

Molecular interactions in solutions of poly vinyl alcohol : an ultrasonic study

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Abstract

Ultrasonic velocity, density, viscosity have been measured experimentally in the binary and ternary mixtures of Poly Vinyl Alcohol (PVA), water and borax with various concentration at 301.32 K. As the acoustical parameters like adiabatic compressibility, intermolecular free length, relaxation time, acoustic impedance, surface tension, Rao's and Wada's constant, ultrasonic attenuation and free volume would be more useful to predict and confirm the molecular interaction, these have been determined by using ultrasonic velocity, density and viscosity of the prepared solution. It has been identified that the molecular interactions in binary mixture were stronger than that of in ternary mixtures. And also there is a strong solute – solvent interaction occurring in both binary and ternary solutions. This may be due to the greater possibility of hydrogen bonding between PVA and Water molecules. When the borax is added, the molecular interaction is getting weaker due to greater affinity of borate ion towards the hydrogen in hydroxyl group of PVA.

Keywords: Binary Mixtures; Ternary Mixtures; Molecular Interactions; Ultrasonic Velocity; Inter Molecular Free Length; Acoustic Impedance.

1. Introduction

In recent years, the study of intermolecular interactions through ultrasonic investigations plays an imperative role in the growth of molecular sciences. Ultrasonic non destructive testing has been served as a realistic technique since it can be appropriate to study many of the aqueous, pure non-aqueous and mixed electrolytic solutions which may lead to new insights into the process of ion-ion and ion-solvent interactions (Bebek, 2005). The ultrasonic study of liquid mixtures have of greater significance in understanding intermolecular interactions between the component molecules as they can locate numerous applications in industrial and technological processes (Acharya et al., 2003; Ali and Abida, 2004). The study of propagation of ultrasonic waves in liquid systems is recognized as a simple and efficient tool in determining the nature of interactions between molecules in liquids and solutions. Nikam et al. (1994) have reported, the ultrasonic studies in binary liquid mixtures of nitrobenzene with several alcohols at 25 and 30% showed that strong dipole-dipole interactions are present in the liquid mixtures. The ultrasonic studies for the binary liquid mixtures of methyl benzoate and 1-octanol system at temperatures 303.15K, 308.15K, 313.15K and 318.15K, it is clear that there exists a strong intermolecular association between the component molecules of the liquid mixtures have reported (SrideviGutta, 2013). Also ultrasonic parameters are directly related to a number of thermodynamic properties. The deviation of ultrasonic sound velocity and several other thermodynamic properties of electrolytic solutions and binary and ternary mixtures with various concentrations has been investigated by many researchers (Oswet and

Patel, 1995; Awasthi and Shukla, 2003). Ravichandran et al. (2010) have reported, the acoustical properties and surface tension study of some potassium salts in polyacrylamide solution at 303K by ultrasonic investigations and concluded the concentration, nature of the solvent and nature of the solute play an important role in determining the interactions occurring in the solutions. Recently, ionic interactions and ion-solvent interactions for the mixtures have been reported from density and viscosity measurements (Kulshrestha and Verghese, 2007). The ultrasonic velocity, density, and viscosity have been measured for ternary mixtures of nitrobenzene, N,N-dimethylformamide, and cyclohexane at temperature $T = 318$ K at different frequencies such as 2, 4, 6, and 8 MHz (Manoj Kumar Praharaj, 2013). The acoustical parameters like adiabatic compressibility, intermolecular free-length, apparent molar compressibility, specific acoustic impedance, relative association and solvation number have been determined as they are functions of ultrasonic velocity (Ali and Nain, 1997). In many industrial applications, liquid mixtures rather than single component liquid system are used in processing units and product formulations. A deviation from linearity in the velocity in liquid mixtures is taken as an indication of the existence of interaction between the different species. During the last few decades, ultrasonic study of liquid mixtures has gained much more importance in assessing the nature of molecular interactions and investigating the physico-chemical behavior of such system (Pankaj and Singh Bhatt, 2010). Extensive ultrasonic velocity measurements have been carried out in a large number of binary liquid mixtures of polar and non-polar solvents (Sunanda et al., 2012; Tadkalkar et al., 2011). These studies have conclusively established the exist-

ence of association, dissociation, complex formation and hydrogen bonding between the molecules.

