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Acoustic and Ultrasonic Studies of Dextran in 2(M) Glycine-Variation with Frequencies and Concentrations

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Abstract

The propagation of ultrasonic waves and the measurement of their velocity in solutions form an important tool for the evaluation of various acoustical and thermo dynamical parameters which give an insight into the nature of miscibility and molecular interactions in polymer. The density and viscosity of dextran in 2(M) glycine solution is measured at temperature of 308K and ultrasonic velocity in this solution has been measured at 1, 5, 9 and 12MHz.frequencies. Various parameters such as acoustic impedance (Z), adiabatic compressibility (β), intermolecular free length (L_f), relaxation time (τ) and Gibb's free energy(ΔG) has been calculated using experimentally determined values of ultrasonic velocity density and viscosity. The variation of these parameters has been discussed in the light of solute-solvent and solute-solute interaction.

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

INTRODUCTION

Ultrasonic study of velocity, density along with acoustic parameters of polymer are essential to understand the molecular interactions between the unlike molecules to develop theoretical models and applications in industrial processes. Propagation of ultrasonic waves through polymer solution reveals many physico-chemical properties of the polymer. These polymers have a wide range of applications in various industries and technology [1]. Ultrasonic investigation of polymer solution of dextran

in 2(M) glycine is of considerable importance because of its extensive use in medical, research and various industrial purposes.

Ultrasonic velocity is measured for polymer solution dextran in 2(M) glycine at four different frequencies (1MHz, 5MHz, 9MHz and 12MHz)at 308K and related parameters are calculated. These parameters provide qualitative information regarding the nature and strength of interaction between solute-solvent molecules which has wide range of industrial applications. We have chosen dextran for our study due to its wide industrial application particularly in pharmaceutical sector. The dextrans which were used initially for conversion into synthetic blood-volume expanders [2,3] human red blood cells aggregation for increasing the degree of polymerization and hence the molecular weight [4,5,6]. Dextrans and their derivatives find an interest in clinical applications, as well as experiments in tablets in the pharmaceutical industry [7].

EXPERIMENTAL SECTION

Materials

The polymer dextran of molecular weight 70,000 which was obtained as a gift sample is of analytical reagent (AR) grade, manufactured by HI Media Laboratories Private Limited, India and solvent such as aqueous solution of 2(M) glycine is of analytical reagent (GR) grade, manufactured by Merck Specialties Private Limited and are used as such throughout the experiments.

Measurements

Velocity Measurement:-The velocity of ultrasonic wave in the solution have been measured using multi-frequency ultrasonic interferometer with an high degree of accuracy operating at 11 different frequencies (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, operating in the temperature range -10^{o}C to 85^{o}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.

Density Measurement: Density was determined with a Pycnometer using a standard equation [9]. The Pycnometer bottle with the experimental mixture was immersed in a temperature controlled water bath.

V**iscosity 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 and calculated using standard equation [9].

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.

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

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

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

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

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

Where ρ density, U velocity, η 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

Table 1: Values of density (ρ) and Viscosity (η) of aqueous solution of dextran in different concentrations at308K temperature

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}
308	1051.885	0.957	1053.469	0.985	1054.261	1.023	1055.053	1.087	1055.845	1.118

Table 2: Values of Ultrasonic velocity (U) and Acoustic impedance (Z)at different concentrations and frequencies ofaqueous solution of dextran in 2(M) glycine at 308Ktemperature

	Ultrasonic velocity (U) m/s^2				Acoustic impedance (Z) 10^6 kg·m^2·s^{-1})			
Conc.	1MHz	5MHz	9MHz	12MHz	1MHz	5MHz	9MHz	12MHz
0.10%	1620.67	1613.00	1609.20	1606.80	1.7048	1.6967	1.6927	1.6902
0.25%	1621.33	1614.75	1611.90	1608.60	1.7080	1.7011	1.6981	1.6946
0.50%	1622.00	1615.50	1612.35	1611.00	1.7100	1.7032	1.6998	1.6984
0.75%	1622.67	1617.75	1615.50	1613.40	1.7120	1.7068	1.7044	1.7022
1%	1623.50	1620.00	1616.00	1614.00	1.7142	1.7105	1.7062	1.7041

