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Effect of pH in aqueous (Hydroxy Propyl Methyl Cellulose) polymer solution

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ABSTRACT

The ultrasonic velocity, density and viscosity have been measured for the aqueous solution of Hydroxy Propyl Methyl Cellulose (HPMC) at different concentration and pH using ultrasonic interferometer at a frequency of 2 MHz and at a constant temperature of 303 K for the entire composition. The various physical parameters were calculated from the measured values of ultrasonic velocity (U), density (ρ) and viscosity (η) using the standard formula and the results are discussed in the light of molecular interaction present in the system. It is found that the ultrasonic velocity values increases with increase in concentration due to the solute – solvent interaction through hydrogen bonding. The increase in velocity near basic pH may be due to the fact that strong interaction between the water-HPMC solutions.

1. Introduction

To know the interesting characteristics features of interaction between biologically energetic substances and water are vibrant to understand the role of these substances in living organisms. In the field of ultrasonic it has been grown enormously in scientific studies and has become a subject of active interest during recent years. Propagation characteristics of an acoustic wave in liquids, solutions or liquid mixtures are widely used to study the intermolecular interactions. Molecular interaction between solvent molecules and long chain polymers have been studied by researchers with one of the main intents of measuring the binding constant of solvents to macromolecules and to relate the constants with chemical structures of the species involved.

Polymers are widely used in foodstuffs, adhesives, paints, textiles and paper. Hydroxy Propyl Methyl Cellulose (HPMC) as a hydrophilic gel matrix have also found widespread in the formulation of different pharmaceutical products. In solid dosage forms, they are usually used as tablet binders, film-coating agents, and controlled released matrix formers [1–6]. Water soluble cellulose ethers, such as, HPMC are effective as hydrophilic matrix forming components.

HPMC is chosen for the present study because of the importance of Hydroxy group in biopolymers, as it binds with water molecule to some extent in the aqueous form. The ultrasonic velocity and its characteristics of aqueous HPMC molecules are of great interest in the field of physical chemistry and biophysics to the extent that these properties are useful in studying molecular interactions [7]. Polymers change their properties depending on factors such as temperature, solvent composition, ionic strength, pH, electric field and light. This effect can be widely applied in a variety of fields such as chemical engineering, medicine pharmacy, life sciences, food and agriculture [8]. These studies have been used as a tool to study the liquid state and to understand the intra and intermolecular interactions in aqueous solutions of HPMC. The ultrasonic velocity measurement as a function of pH in aqueous liquid is useful in gaining insight into the structure and bonding of associated molecular complexes and other molecular process in aqueous HPMC. HPMC is playing an active role in the development for topical treatment of eye. The controlled release of HPMC in hydrophilic matrix depends mainly on the low solubility of drugs [9,10]. An overview of the present study is to identify the range of finest method of concentration and to inculcate the concentration with different pH by using ultrasonic interferometer technique.

2. Experimental method

The pure HPMC samples and pH tablets were bought from Madras scientific company, Salem, Tamilnadu, India. The ultrasonic velocity measurement in the HPMC and in different pH solutions are made in the single frequency continuous wave ultrasonic interferometer (F81-Model, Mittal) using a fixed frequency of 2 MHz and at 303K. The density is determined by using 5 ml specific gravity bottle and the viscosities are

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determined by Ostwald's viscometer with accuracy ±2 parts of 10^4 and 0.1% respectively. The pH of the buffer solution has been measured by using a digital pH meter. In the present investigation, ultrasonic velocity and thermo acoustical values are estimated in these solutions. The experimental solutions are prepared by adding a known weight of HPMC and then stirred by using magnetic stirrer until clear solutions have been obtained. In 100 ml of the solvent the mass by volume percentage of the solution were prepared. For 0.4% of solution 0.10g of the solute dissolved in 25 ml of stock solution. It is purely based on the concentration of solution at 303K. The ultrasonic velocity (u), density (ρ) and viscosity (η) values were measured in Research and Development Center, Department of Physics, Paavai Engineering College, Namakkal, India – 637 018. The ultrasonic velocity, density and viscosity of solutions were determined through the following factors.