In present work an attempt has been made to understand the molecular interaction of (i) PVA with Borax and Water (Ternary Mixture) and (ii) PVA with Water (Binary Mixture). Hence it is planned to report the experimental studies of ultrasonic velocity, density and viscosity of both ternary and binary mixtures and the results of derived thermodynamic parameters like adiabatic compressibility, intermolecular free length, relaxation time, acoustic impedance, space filling factor, refractive index at 301.32 K. These derived thermodynamic parameters will be employed in understanding the nature of the molecular interactions in both ternary and binary mixtures.

2. Experimental details

2.1. Sample preparation for binary mixtures and ternary mixtures

The binary mixtures of samples labeled as system-1 have been prepared by changing the concentration of PVA only with fixed volume of pure distilled water say 100 ml. The binary mixtures have been prepared for the concentrations 0.25, 0.30, 0.35, 0.40, 0.45 and 0.50 gm/lit. The ternary mixtures of samples labeled as system-2, system-3, system-4, and system-5 have been prepared by changing the concentration of PVA only with fixed volume of pure distilled water say 100 ml. The mixtures have been prepared for the concentrations 0.25, 0.30, 0.35, 0.40, 0.45 and 0.50 gm/lit. For each system, the mixtures have been made up with the molality of 0.001, 0.002, 0.003 and 0.004 mol/lit of borax.

2.2. Ultrasonic velocity measurement

Ultrasonic velocity measurements were carried out at 1 MHz using interferometer (Mittal Enterprises) which is a direct and simple device for measuring of sound velocity in liquids. The ultrasonic velocity were measured for the different concentration of the mixed solution at 301.2 K.

2.3. Measurement of density and viscosity

For density measurements, the liquid mixtures were taken in a 10 ml gravity bottle (Borosil). The bottle was immersed in a water bath. In order to obtain a constant temperature, the specific gravity bottle was kept inside the water bath for about 30 minutes. Finally, the densities of the prepared binary and ternary liquid mixtures were measured by using the digital balance. The results of the densities are accurate to $\pm 0.5\%$. The density of water at temperature 301.32 K has been determined by Newton's interpolation statistical method. Viscosity measurement was also carried out for the solutions using Ostwald viscometer and specific gravity bottle of 10ml respectively at 301.32 K. Single pan macro balance with an accuracy of 0.001gm has been employed for mass measure-

ment. The viscosity of the liquid can be determined with the accuracy of $\pm 2\%$. The viscosity of water has been determined by Newton's interpolation statistical method.

2.4. Parameters computed

Parameters such as adiabatic compressibility (β_{ad}), acoustic impedance (Z), intermolecular free length (L_f), relaxation time (τ), relative association (R_A), surface tension (S), ultrasonic attenuation (α), Rao's constant (R), wada's constant (W) and free volume (V_F) have been computed.

3. Results and discussions

In the present study diverse acoustic parameters are measured and tabulated in table 1 at the temperature 301.32 K. These parameters play a major role in perceptive the nature of molecular interactions in liquids. These excess properties are mainly based on several physical and chemical contributions. The variations of ultrasonic velocity with different concentrations of both binary and ternary mixtures are shown in Fig 1. It is observed that the ultrasonic velocity varies non-linearly with concentration and a sudden decrease at a particular concentration. This indicates the presence of molecular interactions in both ternary and binary mixtures. The minimum value of ultrasonic velocity indicates weakening of the molecular association at these concentrations. The variations in density with increase in concentration are calculated. It is revealed that the density of both binary and ternary mixtures increases with the increase of mole concentration due to the presence of ions or particles (Rajagopalan and Sharma, 2002).

