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Molecular interaction studies of aqueous Dextran solution through ultrasonic measurement at 313K with different concentration and frequency

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ABSTRACT

The behavior of ultrasonic wave propagation through liquid solution has become an important tool for studying physical and chemical properties of liquid solutions. The density and viscosity of aqueous Dextran have been measured with different concentrations and ultrasonic velocities have been measured at different concentrations as well as at four different frequencies within range 1-12MHz at 313 K. From the experimental data various thermo acoustical parameters such Acoustic impedance (Z), Adiabatic Compressibility (β), Intermolecular free length (L_f), Relaxation time (τ) and Gibb's free energy(ΔG) have been calculated. Molecular interactions in aqueous Dextran in terms of these thermo-acoustical parameters have been discussed.

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

INTRODUCTION

Acoustical studies in polymer solutions have been the subject of research in recent years. Ultrasonic is the universally accepted technique to study the physical and chemical properties of the liquids, liquid mixtures, electrolytic solutions and polymeric solutions. The different acoustical parameters interpret the nature and strength of molecular interaction that exist in the system.

In this paper, values of η , ρ , U and related thermodynamic and acoustic parameters have been determined and the solute-solvent interactions for the aqueous solution of dextran at different concentration have been studied at four different frequencies - 1MHz,5MHz,9MHz &12MHz at 313K. Measurement of ultrasonic velocity [1] has been adequately employed in understanding the molecular interactions in polymer solution. The propagation of ultrasonic velocity in a medium is a thermodynamic property and has come to be recognized as a very specific and unique tool for predicting and estimating various physico-chemical properties of the systems under consideration. Since ultrasonic velocity data proves to be a very simple and convenient tool to determine various thermodynamic properties of liquid, liquid mixtures and polymer solutions not obtained so accurately through other technique. Significant amount of work has been done in carrying out investigation pertaining to various thermodynamic, physicochemical and liquid state properties by correlating them with ultrasonic velocity in conjunction with density and viscosity.

Dextran, a water soluble polymer is a α -D-1, 6-glucose linked glucan with side chains 1-3 linked to the backbone units of polymer. It has occupied a separate area of investigations by researchers [2-3] because of its versatile pharmaceutical, biomedical and industrial applications.

The fast increasing of these polyglucosans for medical, industrial and research purpose motivated to carry out investigation of thermo acoustic parameters of dextran by ultrasonic technique.

MATERIALS AND METHODS

Experimental Details

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

(i) Velocity Measurement:-

The velocity of ultrasonic wave through aqueous solution of dextran have been measured using multi-frequency ultrasonic interferometer with an high degree of accuracy (Model M-84) supplied by M/s Mittal Enterprises, New Delhi. The measuring cell of interferometer is a specially designed double walled vessel with provision for temperature constancy. An electronically operated digital constant temperature bath (Model SSI-03spl) supplied by M/s Mittal Enterprises, New Delhi, Mittal Enterprises, New Delhi, operating in the temperature range -10° C to 85° C with an accuracy of $\pm 0.1^{\circ}$ C has been used to circulate water through the outer jacket of the double walled measuring cell containing the experimental liquid.

(ii) Density Measurement:-

The densities of the polymer solution were measured using a 25ml specific gravity bottle. The specific gravity bottle with the experimental solution was immersed in a temperature controlled water bath. The density was measured using the formula

$$\rho_2 = \frac{w_2}{w_1} \rho_1$$

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

(iii) Viscosity measurement:-

The viscosities of the aqueous solution of dextran were measured using an Oswald's viscometer calibrated with double distilled water. The Oswald's viscometer with the experimental solution was immersed in a temperature controlled water bath. The time of flow was measured using a digital racer stop watch with an accuracy of 0.01 sec. The viscosity was determined using the relation,

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

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

Theoretical Aspect

The density, viscosity [4] and ultrasonic velocity have been measured and using these experimental data the following thermo acoustic parameters were calculated using standard formula.

