Variation of thermo-acoustic parameters of dextran with concentration and temperature

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ABSTRACT

The acoustic behaviour of aqueous dextran solution has been studied at 303K, 308K, 313K, 318K & 323K at 1MHz frequency in different concentration. Various parameters such as adiabatic compressibility, intermolecular free length, relaxation time, acoustic impedance, and Gibb's free energy have been calculated using experimental determined values of ultrasonic velocity, density and viscosity. The variation of these parameters has been discussed in the light of solute and solvent interactions and structural arrangement of the molecules. The qualitative inter molecular elastic forces between the solute and solvate molecules are explained.

Key words: Aqueous dextran solution, Ultrasonic Velocity, Acoustic impedance (Z), Adiabatic Compressibility (β), Intermolecular free length (L_f), Relaxation time (τ) , Gibb's free energy(ΔG).

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INTRODUCTION

Ultrasonic investigation of polymer solution is of considerable importance in understanding intermolecular interaction between the solute and solvent molecules as that finds application in several industrial and technological processes [1, 2].

Measurement of some bulk properties like viscosity (η),density(ρ) and ultrasonic velocity (U) provides insight into the intermolecular arrangements of the solute and solvent in solutions and helps to understand the thermodynamic and acoustic properties of the solutions.

In this paper, values of η, ρ, U and related acoustic parameters have been determined and the solute-solvent interactions for the aqueous solution of dextran at different concentrations have been studied at five different temperatures i.e. 303K, 308K,313K, 318K & 323K at 1MHz frequency.

Dextran consists of α-D glucose units with a majority of α (1→6) glucosidic linkage between them. Dextran is a branched polysaccharide which is water soluable and is composed of α- D-glucopyranosyl residues. Dextran and their derivatives find wide applications in various industries particularly in pharmaceutical sector [3, 4].

The fast increasing of these polyglucosans for medical, industrial and research purpose motivated to carry out investigation of thermoacoustic parameter of dextran by ultrasonic technique [5-7].

EXPERIMENTAL SECTION

Freshly prepared distilled water has been used as solvent for preparing dextran solution [8, 9]. Dextran of molecular weight 70,000 used as solute, is of analytical reagent (AR) grade, manufactured by HI Media Laboratories Private Limited, India.

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Velocity Measurement
The ultrasonic interferometer model (M-84) used for measuring velocity have been calibrated by taking some standard liquid. The velocity of ultrasonic wave in the aqueous solution of dextran in different concentrations have been measured using multi-frequency ultrasonic interferometer having high degree of accuracy, (Model M-84) supplied by M/s Mittal Enterprises, New Delhi at 1 MHz frequency. The measuring cell consist of a specially designed double walled vessel with provision of maintaining constant temperature. An electronically operated digital constant temperature bath (Model SSI-03spl) supplied by M/s Mittal Enterprises, New Delhi, operating in the temperature range -10°C to 85°C with an accuracy of ± 0.1°C has been used to circulate water through the outer jacket of the double walled measuring cell containing the experimental liquid.

Density Measurement
The densities of solvent and the solution are measured using a 25ml specific gravity bottle. The specific gravity bottle with the aqueous solution of dextran is immersed in the temperature controlled water bath and density is measured at five different temperatures (303K, 308K, 313K, 318K & 323K).

Viscosity measurement
The viscosity of solution is measured using an Oswald's viscometer calibrated with double distilled water. The Oswald's viscometer with the polymer solution is immersed in the temperature controlled water bath. The time of flow was measured using a racer stop watch with an accuracy of 0.01 second at above mentioned temperatures.

Theoretical aspect
The density, viscosity and ultrasonic velocity have been measured and using these experimental data the following thermo acoustic parameters were calculated using standard formula [10].

