A study on Thermodynamic, Acoustic and Elastic properties of aqueous solutions of Hydroxyethyl Cellulose

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Abstract. Hydroxyethyl cellulose is a thickening and gelling derived from cellulose. It is broadly used in household products, cosmetics and cleaning solutions. Hydroxyethyl cellulose is frequently used with hydrophobic drugs in capsule formulations, to improve the drugs dissolution in the gastrointestinal fluids. Ultrasonic technique is one of the basic non-destructive methods for evaluation of materials and structures. A significant part of every ultrasonic inspection is the way in which the ultrasonic energy is transferred between the transducer and the tested object. In the present investigation, we have tried to compute the activation energy, ultrasound investigations, elastic property (bulk modulus) and molecular interaction properties of aqueous solutions of Hydroxyethyl cellulose at different concentrations (0.05%, 0.10%, 0.15%, 0.20%, 0.25%, 0.30%, 0.35%, 0.40%, 0.45% and 5%) for different temperatures (303K, 308K, 313K, 318K) by determining the relative viscosity.

1. Introduction

Ultrasonic technique has been engaged as commendable tool for non-destructive testing and imaging. Although the relationship between material properties and acoustic parameters has been studied for a long period of time [1-5]. In the recent years, the usage of ultrasound sound waves are escalated, because of the advantage it offers to synthetic chemistry. This includes time consumption in reaction, saving energy, higher yield, milder conditions and higher purity of the product. For analyzing the molecular interaction properties, ultrasonic method has the added advantage of being less costly with efficiency comparable to other methods [6-8]. The molecular interaction parameters such as free volume, internal pressure, attenuation, compressibility, acoustic impedance and scattering provide us a clear picture of structural changes in cellulose derivative polymers and biological substances [9]. When ultrasound waves are propagated in polymeric materials, acoustic waves are influenced by the polymer structure and molecular relaxation process [10]. Activation energy is an important thermodynamic property and used to describe the minimum energy that must be available for initiating a chemical process. For analyzing the properties and interactions taking place in polymer-polymer systems, knowledge of rheological properties is essential and viscometry is one of the efficient techniques for studying the properties [11]. Most commonly, the elastic property of the polymer solution particles has been accessed using atomic force microscopy (AFM). In this approach, it is calculated by theoretical method. In the present investigation, we have tried to compute the activation energy of aqueous solutions of Hydroxyethyl cellulose at different concentrations (0.05%, 0.10%, 0.15%, 0.20%, 0.25%, 0.30%, 0.35%, 0.40%, 0.45% and 5%) for different temperatures (303K, 308K, 313K, 318K) by determining the relative viscosity and ultrasound velocity and density studies were taken for the above
concentrations at 303K for aqueous solutions of Hydroxyethyl cellulose. From these experimental values, the acoustical parameters such as adiabatic compressibility, intermolecular free length and internal pressure etc were calculated and effect of solute solvent interaction were analysed. From adiabatic compressibility values, the elastic property (bulk modulus) was calculated for the above concentrations. The important reason for choosing this material is it has variety of applications in household cleaning products, soaps, and shampoos and the detailed literatures showed that no measurements have been previously reported for the mixtures reported in this paper.

2. Experimental Details
The cellulose derived polymer Hydroxyethyl cellulose (HEC – SPECTRA Grade) was purchased from Sri Ganapathy Trading Company, Kanchipuram. The polymer HEC is dissolved in double distilled water and the polymer solutions are prepared for various concentrations (0.05%, 0.10%, 0.15%, 0.20%, 0.25%, 0.30%, 0.35%, 0.40%, 0.45% and 5%). A magnetic stirrer (REMI make) operating at a rate of 1000 rpm is used for preparing the polymer solutions. BROOKFIELD Viscometer (USA) is used to determine the relative viscosity of the prepared polymer solutions at different concentrations at 303K, 308K, 313K & 318K. The viscometer was connected to an electronically controlled thermostat having a thermal stability of ± 0.05K for taking measurements at different temperatures. Pyknometric method is employed to determine the density of the solutions. A K-ROY electronic balance having an accuracy of ±0.001gm is used to measure the mass of the liquid. A digital ultrasonic balance meter (VCT-70A model, VI MICROSYSTEMS) is used to measure the ultrasonic velocity. The measurements were taken at a frequency of 2 MHz (accuracy ± 0.1m/s). The ultrasound velocity measurements are taken at 303K by circulating water from a thermostat having a thermal stability of ± 0.05 K.