Acoustic impedance

 $Z = U.\rho$ (1) $\beta = \frac{1}{\rho U^2}$ (2) $L_f = \frac{K_T}{U\rho^{\frac{1}{2}}}$ (3)

Intermolecular free length

Adiabatic Compressibility

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τ

Relaxation time

$$= \frac{4}{3} \frac{\eta}{\rho U^2}$$

$$\Delta G = kT \ln \frac{kT\tau}{h}$$
(4)
(5)

Gibb's free energy

Where $^{\rho}$ density, U velocity, $^{\eta}$ viscosity KT is the temperature dependent constant. KT = (93.875+0.375T) x10⁻⁸ 'T' is the absolute temperature; 'k' is the Boltzmann's constant and 'h' is the Planck's constant

RESULTS AND DISCUSSION

The experimental data relating to density and viscosity at 313 K for the aqueous solution of dextran is presented in Table 1.

Table 1: Values of density (ρ) and Viscosity (η) of aqueous solution of dextran in different concentrations at 313K

	Concentration									
Т	0.10%		0.25%		0.50%		0.75%		1%	
(Kelvin)	ρ	η	ρ	η	ρ	η	ρ	η	ρ	η
	Kg.m ⁻³	10 ⁻³ N.s.m ⁻²								
313	993.831	0.686	994.227	0.702	994.623	0.739	996.602	0.773	996.998	0.809

The experimental data of ultrasonic velocity and calculated values of acoustic impedance (Z) at different concentrations and frequencies is presented in Table 2

Table 2: Values of Ultrasonic velocity (U) and Acoustic impedance (Z) of aqueous solution of dextran in different concentrations and frequencies at 313K

		Acoustic impedance (Z) $10^6 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1}$)						
Conc.	1MHz	5MHz	9MHz	12MHz	1MHz	5MHz	9MHz	12MHz
0.10%	1532.0000	1530.0000	1527.0000	1528.2000	1.5225	1.5206	1.5176	1.5188
0.25%	1533.0000	1531.0000	1529.5000	1531.2000	1.5241	1.5222	1.5207	1.5224
0.50%	1535.2667	1531.5000	1530.0000	1532.0000	1.5270	1.5233	1.5218	1.5238
0.75%	1536.6000	1532.0000	1530.5000	1533.0000	1.5314	1.5268	1.5253	1.5278
1%	1538.3333	1532.7500	1531.0000	1535.8000	1.5337	1.5281	1.5264	1.5312



Fig.3 Acoustic impedance vs. concentration

Fig.4 Acoustic impedance vs. Frequency

It is observed that, Ultrasonic velocity increases with increase in concentration at a particular frequency. This is due to the structural changes occurring in the polymer solution resulting in decrease of intermolecular forces[5]. For a given concentration and temperature, ultrasonic velocity decreases with increase in frequency from 1MHz-9MHz [6]. Such a decrease in velocity is an indication of existence of weak molecular association between the solute and solvent but the case is just reverse when frequency is high (12MHz) which may be due to thermal agitation.

The increase in acoustic impedance (Z) values with solute concentration can be attributed to the effective solutesolvent 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 solution. In a particular concentration of the solution with increase in frequency, velocity decreases and hence acoustic impedance decreases. This factor is governed by the inertial and elastic properties of the medium and hence supports the possibility of molecular interactions. The decreasing property of acoustic impedance with increase in frequency supports the possibility of weak interaction between unlike molecules but the case is just reverse when frequency is high (12MHz). Acoustic impedance is also given by the product of the ultrasonic velocity and density $Z = U\rho$ and is used for assessing the absorption of sound in a medium.

Calculated values of adiabatic compressibility (β) and intermolecular free length (L_f), are presented in Table 3.

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Table 3: Values of adiabatic compressibility and acoustic impedance at different frequencies and different concentrations of aqueous solution of dextran at 313K

		Adiabatic	Compressi	bility (β)(1	Intermolecular free length (L_f) 10^{-10} m				
C	Conc.	1MHz	5MHz	9MHz	12MHz	1MHz	5MHz	9MHz	12MHz
0	.10%	4.2872	4.2984	4.3153	4.3085	0.4180	0.4185	0.4193	0.4190
0	.25%	4.2799	4.2911	4.2995	4.2899	0.4176	0.4182	0.4186	0.4181
0	.50%	4.2655	4.2865	4.2950	4.2837	0.4169	0.4179	0.4183	0.4178
0	.75%	4.2497	4.2752	4.2836	4.2697	0.4161	0.4174	0.4178	0.4171
1	%	4 2384	4 2694	4 2791	4 2524	0.4156	0.4171	0.4176	0.4163



