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Optical and Conductivity studies of double salt doped Polymer Electrolyte based on Poly Vinyl Alcohol (PVA)

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Abstract

The recent trends in power sources is developing miniature batteries and fuel cells using polymer electrolytes. It is found that the polymers such as PVA, PEO, PVP, PAN etc., doped with ammonium salts or lithium salts have considerable increase in the ionic conductivity of the polymer electrolytes. In the present study, a new combination of electrolytic materials are used and an analysis is made to know the effect of double salt that is Ammonium chloride (NH_4Cl) and Sodium Chloride (NaCl) dissolved in equal proportions in various concentrations of Poly Vinyl Alcohol (PVA). The polymer electrolytes are prepared using chlorine salts such as Ammonium Chloride and Sodium Chloride, PVA as host polymer and distilled water as solvent by Solution Casting Technique since this technique is an easy and useful technique. The prepared polymer electrolytes in the form of film, optical properties is studied by using Ultraviolet Visible Spectroscopic technique and ion conducting properties using AC Impedance Spectroscopy technique are studied. It is found that as the concentration of PVA is decreased their viscosity also decreased. From the UV- Visible Spectra the direct and indirect energy gap have been found. In present work, when pure PVA doped with NH_4Cl and NaCl the direct band gap and indirect band gap values are 5.57 eV and 5.49022 eV respectively for the highest ionic conducting sample. It is found that band gap value is low for 0.8 PVA: 0.1 NH_4Cl: 0.1 NaCl sample. The addition of double salts did not change much the band gap values of the corresponding single salt doped system. AC Impedance Spectroscopic analysis has been used to calculate the dc conductivity. The observed highest conductivity value is in the plateau region which is 4.786×10^{-8} S cm^{-1} for 1g of PVA doped with 0.1 g of NH_4Cl and NaCl each at room temperature which is the highly viscous liquid. It is also observed that when the concentration of PVA is decreased the conductivity value is also decreased. An exponential decay of dielectric constant is in the frequency region log ω = 4.5 to 5.81. Here, there is a sudden hike in the value of ε' after which it gradually decreases. But ε'' has a well-defined peak after the surge at log ω equal to 5.81 which may be due to a relaxation phenomenon.

Keywords: Double Salt; UV;ACImpedance.

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1.INTRODUCTION

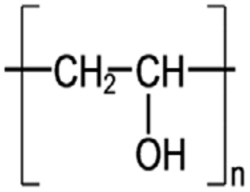
In recent years, researchers are developing miniature batteries, supercapacitors and fuel cells using polymer electrolytes of high ionic conductivity at room temperature. Polymers are the high molecular weight compounds obtained by repeated union of simple molecules. (Monomers). Examples: Starch, Polyvinyl Chloride, Polyethylene, Nylon 6, 6 and etc. This polymer electrolyte should have good mechanical, thermal and optical properties. Polymers such as PVA, PEO, PVP, and PAN etc. are doped with salts [1-6] to have considerable increases in ionic conductivity of the polymer electrolytes. There are various approach to improve the electrical, mechanical, optical and electrochemical properties of the polymer electrolytes.So far research work has been carried out by synthesizing polymer electrolytes doped with single salt; either lithium / metal salts to construct proton batteries [7] or ammonium salts to construct fuel cells.[8] In the present study, a new combination of electrolytic materials are used and an analysis is made to know the effect of double salt that is Ammonium chloride (NH4Cl) and Sodium Chloride (NaCl) dissolved in equal proportions in various concentrations of Poly Vinyl Alcohol (PVA). The polymer electrolytes are prepared using chlorine salts such as Ammonium Chloride and Sodium Chloride, PVA as host polymer and distilled water as solvent by Solution Casting Technique since this technique is an easy and useful technique. [9] In solid state (in the form of film), optical properties by using Ultraviolet Visible Spectroscopic technique and ion conducting properties using AC Impedance Spectroscopy technique are studied.

