Fluorescence Behavior and Specific Interactions of an Ionic Liquid in Ethylene Glycol Derivatives

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The excitation-wavelength- and concentration-dependent fluorescence response of an ionic liquid (IL), 1-octyl-3-methylimidazolium tetrafluoroborate [Omim][BF_4], in the ethylene glycol derivatives, [$CH_3(OCH_2CH_2)_n$−OH, $n = 1-3$], has been critically examined in the entire composition range. The pure IL exhibited a large red shift beyond an excitation wavelength of 390 nm, showing the heterogeneous nature of the liquid. Concentration dependence of the fluorescence spectra in the organic solvent-rich region favors the association of IL molecules into the aggregated structures. The maximum of the fluorescence spectra shifted toward blue with the increase of organic component concentration in all of the mixtures, reflecting an appreciable solute−solvent interaction. Very high concentrations of the organic liquid in the mixtures resulted in the inversion of the spectral shift toward red, indicating the dominance of $\pi-\pi^*$ transitions over the $n-\pi^*$ transitions as a consequence of imidazolium ring stacking. ^{1}H NMR and FT-IR investigations over the whole composition range of the mixtures showed multiple hydrogen-bonded interactions of varying strengths between the unlike molecules and the existence of associated species of the IL in the dilute region. Both the specific interactions between unlike molecules and the tendency of aggregation of IL molecules in the dilute region reduced with the introduction of the $-OC_2H_4$ group in the glycol derivative. A comparison of specific interactions with the volumetric properties of the similar mixtures shows that the packing efficiency depending on differences in the shape and size of the molecules mainly decides the overall magnitude of deviations from ideality.

Sample

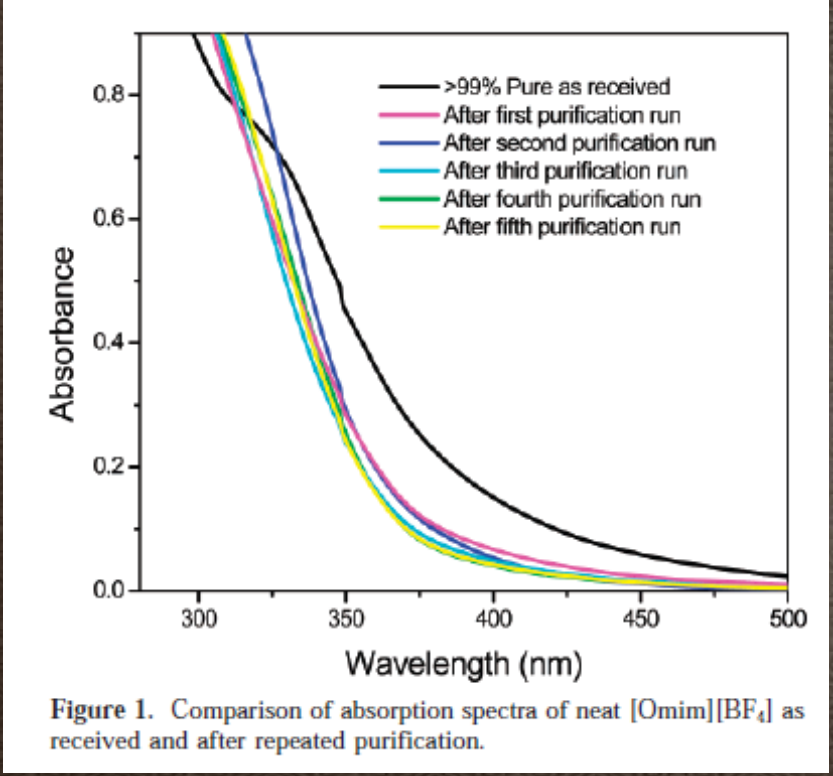


Figure 1. Comparison of absorption spectra of neat [Omim][BF_4] as received and after repeated purification.

