

Studies on electrical conductivity and dielectric behaviour of PVdF–HFP–PMMA–NaI polymer blend electrolyte

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Abstract. Polymer blend electrolytes composed of poly(vinylidene fluoride-co-hexafluoro-propylene), poly(methyl methacrylate) and 1.0 M NaI as salt have been synthesized using solution cast technique by varying the PVdF(HFP)–PMMA blend concentration ratio systematically. A.c. impedance studies were performed to evaluate the ionic conductivity of the polymer electrolyte films. The highest ionic conductivity at room temperature for [PVdF(HFP)–PMMA(4:1)](20 wt%) – [NaI(1.0 M)](80 wt%) system is found to be $1.67 \times 10^{-2} \text{ S cm}^{-1}$. XRD studies reveal complete complexation of the salt in the polymeric blend systems. The temperature dependence conductivity has been performed in the range of 303–373 K and it is observed that it obeys the Arrhenius behaviour. It has been observed that the dielectric constant, ϵ_r and dielectric loss, ϵ_i , increases with temperature in the lower frequency region and is almost negligible in the higher frequency region. This behaviour can be explained on the basis of electrode polarization effects. Plot of real part, M_r and imaginary part, M_i vs frequency indicates that the systems are predominantly ionic conductors. The phenomenon suggests a plurality of relaxation mechanism.

Keywords. Polymer blend electrolytes; PVdF(HFP)–PMMA–NaI; impedance studies.

1. Introduction

The conducting polymer electrolytes have been intensely interesting to physicists, chemists and engineers because of their fundamental physical properties and potential application in various electrochemical devices such as fuel cells, supercapacitor, sensors and display devices (Gray 1991). The development of polymer electrolytes has gone through three stages which are dry solid-state polymers, gel/plasticizer polymer electrolytes systems and composite polymer electrolytes system.

The first category of solid polymer electrolytes e.g. PEO based electrolyte system, shows very low ambient temperature conductivities of the order of $10^{-8} \text{ S cm}^{-1}$ (Fenton *et al* 1973).

The second category of polymer electrolytes is known as gel polymer electrolytes or plasticized polymer electrolytes which consists of both the properties of liquid and solid phases in the same electrolytes system. Combination of both properties i.e. the cohesive properties of solid and the diffusive properties of liquids give unique characteristics of the gel to find various important applications including polymer electrolytes (Bruce and Gray 1995).

Third category of polymer electrolytes are composite electrolytes. These are new categories of multiphase solid systems in which two or more materials are mixed together

to achieve improvement in its mechanical, thermal stability and high ionic conductivity of the polymer electrolytes. The polymer blending is one of the most promising and feasible ways to improve the ionic conductivity, flexibility and mechanical strength of the composite systems. When two or more polymers give rise to a homogeneous mixture, miscible or compatible blend is formed in which one polymer is adopted to absorb the electrolytes active species while another remains as an undissolved inert second phase providing toughness to the polymer electrolytes films (Berthier *et al* 1989).

Many lithium ion based blend polymer electrolyte systems have been studied and reported in the literature. Among them are PVdF–HFP/PMMA (Lee and Park 2000), PVAc/PVdF–HFP (Ulaganathan and Rajendran 2010), PVAc/PMMA (Rajendran *et al* 2010), PVC/PEO (Ramesh *et al* 2007), PVAc/PMMA (Baskaran *et al* 2004, 2006), PVA/PMMA (Rajendran and Sivakumar 2008), PVdF/PVC (Rajendran *et al* 2008), PVC/PMMA (Lee and Park 2000), PVdF–HFP/PAN (Subramania *et al* 2006) and PVdF–HFP/PVAc (Choi *et al* 2001), PVDF–HFP/PEG (Lee *et al* 2003) blend based electrolytes system. These electrolytes are of great importance, because of its possible application in different energy storage/conversion devices, particularly in rechargeable batteries. Many research articles are available which incorporates sodium ion in its polymeric system for its application as electrolyte materials in sodium batteries (Wang *et al* 2007; Kim *et al* 2008). There also exists some sodium ion conducting polymer electrolytes based on poly-ethylene-oxide (PEO) and poly-propylene-