2.1. Ultrasonic velocity measurement

The ultrasonic velocity (U) can be obtained from the relation

$$U = \lambda \times f, \tag{1}$$

where f is the frequency of ultrasonic wave and 'λ' is the wavelength of ultrasonic waves [11,12]. When the solution attains the required temperature, the micrometer is operated and the distance d (mm) is measured and $d = (n\lambda)/2$. Therefore by knowing (λ) from above, U, the ultrasonic velocity can be calculated.

2.2. Density measurement

The density of the samples is measured using relative measurement method. A clean and dry 5 ml specific gravity bottle is taken and its weight is measured as (w_1). The water level in the specific gravity bottle is maintained up to the marked level and then its weight (w_2) is measured. Thus, the mass of water is determined as m_w ($=w_1 - w_2$). By standardizing the specific gravity bottle with water, the experimental liquid whose density is to be determined is taken in it and the mass (m) of the mixture is determined at the experimental temperature as that of water. By using the following relation, the density of the unknown mixture at any experimental temperature can be determined. The density of water (ρ_w) at different temperatures was taken [13].

$$\rho = \frac{m\rho_w}{m_w} \tag{2}$$

The accuracy of the measurement of density in this method depends on the accuracy of the weight.

2.3. Viscosity measurement

By knowing the time taken for the reference liquid (water) and mixture, the viscosity of the unknown mixture is determined using the following relation

$$\eta = \eta_w \frac{\rho t}{\rho_w t_w} \tag{3}$$

Where η_w, ρ_w, t_w are the viscosity, density and the time of flow of water respectively [14]. ρ and t are the density and time of flow of mixture respectively.

3. Physical parameter

Thermodynamical physical parameters such as adiabatic compressibility (β), intermolecular free length (L_f), internal pressure (π_i), acoustic impedance (z_a) and solvation number (S_n) have been calculated from empirical Jacobson's relations [15,16].

(i) Adiabatic compressibility $\beta = 1/u^2 \rho$ (4)

has been calculated from the u-ultrasonic velocity and ρ-density of the medium using the Newton –Laplace equation.

(ii) Intermolecular free length $L_f = K_T \beta^{1/2}$ (5)

Where K_T - temperature dependent constant known as Jacobson's constant ($K_T = 2.131x10^{-6}$), and β - the adiabatic compressibility

(iii) Internal pressure $\pi_i = bRT\,[K\,\eta/u]^{1/2}\,\rho^{2/3}/M^{7/6}$ (6)

(Where, b stands for cubic packing, which is assumed to be 2 for all liquids.

T-absolute temperature in Kelvin, Where M_{eff} - effective molecular weight of the mixture ($M_{eff} = \sum m_i x_i$, where m_i and x_i are the molecular weight and mole fraction of individual constituents, respectively K is a temperature independent constant which is equal to $4.281x10^9$ for all liquids, R is the universal gas constant, η-Viscosity of the solution).

(iv) Rao's constant $R_a = (M/\rho)\,(u)^{1/3}$ (7)

(v) Relaxation time $\tau = 4/3\beta\eta$ (8)

(vi) Acoustic impedance $z_a = \rho u$ (9)

(vii) Absorption coefficient $\alpha/f^2 = (8\pi^2\eta/3\rho u^2)$ (10)

(viii) Free Volume $V_f = (M_{eff}\,u/K\,\eta)^{3/2}$ (11)

(ix) Cohesive energy $CE = V_f \pi_i$ (12)

(x) Solvation number $Sn = M_2/M_1\,[1-((\beta)/\beta o)][(100-x)/x]$ (13)

Where M_1, M_2 - molecular weight of the solvent and solute, β and β_o - adiabatic compressibility of the solution and solvent.

4. Results and discussion

Using the measured values of ultrasonic velocity (u), density (ρ), viscosity (η) of the solution and other acoustical parameters like adiabatic compressibility (β), intermolecular free length (L_f), internal pressure (π_i), Rao's constant (R_a), relaxation time (τ), acoustic impedance (Za), absorption coefficient (α/f^2), free Volume (V_f), cohesive energy (CE), solvation number (Sn) are calculated as shown in Tables 1–4. The plots of ultrasonic velocity (u), adiabatic compressibility (β), absorption coefficient (α/f^2) and free Volume (V_f) versus different concentration and pH of HPMC solution at room temperature 303K are shown in Figs. 1–8. The ultrasonic studies are more useful in illuminating these parameters which may further support us to understand the features of polymer ion interaction in these systems.

