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RESEARCH ARTICLE

AC Impedance Analysis of PVP:(H_2N-C_6H_4-SO_3H) Complexed Polymer Electrolyte Films

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Abstract: A solid polymer electrolyte system based on polyvinyl pyrrolidone (PVP) complexed with amino benzene sulphonic acid isomers have been prepared by solution casting technique. The conductivity measurements were carried out on these films as a function of frequency at various temperatures. The complex impedance spectroscopy results reveal that the high-frequency depressed semicircle is due to the bulk effect of the material. The conductivity is enhanced to the order of 10^{-6} S/cm upon increase in salt concentration at room temperature. The 2 and 4-amino benzene sulphonic acid enhances the conductivity of PVP by donating its proton from the sulphonic acid group very effectively. Thus the maximum ionic conductivity (8.44x 10^{-6} S/cm) is obtained for 9 mol% 2-amino benzene sulphonic acid (2ABSA) complexed PVP polymer electrolyte.

Keywords: Polyvinyl pyrrolidone, 2, 3, 4-Amino benzene sulphonic acid, Impedance spectroscopy, Polymer electrolyte

Introduction

Polymer electrolytes have evolved extensively in the electrochemical field. Intensive research in this discipline is mainly driven by their significant applications in solid state proton battery[1], electrochromic devices[2], fuel cells[3] *etc*. The proton donor, normally organic/inorganic salt is dissolved in the polymer host like PEO[4], PVA[5] and PVP[6] *etc*. Among the polymer host, PVP is an amorphous polymer. The pyrrolidone ring in PVP contains a proton accepting carbonyl group. PVP doped with inorganic salt such as $NaClO_3$,

$LiBF_4$ and ammonium salts that possess high ionic conductivity have been reported[7-9]. The conductivity of pure PVP is ~10^{-10} S/cm at room temperature[10] and its value increases sharply to ~10^{-9}-10^{-4} by complexing with inorganic and organic salts[11].

The poly amino benzene sulphonic acid isomer and their copolymers act as a conducting polymer which was used to prepare nano composite membrane and applied in sensors[12-15]. In the present study amino benzene sulphonic acid (ABSA) salt isomer were used as dopant to enhance the conductivity of PVP, because the sulphonic acid group in ABSA provides the proton for conduction. The polymer electrolyte film has been analysed by AC impedance spectroscopy.

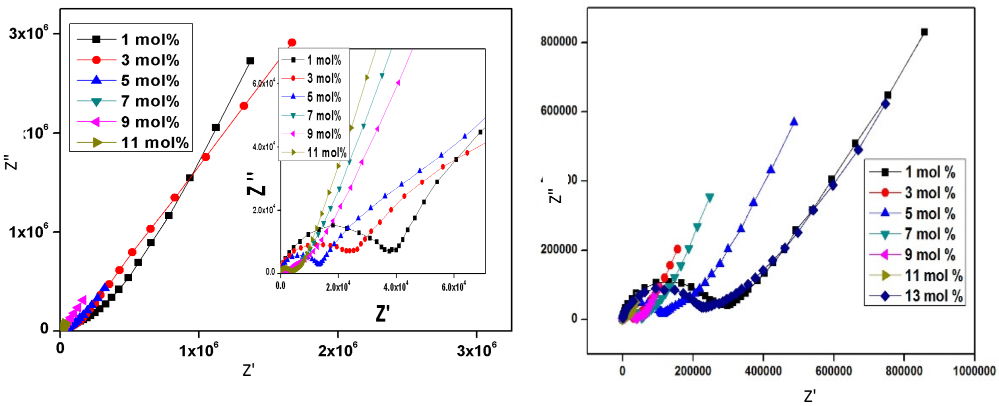
Experimental

Polyvinyl pyrrolidone (PVP) K_{90} (Sd fine – chem. Limited, India.), 2, 3, 4-amino benzene sulphonic acid (ABSA) (Tokyo Chemical Industry –Co. Ltd. Japan.) -99% purity were used as raw materials. Polymer electrolytes have been prepared with different concentrations of PVP complexed with amino benzene sulphonic acid isomers by solution casting technique using water as solvent. The complex impedance measurements were carried out using a computer-controlled electrochemical work station (Biologic Science Instrument France Model – SP 300) in the frequency range of 100 Hz - 5 MHz with an applied voltage of 100 mV at different temperatures.

