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Spectroscopic characterization of a gel polymer electrolyte of zinc triflate and polyacrylonitrile

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Abstract

Fourier transform Raman spectroscopy has been used to understand the changes in the zinc ion co-ordination in the gel polymer electrolyte comprising polyacrylonitrile (PAN), ethylene carbonate (EC), propylene carbonate (PC) and zinc triflate (ZnTr). The metal ions tend to co-ordinate with the solvents that manifest in the form of a shift in the wavenumbers of the ring-breathing vibrational mode of the EC. Band shape analysis clearly indicates a strong interaction of the metal ion with the plasticizers. Once the plasticizer is removed, an interaction between the metal ions and the polymer matrix is observed that manifests in the splitting and shift of CN stretching band to higher wave numbers. Presence of ion-pairs and aggregates is confirmed by analyzing the triflate-stretching band. Curve fitting analysis clearly separates out different ionic components. A correlation between the ionic conductivity values and their variation with respect to increasing salt concentration has been found and it is in tune with the spectroscopic results.

Keywords: Gel polymer; Polyacrylonitrile; Solid electrolyte

1. Introduction

Research in the area of solid polymer electrolytes (SPE) stems from the idea suggested by Wright [1] and Armand [2] where PEO complexed with various metal ions has been shown to possess good ionic conductivity. There has been a considerable amount of research both from a fundamental point of view in understanding the mechanism of ion transport and also from an application point of view in enhancing the performance of devices based on solid electrolytes [3]. Research on SPEs using vibrational spectroscopy would yield information on the ion–polymer, ion–ion and ion–solvent interactions that forms the basis of understanding the mechanism of ionic conduction in SPEs or gel polymer electrolytes (GPE) [4–6]. A well-studied system is polyethyleneoxide (PEO) complexed with different lithium salts [7]. Among the anions, triflate ($CF_3SO_3^-$) is used to probe the finer aspects of the conduction mechanism [8].

Raman spectroscopy has been used as an excellent tool to probe information at the molecular level [9]. This technique is quite sensitive to molecular and intermolecular motions like vibrations, rotations etc. [10]. There have been a lot of computational studies [11,12] on different polyatomic anions to understand the nature of interactions and also determine the minimum-energy geometries, symmetries and their interactions with cations. Interactions between cation–anion and their subsequent changes on the vibrational modes have been calculated [13]. Thus, the results from computational studies can be used to interpret the experimental data concerning shifts and splitting of various vibrational modes upon complexation of the matrix with cations and also to determine the effect of plasticizers in polymer–salt mixtures [14]. Raman scattering studies involving triflate salts reveal that the symmetric SO_3 stretching and the symmetric CF_3 deformation modes of the triflate anion either split or shift in frequency in a triflate salt–solvent–polymer complex as compared to the behaviour of the corresponding free triflate salts in the solvent alone [15]. This is a direct proof that the triflate ions are in different environment in the host polymer and is attributed to the presence of free ions, ion-pairs and multiple aggregates. The SO_3 stretching component observed at 1032 cm^{-1} has been assigned to free anions while the bands

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at 1042 and 1052 cm^{-1} are assigned to contact ion-pairs and aggregates (triple-ions), respectively [16,17]. The analysis of CF_3 band also yields similar information [18]. Studies based on other polyatomic anions like perchlorate (ClO_4) [19] and TFSI ($((CF_3SO_2)_2N^-)$) [20] have also been reported. The symmetric mode [21] (SO_3) of triflate anion is often chosen for the studies since it is non-degenerate thus avoiding complications involved in the lifting of degeneracy in an ionic environment. Band shape and band area analysis of this split component is a direct fingerprint of their environment [22].

Polyacrylonitrile (PAN) [23] based systems containing lithium salts with different counter anions have also been reported [24]. A variety of plasticizers like EC, PC, dimethylformamide (DMF), dimethyl sulfoxide (DMSO) [25] and a mixture of them have been used in this study. Chen and co-workers [26] have reported the mechanism of lithium ion transport in GPEs [27]. The studies clearly indicate that there is a strong interaction between the plasticizer and the Li^+ ion. There is a strong affinity of the metal ion with the plasticizer as compared to the polymer matrix and once the plasticizer is removed from the gel electrolyte, apparent interaction is observed between the metal ion and the polymer matrix. Thus, there is a competition between the polymer and the plasticizer to co-ordinate with the metal ion [28]. The plasticizer seems to dominate the interaction.

