

Ultrasonic Investigation of Dipole- Induced Interactions in Binary Solutions of Cellulose Acetate with Cyclohexanone and Carbontetrachloride (CCl₄)

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Abstract—Dipole- induced dipole interactions has been studied in the polymer binary system of cellulose acetate with carbon tetrachloride and cyclohexanone by ultrasonic velocity (u), density (ρ) and viscosity (η) at five different temperatures (288K to 308K) and at different concentrations (wt.%). Acoustical parameters such as adiabatic compressibility (β_a), Acoustic impedance (Z), Relaxation time (τ), intermolecular free length (L_f), Internal pressure (P_i) and available volume (f) were calculated from the experimental data. The ultrasonic investigations on two binary polymer systems reveal that in the polymer mixture containing polar and nonpolar liquids, there exist weak dipole-induced dipole interactions. The strength of this type of intermolecular interaction depends on the interacting molecules present in the mixture of cellulose acetate with carbon tetrachloride and cyclohexanone.

Index terms – Dipole- induced dipole interactions, Ultrasonic parameters, Cellulose acetate, cyclohexanone, carbontetrachloride, etc.

I. INTRODUCTION

Ultrasonic studies in polymer solutions have been the subject of research in recent years [1-7]. Recently many workers have carried out pioneering work on polymer solution using ultrasonic technique. An acoustical study provides a useful technique to understanding the physico-chemical properties of the interacting components in polymer solution. The different acoustical parameters interpret the nature and strength of molecular interaction that exist in the system. The present paper deals with the ultrasonic studies of polymer solution of cellulose acetate in carbon tetrachloride and cyclohexanone 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 (hydroxyl propyl methylcellulose) dispersions. The nature and strength of cellulose acetate –cyclohexanone and carbon tetrachloride interaction is determined by the interacting molecules. In cellulose acetate some of hydroxyl (OH) group have been replaced by acetyl (-C=O) CH₃) group^[8]. Cyclohexanone and carbon tetrachloride are nonpolar

solvents, hence the nature of the forces responsible for the observed heteromolecular interactions in the binary mixture of polymer cellulose acetate + cyclohexanone and cellulose acetate + carbon tetrachloride are dipole- induced dipole type.

II. MATERIALS AND METHODS

The cellulose acetate solution was prepared by adding a known weight of cellulose acetate to a fixed volume of carbon tetrachloride and cyclohexanone 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 $\pm 0.1^\circ\text{C}$. By using experimental data on ultrasonic velocity, density, viscosity and various acoustical parameters are calculated according to standard relationship given below:

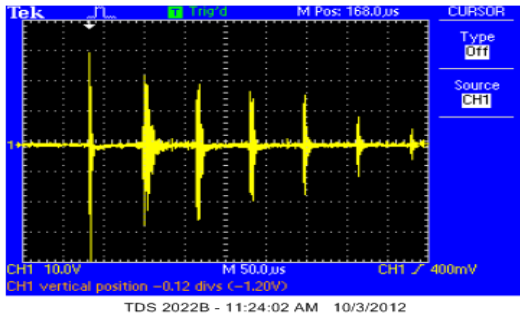
1. Density $\rho = \frac{M_i}{M_w} \rho_w$
2. Viscosity $\eta = \frac{\rho_i t_i}{\rho_w t_w} \eta_w$
3. Adiabatic compressibility $\beta_a = \frac{1}{u^2 \rho}$
4. Relaxation Time $\tau = \frac{4}{3} \eta \cdot \beta_a$
5. Acoustic Impedance $Z = \rho \cdot u$
6. Free Length $L_f = K_j \beta_a^{1/2}$ Where,
 K_j - Jacobson's constant
7. Internal Pressure $P_i = \frac{\alpha T}{\beta_i}$