[OMIM][BF_4] >99.0%

Purification

Decolorization (column comprise of celite, silica, and charcoal)
Drying under 60℃

1cm cuvette

Sample

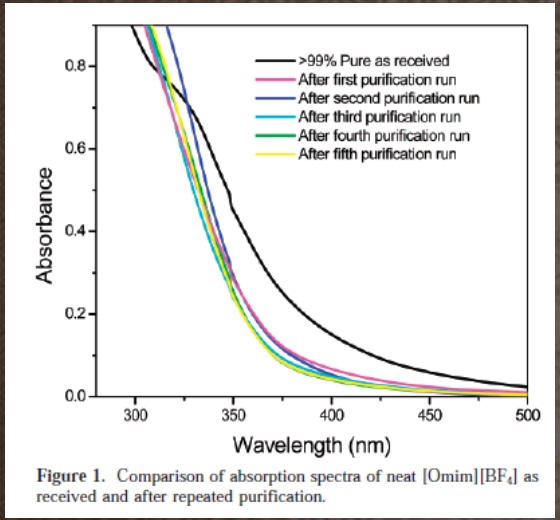
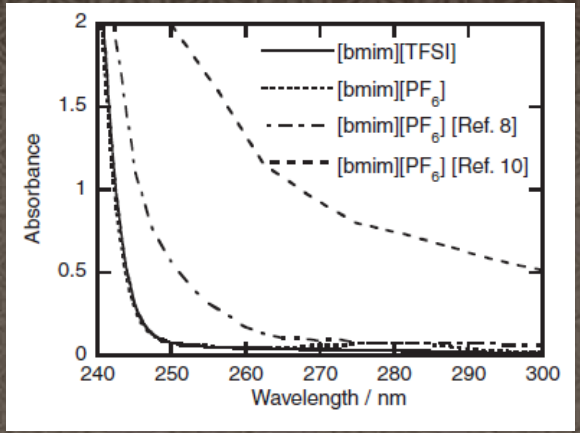
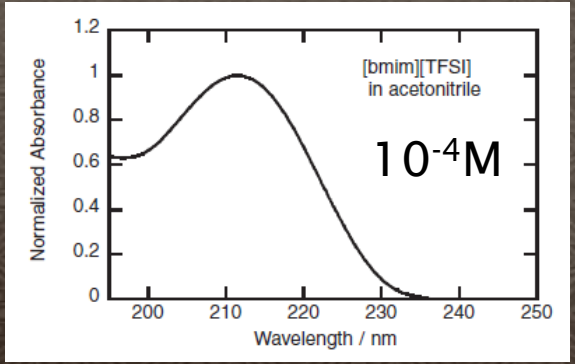
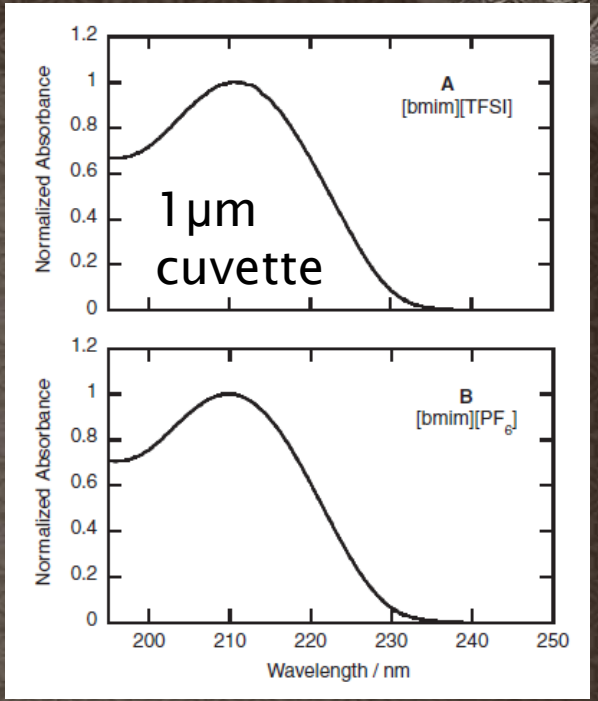


Figure 1. Comparison of absorption spectra of neat [Omim][BF_4] as received and after repeated purification.

[OMIM][BF_4]







