

# Study of Optical, Electrical and Acoustical Properties of $\text{CuSO}_4$ Doped Polyvinyl Pyrrolidone (PVP) based Polymer Solutions

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## ABSTRACT

*The optical, electrical and acoustical properties of a polymer solution based on polyvinyl pyrrolidone (PVP) doped with different concentration of cupric sulphate ( $\text{CuSO}_4$ ) were studied. UV-VIS spectroscopy results reflected that absorption increases in asymmetric manner and the absorption peak showed red shift with increasing Cu ions concentration. The optical band gap (direct and indirect) was found to decrease with increase in Cu ions concentration in the polymer due to increase in the density of localized states in the band-gap. The value of Urbach energy is also evaluated from the transmission spectra and the activation energies are also evaluated from the conductivity measurements and found to decrease with the increase in the concentration of Cu ion in the PVP. The ultrasonic velocity and surface tension are increased while the adiabatic compressibility, acoustic impedance and intermolecular free length decreases with increase in the concentration of  $\text{CuSO}_4$  in the polymer PVP.*

**KEYWORDS:** *Polymer solution, UV-visible spectroscopy, Optical energy band gap, Electrical conductivity, Ultrasonic velocity, Polyvinyl pyrrolidone.*

## 1. INTRODUCTION

Polymeric materials have attracted a growing interest in recent years because of their ability to combine with suitable metal salts resulting into complexes which have wider applications in solid state devices viz. rechargeable

batteries, super-capacitors, electro chromic display devices/smart windows, fuel cells and gas sensors [1-3]. Pioneering work of Wright and his co-workers (1975) of doping the polyethylene oxide (PEO) with sodium iodide and thiocyanates of sodium, potassium and

ammonium brought the global attention towards the conductive nature of polymers [4]. PEO is most widely used as electrolyte due to its exceptional ability to solvate ionic salts. However, there were few drawbacks of PEO [5] and hence research started to improve the properties of inherently insulating polymers. In principle, the polymer is blended with another polymer or a dopant so as to improve its properties. The significant advantage of polymer blending is that the properties of the desired product can be tailored to the requirements of the applications, otherwise which cannot be achieved. However, the inherent problem of low ionic conductivity at ambient temperatures acts as a barrier to their utility. The synthesis of a novel polymer electrolyte exhibiting high ionic conductivity, good electrochemical stability and mechanical strength, is highly desirable to create a new generation of polymer electrolytes for batteries. As PEO-alkali metal salt complexes have significant ionic conductivity, they have been studied extensively. There are several disadvantages of such systems, the major one being that PEO tends to crystallize or form crystalline complexes. Therefore, acceptable levels of ionic conductivity can be achieved above the melting temperature. To overcome these problems and obtain high ionic conductivity at ambient temperatures several polymers such as PVA, PVC, PAN, PMMA and PVP complexed with different alkali metal salts have been investigated [6]. Among these polymers, PVP deserves a special attention because of its good electrical properties, easy processability, moderate electrical conductivity and charge transport mechanism [7]. PVP is an amorphous polymer and possesses high  $T_g$  due to the presence of the rigid pyrrolidone group, which is known to form various complexes with

many inorganic salts. In dry form, PVP is a flaky powder which can absorb water up to 40% of its weight, a non-toxic material and has good environmental stability [8], widely used in medicines, cosmetics, pharmacy and industrial production [9]. It also possesses some unique properties, like transparency and gloss, chemical/biological inertness, crosslinking ability and long-lasting adhesion.

In present study, we have prepared polymer electrolyte while selecting polyvinyl pyrrolidone (PVP) as host polymer and cupric sulphate ( $\text{CuSO}_4$ ) as dopant and studied their optical, electrical and acoustical properties. The dopant  $\text{CuSO}_4$  is easily soluble in almost all polar solvents like water, alcohol etc, and gives  $\text{Cu}^{2+}$  and  $\text{SO}_4^{2-}$  ions in aqueous solution and these ions are responsible for the conductivity in the solution. It is also being used as electrolyte in copper plating process and batteries. All these qualities of  $\text{CuSO}_4$  make it a good material to be used as a dopant. Literature survey shows that there are few studies on copper ion complexed PVP electrolyte systems. Many researchers like Vani *et al.* [10], Kumar *et al.* [11] and Tomar *et al.* [12] have reported the studies on polymer electrolyte for solid state battery applications but scanty of reports are available for the materials chosen in present study. Further, we have reported the acoustical properties of prepared polymer electrolyte as very limited knowledge is available about these properties of the polymer electrolyte.