It is of prime interest to understand whether the cation is co-ordinated with the anion, the plasticizer or with the polymer chain. This will, in turn, dictate the ionic conductivity of the matrix. Each of the coordination will give different species having its own characteristics in the Raman spectra. Thus, vibrational spectroscopy is an appropriate tool for monitoring the coordination of metal ions. Certain bands, which are very specific to co-ordinating species, have been observed to split or shift to different frequencies on co-ordination with the cation [29].

Studies on zinc-based systems are important both from a fundamental and also from an application point of view, especially in areas related to batteries where exhaustive literature is available [30]. Although the zinc electrode potential is only -0.76 V versus SHE with an electrochemical equivalence of 0.82 Ah g^{-1}, there are several advantages associated with zinc-based devices. They are (i) natural resources of zinc are plentiful (ii) zinc is less-toxic, very stable and can be handled safely in oxygen and humid atmosphere (iii) zinc based devices would have high specific and volumetric energy density (iv) safety problems associated with zinc metal are minimal and (v) ionic radii of Li^+ (68 pm) and Zn^{2+}(74 pm) are comparable and hence, insertion compounds used for lithium ions may be used for Zn^{2+}. Although there is considerable amount of data available on the aqueous, alkaline-based electrolytes for rechargeable zinc systems, the study of SPEs related to zinc batteries are scanty [31,32]. Various electrolytes based on PEO such as PEO–$ZnBr_2$, PEO–KOH mixture, polyvinyl alcohol (PVA)—proton/iodide systems have been reported in combination with zinc anode and various cathodes such as V_6O_{13}, MnO_2, *N*,*N*′-dichlorohydantoin and dichloroisocyanuric acid [33]. Recently, we have synthesised a GPE based on PAN and zinc triflate and the gel films are shown to possess good ionic conductivity. The application of the GPEs in rechargeable batteries has also been reported [34].

In the present study, we have spectroscopically characterized the GPEs containing Zn^{2+}ions and PAN matrix that is optimized to contain minimum amount of liquid components. A quantitative band shape analysis has been performed for a series of gel electrolytes with different compositions to understand the formation of the ion-pairs and higher aggregates that are responsible for ionic conductivity.

2. Experimental

2.1. Preparation of the gel polymer films

Polyacrylonitrile (PAN), propylene carbonate (PC), ethylene carbonate (EC) and zinc trifluoromethanesulfonate (zinc triflate, Zntr) were purchased from Aldrich, USA. The solvents PC and EC were vacuum distilled at 110 °C and ZnTr was vacuum dried at 120 °C before use. A mixture containing PAN (0.25 g), PC (0.6 g), EC (0.6 g) and with varying concentrations of ZnTr (0.15–2.5 M) was stirred till a suspension was obtained. On heating this suspension to about 100 °C, a homogeneous solution was formed. This, on subsequent cooling, resulted in a homogeneous film (GPE) [34]. For Raman measurements, the suspension was cast on to a thin transparent glass plate and the thickness of the polymer film was maintained constant for all the samples.

2.2. Techniques

2.2.1. FT-Raman spectroscopy

FT- Raman spectra were recorded on a Bruker RFS-100/S FT-Raman spectrometer. A laser power of 250 mW with a radiation spot of 0.1 mm in diameter was used. The excitation wavelength was 1.064 μm in a 180 degree back scattering geometry at room temperature. A Ge detector, which was cooled to liquid nitrogen temperature, was used. Each spectrum was an average of 512 scans with a wave number resolution of 2 cm^{-1}. Spectral analysis was carried out by fitting the bands to a multiple gaussian function after correcting the base line using origin 6.0 software.

2.3. Conductivity measurements

Symmetrical cells, SS/GPE/SS where SS is stainless steel, were assembled in teflon holders and contained in airtight glass containers. The ambient temperature of the cells was maintained at 27 ± 1 °C. Temperature inside the glass container was measured with an accuracy of ± 1 °C.

