Fluorescence Behavior and Specific Interactions of an Ionic Liquid in Ethylene glycol derivatives

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Tejwant Singh and Arvind Kumar

Introduction

In resent years,

- unique spatial heterogeneity from results (inherent polar/nonpolar segregation)

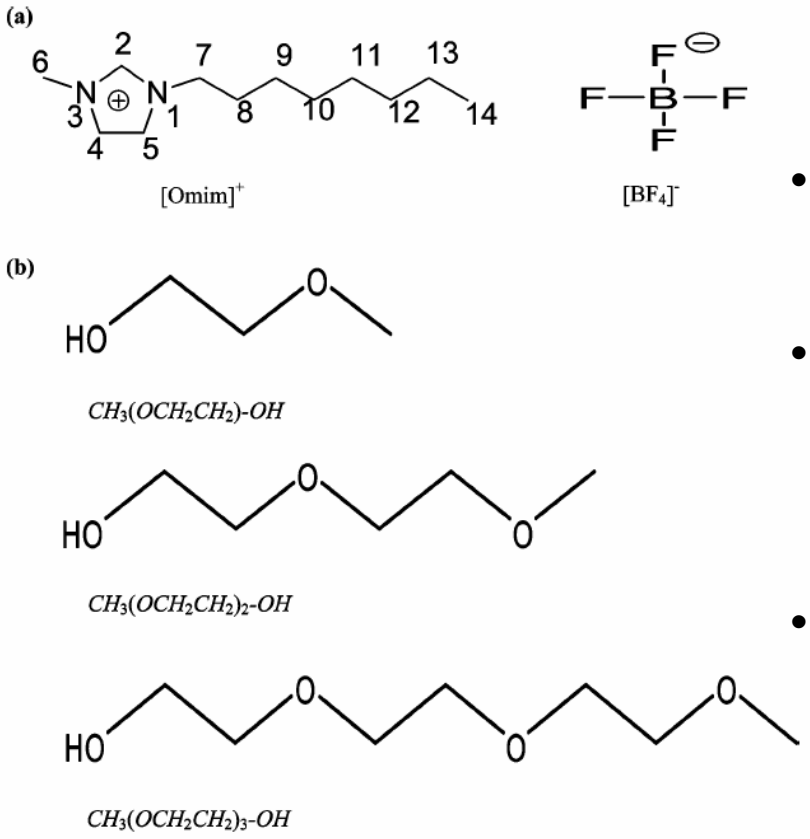
  - Experimental & computer simulation of pure ionic liquids
    (nanostructural organization in ionic liquids with various alkyl chain lengths)

- Water or organic solvent mixture are extensively studied by various techniques.
  (the exact information about the nature of interaction at molecular level)

- ^{1}H NMR and FT-IR measurements
  (the existence of aggregate-like structures of the IL in dilute region and
  comparatively stronger cation-anion interactions in the IL-rich region of the mixture)

Introduction

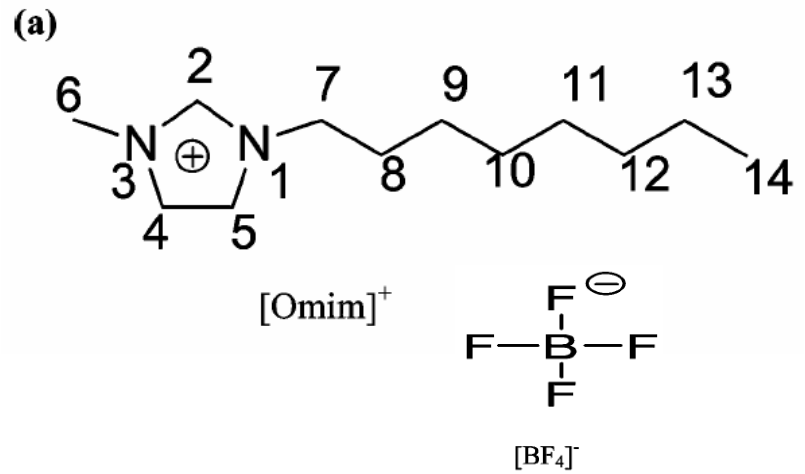
SCHEME 1: (a) Constituent Ions of the Ionic Liquid 1-Octyl-3-methylimidazolium Tetrafluoroborate; (b) Structure of the Organic Liquids



- Absorption (Cary 500, Varian)
  & Fluorescence (Fluorolog, Horiba Jobin Yvon)
- NMR (Bruker 500 and 200 MHz
  - standard : TMS in C_6D_6)
  - Chemical shift, (C-2, C-4,C-5, C-14 of ionic liquid)
    (-OH of glycol derivatives)
- FT-IR (Spectrum GX Series 49387)
  (BF_4^- stretching of the IL in glycol derivatives)

Results & discussion

[OMIM][BF_4]