Table 1: Systems and Mixtures

System	Mixture
1	Poly Vinyl Alcohol + Water
2	Poly Vinyl Alcohol + Borax (0.1 mol) + Water
3	Poly Vinyl Alcohol + Borax (0.2 mol) + Water
4	Poly Vinyl Alcohol + Borax (0.3 mol) + Water
5	Poly Vinyl Alcohol + Borax (0.4 mol) + Water

Also, the adiabatic compressibility values can be used to ascertain the molecular interaction in the solution. In the present systems, the adiabatic compressibility values decrease with the increase in concentration of PVA (Nain, 2007) has shown in Fig. 2. The lower values of adiabatic compressibility reveal that the medium is tightly packed. When the mole value of borax is increased, compressibility decreases. This indicates the formation of bonding or liking between borate ion (formed from borax) and PVA. As expected, the adiabatic compressibility decreases with increase in concentration of borax in PVA-Water mixtures and it may be due to a large portion of solvent molecules being electrostricted and the amount of bulk solvent decreasing.

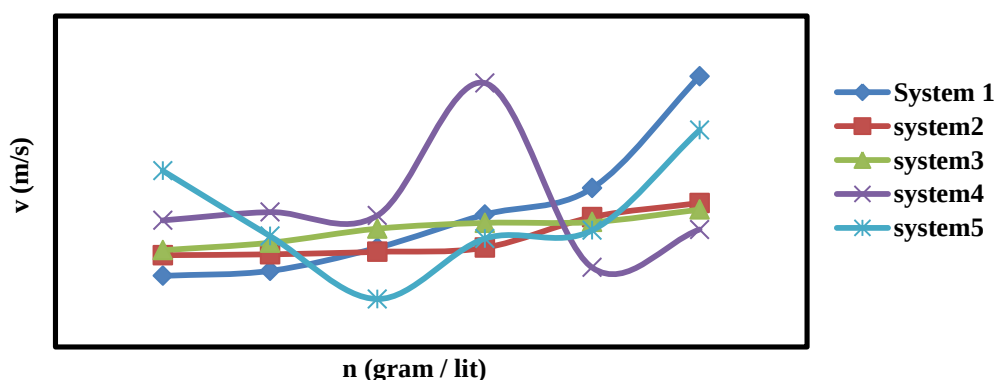


Fig. 1: Variation of Ultrasonic Velocity with Concentration of PVA.

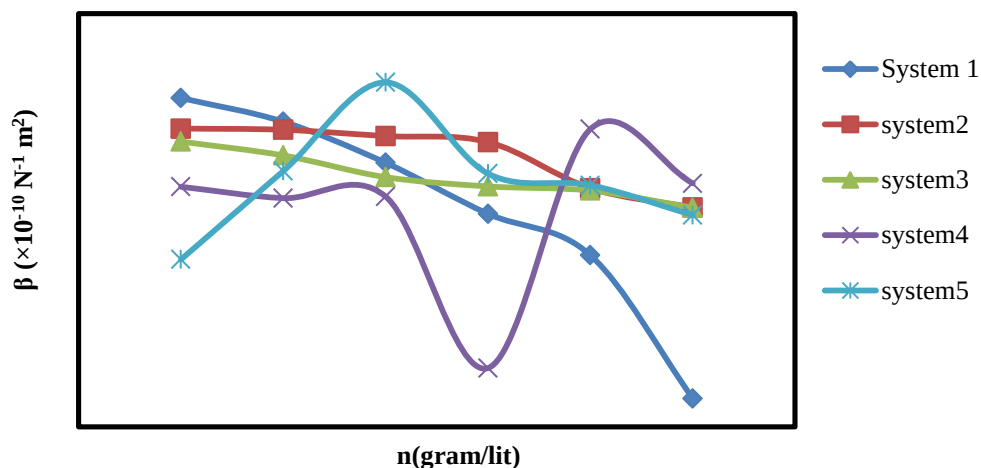


Fig. 2: Variation of Adiabatic Compressibility with Concentration of PVA

The variation of acoustic impedance of both binary and ternary mixtures with various concentrations has shown in Fig.3. It is clearly seen that, the value of acoustic impedance increases with the increase in the concentration in binary mixture. It is interesting to observe that in the case of ternary mixtures it varies non linearly. This is in agreement with the observed values of both ultrasonic velocity and density of both binary and ternary mixtures as they increase with increase in the concentration of solute. The increase in Z values with solute concentration is attributed to the effective solute-solvent interactions (Ali et al., 2006). The variation of relaxation time with concentration of PVA has shown in Fig.4. It is evident from the Fig.4 that the relaxation time increases with in-