The symmetrical cells were subjected to ac impedance measurements using an electrochemical impedance analyser (EG and G PARC model 263A) in the frequency range from 100 kHz to 100 MHz at an excitation signal of 5 mV (rms).

3. Results and discussion

GPEs containing plasticizers (EC and PC), a salt (ZnTr) and a polymer (PAN) form a mixed phase or a composite system where the interaction among the components are very likely to play a role in their performance. Free ions, ion-pairs and higher aggregates are known to be present to varying degrees depending on the properties of the matrix and the ionic component [35]. Hence, it becomes essential to understand the ionic and solvent interactions in the GPEs. In the present study, Fourier transform Raman (FT-Raman) spectroscopic technique has been used to monitor the interactions and an attempt has been made to relate the various properties though the system under investigation is a complicated one. The literature survey reveals the use of vibrational spectroscopy to study systems comprising lithium salts and various polymer electrolytes [36]. For example, Chen and co-workers have extensively investigated PAN based matrices containing various plasticizers and a lithium salt [37]. It is observed that the plasticizers compete with the polymer backbone to co-ordinate with the metal ions. A probable mechanism of ion transport has also been proposed for the GPEs based on PAN. Other published literature on spectroscopy [38–40] includes the use of plasticizers such as PC, EC and DMSO and matrices such as polymethylmethacrylate (PMMA), and polyvinylidenefluoride (PVDF).

3.1. Interaction between polymer and metal ion

The FT-Raman spectra of pure EC, pure PC, mixture of EC, PC and also a mixture of PAN (0.25 g) with EC (0.6 g) and PC (0.6 g) are shown in Fig. 1(a)–(d). It is clearly observed that the spectra of EC, PC and PAN (not shown) correspond to those reported in the literature [41]. The matrix contains plasticizers as well as a polymer host. The interaction between the plasticizers and the polymer in the absence of a salt is found to be negligible in the region 650–1050 cm^{-1}, particularly on the 893 cm^{-1} band (Fig. 1). It is essential to understand whether the metal ion interacts with PAN or EC/PC or both. The –CN stretching region at 2243 cm^{-1} is followed to understand the interaction between PAN and the salt. Fig. 2(a) shows the variation in the –CN stretching region of the Raman spectra with EC and PC as the plasticizer. It is clearly seen that the –CN stretching frequency at 2243 cm^{-1} is little affected with increasing concentration of the salt indicating that there is only a weak interaction of the metal ion with the –CN group of the polymer. Similar results have been reported for PAN–EC–PC Li salt system [42]. Subsequently, the plasticizers have been removed from the matrix by heating the GPE for one week in an evacuated oven at a temperature of 80 °C. Fig. 2(b) shows the Raman spectra of the plasticizer-free solid electrolyte containing various amounts of the salt. Here again, –CN stretching band is not altered substantially. However, the evolution of a weak, broad band at around 2260 cm^{-1} suggests an interaction of PAN and the salt (metal ion) when the plasticizers are absent. This is very similar to the changes observed in the literature for lithium bis(trifluromethane sulfone imide), and PAN–EC system [43] Thus, it can be concluded that zinc ions do not associate

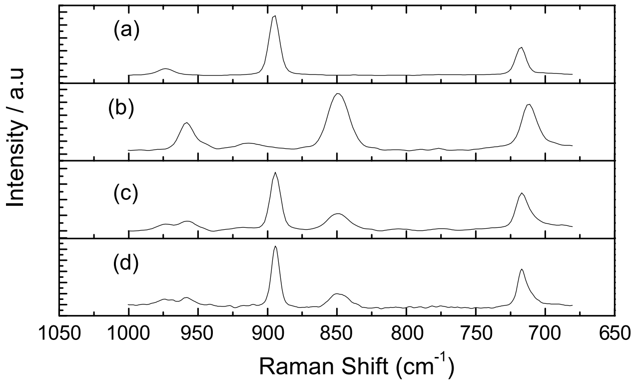


Fig. 1. Raman spectra of EC (a), PC (b), mixture of EC (0.6 g) and PC (0.6 g) (c) and (d) PAN (0.25 g) mixed with EC (0.6 g) and PC (0.6 g).