The prepared metal ion-polymer solution will certainly have improved optical and electrical properties due to metallic ions with the advantages of polymers such as light weight, good flexibility, resistant to corrosion and low cost.

## 2. EXPERIMENT

### Materials and Methods

The Cu salt incorporated polymer samples were prepared by simple chemical route. All the chemicals used were of AR grade. The reagents used were polyvinyl pyrrolidone (PVP) (S.D. Fine-chemical limited, India), Copper sulphate ( $\text{CuSO}_4$ ) (QualiKems Fine Chemicals, India) and distilled water. A stock solution of 3wt% of PVP was prepared by dissolving 3 gm of PVP in 100 ml of distilled water. The  $\text{CuSO}_4$  stock solutions were prepared with different weight concentrations of 0.2%, 0.4%, 0.6%, 0.8% and 1.0% stirred for an hour at room temperature using magnetic stirrer to get homogenous solution. Then, stock solution of PVP and  $\text{CuSO}_4$  solution of concentration 0.2%, 0.4%, 0.6%, 0.8% and 1.0% were mixed in volume ratio 80:20 (PVP: $\text{CuSO}_4$ ), and then stirred at room temperature

using magnetic stirrer for about two hours to get homogeneous and clear solution. The resulting five different 100 ml composite solutions contain 2.4wt% of PVP with 0.04 wt%, 0.08 wt%, 0.12 wt%, 0.16wt% and 0.2wt% of  $\text{CuSO}_4$ , respectively and labelled as  $C_1$ ,  $C_2$ ,  $C_3$ ,  $C_4$  and  $C_5$ , respectively throughout the text. The optical absorption spectra of these samples were observed in the wavelength range 300- 700 nm at room temperature using the Systronics UV-visible spectrophotometer 108 with deuterium and tungsten-halogen lamp as source of UV- visible light as shown in Fig. 1. The obtained optical absorbance data was evaluated to get information about the various band gaps and refractive index. The electrical conductivity was measured by using at wo-probe method using Hanna Instrument HI 98311 having graphite electrodes in the temperature range 283- 333 K. The ultrasonic velocity was also measured using ultrasonic interferometer at a frequency of 1MHz.

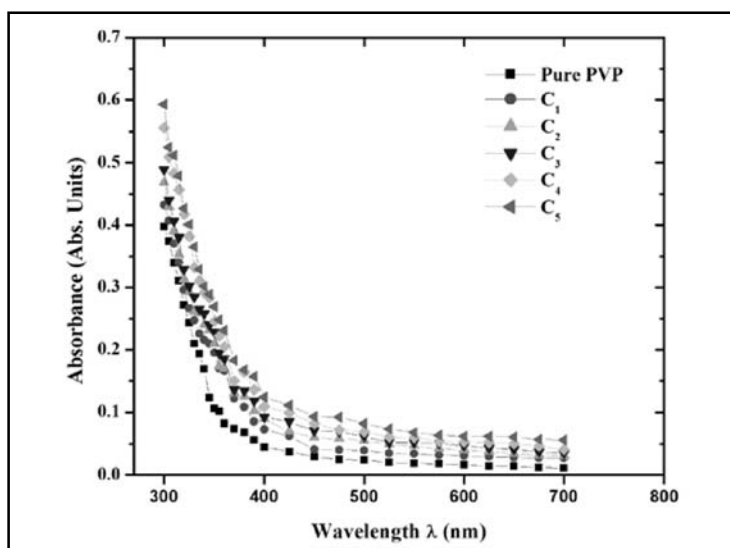


Fig. 1. Absorbance spectra for pure PVP and  $\text{CuSO}_4$  doped polymer solutions.

