International Journal of Modern Agriculture, Volume 9, No.4, 2020
ISSN: 2305 - 7246

MOLECULAR INTERACTION OF AQUEOUS DEXTRAN AT DIFFERENT TEMPERATURES AND FREQUENCIES

Subhraraj Panda

Department of Physics, Centurion University of Technology and Management, Odisha, India
Email: subhraraj4u@gmail.com

Abstract

The propagation of ultrasonic waves in aqueous solution of dextran polymers depends on their viscoelastic behavior and density, which affected significantly with temperature and frequency changes. In this paper, the "density (ρ) and viscosity (η)" of the aqueous dextrane systems were measured at "303K, 3308K, 313K, 318K and 323 K". Ultrasonic speed was measured at five temperatures ranging from 303 K to 323 K and at frequencies at "1MHz, 5MHz, 9MHz, and 12MHz", using ultrasonic interferometer. The acoustic parameters such as "free volume, internal pressure, attenuation coefficient, Rao's constant and Wada's" constant are determined using the experimental parameters "density (ρ) viscosity (η) and ultrasonic speed (U)". The variance of these parameters with different temperatures and frequencies contributes to the study of inter-molecular interaction and its constituent power between the solute (dextran 1 percent) and the solvent (distilled water).The findings in the aqueous dextran solution were viewed in light of structural rearrangement occurring.

Key words: Dextran, ultrasonic velocity, density, viscosity, acoustical parameters

Introduction

Most pharmaceutical and chemical industries use various types of polymer solution and liquid mixtures in their operations, which is why optimum industrial designs and simulations need to be taken into account in thermodynamic studies and modeling research and growth [1].Non-ideal solvent mixing properties are responsible for interactions between different molecules, and these interactions influence the physio-chemical properties of solvents [2-4].

During the last two decades, the practical importance of solution rather than single component liquid systems has gained considerable importance in assessing the nature of molecular interactions and in investigating the physio-chemical behavior of such systems [5-6]. The ultrasonic studies have seen many applications in the characterization of the thermodynamic and physiochemical properties of liquid solutions. The acoustic and thermodynamic parameters were used to test various kinds of interactions, molecular motion and various interaction modes and their effects, influenced by the size of the pure component and the mixtures[7-9] .Attempts have been made in the present work to investigate the behavior of aqueous dextran (1 per cent). Throughout our work we measured acoustic parameters such as "free volume (V_f), internal pressure (πi), absorption or attenuation coefficient (α), Rao's constant(R) and Wada 's constant (W)" at five temperatures ranging from 303 K to 323 K and at frequencies at "1MHz, 5MHz, 9MHz, 12MHz".

We chose a dextran of polymer as a solvent, with water as a solvent [10-11]. This is the "only water-soluble polymer". Dextran and its derivatives consider the rapid growth of these polyglucosans for "medical-industrial and research purposes" in wide-ranging applications in various "industries, in particular in the pharmaceutical sector; inspired by ultrasonic technique to investigate thermo-acoustic parameters of dextran".

Materials and Methods

Materials

Freshly prepared distilled water was used as a solvent for the preparation of dextran (70,000 dalton molecular weight) solution. [12]

Measurements

(a) "Velocity Measurement":-

The velocity of ultrasonic wave in the solution have been measured using "multi-frequency ultrasonic interferometer", "operating in the temperature range -10 ^{0}C to 85 ^{0}C with an accuracy of ± 0.1K" has been used to circulate water through the outer jacket of the double walled measuring cell containing the experimental liquid.[13]

The expression used to determine the ultrasonic velocity is

$$u = 2d/T \text{ (m/s)}$$

$$= 2d \times \nu$$

$$= \lambda \times \nu \quad \text{(Here-2d=}\lambda\text{)}$$

"Where, ν is the frequency of the generator which is used to excite the crystal; (In the present investigation, different frequency frequencies (1MHz, 5MHz, 9MHz and 12MHz interferometer was employed) d- Separation between the reflector and crystal; T-Travel time of ultrasonic wave".

(b) "Density Measurement":-

The "densities" of the mixture were measured using a 10 ml "specific gravity bottle".

The density was measured using the formula [13]

$$\text{“}\rho_2 = \frac{w_2}{w_1}\rho_1\text{”}$$

"Where, w_1 = weight of distilled water, w_2 = Weight of experimental liquid, ρ_1 = Density of water, ρ_2 = Density of experimental liquid"

(c) "Viscosity measurement":-

The "viscosities" of the solution were measured using an "Ostwald's viscometer" calibrated with distilled water, with an accuracy of 0.01s [13]

The "viscosity" was determined using the relation,

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

"Where, η_1 = Viscosity of water, η_2 = Viscosity of solution, ρ_1 = Density of water, ρ_2 = Density of solution, t_1 = Time of flow of water, t_2 = Time of flow of solution".