Acoustic impedance
$$Z = U.\rho \qquad (1)$$

Adiabatic Compressibility
$$\beta = \frac{1}{\rho U^2} \qquad (2)$$

Intermolecular free length
$$L_f = \frac{K_T}{U\rho^{\frac{1}{2}}} \qquad (3)$$

Relaxation time
$$\tau = \frac{4}{3}\frac{\eta}{\rho U^2} \qquad (4)$$

Gibb's free energy
$$\Delta G = kT \ln \frac{kT\tau}{h} \qquad (5)$$

Where ρ density, U velocity, η viscosity K_T is the temperature dependent constant. $K_T = (93.875+0.375T) \times 10^{-8}$ '*T*' is the absolute temperature; '*k*' is the Boltzmann's constant and '*h*' is the Planck's constant.

RESULTS AND DISCUSSION

The density, viscosity, ultrasonic velocity and acoustic impedance (Z) of aqueous solution of dextran of different concentration are represented in **Table-1 and 2** at temperature 303K, 308K, 313K, 318K and 323K.

Table 1 Values of density (ρ) and Viscosity (η) of aqueous solution of dextran in 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	996.866	0.845	998.450	0.857	998.846	0.896	999.639	0.918	1000.827	0.991
308	995.251	0.737	996.439	0.757	996.835	0.800	998.419	0.825	999.212	0.890
313	993.831	0.686	994.227	0.702	994.623	0.739	996.602	0.773	996.998	0.809
318	990.639	0.636	991.035	0.650	993.013	0.690	993.409	0.710	994.597	0.748
323	988.458	0.584	989.249	0.598	989.645	0.625	990.040	0.643	991.621	0.713

Table 2   Values of Ultrasonic velocity (U) and Acoustic impedance (Z) of aqueous solution of dextran in different concentrations and temperatures at 1MHz frequency

T (kelvin)	Ultrasonic velocity (U) m/s^2					Acoustic impedance (Z) 10^6 kg·m^2·s^{-1})				
	0.10%	0.25%	0.50%	0.75%	1%	0.10%	0.25%	0.50%	0.75%	1%
303	1519.000	1517.533	1515.333	1517.467	1518.533	1.514	1.515	1.514	1.517	1.520
308	1527.867	1527.733	1527.533	1527.800	1528.467	1.521	1.522	1.523	1.525	1.527
313	1538.133	1537.000	1535.267	1536.600	1538.333	1.529	1.528	1.527	1.531	1.534
318	1544.200	1543.933	1541.533	1544.067	1545.267	1.530	1.530	1.531	1.534	1.537
323	1550.400	1548.666	1548.000	1549.933	1550.467	1.533	1.532	1.532	1.534	1.537
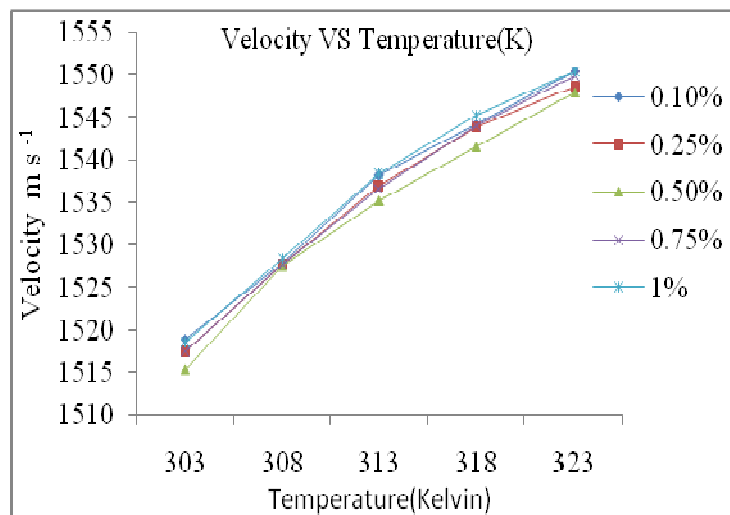
Fig.-1 Variation of ultrasonic velocity with Temperature
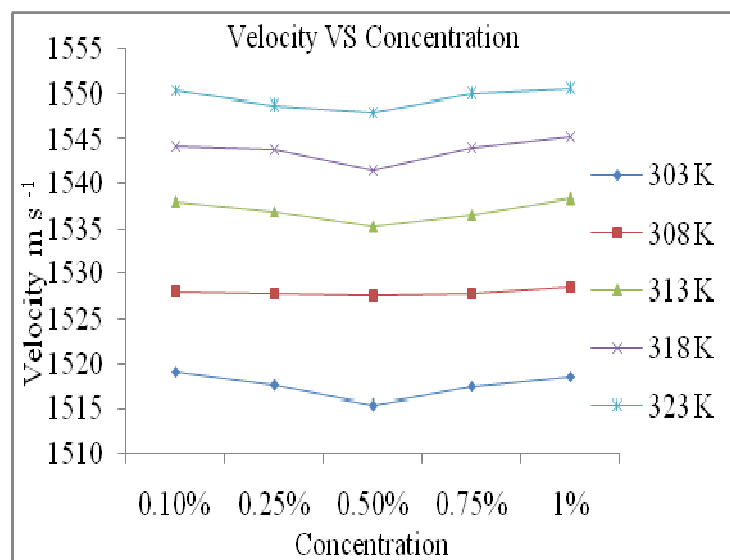
Fig.-2 Variation of ultrasonic velocity with concentration

