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Ultrasonic Investigation on Hydroxy Ethyl Propyl Cellulose (HEPC) Solution at Different Concentration and pH

S. Aruna[1,*], R. Thiyagarajan[2] and A. Panneerselvam[3]

[1]Department of Physics, STET Women's College, Mannargudi-614016, India
[2]Department of Physics, Chikkaiah Naicker College, Erode-638004, India
[3]Department of Physics, Vivekanandha College of Engineering for Women (Autonomous), Elayampalayam, Tiruchengode-637205, India

*Corresponding author: E-mail: shastha.saruna5@gmail.com

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The ultrasonic investigation is one of the most effective and economical technique to analyze the nature of the matter. Ultrasonic techniques provide valuable information about the physico-chemical nature of the aqueous solutions. Thus, the propagation characteristics of an acoustical wave in solutions are used to study the nature of intermolecular interaction. In this work, the ultrasonic velocity, viscosity and density studies were determined to study the effect of concentration and pH in the aqueous hydroxyethyl propyl cellulose (HEPC) solutions at different temperatures (303, 313 and 323 K). From the observed values, the necessary related ultrasonic parameters are calculated and their variations are discussed. The findings from the result say the variations in the velocity and absorption coefficient values are only due to the conformational changes that occur in the HEPC solution.

Keywords: Ultrasonics, Concentration, Hydroxyethyl propyl cellulose.

INTRODUCTION

The propagation of ultrasonic waves in any substance has become a fundamental test to investigate its properties. Thus, the propagation characteristics of the ultrasonic waves in solutions are very useful to study the nature of intermolecular interaction. The ultrasonic technique is thought to be a suitable method for providing information about the molecular behaviours of liquids and solids when compared to other experimental techniques such as infrared spectroscopy, dielectric, nuclear magnetic resonance, refractometry techniques. Due to its sensitivity to very low population densities at higher energy states are found to be complementary to other techniques. Viscometric and density studies are also used to characterize the solutions. The molecular interaction influences the velocity of sound, absorption and other related acoustical parameters. Therefore, it is obvious that the ultrasonic parameters are useful for the study of molecular interaction [1]. The study of the effect of aqueous polymer in solution becomes more important in the scientific and technological points of view. Like almost all polyelectrolytic solutes, generally, the polyhydroxyl compounds are expected to influence water structure and the importance of contribution from structural changes of the solvent to the thermodynamic and kinetic properties of aqueous solutions of the biopolymer molecules has often been stressed [2].

Polymer gels have greater attention in the field of functional polymers. Gels have intermediate properties between solid and liquids since they consist of a three-dimensional network cross-linked polymers and solvent. Some polymers change their properties depending on the factors such as solvent composition, temperature, electric field, ionic strength, pH and light. The structural changes can be widely applied in a variety of fields such as pharmacy, chemical engineering, agriculture, food and medicines [3-5].

The present investigation deals with the effect of concentration and pH in the aqueous hydroxy ethyl propyl cellulose (HEPC) solutions. The HEPC has a various of applications and widely applied in a variety of fields, such as chemical engineering, medicine, pharmacy, life sciences, foods and agriculture. Usually, the data obtained from ultrasonic studies and their variation with pH and concentration at various temperatures of one of the components help to understand the nature of molecular interaction in terms of some physical parameters.

EXPERIMENTAL

Purification of chemicals: The correctness of any experimental measurement is limited not only by the accuracy of the instrument used but also to a considerable extent by the purity of the substances used. In general, the impurities change the behaviour of the liquids and liquid mixtures drastically. The chemicals used in this work are AnalaR (AR) grade and are purified by the standard methods [6,7]. Extra pure quality buffer salts are used for preparing pH solutions and fresh double distilled water is also used throughout the investigation.