THEORETICAL ASPECT

The following thermodynamic and acoustic parameters have been calculated [14]

"Free volume"

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

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

"Where M_{eff} is the effective molecular weight of the mixture ($M_{eff} = \Sigma m_i X_i$, where mi and Xi are the molecular weight and mole fraction of individual constituents respectively), K is the temperature independent constant which is equal to 4.281×10^9 [11] for all liquids".

"Internal pressure"

It can be calculated using the relation as given below

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

"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".

"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".

"Rao's constant"

"Rao has established the empirical relation between molecular weight, density and ultrasonic velocity" of liquids as

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

"This equation is called Rao's rule and R is also called as 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"

"Wada had analyzed the variation of molar compressibility" with concentration for many liquid systems .He derived the empirical relation,

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

Results and Discussion

Table-1 shows the "density (ρ) and viscosity (η)" of polymer dextran at temperature "303 K, 308 K, 313 K, 318 K and 323 K"

Table 1. The experimental values of "density (ρ) and viscosity (η)" at 303K, 308K, 313K and 318K of solution

T in kelvin	(ρ) $Kg.m^{-3}$	(η) 10^{-3} $N.s.m^{-2}$
303	1000.83	0.991
308	999.21	0.890
313	997.00	0.809
318	994.60	0.748
323	991.62	0.713

Table 2. Values of "ultrasonic speed (U) and free volume (V_f)"at different temperature and frequencies

T in kelvin	U $m.s^{-1}$				V_f ($x10^{-3}m^3 \cdot mol^{-1}$)			
	1MHz	5MHz	9MHz	12 MHz	1MHz	5MHz	9MHz	12 MHz
303	1520.0	1516.0	1514.0	1519.0	5.261	5.240	5.230	5.256
308	1528.5	1523.0	1521.0	1526.0	6.227	6.193	6.181	6.212
313	1538.3	1532.8	1528.0	1535.0	7.262	7.222	7.189	7.238
318	1545.3	1540.0	1538.0	1542.0	8.218	8.176	8.160	8.192
323	1552.0	1548.0	1543.5	1550.0	8.897	8.863	8.824	8.880

Table 3. Values of "internal pressure (πi) and absorption coefficient (α)" at different temperature and frequencies

T in kelvin	π_i ($\times 10^3$ $N \cdot m^{-2}$)				α ($x10^6(np \cdot m^{-1})$			
	1MHz	5MHz	9MHz	12 MHz	1MHz	5MHz	9MHz	12 MHz
303	903.18	904.37	904.96	903.47	1.13	28.36	92.13	162.70
308	866.98	868.54	869.11	867.68	1.00	25.33	82.17	145.12
313	835.78	837.30	838.60	836.68	0.90	22.74	73.93	130.57
318	813.51	814.90	815.43	814.37	0.83	20.88	68.15	119.98
323	803.10	804.13	805.30	803.61	0.79	19.75	64.36	113.46

Table 4. Values of "Rao's constant (R) and Wada's constant (W)" at different temperature and frequencies

T in kelvin	R $(m^3/mole)(m/s)^{1/3}(10^{-3})$				W $(m^3/mole)(N/m^2)^{1/7}(10^{-3})$			
	1MHz	5MHz	9MHz	12 MHz	1MHz	5MHz	9MHz	12 MHz
303	2.089	2.087	2.086	2.088	3.954	3.951	3.949	3.953
308	2.096	2.094	2.093	2.095	3.965	3.961	3.960	3.964
313	2.105	2.103	2.101	2.104	3.980	3.976	3.973	3.978
318	2.114	2.111	2.110	2.112	3.994	3.990	3.988	3.991
323	2.123	2.121	2.119	2.122	4.009	4.006	4.003	4.008