Density and viscosity decreases with increase in temperature indicates decrease in inter molecular forces due to increase in thermal energy of the system. This causes an increase in volume and hence decrease in density and viscosity [11,12].

By addition of dextran in water the structure of both solute and solvent being disrupted. Dextran occupies the interstitial space of water and tends to break the original order state of water. Interaction between solute and solvent molecules results in decrease in free length and increase in density and viscosity with increase of solute concentration at all temperatures. With increase in temperature there occurs a structural rearrangement as well as a result of hydration leading to a comparatively more order state therefore ultrasound speed increases with increase in temperature **Fig.1 &Fig.2**
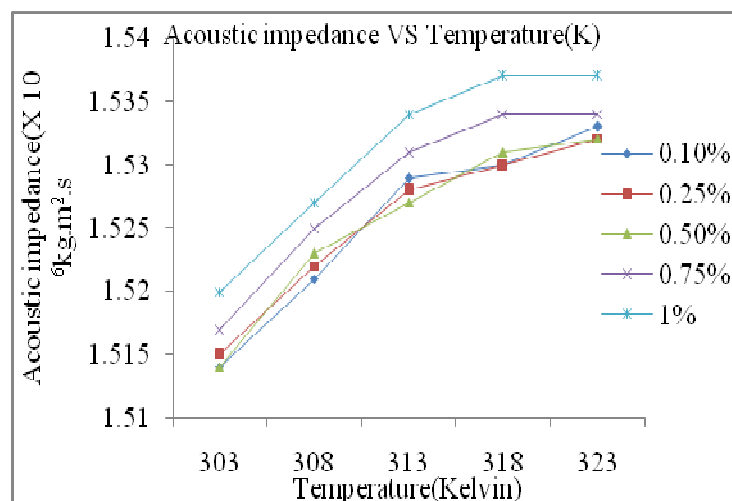
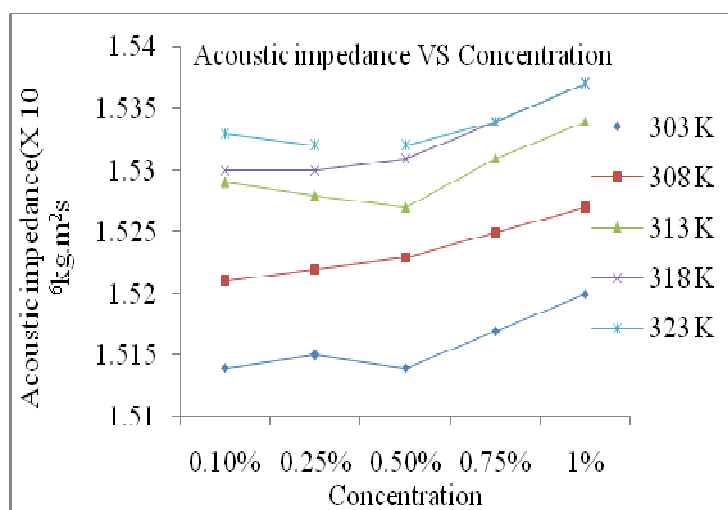**Fig.-3 Variation of Acoustic impedance with Temperature**

