

Plasticizer as a salt dissociator: a FT-IR investigation

Winie Tan^{*1}

¹Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Malaysia

*Corresponding author's phone: +603-55435738

E-mail: tanwinie@salam.uitm.edu.my

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ABSTRACT

Fourier transform infrared (FT-IR) spectroscopic studies have been undertaken to investigate the interactions between plasticizer ethylene carbonate (EC) and propylene carbonate (PC) with lithium trifluoromethanesulfonate (LiCF_3SO_3) salt. Evidences of EC- LiCF_3SO_3 and PC- LiCF_3SO_3 interactions have been manifested as frequency shifts and alteration in band shapes. Differences in the interactions of EC and PC with LiCF_3SO_3 are noted. The PC- LiCF_3SO_3 interaction tends to favor the formation of ion aggregates as compared to EC- LiCF_3SO_3 interaction.

Keywords: Ethylene Carbonate; Propylene Carbonate; LiCF_3SO_3 ; FT-IR.

1.0 INTRODUCTION

Low molecular weight solvents such as ethylene carbonate (EC) and propylene carbonate (PC) have been the most widely used plasticizing solvents for electrolyte system in a lithium ion battery. The role of a plasticizer is to help in the dissociation of lithium salt, which allows greater numbers of free ions for conduction [1]. The explanation to the mechanism of ionic conduction requires knowledge of the interactions existing between the cation and anion of salt with the plasticizing solvent. These interactions could be manifested

through FT-IR spectra as frequency shifts, alteration in band shapes, intensities and splitting of the internal vibrational modes. The work reported here involves a comprehensive spectroscopic study on ion-solvent interactions in EC-LiCF₃SO₃ and PC-LiCF₃SO₃ electrolytes.

2.0 EXPERIMENTAL

LiCF₃SO₃ with purity >96% from Aldrich was dried for 24 h at 120 °C prior to use. EC with high purity (>99%) from Fluka and PC with purity >99.7% from Aldrich were used as received. Various mixtures of EC (or PC):LiCF₃SO₃ with mass ratio of 2:1, 1:1 and 1:2 were prepared. ATR-FTIR spectroscopic studies were carried out using a Thermo Nicolet Avatar 370 FT-IR spectrophotometer in the frequency range from 650 to 4000 cm⁻¹ and at a resolution of 1 cm⁻¹.

3.0 RESULTS AND DISCUSSION

Characteristic frequencies exhibited by LiCF₃SO₃ are observed at 1293 cm⁻¹, 1252 cm⁻¹ (ν_{as}(SO₃)), 1224 cm⁻¹ (ν_s(CF₃)), 1188 cm⁻¹ (ν_{as}(CF₃)), 1044 cm⁻¹ (ν_s(SO₃)) and 776 cm⁻¹ (δ_s(CF₃)). The characteristic bands of EC and PC observed in the present study were assigned based on [2-5].