1.1.1 ELECTROLYTE CONSTITUENT

(i) POLY (VINYL ALCHOL)-HOST POLYMER

Polyvinyl alcohol polymers are well known for various applications. They are widely used for electroplating their ion-exchange properties and also in batteries. Potential applications in early stage of development include their use as electrolyte for capacitor as well as in electrochemical cell.

STRUCTURE OF PVA

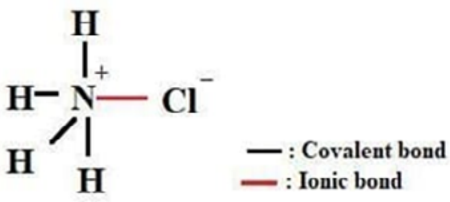


PROPERTIES OF PVA (POLY VINYL ALCHOL)

Alternate Names - PVA, PvOH, Poly (Ethenol), Ethenol, Hemopolymer, Polyviol, Vinol, Alvyl, Alkotex, Covol, Gelvatol, Lemol
Formula - (C2H4O)n
MolecularWeight - 44.05 g/mol
Appearance - White Granular, odorless
Density - 1.19 to 1.31 g/cm3
Solubility -Soluble in water, Glycols (hot), Glycerol (hot),Piperazine, Foramide, DMF, DMSO
Meltingpoint - 513 ° C
Properties - Watersoluble, resistant to solvents, oil and grease, Exceptional adhesion to cellulosic and other hydrophilic surfaces

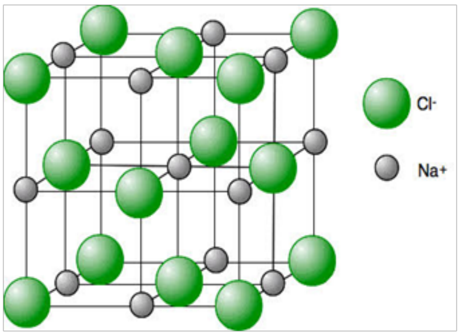
(ii) CHLORINE SALT AS IONIC DOPANT FOR PROTON ELECTROLYTE

(a) STRUCTURE OF AMMOUIUM CHLORIDE



Formula - NH4Cl
MolecularWeight - 53.491 g/mol
Appearance - White crystal solid
Density - 1.53 g/cm3
Solubility - Soluble in water, Ammonia, Alcohol, Methanol, Glycerol, ydrazine
Meltingpoint - 338 o C
Boilingpoint - 520o C

(b) STRUCTURE OF SODIUM CHLORIDE



Formula -NaCl
Molecular Weight -58.44 g/mol
Appearance - White crystal solid
Density - 2.16 g/cm3
Solubility - Soluble in water, Ammonia, Methanol, Glycerol, Formic acid, Propylene glycol, Foramide
Meltingpoint - 801 o C
Boilingpoint - 1465 o C

1.2 EXERIMENTAL TECHNIQUES FOR CHARACTERISATION

1.2.1SOLUTION CASTING METHOD:

This method is the simplest one. The essential criteria for solvent selection is that it should be water-free, having boiling point not more than 65oC and at the same time should be a common solvent for both salt and polymer. The main advantage of this method is that drying can be performed at temperatures of around 65oC. This is necessary since most the polymers used in these studies have a melting point of maximum value around 65oC. Following steps are involved in this method:

a. Addition of polymer in the solvent.
b. Adding salts in the mixture.
c. Mixing by means of magnetic stirrer.
d. Casting the mixture homogeneously on a substance.
e. Finally drying in vacuum.

In present study, ammonium chloride and sodium chloride doped with PVA and dissolved in distilled water as solvent to form thin film electrolytes and the thin film electrolyte have been prepared by solution casting technique to make flexible plastic components. In this technology, the suitable amount of the polymer PVA with different concentrations of weight 1g, 0.9g, 0.8g, 0.7g, 0.6g, 0.5g are dissolved in 40 ml of distilled water and continuously stirred with the help of a magnetic stirrer at 60 o C for 4 hours.