## 3. RESULTS AND DISCUSSIONS

### 3.1 Optical properties

The absorption coefficient ( $\alpha$ ) for the prepared

polymer solutions was calculated from the measured values of optical absorbance (A) in the wavelength range 300- 700 nm. The absorption coefficient was calculated using the

following equation:

$$\alpha = \frac{2.303 * A}{t} \quad (1)$$

where A is the optical absorbance and t is the thickness of the sample. Figure 2 depicts the variation of absorption coefficient ( $\alpha$ ) for pure PVP and polymer solutions with different concentrations of Cu ions with change in wavelength ( $\lambda$ ). As can be seen from the graph that absorption coefficient decreases with increase in wavelength. The high absorbance

at lower wavelength (UV region) simply depicted that the energy of incident photons matches with the energy required by electrons for the transition to higher energy state. At a particular wavelength, the absorption coefficient increases with increase in the concentration of  $\text{CuSO}_4$ . This increase in absorbance confirmed the significant complexation between dopant and polymer molecules. The absorption spectra also exhibit sharp absorption edge, which shifts towards longer wavelength as the incorporation

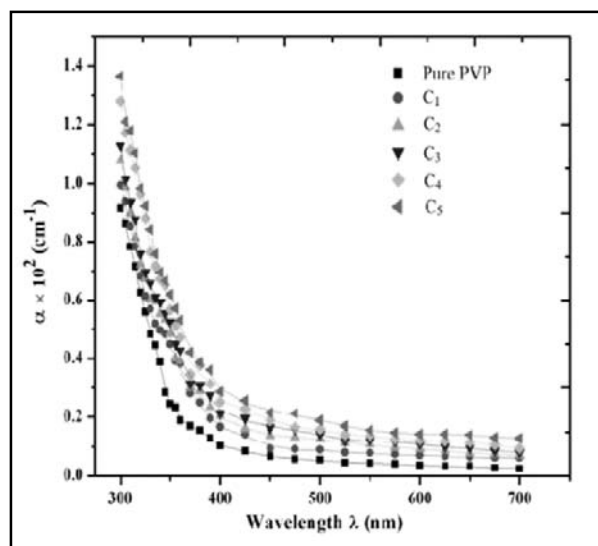


Fig. 2. Variation of absorption coefficient ( $\alpha$ ) with wavelength ( $\lambda$ ) for pure PVP and  $\text{CuSO}_4$  doped polymer.

of Cu salt is increased in the polymer. These absorption edges are assigned to the band excitonic absorption. The shift in the absorption edge may be due to the change in lattice bond rearrangements and local structure of the material. The study of the optical absorption provides a simple method for the study of band structure, band gap value and other optical parameters. The following Tauc's relation has

been used to evaluate the optical band gap ( $E_g$ ):

$$(\alpha h\nu) = (h\nu - E_g)^p \quad (2)$$

where  $\alpha$  is absorption coefficient,  $\beta$  is constant depending on specimen structure,  $E_g$  is optical energy band gap,  $h\nu$  is incident photon energy and p is the exponent that depends on the type of transition. The exponent  $p$  can take values

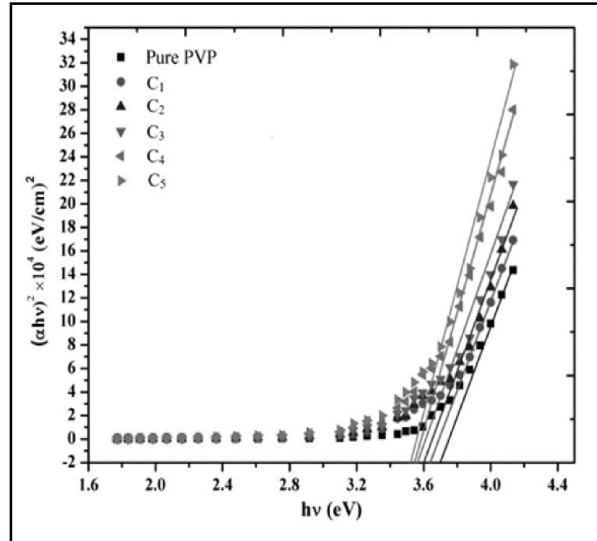


Fig. 3. Direct band gap variation with photon energy ( $h\nu$ ) for pure PVP and  $\text{CuSO}_4$  doped polymer solutions.