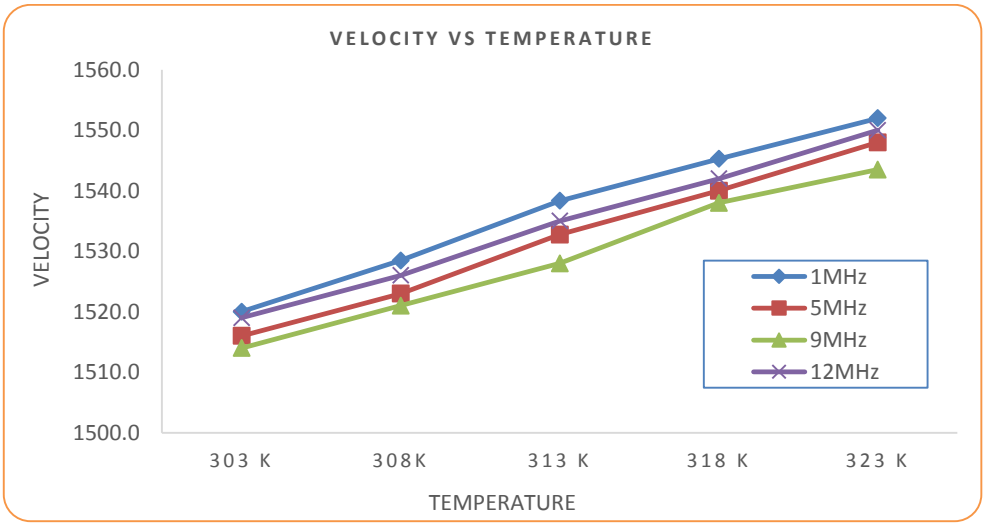

Figure 1. Plot of "velocity with temperature"

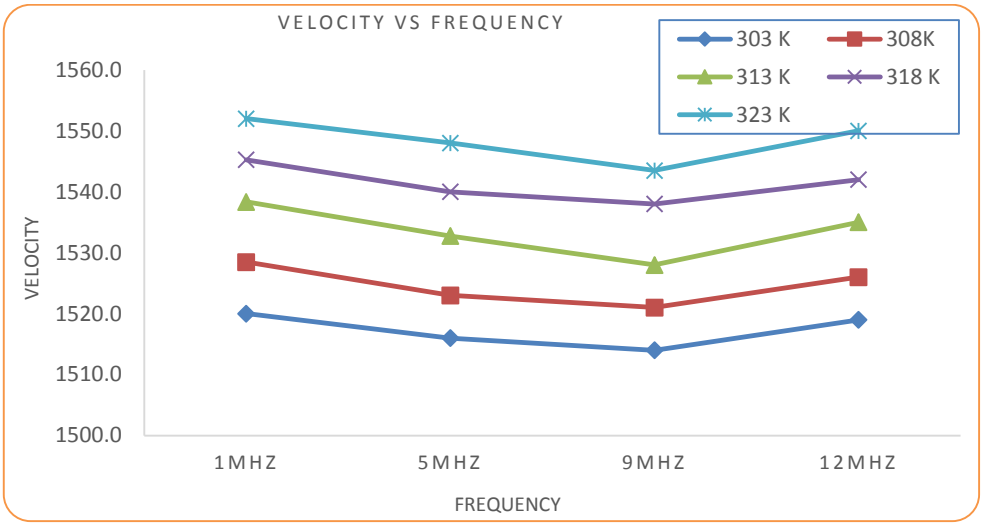

Figure 2. Plot of "velocity with frequency"

Figure 1 presents the "ultrasonic velocity plot versus temperature". "Ultrasonic velocity" is observed to increase with temperature rise suggesting interaction in the constituent. The electrons in the atom of each dextran molecule surrounding the nucleus are symmetrical, distributed around the nucleus. According to London, these electrons are in continuous and rapid motion in relation to the nucleus due to an increase in temperature and it is therefore possible that the electron density around the nucleus can be concentrated in the other region of the same molecule at any moment. This results in an unsymmetrical distribution of the electron density around the nucleus, and the permanent dipoles in the water molecules are thus induced [15].

"Ultrasonic velocity" decreases with increasing frequency, for a temperature. These velocity reduction is an indicator of a weak molecular interaction between the solvent components and the solvent molecules, due to increase in agitation between molecules give rise to decreases, in speed at higher frequency the trend is reverse (Figure 2).