4.1. The effect of different concentration on aqueous HPMC

From the observed values of ultrasonic velocities (u) with change in concentration of Fig. 1 it is evident that the velocity increases suddenly with addition of water – HPMC solution. On further adding up of the solute to water leads to a gradual increase of velocity with concentration. As the concentration increases the velocity also increases and variation of velocity with concentration is due to intermolecular forces. This indicates increase in cohesion forces due to powerful polymer solvent interactions. This observation confirms the existence of polymer-solvent interaction [17].

Density (ρ) increases with increase in concentration of aqueous HPMC solution due to the presence of ions or particles. When an ion is added to a solvent it charms certain solvent molecules towards itself by drawing the molecule from the compressibility of a solvent is greater than that of a solution and it decreases with the increase in concentration of the solution. Dipole-Dipole interaction of hydrogen bonded complex formation between different molecule which leads to increase the sound velocity and decrease of compressibility [18,19].

Viscosity (η) is another important parameter that contributes to

Table 1
Ultrasonic velocity and related acoustical parameters in aqueous HPMC solution at 303K.

Temp. K	Conc. %	U ms^{-1}	ρ kgm^{-3}	η x10^{-3} Nsm^{-2}	β x10^{-10} $N^{-1}m^2$	L_f Å	π_i x10^6 Pascal	R x10^{-3}
303	0	1504	998	0.810	4.429	0.419	0.002	0.206
	0.4	1569	1057	0.908	3.843	0.391	0.010	3.339
	0.8	1582	1076	0.925	3.713	0.384	0.489	6.355
	1.2	1588	1081	0.952	3.668	0.382	0.315	9.359
	1.6	1594	1094	0.989	3.597	0.378	0.234	12.225
	2.0	1601	1111	1.092	3.511	0.373	0.193	14.951

Table 2
Ultrasonic absorption and related acoustical parameters in aqueous HPMC solution at 303K.

Temp. K	Conc. %	α/f^2 x10^{-10} $Npm^{-1}s^2$	V_f x10^{-6} m^3mol^{-1}	Cohesive energy $kjmol^{-1}$	τ x10^{-12}s	z_a x10^6 $kgm^{-2}s^2$	S_n
303	0	0.943	0.021	0.470	4.782	1.500	–
	0.4	0.917	1.363	0.298	4.651	1.658	557
	0.8	0.903	3.604	0.267	4.578	1.702	654
	1.2	0.918	6.236	0.253	4.655	1.716	682
	1.6	0.935	8.989	0.245	4.742	1.714	736
	2.0	0.010	10.767	0.246	5.111	1.778	802

Table 3
Ultrasonic velocity and related acoustical parameters in 0.4% concentration of aqueous HPMC in different pH values.

Temp. K	pH	U ms^{-1}	ρ kgm^{-3}	η x10^{-3} Nsm^{-2}	β X10^{-10} $N^{-1}m^2$	L_f Å	π_i X10^8 Pa	R X10^{-3}
303	4.2	1484	1052	1.163	4.316	0.414	1.202	3.294
	5.5	1541	1073	1.210	3.924	0.395	1.219	3.270
	7	1566	1086	1.352	3.754	0.386	1.289	3.248
	8	1597	1107	1.420	3.541	0.375	1.325	3.207
	9.2	1674	1146	1.513	3.113	0.352	1.367	3.147

Table 4
Ultrasonic absorption and related acoustical parameters in 0.4% concentration of aqueous HPMC in different pH values.