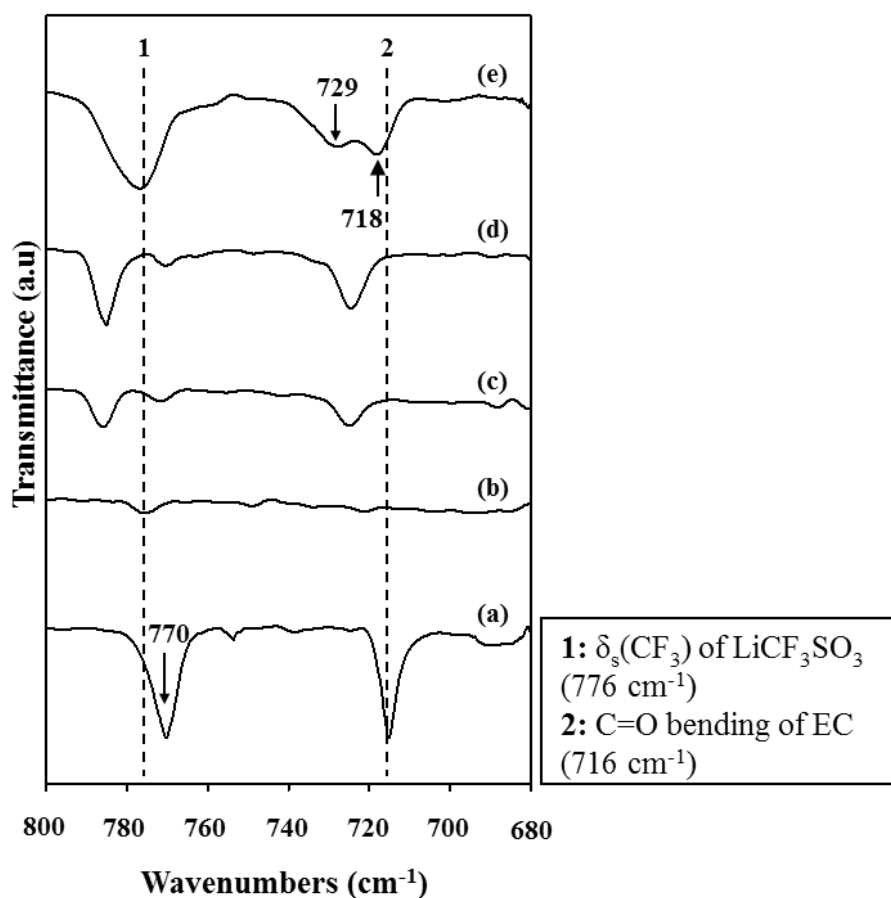


Figure 1: Infrared spectra of (a) pure EC; (b) LiCF_3SO_3 and LiCF_3SO_3 :EC complexes at the mass ratio of (c) 2:1 (d) 1:1 (e) 1:2 in the region between 680 and 800 cm^{-1}

The infrared spectra of the LiCF_3SO_3 and EC mixture at the mass ratio of 2:1, 1:1 and 1:2 in the region between 680 and 800 cm^{-1} are presented in Figure 1. The spectra of pure LiCF_3SO_3 and EC are also included for comparison purpose. The peak at 776 cm^{-1} due to $\delta_s(\text{CF}_3)$ of the salt was found to shift to 786 cm^{-1} with increased intensity when LiCF_3SO_3 interacts with EC as shown in Figure 1(c). The interaction between LiCF_3SO_3 and EC is also revealed by the changes in the band shape, the band width, the relative intensity and the vibrational frequency of the C=O bending mode of EC. The C=O bending mode located at 716 cm^{-1} has shifted to a higher wavenumber region and became a doublet at 718 and 729 cm^{-1} in the spectrum of LiCF_3SO_3 :EC at the ratio of 1:2.

The lower frequency wagging mode has become a weak shoulder of the merged band.

The perturbation of EC's vibrational modes in the presence of LiCF_3SO_3 reflects the EC- LiCF_3SO_3 interaction.