Measurement of density (ρ): The density of the samples can be measured using the relative measurement method. A clean and dry 10 mL specific gravity bottle is taken and its weight is measured as w_1. The specific gravity bottle is now filled with the reference liquid *e.g*. double distilled water and then immersed into a temperature-controlled water bath. The temperature of the bath can be maintained at any desired constant temperature. The specific gravity bottle is immersed for a period of time into the bath so that the water in the specific gravity bottle attains the temperature of the bath. 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 ($= w_2 - w_1$) *i.e.* the volume of the specific gravity bottle was ascertained by weighing the water at the experimental temperature(s). After standardizing the specific gravity bottle with water, the experimental liquid whose density is to be determined is taken in the specific gravity bottle and the mass of the mixture (m) is determined at the experimental temperature(s) as that of water. By using the following relation, the density of the unknown mixture at any experimental temperature(s) can be determined. The density of reference liquid say water (ρ_w) at different temperatures is calculated using the relation [7]:

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

The accuracy of the measurement of density in this method depends on the accuracy of the weight. The accuracy in the measurement of density is in the order of ± 0.1 kg m^{-3}.

Measurement of viscosity (η): Similar to the density measurement, the viscosity of the mixture can also be measured using the relative method. The viscosity of the samples was measured using Ostwald's viscometer of capacity 10 mL. The viscometer is filled with double distilled water and then immersed into the water bath. To attain the experimental temperature, the water in the viscometer is allowed for some time. Employing a suitable arrangement, the water is sucked above the marked level and then it's allowed to flow freely. The time taken for water flow between the marked levels is noted. The same procedure is repeated for various experimental temperatures. The water is replaced with a solution whose viscosity to be determined. Using the same procedure, the time taken for the solution at the experimental temperature was determined. By knowing the time taken for the reference liquid (water) and the solution, the viscosity of the unknown mixture is determined using the following relation:

$$\eta = \eta_w \frac{\rho_t}{\rho_w t_w}$$

The viscosity, density and the time flow of the reference liquid say water is represented as η_w, ρ_w, t_w respectively. ρ and t are representing the density and time flow of the solution respectively. The viscosity of water at various temperatures has been taken from the available literature [7,8].

The accuracy of the viscosity measurement depends on the accuracy in the time determination and density of water. The overall accuracy of the measured viscosity using Oswald's viscometer is ± 0.001 Ns m^{-2}.

Measurement of ultrasonic velocity (U): The velocity of the ultrasonic waves in liquids has been measured using an ultrasonic interferometer made in India by Mittal Enterprises, New Delhi which is working at 2 MHz. The accuracy of the measurement from the interferometer is 0.1 m s^{-1} [9].

The ultrasonic velocity measurements in the aqueous HEPC solutions are made by using a low amplitude continuous-wave variable path interferometer at 303, 313 and 323 K. Throughout the experiment the sample cell is maintained at a required temperature by circulating water from a thermostatically controlled (± 0.1 ºC) water bath. The density is determined by using a specific gravity bottle and the viscosities are determined by Ostwald's viscometer, with an accuracy of the density should be in the order of ± 0.1 kg m^{-3}. The pH of the buffer solution has been measured by using a digital pH meter.

The adiabatic compressibility (β), intermolecular free length (L_f), absorption coefficient (α/f^2), free volume (V_f) and solvation number (S_n) are calculated by using the relations from the available literature.

$$\beta = \frac{1}{v^2\rho} \tag{1}$$

$$L_f = K_T\beta^{1/2} \tag{2}$$

Tacobson constant ($K_T = 2.131 \times 10^{-6}$)

$$\left(\frac{\alpha_A}{f^2}\right)_{class} = \frac{8\pi^2\eta}{3\rho U^2} \tag{3}$$

$$V_f = \left(\frac{M_{eff}.u}{K\eta}\right)^{1/3} \tag{4}$$

$$S_n = \frac{M_2}{M_1}\left[1 - \left(\frac{\beta}{\beta_0}\right)\right]\left(\frac{100 - x}{x}\right) \tag{5}$$

RESULTS AND DISCUSSION

The values of ultrasonic velocity, density and viscosity and other acoustical parameters were determined and tabulated in Tables 1-4. The above said mathematical relations are used to calculate the adiabatic compressibility (β), intermolecular free length (L_f), internal pressure (π_i), Rao's constant (R), absorption coefficient (α/f^2), free volume (V_f), Cohesive energy (CE), relaxation time (τ) and solvation number (S_n), respectively.