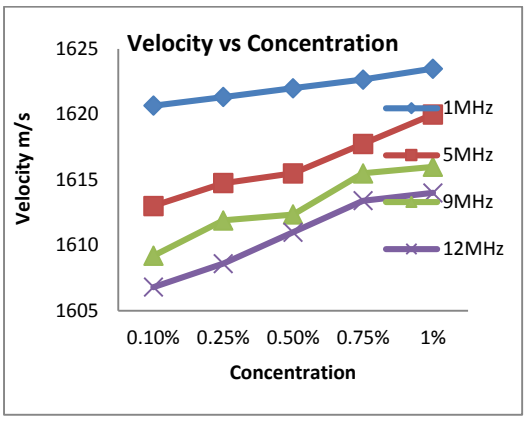

Fig.1 Variation of ultrasonic velocity with concentration of dextran in 2(M) glycine

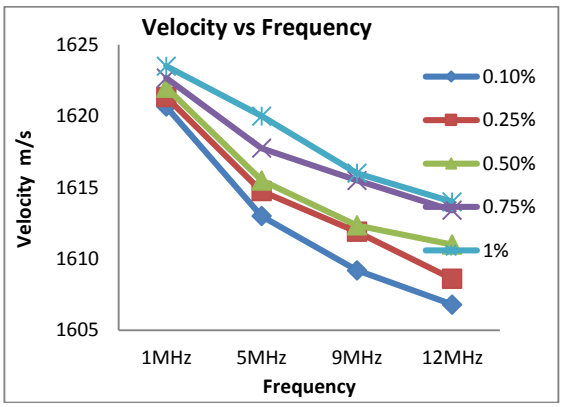

Fig.2 Variation of ultrasonic velocity with frequency of dextran in 2(M) glycine

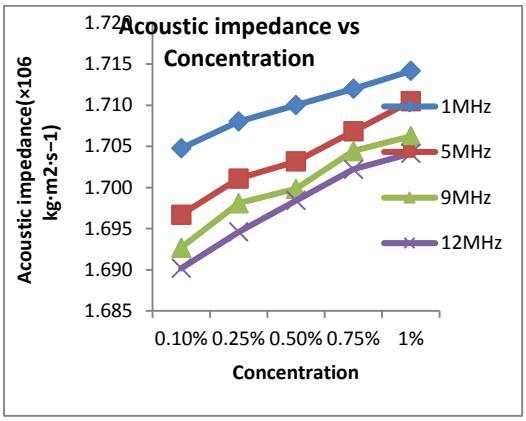

Fig.3 Variation of acoustic impedance with concentration of dextran in 2(M) glycine

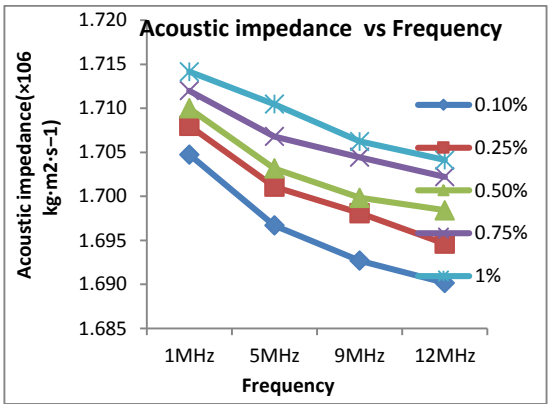

Fig.4 Variation of acoustic impedance with frequency of dextran in 2(M) glycine

It is observed that, ultrasonic velocity increases with increase in concentration at 308K as shown in figure-1 for all the frequencies 1MHz, 5MHz, 9MHz, and 12MHz.The variation of velocity with concentration of dextran is nonlinear which indicates the existence of molecular association. Variation in the velocity is due to self-association of the solvent molecules and dipole-induced dipole interaction between the component molecules, which is concentration dependent. With increase in dextran concentration, dipole-induced dipole interaction increases making the system less compressible resulting increase in velocity. From figure-2 it is observed that ultrasonic velocity decreases with increase in frequency. Increase in frequencies weakens the interaction which may be due to increase in agitation between molecules resulting decrease in ultrasonic velocity at higher frequencies. It is observedfromfigure-3 that values of acoustic impedance increase with increase in