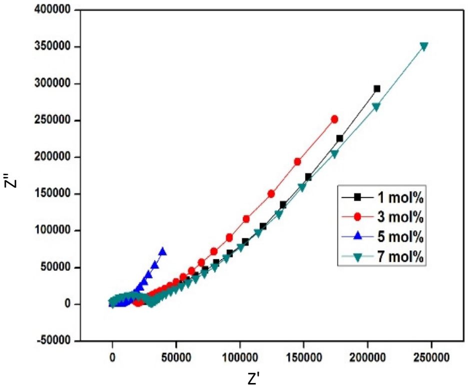
Results and Discussion

Impedance analysis

Figure 1(a-c) show the impedance spectra for different concentrations of PVP complexed with amino benzene sulphonic acid (ABSA) isomers based polymer electrolytes at ambient temperature. Typical ac impedance plot shows two well-defined regions: (1) depressed semi-circle at high frequency side and (2) inclined line at low frequency side. In PVP-2ABSA, the depressed semicircle, observed in the high-frequency region at low temperature is due to the bulk effect of the electrolytes and the linear region in the low-frequency range is attributed to the effect of the blocking electrodes[16]. The disappearance of high frequency semicircular portion leads to a conclusion that the current carriers are ions and hence the total conductivity is mainly the result of ion conduction. The bulk resistance (R_b) can be retrieved from the intercept of high frequency semi-circle or the low frequency spike on the Z′-axis[17].



(a) (b)



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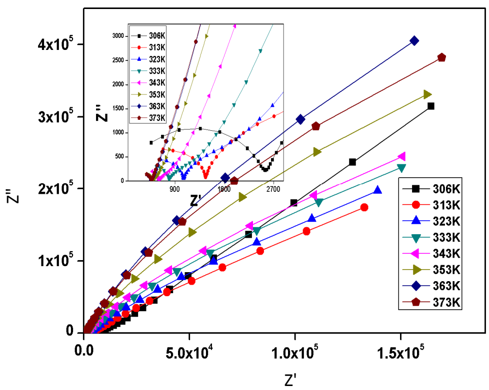

(d)

Figure 1. Impedance Plot of PVP with (a) 2ABSA (b) 3ABSA (c) 4ABSA at ambient temperature (d) PVP- 9 mol% of 2ABSA at different temperature

The ionic conductivity values of the electrolytes were calculated by using the equation: $\sigma = d/ R_bA$; where d and A are the thickness and known area of the electrolyte film respectively and R_b is the bulk resistance of the electrolyte film. The dc conductivity values for PVP:ABSA isomers doped polymer electrolytes at different temperatures have been listed in Table 1, 2 & 3. The highest conductivity has been found to be $8.46x10^{-6}$ S/cm at ambient temperature for PVP-9 mol% 2ABSA. Figure 1 (d) shows the impedance plot for the highest conductivity sample at different temperatures. It has been found that the impedance value decreases with increase in temperature. As the temperature increases, the dissociation of the acid increases resulting in the decrease in impedance, hence high conductivity[18,19].