Where α is volume expansivity
 T- Temperature
 β_i - Isothermal compressibility

8. Available volume

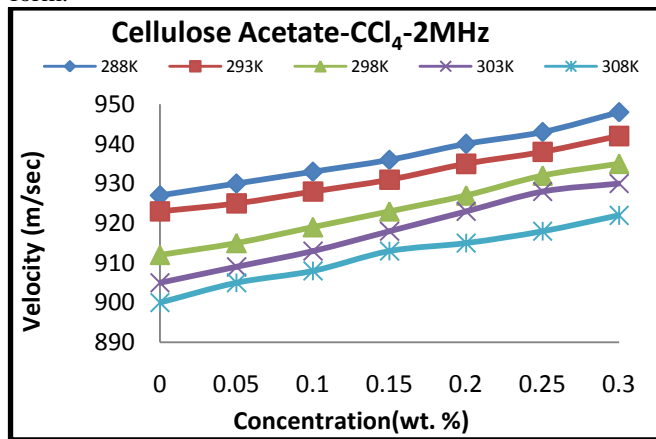
$$f' = 2(J_x + 2)^{-1}$$

ECHO PATTERN

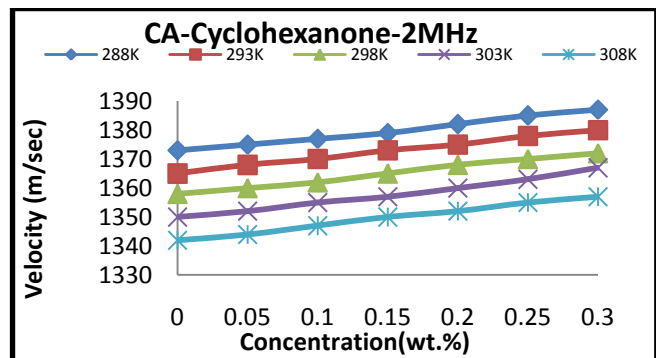


III RESULTS AND DISCUSSION

The various thermo-acoustic parameters such as ultrasonic velocity (u), density (ρ), viscosity (η), adiabatic compressibility (β_a) acoustic impedance (z), relaxation time(τ), intermolecular free length (L_f), Internal pressure (P_i) and available volume (f') at concentrations (X) in weight % of cellulose acetate with carbon tetrachloride and cyclohexanone at frequency 2MHz and at temperatures 288K, 293K, 298K, 303K & 308K are presented in graphical form.