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oxide (PPO) complexed with NaSCN, NaI, NaClO₃, NaPF₄, NaYF₄, NaCF₃SO₄, NaNO₃ and NaClO₄ (Sreepathi Rao *et al* 1995; Sreekanth *et al* 1999) which has been reported for its application as electrolyte materials in sodium batteries. Usually, low-evaporation solvents, like organic solvents, ethylene carbonate, propylene carbonate (PC), dimethyl carbonate (DEC), dimethyl formamide (DMF), dimethyl carbonate (DMC) etc are used as plasticizers (Agrawal and Pandey 2008). The plasticizers should possess some specific properties like an increase in conductivity, increases of amorphous regions, a wide redox stability, ionic mobility, behaviour of cells etc (Sheldon *et al* 1989; Michael *et al* 1997).

In the present study, PVdF–HFP/PMMA polymer blend electrolytes were prepared by incorporating NaI as the doping salt. PVdF–HFP has been chosen because of its appealing properties. It has high dielectric constant, ϵ' , of 8.4 reported by Lee and Park (2000) which occurred in two phases (amorphous and crystalline). Amorphous phase enhances higher ionic conduction in the system meanwhile crystalline phase provides strong mechanical support to the polymer electrolytes (Stephan *et al* 2006; Hwang *et al* 2007). In order to improve the ionic conductivity, PMMA was used because it has good amorphous and compatible nature. It is also known that PMMA gels were found to have better interfacial properties for electrodes and provides good mechanical properties with another polymer. Poly (methyl methacrylate) (PMMA) was first reported by Iijima *et al* (1985). Sodium is much more abundant and lower priced than lithium and the softness of sodium metal promotes the stability of electrode – electrolytes interface in solid state ionic devices (Hunter and Ingram 1984).

Combining all of the above said properties of polymers and salt, we have chosen PVdF(HFP)–PMMA–NaI based blend system for our present investigations.

2. Experimental

2.1 Sample preparation

The polymer blend electrolyte has been prepared by using polymers, PVdF–HFP with an average molecular weight of 4,00,000 (Aldrich), PMMA with an average molecular weight of 1,30,000 (Aldrich) and inorganic salt, NaI (Merck) which has been used as such without further purification. DMF (*N–N* dimethyl formamide) has been used as the solvent (Deepa *et al* 2002). The polymer films were developed by using the well known solution cast techniques. The mixture of polymers and doping salt in suitable amounts were stirred continuously with a magnetic stirrer for 10 h at a temperature of 60 °C until homogenous solutions were obtained. The solutions were poured into glass petri dishes and left to dry at room temperature to form a film for about 35–40 days. The films were kept in desiccators for further drying.

2.2 Conductivity measurement

To study the conductivity behaviour of the polymer electrolytes, impedance spectroscopy was performed using LCR HiTESTER [HIOKI, 3522–50, Japan]. The samples were cut into a proper size and sandwiched between two stainless steel electrodes. The conductivity (σ) was calculated using the following equation

$$\sigma = t/R_b A, \quad (1)$$

where t is the thickness of the electrolyte, A the electrolytes contact area and R_b the bulk resistance which was obtained from the plots of real impedance Z' against imaginary impedance Z'' . The mathematical equation of impedance can be written as

$$Z^* = Z' + i Z'' \quad (2)$$

Using the impedance data, the dielectric constant (ϵ^*), electrical modulus (M^*) was obtained using the following equations.

$$\epsilon'(\omega) = Z''/\omega C_0 (Z'^2 + Z''^2), \quad (3)$$

$$\epsilon''(\omega) = Z'/\omega C_0 (Z'^2 + Z''^2), \quad (4)$$

$$M'(\omega) = \epsilon'/(\epsilon'^2 + \epsilon''^2), \quad (5)$$

$$M''(\omega) = \epsilon''/(\epsilon'^2 + \epsilon''^2), \quad (6)$$

where ϵ_0 is vacuum space permittivity, ϵ' the dielectric loss and ω the $2\pi f$, f is the frequency in Hz, $C_0 = \epsilon_0 A/t$, A is the electrode–electrolyte contact area and t the thickness of electrolyte.

