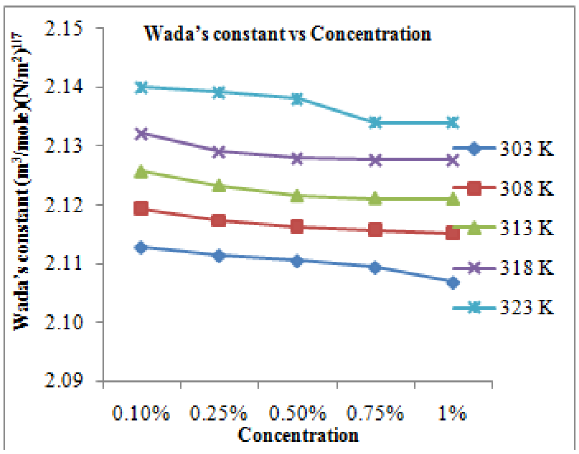

Figure 11: Variation of Wada's Constant (W) with Concentration

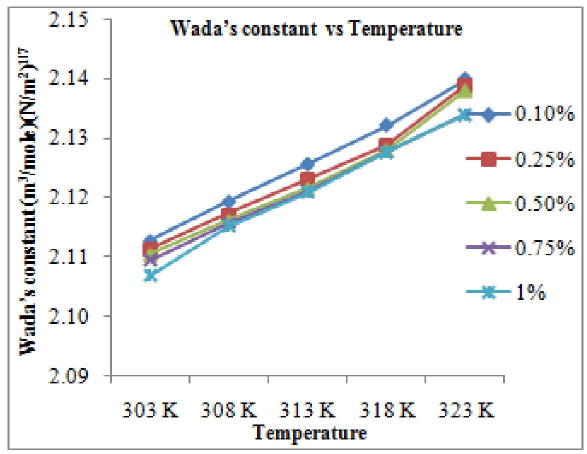

Figure 12: Variation of Wada's Constant (W) with Temperature

The variation of Rao's constant with concentration is shown in figure 9 it is also observed that Rao's constant decreases with the rise in concentration but the variation is negligible which supports the facts shown by other thermo acoustical parameters (Nikam and Hasan, 1993; Panda and Mahapatra, 2014).

It is observed that Wada's constant decreases with the increasing concentration but the variation is negligible. This indicates that solute-solvent molecules are very close to each other and hence, the interaction increases which leads to the increase in compressibility, but both Rao's and Wada's constant increases with increase in temperature.

Conclusion

Ultrasonic velocity, density and viscosity have been measured for dextran of different concentrations with 2(M) glycine at different temperatures in 5 MHz frequency. Viscosity, velocity, free volume, attenuation coefficient and internal pressure increases with increase in concentration, whereas Wada's constant and Rao's constant decrease with the increase in concentration and the trend reverse with increase in temperature.. These results show that the specific solute-solvent interactions play a significant role in explaining thermo acoustic parameters. Therefore, the detailed study of thermo dynamical parameters and acoustic parameter suggests that there is molecular associations exist in the solution. The addition of solute into the solvent brings about a strong solute-solvent interaction and necessary structural changes takes place in the respective system.

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