concentration of dextran none uniformly as in velocity which is in agreement with the theoretical requirement**.** Increase in impedance with solute concentration can be attributed to the effective solute solvent interactions [8]**.**From figure-4 it is clear that with increase in frequency acoustic impedance decreases, which is in conformity with the theory.

Table 3: Values of adiabatic compressibility and intermolecular free length at different frequencies and different concentrations of aqueous solution of dextran in 2(M) glycine at 308Ktemperature

	Adiabatic Compressibility (β)($10^{-10}N^{-1}.m^2$)				**Intermolecular free length (L_f) 10^{-10} m**			
Conc.	1MHz	5MHz	9MHz	12MHz	1MHz	5MHz	9MHz	12MHz
0.10%	3.6195	3.6540	3.6712	3.6822	3.8075	3.8256	3.8347	3.8404
0.25%	3.6111	3.6406	3.6534	3.6684	3.8031	3.8186	3.8254	3.8332
0.50%	3.6054	3.6344	3.6487	3.6548	3.8001	3.8154	3.8229	3.8261
0.75%	3.5997	3.6216	3.6317	3.6412	3.7971	3.8087	3.8140	3.8189
1%	3.5933	3.6089	3.6267	3.6357	3.7938	3.8020	3.8114	3.8161

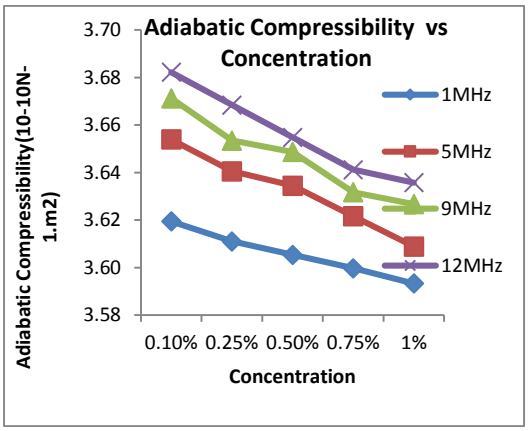

Fig.5 Variation of adiabatic compressibility with. concentration of dextran in 2(M) glycine

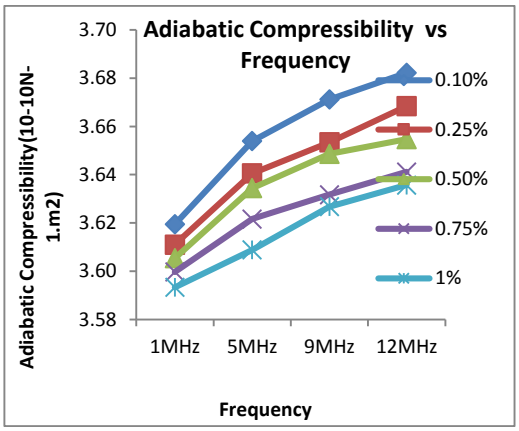

Fig.6 Variation of adiabatic compressibility with. frequency of dextran in 2(M) glycine