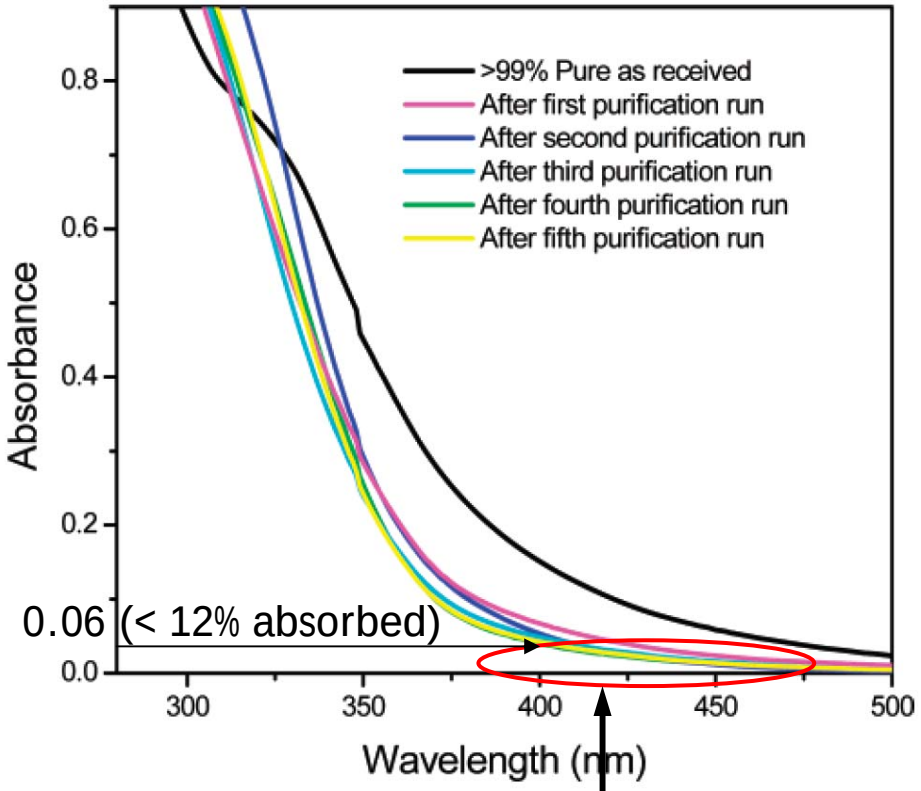


Figure 1. Comparison of absorption spectra of neat [Omim][BF_4] as received and after repeated purification.

Long tail of absorption spectra
(Due to the Imidazolium moiety of ionic liquid and not due to the impurities)

Results & discussion

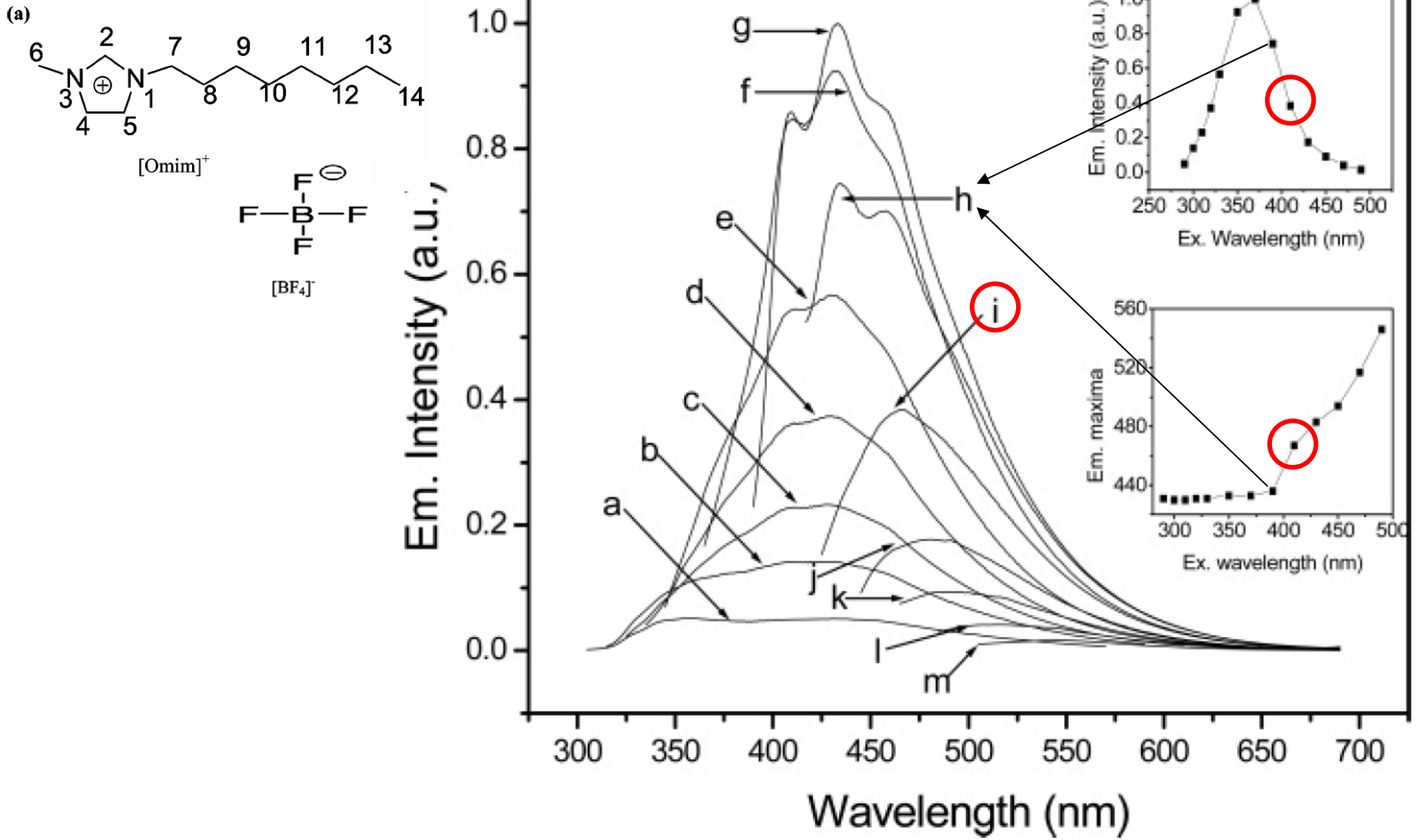


Figure 2. Excitation-wavelength-dependent [λ_{exc} (nm) = 280−490 (a−m)] emission behavior of neat [Omim][BF_4].

Results & discussion

CPL 402, 375 (2005), JPCB 109, 9148 (2005) by samanta

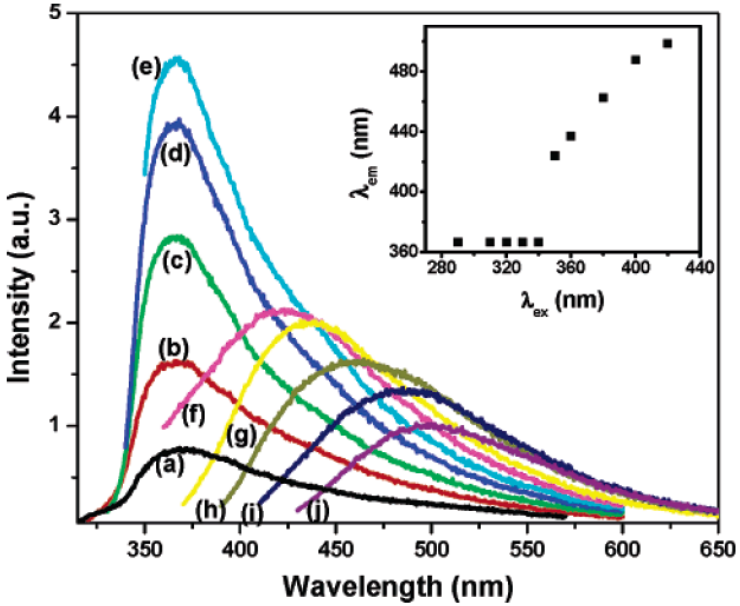


Figure 3. Excitation wavelength-dependent emission behavior of neat [bmim][BF_4]. λ_{exc} (nm) = 290 (a), 310 (b), 320 (c), 330 (d), 340 (e), 350 (f), 360 (g), 380 (h), 400 (i), and 420 (j).