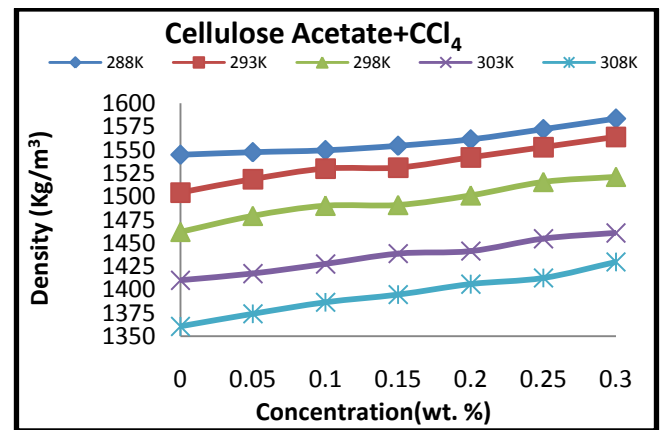


Graph 1

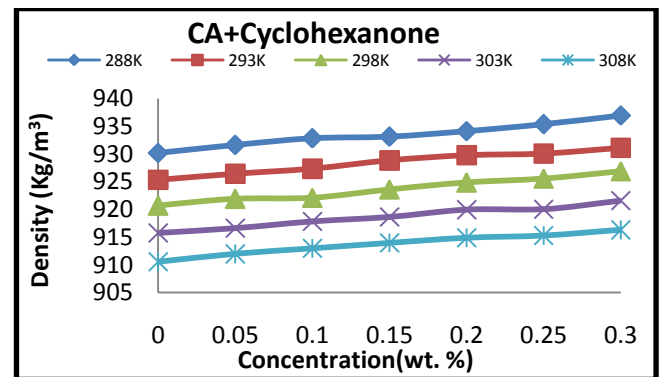


Graph 2

Graph (1) and (2) shows the variation of ultrasonic velocity (u), versus concentration (wt. %). It is observed that ultrasonic velocity increases with increase in concentration (wt.%) of cellulose acetate (CA) in carbon tetrachloride and cyclohexanone. This behavior is due to dipole- induced dipole interactions between cellulose acetate and solvent (carbon tetrachloride and cyclohexanone) molecules^[9]. The large molecular weight of cellulose acetate is also responsible for slow variation of ultrasonic velocity (u). Moreover, the chains of cellulose acetate are stiff and more extended in the solution. It is observed that ultrasonic velocity of cellulose acetate decreases with increase in temperature at all frequencies in both carbon tetrachloride and cyclohexanone. As the concentration (wt.%) increases along with the chain entanglements, the ultrasonic velocity does not vary much with increase in temperature. With increase in temperature, few chains are broken and monomers occupy the space thereby decreasing the ultrasonic velocity. It may be due to disruption of cellulose acetate structure is increased with the addition of carbon tetrachloride (CCl₄) and cyclohexanone respectively.



Graph 3

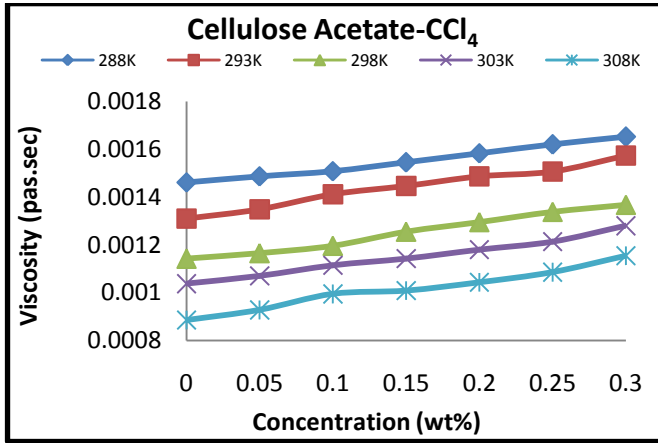


Graph 4

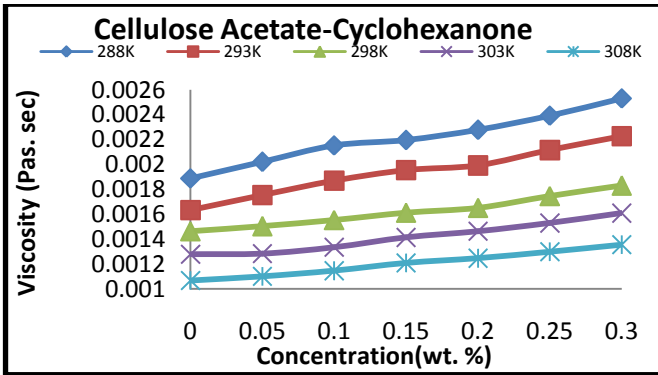
Graph (3) and (4) shows the plot of density with concentration (wt. %) of cellulose acetate in cyclohexanone and carbon tetrachloride (CCl₄) respectively. It is observed that density increases with increase in concentration (wt.%) of cellulose acetate (CA) in respective solvents. This is obvious due to the fact that the number of polymer chain added to the solution

increases with increase in cellulose acetate concentration. The density-temperature dependence shows the density decreases with increase in temperature of the cellulose acetate in carbon tetrachloride and cyclohexanone. This variation is attributed to the dilation effect. This density – temperature variation can be used to evaluate the volume expansivity^[10], α as

