Ultrasonic Investigation of Dipole- Dipole Interaction in Binary Solution of Cellulose Acetate + Water

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Abstract: Dipole- Dipole interactions have been studied in the binary solution of cellulose acetate and water by ultrasonic velocity (u), density (ρ) and viscosity (η) measurements at temperature range 288K- 308K and at concentration range 0.05- 0.3 (wt.%) at three different frequencies 1MHz, 2MHz & 5MHz respectively. All these measurements were carried out using ultrasonic pulse echo technique. Acoustical parameters such as adiabatic compressibility (β), isothermal compressibility, acoustic impedance (Z), intermolecular free length (Lf), relaxation time (τ), internal pressure (Pi), volume expansivity (α), Moelwyn Hughes parameter (C1) etc. were calculated using experimental data. The ultrasonic investigations on present binary polymer system reveals that in the polymer mixture containing both polar liquids, there exist weak dipole-dipole interactions. The strength of this type of intermolecular interaction depends on the interacting molecules present in the aqueous solution of cellulose acetate.

Keywords: Cellulose acetate, dipole- dipole interaction, pulse echo technique, Velocity.

1. Introduction

Forces of attraction due to dipole- dipole interaction is strong and optical method is used to detect and access such type of interactions. Literature survey shows that very few study have been done on the dipole-dipole interactions in the binary liquid mixtures. Hence, an attempt have been made to measure the ultrasonic velocity, density and viscosity in order to access the strong molecular interaction existing between the molecules of the components in the liquid binary solution.

The present paper deals with the ultrasonic studies of polymer solution of cellulose acetate with distilled water as a function of increasing concentration (wt.%) at different temperatures and frequencies. Cellulose acetate is a very valuable manufactured fiber that is low in cost and has good draping qualities. Water soluble cellulose acetate is a versatile polymer used for film coating material for tablets. Aspirin (ASA) tablets were prepared by direct compression and coated with either WSCA or HPMC (hydroxypropyl methylcellulose) dispersions. The nature and strength of cellulose acetate with water interaction is determined by the interacting molecules. In cellulose acetate some of hydroxyl (OH) group have been replaced by acetyl (-CO-CH3) group. Water is polar solvent; hence the nature of the forces responsible for the observed homomolecular interactions in the binary solution of polymer cellulose acetate with water is dipole- dipole type.

2. Experimental Study

The cellulose acetate solution was prepared by adding a known weight of cellulose acetate to a fixed volume of distilled water then stirring until clear solution were obtain. The concentration range chosen in the solution are 0, 0.05 wt%, 0.1 wt%, 0.15wt%, 0.2wt%, 0.25 wt% & 0.3%. The ultrasonic velocity, density and viscosity measurements are carried out by pulse echo technique using MHF-400 pulser receiver at frequencies 1MHz, 2MHz and 5MHz and at temperature range 288K- 308K. The density and viscosity were measured by pycnometer method and Oswald’s viscometer respectively. Thermostatically controlled water circulation system Plasto Craft thermostat LTB-10 is used to maintain the temperature at 293K with an accuracy of ± 0.1°C. By using experimental data on ultrasonic velocity, density, viscosity and various acoustical parameters are calculated according to standard relationship given below:

FORMULAE
1. Density ρ = \frac{M_l}{M_w} \rho_w
Where M_l- mass of experimental liquid, M_w- mass of water & \rho_w- density of water
2. Viscosity η = \frac{\rho_k \eta_k}{\rho_w \eta_w}
3. Adiabatic compressibility β_a = \frac{1}{u^2 ρ}
4. Relaxation Time τ = \frac{4}{3} η β_a
5. Acoustic Impedance Z = ρ u
6. Free Length L_f = K_j β_a^{3/2} Where, K_j - Jacobson’s constant
7. Volume Expansivity α = -\frac{1}{ρ} \left(\frac{\partial ρ}{\partial T}\right) Where, T- temperature
8. Moelwyn-Hughes parameter C_1 = \left[\frac{13}{3} + (αT)^{-1} + \frac{4}{3} αT\right]

3. Results and Discussion

Below graph shows the plot of ultrasonic velocity (u) and adiabatic compressibility (β_a) versus concentration (wt.%). It is observed that ultrasonic velocity increases with increase in concentration (wt.%) of cellulose acetate (CA) in water.
This behavior is due to interaction between cellulose acetate and solvent (water) molecules.