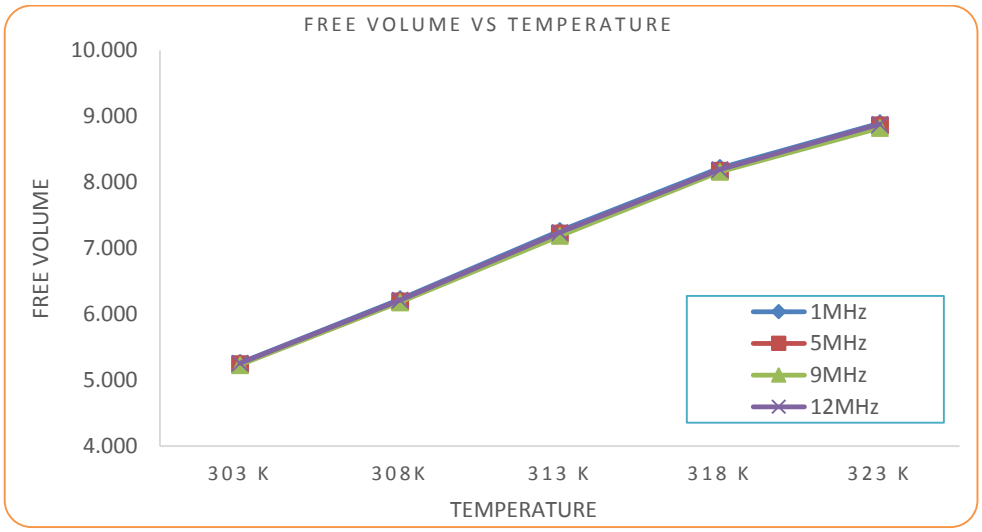

Figure 3. Plot of "free volume with temperature"

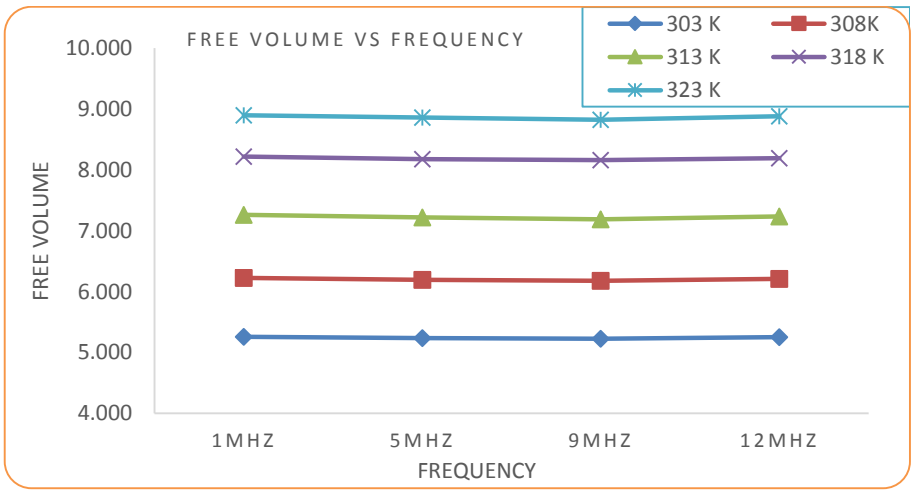

Figure 4. Plot of "free volume with frequency"

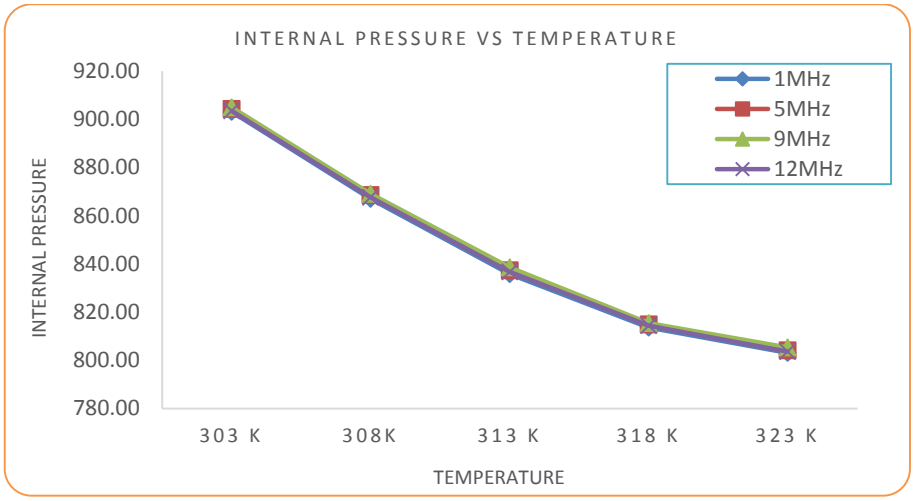

Figure 5. Plot of "internal pressure with temperature"