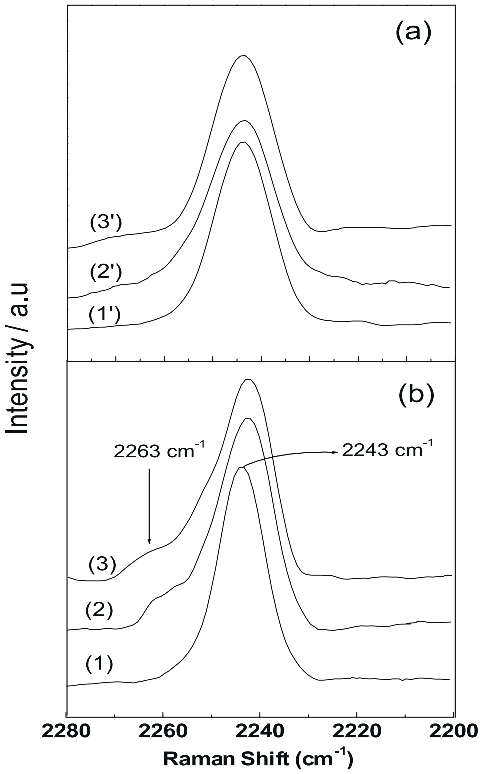


Fig. 2. (a) FT-Raman spectra of the symmetric nitrile stretching mode of PAN in (1′) pure PAN, (2′) PAN (0.25 g), EC (0.6 g), PC (0.6), ZnTr (1.87 M) (3′) PAN (0.25 g), EC (0.6 g), PC (0.6 g), ZnTr (2.18 M). (b) After removing the plasticizers completely, (1) pure PAN, (2) PAN (0.25 g), ZnTr (1.87 M), (3) PAN (0.25 g), (2.18 M) ZnTr in GPE.

themselves with the CN groups of the polymer in the presence of plasticizers and once the plasticizers are removed, the metal ion tends to coordinate with the CN group of the polymer. The extent of interaction of Zn^{2+} ions with the CN group of the polymer is not as significant as observed with that of Li^+ ions. This is likely to be due to the difference in the polarizing ability of the two ions.

3.2. Interaction between plasticizer and zinc triflate

The interaction of the plasticizers with the metal ion is followed in a similar way. The ring breathing mode of EC that is observed around 893 cm^{-1} is unaffected by the presence of other components in the matrix (Fig. 1(d)), while the C=O stretching mode of EC is affected by the presence of PAN (not shown). Fig. 3(a) shows the ring-breathing mode of EC at 893 cm^{-1} and this is observed to be very intense. With an increase in the concentration of the salt, the intensity of this band decreases and a new band is formed. The variation in the region 890–915 cm^{-1} as a function of the salt concentration is given in Fig. 3(b)–(j). The new band is found to increase in intensity and shifts its position to 902 cm^{-1} as the concentration of the salt is increased to 2.2 M. These changes observed in the ring-breathing mode in the presence of ZnTr clearly indicate that there is a strong interaction between the plasticizer (EC) and the zinc salt. Splitting of the band is a clear manifestation of the changes in the ionic environment. Similar observations have been reported for lithium-based systems [44].

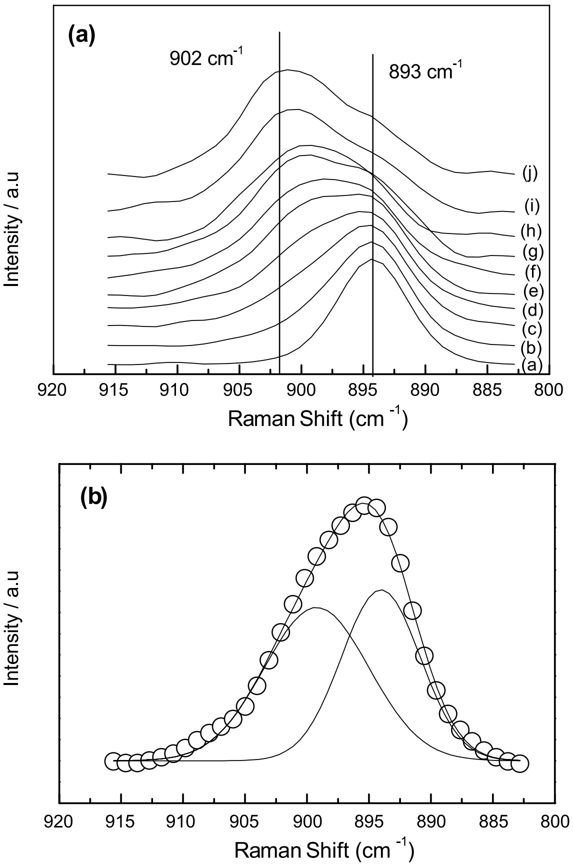
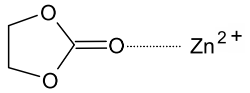


