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Molecular interaction of novel polymer dextran with 1(N) sodium hydroxide solution: Ultrasonic studies

Subhraraj Panda[1,*]

[1]Department of Physics, SoAS, Bhubaneswar campus Centurion University of Technology and Management, Odisha, India
[*]Corresponding author: subhraraj4u@gmail.com

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Abstract

The purpose of this experiment was to look at the molecular interionic interactions that could occur of novel polymer with aqueous sodium hydroxide solution at 303K, 308K, 313K, 318K & 323K. The solutions containing different thermo acoustical properties have been studied at various temperature and frequency. The physical parameters like "free volume, internal pressure, absorption coefficient, Rao's constant and Wada's constant" are determined from ultrasonic velocity, density and viscosity measurements at atmospheric pressure. The result is explained in terms of molecular interactions such as dipole-dipole, ion-ion, and ion-dipole interactions between solution components due to hydrogen bonding.

Keywords: Ultrasonic Velocities, Thermodynamic Parameters, Ultrasonic Interferometer, Molecular Interactions

1. Introduction

Ultrasonic research can be used to recognise molecular connections and structural behaviour of molecules. The combination of ultrasonic velocity, density, and viscosity data provides a plethora of information on ion interactions, dipoles, hydrogen bonding, multi-polar, and dispersive forces [1-3].

Ultrasonic velocity measurements have proved useful in determining the type of molecular interaction of fluids. However, the derived parameters from sound velocity (U) using density (ρ), viscosity (η), such as free volume (V_f), internal pressure (πi), absorption coefficient or attenuation coefficient (α), Raos constant (R) and Wadas constant (W), to gain a better grasp of the molecular environment of fluids [4]. The ultrasonic interferometer produces precise and reliable data, from which one can determine the velocity of ultrasonic sound in a liquid medium with a high degree of accuracy. The non-destructive technique, ultrasonic is highly useful for the investigation of various physic-chemical properties [5].

In present study, Dextran, a new polymer with a molecular weight of 70,000 Da, was studied for ρ, η, and U for concentration of 1% in 1(N) sodium hydroxides have been measured at temperatures 303K, to 323K in 5K interval range in various frequencies such as 1 MHz, 5 MHz, 9 MHz and 12 MHz frequency [6].

We have chosen dextran for our study due to its wide industrial application particularly in pharmaceutical sector. It is the only water-soluble polysaccharide. The dextrans which were used initially for conversion into synthetic blood-volume expanders human red blood cells aggregation for increasing the degree of polymerization and hence the dextran and their derivatives find an interest in clinical applications, as well as experiments in tablets in the pharmaceutical industry. The rising use of these polyglucosans for medical, industrial, and research applications motivates ultrasonic examination of dextran's thermo acoustic parameters [7-8].

In continuation of our prior work dextran with water medium [9-10]. We have made a further endeavor to contemplate efficiently the physical-chemical behavior of dextran in sodium hydroxide i.e., in an alkaline medium. We have chosen a polymer dextran as a solute with 1(N) sodium hydroxide as a solvent. The outcomes give subjective data with respect to nature and quality of the particles interactions between solute and solvent in the liquids solutions. It has involved a different region of examinations by analysts due to its flexible "pharmaceutical, biomedical and modern application". As Industry demands reliable data on the physical and chemical properties of a wide variety of liquid solutions.

2. Materials and methods

2.1 Materials

The polymer dextran of molecular weight (M_W) 70,000 Da and 1(N) sodium hydroxide are used for experiments [11].

2.2 Measurements

The density of the solution is estimated using a standard equation and a 25 mL specific gravity bottle with an accuracy of 0.1 kg/m^3[12]

$$\text{“}\rho_2 = \frac{w_2}{w_1}\rho_1\text{”} \tag{1}$$

where w_1 denotes the weight of distilled water, w_2 denotes the weight of experimental solution, ρ_1 denotes the density of distilled water, ρ_2 denotes the density of experimental solution

The viscosity of the polymer solution was measured with viscometer an accuracy of 0.001 N s/m^2. The time of flow was measured with a digital racing stop watch with an accuracy of 0.01 s at the temperatures stated, and the equation was used to calculate it. [12]

$$\text{“}\eta_2 = \eta_1 \left(\frac{t_2}{t_1}\right)\left(\frac{\rho_2}{\rho_1}\right)\text{"} \tag{2}$$

where, η_1 is the viscosity of water, η_2 is the viscosity of the aqueous solution of dextran, ρ_1 is the density of water, ρ_2 is the density of aqueous solution of dextran, t_1 is the time of flow of water, t_2 is the time of flow of solution of dextran.