This also suggests that disruption of water structure is enhanced further with the addition of cellulose acetate in water. 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 polymers acetate \((-\text{C}=\text{O}) \text{CH}_3\) group. The association in the constituent molecules may involve due to hydrogen bonding between the constituent molecules. All these process may lead to strong interaction forces. Ultrasonic velocity increases with increase in temperatures. It may be due to disruption of cellulose acetate structure is increased with the addition of water in cellulose acetate. It indicates the strong association between solute and solvent.

The adiabatic compressibility reduces due to formation of molecular aggregates. It is also observed from the plot that there is a gradual decrease of adiabatic compressibility with increase in temperature, which is due to strengthening of intermolecular forces with the supply of heat energy.

Above graph shows the plots of density and viscosity versus concentration (wt. %). It is observed that density increases with increase in concentration of cellulose acetate (CA) in water. This is obvious due to the fact that the number of polymer chain added to the solution increases with increase in cellulose acetate concentration. Polymers are characterized by the large molecular weight compared to the solvents. This also contributes to the increase in the density of the solution. The density-temperature dependence shows the density decreases with increase in temperature of the cellulose acetate in water. This variation is attributed to the dilation effect. As the temperature increases more and more bonds are broken or bonds are elongated which result in the dilation of the polymer chain. This density – temperature variation can be used to evaluate the volume expansivity, \(\alpha\) as

\[
\alpha = -\frac{1}{\rho} \frac{\partial \rho}{\partial T}
\]

It is observed that viscosity linearly increases with increase in concentration (wt. %) and decreases with increase in temperature of cellulose acetate (CA) in water. It suggests the formation of a more rigid structure with increase in cellulose acetate concentration. 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.
Above graph shows the variation of acoustic impedance (Z) and relaxation time (τ) with concentration (wt.%) of cellulose acetate with water. The acoustic impedance (Z) with concentration is attributed to increase of ultrasonic velocity with concentration (wt.%). Z shows increase with increase in temperature due to increase in ultrasonic velocity with increase in temperature. This kind of behavior is due to association of molecules and formation of molecular aggregates\textsuperscript{10}. The increase in acoustic impedance (Z) with concentration also 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.

It is observed that relaxation time slightly increases with increase in the concentration of cellulose acetate in water indicating high stability of cellulose acetate molecules. Motion of acetate side groups on the cellulose acetate polymer chain may also contribute to relaxation processes. In this case energy exchange can occur between the wave and vibrational and rotational energy associated with motion of the chain side groups. The relaxation time (τ) varies with concentration of the cellulose acetate in the solution. The relaxation time increases with increase in concentration at temperature range 288K-308K. This may be interpreted in terms of increase in intermolecular forces due to increase in concentration and subsequent increase in relaxation of the molecules. The decrease in relaxation time with temperature is due to supply of thermal energy\textsuperscript{10}.

Free length shows same variation as that of (β\textsubscript{a}) and (β\textsubscript{i}) but free length (L\textsubscript{f}) increases with increase in temperature. 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)\textsuperscript{11}.

The small decrease in volume expansivity (α) at particular concentration shows weak orientation of the solvent (H\textsubscript{2}O) 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\textsuperscript{11}. (α) and C\textsubscript{1} parameter shows opposite behavior as shown in above graph.

4. Conclusions

1) Water soluble cellulose acetate is a versatile polymer used for film coating material for tablets.
2) Density and viscosity measurement are important for clarification of ion-solvent, ion-ion and solvent- solvent interactions in mixed solvent systems.
3) The linear nature of ultrasonic velocity suggests miscibility of polymers indicated by single phase formation and thus suggesting compatibility of the polymers.
4) Thermo-acoustic parameters such as ultrasonic velocity, density, viscosity, adiabatic compressibility, acoustic impedance, relaxation time, free length, etc indicates the strength of molecular interactions in the binary liquid mixtures of polymer.

References