$1/2$  and  $2$  for direct and indirect allowed transitions, respectively [13-14]. To obtain direct and indirect band gap for different polymer solutions,  $(\alpha h\nu)^2$  and  $(\alpha h\nu)^{1/2}$  values were plotted against incident photon energy  $h\nu$  respectively as shown in Figs. 3 and 4. The band gap values were obtained by extrapolating the linear portions of the curves in Figs. 3 and

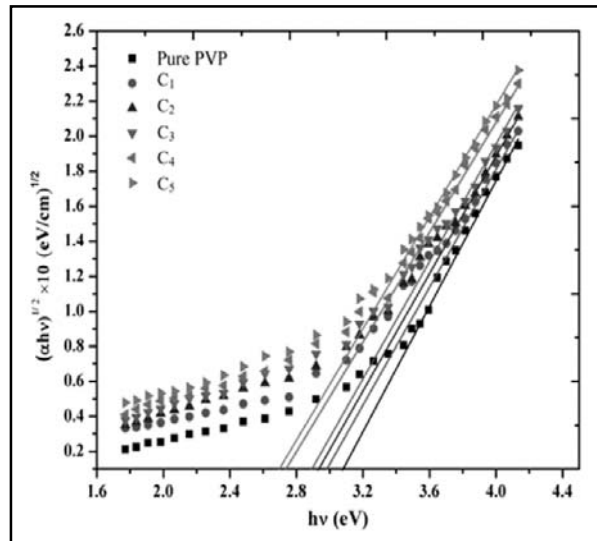


Fig. 4. Indirect band gap variation with photon energy ( $h\nu$ ) for pure PVP and  $\text{CuSO}_4$  doped polymer solutions.

4 to zero absorption values. The direct band gap involves the transitions between the valance and conduction band at the same momentum vector while the indirect band gap indicates that there exist transitions between the valance and conduction band at different momentum vector

by phonon assistance process. The direct and indirect band gap values obtained from the plots are listed in Table 1. The direct and indirect band gap of the pure PVP polymer is found to be 3.70 eV and 3.08 eV,

TABLE 1. Optical parameters for PVP and CuSO<sub>4</sub> incorporated PVP solutions

Polymer solutions	Direct band gap (eV)	Indirect band gap (eV)	Urbach energy (eV)	Refractive index (n) at 500nm
Pure PVP	3.70	3.08	2.28	1.41
C <sub>1</sub>	3.64	2.93	2.15	1.55
C <sub>2</sub>	3.60	2.89	2.09	1.67
C <sub>3</sub>	3.57	2.84	2.08	1.72
C <sub>4</sub>	3.55	2.74	2.88	1.77
C <sub>5</sub>	3.52	2.70	2.62	1.85

respectively. It has been observed that the indirect band gap of the investigated samples is less than the direct band gap of the materials. With the incorporation of Cu in PVP, the band gap is found to decrease as the Cu concentration increases. The decrease in band gap can be attributed due to the filling of low-level conduction electrons<sup>[15]</sup>. The phonon assisted electronic transitions given rise to the tail states near the mobility band edge. The width of these localized tail states is evaluated using the absorption coefficient in the low absorption region. The optical absorption in the low energy region corresponds to an exponential tail obeying the equation<sup>[16]</sup>:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_U}\right) \quad (3)$$

where  $E_U$  is the Urbach energy which corresponds to the width of tail states in the

mobility gap and related to structural disorderness in the material. The value of Urbach energy has been evaluated by exponential fitting of the sub-band gap absorption coefficient and given in Table 1. It has been found that Urbach energy decreases as the concentration of Cu ions increases in the PVP. The disordered arrangement of atoms causes the mobility edges to enter in the mobility gap and give rise to the tail states.

