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Study of Thermodynamical Properties of Aqueous Polyvinyl Pyrrolidone (PVP) Solution

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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 solutions. In the present study, the ultrasonic velocity, density, viscosity measurements have been made in polyvinyl pyrrolidone solution using pulse echo technique at temperature range 288K- 308K at the different concentrations (wt.%) of PVP in water. Thermo- acoustical parameters viz., adiabatic compressibility (βa), acoustic impedance (z), relaxation time (τ), free length (L_f), isothermal compressibility (β_i), volume expansivity (a), Moelwyn-Hughes parameter (C_1) and internal pressure have been computed from the experimental data. The nature of polymer solvent interaction and the effect of concentration on the molecular interaction are studied. The nonlinear variations of polyvinyl pyrrolidone in water have been studied. The variation of ultrasonic velocity and other thermo-acoustical parameters shows linear increase or decrease with concentration (wt.%) which suggest compatibility of the polymer in the given solvent.

KEYWORDS : Acoustical parameters; polyvinyl pyrrolidone (PVP); pulse echo technique, etc.

INTRODUCTION

Propagation of ultrasonic waves in polymer solution forms the basis of qualitative characterization. Acoustical studies in polymers solutions and in solid polymers have been the subject of research in recent years. Recently, Pandey[1], Jayakumar[2-4], Kalyansundaram [5–8] have carried out pioneering work on polymer solution using ultrasonic technique. Ultrasonic is the universally accepted technique to study the physico- 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 sysetm[9]. Being fast, nondestructive and versatile, ultrasonic technique is useful for testing structure property relationship of macromolecules. Polyvinyl pyrrolidone (PVP) having molecular formula $(C_6H_9NO)_n$ and used as binders for the formulation of pharmaceutical tablets, for moistening various personal care products, as food additives and adhesives, etc. It is readily soluble in water, physiologically compatible, non-toxic, essentially chemically inert, temperature-resistant, pH-stable, non-ionic, and colorless. This remarkable combination of properties predestined its use in numerous applications in medicine, pharmaceutical technology, cosmetics and in the technical industry. Even as early as 1939, PVP was used as a plasma expander and was widely used in this form during World War II[10]. During the 1950s, PVP replaced the schellac hitherto used in hair sprays. This article, however, deals with the applications of PVP in the pharmaceutical industry.

Ultrasonic Measurements

Velocity measurement

The ultrasonic velocity measurements were carried out using highly versatile accurate pulse echo technique by using MHF-400 High frequency pulser- receiver supplied by Roop Telsonic Ultrasonic Limited, Mumbai- (India). The frequency of the pulses is kept at 1MHz, 2MHz and 5MHz. The accuracy in the measurement of velocity is about $\pm$ 0.1 m/sec.

Density Measurement

The density of the solutions was determined using pycnometer method with an accuracy of $\pm$0.1mg/cm^3.

Viscosity measurement

The viscosity of liquid was measured by using Oswald's viscometer.

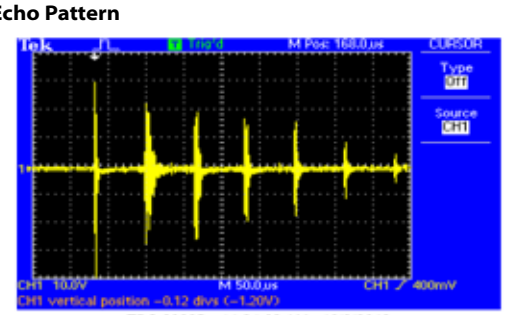
Temperature measurement

Temperature is maintain at 288K, 293K, 298K, 303K and 308K using Plasto Crafts Thermostat (accuracy $\pm$0.1^{0}C).The experimental set up and observed wave pattern for calculating acoustical parameters are shown in the images below. The measured ultrasonic velocity, density, viscosity and various other parameters were calculated by using the standard formulae listed below [9-10].