crease in the concentration of a binary mixture. In the case of ternary mixtures it varies nonlinearly. From the Fig. 5, it has been observed that the intermolecular free length decreases nonlinearly on increasing the mole value of borax in PVA-Water mixtures. This indicates the significant interaction between solute and solvent molecules suggesting a structure promoting behavior on the addition of electrolyte (Awasthi and Shukla, 2003). The variation of relative association with various concentrations has shown in Fig. 6. It is clearly seen that it shows a random variation with increase in concentration of both the mixtures.

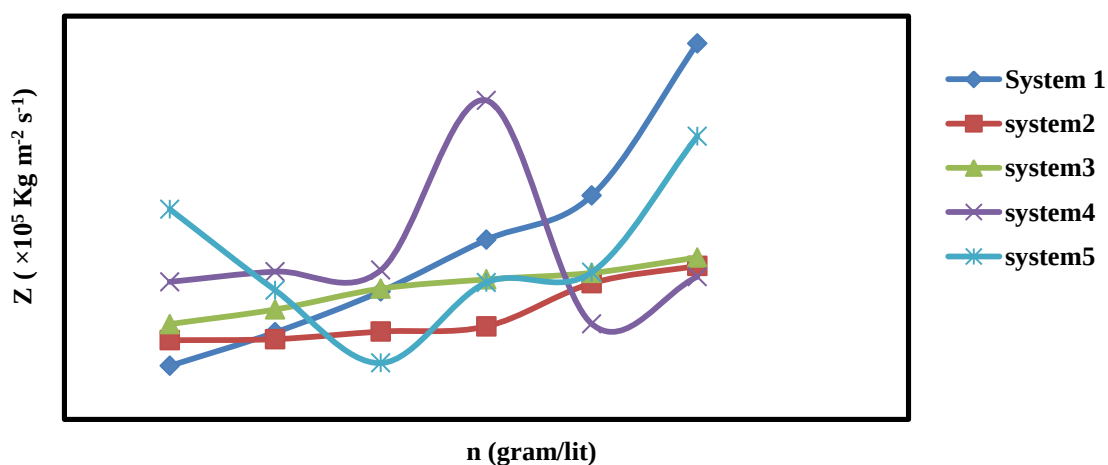


Fig. 3: Variation of Acoustic Impedance with the Concentration of PVA.

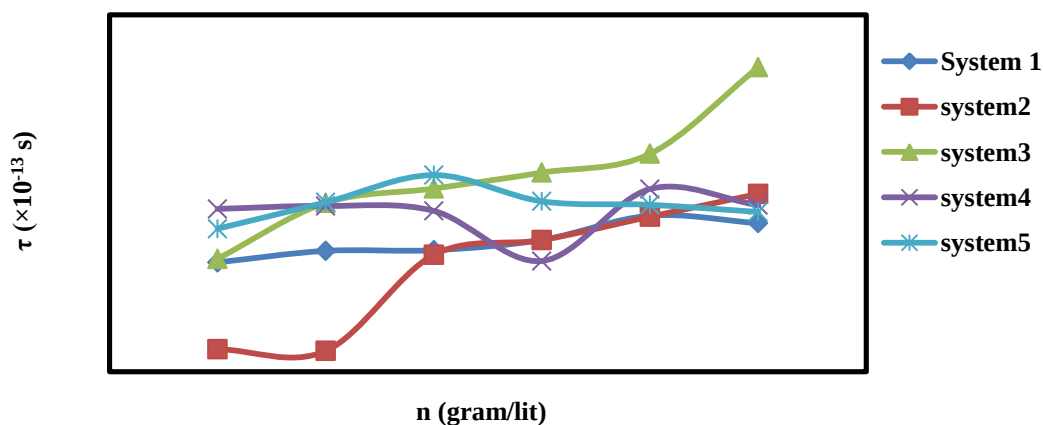


Fig. 4: Variation of Relaxation Time with Concentration of PVA.