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Fluorescence

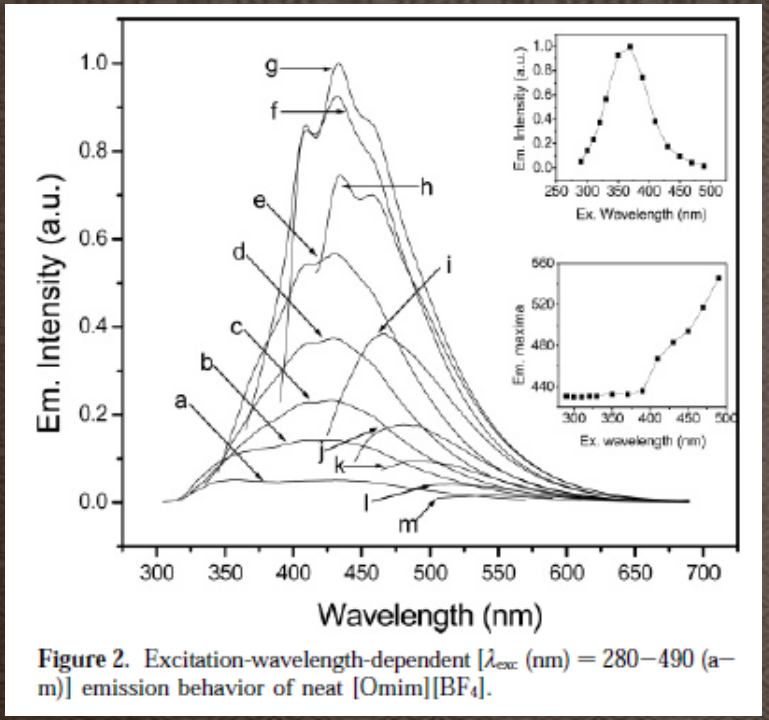


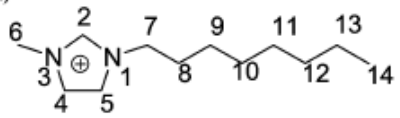
Figure 2. Excitation-wavelength-dependent [λ_{exc} (nm) = 280−490 (a−m)] emission behavior of neat [Omim][BF_4].

2.5nm slit resolution

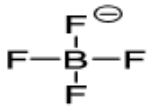
Dilution Experiments

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

(a)



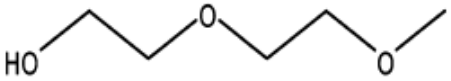
[Omim]$^+$



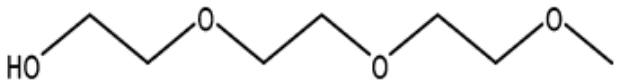
[BF_4]$^-$

(b)

$CH_3(OCH_2CH_2)$-OH



$CH_3(OCH_2CH_2)_2$-OH



$CH_3(OCH_2CH_2)_3$-OH

Dilution Experiments

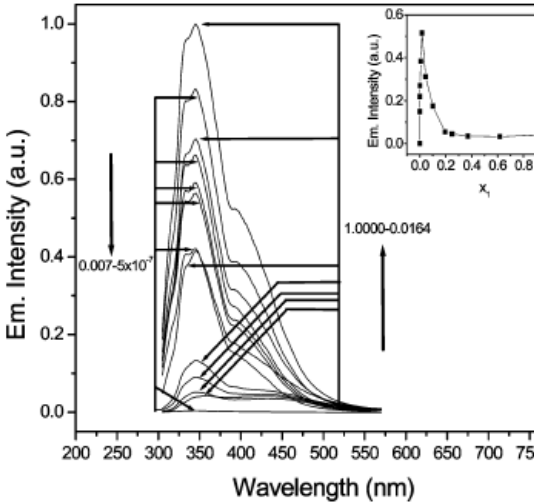


Figure 3. Emission spectra at an excitation wavelength of 290 a function of the mole fraction of the ionic liquid in the mixtu [Omim][BF_4] + $CH_3(OCH_2CH_2)$−OH}.

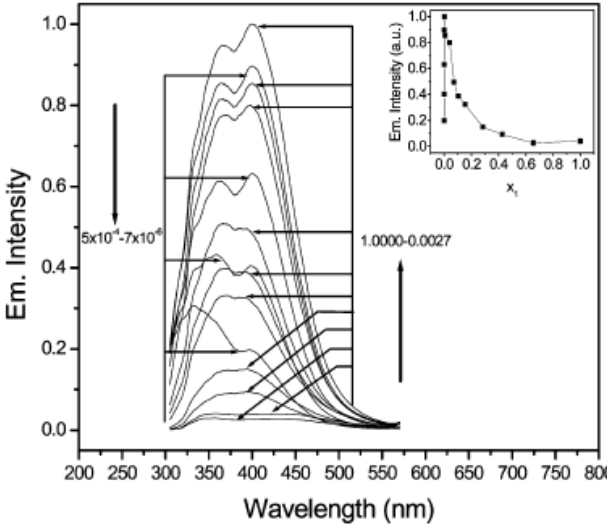


Figure 4. Emission spectra at an excitation wavelength of 290 nm as a function of the mole fraction of the ionic liquid in the mixtures {- [Omim][BF_4] + $CH_3(OCH_2CH_2)_2$−OH}.

