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FTIR investigations on ion–ion interactions in liquid and gel polymeric electrolytes: $LiCF_3SO_3$-PC-PMMA

M. DEEPA, N. SHARMA, S. A. AGNIHOTRY
National Physical Laboratory, Dr. K. S. Krishnan Road, New Delhi 110012, India
E-mail: agni@csnpl.ren.nic.in

R. CHANDRA
Chaudhry Charan Singh University, Merrut, India

FTIR spectroscopy and ionic conductivity measurements have been employed to study the solvation and conduction mechanism of lithium ions in aprotic liquid electrolytes of $LiCF_3SO_3$-PC (lithium trifluromethanesulfonate-propylene carbonate) and gel electrolytes containing poly(methylmethacrylate) (PMMA) additionally. Cation solvation occurs via interactions between Li^+ ions with the ring oxygens as well as the carbonyl oxygen of PC molecules over the entire salt concentration range under investigation (0.025–2 M) for both liquid and gel electrolytes. The ionic conductivity decline for concentrations $\geq$0.8 M $LiCF_3SO_3$-PC is attributed to the formation of ion pairs and/or triplets. Presence of (a) free $CF_3SO_3^-$ ions in 0.025 and 0.05 molar $LiCF_3SO_3$-PC solutions, (b) the $LiCF_3SO_3$ structure with a monodentate coordinated lithium ion for concentrations $\geq$0.5 molar $LiCF_3SO_3$-PC systems and (c) ion triplets comprising two cations and an anion with a bidentate bridging structure in 2 M $LiCF_3SO_3$-PC electrolytes, has been established. Ionic conductivity performance concurs with our infrared results. Gel electrolytes containing upto 15 wt% of PMMA have been found to exhibit liquid like behavior but 2 M $LiCF_3SO_3$-PC systems that incorporate 25 wt% of polymer show a distinct Li^+–O=C (of PMMA) interaction which is unambiguously determined from the remarkable changes observed for the ν_s(C=O) and $\nu_s(SO_3)$—the symmetric stretching vibrational modes. © *2002 Kluwer Academic Publishers*

1. Introduction

Lithium ion conductive gel polymeric electrolytes which are seen as an attractive alternative to solvent free polymer-salt complexes have been generating tremendous interest from both theoretical and practical view points as they encompass several technologically desirable characteristics [1–3]. Since they possess high room temperature ionic conductivity ($\sim10^{-3}$ Scm^{-1}), high cation transport number, amorphous nature and good mechanical and dimensional stability, they are most conducive for use in electrochromic devices (ECDs) [4], batteries [2, 5] and supercapacitors [2]. The mechanism of fast ionic diffusion in polymer electrolytes is much debated and has been the focus of considerable research since the discovery of ionic conductivity in polymer-salt complexes [6]. Although, the free volume model [6, 7] has been successful in describing the macroscopic behavior of polymer electrolytes and especially the overall temperature dependence of σ and η, it does not account for the interactions at the microscopic level. It is believed that effects such as ion-polymer interaction, ion-pairing and ion solvation are all important factors that control conductivity although it is difficult to measure them independently. Information pertaining to free ions, ion-pairs and multiplets formation can be obtained from vibrational spectroscopic studies.

Raman scattering [8] and Infrared spectroscopy [9] have been employed extensively to study the ion-pairing phenomena in polyether-salt systems and quantitative measurements have been reported for the amount of ions locked in various ion-ion formations. Similarly, Raman and Li NMR studies for investigating the structure and dynamics of Li^+ ions in concentrated solutions of $LiClO_4$-(EC + PC) have been reported by Cazzanelli *et al.* [10].

Li^+ conductive gel polymeric electrolytes with ionic conductivity exceeding 10^{-3} Scm^{-1} (at 25°C) have been synthesized by us by immobilizing liquid electrolytes {lithium triflate ($LiCF_3SO_3$) in propylene carbonate (PC)} in an appropriate polymer matrix such as PMMA. Recent literature [11] shows that non aqueous liquid electrolytes and complexes of lithium triflate with polyethers have been the central theme of numerous spectroscopic investigations. However the coordination phenomenology of the lithium metal cation with (a) the triflate anion, (b) solvent PC molecules and (c) the polymer (PMMA) in gel polymeric electrolytes

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has seldom been probed into. It is presumed that each type of ionic species present makes a contribution to the total ionic conductivity, i.e. while the formation of neutral ion pairs and aggregates decreases the number of charge carriers, the existence of charged associated species affects ionic mobility adversely. Decline of ionic conductivity is a repercussion of such unfavourable coordinations.

This work reports conductivity measurements corroborated by a detailed FTIR study on aprotic liquid electrolytes ($LiCF_3SO_3$-PC) and the same gelatinized by PMMA incorporation over a wide range of salt (0.025 M–2 M) and polymer (5–25 wt%) concentration. Central to the following discussion of the spectroscopic data will be its relevance for interpreting ionic conductivity behavior. Ion association in pairs and/or in higher order aggregates has been verified from the observations of the internal vibrational modes in the case of molecular ions. The present comprehensive study based on FTIR spectroscopic findings and ionic conductivity performance attempts, to propound a likely model for cation solvation in the quasiternary system of $LiCF_3SO_3$-PC-PMMA. This conjecture alongwith the detailed knowledge of the interactions existing between the cations, anions, solvent and the polymer will help in understanding the mechanism of ionic conduction in gel polymeric electrolytes.