Formulae

1. Adiabatic compressibility $\beta_a = \frac{1}{u^2\rho}$,
   where u is ultrasonic velocity and ρ is density of given solution.
2. Acoustic Impedance $Z = \rho . u$
3. Relaxation Time $\tau = \frac{4}{3}\eta . \beta_a$
   where η is viscosity
4. Free Length
   $L_f = K_j \beta_a^{1/2}$ *Where, K_j - Jacobson's constant*
5. Isothermal compressibility $\beta_i = \gamma \beta_a$
6. Volume Expansivity
   $\alpha = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)$ *Where, T- temperature*
7. Moelwyn-Hughes parameter
   $C_1 = [{}^{13}/_{3} + (\alpha T)^{-1} + {}^{4}/_{3}\,\alpha T]$
8. Internal Pressure
   $P_i = \frac{\alpha T}{\beta_i}$

Echo Pattern



Results and discussion

The values of βa, Z, τ, Lf, α, C1, Pi were calculated using equation (1)-(8). Figures (1 – 10) shows the plots of experimental velocity (u), density (ρ), viscosity (η) and the calculated values of all the above acoustical parameters at different concentrations (wt.%) for polymer solution of polyvinyl pyrrolidone with water at temperature range 288K-308K and 2MHz frequency.

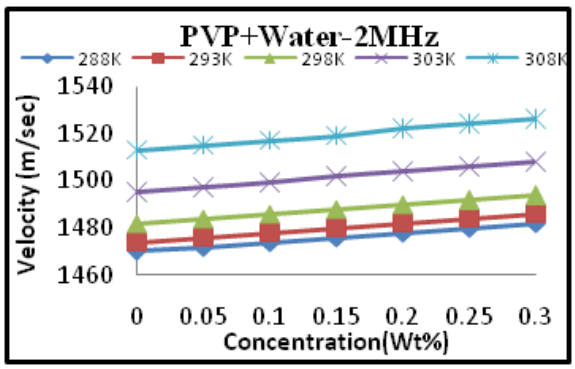


Figure 1

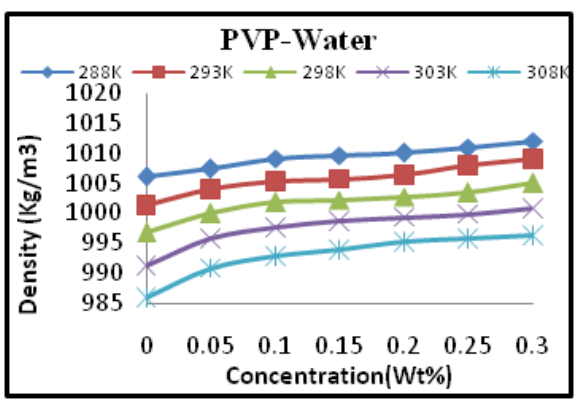


Figure 2

The variation of u with concentration (wt.%) as shown in figure 1. It is observed that variation of u is linearly increasing with increase in concentration (wt. %) indicates the association in the component molecules. This also suggests that disruption of water structure is enhanced further with the addition of PVP in water[11]. The increment in velocity with concentration implies a decrement in the compressibility. This behavior suggests the formation of a more rigid structure, possible due to polymer-water bonding at sites on the polymer's carbonyl (C=O) group. In polyvinyl pyrrolidone oxygen atom contains lone pair to the electron act as nucleophile and provides a lone pair to the electron deficient β- carbonation of polyvinyl pyrrolidone and the constituent molecule gets associated. The association in the constituent molecules may involve due to hydrogen bonding or due to dipole-dipole interaction between the constituent molecules. All these process may lead to strong interaction forces.