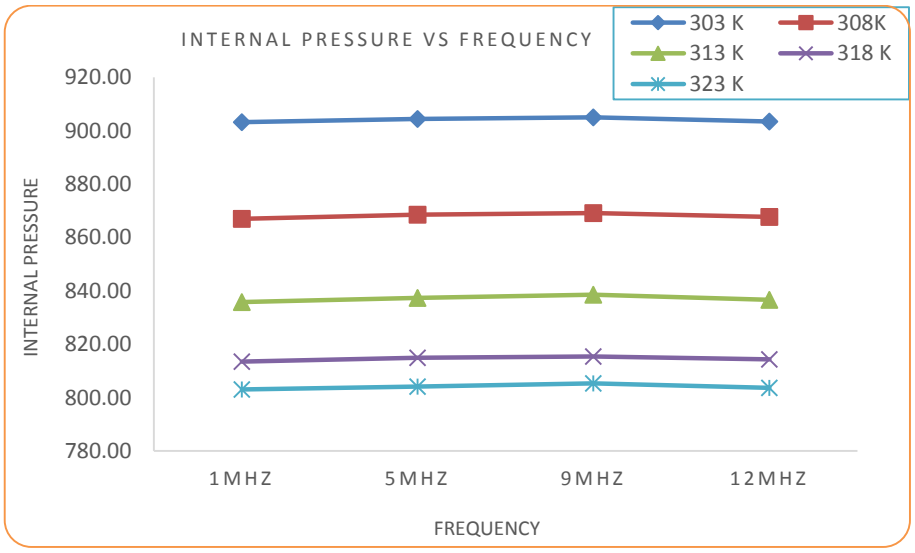

Figure 6. Plot of "internal pressure with frequency"

It is observed that 'V_f 'and 'π_i' in general expected to show a reverse trend with each other for rise in temperature. Which indication of a weak molecular relationship between the solvent and solvent components. That means the molecules are organizing themselves in such a way that void space is more accessible, suggesting that "free volume "is growing. As the attractive force among the molecules decreases which give rise to decrease in internal pressure with rise in temperature. The variation of free volume and internal pressure with frequency is almost parallel to frequency axis (Figure 4 and Figure 6).This conforms that there are little variations of these parameters with respect to frequencies where cohesive force does not affect the system [16].

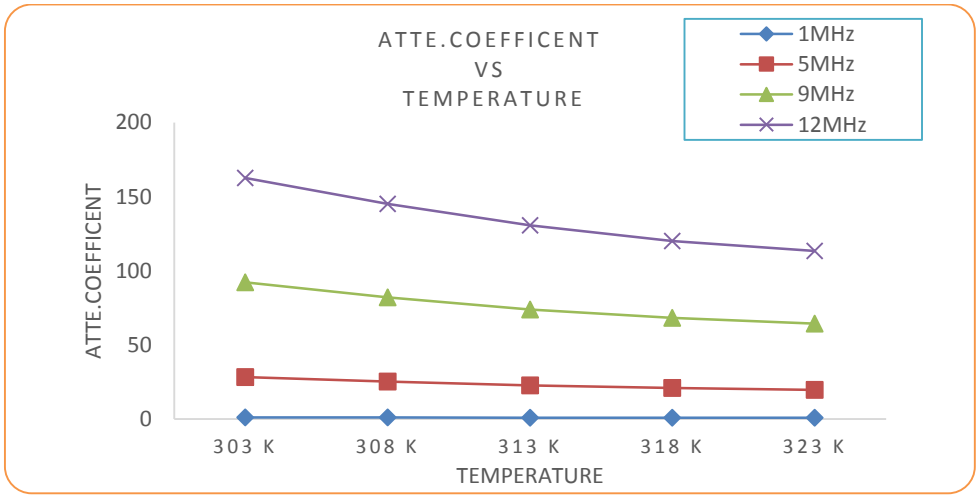

Figure 7. Plot of "attenuation coefficient with temperature"