2. Experimental procedure

High purity $LiCF_3SO_3$ (Lithium trifluromethanesulfonate or triflate) from Aldrich Chemical Co. was used after drying at 110°C under vacuum for 12 hours. PMMA (Avg. mol. wt = 9,96,000 and $T_g = 95°C$) from Aldrich Chemical Co. was used after drying at 80°C under vacuum for 12 hours. The solvent used was propylene carbonate (PC) from Merck after being dried over 4 Å molecular sieves. All liquid and gel electrolytes were prepared and studied under controlled temperature and humidity conditions (25°C and RH ∼ 50%). PMMA was dissolved upto 25 wt% of the liquid electrolyte in PC to obtain homogeneous and transparent gels.

After calibration with standard aqueous KCl solutions, conductivity measurements for both liquid and gel electrolytes were carried out with Cyberscan Con 100 conductivity meter at 25°C. Vibrational spectroscopic studies were carried out for the solvent PC and liquid electrolytes: xM $LiCF_3SO_3$-PC with $x = 0.025$, 0.05, 0.5, 1, and 2. FTIR spectra were recorded for gel electrolytes based on 1 M and 2 M $LiCF_3SO_3$-PC containing x wt% of PMMA with $x = 5$, 15 and 25. All liquid and gel electrolytes were used in the form of a thin layer formed between two KBr windows in the 2000–500 cm^{-1} region using Perkin Elmer GX 2000 OPTICA FTIR spectrophotometer.

3. Results and discussion

3.1. Conductivity measurements

The ionic conductivity dependence of liquid and gel electrolytes (at 25°C) on varying $LiCF_3SO_3$ concentration (0.025–2 M) in PC is shown in Fig. 1. Influence of PMMA addition on conductivity of (a) one and (b) two molar $LiCF_3SO_3$-PC liquid electrolytes is also displayed in the same figure.

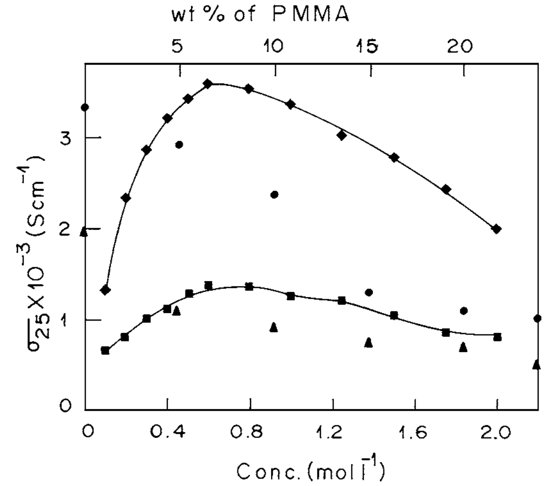

Figure 1 Ionic conductivity variation as a function of $LiCF_3SO_3$ concentration in PC (◆), PC + 15 wt% PMMA (■) and effect of addition of PMMA on σ_{25} of 1 M (●) and 2 M (▲) $LiCF_3SO_3$ in PC.

As salt concentration is raised, ionic conductivity of the electrolyte solutions and gels increases steadily, acquires a maximum value and then decreases gradually. The existence of a conductivity maximum at ∼0.6 molar triflate salt concentration is indicative of two competing effects occurring as salt concentration is increased: (a) increase in the concentration of charge carriers and (b) the viscosity of the medium. The σ_{25} decline at higher salt concentrations, i.e. at values >0.6 M $LiCF_3SO_3$-PC, is most likely due to cation (Li^+) and anion ($CF_3SO_3^-$) recombination or ion-aggregation, which tends to play a pivotal role in determining the number of charge carriers or "free ions" in the electrolyte [12, 13].

Incorporation of 25 wt% of PMMA in liquid electrolyte enhances its macroscopic viscosity by several orders of magnitude thereby imparting mechanical stability to the system [14, 15]. Since the decrease of σ_{25} occurs only by a factor and not by an order, it is assumed that polymer addition does not alter the conduction mechanism that prevails in liquid electrolytes significantly [15]. The elucidation of how the interrelationship that persists between conductivity and viscosity of gel electrolytes influences the ion-transport properties of gel systems has been described elsewhere [14, 15]. Vibrational frequency shifts, alteration in band intensities, shapes and splittings for the anion's bands observed upon varying salt concentration (from 0.025 M to 2 M) and polymer content (from 5 to 25 wt%) are of tremendous importance in predicting the nature of intermolecular interactions and the conductivity performance of electrolytes. Thus, information obtained from our FTIR studies of liquid and gel electrolytes helps in correlating and discerning the ionic conductivity trends with the microstructural features of ion-solvent-polymer systems.