At higher temperature ultrasonic velocity is high and at lower temperature ultrasonic velocity is low indicates the strong association between solute and solvent. As the temperature increases, more and more bonds are broken or the bonds are elongated which results in dilation of polymer chains. As the temperature increases, hydrogen bonds in solvent break, more and more monomers occupy the vacant space and increase the cohesion among the molecules, thereby increasing the ultrasonic velocity. There is a tendency for breaking the complex at higher temperature in the synthetic polymer[11]. Carbon atom (C) in polyvinyl pyrrolidone can form double bond with oxygen atom of carbonyl (C=O) group.

Figure (2) shows the plot of density versus concentration (wt.%). It is observed that density increases with increase in concentration of polyvinyl pyrrolidone (PVP) in water, increase in density decreases the volume indicating association in component molecules. This increase in density is due to the fact that the number of polymer chain added to the solution increases with increase in concentration (wt. %) of polymer solution. Polymers are characterized by large molecular weight compared to the solvents. This also contributes to increase in the density of the solution[12].

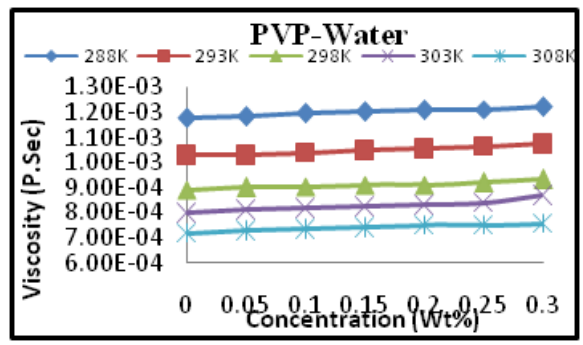


Figure 3

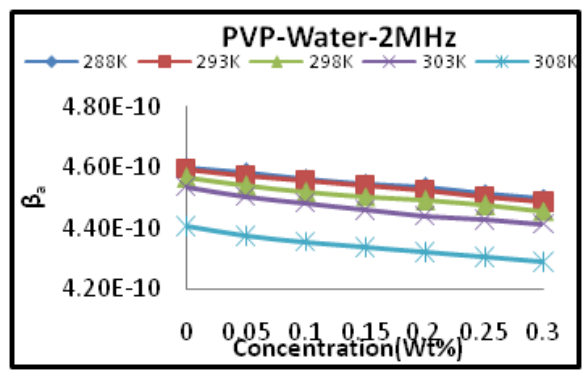


Figure 4

Figure (3) consists the plot of viscosity (η) versus concentration (wt. %). It is observed that viscosity linearly increases with increase in concentration (wt. %) of polyvinyl pyrrolidone (PVP) in water. According to Kauzman and Eyring[13], the viscosity of a mixture strongly depends on the entropy of mixture, which is related with the liquid structure as well as molecular interactions between the components of the mixtures. Thus the viscosity depends upon the molecular interaction as well as on the shape and size of the molecules.

Increasing the pressure on an object decreases the volume of the object and therefore increases its density (ρ), increasing the temperature of the substance decreases its density (ρ) and viscosity (η). Decrease in density (ρ) and viscosity (η) with increase in temperature indicated decrease in cohesive forces. The increasing temperature has two opposite effects namely increase of molecular interactions (structure formation) and destruction of structure formed previously as a result of thermal fluctuation. Thus, increase of temperature favors increase of kinetic energy and volume expansion and hence decrease of density (ρ) and viscosity (η), while it increases intermolecular distance (free length)[14].

The carbonyl group of PVP attract strongly or electrostatically[14] surrounding the water molecules. As a result, the electrostricted water is much less compressible than bulk water and leads to a large decrease in compressibility of aqueous solution. Adiabatic compressibility (β_a), and free length (L_f) decreases with concentration of PVP in water which indicates the enhancement of degree of association among the liquid molecules. Intermolecular distance decreases with increase in concentration due to large cohesive forces. Figure (4) and (5) shows the plot of adiabatic compressibility and free length. Adiabatic compressibility and Isothermal compressibility shows less value at higher temperature while free length shows high value at higher temperature in aqueous polyvinyl pyrrolidone solution. Because increase of temperature favors increase in kinetic energy and volume expansion and hence it increases the free length[14].