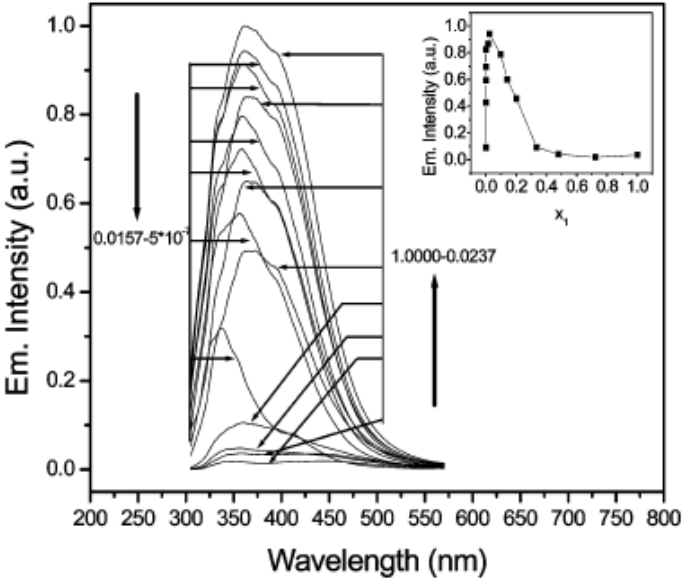
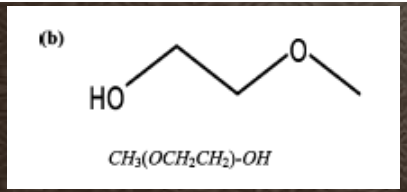
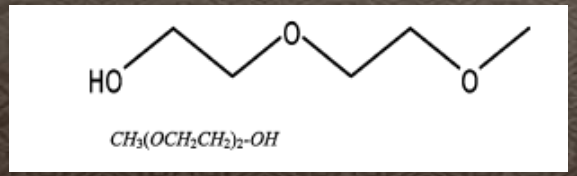
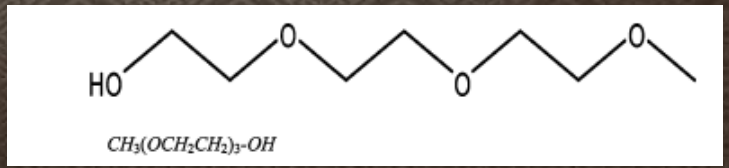


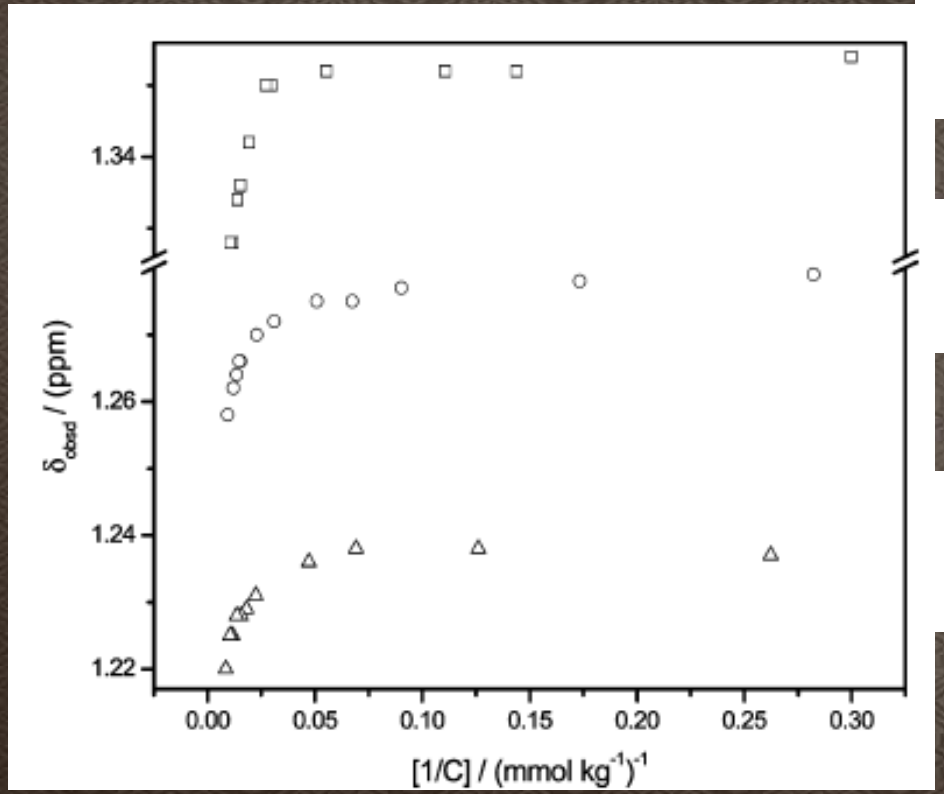
Figure 5. Emission spectra at an excitation wavelength of 290 nm as a function of the mole fraction of the ionic liquid in the mixtures {- [Omim][BF_4] + $CH_3(OCH_2CH_2)_3$−OH}.