Fig. 3. (a) Ring breathing mode of (a) EC in a mixture of PAN (0.25 g), EC (0.6 g), PC (0.6 g) and (b) 0.15 M, (c) 0.31 M, (d) 0.62 M, (e) 0.93 M, (f) 1.25 M, (g) 1.56 M, (h) 1.87 M, (i) 2.18 M, and (j) 2.5 M of ZnTr. (b) Deconvoluted spectrum of the ring breathing mode of EC in a mixture of PAN (0.25 g), PC (0.6 g) EC (0.6 g) and ZnTr (0.62 M) ($\chi^2 = 1.39$ e^{-8} and $R^2 = 0.9974$).

Band shape analysis of the spectra has been carried out to quantitatively evaluate the interaction between the plasticizer and the zinc metal ion. The analysis is carried out by fitting the respective regions using two components. The ring-bending mode of EC at 893 cm^{-1} is quite sensitive to the co-ordinated species. It is known that the free EC moiety and the metal ion co-ordinated moiety are observed at 894 and 902 cm^{-1} for lithium based systems [45]. Fig. 3(b) shows the deconvoluted spectrum of 890–915 cm^{-1} region for a composition of PAN (0.25 g), EC (0.6 g), PC (0.6 g) and ZnTr (0.62 M). The band at 894 cm^{-1} corresponds to the free EC moiety while that of 902 cm^{-1} corresponds to the metal ion co-ordinated moiety as shown.



The ratio of free EC to the co-ordinated EC varies as a function of the salt concentration. Fig. 4 show the results of the ratio of the quantitative band area analysis with increasing concentration of the metal salt. The ratio of areas under the peak for the pure and the coordinated EC bands decreases with increasing concentration of the salt and reaches a minimum. This is likely since the increase in salt concentration leads to a large amount of metal ions. The dissociated metal ions tend to bind with the EC moiety thereby reducing the concentration of the free EC moiety. The ratio of the free to the coordinated species is 1.9 at a concentration of 0.28 M, and this decreases very rapidly and

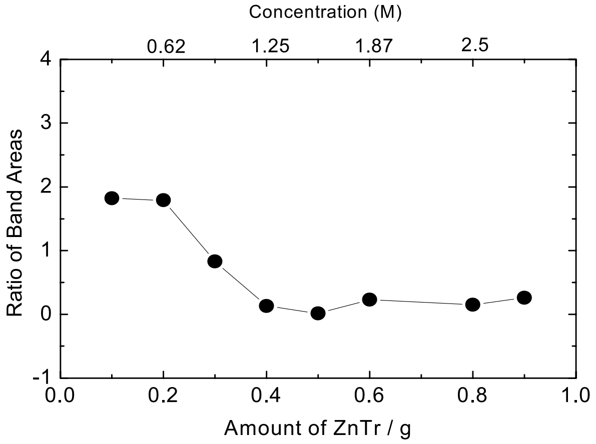


Fig. 4. Results of the quantitative band shape analysis of polymer PAN (0.25 g), with EC (0.6 g) and PC (0.6 g) as plasticizers, showing the calculated ratio of the band areas of pure EC band (893 cm^{-1})/co-ordinated EC band (902 cm^{-1}).

reaches a minimum of 0.01 for 1.56 M concentration of the salt. Incidentally, this is the concentration at which maximum ionic conductivity is observed. With further increase in the concentration of the salt, the ratio remains almost constant. Thus, the band shape analysis clearly reveals the interaction of the metal ion with the solvent and further substantiates the conclusion that the binding is dominant with the plasticizer rather than with the polymer host. It should, however, be noted that the present analysis pertains only to the interactions involving EC and the metal ion.