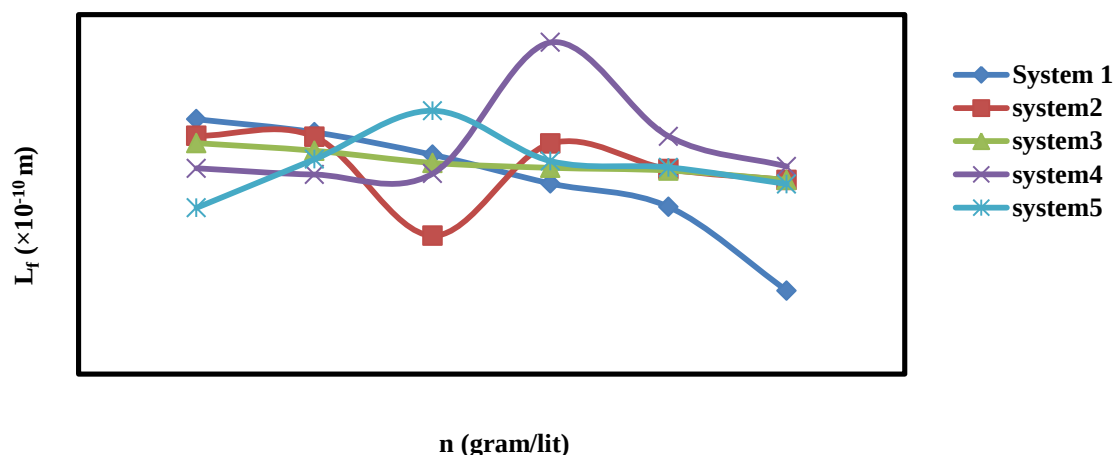


Fig. 5: Variation of Intermolecular Free Length with the Concentration of PVA.

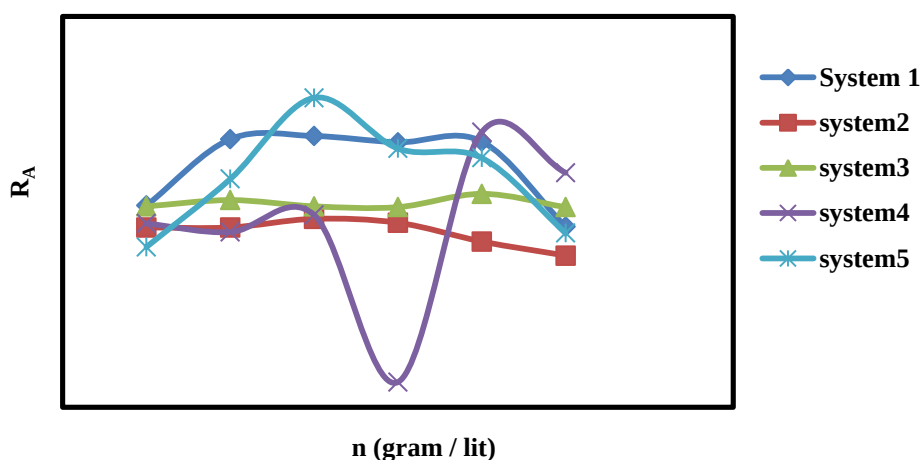


Fig. 6: Variation of Relative Association with the Concentration of PVA.

The increase in ultrasonic velocity and acoustic impedance with the decrease in adiabatic compressibility and intermolecular free length indicate that the intermolecular force increases with the addition of electrolyte (mole value of borax). As a result, a strong interaction occurs among the different species involved in the system. The interaction may tend to form the hydrogen bond among the species as the hydroxyl groups on the sides of PVA may also form hydrogen bond with borate ion (Srinivaslu et al., 1995). When the mole value of borax increases above certain value in PVA - water mixtures, ultrasonic velocity, adiabatic compressibility, relaxation time, acoustic impedance show a random variation.

It is suggested that the hydrogen bonds are relatively strong and quite dynamic such that they are constantly forming and dissociating the bonding or cross linking randomly among PVA molecules. This dynamic nature of cross links allows the PVA molecules to move relatively each other allowing the slime to ooze. As the slime remains fluid, the interactions among the species are non covalent and hence there will be no actual chemical reaction between the PVA molecules and borate ions. In concern to the above, it is evident that no product has been formed from the relation of borate ion and PVA. In order to study the molecular interactions among the different types of molecules (Ravichandran and

Ramanathan, 2012), the binary mixture of PVA has been studied (System-1). The velocity of ultrasound, density, shear viscosity of the solution are observed to be greater than the ternary mixtures (System-2 to System-5).