3. Results and Discussions
3.1. Determination of Activation Energy
Viscosity studies are performed for aqueous solutions of Hydroxyethyl cellulose for different concentrations at different temperatures as mentioned above. Fig. 1 shows the variation of relative viscosity against concentration for aqueous solutions of Hydroxyethyl cellulose at different temperatures.

In this system, the relative viscosity shows a non-linear variation with increase in concentration and temperature. The nonlinear variation of viscosity with concentration of HEC indicates presence of intermolecular interaction within the system. The decreasing trend of viscosity indicates that water is a
poor solvent for HEC. Arrhenius expression is valid for pure solvents and also for dilute polymer solutions. According to Venkatramanan et al. [12],

\[ \eta = A e^{Q/kT} \]

Where \( Q \) is the apparent activation energy of flow and \( A \) is the pre-exponential term with an activation entropy significance.

The logarithm of this equation leads to a straight-line type given by

\[ \ln \eta = \ln A + \left( \frac{Q}{R} \right) \frac{1}{T} \]

The graph is drawn between \( \ln \eta \) against \( 1/T \). The slope of these straight lines gives the value for activation energy. The variation of activation energy (\( Q \)) with concentration (\( C \)) of aqueous solutions of HEC is shown in Fig. 2.

In this system, it is observed that there is a sudden decrease in the activation energy for 0.2% and 0.35% concentration. In most cases, activation energy for the viscous flow of polymer solution increases continuously with increasing polymer concentration, except in particular cases of critical mixtures [13]. The reason being the activation energy for the viscous flow of polymer solutions in poor solvent decreases with polymer concentration at high dilution and this is ascribed to the temperature dependence of the limiting viscosity number [14, 15].

The experimentally observed values of density and ultrasonic velocity of the above systems are presented in Table 1. It is observed that the density and ultrasonic velocity values are non-linear. The pronounced increase or decrease in these parameters with composition of mixtures indicates the presence of interactions between the components of molecules [16].

### Table 1. Values of density and ultrasonic velocity of aqueous solutions of HEC

| Concentration (w/v) | Density (kg/m³) | Ultrasonic Velocity (m/s) |
|---------------------|-----------------|----------------------------|
| 0.05                | 995.6609        | 1493.675                   |
| 0.10                | 995.8627        | 1493.762                   |
| 0.15                | 995.9636        | 1493.159                   |
| 0.20                | 996.3673        | 1494.364                   |
| 0.25                | 996.0645        | 1493.762                   |
| 0.30                | 996.8718        | 1494.967                   |
| 0.35                | 996.2663        | 1494.967                   |
| 0.40                | 996.5691        | 1494.967                   |
| 0.45                | 996.7709        | 1493.762                   |
| 0.50                | 997.1745        | 1494.967                   |

### 3.2. Determination of Molecular Interaction Parameters

Normally a decrease in adiabatic compressibility indicates closed packing and decreased ionic repulsion. The variation of adiabatic compressibility for aqueous solutions of HEC with concentration is shown [Fig. 3]. It is observed that there is a non-linear variation with increase in concentration of HEC. The actual deviation depends on the resultant effect. The observed decrease or increase in adiabatic compressibility with composition is an evidence of significant interaction between the component molecules in the binary mixtures. This shows the complex formation and molecular dissociation. It also indicates weakening of hydrogen bond at this molar concentration [17]. Intermolecular free length shows a similar behavior as reflected by adiabatic compressibility. Free length varies nonlinearly with increasing concentration of HEC at lower concentration which suggests that there is a significant interaction between solute and solvent molecules due to which structural arrangement is also affected [Fig. 4]. Free volume refers to the void space between the molecules, i.e., the volume present as holes because of irregular packing of the molecules. It may be defined as the average volume in which the central molecule can move inside the hypothetical cell freely without
affected by the repulsion of surrounding molecules. The free volume plot follows reverse trend of viscosity. Therefore viscosity rather than velocity determines the free volume of our system. The free volume reduces when the internal pressure increases [6]. In the present case, free volume for aqueous solutions of HEC is maximum at 0.05% and minimum at 0.50% [Fig. 5] and this variation is found to be nonlinear. The reverse trend of free volume with internal pressure is clearly shown in Fig.5.