3.2. Liquid electrolytes

The FTIR spectra of: (a) the pure solvent PC and (b) the electrolyte solutions of xM $LiCF_3SO_3$-PC with $x = 0.025$, 0.05, 0.5, 1, and 2, in the 2000–500 cm^{-1}

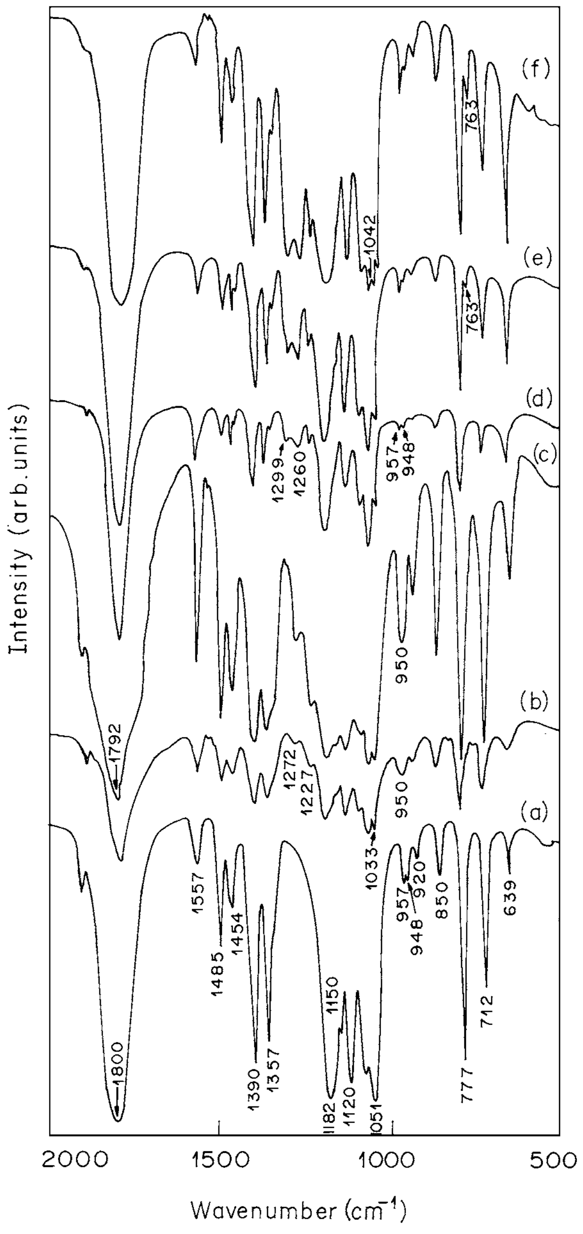

Figure 2 FTIR spectra of (a) solvent PC, (b) 0.025 M, (c) 0.05 M, (d) 0.5 M, (e) 1 M and (f) 2 M-LiCF$_3$SO$_3$ in PC in the 2000–500 cm^{-1} region.

region, have been illustrated in Fig. 2. Characteristic group frequencies of PC, triflate salt, PMMA, molecular ions and electrolytes and their corresponding assignments are listed in Table I.

The interpretation of the vibrational modes and characteristic infrared frequencies of PC have been summarized by Battisti and co-workers in great detail [16]. Therefore, an in-depth and an intricate analysis of the group frequencies of PC alongwith their assignments was considered to be unnecessary as Battisti's results are validly comparable with the results of our spectroscopic studies on PC. The following discussion will instead focus on the frequency shifts and band splittings of some vibrational modes of lithium triflate upon coordination with PC. This will enable us to sketch a tentative model for the structural dynamics of the triflate salt in the pesudobinary system of LiCF$_3$SO$_3$-PC.

TABLE I Group frequencies and assignments of PC, LiCF$_3$SO$_3$, PMMA (ν_s and ν_a-symmetric & antisymmetric stretching; δ-bending or deformational mode; ρ_w and ρ_t-wagging & twisting)

Wavenumber (cm^{-1})	Assignment	Group/species/molecular ions
1896	2 × ring breathing mode of PC (948 cm^{-1})	Solvent PC
1800	ν(C=O)	Solvent PC
1792	ν(C=O)	Liquid electrolytes
1790	ν(C=O)	Gel electrolytes
1737	ν(C=O)	PMMA
1734	ν(C=O)	PMMA
1727	ν(C=O)	PMMA
1557	δ(C—H)	Ring structure of solvent PC
1485	δ(C—H) + δ(CH$_3$)	PC + PMMA
1454	δ(C—H) + δ(CH$_3$)	PC + PMMA
1390	δ(C—H) + δ(CH$_3$)	PC + PMMA
1357	δ(C—H)	PC
1299	ν_a(SO$_3$)	Coordinated triflate ion/ion-pair
1272	ν_a(SO$_3$)	Free triflate ion
1260	ν_a(SO$_3$)	Coordinated triflate ion/ion-pair
1227	ν_s(CF$_3$)	Free triflate ion
1182	ν(C—O) + ρ_w(C—H)	Solvent PC
1150	ν(C—O) + ν(C—H)	Solvent PC
1120	ρ_w(C—H) + δ(C—H)	Solvent PC
1051	ρ_t(C—H) + δ(C—H)	Solvent PC
1042	ν_s(SO$_3$)	Coordinated triflate ion/ion-pair
1033	ν_s(SO$_3$)	Free triflate ion
990	ν_s(C—O—C)	PMMA
957	Ring breathing mode	Solvent PC
948	Ring breathing mode	Solvent PC
777	Ring breathing mode	Solvent PC
763	δ_s(CF$_3$)	Ion triplets (Li$^+$—CF$_3$SO$_3^-$—Li$^+$)
712	Symmetric ring deformation	Solvent PC