$$\alpha = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)$$

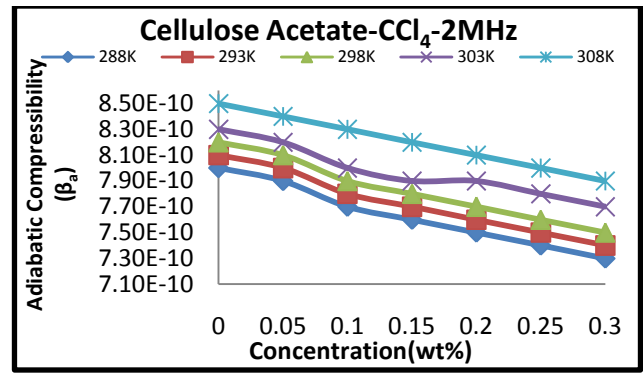


Graph 5

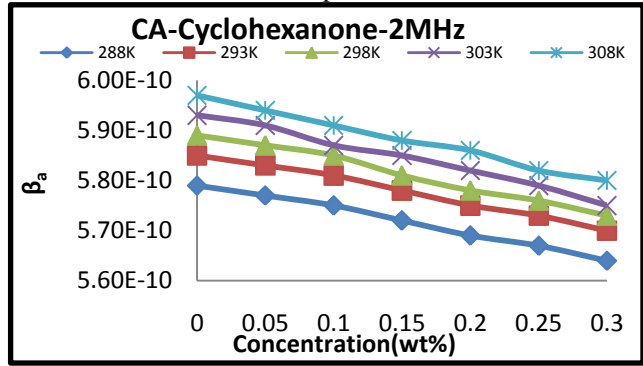


Graph 6

Graph (5) and (6) consists of the plot of viscosity (η) versus concentration (wt. %) of cellulose acetate in carbon tetrachloride and cyclohexanone. It is observed that viscosity linearly increases with increase in concentration (wt. %) and decreases with increase in temperature of cellulose acetate (CA) in both the solvents. It suggests the formation of a more rigid structure with increase in cellulose acetate concentration (wt%). 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.

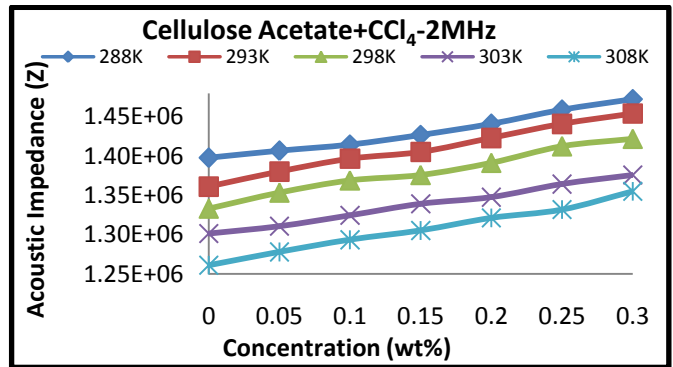


Graph 7

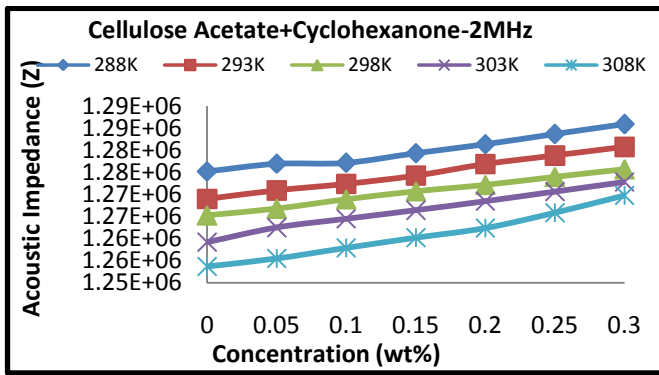


Graph 8

Graph (7) and (8) consists of the plot of adiabatic compressibility (β_a) versus concentration (wt%) of cellulose acetate in carbon tetrachloride (CCl_4) and cyclohexanone respectively. It shows linear decrease with increase in concentration of cellulose acetate with both the solvents. The adiabatic compressibility reduces due to formation of molecular aggregates. It is also observed from the plot that there is a gradual increase of adiabatic compressibility with increase in temperature, which is due to weakening of intermolecular forces with the supply of heat energy^[11]. Free length shows same variation as that of (β_a) but it is decreases with increase in temperature. In cellulose acetate + carbon tetrachloride and in cellulose acetate +cyclohexanone systems, there is very small reduction in adiabatic compressibility. This may be due to dipole- induced dipole interactions in both the systems.