Fig.-4 Variation of acoustic impedance with concentration

With increase in concentration of dextran, density of dextran of the solution increases and volume variation is negligible, where as ultrasonic velocity initially decreases and then increases with increase in concentration of dextran in distilled water as shown in fig.2. The initial decrease in ultrasonic velocity shows structure breaking tendency between solute and solvent molecules and increase in ultrasonic velocity at higher concentration of dextran in distilled water shows structural readjustment of molecular packing taking place in solution [13]. The variation of acoustic impedance (Z) with concentration of dextran is negligible for low concentrations of dextran and increases linearly for higher concentrations of dextran as shown in. fig.4. This increase in Z values with solute concentration can be attributed to the effective solute-solvent interaction, since acoustic impedance is a measure of the resistance offered by the liquid medium to the solvent concentration and a function of the elastic property of one medium i.e. the bulk modulus of elasticity depend on the structural changes of the solution, the higher Z values in the equivalent dextran solution as compared to that in water and increasingly higher values with increase in the solute concentration.

Table 3 Values of adiabatic compressibility and acoustic impedance at different temperatures and different concentrations of aqueous solution of dextran at 1MHz frequency

| T (kelvin)	Adiabatic Compressibility $(\beta)(10^{-10}N^{-1}.m^2)$					Intermolecular free length $(L_f)\ 10^{-10}$ m				
	0.10%	0.25%	0.50%	0.75%	1%	0.10%	0.25%	0.50%	0.75%	1%
303	4.348	4.349	4.360	4.344	4.333	0.41370	0.41377	0.41429	0.41355	0.41301
308	4.304	4.300	4.299	4.291	4.283	0.41521	0.41500	0.41497	0.41457	0.41418
313	4.253	4.258	4.266	4.250	4.238	0.41629	0.41652	0.41691	0.41613	0.41558
318	4.233	4.233	4.238	4.222	4.211	0.41888	0.41886	0.41910	0.41833	0.41775
323	4.209	4.215	4.217	4.205	4.195	0.42120	0.42150	0.42160	0.42099	0.42051

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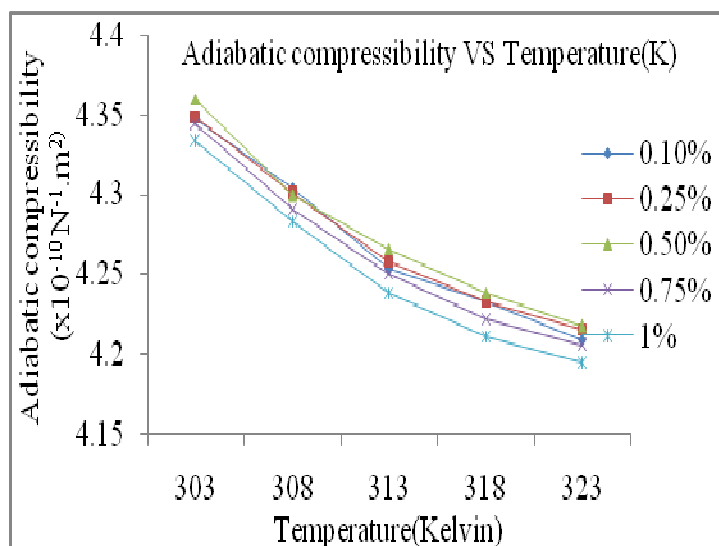
Fig.-5 Variation of Adiabatic Compressibility with Temperature