Normal saturated esters with an α-electronegative substituent exhibit an intense absorption band in the 1750–1800 cm^{-1} region ascribable to the C=O stretching vibrational mode [17]. PC, being one such ring compound shows a doublet with a very strong and a broad band peaking at 1800 cm^{-1} corresponding to ν(C=O) [14, 16, 18]. This high carbonyl frequency in PC is undoubtedly related to the ring strain in five membered ring structures [19]. The second component of the doublet appears as a weak band at 1896 cm^{-1}. In cyclic compounds, it has been observed that splitting is caused by coupling between the carbony1 stretching mode and the overtone of an another low lying vibrational mode. This type of accidental degeneracy or Fermi resonance occurs in PC, between the first overtone of ring breathing mode and the carbony1 stretching vibration. The ring breathing mode at ~948 cm^{-1} with its overtone at 1896 cm^{-1} is also infrared active owing to vibrational anharmonicity [20, 21].

The C=O stretching frequency experiences a downshift by 8 cm^{-1} upon incorporation of lithium triflate in PC. The magnitude of this shift to lower wavenumbers, i.e. from 1800 to 1792 cm^{-1} is apparently independent of salt concentration, as the extent of this shift virtually remains intact for all values of x in xM LiCF$_3$SO$_3$-PC systems. Model studies of LiClO$_4$-(PC + EC) have been conducted previously by Cazzanelli *et al.* [10]. Their studies revealed that at low salt concentrations, the salt is completely dissociated and the cations are solvated by solvent molecules via strong interactions between the Li$^+$ ions and the oxygens of the carbonate rings. As the position of the carbonyl stretching band is determined by the molecular structure in its immediate vicinity [22], the observed $\Delta\nu = 8$ cm^{-1}, is in all likelihood induced by Li^{+}—O (ring oxygens) and Li^{+}—O=C interactions. Although the specificity of the position of the 1896 cm^{-1} band is retained in all the liquid electrolytes, its intensity diminishes with increasing salt concentration. For solutions of low strengths (0.025 and 0.05 M LiCF$_3$SO$_3$-PC), this band is seen as a week peak. For concentrations $\geq$0.5 M LiCF$_3$SO$_3$-PC, this band appears as a very weak shoulder, indicative of triflate salt's spectral features overriding those of PC.

For all solutions with different LiCF$_3$SO$_3$ concentrations, strong absorption bands seen at ~1557, ~1485, ~1454, ~1390 and 1357 cm^{-1} are characteristic of the various C—H deformational modes pertaining to the ring structure of the solvent. The precise assignments can be obtained from Battisti's work [16]. Remarkably, these bands remain largely unperturbed except for some minor insignificant shifts, which render them to be most unsuitable for probing into ion-solvent interactions in xM LiCF$_3$SO$_3$-PC systems.

Bernson *et al.* [9] observed that when non coordinated to a cation, the triflate ion is assumed to have a point group symmetry $C_{3\text{v}}$. The antisymmetric SO$_3$ stretching mode, ν_a(SO$_3$) with E symmetry is doubly degenerate, while the symmetric mode, ν_s(SO$_3$), with A$_1$ symmetry is non degenerate; both modes are infrared active [9]. When the triflate ion is coordinated to a cation, the degenerate ν_a(SO$_3$) band splits into two bands. According to Bernson *et al.*, at low salt concentrations, the cations are completely coordinated to the solvent molecules and the triflate anions are free. This is evidenced from their spectra, as two weak free triflate ion bands are seen at 1272 and 1033 cm^{-1} which are attributable to ν_a(SO$_3$) and ν_s(SO$_3$) [9]. Our observations for low concentration (0.025 M and 0.05 M LiCF$_3$SO$_3$-PC) systems (Table I) conform very well with Bernson's data. These two bands are extremely useful tools to establish the formation of ion pairs and clusters at high salt concentrations. Strangely, for 0.5 M LiCF$_3$SO$_3$ concentrations and above only one clear component is observed at 1033 cm^{-1}, indicative of free triflate ions, whereas no band is found at 1272 cm^{-1}, the expected location of ν_a(SO$_3$) for free triflate. This observation is in complete concordance with Bernson's findings [9]. Possible causes involve a splitting of the asymmetric mode due to an inhomogeneous electrostatic field produced around a non-coordinated triflate ion by more distant lithium ions [9].