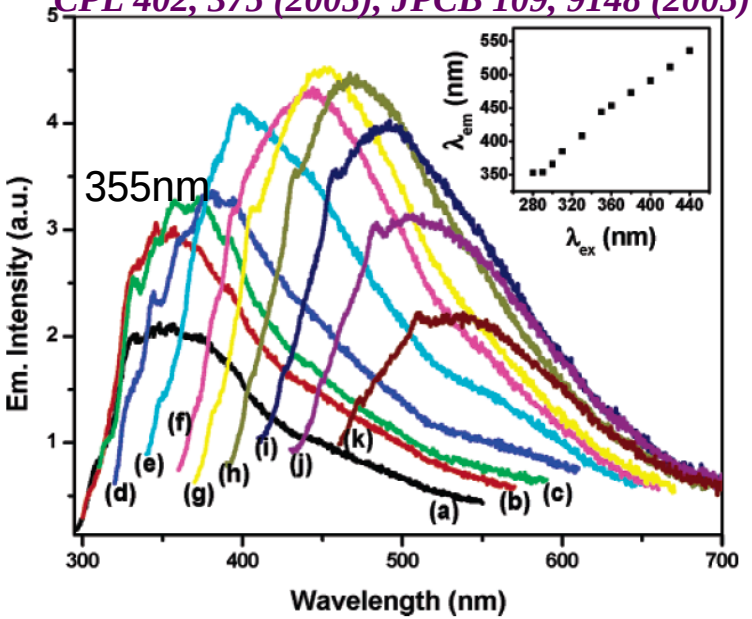
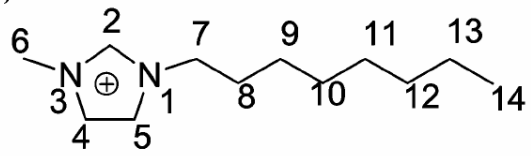
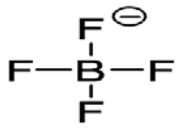


Figure 4. Excitation wavelength-dependent emission behavior of neat [emim][BF_4]. λ_{exc} (nm) = 280 (a), 290 (b), 300 (c), 310 (d), 330 (e), 350 (f), 360 (g), 380 (h), 400 (i), 420 (j), and 440 (k).

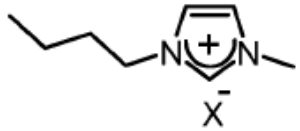
Red edge effect (excitation wavelength)

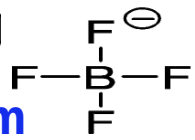
(a)