Temp. K	pH	α/f^2 x10^{-10} $Npm^{-1}s^2$	V_f x10^{-7} m^3mol^{-1}	Cohesive energy $kjmol^{-1}$	T x10^{-12} s	z_a x10^6 $kgm^{-2}s^2$	S_n
303	4.2	0.013	8.651	0.104	6.691	1.561	107
	5.5	0.012	8.626	0.105	6.330	1.653	479
	7	0.013	7.482	0.096	6.766	1.700	641
	8	0.013	7.158	0.094	6.704	1.767	843
	9.2	0.012	6.985	0.095	6.280	1.918	125

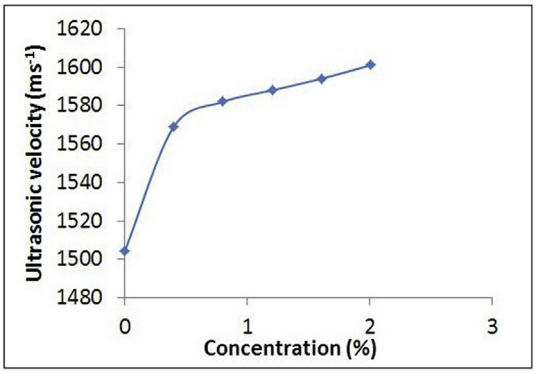


Fig. 1. Ultrasonic velocity Vs concentration of HPMC in aqueous solution at 303K

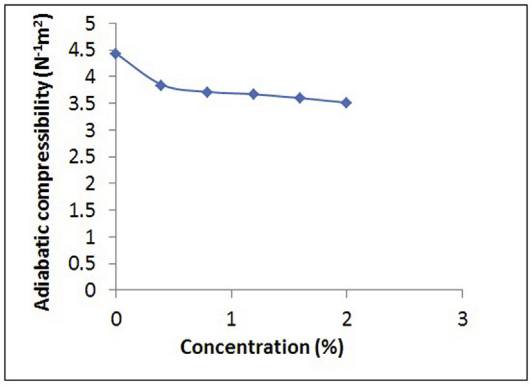


Fig. 2. Adiabatic compressibility Vs concentration of HPMC in aqueous solution at 303K

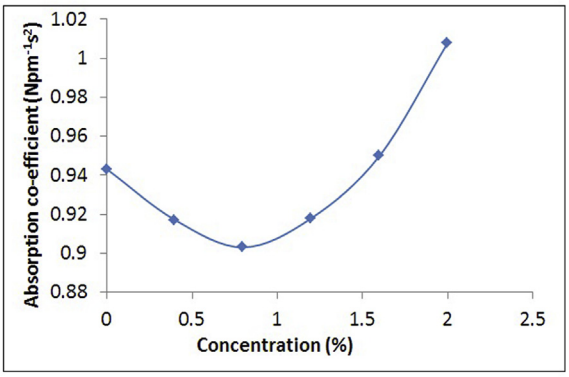


Fig. 3. Absorption coefficient Vs concentration of HPMC in aqueous solution at 303K

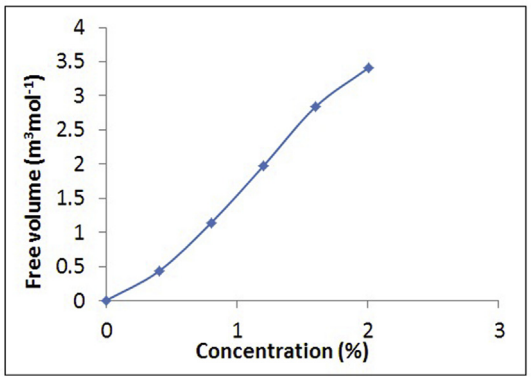


Fig. 4. Free Volume Vs concentration of HPMC in aqueous solution at 303K

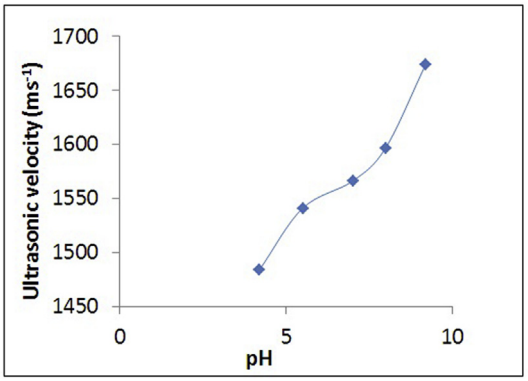


Fig. 5. Ultrasonic velocity Vs pH values of aqueous HPMC in solution at 0.4% concentration at 303K