The velocity of ultrasonic waves in the solution was measured with an accuracy of 0.1K using a multi-frequency ultrasonic interferometer working in the temperature range of -10 °C to 85 °C [12]. The expression used to determine the ultrasonic velocity

$$U = 2d/t = 2d\,v = \lambda\,v \text{ where } 2d = \lambda \tag{3}$$

where v is the frequency of the generator to stimulate the crystal, d-distance between the reflector and the crystal, t-ultrasonic wave travel period.

2.3 Theoretical aspect

We have measured the following thermodynamic and acoustic parameters [13].

$$\text{Free volume } (V_f) \text{ is as } V_f = \left(\frac{M_{eff}U}{K\eta}\right)^{\frac{3}{2}} \tag{4}$$

where M_{eff} is the solutions effective molecular weight, and K is the temperature independent constant, which is 4.281 x 10^9 for all liquids.

$$\text{Internal pressure is } \pi_i = bRT\left(\frac{k\eta}{U}\right)^{3/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right) \tag{5}$$

where b stands for cubic packing, which is assumed to be 2 for all liquids T is the absolute temperature in Kelvin R is the universal gas constant.

Absorption coefficient or attenuation coefficient is given by the relation

$$\propto = \frac{8\pi^2\eta f^2}{3\rho U^3} \tag{6}$$

where f is the frequency of ultrasonic wave.

Rao's constant developed by

$$R = \frac{M_{eff}}{\rho} U^{1/3} \tag{7}$$

Wada's constant derived the empirical relation,

$$W = \frac{M_{eff}}{\rho} \beta^{-1/7} \tag{8}$$

3. Results and discussion

The experimental values of ρ, η, and U at different temperatures for frequencies 1, 5, 9, and 12 MHz for experimental solutions were used to calculate the acoustical parameters data are given in Table 1-4 and displayed in Figure 1 to 6.

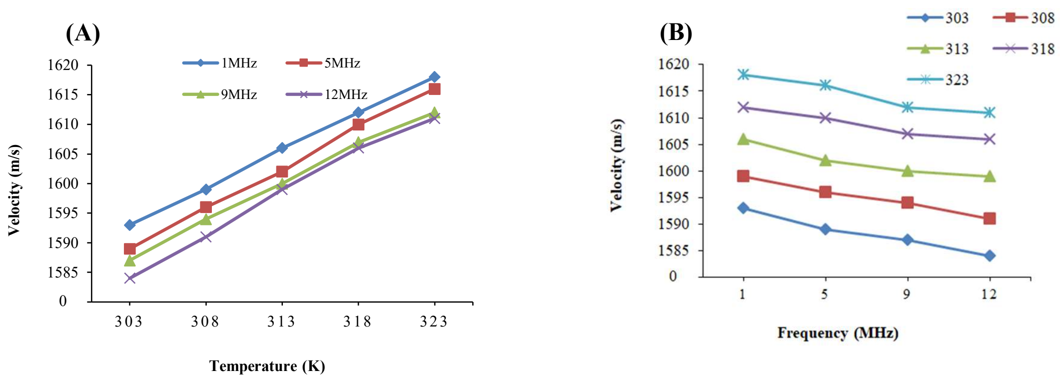

Figure 1 Variation of (A) velocity with temperature, and (B) velocity with frequency in sodium hydroxide as solvent.

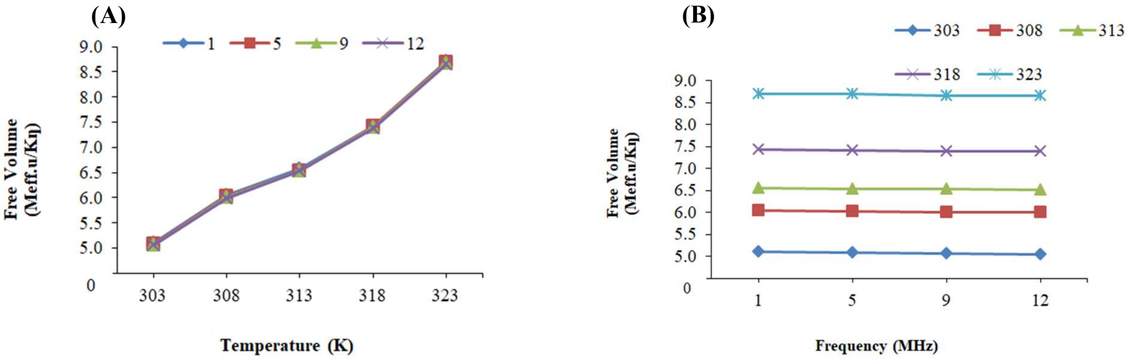

Figure 2 Variation of (A) Free volume with temperature, and (B) Free volume with frequency in sodium hydroxide as solvent.