For our 0.5 M–2 M LiCF$_3$SO$_3$-PC systems, two bands are observed at ~1299 and ~1260 cm^{-1} as observed by Bernson [9] in LiCF$_3$SO$_3$-PPO$_\text{n}$ systems at 1300 and 1258 cm^{-1}. The intensities of these two bands increase as salt concentration increases from 0.5 M < 1 M < 2 M LiCF$_3$SO$_3$. The presence of two bands instead of one band at 1272 cm^{-1} for low salt concentration in this frequency region can be ascribed to the splitting of ν_a(SO$_3$) mode [9]. In the ν_s(SO$_3$) region, it is seen that increasing salt concentration causes a split of the 1033 cm^{-1} band with two distinct components at 1033 and 1042 cm^{-1} [9, 23]. The presence of a double peak is suggestive of the existence of different environments for the anions [23]. Increasing salt concentration increases the probability of ion-ion interactions and one therefore expects growing intensities of the corresponding infrared modes. The low frequency component at ~1033 cm^{-1} (seen for all values of x in xM LiCF$_3$SO$_3$-PC) is attributed to free ions [9, 23] and the mode at ~1042 cm^{-1} to ion-pairs [24, 25]. The 1042 cm^{-1} component is observed only for the 2 M LiCF$_3$SO$_3$-PC solution. Perhaps the solvent's strong absorption at ~1051 cm^{-1} overlaps with the 1042 cm^{-1} band and inhibits it from being dominant below ~1 M LiCF$_3$SO$_3$ salt concentration. But for the 2 M LiCF$_3$SO$_3$-PC system, which has a substantially high salt proportion, the ν_a(SO$_3$) band exhibits a doublet with a weak peak at 1033 cm^{-1} corresponding to free CF$_3$SO$_3^-$ ions and the second component at 1042 cm^{-1} corresponding to triflate ions locked in ion pairs [9, 23–25].

Ab initio studies of the vibrational frequencies of Li^{+}-CF$_3$SO$_3^-$ ion pairs by Gejji *et al.* [24] have shown that ν_s(SO$_3$) shifts to higher wavenumbers ($\geq$1040 cm^{-1}) when involved in monodentate coordination and to still higher wavenumbers, i.e. to ~1053 cm^{-1} when associated in the form of ion-triplets. Huang *et al.* [25] proposed a bidentate bridging structure involving two cations and an anion (Li^{+}—CF$_3$SO$_3^-$—Li^{+}) for this triplet. In our systems with salt concentration >0.6 M LiCF$_3$SO$_3$, the possibility of the triplet's band at 1053 cm^{-1} being superimposed by PC's absorption is quite strong especially for concentrations above one molar LiCF$_3$SO$_3$. This is also exemplified from the increasing intensity of the 1051 cm^{-1} band with increasing salt content in the electrolyte (from 0.025 M to 2 M LiCF$_3$SO$_3$-PC) when compared with that of the 1033 cm^{-1} band. The existence of similar ion-aggregates has been established in the latter part of this discussion. Also, our conductivity results do favour the formation of ion-pairs and aggregates (Fig. 1).

In the free triflate ion, ν_s(CF$_3$) and ν_a(CF$_3$) are located at 1226 cm^{-1} and 1156 cm^{-1} respectively [9]. When coordinated, the ν_a(CF$_3$) band of the triflate ion shifts to 1165 cm^{-1} [9]. The complex character of the 1200–1000 cm^{-1} region in our spectrum for PC owing to several closely placed bands makes the deconvulation of the juxtapositioned bands from the triflate salt and the solvent, a cumbersome task. As a result, the 1156 cm^{-1} band due to ν_a(CF$_3$) for the free triflate ion cannot be identified reliably in any of the spectra of liquid electrolytes, as it seems to have merged with PC's bands that are seen at 1150 and 1182 cm^{-1}. For the free CF$_3$SO$_3^-$ ion, the ν_s(CF$_3$) band is observed at 1227 cm^{-1} as a weak peak whose position is obviously independent of the presence of solvent, as none of the pure solvent's frequencies are found in the 1200–1300 cm^{-1} region. Intensity of the 1227 cm^{-1} band enhances by small extents in accordance with increasing salt concentration (0.025 < 0.05 < 0.5 < 1 < 2 M LiCF$_3$SO$_3$) in the samples.

In all solution spectra, there exists a very strong band with a broad spread over the 1200–1000 cm^{-1} region. This band is embedded with many prominent peaks that are characteristic of solvent's absorptions. These have been assigned to ν(C—O) + ρ_w(C—H) at ~1182 cm^{-1}, ν(C—O) + ν(C—C) stretch at ~1150 cm^{-1}, ρ_w(C—H) + δ(C—H) at ~1120 cm^{-1} and ρ_t(C—H) + δ(C—H) at ~1051 cm^{-1} [16]. Their positions as well as their intensities remain unaffected in the presence of salt as these bands more or less appear at the same positions in all the cases {0.025 M–2 M(LiCF$_3$SO$_3$-PC)}. This implies that the triflate salt hardly forms any strong linkages with C—C and C—H groups of PC.