X-ray diffraction patterns were recorded at room temperature by Bruker Advance (D8) X-ray diffractometer with Cu K α radiation over a Bragg angle (2θ) range of 10°–60°.

3. Results and discussion

3.1 X-ray diffraction studies

In order to examine the influence of PMMA contents on the semicrystalline structure of PVdF–HFP based blend polymer electrolyte system, the X-ray diffraction patterns of pure NaI salt, PVdF–HFP, PMMA, PVdF–HFP/PMMA blend polymer films recast from its DMF, PVdF–HFP/PMMA/NaI blend polymer electrolytes film are shown in figure 1. XRD pattern of the PVdF–HFP film shows typical characteristic of a semicrystalline microstructure i.e. the co-existence of mixed crystalline and amorphous regions with predominant peaks at $2\theta = 20^\circ$ and 38° (Saikia and Kumar 2004). Further the absence of sharp Bragg peaks and the presence of broader peaks in XRD pattern of PMMA shows predominant amorphous nature of the PMMA polymer (figure 1c). It is observed that when PVdF–HFP is blended with PMMA,

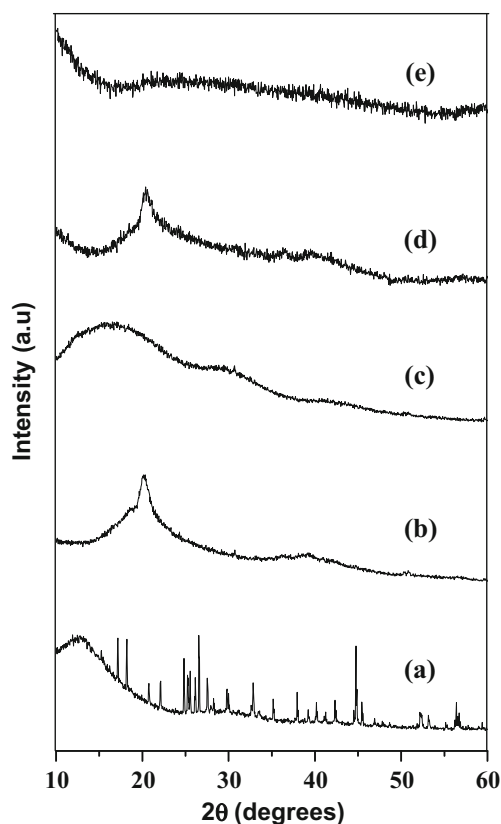


Figure 1. XRD spectra of (a) pure NaI, (b) PVdF(HFP) film, (c) PMMA film, (d) PVdF(HFP)/PMMA optimized film and (e) PVdF(HFP)/PMMA/NaI optimized film.

no additional peak in the blend system appears, but only the intensity of crystalline peak of the PVdF–HFP decreases (figure 1d), suggesting that the amorphicity of the blend system increases to some extent (Leo *et al* 2002). Finally, it is observed that by mixing of NaI with PVdF–HFP/PMMA blend, the NaI and PVdF–HFP peaks get completely disappeared in the optimized composition of polymer blend electrolytes (figure 1e). This indicates that the salts, NaI most likely blends with the PVdF–HFP/PMMA polymer blend at the molecular level and it gives a clear indication of complexation of the salt in the polymer blend system.