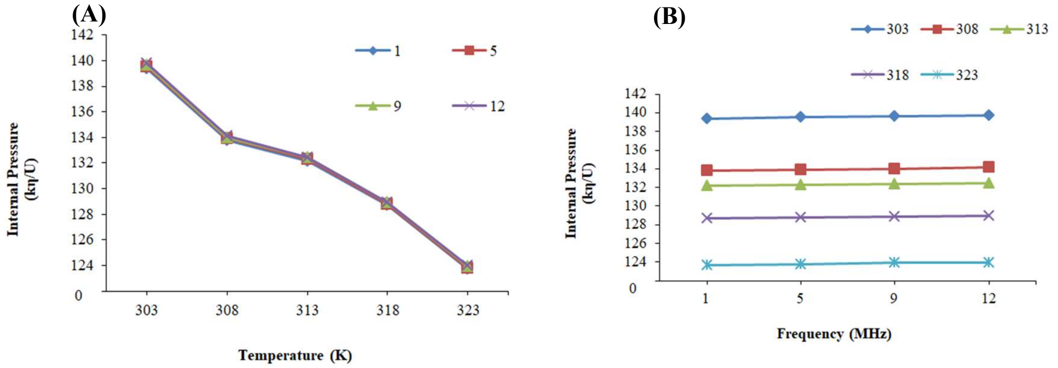

Figure 3 Variation of (A) Internal pressure with temperature, and (B) Internal pressure with frequency in sodium hydroxide as solvent.

Table 1 The experimental values of "density (ρ) and viscosity (η).

T in (kelvin)	(ρ) kg/m^3	(η) 10^3/N.s.m^2
303	1039.00	1.256
308	1038.21	1.126
313	1036.78	1.070
318	1034.76	0.989
323	1031.74	0.893

Table 2 The "ultrasonic velocity (U) and free volume (V_f)".

T in kelvin	U (m/s)				V_f (x10^{3}m^3/mol)			
	1 MHz	5 MHz	9 MHz	12 MHz	1 MHz	5 MHz	9 MHz	12 MHz
303	1593	1589	1587	1584	5.101	5.082	5.072	5.058
308	1599	1596	1594	1591	6.044	6.027	6.016	5.999
313	1606	1602	1600	1599	6.566	6.542	6.529	6.523
318	1612	1610	1607	1606	7.428	7.414	7.393	7.386
323	1618	1616	1612	1611	8.709	8.693	8.661	8.653

Table 3 The "internal pressure (πi) and attenuation coefficient (α)".

T in kelvin	π_i (×10^3 N/m^2)				α (x10^6(np/m)			
	1MHz	5MHz	9MHz	12 MHz	1MHz	5MHz	9MHz	12 MHz
303	139.369	139.544	139.632	139.764	6.371	159.474	525.297	929.054
308	133.809	133.935	134.019	134.145	5.469	137.043	450.199	792.583
313	132.159	132.324	132.406	132.448	5.019	126.729	413.838	733.980
318	128.696	128.776	128.896	128.937	4.593	116.440	381.718	673.582
323	123.723	123.799	123.953	123.991	4.173	105.410	343.526	609.527

Table 4 The "Rao's constant (R) and Wada's constant (W)".

T in kelvin	R (m^3/mole) (m/s)$^{1/3}$/(10^3)				W (m^3/mole) (N/m^2)$^{1/7}$/(10^3)			
	1 MHz	5 MHz	9 MHz	12 MHz	1 MHz	5 MHz	9 MHz	12 MHz
303	1.124	1.123	1.123	1.122	2.134	2.133	2.132	2.131
308	1.126	1.126	1.125	1.124	2.138	2.137	2.136	2.135
313	1.130	1.129	1.128	1.128	2.143	2.142	2.141	2.140
318	1.133	1.133	1.132	1.132	2.149	2.148	2.147	2.147
323	1.138	1.137	1.136	1.136	2.157	2.156	2.154	2.154