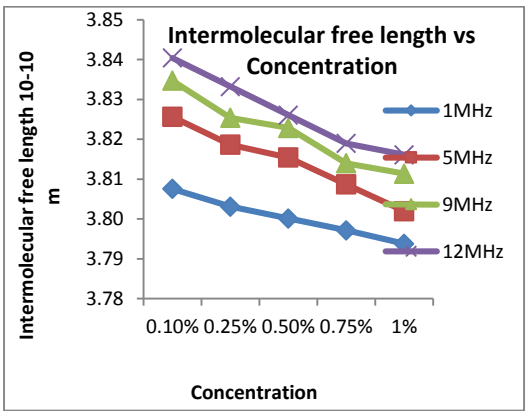

Fig.7 Variation of intermolecular free length with concentration of dextran in 2(M) glycine

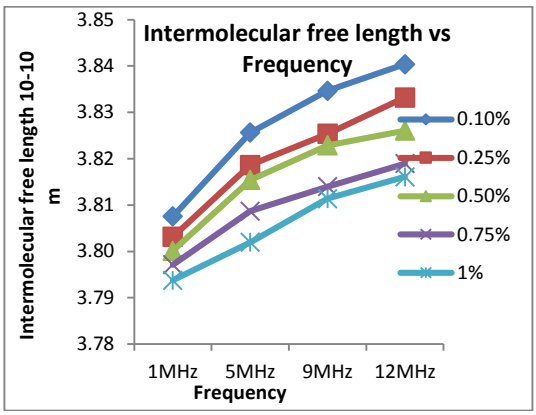

Fig.8 Variation of intermolecular free length with frequency of dextran in 2(M) glycine

As expected adiabatic compressibility decreases with increase in concentration of dextran which shows a reverse trend to velocity graph in figure-5 This behavior may be due to breaking up of associated clusters of dextran releasing several dipoles, which in turn induces dipole moment in glycine resulting dipole- induced dipole interaction [10].When frequency increases from1MHz to 12 MHz the compressibility increases which shows an irregular trend as shown in figure-6 due to the dominance of dispersive interaction forces.

From figure-7 and figure-8 it is observed that the value of intermolecular free length decreases steadily with increase of concentration of dextran and increases with increase in frequency. This indicates the significant dipole–induced dipole interaction between solute and solvent due to which structural arrangement is affected. Dextran have higher molar volume, therefore, molar volume of dextran part rises with increase in concentration of dextran and occupies larger spatial arrangement in the molecular core of the solution[11] which leaves less intermolecular space in between the associated structure present in the system. Further, in higher frequency range intermolecular gap decreases which leads to decrease in velocity.

Table 4: Values of relaxation time and Gibb's free energy (ΔG)of aqueous solution of dextran in 2(M) glycine at different frequencies and concentrations at 308K Temperature

	Relaxation time (τ)(10^{-13}Sec.)				**Gibb's free energy(ΔG)10^{-20}kJ·mol^{-1}**			
Conc.	1MHz	5MHz	9MHz	12MHz	1MHz	5MHz	9MHz	12MHz
0.10%	4.6163	4.6603	4.6823	4.6963	200.5752	202.3266	203.1978	203.7490
0.25%	4.7437	4.7825	4.7994	4.8191	205.6030	207.1058	207.7583	208.5153
0.50%	4.9159	4.9556	4.9750	4.9833	212.1903	213.6735	214.3944	214.7038
0.75%	5.2189	5.2507	5.2653	5.2790	223.2347	224.3555	224.8696	225.3500
1%	5.3567	5.3798	5.4065	5.4199	228.0463	228.8435	229.7566	230.2140