Table 1. Ionic conductivity of PVP: 2ABSA system at different temperature

	Conductivity σ(S/cm)							
Temperature→ Concentration↓	33 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C	100 °C
1 mol%	$6.56x10^{-7}$	$3.22x10^{-6}$	$6.10x10^{-6}$	$9.21x10^{-6}$	$1.13x10^{-5}$	$1.37x10^{-5}$	$1.54x10^{-5}$	$1.18x10^{-5}$
3 mol%	$5.29x\ 10^{-7}$	$1.08x10^{-6}$	$2.55x10^{-6}$	$3.36x10^{-6}$	$4.02x10^{-6}$	$4.76x10^{-6}$	$5.21x10^{-6}$	$4.46x10^{-6}$
5 mol%	$9.11x10^{-7}$	$1.92x10^{-6}$	$4.14x10^{-6}$	$5.29x10^{-6}$	$4.01x10^{-6}$	$3.30x10^{-6}$	$2.54x10^{-6}$	$1.66x10^{-6}$
7 mol%	$7.00x10^{-6}$	$1.19x10^{-5}$	$1.99x10^{-5}$	$2.96x10^{-5}$	$3.89x10^{-5}$	$4.94x10^{-5}$	$5.63x10^{-5}$	$6.29x10^{-5}$
9 mol%	$8.44x10^{-6}$	$1.47x10^{-5}$	$2.01x10^{-5}$	$2.74x10^{-5}$	$3.62x10^{-5}$	$4.37x10^{-5}$	$4.69x10^{-5}$	$4.66x10^{-5}$
11 mol%	$3.06x10^{-6}$	$4.70x10^{-6}$	$7.25x10^{-6}$	$1.12x10^{-5}$	$1.33x10^{-5}$	$1.70x10^{-5}$	$2.01x10^{-5}$	$2.15x10^{-5}$

Table 2. Ionic conductivity of PVP: 3ABSA system at different temperature

	Conductivity σ(S/cm)							
Temperature→ Concentration↓	33 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C	100 °C
1 mol%	$4.87x10^{-8}$	$5.39x10^{-8}$	$6.97x10^{-8}$	$8.65x10^{-8}$	$7.31x10^{-8}$	$3.54x10^{-8}$	$1.87x10^{-8}$	$5.49x10^{-9}$
3 mol%	$4.76x10^{-7}$	$7.32x10^{-7}$	$1.33x10^{-6}$	$1.87x10^{-6}$	$2.40x10^{-6}$	$2.24x10^{-6}$	$2.27x10^{-6}$	$2.35x10^{-6}$
5 mol%	$1.23x10^{-7}$	$1.71x10^{-6}$	$1.22x10^{-5}$	$2.49x10^{-5}$	$3.69x10^{-5}$	$3.64x10^{-5}$	$2.42x10^{-5}$	$4.28x10^{-6}$
7 mol%	$3.02x10^{-7}$	$1.31x10^{-6}$	$5.54x10^{-6}$	$1.27x10^{-5}$	$2.45x10^{-5}$	$4.27x10^{-5}$	$6.32x10^{-5}$	$7.32x10^{-5}$
9 mol%	$6.81x10^{-7}$	$2.14x10^{-6}$	$4.79x10^{-6}$	$8.25x10^{-6}$	$1.55x10^{-5}$	$2.24x10^{-5}$	$2.98x10^{-5}$	$3.49x10^{-5}$
11 mol%	$2.68x10^{-6}$	$5.81x10^{-6}$	$1.42x10^{-5}$	$2.50x10^{-5}$	$4.25x10^{-5}$	$5.53x10^{-5}$	$6.28x10^{-5}$	$7.96x10^{-5}$
13 mol%	$1.72x10^{-7}$	$2.30x10^{-6}$	$1.42x10^{-5}$	$4.05x10^{-5}$	$7.49x10^{-5}$	$1.24x10^{-4}$	$1.72x10^{-4}$	$2.06x10^{-4}$