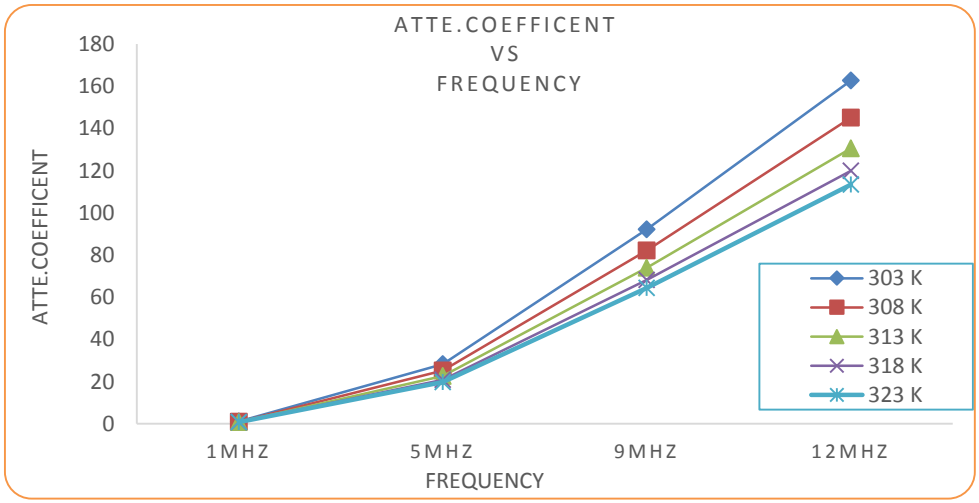

Figure 8. Plot of "attenuation coefficient with frequency"

At a lower frequency "(1 MHz and 5 MHz) the absorption coefficient" is parallel to temperature axis indicating very small effective with temperature, and gradually decreases with rise in temperature. It is observed that 'α' gradually rises with rise in concentrations at higher frequency and the effects are negligible at low frequencies. [17].

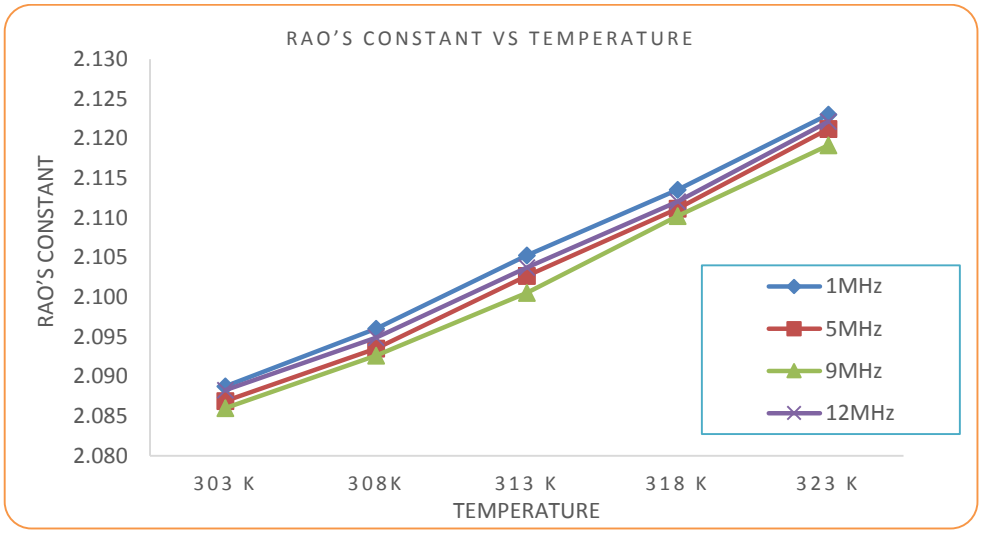

Figure 9. Plot of "Rao's constant with temperature"

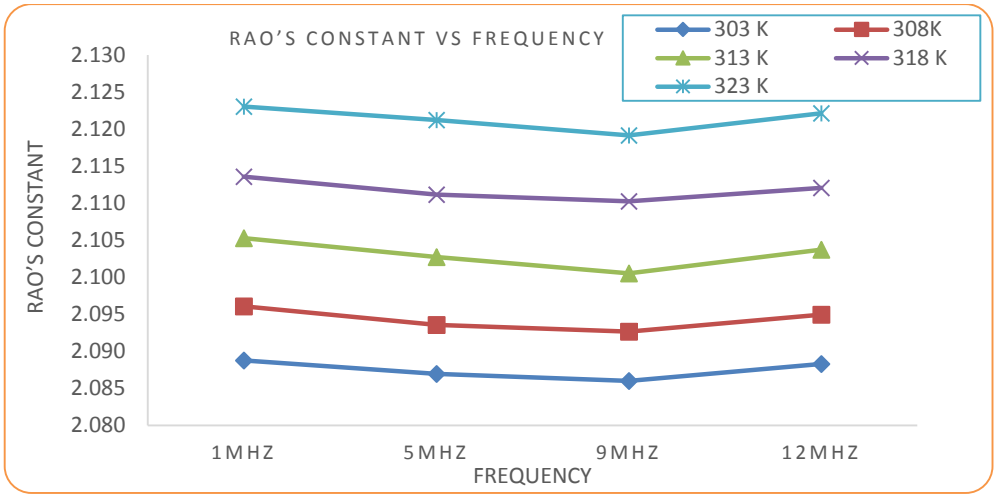

Figure 10. Plot of "Rao's constant with frequency"