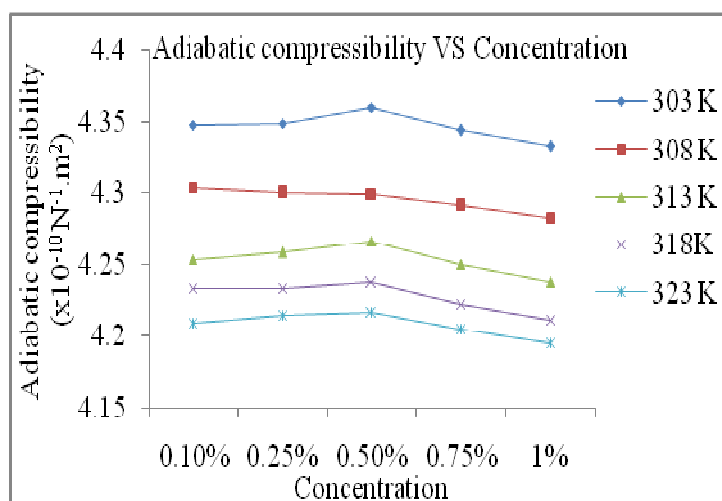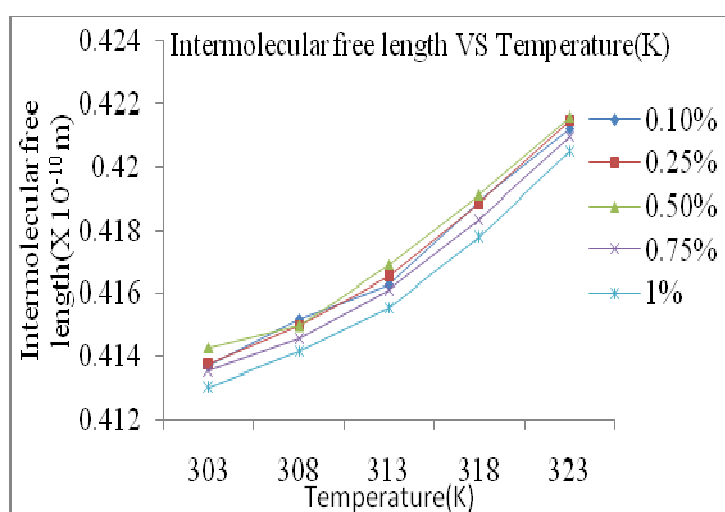**Fig.-6 Variation of Adiabatic Compressibility with Concentration**

Fig.-7 Variation of Intermolecular free length with Temperature
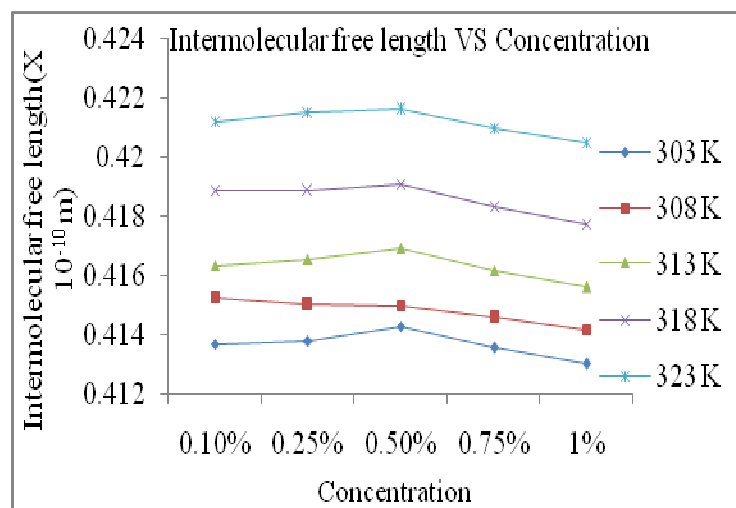
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Fig.-8 Variation of Intermolecular free length with Concentration