Fig.5 Adiabatic compressibility vs. concentration

Fig.6 Adiabatic compressibility vs. Frequency



Fig.7Intermolecular free length vs. concentration

Fig.8 Intermolecular free length vs. Frequency

Adiabatic compressibility decreases with increase in concentration (Fig.5), it indicates strong interaction between solute and solvent molecules at a particular frequency. Increasing trend of adiabatic compressibility is observed with increasing frequency in the range from 1MHz to 9MHz. When frequency increases, the interaction between the molecules in the solution changes causing a structural change and hence increase in adiabatic compressibility but reverse in high frequency i.e 12MHz. The increase in adiabatic compressibility (Fig.6), suggests minimum interaction between unlike molecules.

Intermolecular free length depends on adiabatic compressibility (β) and shows a similar behavior as that of compressibility. Hence free length also increases but at a slower rate. On the basis of a model for sound propagation proposed by Eyring and Kincaid [7] Ultrasonic velocity should decrease if the intermolecular free length increases and vice versa. The decrease in free length with rise in concentration shows that solute-solvent molecules are coming closer to each other and this may be attributed to dipole-dipole interaction, H-bonding between the solute and solvent molecules. Calculated values of relaxation time (τ) and Gibb's free energy (ΔG) are presented in Table 4.

	Relaxati	on time (t)(10 ⁻¹³ Sec.)	Gibb's free energy(ΔG)10 ⁻²⁰ kJ·mol ⁻¹				
Conc.	1MHz	5MHz	9MHz	12MHz	1MHz	5MHz	9MHz	12MHz	
0.10%	3.9234	3.9337	3.9492	3.9430	176.3323	176.8226	177.5593	177.2644	
0.25%	4.0063	4.0167	4.0246	4.0157	180.2538	180.7438	181.1118	180.6948	
0.50%	4.2042	4.2249	4.2332	4.2222	189.3046	190.2266	190.5944	190.1041	
0.75%	4.3819	4.4083	4.4169	4.4025	197.0755	198.2008	198.5685	197.9559	
1%	4.5702	4.6035	4.6141	4.5853	204.9697	206.3345	206.7633	205.5883	

Table 4: Values of relaxation time and Gibb's free energy (ΔG) at different frequencies and concentrations of aqueous solution of
dextran at 313K



Fig.9 Relaxation time vs. concentration

Fig.10 Relaxation time vs. Frequency



Fig.11: Gibb's free-energy vs. concentration

Fig.12: Gibb's free-energy vs. Frequency

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Relaxation time increases with increase in concentration of dextran. Such a situation suggests that, the molecules get rearranged due to co-operation process [8] Free length also increases but at a slower rate as frequency increases. Relaxation time increases with increase in frequency in the lower frequency range i.e. 1MHz-9MHz but decreases at high frequency (12MHz) and this may be due to thermal agitation at high frequency the relaxation time decreases.

The Gibbs free energy (ΔG) increases with the increase in concentration of Dextran as well as frequency but higher frequency it shows reverse trend. An increasing value of ΔG suggests that the closer approach of unlike molecules is due to hydrogen bonding[9]. The increase in ΔG suggests shorter time for the rearrangement of molecules in the solution. When frequency increases, the energy imparted to the molecules obviously expedites the rearrangement process. This indicates existence of molecular association between the solute and solvent.[10]

CONCLUSION

It is concluded that ultrasonic studies provide a comprehensive investigations of molecular association in polymer solution. When an acoustic wave travels in a medium, there is a variation in pressure from particle to particle. When the frequency of the ultrasonic wave changes, the pressure also changes leading to a change in the velocity as well as the associated thermodynamics parameters[11]. The trends and variations of thermodynamic parameters with frequency of the ultrasonic wave and concentration have been studied in detail which gave an idea about the nature of molecular interactions in the aqueous dextran solution.

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