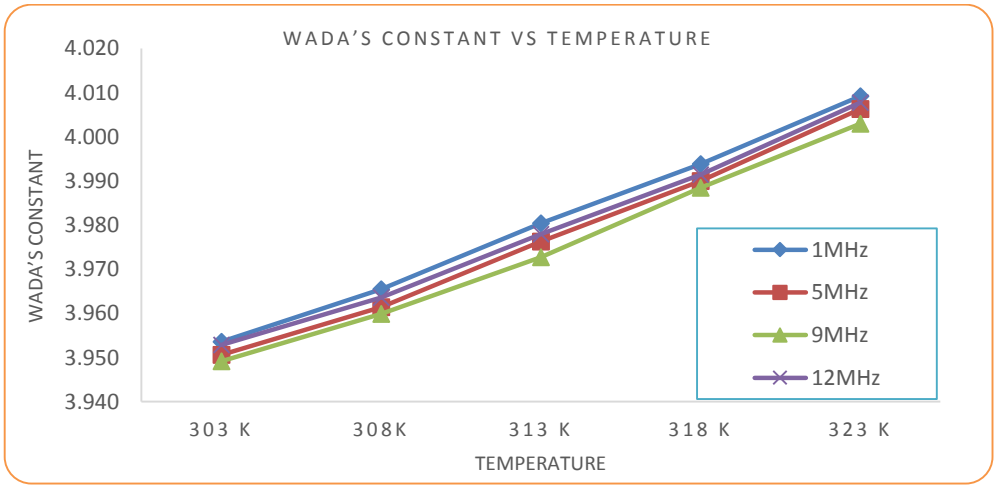

Figure 11. Plot of "Wada's constant with temperature"

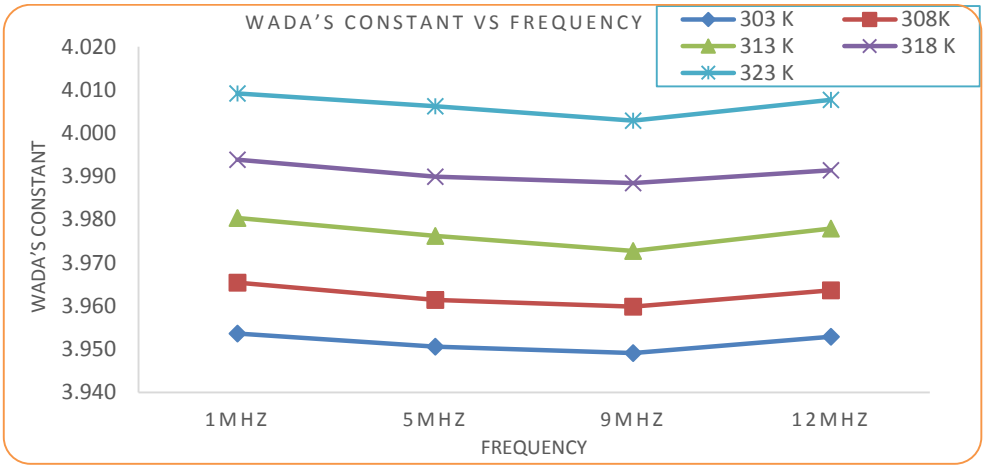

Figure 12. Plot of "Wada's constant with frequency"

The calculated values of dextran solution of at different temperature for 'R' and 'W' show increasing trends with temperature as the availability of more components in a given region result in the medium becoming tightly packed and thus increasing interaction.. Fig 10 and Fig.12 highlight that there is presence of small complex formation at low frequency and the complex formation becomes week at higher frequency due to agitation of the molecules [18].

Conclusion

"Ultrasonic speed, density and viscosity" have been measured for aqueous dextran solution at different frequencies and temperature. When the temperature increases, more and more solute molecules move closer to the solvent molecules and thereby increasing the solute-solvent interactions. This is a clear indication of intermolecular interactions because of hydrogen bonding of aqueous dextran solution. Summarizing the trends and variation of thermodynamic parameters with the frequency of the ultrasonic wave have also been studied and the effects are negligible at low frequencies.

Acknowledgement

The authors are thankful to department of Physics, ABIT Cuttack for their kind support in the present research work.