3.3. Ion association in the GPE

The triflate anion belongs to the C_{3v} point group with an irreducible representation of 5A1 + A2 + 6E. All the modes except the A2 modes are spectroscopically active. The bands from A1 and A2 representations are non-degenerate bands while the ones arising from E representations are degenerate. These bands can split into multiple bands upon lifting of degeneracy or distortion of the crystal symmetry [46]. The observed bands arise due to the internal vibrations of different bonds in triflate anion and all assigned values are given in Table 1. The spectrum corresponding to the region at 1100–1000 cm^{-1} is chosen to decipher the ionic interactions in the GPE. The band at 1034 cm^{-1} for a free triflate anion arises due to the symmetric SO_3 stretching [47]. This region is particularly chosen for the reason that the intensity of this band is high.

The FT-Raman spectra in the region 1100–1000 cm^{-1} shows the presence of a band at 1032 cm^{-1} that is assigned to the free triflate and bands at 1043 and 1053 cm^{-1} that are assigned to the ion pairs and higher aggregates, respectively [48]. The bands at 1043 and 1053 cm^{-1}, however, start to appear and grow in intensity with an increase in the concentration of the salt in the matrix (not shown). The assignment is in accordance with the values reported in the literature for lithium triflate-based systems [49]. The shift in the frequency towards lower as well as higher wavenumbers is documented for co-ordination of different metal ions [50]. Depending on the nature of the co-ordination (monodendate or bidendate), the shift can be to lower or higher wavenumbers [51]. A detailed curve fitting analysis to separate the various components is carried out. Fig. 5(a) shows the deconvoluted spectrum of the components corresponding to the free ion, ion-pair and higher aggregates for a composition of PAN (0.25 g), PC (0.6 g), EC (0.6 g) and 1.25 M concentration of ZnTr.

Table 1
FT- Raman band frequencies and vibrational assignment of ZnTr, where ν_{as}, ν_s, δ_s, δ_{as}, and ρ refer to asymmetric stretching, symmetric stretching, symmetric deformation asymmetric deformation and rocking mode, respectively

Frequency (cm^{-1})	Assignment
1257	ν_{as} (SO_3)
1227	ν_s (CF_3)
1185	ν_{as} (CF_3)
1035	ν_s (SO_3)
764	δ_s (CF_3)
584	δ_{as} (CF_3)
354	ρ (SO_3)
313	ν_s (C–S)
220	ρ (CF_3)

Fig. 5(b) shows the percentage of free ions, ion-pair and higher aggregates based on the areas under the deconvoluted spectra. It is clearly observed that the percentage of free ions increases as a function of salt concentration, attains a maximum at about 1.56 M of ZnTr, and then begins to