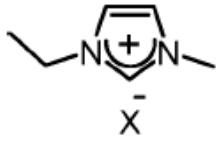


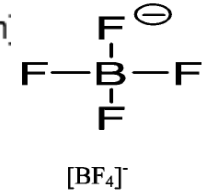
390nm >





340nm >

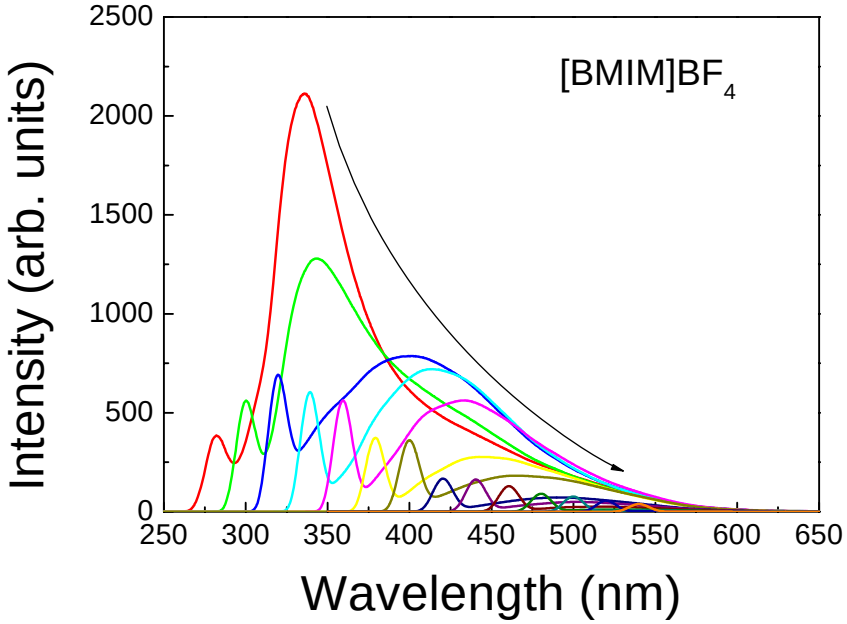


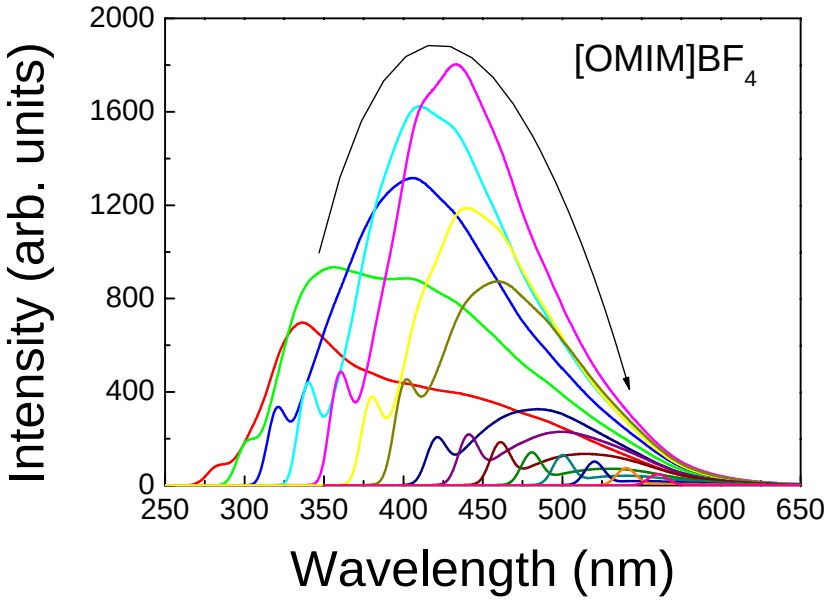


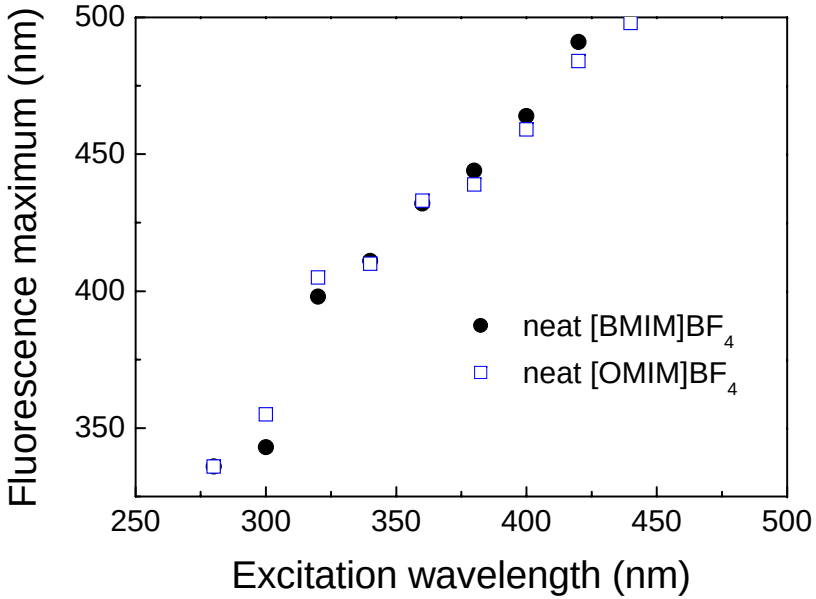
300nm

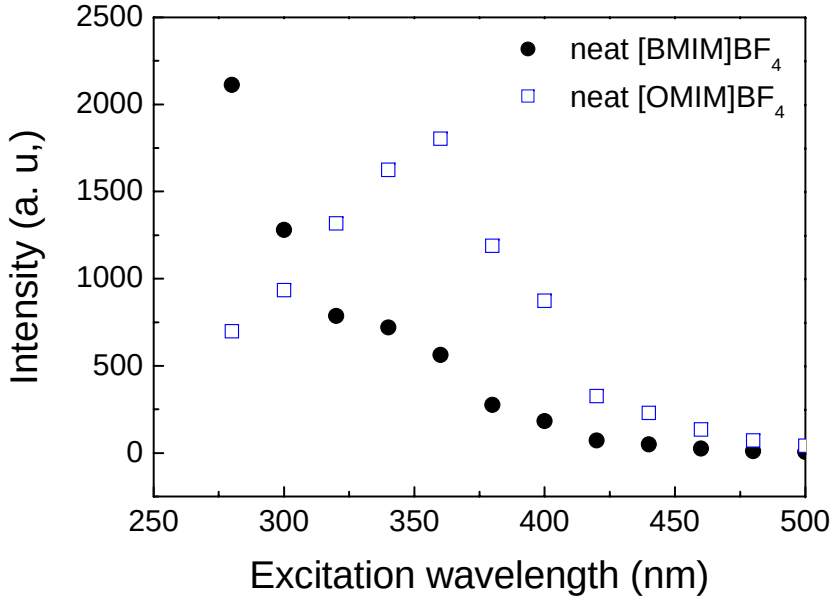
Higher viscosity of the longer alkyl chain IL
or the associated structure with polar/nonpolar segregation

Results & discussion

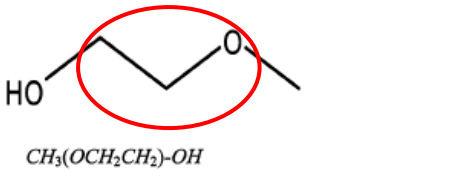








Results & discussion



$CH_3(OCH_2CH_2)$-OH

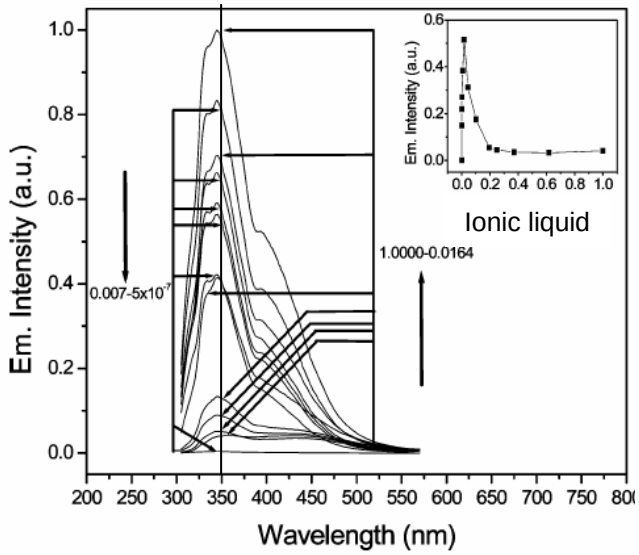
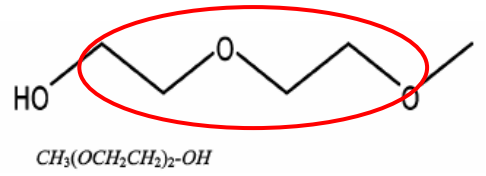


Figure 3. Emission spectra at an excitation wavelength of 290 nm as a function of the mole fraction of the ionic liquid in the mixtures {[Omim][BF_4] + $CH_3(OCH_2CH_2)$−OH}.