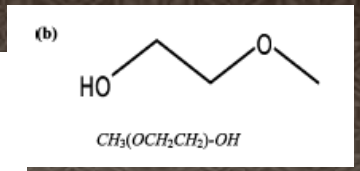


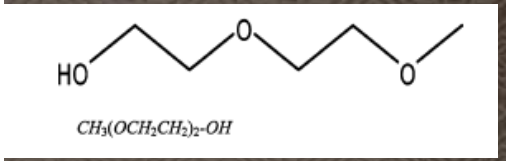


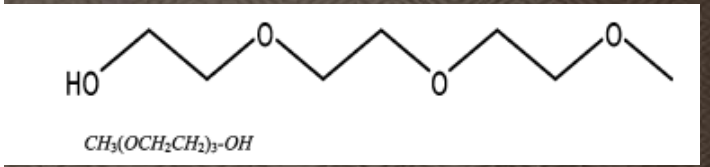


Dilution Experiments



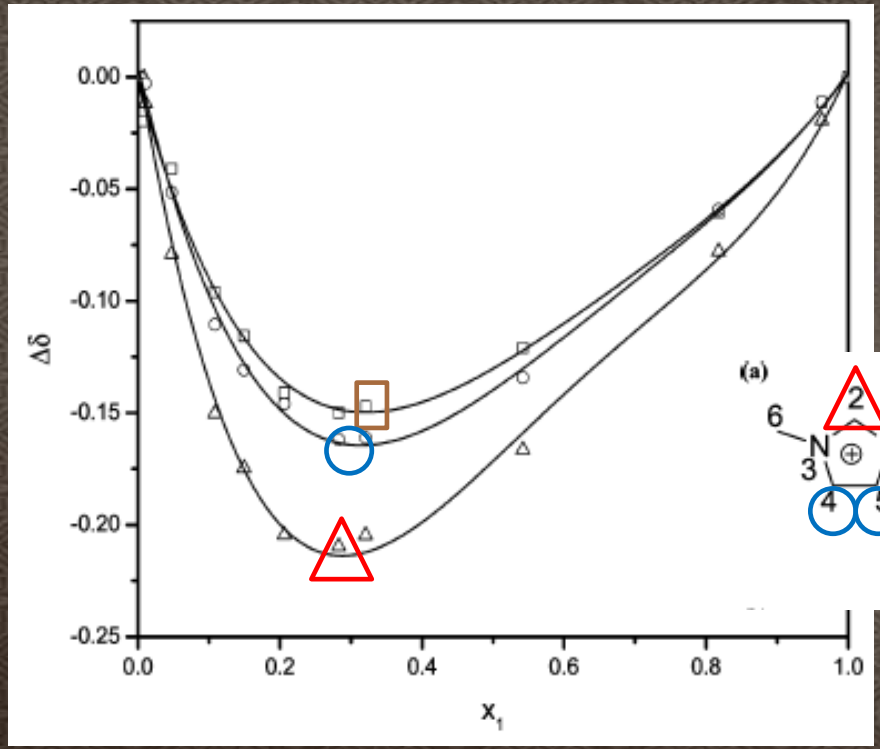