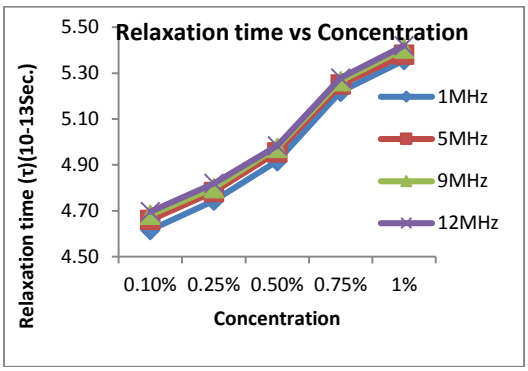

Fig.9 Variation of relaxation time with concentration of dextran in 2(M) glycine

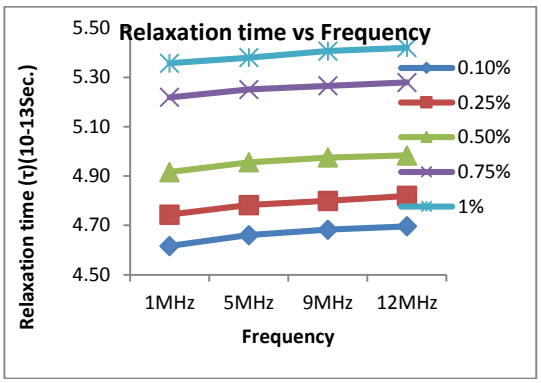

Fig.10 Variation of relaxation time with frequency of dextran in 2(M) glycine

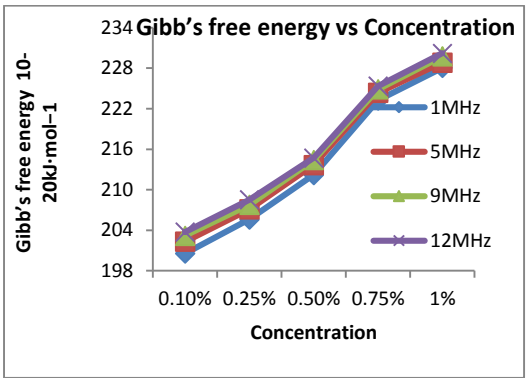

Fig.11 Variation of Gibb's free-energy with concentration of dextran in 2(M) glycine

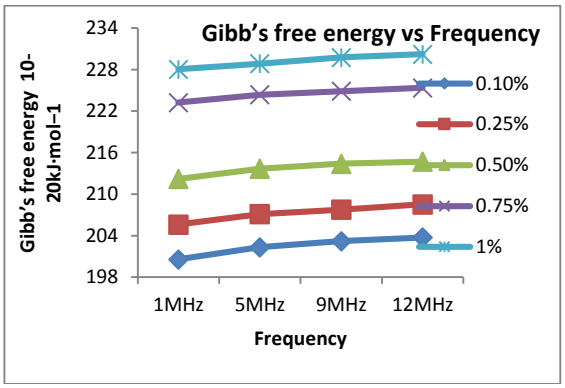

Fig.12 Variation of Gibb's free-energy with frequency of dextran in 2(M) glycine

From figure-9 Relaxation time increase with increase in concentration of dextran. Such situation suggests that, the molecules get rearranged due to co-operation process [12]. Relaxation time also increases but at a slower rate as frequency increases as shown in figure-10.

The Gibbs free energy (ΔG) increases with the increase in concentration of dextran as well as frequency as shown in figure-11 & figure-12. An increasing value of ΔG suggests that the closer approach of unlike molecules is due to hydrogen bonding. The increase in ΔG suggests shorter time for the rearrangement of molecules in the mixture. When frequency increases, the energy imparted to the molecules obviously expedites the rearrangement process. This indicates existence of molecular association between the components of the liquid mixture [13].

CONCLUSION

The experimental data relating to density and viscosity at308K for the dextran in 2(M) glycine have been presented in table1 and experimental data relating to velocity is represented in table 2. Calculated values of acoustic impedance (Z), adiabatic Compressibility (β), intermolecular free length (L_f), relaxation time (τ), and Gibb's free energy (ΔG) are presented in tables 2, 3 and 4.Ultrasonic method is a powerful probe for characterizing the physico-chemical properties and existence of molecular interactions in the liquid mixture. In the solution the evaluated values of ultrasonic velocity and other derived thermodynamic parameters indicate the presence of molecular interaction between component molecules at constant temperature and at different frequencies. Summarizing the trends and variation of thermodynamic parameters with frequency of the ultrasonic wave has been studied in detail which will give us an idea about the nature of molecular interactions between the solute(dextran) and solvent (glycine).

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