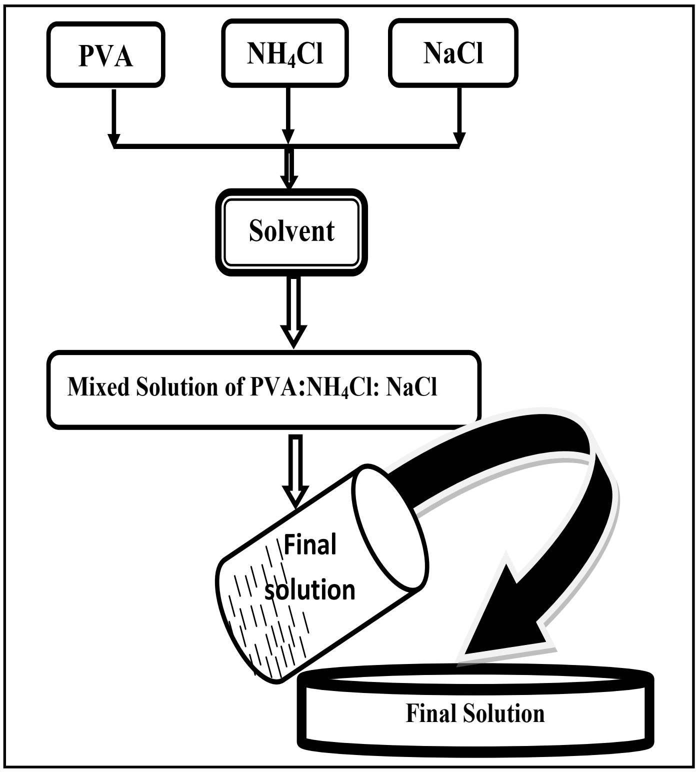


Figure 2.1 Preparation procedure of polymer blend electrolyte

Then the salt NH4Cl and NaCl of weight 0.1 g of each are added and stirred well until they become homogeneous. Then the homogeneous solution is poured in polypropylene petri dishes and kept in vacuum oven for solvent evaporation at 80 o C for three hours. After the complete evaporation of the solvent, the polymer films are carefully removed from the Petri dishes and sealed in air tight cover.

1.3 RESULT AND DISCUSSION

1.3.1 UV-VISIBLE ANALYSIS

The characteristic of electronic band structure of the polymer electrolyte is analyzed using UV-Visible analysis.[10] Figure 3.1. Shows the optical absorption spectra in the region 200 to 896 nm for PVA of different weights 1g, 0.9g, 0.8g, 0.7g, 0.6g and 0.5g with dopants of 0.1g NH4Cl and NaCl of each

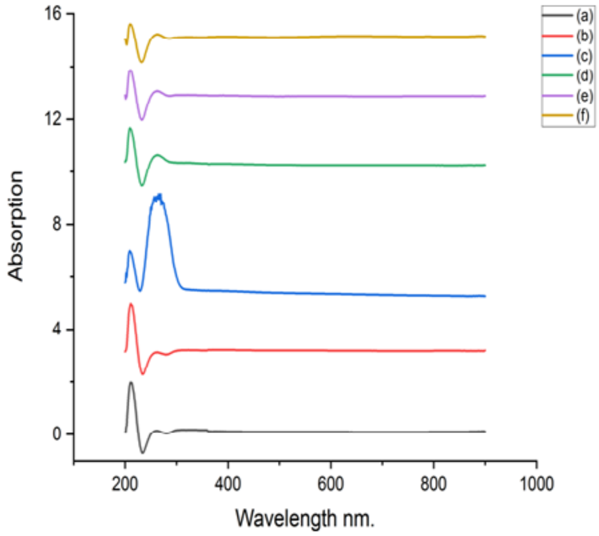


Figure.3.1 Optical absorption spectra of (a) 1g of PVA: 0.1g of NH4Cl and NaCl of each (b) 0.9g of PVA: 0.1g of NH4Cl and NaCl of each (c) 0.8g of PVA: 0.1g of NH4Cl and NaCl of each (d) 0.7g of PVA: 0.1g of NH4Cl and NaCl of each (e) 0.6g of PVA: 0.1g of NH4Cl and NaCl of each (c) 0.5g of PVA: 0.1g of NH4Cl and NaCl of each