Table 3. Ionic conductivity of PVP: 4ABSA system at different temperature

Conductivity σ(S/cm)								
Temperature→ Concentration↓	33 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C	100 °C
1 mol%	$4.87x10^{-8}$	$5.39x10^{-8}$	$6.97x10^{-8}$	$8.65x10^{-8}$	$7.31x10^{-8}$	$3.54x10^{-8}$	$1.87x10^{-8}$	$5.49x10^{-9}$
3 mol%	$4.76x10^{-7}$	$7.32x10^{-7}$	$1.33x10^{-6}$	$1.87x10^{-6}$	$2.40x10^{-6}$	$2.24x10^{-6}$	$2.27x10^{-6}$	$2.35x10^{-6}$
5 mol%	$1.23x10^{-7}$	$1.71x10^{-6}$	$1.22x10^{-5}$	$2.49x10^{-5}$	$3.69x10^{-5}$	$3.64x10^{-5}$	$2.42x10^{-5}$	$4.28x10^{-6}$
7 mol%	$3.02x10^{-7}$	$1.31x10^{-6}$	$5.54x10^{-6}$	$1.27x10^{-5}$	$2.45x10^{-5}$	$4.27x10^{-5}$	$6.32x10^{-5}$	$7.32x10^{-5}$
9 mol%	$6.81x10^{-7}$	$2.14x10^{-6}$	$4.79x10^{-6}$	$8.25x10^{-6}$	$1.55x10^{-5}$	$2.24x10^{-5}$	$2.98x10^{-5}$	$3.49x10^{-5}$
11 mol%	$2.68x10^{-6}$	$5.81x10^{-6}$	$1.42x10^{-5}$	$2.50x10^{-5}$	$4.25x10^{-5}$	$5.53x10^{-5}$	$6.28x10^{-5}$	$7.96x10^{-5}$
13 mol%	$1.72x10^{-7}$	$2.30x10^{-6}$	$1.42x10^{-5}$	$4.05x10^{-5}$	$7.49x10^{-5}$	$1.24x10^{-4}$	$1.72x10^{-4}$	$2.06x10^{-4}$

Conductance spectra analysis

The frequency dependence of conductivity for the entire polymer electrolytes at ambient temperature are shown in Figure 2(a-c). Typical conductance spectra consists of three distinct regions: the low frequency spike describing electrode–electrolyte interfacial phenomena, followed by the frequency independent plateau region connected with the σ_{dc} of the complexed polymer electrolyte and the high frequency region corresponding to the bulk relaxation phenomena. The dc conductivity of the prepared polymer electrolyte has been obtained by extrapolating the plateau region on the log σ axis. The calculated dc conductivity values from the conductance spectra are in good agreement with those obtained from the Cole–Cole plot[20].

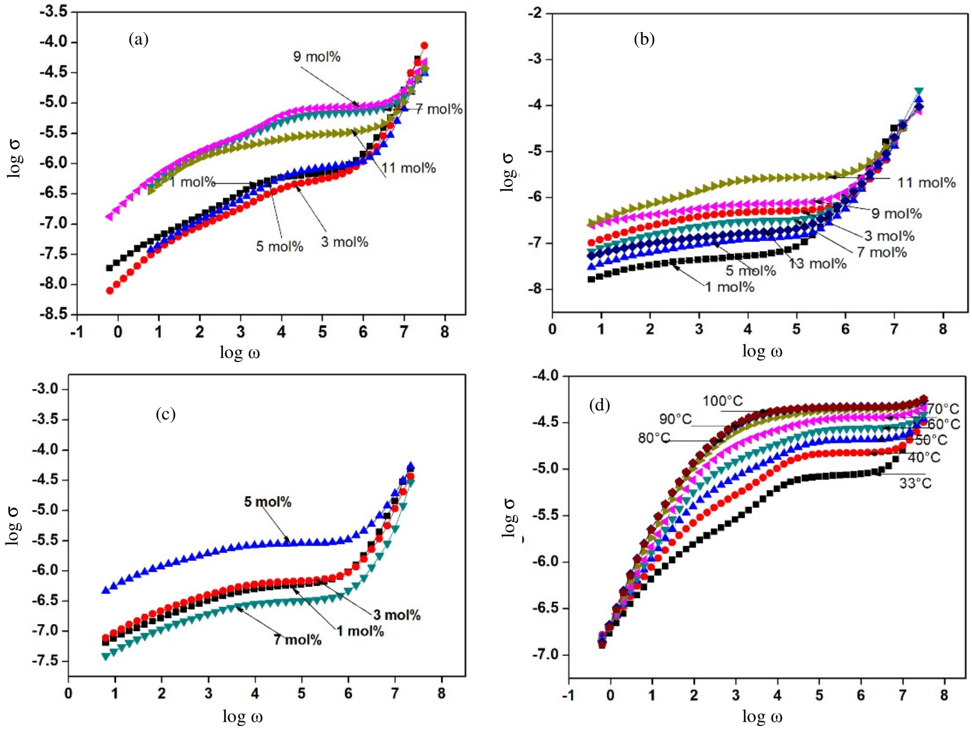

Figure 2. Conductance spectra of PVP with (a) 2ABSA (b) 3ABSA (c) 4ABSA at ambient temperature (d) PVP- 9 mol% of 2ABSA at different temperature