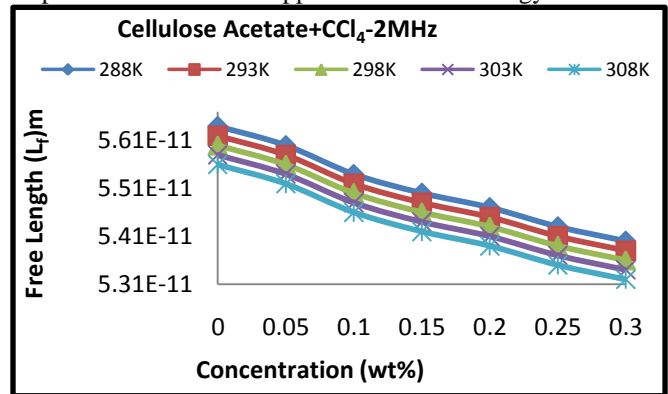
Graph 9



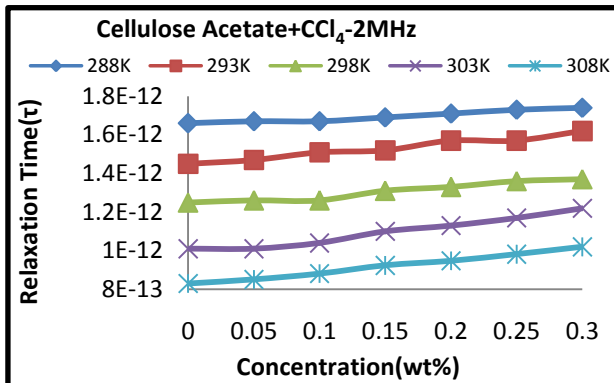
Graph 10

Graph (9) and (10) consists of the plot of acoustic impedance (Z) versus concentration (wt. %) of cellulose acetate in carbon tetrachloride and cyclohexanone. The acoustic impedance (Z) with concentration is attributed to increase of ultrasonic velocity with concentration (wt.%)^[11]. It shows decrease with increase in temperature due to decrease in ultrasonic velocity with increase in temperature in both the system. This kind of behavior is due to association of molecules and formation of molecular aggregates^[12]. The increase in acoustic impedance (Z) with concentration also can be explained on the basis of dipole-induced dipole interaction present between component molecules, which decreases the intermolecular distance, making relative fewer gaps between the component molecules. This also indicates significant interactions in these liquid systems.

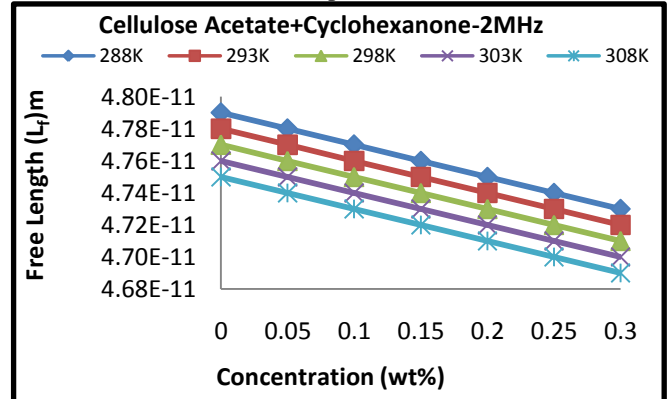
Variation of relaxation time (τ) versus concentration (wt%) shown in graph 11 and 12 for both the systems. It is observed that relaxation time slightly increases with increase in the concentration (wt%) of cellulose acetate in carbon tetrachloride and cyclohexanone, indicating high stability of cellulose acetate molecules in respective solvents. 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 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 unsupplied of thermal energy.