In the UV region, the strong absorption bands for the different weights of 1g, 0.9g, 0.8g, 0.7g, 0.6g and 0.5g with the dopants of 1g NH4Cl and NaCl of each are observed at 212nm, 211nm, 210nm, 210nm, 210nm and 210 nm respectively. The absorption band at 210 nm may be attributed to the n → π* transition. [11]

Max Plank Equation is used to calculate energy gap from wavelength. [4]

$$E_g = hc / \lambda$$

Where,

E_g is the band gap energy

h is Planck's constant (6.62 x 10-34Js)

c is velocity of light (2.999 x 108 ms-1)

λ is the wavelength corresponding to the sharp rise in absorption

The width of the band gap are determined using Tauc-Plot method. [12] In this plot energy is on x-axis while $(\alpha h\upsilon)^n$ on y-axis.

Then the target line is drawn on the curve where α =0.

The point where it touch the x-axis is the optical bandgap energy of the material. [1]

Here, α is the absorbance coefficient.

The absorbance coefficient (α) can be calculated using by Beer Lambert's law [12]

α = 2.303 x A (cm^{-1})

The unit of the absorbance coefficient is cm^{-1} and the Absorbance id dimensionless quantity.

Then the Tauc relation for calculating direct bandgap and indirect bandgap is

$(\alpha h\upsilon)^n$ = (Absorbance coefficient x Energy)^n

Its unit is eVcm^{-1}.

For the direct bandgap, n = 2

For the indirect bandgap, n = 1/2

The width of direct optical bandgap and indirect optical bandgap are calculated by plotting the photon energy (hυ) vs $(\alpha h\upsilon)^2$ and the photon energy (hυ) vs$(\alpha h\upsilon)^{1/2}$ respectively.

From the table, it is seen that the direct band gap value is from 4.2116 to 5.649 and the indirect band gap value is from 4.0666 to 5.5627.

Many researchers has reported that, for pure PVA the direct band gap energy is 5.44 eV and indirect band gap energy is 4.84 eV. [1] But in present work, when pure PVA doped with NH4Cl and NaCl the direct band gap and indirect band gap values are 5.57 eV and 5.49022 eV respectively for the highest ionic conducting sample. It is found that band gap value is low for 0.8 PVA: 0.1 NH4Cl: 0.1 NaCl sample.

1.3.2 AC IMPEDANCE ANALYSIS

AC Impedance Spectroscopy is used to analyze electrical properties of ion (Sodium ion and Proton) [1] conducting material. In terms of emittance parameters, the total conductivity of various contributions are described. All these parameters are used to analyze the conductivity of various PVA conduction with 0.1g of NH4Cl and 0.1g of NaCl polymer electrolytes as a function of frequency.

(i) CONDUCTANCE SPECTRA ANALYSIS

The conductance Spectra analysis determines the DC conductivity of the ions present in polymer electrolytes because the AC conductivity spectra obeys Jonschers Universal power law. [13]

Figure 3.3 shows a conductance spectra which depends on frequency at different concentration of PVA with 0.1 g of NH4Cl and NaCl each at room temperature.

Plateau region is observed for log ω values is between 4.5 to 5.81 above that there is a sudden increase in the conductivity value and again a plateau region is observed for log ω value approximately equal to 6.11.

Most of the researchers reported that, when PVA is doped with Ammonium Chloride, the ionic conductivity of the (PVA-NH4Cl) is in the order of 10-3 S cm-1 and when PVA is doped with Sodium Chloride, the ionic conductivity of the (PVA-NaCl) is in the order of 10-4 S cm-1. Even though NH4Cl doped system had conductivity in the order of 10-3 S cm-1 and NaCl doped system had conductivity in the order of 10-4 S cm-1[1], in the present work, the conductivity is found to be low which is 4.786 x 10-8 S cm-1 for pure PVA doped with 0.1g of NH4Cl and NaCl each. It is also observed that when the concentration of PVA is decreased the conductivity value is also decreased.