TABLE-1
ULTRASONIC VELOCITY AND RELATED ACOUSTICAL PARAMETERS IN AQUEOUS HEPC SOLUTION AT DIFFERENT TEMPERATURES

Temp. (K)	Conc. (%)	U (m s^{-1})	ρ (kg m^{-3})	$\eta \times 10^{-3}$ (Ns m^{-2})	$\beta \times 10^{-10}$ (N^{-1} m^2)	L_f (Å)	$\pi_i \times 10^6$ (Pascal)	$R \times 10^{-3}$
303	0	1505	998	0.795	4.423	0.419	8.16	0.206
	0.5	1536	1051	0.876	4.032	0.400	2.60	4.030
	1.0	1554	1076	0.902	3.848	0.391	1.25	7.513
	1.5	1567	1085	0.938	3.753	0.386	0.83	10.831
	2.0	1574	1097	0.967	3.679	0.382	0.62	13.891
	2.5	1579	1116	1.025	3.593	0.378	0.52	16.629
313	0	1510	992	0.782	4.421	0.419	8.32	0.207
	0.5	1539	1040	0.851	4.059	0.402	2.62	4.075
	1.0	1562	1061	0.887	3.862	0.392	1.27	7.632
	1.5	1573	1072	0.915	3.770	0.387	0.84	10.976
	2.0	1581	1084	0.944	3.690	0.383	0.63	14.078
	2.5	1588	1098	0.982	3.611	0.379	0.51	16.934
323	0	1515	988	0.687	4.409	0.419	8.01	0.208
	0.5	1544	1031	0.761	4.068	0.402	2.54	4.115
	1.0	1566	1047	0.819	3.894	0.393	1.25	7.740
	1.5	1579	1059	0.864	3.787	0.388	0.83	11.125
	2.0	1587	1071	0.908	3.707	0.384	0.63	14.267
	2.5	1596	1086	0.943	3.614	0.379	0.52	17.150

TABLE-2
ULTRASONIC ABSORPTION AND RELATED ACOUSTICAL PARAMETERS IN AQUEOUS HEPC SOLUTION AT DIFFERENT TEMPERATURES

Temp. (K)	Conc. (%)	$\alpha/f^2 \times 10^{-15}$ (Np m^{-1} s^2)	$V_f \times 10^{-15}$ (m^3 mol^{-1})	Cohesive energy $\times 10^{-8}$	$\tau \times 10^{-12}$ (s)	$z_a \times 10^6$ (kg m^{-2} s^2)	S_n
303	0	6.144	3.574	2.9183	0.468	1.501	–
	0.5	6.047	3.946	1.0235	0.470	1.614	300
	1.0	5.873	11.121	1.3816	0.462	1.672	560
	1.5	5.907	12.067	1.7146	0.469	1.700	710
	2.0	5.943	13.195	2.009	0.474	1.726	817
	2.5	6.133	14.729	2.4460	0.491	1.762	923
313	0	6.019	3.524	2.9142	0.460	1.497	–
	0.5	5.902	3.783	9.9278	0.460	1.600	278
	1.0	5.767	11.084	1.3743	0.456	1.657	544
	1.5	5.765	11.992	1.6783	0.459	1.686	690
	2.0	5.793	13.124	1.9716	0.464	1.713	802
	2.5	5.872	4.443	2.3073	0.472	1.743	1082
323	0	5.257	2.9226	2.3229	0.403	1.496	–
	0.5	5.272	3.216	8.1718	0.412	1.591	262
	1.0	5.355	9.672	1.2015	0.425	1.639	503
	1.5	5.448	11.842	1.5376	0.436	1.672	661
	2.0	5.576	12.946	1.8743	0.448	1.699	773
	2.5	5.615	14.218	2.1906	0.454	1.733	1064