3.2 Polymer concentration dependence conductivity

Figure 2 shows variation of ionic conductivity of PVdF(HFP)–PMMA–NaI polymer blend electrolyte system. It is observed that [PVdF(HFP) (80 wt%)–PMMA (20 wt%)] (20 wt%)–[NaI (1.0 M)] (80 wt%) composition of polymer blend electrolytes having free-standing film exhibits maximum conductivity of about $1.67 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature. They are very much suitable for device fabrication. The maximum conductivity is due to the proper PVdF(HFP)–PMMA polymer blend and salt interaction. Higher conductivity in polymer electrolyte system could be attributed to the higher amorphicity due to steric hindrance.

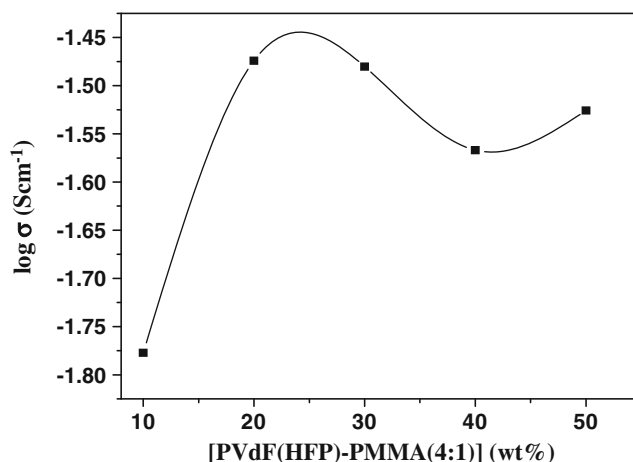


Figure 2. Variation of ionic conductivity of blend polymer electrolyte PVdF(HFP)–PMMA–NaI as a function of different weight percent of [PVdF(HFP)–PMMA](4:1 wt %) polymer blend concentration.

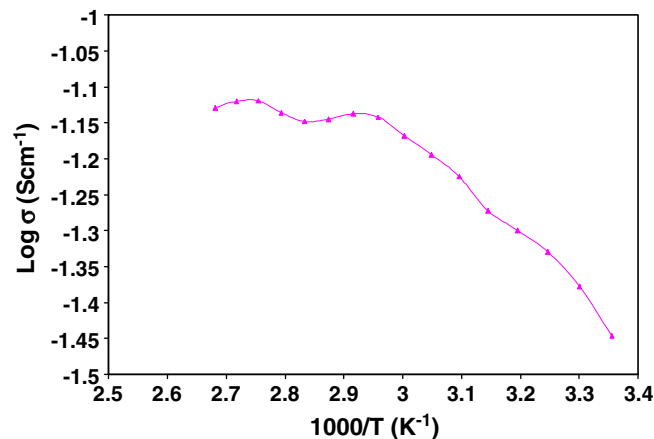


Figure 3. Variation of ionic conductivity of blend polymer electrolyte [PVdF(HFP)–PMMA(80:20)] (20 wt%)–[NaI(1M)] (80 wt%) as a function of different temperatures.

Higher amorphicity provides mobile Na^+ ion more free volume giving rise to higher conductivity of the electrolyte system.

3.3 Temperature dependence conductivity

Figure 3 shows temperature dependent ionic conductivity of polymer electrolytes system. From the plot it is evident that as the temperature increases the ionic conductivity also increases for the complex systems. The increase in conductivity with temperature may be due to the decrease in viscosity and hence increased chain flexibility (Michael *et al* 1997). The conductivity pattern shows almost Arrhenius behaviour up to 70°C which can be expressed as

$$\sigma = \sigma_0 \exp(-E_a/kT),$$

where σ_0 is the pre-exponential factor, E_a the activation energy and T the absolute temperature in Kelvin scale. The activation energy is found to be of the order of 0.06 eV in polymer electrolyte system which has been calculated by fitting the curve in lower temperature region up to 70 °C. The variation in ionic conductivity with temperature has been explained in terms of segmental motion that results in an increasing free volume of the sample and hence the motion of ionic charge. The amorphous nature of polymer blend provides a greater free volume of the system upon increasing the temperature (Tsunemi *et al* 1983). Thus the segmental motion either permits the ions from one site to another or provides the pathway for ions to move. This inter-chain or intra-chain ion movements are responsible for high ionic conductivity.