$CH_3(OCH_2CH_2)_2$-OH

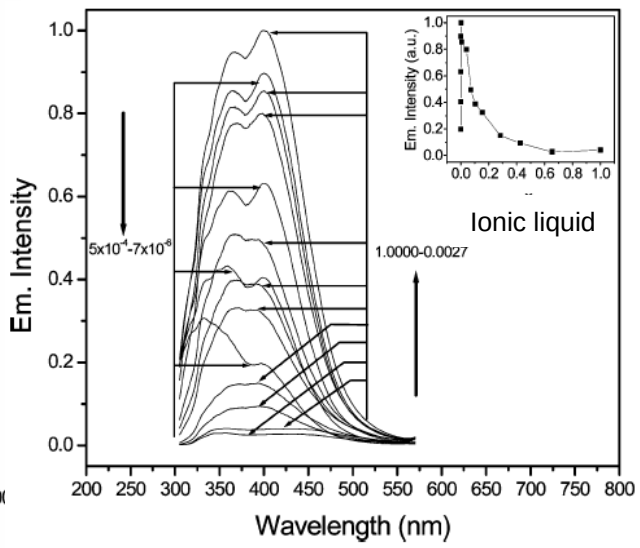
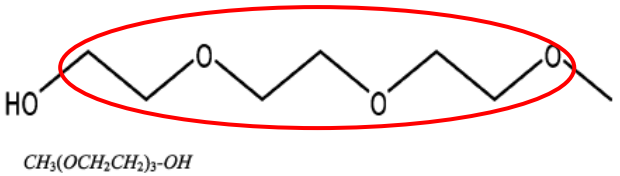


Figure 4. Emission spectra at an excitation wavelength of 290 nm as a function of the mole fraction of the ionic liquid in the mixtures {[Omim][BF_4] + $CH_3(OCH_2CH_2)_2$−OH}.



$CH_3(OCH_2CH_2)_3$-OH

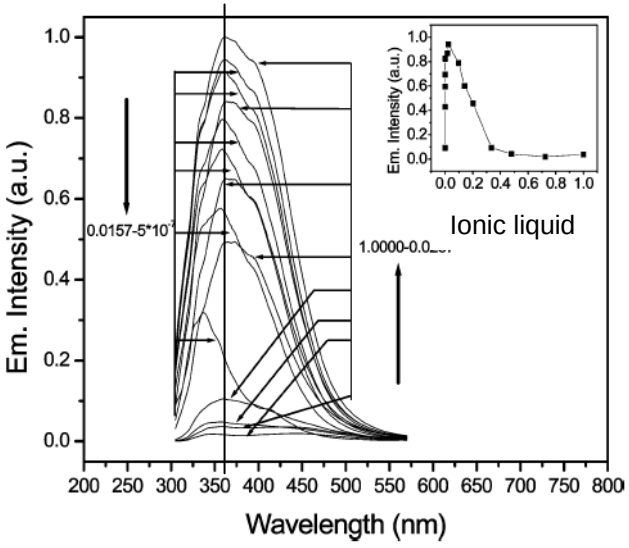


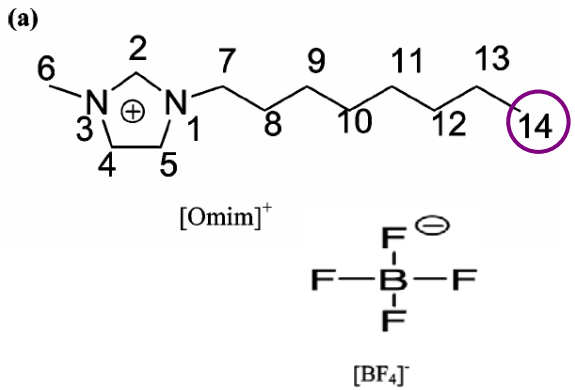
Figure 5. Emission spectra at an excitation wavelength of 290 nm as a function of the mole fraction of the ionic liquid in the mixtures {[Omim][BF_4] + $CH_3(OCH_2CH_2)_3$−OH}.

Excitation wavelength : 290nm

Blue shift (with increase of organic concentration) in the spectra

- intermolecular hydrogen bonding between [OMIM][BF_4] and glycol derivatives in the mixtures
- decrease in the viscosity of the medium
  (which makes the relaxation of the photo excited species more efficient)