The refractive index of prepared polymer solution was also calculated from the reflectance values (R) in the wavelength range 300- 700 nm. The reflectance values were obtained from absorbance (A) and transmittance (T) values by following equations:

$$A = 2 - \log_e(\%T) \quad (4)$$

$$R + T + A = 1 \quad (5)$$

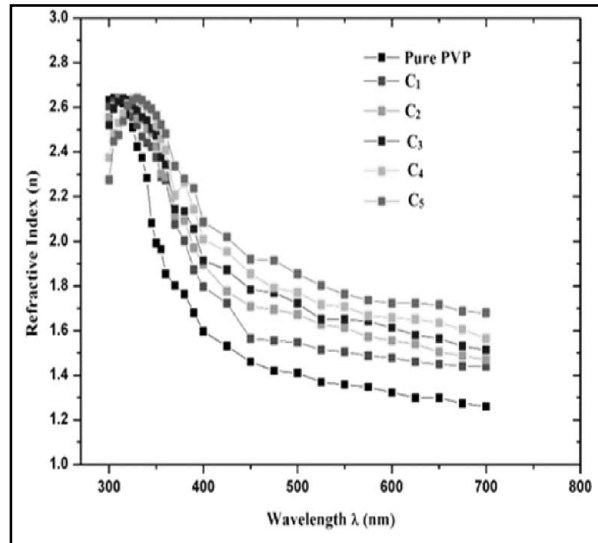


Fig. 5. Variation of refractive index (n) with wavelength (λ) for pure PVP and for PVP with different concentration of CuSO<sub>4</sub>.

where A is absorbance, T is transmittance and R is reflectance of light. By obtaining the reflectance value (R) at each wavelength in region 300- 700 nm, the refractive index (n) of polymer solution was calculated using following equation:

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \quad (6)$$

The variation of refractive index (n) as a function of wavelength (λ) for pure PVP and polymer solutions with different concentrations of CuSO<sub>4</sub> is shown in Fig. 5. The refractive index was found to first increase and then decrease with increase in wavelength. The maximum shows redshift with increasing concentration of Cu ions. At a particular wavelength, the refractive index (n) increases with increase in concentration of dopant. As can be seen from the Table 1 that at wavelength 500 nm, the refractive index for pure PVP was found to be 1.41 and it increased

to 1.55 for 0.04wt% Cu ions and to 1.85 for 0.2 wt% Cu-ions. However, some anomalous dispersion can be seen in the Fig. 5 in the wavelength region 300 - 335 nm and after that normal dispersion. The anomalous dispersion is not significant in case of pure PVP but this effect can be seen significantly when PVP doped with 0.16wt% and 0.2wt% CuSO<sub>4</sub>. The refractive index tends to increase with wavelength or anomalous dispersion occurs when light is absorbed by the medium and normal dispersion occurs when the light is very less or not absorbed by medium. This increase in refractive index confirms the complexation of CuSO<sub>4</sub> with polymer PVP [17, 18].

### 3.2 Electrical properties

The electrical conductivity as a function of temperature (in the range 283- 333 K) for different compositions of (PVP:CuSO<sub>4</sub>) polymer solution was studied. The electrical conductivity

( $\sigma$ ) varies with temperature (T) in accordance to the Arrhenius equation as:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \quad (7)$$

where  $\sigma_0$  is the pre-exponential factor,  $E_a$  is the activation energy,  $k$  is the Boltzmann constant and  $T$  is the absolute temperature [5]. Figure 6 shows the variation in the electrical conductivity ( $\ln \sigma$ ) of polymer solution with temperature for different concentrations. The magnitude of electrical conductivity was found to increase

with temperature as well as concentration of  $\text{CuSO}_4$  in the polymer solution [19-20]. The former increase in conductivity is attributed to the increase of free ion mobility due to thermal energy  $kT$  and the later increase may be due to increase in concentration of charge carriers in the polymer solutions with the additions of Cu ions [21]. The activation energy ( $E_a$ ) was calculated by multiplying the Boltzmann Constant ( $k$ ) with the slope of lines in Fig. 6. The activation energy values for pure PVP and all the compositions of PVP and Cu ions