Figure 1 (A) shows the ultrasonic velocity as a function of temperature. The ultrasonic velocity appears to increase as the temperature rises, implying that the component is interacting. Each dextran molecule's electrons surrounding the nucleus are symmetrical and distributed evenly around the nucleus. According to London (1948), due to an increase in temperature, these electrons are in continuous and rapid motion in relation to the nucleus, and it is thus possible for the electron density around the nucleus to be concentrated in the other region of the same molecule at any time. This causes an asymmetrical distribution of electron density around the nucleus, resulting in the formation of permanent dipoles in water molecules. This shows that sodium hydroxide and water have a molecular interaction, such as hydrogen bonding or dipole-dipole interactions. The dipole-ion contact between sodium hydroxide Na+ and dextran molecules is responsible for the relationship between sodium hydroxide Na+ and H_2O molecules [14].

The interaction between molecules that may be due to a rise in agitation results in a decrease in “U’ at advanced frequencies and detachment is also weakened by an increase in frequencies. This is due to a decrease in the amount of dextran molecules, and the strong dipole-ion communication between Na+ of NaOH and dextran does not have enough polarised molecules. This mechanism leads to weak forces of interaction. In addition, the intermolecular difference decreases in the greater frequency range, leading to a decrease in velocity (Figure 1 B) [15].

The power of the interaction is well expressed in the ‘V_f ‘and ‘π_i’ deviations. Strong repulsive forces in the fluid solution are responsible for the ‘π_i’ that held the solution together. The ‘π_i’ is more responsive to attracting forces, whereas the ‘V_f' is more susceptible to repulsive forces. The entropy of the system is determined extraordinarily by these two acoustic parameters combined. It is observed that ‘V_f ‘and ‘π_i’ temperature rises are likely to show a broad tendency in the opposite direction. The free volume is the space available for the molecule to move in an imaginary unit cell. The increase in free volume and decrease in internal pressure in system shows that the strength of interaction increases gradually with the increase temperature. Free volume is the average volume in which the center of a molecule can move due to the repulsion of the surrounding molecules. At constant concentration of components liquid and constant temperature, viscosity remains constant, hence V_f is directly proportional to $U^{3/2}$. As velocity decreases as frequency increases, therefore the free volume also decreases. Internal pressure is a broader concept and is a measure of the totality of the forces (dispersion + ionic + dipolar) of interaction that contribute to the overall cohesion / adhesion of the liquid system. When temperature increases, the force of cohesion also decreases, hence internal pressure decreases. 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 2 and Figure 3). This conforms that there are little variations of these parameters with respect to frequencies where cohesive force does not affect the system. Because of further solvent interaction [16].

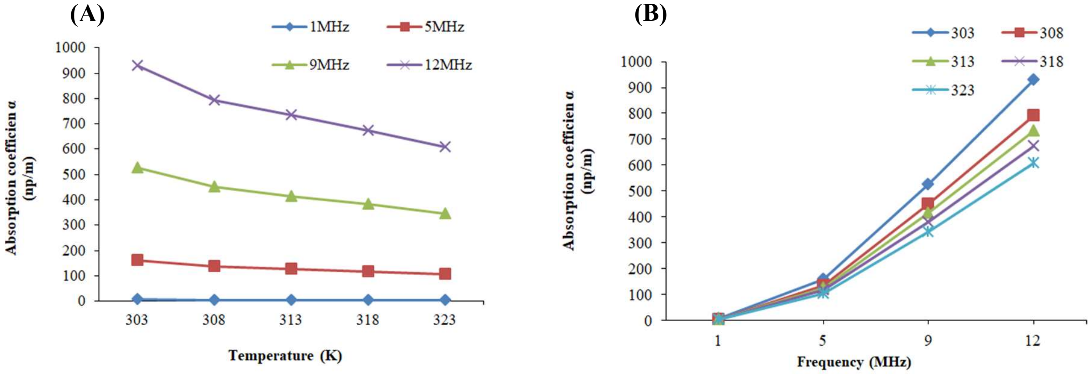

Figure 4 Variation of (A) Attenuation coefficient with temperature, and (B) Attenuation coefficient with frequency in sodium hydroxide as solvent.