TABLE-3
ULTRASONIC VELOCITY AND RELATED ACOUSTICAL PARAMETERS IN 0.4% CONCENTRATION OF AQUEOUS HEPC IN DIFFERENT pH VALUES AT 303 K

pH	U (m s^{-1})	ρ (kg m^{-3})	$\eta \times 10^{-3}$ (Ns m^{-2})	$\beta \times 10^{-10}$ (N^{-1} m^2)	L_f (Å)	$\pi_i \times 10^6$ (Pascal)	$R \times 10^{-3}$
4	1469	1091	1.162	4.247	0.411	3.99	3.113
6	1556	1101	1.237	3.751	0.386	4.02	3.144
7	1579	1011	1.324	3.967	0.397	3.90	3.441
9	1594	1120	1.421	3.514	0.374	4.31	3.116
11	1621	1136	1.513	3.350	0.365	4.45	3.089

Effect of concentration and temperature on aqueous HEPC: From the measured values of ultrasonic velocity with the change in concentration is shown in Fig. 1 and the velocity increases suddenly on the addition of HEPC to water. On further addition of the solute to water leads to a gradual increase of velocity with concentration. At lower concentrations, the inter-

TABLE-4
ULTRASONIC ABSORPTION AND RELATED ACOUSTICAL PARAMETERS IN
0.4% CONCENTRATION OF AQUEOUS HEPC IN DIFFERENT pH VALUES AT 303 K

pH	$\alpha/f^2 \times 10^{-15}$ (Np m^{-1} s^2)	$V_f \times 10^{-15}$ (m^3 mol^{-1})	Cohesive energy $\times 10^{-8}$	$\tau \times 10^{-12}$ (s)	$z_a \times 10^6$ (kg m^{-2} s^2)	S_n
4	8.833	4.132	1.648	0.657	1.602	190
6	7.841	4.946	1.991	0.618	1.713	280
7	8.746	5.621	2.186	0.700	1.596	379
9	8.236	6.313	2.722	0.665	1.785	448
11	8.221	7.114	3.168	0.675	1.841	733

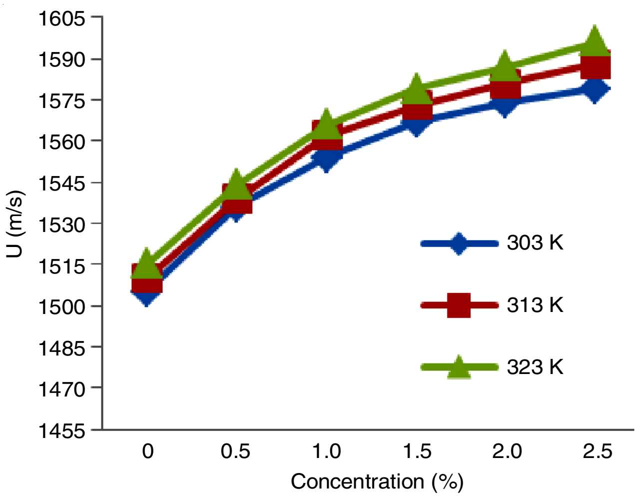

Fig. 1. Ultrasonic velocity *vs.* concentration of aqueous HEPC solution at different temperatures

action is between the polymer HEPC and water molecules. The number of solvated molecules around a polymer repeat unit is found to be more at lower concentrations than at higher concentrations. These numbers of solvated molecules of water and polymer HEPC repeat units could be interpreted in terms of propagated attractions [10]. The viscosity values also change in the same fashion as that of the ultrasonic velocity as shown in Fig. 2, as the temperature increases the viscosity decreases for the same concentrations and temperature. In the present study, hydrodynamic screening is more effective which causes an enhanced increase in the value of viscosity at dilute concentrations. In more concentrated solution direct segment-segment interaction may exist [11].

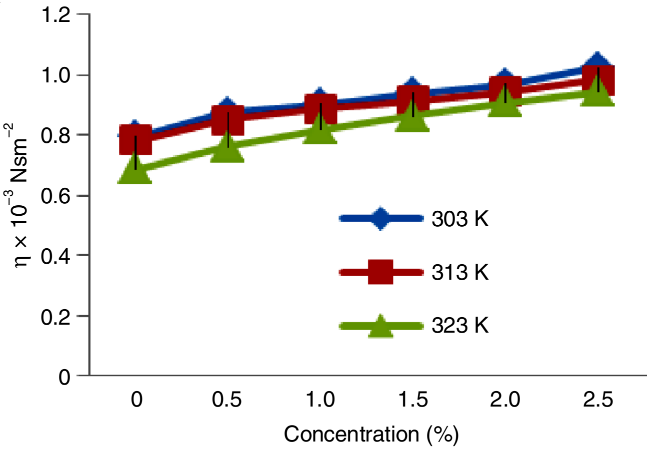

Fig. 2. Viscosity *vs.* concentration of aqueous HEPC solution at different temperatures