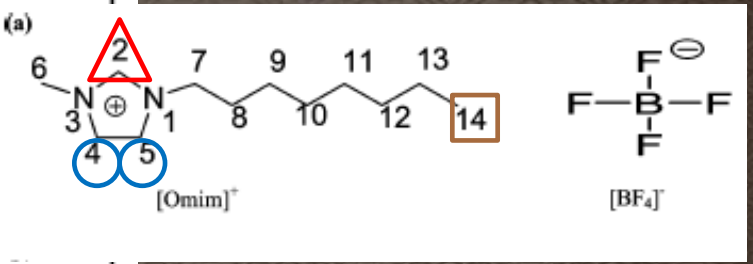




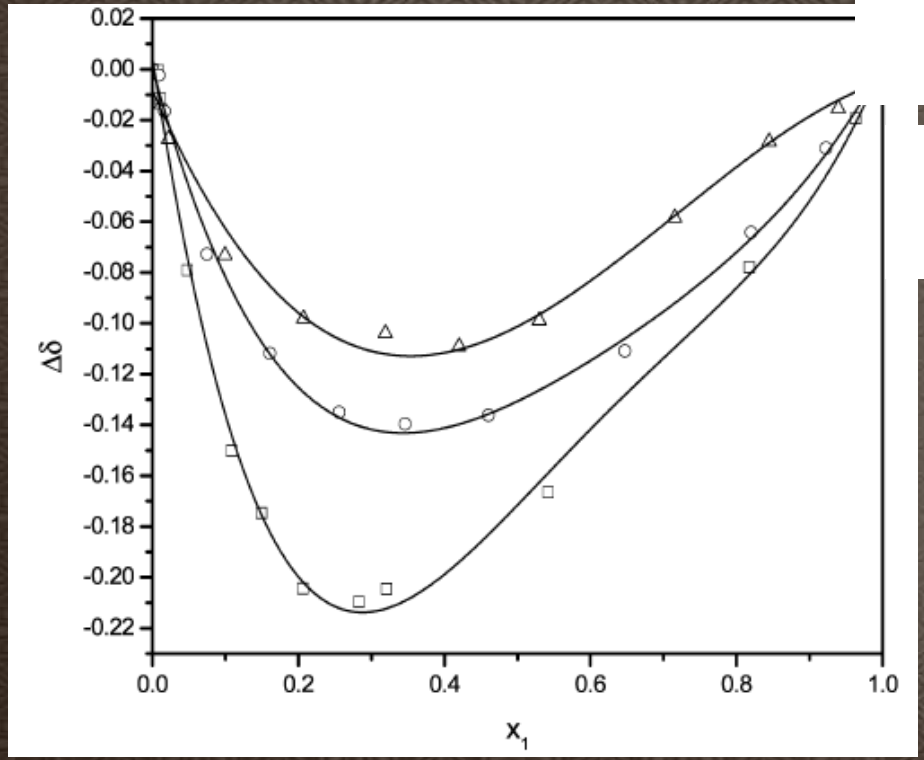
Dilution Experiments

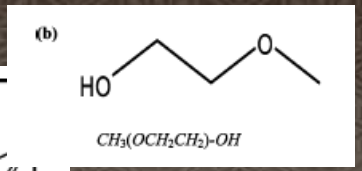
$$\Delta\delta = \delta - x_1\delta_1^{\infty} - x_2\delta_2^{\infty}$$