Absorption coefficient (Figure 4), which is a characteristic of the medium, increases with increase in frequency. This shows a similar behaviour to that of the passage of electromagnetic waves through a conductor where the skin depth decreases with frequency of the incoming wave. Decrease in skin depth means increase in absorption. 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. [17]. The ‘α’ gradually growths with rise in frequencies at higher frequency and the effects are negligible at low frequencies, because of its proportionality to the frequency square, the absorption coefficient rapidly increases.

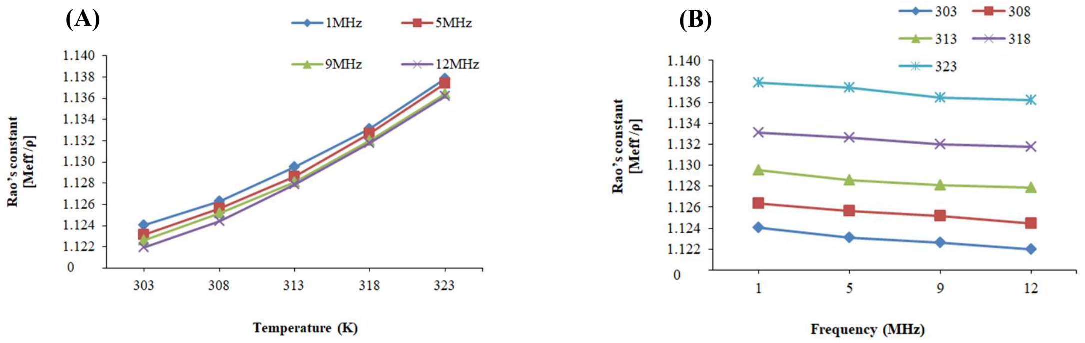

Figure 5 Variation of (A) Rao's constant with temperature, and (B) Rao's constant with frequency in sodium hydroxide as solvent.

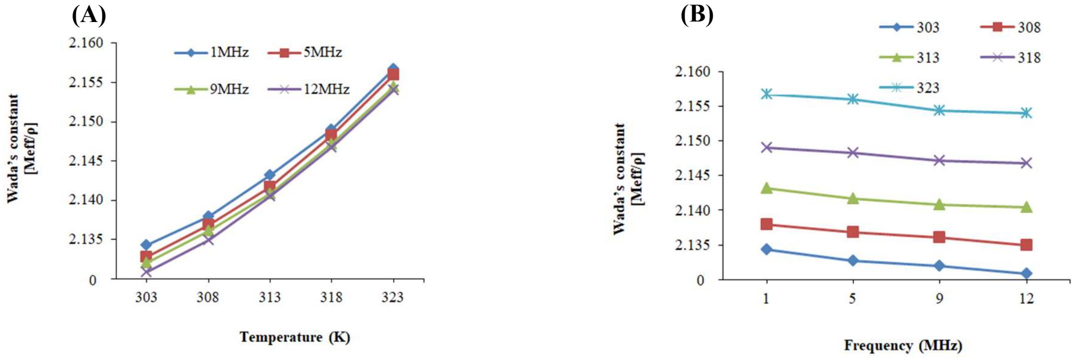

Figure 6 Variation of (A) Wada's constant with temperature, and (B) Wada's constant with frequency in sodium hydroxide as solvent.

In order to research the role of molecular collaboration, R and W are also equally important. The calculated values of dextran solution of at different temperature for 'R' and 'W' show increasing trends as more components become available in each region, the medium becomes more densely packed, enhancing interaction indicates the availability of a greater number of components in a given region, thus leading to a tight packing of the medium and thereby increasing the interactions. Figure 5 and Figure 6 highlight that due to agitation of the molecules, Rao's constant (R) and Wada's constant (W) indicate linear forecasting the absence of complex formation and only weak contact exists in all these scenarios at higher frequencies. [18-19].

4. Conclusion

Internal pressure and free volume have been evaluated which gives an idea about the effect of cohesive force in ion-solute interaction and structure maker and predominant in solute-solvent interactions. The absorption coefficient also indicates that interaction slower with temperature but increases with a rise in the frequencies. Rao's and Wada's constant with temperature suggest the availability of a greater number of components in each region leading to a close packing of the medium thereby increasing the interactions. The vitiation of thermo-dynamical parameters with temperature and frequencies provides useful information about the nature of intermolecular interaction existing in the solutions. The interactions that result in dextran interstitial accommodation with sodium hydroxide have a greater influence than dipole-ion interactions. In such interaction, the relatively large size of polymer dextran can cause hindrance and hence the association is comparatively strong in sodium hydroxide, Solute–solvent interaction predominates over the other type of interactions.

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