It is interesting to note that the interaction in binary mixtures may be stronger than that of in ternary mixtures. This may be due to the greater possibility of hydrogen bonding between PVA and water molecules. Further, the bulkiness of the both the molecules lead to closer packing thereby facilitating the above said molecular interactions. When the borax is added, the molecular interaction is getting weaker due to greater affinity of borate ion towards the hydrogen in hydroxyl group of PVA (Baluja et al., 2002). The non linear variations of Rao's constant (molar sound velocity) and Wada's constant (molar compressibility) are observed in both binary and ternary mixtures as shown in Fig. (7,8). It indicates that there is a strong solute – solvent interaction occurring in both binary and ternary solutions (Syal et al., 2005). The free volume plays an important role in ultrasonic wave propagation of liquids. The calculated free volume of both binary and ternary mixtures show a linearly increasing order with increase in concentration as shown in Fig. 9, which indicate the association through ionic bonding (Sanariya and Parsania, 2010).

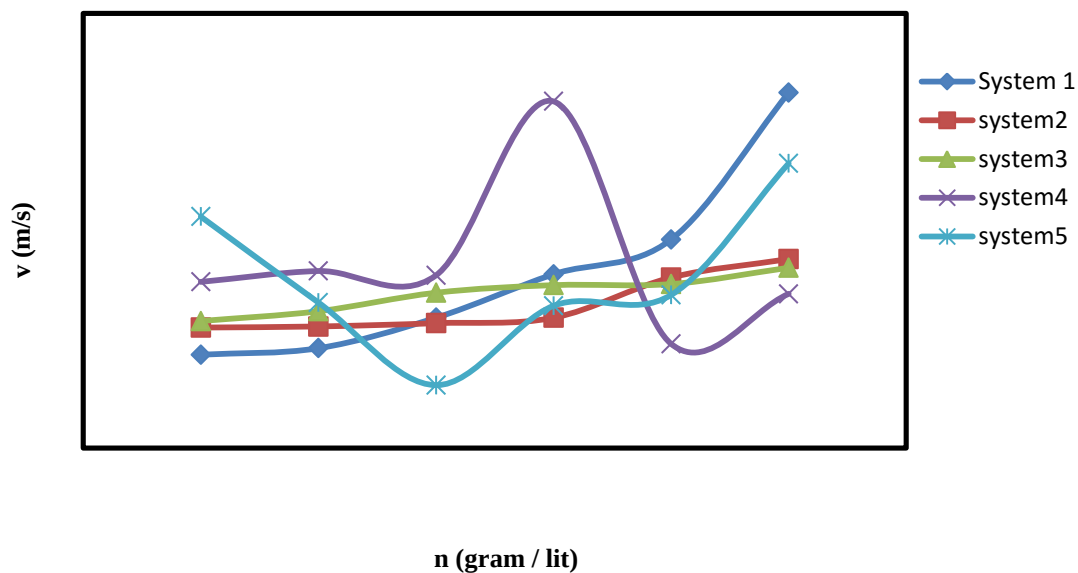


Fig. 7: Variation of Rao's Constant with PVA Concentration.