From Fig. 3, it is clear that the adiabatic compressibility found to be decreased with the increase of concentration and temperatures. The adiabatic compressibility with the compressibility of the solvent molecules concerned in the solvation and decrease in the intermolecular free length indicates that the solvent molecule forms an incompressible sheath around the polymer chain. In the present case, intermolecular free length decreases linearly with increasing velocity, concentration and temperature [12]. The variations of an absorption coefficient, free volume and solvation number are shown in Figs. 4-6. From Fig. 4, as the temperature is increased the ultrasonic absorption coefficient also increased at higher concentrations. The beha-

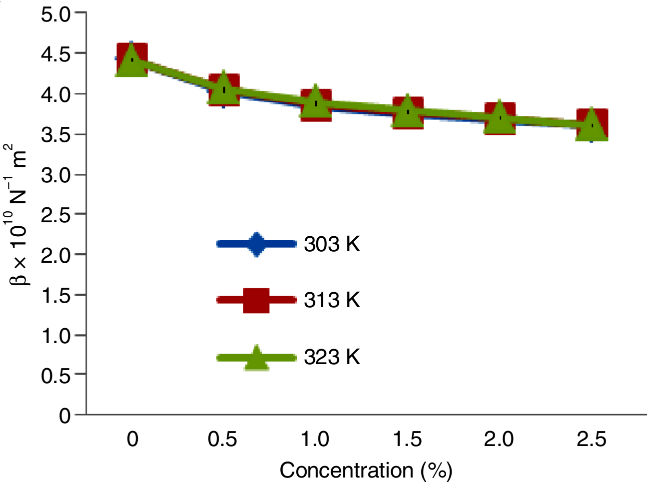

Fig. 3. Adiabatic compressibility *vs.* concentration of aqueous HEPC solution at different temperatures

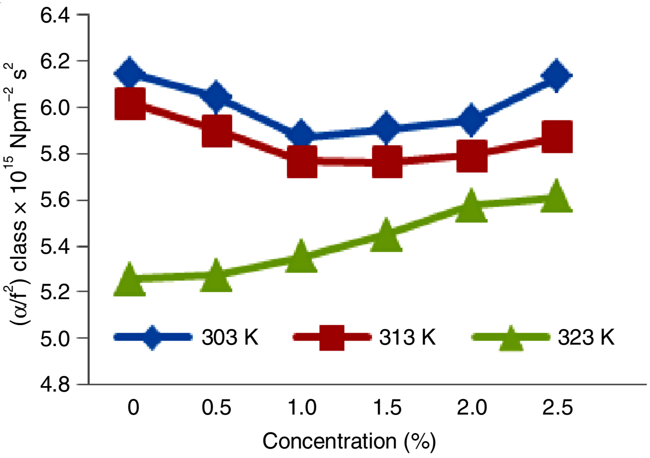

Fig. 4. Absorption coefficient *vs.* concentration of aqueous HEPC solution at different temperatures

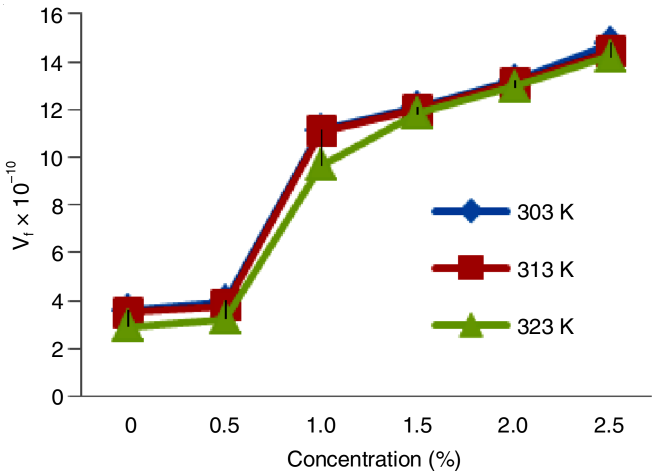

Fig. 5. Free volume *vs.* concentration of aqueous HEPC solution at different temperatures