Figure (5) and (6) shows the plot of free length and acoustic impedance with concentration (wt%) of polyvinyl pyrrolidone (PVP) in water

at 2MHz frequency.

Acoustic impedance (z) is found to be almost reciprocal of adiabatic compressibility. It is observed that, the variation of acoustic impedance and ultrasonic velocity is almost same. Values of acoustic impedance increases with increase in concentration (wt. %). It is in good agreement with the theoretical requirements because ultrasonic velocity increases with increase in concentration. The increase in acoustic impedance (z) with concentration(wt. %) can be explained on the basis of intermolecular interaction between component molecules, which decreases the intermolecular distance, making relative fewer gaps between the component molecules. This also indicates significant interactions in this liquid system.

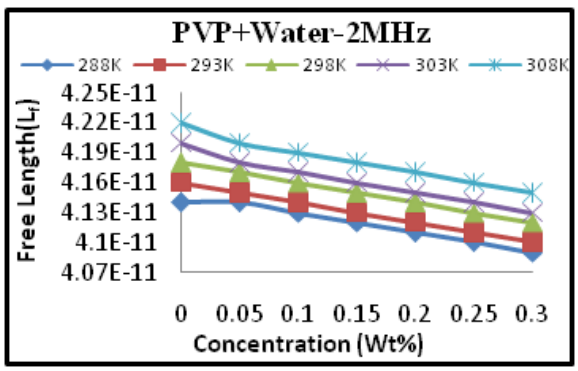


Figure 5

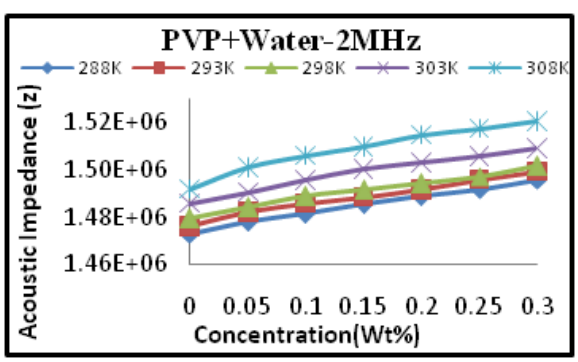


Figure 6

Figure (7) contains the plot of relaxation time (τ) versus concentration (wt. %). It is observed that relaxation time slightly increases with increase in the concentration of polyvinyl pyrrolidone in water indicating high stability of polyvinyl pyrrolidone molecules. Polyvinyl pyrrolidone (PVP) is a highly polar & biocompatible[14]polymer having compact structure and hence molecules are not stable which increases the relaxation time. The relaxation can be caused by the energy transfer between translational and vibrational degrees of freedom and all these degrees take part in the observed process. Its behavior depends on viscosity and adiabatic compressibility of the liquid solution. In this system viscosity plays very important role for increasing relaxation time with increase in concentration (wt. %).