Adiabatic compressibility decreases with increase in higher concentration range Fig.6 which indicates strong interaction between solute and solvent molecules. It is a well known fact that when a solute dissolves in a solvent some of the solvent molecules are attached to the ions (produced from the solute) because of ion-solvent interactions. Since the solvent molecules are oriented in the ionic field (i.e. electrostatic fields of ions) the solvent molecules are more compactly packed in the primary salvation shell as compared to the packing in the absence of the ions, this is the reason why the solvent is compressed by the introduction of ions. Thus, the electro static field of the ions causes compression of the medium giving rise to a phenomenon called electrostriction. Since the solvent molecules are compressed they do not respond any further application of pressure so the solution becomes harder to compress i.e. the compressibility decreases with concentration.

Inter molecular free length increases(Fig.7) with increase in temperature [14,15] as the temperature increases it leads to the less order structured and more spacing between the molecules due to increase in thermal energy of the system which increases in volume expansion and hence increase in inter molecular free length. Inter molecular free length increases initially and then decreases linearly on increasing the concentration as shown in fig.8. The decrease in free length with concentration may be attributed to dipole-dipole interaction, H-bonding association between the solute and Solvent molecules.
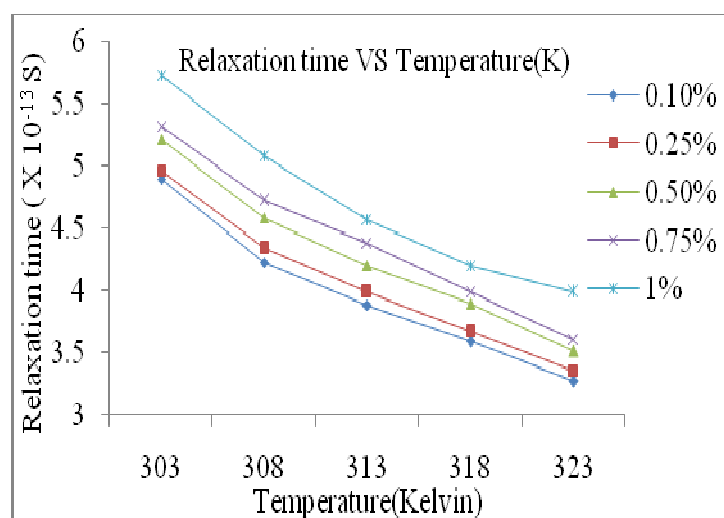

Fig.-9 Variation of Relaxation time with Temperature

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Table 4 Values of relaxation time and Gibb's free energy (ΔG) at different temperatures and concentrations of aqueous solution of dextran at 1MHz frequency