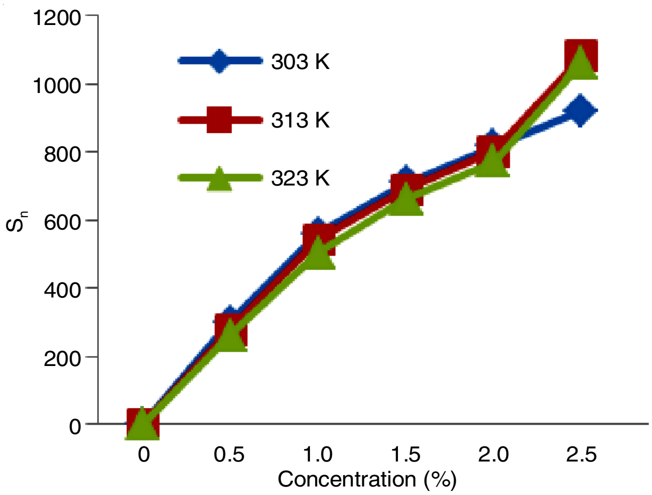

Fig. 6. Solvation number *vs.* concentration of aqueous HEPC solution at different temperatures

viour is the result of an increase in vibrational heat capacity of the solution with an increase in temperature leading to an increase in the value of absorption [13]. Thereby reducing the hydrodynamic volume may increase in internal pressure.

Free volume is the average volume in which center of the molecule can move due to the repulsion of the surrounding molecules. The volume increases with an increase in concentration as shown in Fig. 5. The decrease in molecular association causes an increase in the free volume [14]. The increase in free volume is attributed to losing the packing of the molecules inside the shield. Acoustic impedance [Z_a], increases with increasing concentration and non-linear variation of Rao's constant (R) with concentration predicts strong intermolecular interaction [13].

From Fig. 6 solvation number (S_n) increases with solute concentration, because the solutes may have two lone pairs for the interaction with the solvent molecules. The increase of S_n with solute concentration is more powerful than solute-solvent interaction in some systems. The positive values of S_n confirm an increase in cohesive force, it again supports the structure forming tendency of solute [12].

Effect of pH on aqueous hydroxy ethyl propyl cellulose (HEPC): Velocity is the most often measured parameter in the solution of polymeric materials. The properties of any polymeric solution are affected by environmental changes such as pH, concentration and temperature. In the present study, the effect of pH on the aqueous solution of HEPC is carried out at the lowest concentration *i.e.* 0.2% in the pH range from 4 to 11. The velocity and viscosity values are found to be very low in the lower pH (acidic) and then increases remarkably when compared with neutral pH as shown in Figs. 7 and 8.

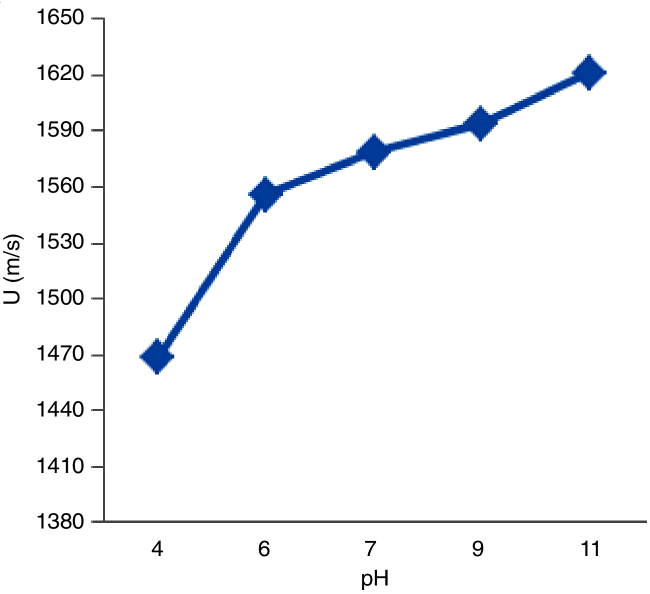

Fig. 7. Ultrasonic velocity *vs.* different pH value of aqueous HEPC at 0.2% concentration at 303 K