Figure 2(d) shows the frequency dependent conductivity spectra of 9 mol% 2ABSA – PVP polymer electrolyte at various temperatures in the range of 33-100 °C. From Figure 2(d) it has been found that as the temperature increases, the low- frequency dispersion region becomes prominent and shifts to higher frequency region and the frequency-independent plateau region decreases. Hence, the polarization effect becomes dominant as the temperature increases[21-23].

Concentration dependence Conductivity

The conductivity at ambient temperature of the pure PVP is found to be 6.03×10^{-10} S/cm. This study shows that the addition of amino benzene sulphonic acid isomers increases the ionic conductivity of PVP. Figure 3 shows that the variation of ionic conductivity of PVP: ABSA polymer electrolyte system with different concentration of ABSA isomer. The spectra show that the conductivity increases with an increase in concentration and then decreases at higher concentration. The initial increase in conductivity is due to the availability of free mobile ions[24], whereas decrease in conductivity at higher concentration is due to the influence of ion pairs and ion aggregation leading to the formation of ion clusters, thus decreasing the number of mobile charge carriers and the overall mobility[25,26]. From this analysis 9 mol% of PVP-2ABSA system possesses highest conductivity at ambient temperature (8.44×10^{-6} S/cm).

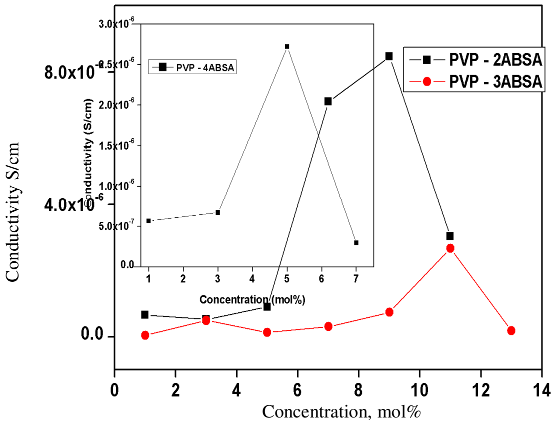

Figure 3. Variation of Ionic conductivity of PVA:ABSA polymer electrolyte system with different concentration

Temperature dependence conductivity

From the literature studies the solid polymer electrolytes follow Arrhenius as well as Vogel-Tamman-Fulcher (VTF) types of ionic conduction which depends on the type of the salt, polymer and the temperature range[27]. Figure 4(a-c) represent that the temperature dependence of proton conductivity for all compositions of PVP: ABSA systems. From the plot it has been observed that as temperature increases the conductivity values also increases for all the compositions.

The experimental data indicate that the ionic conductivity is enhanced with increasing temperature at high salt concentration. When the temperature is increased, the mobility of polymer chain is enhanced, and the fraction of free volume in the polymer electrolyte system increases accordingly, which facilitates the transitional motion of ions[28]. Thus the segmental motion either allows the ions to hop from one site to other site, or it provides pathway for ions to move, which leads to an increase in ionic conductivity of the polymer electrolyte.