| (kelvin)	Relaxation time (τ)(10^{-13}Sec.)					Gibb's free energy(ΔG)10^{-20}kJ·mol^{-1}				
	0.10%	0.25%	0.50%	0.75%	1%	0.10%	0.25%	0.50%	0.75%	1%
303	4.898	4.970	5.211	5.318	5.723	205.121	207.740	216.376	220.061	233.388
308	4.230	4.341	4.587	4.721	5.084	184.417	189.206	199.384	204.726	218.387
313	3.892	3.985	4.204	4.382	4.570	174.831	179.274	189.303	197.073	204.968
318	3.590	3.669	3.897	3.995	4.200	165.236	169.360	180.877	185.593	195.150
323	3.275	3.358	3.513	3.607	3.986	153.046	157.911	166.670	171.787	191.114
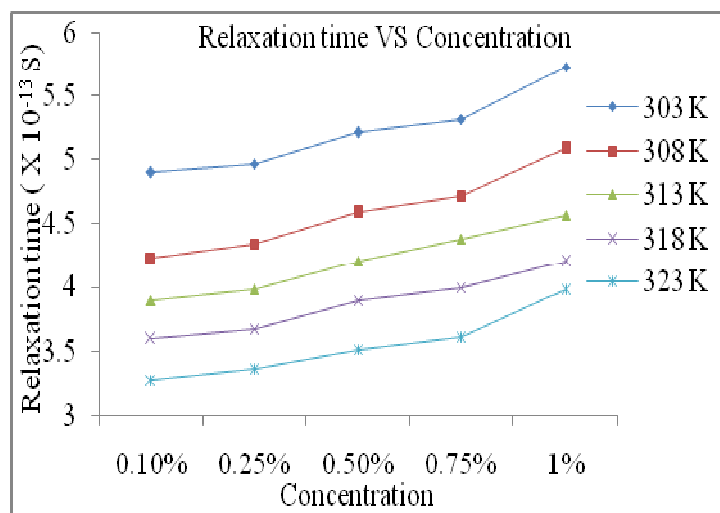
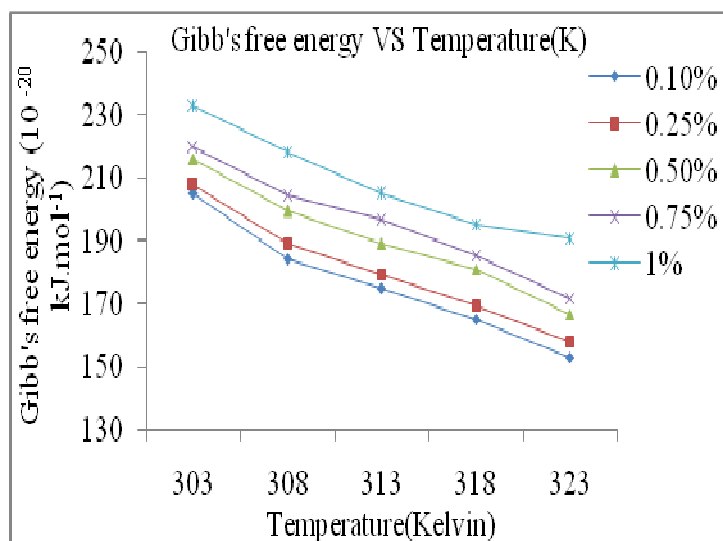**Fig.-10 Variation of Relaxation time with Concentration**

Fig.-11 Variation of Gibb's free energy with Temperature

Gibbs free energy increases with increase in concentration of dextran (Fig.12). Increasing value of Gibbs free energy suggests that the closer approach of unlike molecules due to hydrogen bonding [16]. The increase in Gibb's free energy with concentration suggests shorter time for rearrangement of the solute molecules in the solution. Increase in relaxation time with increase in concentration indicates (Fig.10) that the solution is highly ordered due to excellent hydration.

Viscous relaxation time and Gibbs free energy both decreases as temperature increases as shown Fig.9 & fig.11 respectively. With increase in temperature   excitation energy increases and hence relaxation time decreases [17]. Further as the kinetic energy of the molecule increases, it takes long time for rearrangement of molecule and this suggests a decrease in Gibb's free energy.
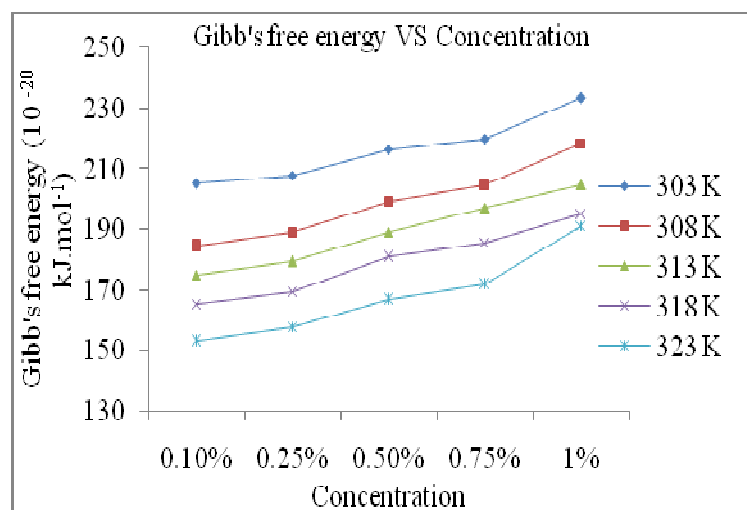
Fig.-12 Variation of Gibb's free energy with Concentration