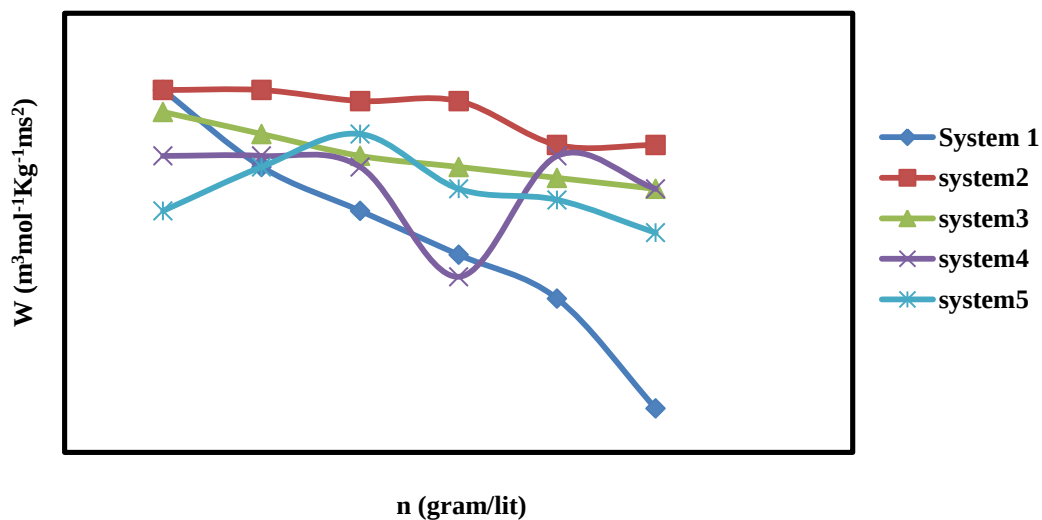


Fig. 8: Variation of Wada's Constant with PVA Concentration.

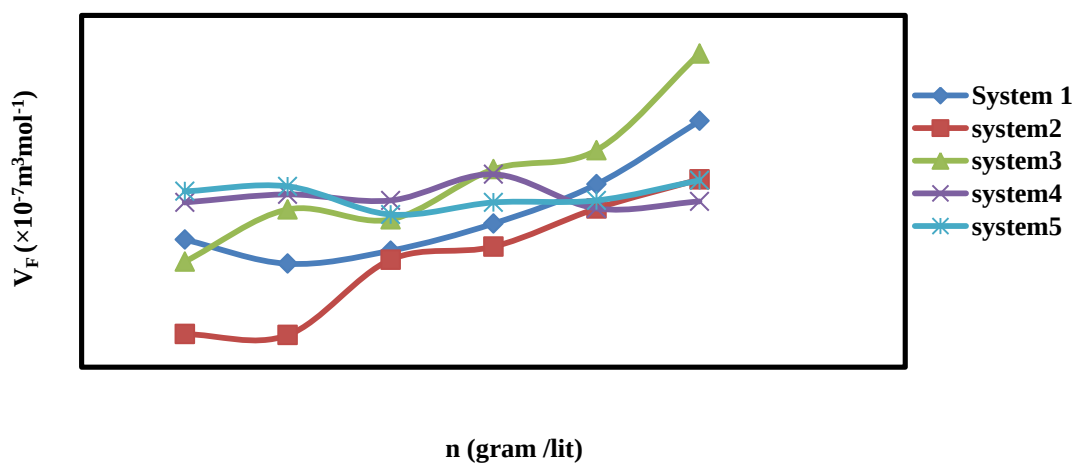


Fig. 9: Variation of Free Volume with PVA Concentration.

The variation of ultrasonic attenuation with various concentrations of both binary and ternary mixtures is shown in Fig. 10. It is seen that ultrasonic attenuation of the solutions is found to vary nonlin-

early with increase in concentration. This shows a similar trend to that of acoustical relaxation time which is due to a modification in the nature of the molecular interaction. The measurements of ul-

trasonic attenuation and relaxation time seem to indicate that viscosity contributes in a significant way to the absorption. The above behavior is noticeable as per kinetic theory of fluids, ultrasonic velocity, viscosity, density studies in both the solutions of binary and ternary systems revealed the presence of solute-solvent interaction (Pandey et al 2005).

The surface tension of both binary and ternary mixtures of system1 to system 5 has been measured and as shown in Fig.11. It is clearly seen that the surface tension values vary non linearly with

increase in concentration. A variation of surface tension shows the attractive interactions between the two solutions. At the interface, there is migration of the species having the lowest surface tension, or free energy per unit area, at the temperature of the system. This migration at the interface results in a liquid phase rich in the component with the highest surface tension and a vapor phase rich in the component with the lowest surface tension (Ravichandran and Ramanathan, 2010).