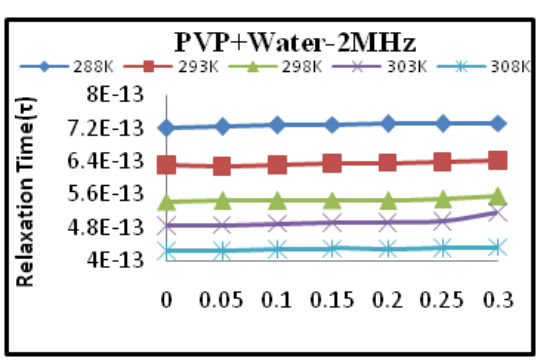


Figure 7

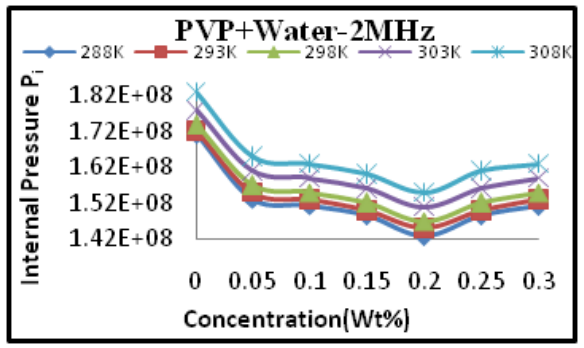


Figure 8

The internal pressure is the resultant of attractive and repulsive forces between the molecules. It measures the molecular cohesion and the instantaneous volume derivatives of cohesive energy associated with an isothermal expansion of the solution. The internal pressure of hydrogen bonded liquids such as water is large as compared to non-hydrogen bonded liquid. This study indicates that the internal pressure in solution could also be used for studying the molecular association through hydrogen bonding. Figure (8) shows nonlinear decrease of internal pressure with increase in concentration (wt. %) of PVP in water. From the non-linearity of internal pressure solute-solvent interactions have been confirmed[14].

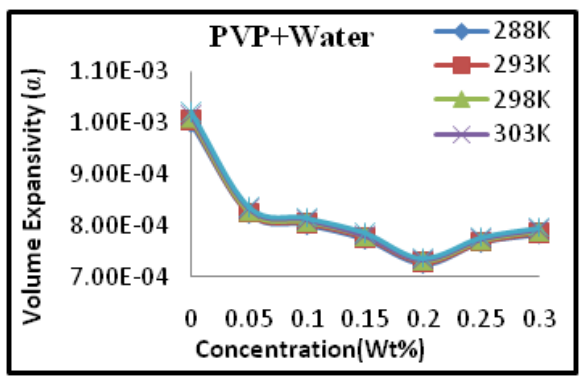


Figure 9

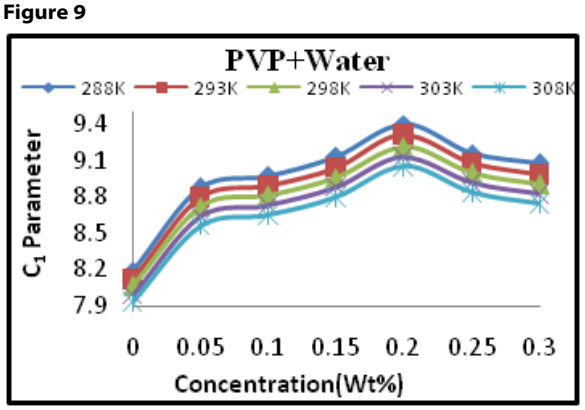


Figure 10

The small decrease in volume expansivity (α) at particular concentration (wt.%) shows weak orientation of the solvent (H_2O) molecules around the polymer ions, which may be due to the influence of the electrostatic field of ions. This means solution becomes less compressible. It indicates the weak associating tendency of the molecules in the polymer solutions.

The variation of C_1 and volume expansivity (α) shows the opposite behavior with increase of concentration (wt. %). If C_1 increases then α is found to be decrease with concentration (wt. %) and vice-versa. This may be due to associating tendency of the liquid molecules. Figure (9) and (10) contains the plot of volume expansivity (α) and Moelwyn-Hughes parameter (C_1) versus concentration (wt. %) respectively.

Conclusions

1. The linear variation in ultrasonic velocity with increasing concentration (wt.%) suggests the miscibility/compatibility of polyvinyl pyrrolidone in water. It enhance the ability of polyvinyl pyrrolidone to form a water-soluble complex within soluble active substances can be used in pharmaceuticals to improve the release rate and solubility of drugs.
2. Ultrasonic velocity measurement have been extensively applied for assess the molecular interactions in pure binary liquid mixture. It also determines the elasticity of the medium.
3. Thermo-acoustic parameters can be used to analyze a broad range of molecular processes.
4. Ultrasonic study of polymer is used to determine the intermolecular interactions and different types of forces exist in the medium.

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