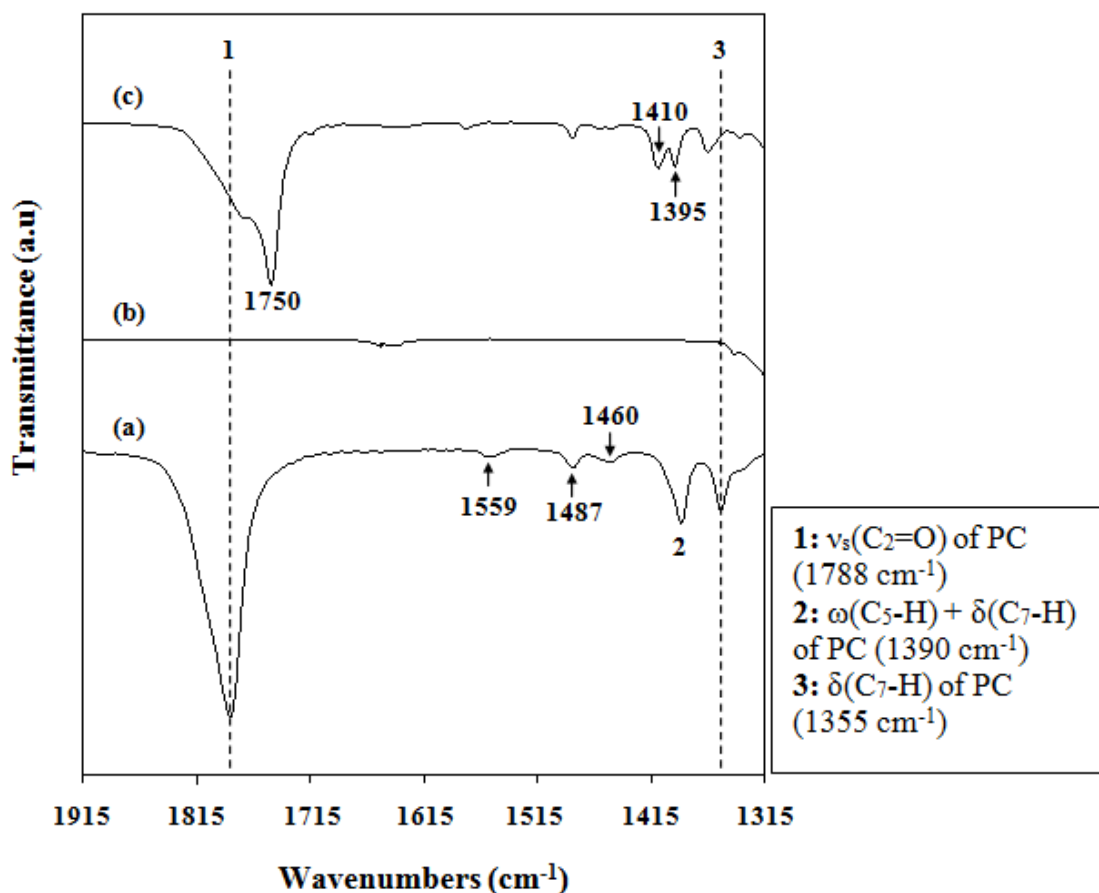


Figure 3: Infrared spectra of (a) pure PC (b) LiCF_3SO_3 and (c) LiCF_3SO_3 -PC complexes at the ratio of 1:1 in the region between 1315 and 1915 cm^{-1}

Figure 3 depicts the infrared spectra of pure PC and LiCF_3SO_3 and their complexes in the ratio of 1:1 from 1315 to 1915 cm^{-1} . Upon the incorporation of LiCF_3SO_3 to PC, a doublet with a strong band characteristic of $\nu_s(\text{C}_2=\text{O})$ at 1750 cm^{-1} , which is shifted from 1788 cm^{-1} in pure PC and a weak peak at 1776 cm^{-1} can be observed. Deepa and co-workers [6] suggested that the existence of this weak peak at the higher wavenumber region is a result of interaction of $\nu_s(\text{C}_2=\text{O})$ with the ring breathing mode via Fermi resonance. This observation indicates the

interaction between Li^+ ions of LiCF_3SO_3 and the oxygen atoms of $\text{C}=\text{O}$ groups of PC molecules.

The 1390 cm^{-1} ascribable to $\omega(\text{C}_5\text{-H}) + \delta(\text{C}_7\text{-H})$ in the spectrum of pure PC is found to split into two components at 1410 and 1395 cm^{-1} , subsequent to the addition of LiCF_3SO_3 . The 1355 cm^{-1} band upshifted to 1367 cm^{-1} as seen in the spectrum of LiCF_3SO_3 -PC complexes. On the other hand, various C-H deformational modes of PC located at 1559 , 1487 and 1460 cm^{-1} experience insignificant changes in vibrational frequencies when LiCF_3SO_3 is added to PC.

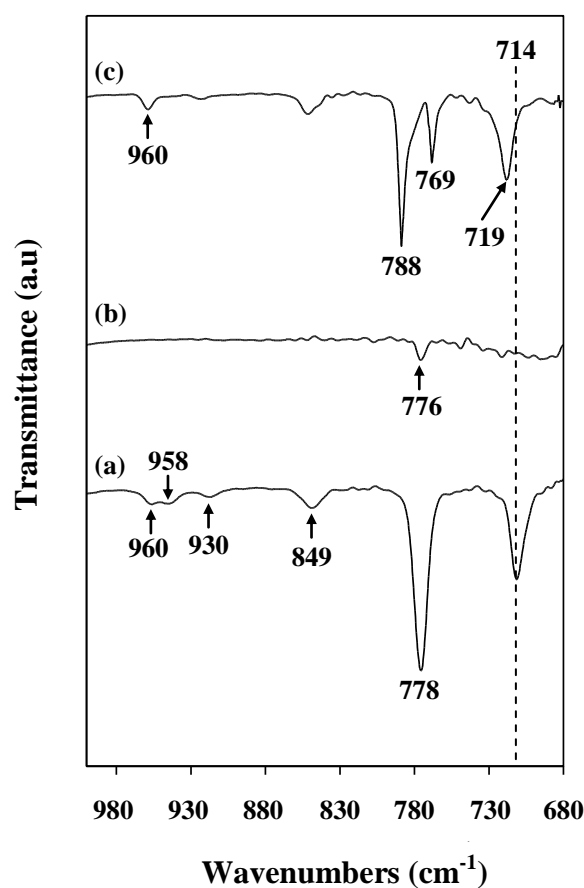


Figure 4: Infrared spectra of (a) pure PC (b) LiCF_3SO_3 and (c) LiCF_3SO_3 -PC complexes at the ratio of 1:1 in the region between 680 and 1000 cm^{-1}