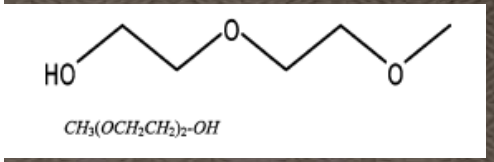


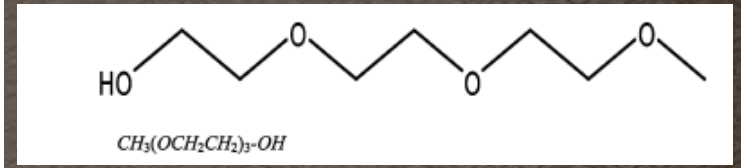


Dilution Experiments









FT-IR Experiments

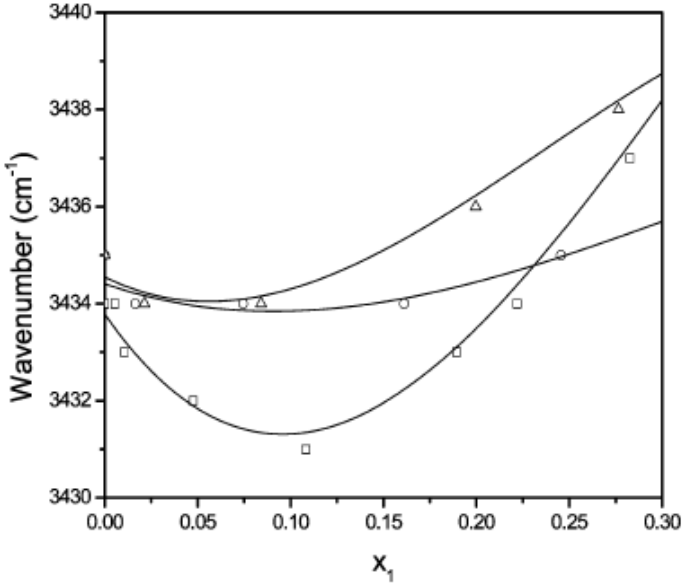


Figure 9. Comparison of the −OH stretching of the different glycol derivatives in the IL-dilute region of the mixtures: (□) $CH_3(OCH_2CH_2)-OH$; (○) $CH_3(OCH_2CH_2)_2-OH$; and (△) $CH_3(OCH_2CH_2)_3-OH$. Solid lines represent the polynomial fits to the experimental data.

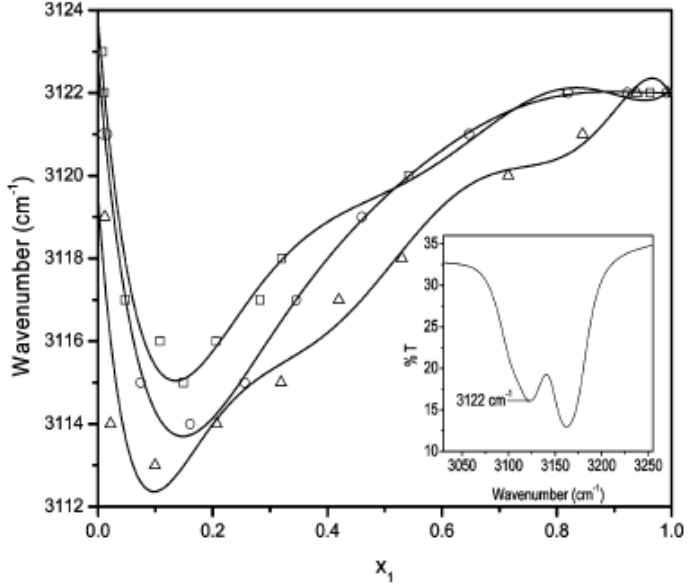


Figure 10. Comparison of the H−C-2 stretching of the IL in different glycol derivatives: (□) $CH_3(OCH_2CH_2)-OH$; (○) $CH_3(OCH_2CH_2)_2-OH$; and (△) $CH_3(OCH_2CH_2)_3-OH$.

Speculation

The long tail of the absorption spectra might be due to the presence of various associated species that are energetically different

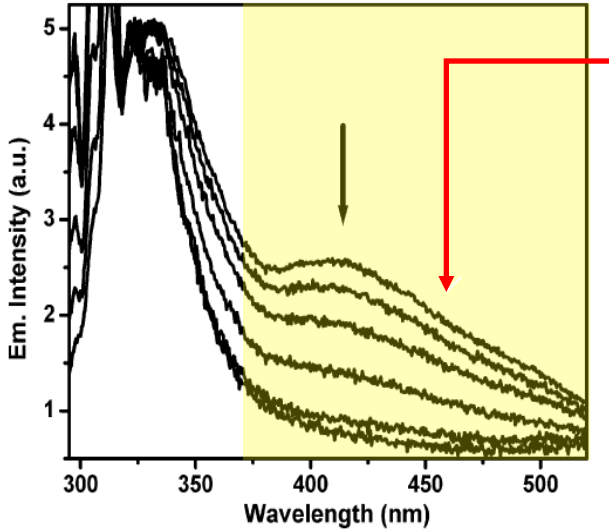


Figure 8. Effect of dilution (using acetonitrile) on the fluorescence profile of [bmim][PF_6]. λ_{exc} = 285 nm. The spectra are normalized at the lower wavelength emission maximum. The concentrations of [bmim][PF_6] in decreasing order of the fluorescence intensity at 425 nm are 0.35, 0.15, 0.07, 0.03, 0.007, and 0.0015 M.

Complete disappearance of the long wavelength emission band indicating the breaking of different kinds of associated structures of the ionic liquid.