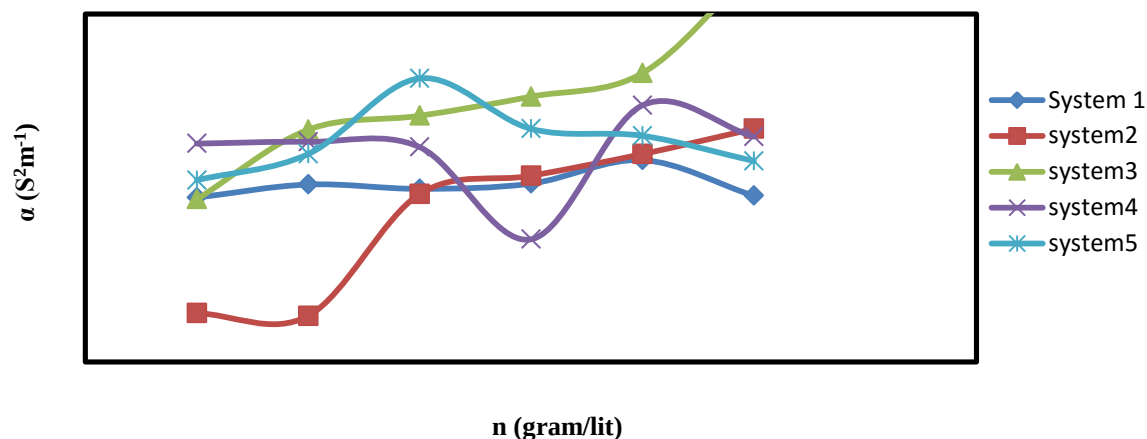


Fig. 10: Variation of Ultrasonic Attenuation with PVA Concentration.

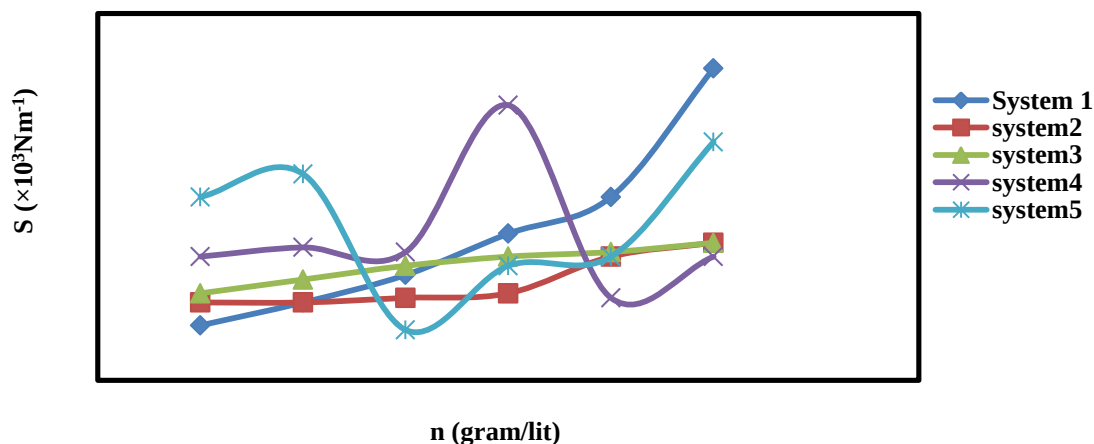


Fig.11: Variation of Surface Tension with PVA Concentration.

4. Conclusion

The derived parameters like adiabatic compressibility, acoustic impedance, intermolecular free length, ultrasonic relaxation time, surface tension, Rao's and Wada's Constant, ultrasonic attenuation and free volume have confirmed the existence of molecular interactions in the system. It has been identified that the molecular interactions in binary mixture were stronger than that of in ternary mixtures. The competitive mechanism in establishing hydrogen bonding between solute-solvent has been identified. Accordingly, the hydrogen bonds are relatively strong and dynamic such that they are constantly forming and dissociating the bonding among PVA molecules. So, it is evident that there is no product of PVA and borate ion formed. Hence, the polymer chains distort to allow these hydrogen bonds to occur and water molecules dispersed throughout the mess add to the hydrogen bondings.

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