The same spectrum in the region between 680 and 1000 cm^{-1} is presented in Figure 4. The 960 , 958 , 930 and 849 cm^{-1} observed in the spectrum of PC are attributed to the ring

breathing modes of PC molecules. The doublet with peaks at 960 and 958 cm^{-1} has merged to form a single band at 960 cm^{-1} in the presence of LiCF_3SO_3 . This demonstrates that Li^+ ions are also interacting with the ring oxygen of PC molecule.

In the spectral region between 680 and 830 cm^{-1} , PC exhibits two intense peaks at 714 cm^{-1} (symmetric ring deformation mode) and 778 cm^{-1} (ring deformation mode), whereas LiCF_3SO_3 shows a band at 776 cm^{-1} , which has been assigned to the $\delta_s(\text{CF}_3)$ mode. A frequency upshift is observed for the 714 cm^{-1} peak of PC (i.e. to 719 cm^{-1}), subsequent to the incorporation of LiCF_3SO_3 . This observation is in agreement with the spectroscopic results obtained for LiClO_4 -PC system by Battisti and co-workers [7]. Due to the nearness of 778 cm^{-1} of PC and 776 cm^{-1} of LiCF_3SO_3 , it is strongly believed that the 778 cm^{-1} has superimposed with 776 cm^{-1} and splits into two components at 788 and 769 cm^{-1} as observed in the spectrum of LiCF_3SO_3 -PC complexes. In summary, the perturbation of LiCF_3SO_3 and PC's vibrational modes as discussed above reflects the LiCF_3SO_3 and PC interaction.

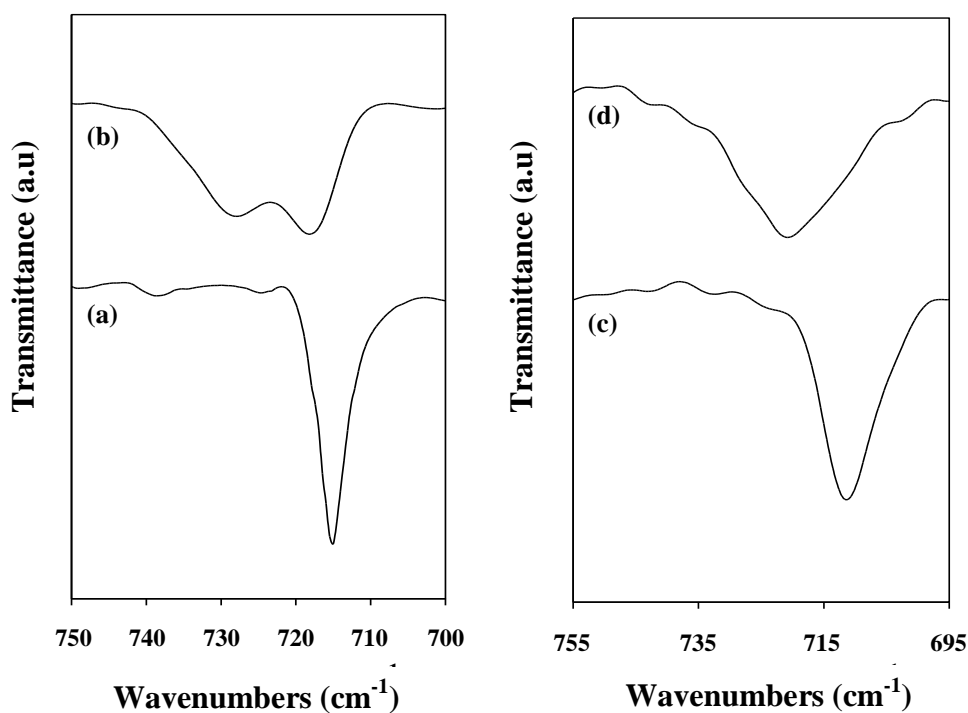


Figure 5: Infrared spectra of (a) pure EC; (b) EC- LiCF_3SO_3 (2:1); (c) pure PC and (d) PC- LiCF_3SO_3 (2:1) in the ring deformation region

In the present study, the differences in the interaction of EC and PC with LiCF_3SO_3 were analyzed from the angle of ring deformation and ring breathing region of EC and PC. Figure 5 shows the infrared spectra of EC- LiCF_3SO_3 and PC- LiCF_3SO_3 in the ring deformation region. It is important to note here that the mixture of EC and PC with LiCF_3SO_3 is fixed at the ratio of 2:1. For comparison, the spectra of pure EC and PC are also included. The C=O bending mode of EC and PC are located at 716 and 714 cm^{-1} , respectively. Besides the frequency shift of the C=O bending mode of EC and PC, a second peak is also observed to appear at 729 cm^{-1} in the EC- LiCF_3SO_3 complex and at 728 cm^{-1} in the spectrum of PC- LiCF_3SO_3 . These observations are consistent with earlier studies [7,8].