Table 3.2. The direct bandgap and indirect bandgap of the various concentration of PVA and 0.1 g of NH4Cl and NaCl of each are tabulated.

Sample PVA:NH4Cl:NaCl(by weight in g)	Band Gap Energy (eV)	
	Direct	Indirect
1:0.1:0.1	5.5714	5.4902
0.9:0.1:0.1	5.5883	5.3671
0.8:0.1:0.1	4.2116	4.0666
0.7:0.1:0.1	5.6206	5.4323
0.6:0.1:0.1	5.6498	5.5540
0.5:0.1:0.1	5.0885	5.5627

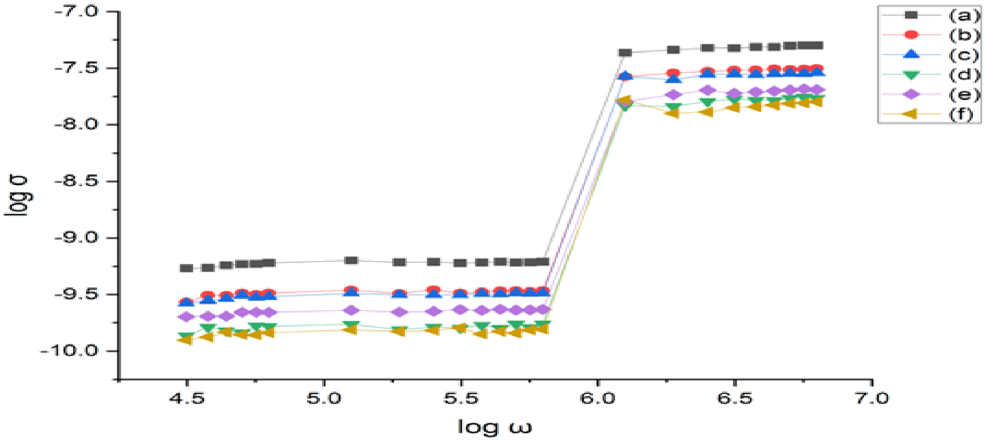


Figure 3.3. Conductance spectra shows high frequency response od conductance (a) 1g of PVA: 0.1g of NH4Cl and NaCl of each (b) 0.9g of PVA: 0.1g of NH4Cl and NaCl of each (c) 0.8g of PVA: 0.1g of NH4Cl and NaCl of each (d) 0.7g of PVA: 0.1g of NH4Cl and NaCl of each (e) 0.6g of PVA: 0.1g of NH4Cl and NaCl of each (c) 0.5g of PVA: 0.1g of NH4Cl and NaCl of each

Table 3.4. DC conductivity for all the sample in the high frequency plateau region is tabulated below

Sample PVA:NH4Cl:NaCl(by weight in g)	Conductivity (S cm-1)
1:0.1:0.1	4.786 x 10 -8
0.9:0.1:0.1	3.236 x 10 -8
0.8:0.1:0.1	2.692 x 10 -8
0.7:0.1:0.1	2.042 x 10 -8
0.6:0.1:0.1	1.698 x 10 -8
0.5:0.1:0.1	1.349 x 10 -8

(ii) DIELECTRIC SPECTRA ANALYSIS

The study of dielectric properties concerns the amount of charge stored by a material. This dielectric used as an indicator to prove that the increase in conductivity is due to an increase in the charge carriers or free mobile ions. When the materials dielectric property increases the amount of charge stored in the materials also increases. Dielectric spectrum is used to study the response of a polymer electrolyte when the frequency is changed or electric field is applied. The dielectric response is described by the complex permittivity.

$$\varepsilon = \varepsilon' - i\,\varepsilon''$$

where, real ε’ is the storage of energy in each cycle of applied electric field and the imaginary ε” is the loss of energy in each cycle of applied electric field. [11]

Many researchers have reported an exponential decay of dielectric constants in the frequency region log ω equal to 2 to 7. [1] But in the present study this exponential decrease in ε’ and ε” is found in the frequency region from log ω equal to 4.5 to 5.81. Above this frequency there is a sudden hike in the value of ε’ after which it gradually decreases. But ε” has a well-defined peak after the surge at log ω equal to 5.81. It indicates a relaxation phenomenon. [1]