Raman studies performed previously on LiClO$_4$/EC/PC samples have revealed a strong interaction of cations with such ring based organic solvents on the basis of the perturbations of the ring breathing and ring bending modes of the solvent molecules which induce observable changes in the spectral parameters such as frequency shifts by 10 cm^{-1} [10, 20, 26]. Infrared bands of PC molecules appear at ~850 and ~920 cm^{-1} and a doublet with peaks at 957 and 948 cm^{-1} of comparable intensities can also be seen (Fig. 2a). These bands correspond to the ring breathing modes of PC [16, 26, 27]. Amongst all these bands, the main effects of the mobile ionic species on the vibrational dynamics of the solution concern only the doublet that arises due to PC's ring breathing mode. This doublet: (a) merges to form a single broad peak at ~950 cm^{-1} (for 0.025 and 0.05 M LiCF$_3$SO$_3$-PC) and (b) reassumes its double peak character for concentrations ≥0.5 M LiCF$_3$SO$_3$-PC. Noticeably, the intensity of the 957 cm^{-1} component increases as the salt concentration increases from 0.5 M to 2 M LiCF$_3$SO$_3$. Perhaps these complex evolutions of the ring breathing mode of PC demonstrate that Li$^+$ ions are chiefly involved in the interaction with the ring oxygens of the solvent. This is supported by similar results obtained for LiClO$_4$/EC/PC systems by Cazzanelli [10] and Hyodo [26]. Authors of [28] have also claimed that the solvation number of ClO$_4^-$ ion is zero in PC, thereby affirming the poor solvation of anions in non aqueous electrolytes.

The δ_s(CF$_3$) band which lies in the 750–770 cm^{-1} region was found to be highly sensitive to the environmental changes and serves as a good complement to the SO$_3$ bands in determining the coordination of triflate ions [29]. Three δ_s(CF$_3$) bands were found for LiCF$_3$SO$_3$ dissolved in a PPO trimer [25, 29]; one small band at 752 cm^{-1} assigned to free triflate ions, a large band at 758 cm^{-1} assigned to ion-pairs and a small band at 763 cm^{-1} assigned to higher aggregates like ion-triplets, as described earlier. Till 0.5 M concentration of LiCF$_3$SO$_3$ in PC, no bands corresponding to δ_s(CF$_3$) can be seen, but for 1 M and 2 M LiCF$_3$SO$_3$ in PC, a weak band at ~763 cm^{-1} develops with increasing intensity as a function of salt concentration. Ion triplets in samples with a huge proportion of LiCF$_3$SO$_3$, are responsible for this band's appearance [29].

PC shows some very strong fundamental absorptions at 777 cm^{-1} (ring deformation or breathing mode) [16] at 712 cm^{-1} (symmetric ring deformation or breathing) [16], and at 639 cm^{-1} (Fig. 2a). Contrary to the Raman spectroscopic results obtained by Cazzanelli [10] and Hyodo [26], which showed phenomenal changes for the 712 cm^{-1} ring breathing mode of PC in LiClO$_4$/EC/PC solutions, we found absolutely no appreciable changes in the form of band shape, intensity or position for all the three IR active bands of PC at 777 cm^{-1}, 712 cm^{-1} and 640 cm^{-1} in all of our LiCF$_3$SO$_3$-PC systems.

Briefly, for LiCF$_3$SO$_3$ concentrations such as: O M < strength of LiCF$_3$SO$_3$-PC ≤0.5 M, the salt is apparently completely dissociated and the cations are predominantly solvated by the high dielectric solvent {for PC, ε (at 25°C) = 64.4} molecules [4]. The interactions are likely to occur between the Li$^+$ ions and the oxygens of the carbonate rings. For LiCF$_3$SO$_3$ concentrations exceeding one molar in PC, reassociation of some cations and anions takes place manifesting in the formation of monodentate ion pairs and higher order aggregates such as bidentate bridging ion triplets.

3.3. Gel electrolytes

FTIR spectra of gel electrolytes containing x wt% of PMMA (x = 5, 15, 25) dissolved in: (a) one molar (Fig. 3) and (b) two molar (Fig. 4) solutions of LiCF$_3$SO$_3$ in PC are illustrated in Figs 3 and 4 respectively.

In PMMA, which is a saturated polymeric ester, the C=O symmetrical stretching frequency gives rise to an intense, a very strong and a sharp peak at ~1730 cm^{-1} [30, 31]. For both salt concentrations and irrespective of the amount of PMMA incorporated in these gel electrolytes, no significant perturbation is observed for the doublet appearing as consequence of Fermi resonance in PC at ~1790 cm^{-1} (due to ν(C=O) of PC) and at ~1900 cm^{-1} (due to an overtone of PC). Thus, the neutral PMMA polymer chains are unable to influence the Fermi doublet of the solvent regardless of salt or polymer concentration. From Fig. 3, for a fixed

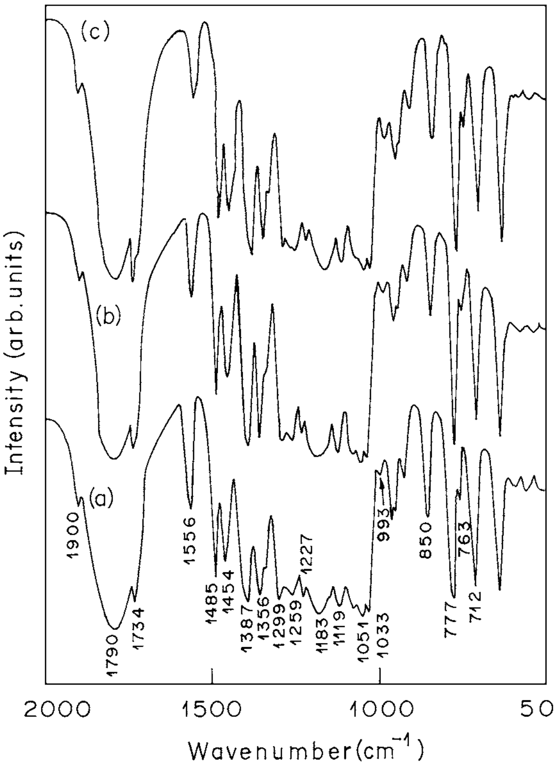

Figure 3 FTIR spectra of gel electrolytes based on 1 M LiCF$_3$SO$_3$ in PC containing (a) 5, (b) 15 and (c) 25 wt% of PMMA in the 2000–500 cm^{-1} region.