CONCLUSION

From the experimental measured parameters(i.e. density, viscosity and ultrasonic velocity) of the aqueous solutions of dextran at different concentrations and temperatures, thermo-acoustic parameters like acoustic impedance (Z), adiabatic compressibility (β), intermolecular free length (L_f), relaxation time (τ), Gibb's free energy (ΔG), have been calculated at 1MHz frequency .The results show that the specific solute-solvent interactions play an important role for explaining acoustic parameters [14]. However, any deviation from the usual behaviour is probably due to characteristic structural changes in the respective system.

REFERENCES

[1] UN Dash; GS Roy; M Talukdar; D Moharatha. *Ind. J. Pure & Appl. Phys*. **2010**, 48(09), 651-657

[2] D Kim; JF Robyt; SY Lee; JH Lee; YM Kim. Carbohydrate Research, ELSEVIER. **2003**,338, 1183-1189.

[3] Gil Castellanos; EE Iraizoz; AEl Colarte; A Ghzaoui; D Durand; JL Delarbre; B Bataille. *European Journal of Pharmaceutics and Bio pharmaceutics*. **2008**, 68, 308-319.

[4] S Aswale; S Aswale; B Ramteke. *Journal of chemical, Environmental and Pharmaceutical research* . **2012**, l3, 58-63.

[5] RP Singh. *Acoustic Society India*. **1993**, 21(3),159-170.

[6] VA Tabhane; S Agrawal; KG Reuatkar; *J.Accoustic Society of India*. **2000**, 28, 369-372.

[7] S Thirumaran; KJ Sabu*; J .Exp.Sc*. **2012**, 3, 10-18.

[8] AP Mahapatra; RK Samal; RN Samal; GS Roy. *Journal applied polymer science*. **2001**,81(2), 440–452 .

[9] AP Mahapatra; RK Samal; RN Samal; GS Roy. *Physics chemistry of liquids*. **2001**, 39(3), 343-356.

[10] RJ Fort; WR Moore. *Trans faraday Soc*. **1965**, 61, 2102-2111.

[11] S Panda; AP Mohapatra. Study of acoustic and thermodynamic properties of aqeous solution of dextran at different frequencies and temperatures through ultrasonic technique. Proceeding of National Symposium on Ultrasonic. Ravenshaw University Cuttack. **2013**, 203-207.

[12] MK Praharaj; P Mishra; S Mishra; A Satapathy. *Journal of Chemical and Pharmaceutical Research*, **2013**, 5(1):49-56

[13] P Tabhane; OP Chimankar; VA Tabhane. *Chem.Pharma.Res*. **2012**, 4(6),3051-3056

[14] MK Praharaj; P Mishra; S Mishra; A Satapathy. *Adv. Applied science Researcher*. **2012**, 3(3),1518-1530.

[15] MK Praharaj; A Satapathy; S Mishra; PR Mishra. *Journal of Chemical and Pharmaceutical Research*, **2012**, 4(4):1910-1920

[16] Amatendy Pal; Hash Kumar; BR Arbadb; AB Takal. *Ind. J. Pure & Appl. Phys*. **2003**, 41,113-120 .

[17] A Ali; S Hyder; AK Nain. *Indian Journal of Physics and Proc of the Indian Assoc for the Cultivation of Science*-B. **2000**, 74(1), 63-68.