1.4 SUMMARY AND CONCLUSION

New polymer electrolytes with PVA as polymer doped with double salt Ammonium chloride and sodium chloride with distilled water as solvent by solution casting technique are synthesized which are flexible plastic films. Keeping the salt content and the volume of the solvent constant, the polymer amount is varied and six samples are prepared and when PVA is decreased their viscosity also decreased. From the UV- Visible Spectra the direct and indirect energy gap have been found. The addition of double salts did not change much the band gap values. AC Impedance Spectroscopy analysis has been used to calculate the conductivity. The observed highest conductivity value is 4.786 x 10^{-8} S cm-1 for 1g of PVA doped with 0.1 g of NH_4Cl and NaCl each at room temperature whereas NH_4Cl doped system had conductivity in the order of 10^{-3} S cm^{-1} and NaCl doped system had conductivity in order of 10^{-4} S cm^{-1}. The conductivity study conclude that the conductivity of electrolyte is affected greatly when the double salts are used. An exponential decay of dielectric constant is in the frequency region 4.5 to 5.81.

Figure 3.4. shows the variation of Ɛ' and Ɛ" with frequency.

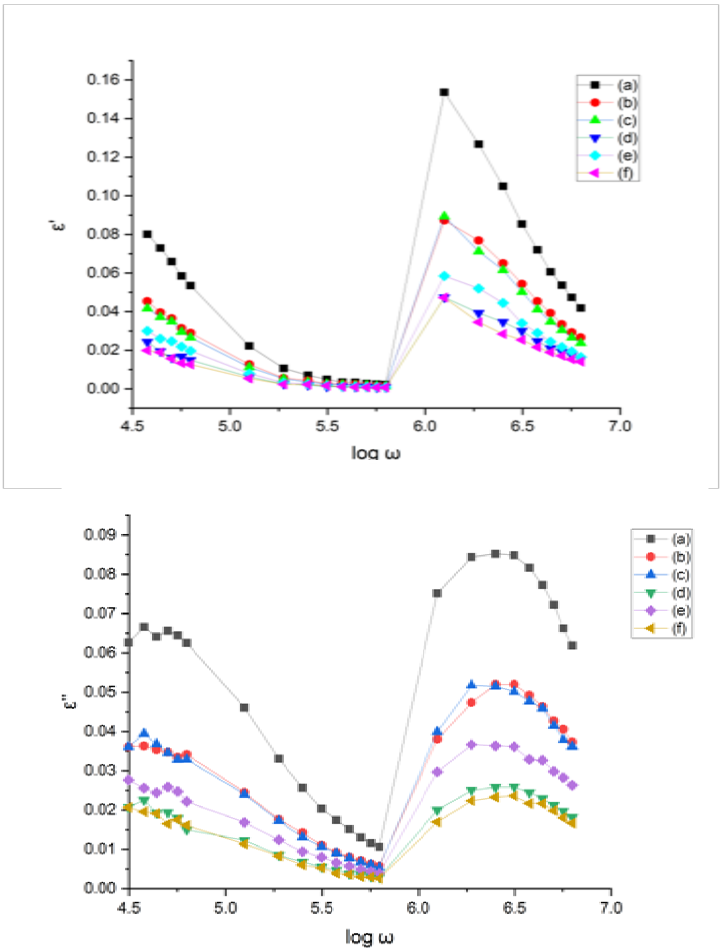


Figure 3.4. Dielectric spectra of Ɛ’ and Ɛ” with variation in frequency. (a) 1g of PVA: 0.1g of NH4Cl and NaCl of each (b) 0.9g of PVA: 0.1g of NH4Cl and NaCl of each (c) 0.8g of PVA: 0.1g of NH4Cl and NaCl of each (d) 0.7g of PVA: 0.1g of NH4Cl and NaCl of each (e) 0.6g of PVA: 0.1g of NH4Cl and NaCl of each (c) 0.5g of PVA: 0.1g of NH4Cl and NaCl of each

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