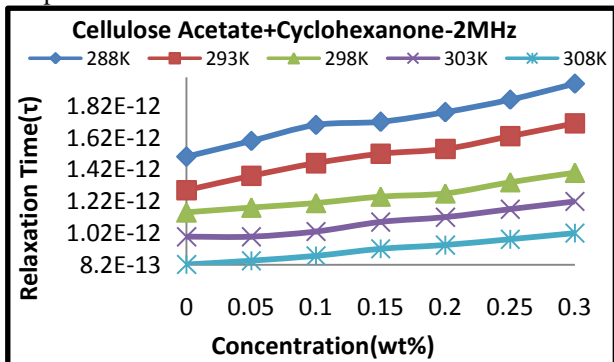
Graph 13



Graph 11

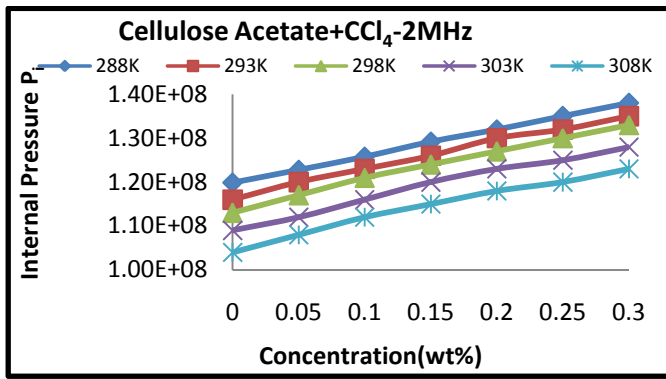


Graph 14

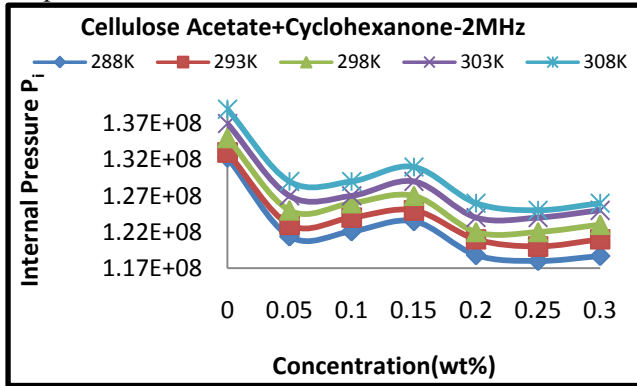


Graph 12

Linear variation of free length with concentration (wt%) of cellulose acetate in carbon tetrachloride and cyclohexanone solution shown in graph 13 & 14 respectively. It decreases linearly with increase in concentration of cellulose acetate solution indicates that the strong interactions, association and non-dominance of cellulose acetate in solvents, because there is no abrupt change in the variation at any concentration (wt%).

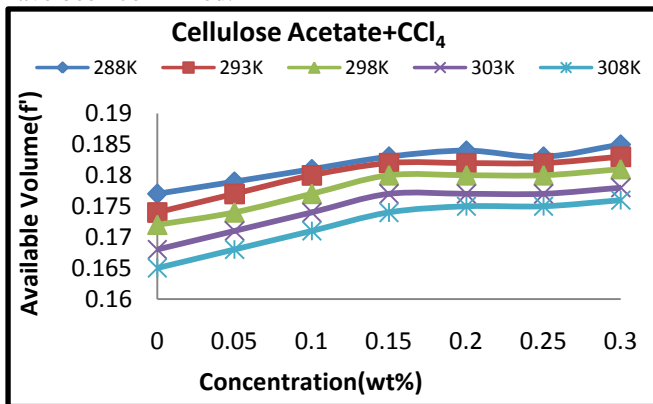


Graph 15

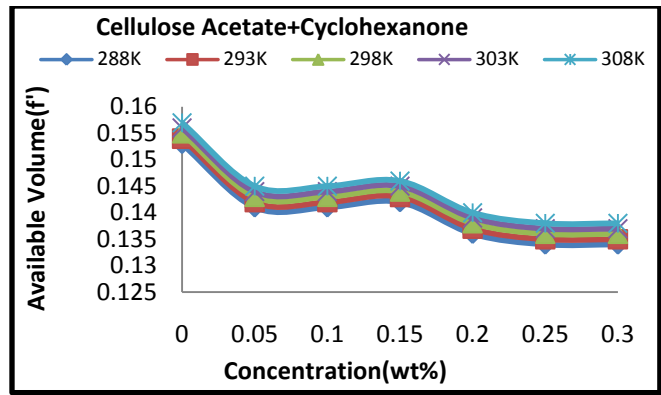


Graph 16

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. This study indicates that the internal pressure in solution could also be used for studying the molecular association through hydrogen bonding. Graph 15 and 16 shows nonlinear variation of internal pressure with increase in concentration (wt. %) of cellulose acetate in carbon tetrachloride and cyclohexanone respectively. From the non-linearity of internal pressure solute-solvent interactions have been confirmed.