Figure 3. Variation of Adiabatic compressibility against concentration of aqueous solutions of HEC

Figure 4. Variation of Intermolecular free length against concentration of aqueous solutions of HEC

The internal pressure of a liquid reflects the molecular interaction. Internal pressure studies show a nonlinear variation with increase in concentration of HEC and thus it is the evidence for the existence of significant interaction between the solvent – polymer molecules. Internal pressure shows dip at 0.25% concentration, whereas the free volume shows peak at corresponding concentration. This shows the complex formation and molecular dissociation. It also indicates weakening of hydrogen bond at this molar concentration. In the present study the classical absorption coefficient has been calculated for Aqueous HEC at different concentrations of 0.05%, 0.10%, 0.15%, 0.20%, 0.25%, 0.30%, 0.35%, 0.40%, 0.45% and 0.50% at 303 K and it is shown in Fig 6. A non-linear variation is observed. The values of viscous relaxation time, specific acoustical impedance, relative association, Rao’s constant and Wada’s constant are reported in Table 2.

Figure 5. Variation of Free volume and Internal pressure against concentration of aqueous solutions of HEC

Figure 6. Variation of Classical absorption co-efficient against concentration of aqueous solutions of HEC
Table 2. Values of Molecular Interaction Parameters

| Concentration (w/v) | Specific Acoustical Impedance (x 10^6 kg m^-2 s^-1) | Relaxation Time (x 10^-12 sec) | Relative Association | Rao’s Constant (X 10^-4 [m^3mol^-1][ms^-1]^-1/3) | Wada’s Constant (X 10^2 m^3 mol^-1 [Nm^-2]^-1/7) |
|---------------------|-----------------------------------------------------|--------------------------------|----------------------|-------------------------------------------------|-------------------------------------------------|
| 0.05                | 1.4871                                              | 0.6482                         | 0.9996              | 2.0168                                          | 3.8817                                          |
| 0.10                | 1.4875                                              | 0.7080                         | 0.9999              | 2.0164                                          | 3.8826                                          |
| 0.15                | 1.4871                                              | 0.7986                         | 1.0001              | 2.0160                                          | 3.8826                                          |
| 0.20                | 1.4889                                              | 1.2764                         | 1.0002              | 2.0157                                          | 3.8853                                          |
| 0.25                | 1.4878                                              | 0.7618                         | 1.0001              | 2.0160                                          | 3.8835                                          |
| 0.30                | 1.4902                                              | 1.1310                         | 1.0006              | 2.0149                                          | 3.8880                                          |
| 0.35                | 1.4893                                              | 1.2335                         | 1.0000              | 2.0162                                          | 3.8853                                          |
| 0.40                | 1.4889                                              | 1.2751                         | 1.0003              | 2.0156                                          | 3.8866                                          |
| 0.45                | 1.4889                                              | 1.5286                         | 1.0008              | 2.0146                                          | 3.8866                                          |
| 0.50                | 1.4907                                              | 2.0700                         | 1.0009              | 2.0143                                          | 3.8893                                          |

Figure 7. Variation of Bulk modulus against concentration of aqueous solutions of HEC

The relaxation time depends upon the size and shape of the rotating molecular entities in the solution. From Table 2, it is observed that the viscous relaxation time shows non-linear variation with increase in concentration throughout the system. This nonlinear variation with increase in concentration is due to the existence of significant molecular interaction between the solute and solvent molecules [18]. Specific acoustic impedance is defined as impedance offered to the sound wave by the components of mixture. Mathematically it is directly proportional to ultrasonic velocity and inversely proportional to adiabatic compressibility. The non-linear decrease of impedance with concentration shows that the
molecular interaction of aqueous solutions of HEC is dissociative [17]. Relative association is influenced by two factors (i) breaking up of the associated solvent molecules on addition of solute and (ii) the solvation of solute molecules. The former leads to decrease and latter leads to increase in relative association. In the present system, the Relative Association is minimum at 0.05% concentration and maximum at 0.50% concentration. Rao’s constant and Wada’s constant also show a non-linear variation with increase in concentration.

3.3 Determination of Bulk modulus

The variation of bulk modulus with different concentration of HEC in binary mixture with water at room temperature is plotted in Fig. 7, which shows the non-linear variation with increase in concentration of HEC. Bulk modulus determines how compressible a fluid is. In other words, it tells us how the density of a liquid changes when the liquid is subjected to pressure. Higher the values of Bulk modulus indicate that it is difficult to compress the fluid [19].

4. Conclusion

The nonlinear variation of ultrasonic velocity and other thermo acoustical parameters with increase in concentration of HEC in water provides useful information about the nature of intermolecular forces existing in the mixture. The observed complex formation in the binary liquid mixture may be due to the formation of hydrogen bonding and the tendency of solute-solvent interaction. This complex formation is very much important in solid pesticides in water-based sprays for agriculture formulations.

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