Results & discussion



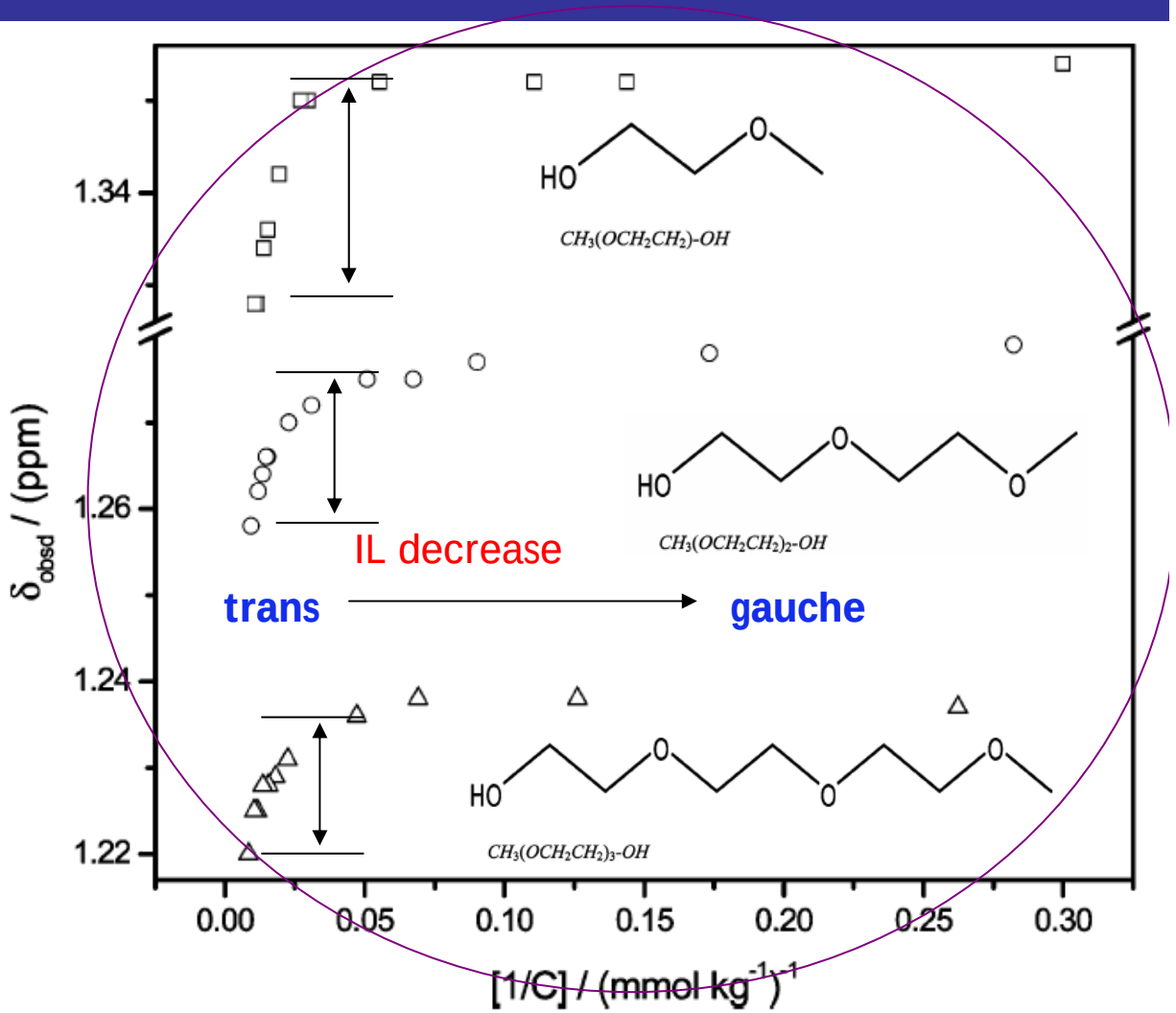


Figure 6. Variation of δ_{obsd} for the protons of the terminal methyl group of the imidazolium cation at C-14 against the reciprocal concentration of the IL in various binary mixtures in the IL-dilute region: (□) $CH_3(OCH_2CH_2)-OH$; (○) $CH_3(OCH_2CH_2)_2-OH$; and (△) $CH_3(OCH_2CH_2)_3-OH$.

Results & discussion (NMR)

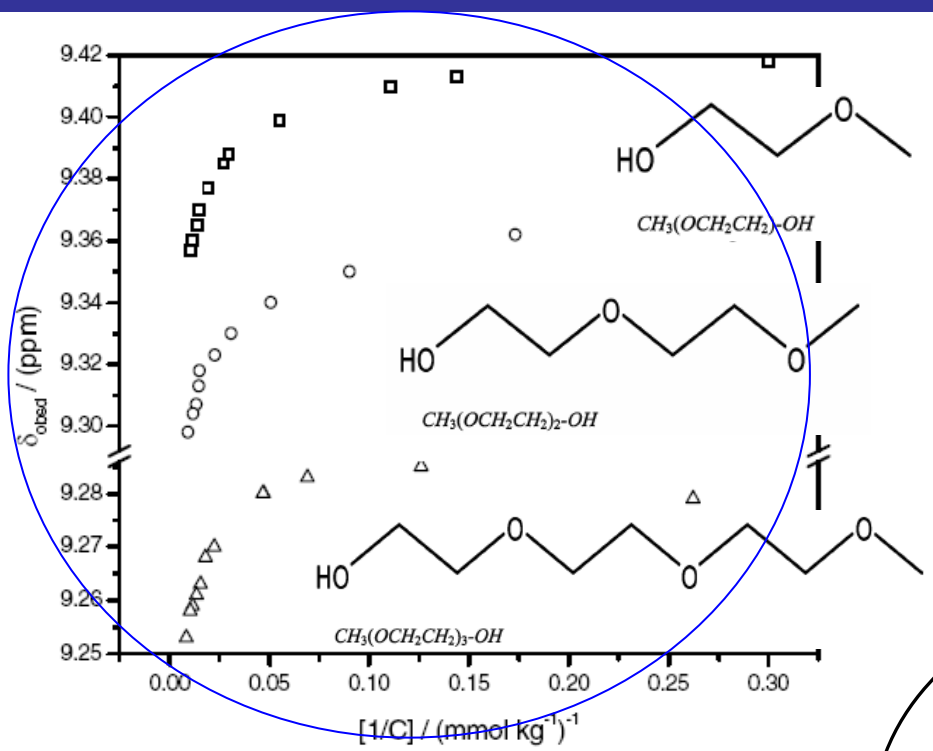


Figure S2. Variation of δ_{obsd} for the protons of imidazolium cation at C-2 against the reciprocal concentration of the IL in various binary mixtures in IL dilute region: (□) $CH_3(OCH_2CH_2)$-OH; (○) $CH_3(OCH_2CH_2)_2$-OH; and (△) $CH_3(OCH_2CH_2)_3$-OH.