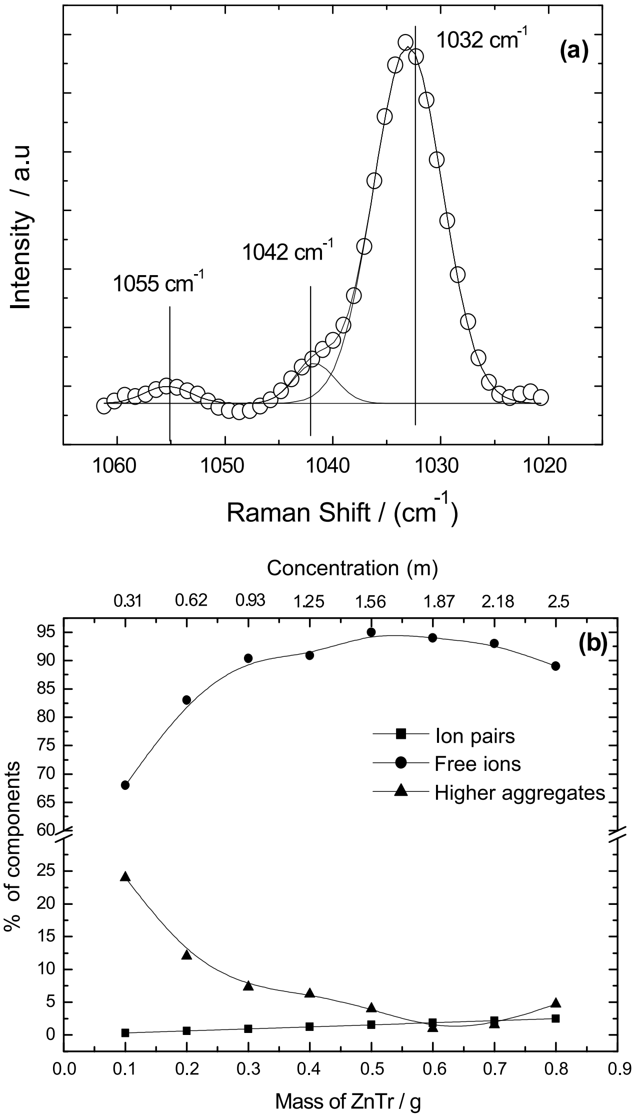


Fig. 5. (a) Deconvoluted spectra of the symmetric SO_3 stretching region. The region at 1032 cm^{-1} corresponds to that of free triflate, 1042 cm^{-1} to ion-pairs and 1055 cm^{-1} to higher aggregates. The spectra correspond to a concentration of PAN (0.25 g), PC (0.6 g) EC (0.6 g) with ZnTr (1.25 M). (b) Percentage variation of free ions, ion-pairs and higher aggregates (PAN 0.25 g, EC 0.6 g, PC 0.6 g) with increasing salt concentrations.

decrease to a small extent. Ion-pairs and higher aggregates are present to a small extent initially. As the concentration the salt is increased, they tend to decrease first and a small increase is observed at about 1.56 M of ZnTr in the matrix. An interesting correlation is that the maximum conductivity is observed at the same composition.

Fig. 6 shows the variation in specific conductivity with increasing concentration of metal salts. Based on the evidence from both electrochemical and spectroscopic techniques, an interesting correlation is observed. The maximum conductivity is noticed at the same composition where the band area analysis of EC (Fig. 4) shows that the coordinated EC moiety is very high. This is likely to assist the motion of cations through hopping resulting in good ionic conductivity. The analysis based on the triflate anion leads to the presence of ion-pairs and aggregates that show an initial decreasing trend. At about 1.56 M of ZnTr, an increasing trend is observed. This relates well with the maximum conductivity observed around the same composition.

4. Conclusions

Changes in the zinc ion co-ordination in GPE have been followed by FT-Raman spectroscopy as a function of the concentration of the salt. The metal ions tend to co-ordinate with the solvents that manifest in the form of a shift in the wavenumbers of the ring-breathing vibrational mode of the plasticizer. Band shape analysis reveals that the ratio of the uncomplexed to the complexed EC moiety decreases with an increase in the concentration of the salt in the matrix. A correlation is found between the electrochemical and spectroscopic data. The composition at which maximum conductivity is observed corresponds to the composition where ion-pairs and aggregates are minimum.

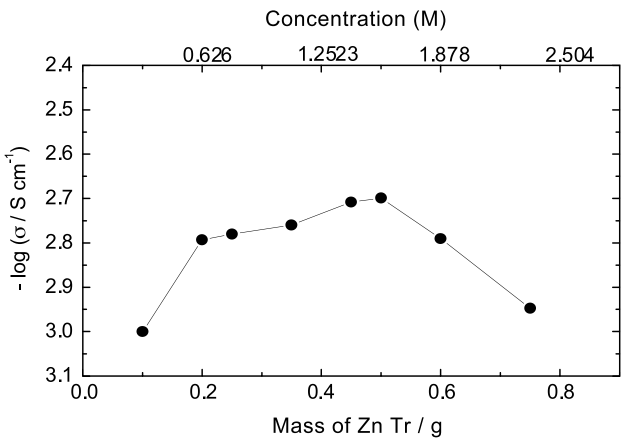


Fig. 6. Specific conductivity (σ) of the GPE (PAN (0.25 g), PC (0.6 g), EC (0.6 g) as a function of mass and concentration (M) of ZnTr.

Acknowledgements

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