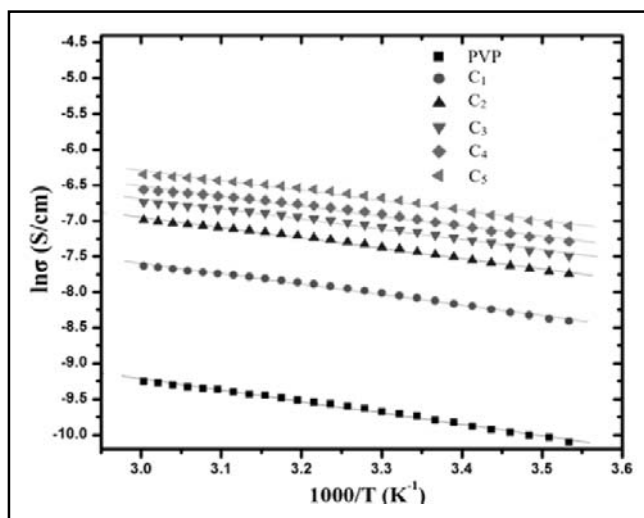


Fig. 6. DC conductivity variation with temperature for pure PVP and  $\text{CuSO}_4$ -doped polymer solutions.

TABLE 2. Activation energy of electrical conduction for pure PVP and  $\text{CuSO}_4$  incorporated PVP solutions.

Polymer solutions	Activation energy $E_a$ (eV)
Pure PVP	0.136
$C_1$	0.126
$C_2$	0.125
$C_3$	0.123
$C_4$	0.121
$C_5$	0.120



are listed in Table 2. The activation energies were found to decrease with increase in concentration of CuSO<sub>4</sub> in the host polymer PVP. These low values of E<sub>a</sub> may be due to amorphous nature and tends to provide more free volume for the motion of charge carriers. Hence, more the mobility of charge carriers, more is the electrical conductivity and lesser the activation energy of electrical conduction [7, 22].

### 3.3 Acoustical properties

Ultrasonic velocity and density measurements of pure PVP and CuSO<sub>4</sub> doped polymer solutions were carried out at room temperature, 300 K. The measured and calculated acoustical parameters are listed in Table 3. The ultrasonic velocity (U) was measured using an ultrasonic interferometer and the density (ρ) of the polymer solutions was measured using a specific gravity method. As clear from the Table 3 that ultrasonic velocity increases with increase in concentration of CuSO<sub>4</sub>. Due to specific molecular interactions such as association,

expansion, and unfolding the variation of U, Z and <sup>1/4</sup> with concentration is considerably more than that of density ρ. The attractive interactions between the molecules decrease the compressibility and intermolecular free length and hence the velocity of sound waves increase in the mixture. It is due to highly polar forces between polymer and dopant molecules come into play and are responsible for intermolecular interactions [23, 24]. Other acoustical parameters like adiabatic compressibility (β<sub>ad</sub>), acoustic impedance (Z), intermolecular free length (L<sub>f</sub>) and surface tension (σ) were also calculated using the measured values of ultrasonic velocity (U) and density (ρ). These acoustical parameters are also listed in the Table 3.

The adiabatic compressibility (β<sub>ad</sub>) was calculated using the following relation:

$$\beta_{ad} = \frac{1}{\rho U^2} \quad (8)$$

where ρ is density and U is ultrasonic velocity. The adiabatic compressibility was found to

TABLE 3. Density (ρ), Ultrasonic velocity (U), adiabatic compressibility (β), acoustic impedance (Z), intermolecular free length (L<sub>f</sub>) and surface tension (s) of pure PVP and different polymer solutions with 0.2, 0.4, 0.6, 0.8 and 1.0% CuSO<sub>4</sub> concentration mixed in ratio 80:20 at 300 K.

Polymer solutions	Density ρ(kgm <sup>-3</sup> )	Ultrasonic velocity U (ms <sup>-1</sup> )	Adiabatic compressibility β×10 <sup>-10</sup> (kg <sup>-1</sup> ms <sup>2</sup> )	Acoustic Impedance Z ×10 <sup>6</sup> (kg <sup>-1</sup> m s <sup>-2</sup> )	Intermolecular free length L <sub>f</sub> ×10 <sup>-11</sup> (m)	Surface tension σ (Nm <sup>-1</sup> )
Pure PVP	1190.8	1484	3.81	1.77	3.85	42887.5
C <sub>1</sub>	1189.9	1518	3.65	1.80	3.77	44337.0
C <sub>2</sub>	1190.2	1532	3.58	1.82	3.73	44963.8
C <sub>3</sub>	1190.5	1538	3.55	1.83	3.72	45240.4
C <sub>4</sub>	1190.9	1568	3.42	1.87	3.65	46586.2
C <sub>5</sub>	1191.2	1592	3.31	1.89	3.59	47672.6