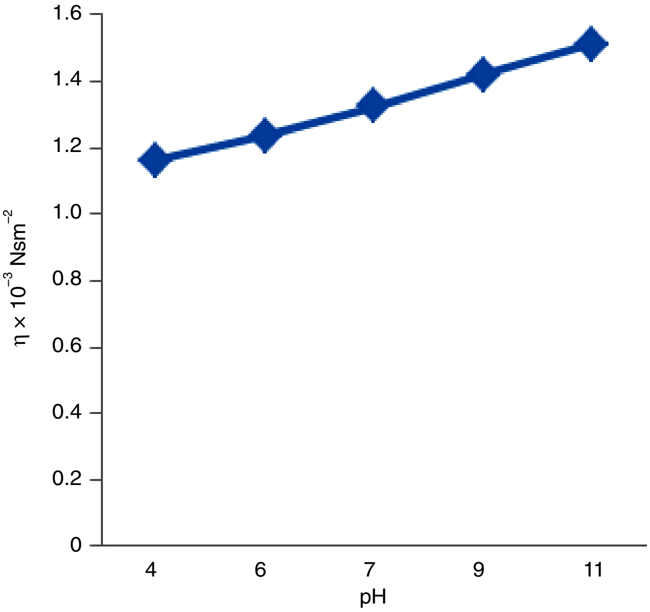

Fig. 8. Viscosity *vs.* different pH value of aqueous HEPC at 0.2% concentration at 303 K

The reduction in viscosity at lower pH is mainly due to the more coiling nature of HEPC when ionic strength is increased. In the case of basic pH, the HEPC molecules are relatively extended. It causes a decrease in adiabatic compressibility (Fig. 9) and an increase in velocity and viscosity at higher pH values [15]. Adiabatic compressibility (β) and intermolecular free length (L_f) are found to vary in a reverse manner as that of velocity. The absorption coefficient (α/f^2) also decreases as one moves from neutral pH to the acidic side and it is increased when pH is raised to the basic side as shown in Fig. 10. From Fig. 11, free volume increases with an increase in pH indicating the association through hydrogen bonding.

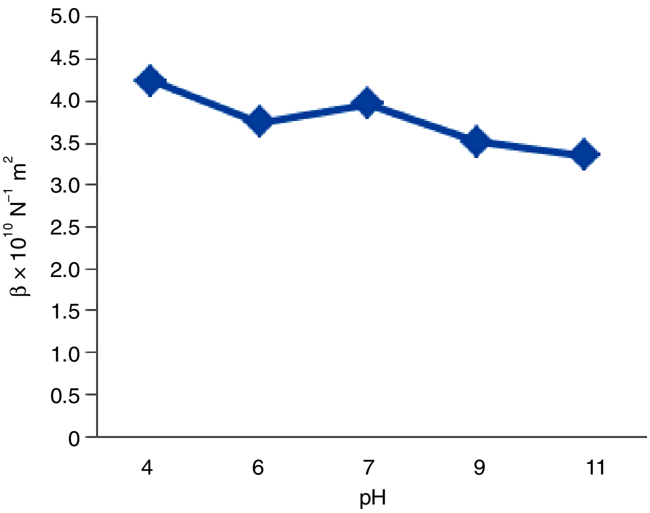

Fig. 9. Adiabatic compressibility *vs.* different pH values aqueous HEPC at 0.2% concentration at 303 K