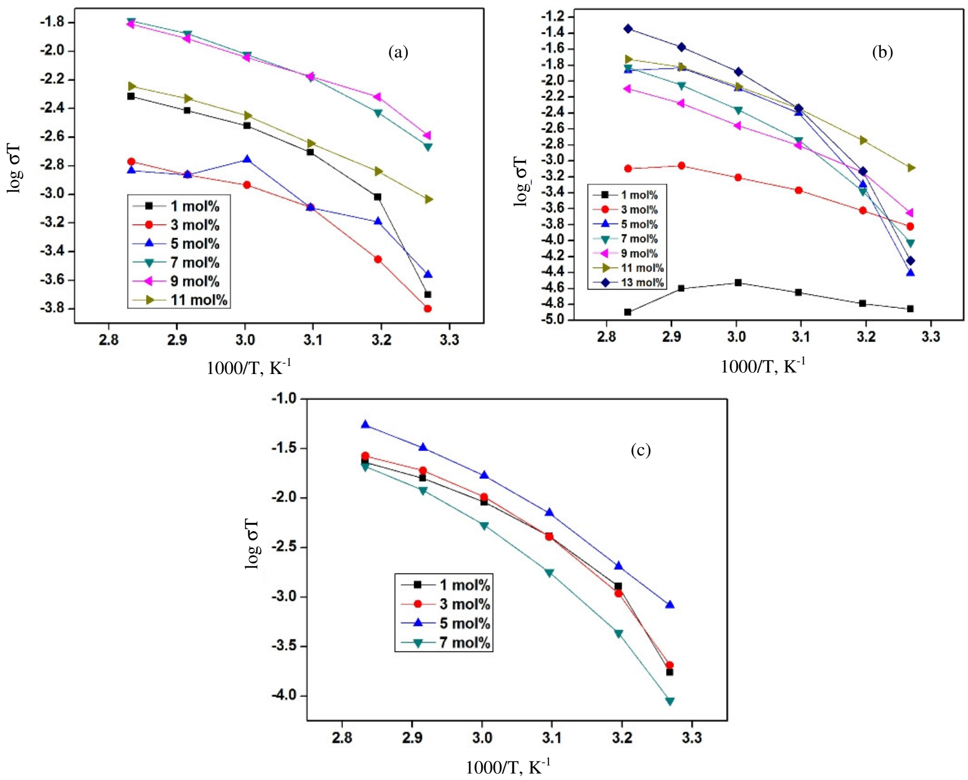

Figure 4. Temperature dependence conductivity of (a) PVP-2ABSA (b) PVP-3ABSA (c) PVP-4ABSA system

The activation energy is calculated for all the prepared polymer electrolytes by linear fit of the Arrhenius plot. The regression values of linear fit of the plots are close to unity (above 0.9) suggesting that the temperature dependent ionic conductivity for some compositions of the PVP-ABSA polymer electrolyte complexes obeys the Arrhenius rule at high temperature. But some compositions of the linear plot have been deviated and their regression values are not close to unity (below 0.8), so that it may be follows free volume based theory.

Table 4. Activation energies for PVP-ABSA polymer electrolyte systems

S. No	Concentration mol%	2ABSA		3ABSA		4ABSA	
		Ea, eV	Regression value	Ea, eV	Regression value	Ea, eV	Regression value
1	1	0.569	0.809	0.172	0.761	0.909	0.886
2	3	0.453	0.879	0.430	0.983	0.940	0.920
3	5	0.317	0.718	1.399	0.864	0.837	0.978
4	7	0.397	0.965	1.099	0.957	1.065	0.960
5	9	0.335	0.957	0.735	0.955		
6	11	0.363	0.977	0.709	0.984		
7	13			1.454	0.903		

The maximum conductivity has been observed $8.44x10^{-6}$ S/cm for 9 mol% 2ABSA – PVP system and the activation energy has been found to be 0.335 eV. The low activation energy for the polymer electrolyte facilitates the fast H^{+} ion motion in the polymer network. It also provides a bigger free volume in the polymer electrolyte system upon increasing the temperature.

Conclusion

PVP – ABSA based polymer electrolytes were prepared by solution – casting method. The ionic conductivity of the electrolytes has been measured by ac impedance technique at different temperature. The influence of the salt concentration on the polymer has been discussed. The maximum conductivity value $8.44x\ 10^{-6}$ S/cm is obtained for PVP – 9 mol% 2ABSA systems and the activation energy has been found to be 0.335 eV.

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