References

1. J. P. Idoux, C. K. Mccurry and T. M. Aminabhavi "Densities, viscosities, speeds of sound, and water solubilities of some piolypropylene ether glycol derivatives in the temperature range 273. 15 to 323.15K", j. chem.eng. Data, vol.39, **(1994),** pp.261-267
2. S.Nithiyanantham ,L.Palaniappan. Ultrasonic study on some monosaccharides in aqueous media at 298.15 K, Arabian J of Chemistry,2012; 5: 25–31.
3. R. K. Shukla, S. K. Shukla, V. K. Pandey, and Piyush Awasthi, "Excess internal pressure, excess energy of vaporization and excess pseudo gruneisen parameter of binary, ternary, and quaternary liquid mixtures," Journal of Molecular Liquids, vol. 137, 2008. ,pp. 104-109,
4. Ranjan Dey, Anjan Chattopadhyay, Ashish K Sharma, and J. D. Pandey," Study of excess thermodynamic properties of multicomponent liquid mixtures," Journal of Molecular Liquids, vol. 147, , 2000,pp. 155-161.
5. M. V. Rathnam, Kavita R. Bhanushali, Reema T. Sayed, and M. S. S. Kumar, "Acoustic, thermodynamics and transport properties of binary liquid mixtures of isopentyl acetate with aryl halides at 303.15 K and 313.15 K," Journal of Molecular Liquids, vol. 173,2012 pp. 35-41,

6. M. M. Papari, H. Ghodrati, F. Fadaei, R. Sadeghi, S. Behrouz, M. N. Soltani Rad and J. Moghadasi, "Volumetric and ultrasonic study of mixtures of 2- phenylethanol with 1-butanol and 2-methyl-1-butanol at T=(298.15 – 323.15)K and atmospheric pressure: Measurement and prediction," Journal of Molecular Liquids, vol. 180,2013, pp. 121-128.
7. S Panda and M K Praharaj, "Evaluation of ultrasonic parameters in binary solution of dextran and urea at various concentration and temperatures", Indian Journal of Natural Sciences, vol.10, no.59, **(2020)**, pp. 18552-18557.
8. S Panda and A.P.Mahapatra, "Study of acoustical parameters of dextran in 2 (M) glycine using ultrasonic technique at different frequencies", J. Pure Appl. ultrason, vol.39,**(2017),**pp.83-87.
9. R.T Langemann., W.S Dunbar, "Relationships between the velocity of sound and other physical properties of liquids". J. Phys.Chem., vol. 49, no.5, **(1945),** pp.428–436.
10. K.Rajagopal, and S.Chenthilnath, ,"Molecular interaction studies and theoretical estimation ofultrasonic speeds using scaled particle theory in binary mixtures of toluene withhomologous nitriles at different temperatures", Thermochimica Acta, Vol.498,no(1-2),**(2010)**,pp.45-53.
11. G.R.Bedare,V.D. Bhandakkar, B.M.Suryavanshi, "Studies of Acoustic and Thermodynamic Properties of Binary liquid Mixtures at 308K", Journal of chemical & pharmaceutical Research, vol.4,no.2,(2012),pp.1028-1032.
12. S Panda and A. P. Mahapatra, "Molecular interaction studies of aqueous Dextran solution through ultrasonic measurement at 313K with different concentration and frequency", Archives of Physics Research, vol.6 no.2, **(2015),**pp. 6-12**.**
13. S Panda ," Molecular Interaction of Polymer Dextran in Sodium Hydroxide through Evaluation of Thermo Acoustic Parameters. Indian Journal of Pharmaceutical Education and Research, 54(3),(2020): 630-636
14. S Panda and A. P.Mahapatra, "Study of Acoustic and Thermodynamic Properties of Aqueous Solution of Dextran at Different Concentration and Temperature through Ultrasonic Technique" International Journal of Science and Research, International Symposium on Ultrasonic, (2015) pp.503-508
15. S Panda and A. P.Mahapatra,"Molecular Interaction of Dextran with Urea through Ultrasonic Technique", Clay Research, vol.38, no.1, **(2019),** pp.35-42.
16. P.S.Nikam, Mehdi Hasan and R.B.Pathak "Densities and speeds of sound for aniline + aliphatic alcohols (c1-c2) at different temperatures", journal of pure and applied ultrasonics.vol.18, **(1996)**, pp.19- 25.
17. S. P. Wankhade and S. G. Kene, "molecular interaction study in binary liquid solution using ultrasonic technique", sci. Revs. Chem. Commun.: vol.2, no.3, **(2012),** pp. 355-360.
18. Rajulu AV, Sreenivasulu G, K S Raghuramam KS. Ultrasonic attenuation in aqueous dispersion of Polytetrafluoroethylene. Indian J of Chemical Technology. 1,1(994),pp302-304.