3.4 Dielectric analysis

Figures 4(a) and (b) show dielectric constant (ϵ') and dielectric loss (ϵ'') as a function of frequency at various temperatures for polymer blend electrolytes [PVdF(HFP) (80 wt%) – PMMA (20 wt%)] (20 wt%) – [NaI (1.0 M)] (80 wt%) system. Both the dielectric constant and dielectric loss part increase with decreasing frequency. This is attributed to the high contribution of charge accumulation at the electrode–electrolytes interfaces (Baskaran *et al* 2004). At higher frequencies the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field. Hence the polarization due to charge accumulation decreases and results in a decrease in both the dielectric constant and dielectric loss. The increase in the

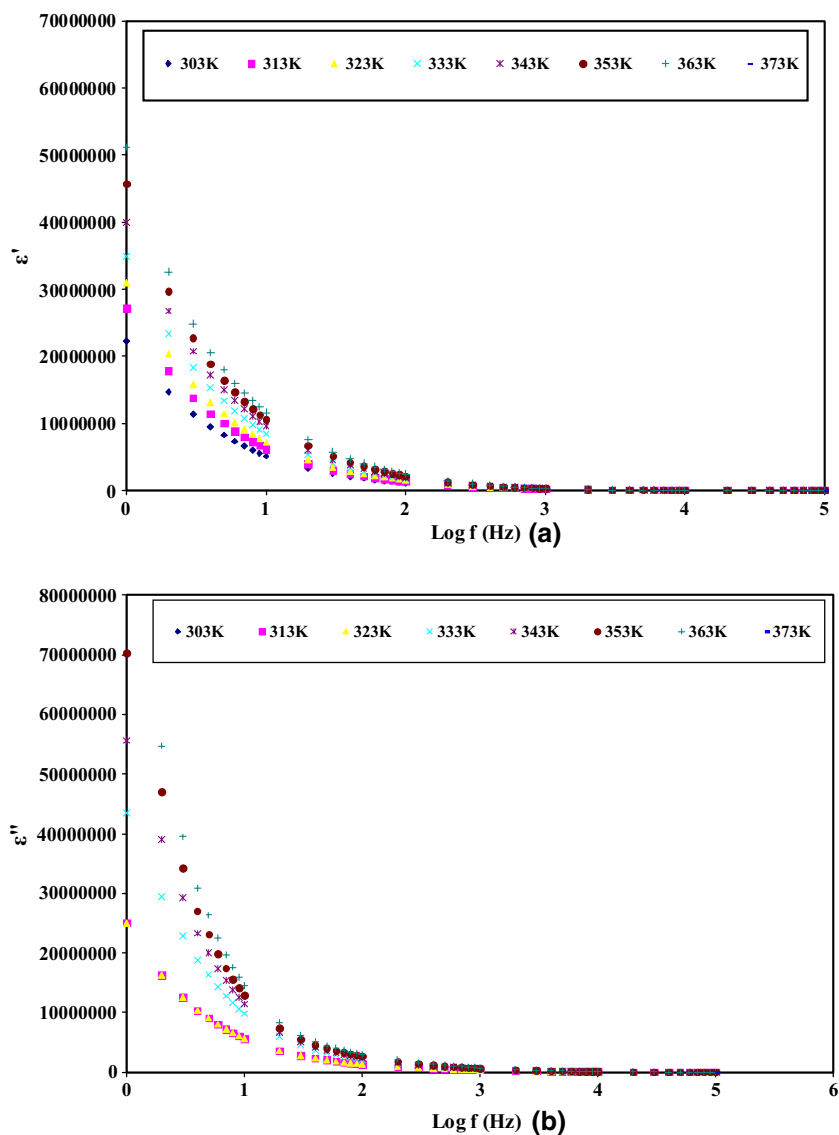


Figure 4. Variation of (a) dielectric constant; and (b) dielectric loss of polymer blend electrolyte system [PVdF(HFP)–PMMA (80:20)] (20 wt%)–[NaI (1M)] (80 wt%) at different frequencies.

dielectric constant and dielectric loss with temperature can be attributed to the increase in charge carrier density due to the increase in dissociation of ion aggregates.