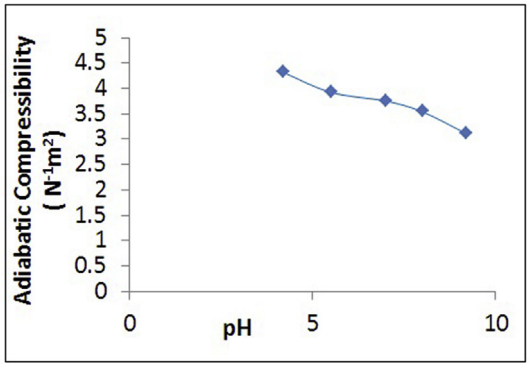


Fig. 6. Adiabatic compressibility Vs pH values of aqueous HPMC in solution at 0.4% concentration at 303K

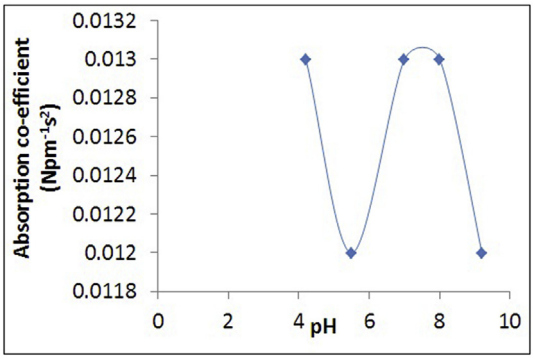


Fig. 7. Absorption coefficient Vs pH values of aqueous HPMC in solution at 0.4% concentration at 303K

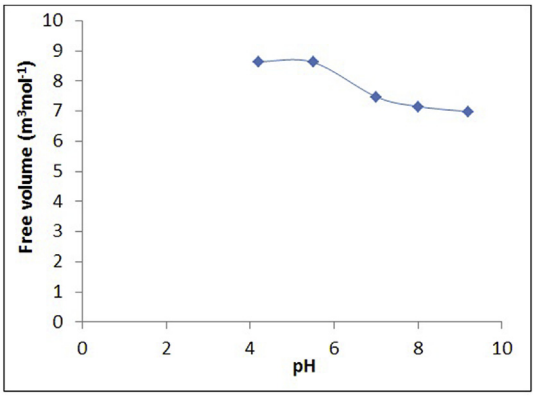


Fig. 8. Free Volume Vs pH values of aqueous HPMC in solution at 0.4% concentration at 303K

understanding the structure and molecular interaction occurring in the solutions. The viscosity increases with concentration of HPMC at 303K. The solutions become more and more viscous, as solute is added. At low concentration there is a sudden increase in the viscosity which indicates a strong hydrodynamic showing which exists between HPMC and water molecules due to mutual interaction. This increasing trend indicates the presence of molecular interaction in aqueous HPMC solution [20].

The increase in velocity and decrease in the adiabatic compressibility with increase of concentration of polymer is an indication that the intermolecular forces increase with the addition of polymer aqueous solution [21,22]. The interaction may either result from hydrogen bonding between the solute and solvent molecule. From the Fig. 2 adiabatic compressibility (β) decreases non-linearly with increase of concentration indicates greater interaction between the components of mixtures [23–25]. The decrease in compressibility denotes that there is enhanced molecular connotation in the above system upon increase in solute content.

The intermolecular free length (L_f) decreases with increase in the solute concentration recommend that there is a significant interaction between solute and solvent molecules suggesting a structure promoting behaviour on the addition of solute as shown in Table 1. Internal pressure plays an important role in elucidating molecular interaction as this

represents the resultant of the forces of attraction and repulsion between the molecules as shown in Table 1. The internal pressure (πi) is found to decreases with increase of concentration [26]. Rao's constant (R) values increases with increase in concentration, forecast the strong intermolecular link between the molecules of water- HPMC solution.