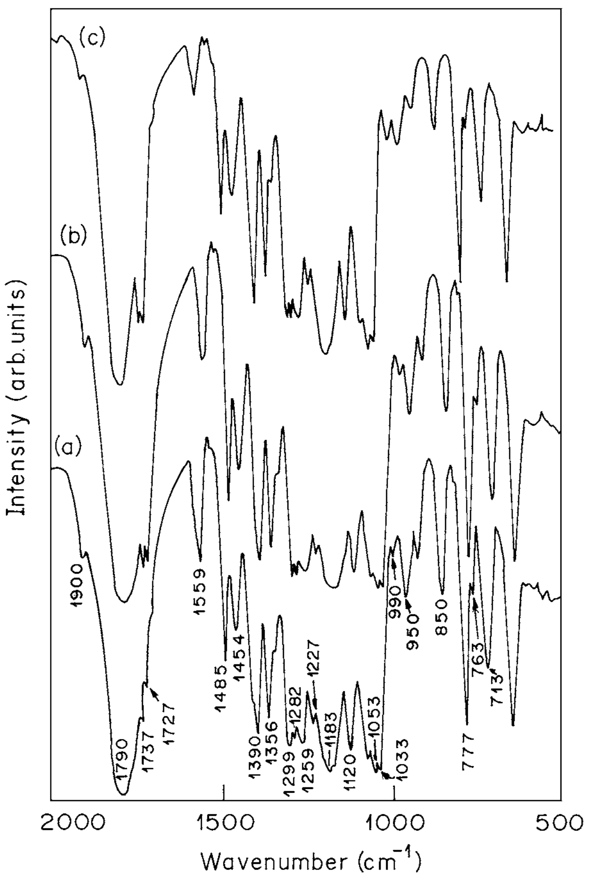

Figure 4 FTIR spectra of gel electrolytes based on 2 M $LiCF_3SO_3$ in PC containing (a) 5, (b) 15 and (c) 25 wt% of PMMA in the 2000–500 cm^{-1} region.

one molar $LiCF_3SO_3$ concentration, a new band is observed at ~1734 cm^{-1} which is attributable to ν(C=O) of PMMA. Its intensity increases with the increasing polymer content in the liquid electrolyte. But for 2 M $LiCF_3SO_3$-PC systems, (Fig. 4), the ν(C=O) of PMMA splits into two components at ~1737 cm^{-1} and ~1727 cm^{-1}. These two bands are seen: (a) as weak shoulders for gel electrolytes with 5 wt% of PMMA, (b) as a weak doublet with unequal intensities with the 1737 cm^{-1} band possessing greater intensity for the gel with 15 wt% of PMMA and (c) as a medium strong doublet with both peaks of comparable intensities for gels with 25 wt% of PMMA.

Probably, in the 2 M $LiCF_3SO_3$-PC + 25 wt% PMMA system, which is a salt rich gel and also encompasses a large quantity of the polymer, there exists insufficient amount of solvent to satisfy the solvation requirements of the cations and the other solute, namely PMMA [2]. It is worth remarking that the transformation of a single ν(C=O) band of PMMA into a doublet for gels with high salt and polymer content could be ascribable to the coordination of the Li^+ ions with the carbonyl oxygens on the ester side of PMMA along with the $CF_3SO_3^-$ ions acting as transient crosslinks [13]. A schematic representation of this ion-polymer interaction is shown in Fig. 5.

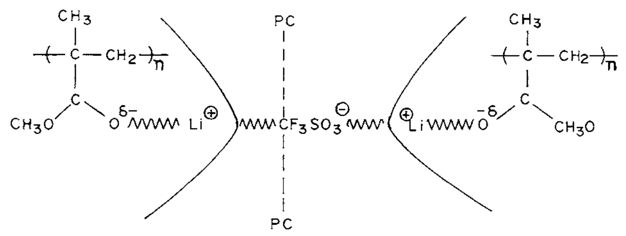

Figure 5 Schematic diagram showing interaction of Li^+ ions with PMMA in the 2 M $LiCF_3SO_3$ in PC + 25 wt% PMMA gel.

This is also consistent with the Bohnke's argument [15] who found that the microscopic viscosity which predominantly governs the conduction mechanism in gel electrolytes increases enormously for $LiClO_4$-PC gels containing 45 wt% of PMMA. Enhancement of microscopic viscosity implies an ion-polymer association that impedes ionic mobility considerably. The net ramification is a decline in the ionic conductivity of the same system. As the system under present investigation, involves a different salt i.e. $LiCF_3SO_3$, whose anion has an electronic charge density and lattice energy characteristics different from those of ClO_4^-, it is plausible that the inception of the Li^+—O=C (of PMMA) coordination occurs at a relatively low concentration of polymer i.e. 25 wt%, in our case. Conductivity plots and FTIR spectra strongly hint at the occurrence of such a phenomenon. It can be presumed that a redissociation of a few Li^+—$CF_3SO_3^-$ ion pairs could be facilitated by PMMA's solvating ability, which comes into action at high polymer levels.