decreases with an increase in concentration of  $\text{CuSO}_4$  dopant which indicate a complex formation in the PVP solution. This decrease in adiabatic compressibility may be due to two effects- electrostatic attraction and association between molecules<sup>[25]</sup>. These effects led to aggregation between the molecules and decreases the compressibility which increases the ultrasonic velocity in polymer solutions.

Acoustic impedance (Z) is the resistance offered by medium to the wave propagation. The acoustic impedance value is related to ultrasonic velocity (U) and density (P) values as:

$$Z = U * \rho \quad (9)$$

The acoustic impedance was found to increase with an increase in concentration of dopant in the polymer which indicates an increase in the intermolecular interactions [26] between PVP and dopant. Intermolecular free length ( $L_f$ ), which is the average distance between the surfaces of adjacent molecules, was obtained by using the following equation:

$$L_f = K * \sqrt{\beta_{ad}} \quad (10)$$

where  $K(= 93.875+0.345*T) \times 10^{-8}$  is temperature dependent Jacobson's constant has value  $197.375 \times 10^{-8}$  at 300K. As from Table 3, the intermolecular free length decreases with increase in the concentration of  $\text{CuSO}_4$  in the polymer PVP. The increase in concentration of dopant led to decrease the intermolecular spacing<sup>[25]</sup> because of the close packing of molecules. This decrease in  $L_f$  supports the formation of new structure with the addition of dopant in the polymer solution.

The surface tension ( $\sigma$ ) was also calculated using following equation:

$$\sigma = (6.3 \times 10^{-4}) \rho U^{3/2} \quad (10)$$

where  $\rho$  is density and U is ultrasonic velocity. This parameter is used to study the surface composition of the polymer solution. As can be seen from the Table 3, surface tension increases with increase in concentration of  $\text{CuSO}_4$  in the polymer. This increase in surface tension showed the significant attractive interactions between solute and solvent molecules.

Vander Waals, H-bonding, dipolar, and London types forces between solvent and solute molecules result in the aggregation of solvent molecules around solute molecules. It shows that the density, ultrasonic velocity, impedance and surface tension of the solution increases with increase in concentration. This linear increase of  $\rho$ , U, Z and  $\sigma$  with concentration confirms an increase of cohesive forces because of strong molecular interactions.

#### 4. CONCLUSIONS

Polymer solutions were prepared by a simple approach with different concentrations of  $\text{CuSO}_4$  in the host polymer, PVP. The optical band gap (direct and indirect) was found to decrease with increase in Cu ions concentration in the polymer due to increase in the density of localized states in the band-gap. The dc conductivity was found to increase with temperature as well as concentration of Cu ions. The electrical conductivity of pure PVP solution is  $9.6 \times 10^{-5}$  S/cm which increases to maximum value of  $1.755 \times 10^{-3}$  S/cm by adding 0.2wt% concentration of Cu ions at 333 K. The refractive index (n), the ultrasonic velocity (U),

acoustic impedance (Z) and surface tension ( $\sigma$ ) of the polymer solution was found to increase with increase in concentration of Cu ions while the activation energy of electrical conduction, the adiabatic compressibility ( $\beta_{ad}$ ) and intermolecular free length ( $L_f$ ) was observed to decrease with increase in concentration of Cu ions. The variations in all these parameters confirmed that attractive intermolecular interactions between PVP and Cu ions which increases with increase in the concentration of CuSO<sub>4</sub>. These studies will help to explore the potential applications of PVP:CuSO<sub>4</sub> as a polymer electrolyte in ionic devices due to its adaptation to various geometries, environmental and other safety measures. Further, liquid electrolytes produce high conductivity at room temperature, hence, have been frequently used in many energy devices. Although a solid polymer electrolyte possesses good mechanical strength, it exhibits poor conductivity at room temperature.

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