Graph 17



Graph 18

Available volume (v_a) shows a nonlinear increase and decrease with concentration (wt%) of cellulose acetate with both the solvents respectively. The increased value f' with concentration (wt%) shows the enhancement in the liquids, because of the increased mobility of the molecules. If the available volume has a small value then fractional free volume would also have a small value. This shows the larger size of the molecules in liquid state^[13]

communicate directly with one another without using an Access Point (AP) or any connection to a wired network. The nodes are free to move randomly and organize themselves arbitrarily. Every node communicates via wireless radios that have limited transmission capabilities. Due to this constraint on transmission, not all nodes are within the transmission range of each other. If a node wishes to communicate with a node outside its transmission range, it needs the help of other nodes in constructing a multihop route. A key challenge in MANET is that communication has to be carried out with changing network topology due to node mobility.

VI. CONCLUSION

In this research work, following conclusions are drawn.

1. Cyclohexanone and carbon tetrachloride are nonpolar solvents, hence the nature of the forces responsible for the observed heteromolecular interactions in the binary mixture of polymer cellulose acetate + cyclohexanone and cellulose acetate + carbon tetrachloride are dipole- induced dipole type.
2. Thermo-acoustic parameters such as ultrasonic velocity, density, viscosity, adiabatic compressibility, acoustic impedance, relaxation time, free length, internal pressure, etc indicates the strength of molecular interactions are dipole- induced dipole type present in the binary liquid mixtures of cellulose acetate with cyclohexanone and carbon tetrachloride.
3. The linearity in given acoustic parameters indicates there is a single phase formation. It predicts strong polymer-solvent interaction and strong association in the cellulose acetate solutions.

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REFERENCES

- [1]. O.P. Chimankar, R. Shriwas, V. A. Tabhane, Pelagia Research Library, Advance in Applied Research., 2010, 1(3), 78-85.
- [2]. V. D. Bhandakkar, O. P. Chimankar and A. A. Mistry, Pelagia Research Library, Advance in Applied Research., 2011, 2(63), 70-76.
- [3]. V. D. Bhandakkar, G. R. Bedare, V. D. Muley and B. M. Suryavanshi, Pelagia Research Library, Advance in Applied Research., 2011, 2(4), 338-347.
- [4]. Kant Shashi, Kumar Sunil, Kumar Manish, Bharti Vikas, Pelagia Research Library, Der Chemica Sinica, 2012, 3(1), 166-174.
- [5]. Shashi Kant, Anuradha Kapil and Kamini Sharma, Pelagia Research Library, Der Chemica Sinica, 2012, 3(3), 667-676.
- [6]. Jayakumar, N. Karunanidhi & V. Kannappan, J. Pure Appl. Ultrason., 1998, 20, 79.
- [7]. Mallika S., K.M.E. Pia and S. Kalyansundaram, J. Pure Appl. Ultrason., 2008, 30, 54.
- [8]. Khangar Sugandha, "Ultrasonic and related studies in advanced organic polymer solutions", Ph.D Thesis submitted to RTM Nagpur university, (December 2013).
- [9]. S. RAJAGOPALAN and S. J. SHARMA; J. Pure Appl. Ultrason. 22 (2000) pp. 60-63.
- [10]. Nambinarayan T K and Shrinivasa Rao A, 1979, Curr.Sci, 48 203.
- [11]. S. Venkata Naidu, K. John and P. Veera Brahmam, International journal of polymer Anal. Charact., 9: 351-359, 2005.
- [12]. Johri, G.K. and R.C. Misra. (1985). Acoustica 57, 292.
- [13]. O. P. Chimankar, Ranjeeta S. Shriwas, Sangeeta Jajodia and V. A. Tabhane, Pelagia Research Library, Advance in Applied Research., 2011, 2(3), 500-508.

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