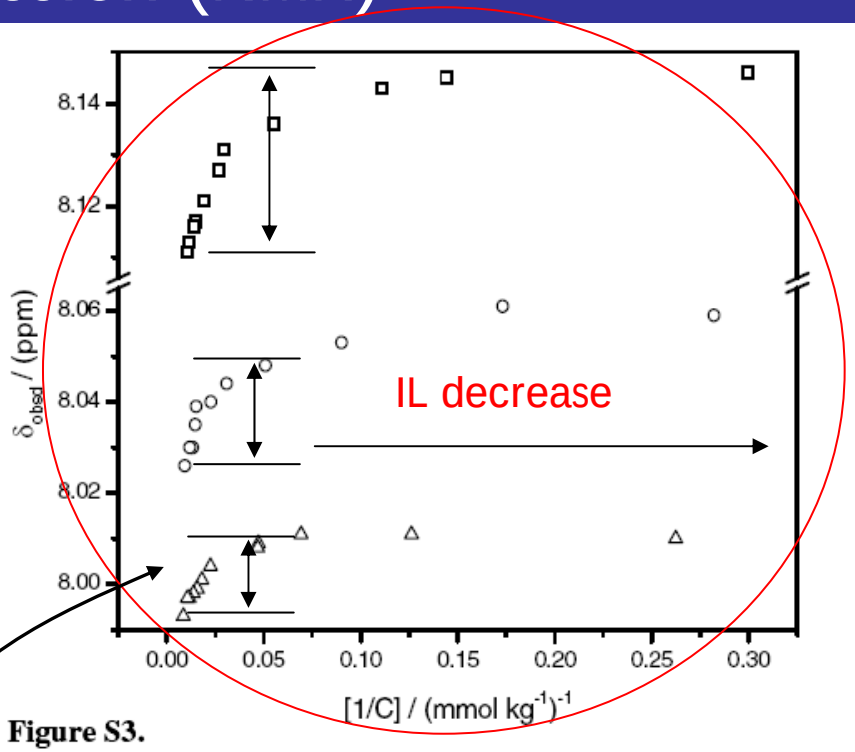
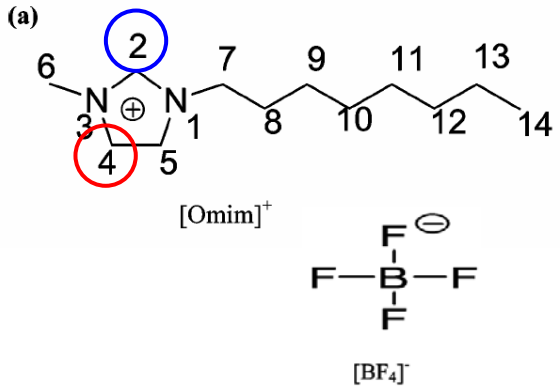


Figure S3.

Figure S3. Variation of δ_{obsd} for the protons of imidazolium cation at C-4 against the reciprocal concentration of the IL in various binary mixtures in IL dilute region: (□) $CH_3(OCH_2CH_2)$-OH; (○) $CH_3(OCH_2CH_2)_2$-OH; and (△) $CH_3(OCH_2CH_2)_3$-OH.

Ring stacking through π-π interaction



Aggregated structures decreases with –OC_2H_4 group

Results & discussion (NMR)

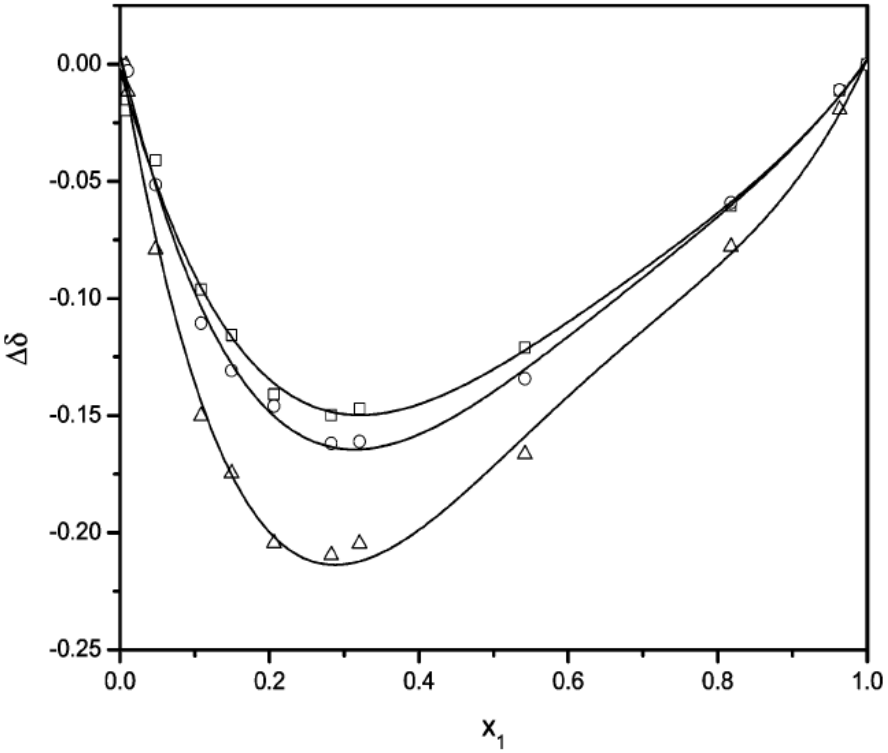


Figure 7. Comparison of the deviation in chemical shift $\Delta\delta$ for various protons of the IL in $CH_3(OCH_2CH_2)-OH$: (□) terminal methyl protons at C-14; (○) ring protons at C-4,5; and (△) ring proton at C-2.

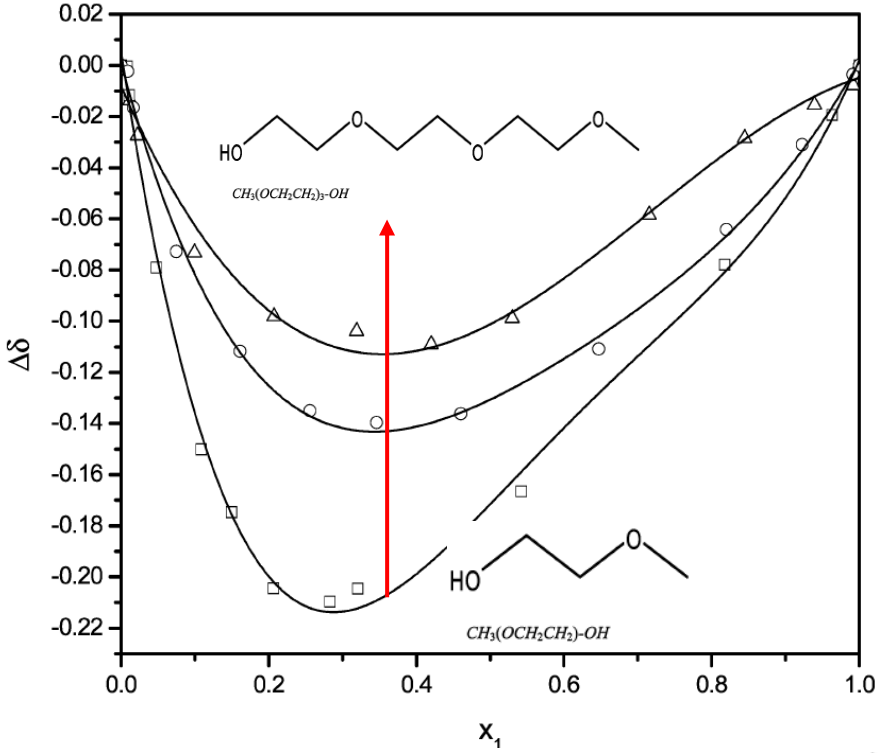


Figure 8. Comparison of the deviation in chemical shift $\Delta\delta$ for the ring proton at C-2 of the IL in different glycol derivatives: (□) $CH_3(OCH_2CH_2)-OH$; (○) $CH_3(OCH_2CH_2)_2-OH$; and (△) $CH_3(OCH_2CH_2)_3-OH$.