3.5 Modulus spectra

Figures 5(a) and (b) show the real part (M') and imaginary part (M'') of electrical modulus as a function of frequency at various temperatures for polymer blend electrolytes. Both M' and M'' are observed to increase in the high frequency region and give a long tail at lower frequencies. The peaks in the modulus formalism at high frequencies show that the polymer electrolytes films are ionic conductors. The peak curve at higher frequencies may be due to bulk effect. It is observed from the plots that M' and M'' decrease towards low frequen-

cies. This is due to the electrode polarization phenomenon which makes a negligible contribution. The plots that show long tails at low frequencies are probably due to their large capacitance values associated with the electrodes.

3.6 Conductance spectra

The conductance spectra for [PVdF(HFP) (80 wt%) – PMMA (20 wt%)] (20 wt%) – [NaI (1.0 M)] (80 wt%) polymer blend electrolytes with different temperatures is shown in figure 6. The spectra consist of two regions, a low frequency dispersive region due to electrode–electrolyte interfacial phenomena and the plateau representing the d.c. conductivity. As the frequency decreases, more and more charge accumulation occurs at the electrode–electrolyte interface

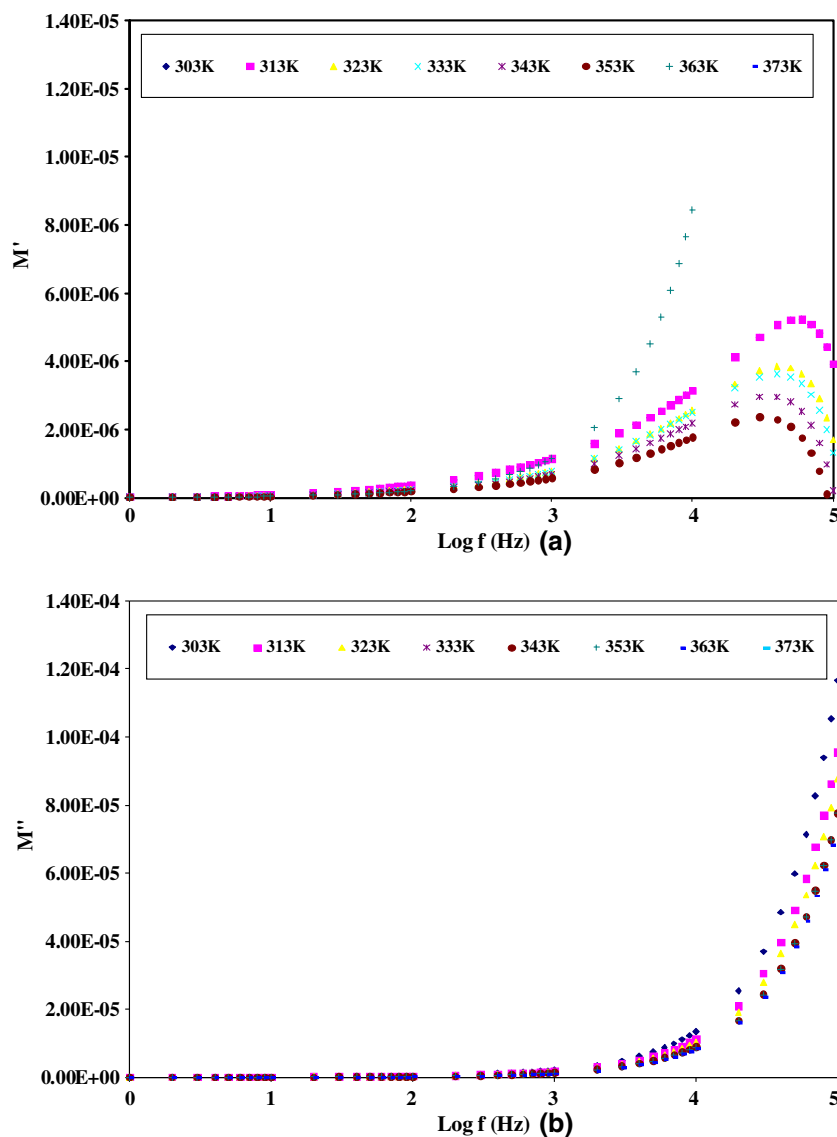


Figure 5. Variation of (a) real part and (b) imaginary part of electrical modulus for [PVdF(HFP)–PMMA (80:20)] (20 wt%)–[NaI (1M)] (80 wt%) based polymer blend electrolyte system at different frequencies.

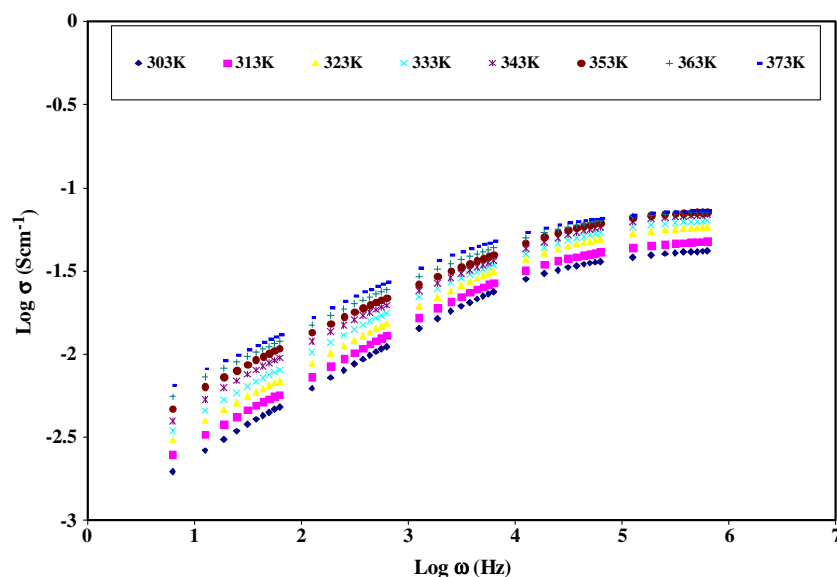