The absorption co-efficient (α/f^2) usually increases with increase in concentration [27,28] and this trend recommends that the extent of complexation increases with increase in concentration as shown in Fig. 3. Free volume is a usual volume in which the central molecule can transfer inside the hypothetical cell due to repulsion of adjacent molecules. It is also referred as the void space between the molecules that is volume present as holes of monomer size due to irregular packing of solvent molecules. From the Fig. 4, the free volume (V_f) increases and internal pressure (π_i) decreases with increase in molar concentration indicate the association through hydrogen bonding. A force is required to overcome the mutual attraction of the molecules so that the displacement of the molecules undergoes shearing stress [29]. It shows the increasing magnitude of interaction between the HPMC and water. Cohesive energy decreases with increase in concentration at temperature 303K indicate the existence of molecular interaction.

Non-linear difference of relaxation time with increase in concentration is due to the existence of momentous molecular interaction between the solute and solvent molecules. This similar change is found in viscosity showing that various forces play a dominant role in the relaxation process [30]. The acoustic impedance increases with increase in concentration and linear variation of acoustic impedance with concentration confirms the presence of molecular association between the solute and solvent molecules such increasing trends of impedance specifies the interaction between the solute –solvent molecules [31]. Solvation number (Sn) increases with increase in concentration depend upon solvent-solute interaction in the aqueous HPMC solution. Increase in Sn depends with concentration indicates predominant solvent-polymer interaction [32].

4.2. The effect of different pH on aqueous HPMC

Velocity, density and viscosity are most often measured parameters in the solutions of polymeric materials. The properties of any polymeric solution are affected by conformational changes. In addition, environmental changes such as concentration, temperature and pH also affect the properties of the polymer. When pH is altered to acidic or basic side the conformational changes occurs in the molecules can be well understood with the help of velocity variations. In the present study the effect of pH on the aqueous solutions of HPMC is carried out at lowest concentration i.e., 0.4% in the pH range 4.2–9.2. The velocity values are found to be very low in the lower pH (acidic). In the basic pH range the velocity values is found to increase remarkably when compared with neutral pH as shown in Fig. 5. The reduction in viscosity at lower pH is mainly because of the more coiling nature of HPMC when ionic strength increased. At the lowest pH the HPMC macromolecules are more and the possibility for polymer-polymer interaction is less pronounced. In the case of basic pH the HPMC molecules are relatively extended and hence they come into contact with each other even at lower concentration, which leads to polymer-polymer interactions. Thus cause decreases in compressibility with increase in pH are as shown in Fig. 6 and also increase in velocity and viscosity at higher pH range.

Hence the alteration in the pH alter the orientation and structural conformation of HPMC molecules which brings weak and strong interaction between water-polymer and polymer polymer molecules respectively [33,34]. The increase in absorption with increase of pH is mainly because of the increase in the free monomer. At higher pH the interaction is mainly between the HPMC molecules, which naturally enhance the availability of free water molecules. It is well known fact that absorption co-efficient increases with increase of non-hydrated water molecules are shown in Fig. 7. HPMC is the prevalent cellulose widely used in pharmaceutical industry [35]. The present work has been estimated to analyze the pH behaviour and concentration character of HPMC.

Hence it may be concluded that at lower pH the coiling of polymer molecules takes place which favours HPMC-water interaction. In the higher pH due to the extended conformation of polymer molecules the polymer-polymer interaction is favoured which leads the molecules to overlap and coiling and then entangles to become a thermo co reversible gel.

5. Conclusion

From the structure of HPMC and the solvent, the interaction is mainly between the OH group of solvent and methyl group of HPMC. Hence, the HPMC in 9.2 pH solution have more hydrogen bond, which not only strengthen the intermolecular forces resulting in decrease of compressibility, but also increase the velocity in that formulation. From the above findings, it is observed that the molecular association between the HPMC – solvent molecules arising from intermolecular hydrogen bonding and the variation of acoustical parameters with concentration at 303K strongly supports the molecular association occurring in these systems.

Author contribution statement

S.Punitha: Conceived and performed the experiments; Wrote the paper, R.Uvarani: Analyzed and interpreted the data A.Panneerselvam: Contributed reagents and designed materials

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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