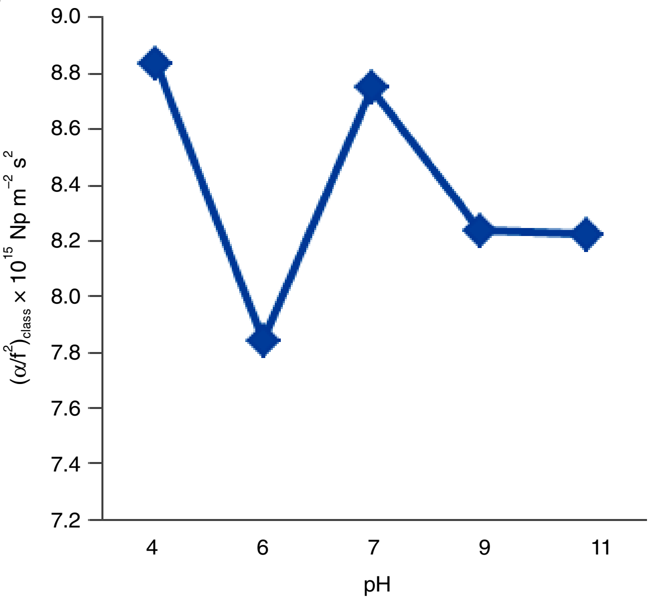

Fig. 10. Absorption coefficient *vs.* different pH value ofaqueous HEPC at 0.2% concentration at 303 K

Fig. 12 shows that the solvation number is increasing with an increase of pH because the pH solution may have two lone pairs for the interaction with the solvent molecules. From the above discussion, it is confirmed that the increase in the value of acidic pH to the base side enhances the property of gel formation of HEPC molecules even at low concentrations.

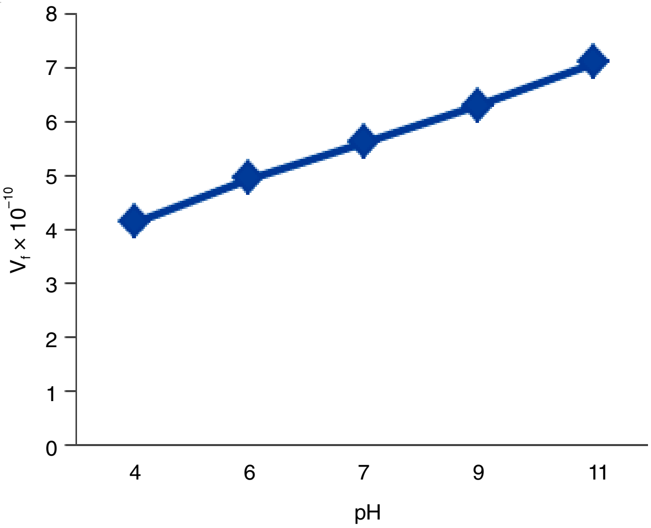

Fig. 11. Free volume *vs.* pH value of aqueous HEPC at 0.2% concentration at 303 K

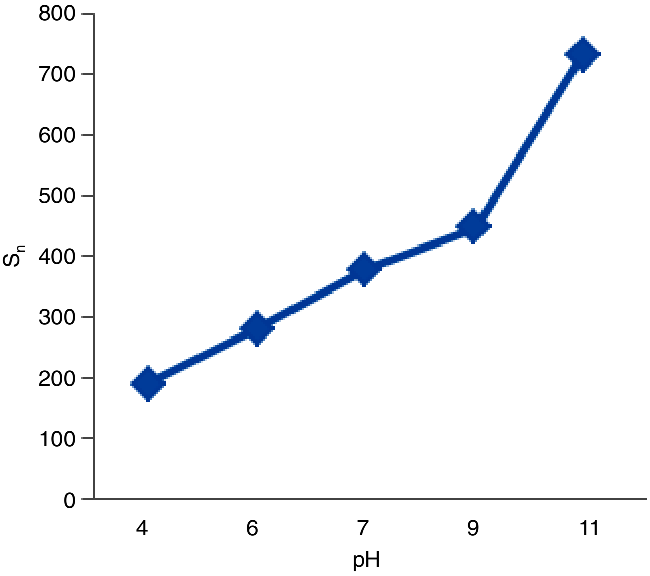

Fig. 12. Solvation number *vs.* pH value of aqueous HEPC at 0.2% concentration at 303 K

Conclusion

From the above findings, it is concluded that the molecular association between the polymer-water molecules arising from intermolecular hydrogen bonding and the variation of acoustical parameters with concentration and temperatures strongly supports the molecular association occurring in these systems.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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