Pure PMMA produces three medium strong bands at ~1487, ~1449 and ~1438 cm^{-1} [31]. For gels, these bands overlap with PC's dominant absorptions at ~1485 and ~1454 cm^{-1}, as presence of polymer does not perturb these bands at all as they exhibit neither positional nor an intensity variation even at high polymer levels (Figs 3 and 4). An independent contribution from PMMA is totally inhibited by the solvent in this range. The bands at ~1390 and ~1357 cm^{-1} of the liquid electrolyte are not affected severely upon polymer addition although PMMA's symmetric $\delta(CH_3)$ deformation mode of CH in OCH_3/CCH_3 makes a significant contribution to the former band [33, 34]. The doubly degenerate $\nu_a(SO_3)$ mode for the free triflate ion splits into two bands for triflate ion-pairs as has been elaborated earlier. Seen at ~1299 cm^{-1} and ~1259 cm^{-1} are the bands corresponding to this mode for both 1 M and 2 M $LiCF_3SO_3$-PC gels with different PMMA concentrations (Figs 3 and 4). But for 2 M $LiCF_3SO_3$-PC systems, a band at 1282 cm^{-1} whose intensity increases as polymer concentration increases from 5 to 25 wt%, is observed. Its evolution and later its distinct preponderance for the 25 wt% PMMA gel is indicative of salt-polymer interaction as any Li^+-PMMA coordination will perturb the SO_3 modes more than the CF_3 modes. This is because only the oxygen atoms of SO_3 are directly linked with the cation and the CF_3 group is shielded from lithium ion's charge density [29]. This is also confirmed by the fact that $\nu_s(CF_3)$ for the $CF_3SO_3^-$ ion hardly undergoes any change with polymer addition as it continues to appear at ~1227 cm^{-1} in all the six gels under study.

Pure PMMA shows strong absorptions at ~1242, ~1150 and ~1192 cm^{-1}. The former two bands are ascribed to the asymmetric stretching vibration of the C—O—C bond {ν_a(C—O—C)} whereas the latter arises due to ν(C—O) of the OCH_3 group [31]. The bands due to PC are also seen in the same region owing to which the polymer's absorption bands are heavily superimposed by those due to the solvent. Precise assignments inclusive of polymer's contribution are difficult to make out as all the six spectra of gel electrolytes are nearly similar to those of the liquid electrolytes from which they have been derived.

In two molar gel electrolytes, the doublet expected to be observed just below 1000 cm^{-1}, is seen as a single peak at 950 cm^{-1}. Apart from the formation of a new band at ∼993 cm^{-1} (Fig. 3) and at ∼990 cm^{-1} (Fig. 4) in the spectra of all the gel electrolytes, whose intensity increases as PMMA's proportion in the system is raised, all other bands in the 1000–500 cm^{-1} region are unperturbed as their spectral features are retained from their parent liquid electrolytes. The band at ∼990 cm^{-1} is attributed to the symmetrical stretching of the C–O bond in the C–O–C linkage of PMMA [35].

4. Conclusions

Experimentally obtained vibrational spectra for lithium triflate dissolved in a polar, aprotic solvent (PC) show evidence of at least three species: free triflate ions, Li^+-$CF_3SO_3^-$ ion pairs and ion triplets or aggregates (Li^+—$CF_3SO_3^-$—Li^+). Ion pairs are identified by the splitting of the doubly degenerate $\nu_a(SO_3)$ modes (at 1272 cm^{-1} for free triflate in 0.025 and 0.05 M $LiCF_3SO_3$-PC) into two distinct bands at 1260 and 1299 cm^{-1} for $LiCF_3SO_3$ concentrations $\geq$0.5 M $LiCF_3SO_3$-PC. Existence of ion triplets in 2 M $LiCF_3SO_3$-PC electrolytes is confirmed by the $\delta_s(CF_3)$ component appearing at 763 cm^{-1}. The perturbed ring breathing and $\nu(C{=}O)$ modes of PC also ratify the aforesaid associations. Gel electrolytes with a low polymer content (upto 15 wt% of PMMA) can be regarded as organic non aqueous electrolytes constrained within a polymer matrix for which the liquid electrolyte like behavior is retained, thus affirming that PMMA does not play a crucial role in controlling conduction mechanism. But for the 2 M $LiCF_3SO_3$-PC + 25 wt% PMMA gel, although PMMA does not obstruct the conduction pathway of Li^+ ions through PC molecules drastically, a surprisingly complex pattern of Li^+-PMMA interactions is revealed. This motivated the proposal of a tentative model for cation solvation in the same gel which advocates a strong Li^+ interaction with the carbonyl oxygen of PMMA. Spectroscopic results fully support the claim that ion pairing/aggregation in liquid and gel electrolytes reduces their ionic conductivity. Future studies will therefore emphasize on the dependence of ionic mobility on viscosity at high salt and polymer concentrations and how it affects ionic conductivity.

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