Figure 6 depicts the same spectra in the ring breathing region. The ring breathing mode of EC and PC are located at 894 and 849 cm^{-1} , respectively. Upon incorporation of LiCF_3SO_3 to EC, only one peak is observed at 903 cm^{-1} as shown in Figure 6(b). On the other hand, a pair of doublet peaks at 846 and 851 cm^{-1} are seen in the spectrum of PC- LiCF_3SO_3 . The FWHM of the doublets of PC- LiCF_3SO_3 are broader as compared to the band in the spectrum of EC- LiCF_3SO_3 . This demonstrates that the interaction between EC and LiCF_3SO_3 is highly specific while the PC and LiCF_3SO_3 interaction favors a broad distribution of LiCF_3SO_3 ionic species [8]. In other words, the PC- LiCF_3SO_3 complexes tend to favor the formation of ion aggregates. This is due to the lower dielectric constant of PC which does not favor the complete dissociation of LiCF_3SO_3 [9].

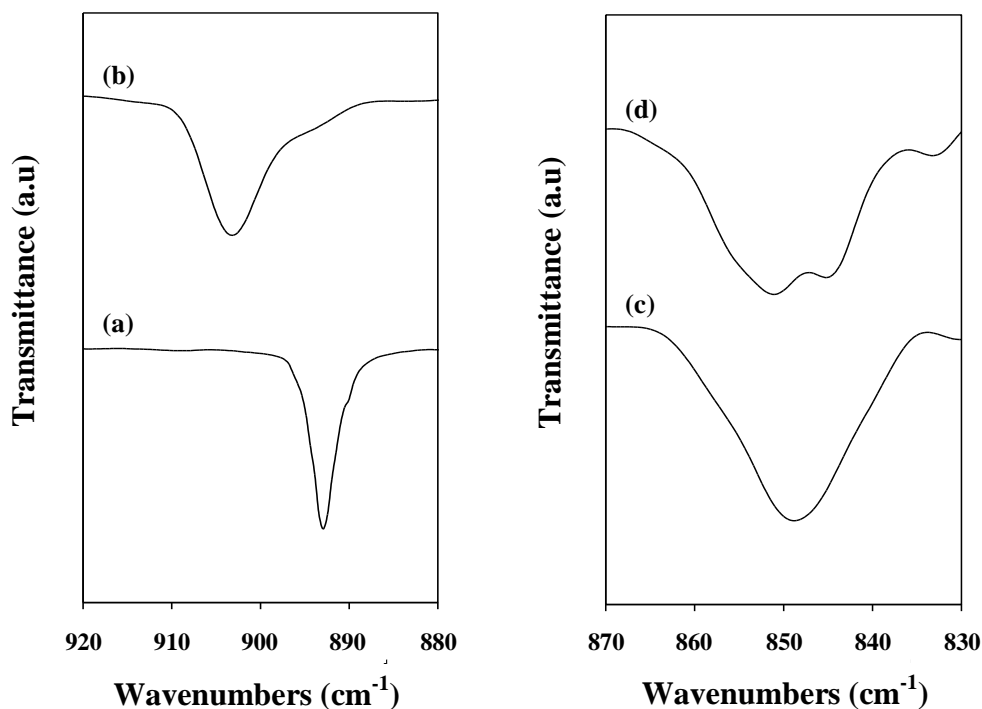


Figure 6: Infrared spectra of (a) pure EC; (b) EC-LiCF₃SO₃ (2:1); (c) pure PC and (d) PC-LiCF₃SO₃ (2:1) in the ring breathing region

4.0 CONCLUSIONS

EC-LiCF₃SO₃ and PC-LiCF₃SO₃ interactions were manifested experimentally in FT-IR study as frequency shifts, alteration in band shape and intensities as well as splitting of the internal vibrational modes. Preferential formation of ion aggregates in PC-LiCF₃SO₃ interaction has been noted.

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