Figure 6. Variation of ionic conductivity for polymer blend electrolyte system [PVdF(HFP)–PMMA (80:20)] (20 wt%)–[NaI (1M)] (80 wt%) at different frequencies.

which leads to decrease in number of mobile ions and eventually to a drop in conductivity at low frequency. In high frequency region, the mobility of charge carriers is high and hence the conductivity increases with frequency (Ramesh and Arof 2001). It has been observed that the d.c. conductivity increases with temperature which suggests that the free volume around the polymer chain causes the mobility of ions and polymer segments (Miyamoto and Shibayama 1973).

4. Conclusions

The polymer blend electrolytes PVdF(HFP)–PMMA–1M NaI with different compositions have been prepared by solution cast technique. The highest conductivity, $\sigma = 1.67 \times 10^{-2} \text{ S cm}^{-1}$, at room temperature is obtained for PVdF(HFP):PMMA(80:20) polymer blend system. XRD studies show complete complexation of the salts in the polymer blend system. The dielectric and a.c. conductivity of the sample was studied and it was found that the synthesized polymer blend electrolyte material is suitable having acceptable properties for its application in energy storage/conversion devices like batteries, supercapacitor, fuel cell, solar cell etc. The polymeric system under present investigation is a very promising material for its application as electrolyte materials particularly in sodium batteries by offering ionic conductivity of the order of $10^{-2} \text{ S cm}^{-1}$.

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