Ring proton at C2

V

Ring proton at C-4,5

V

Ring proton at C-14

- Hydrogen-bonded interactions decrease with $-OC_2H_4$ group

- Intramolecular hydrogen bonding increases with nunmber of oxygen atoms in the ethylene glycol derivative

- Reduces the number of possible intermolecular H-bonds

Results & discussion (FT-IR)

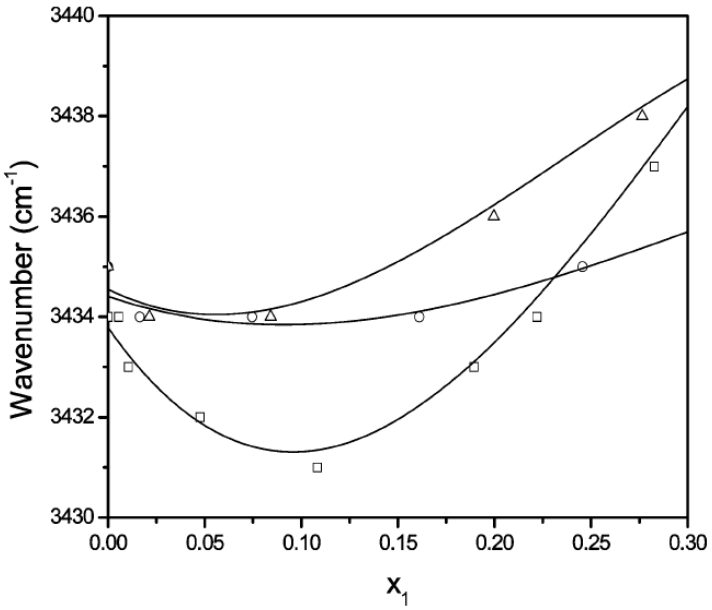


Figure 9. Comparison of the −OH stretching of the different glycol derivatives in the IL-dilute region of the mixtures: (□) $CH_3(OCH_2CH_2)-OH$; (○) $CH_3(OCH_2CH_2)_2-OH$; and (△) $CH_3(OCH_2CH_2)_3-OH$. Solid lines represent the polynomial fits to the experimental data.

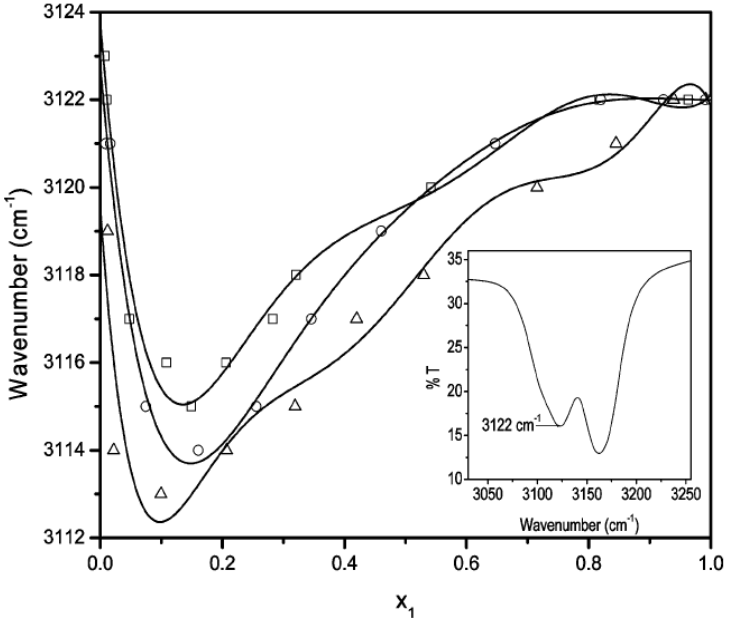


Figure 10. Comparison of the H−C-2 stretching of the IL in different glycol derivatives: (□) $CH_3(OCH_2CH_2)-OH$; (○) $CH_3(OCH_2CH_2)_2-OH$; and (△) $CH_3(OCH_2CH_2)_3-OH$.

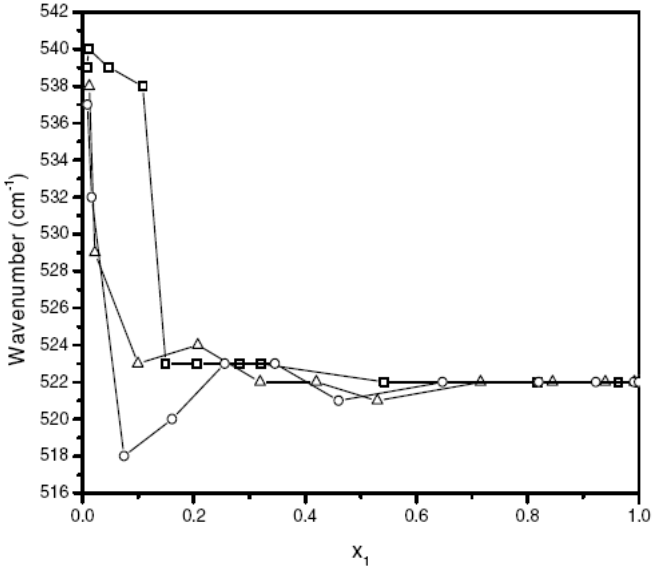


Figure S7. Comparison of the BF_4 stretching of the IL in different glycol derivatives: (□) $CH_3(OCH_2CH_2)$-OH; (○) $CH_3(OCH_2CH_2)_2$-OH ; and (△) $CH_3(OCH_2CH_2)_3$-OH .

Conclusions

[OMIM][BF4]+ethylene glycol derivatives

: steady-state fluorescence, ^{1}H NMR, and FT-IR

Results & discussion