

Spectroscopic Studies For The Different Interactions Between Binary Mixtures of Imidazolium Based Ionic Liquids In 1,2-Propanediol

Dr. Wazir Singh¹

¹Department of Applied Science & Humanities, Ch. Devi Lal State Institute of Engineering & Technology, Panniwala Mota, Sirsa, Haryana, INDIA-125077

*Corresponding author: Dr. Wazir Singh

Abstract: Binary mixtures of room-temperature ionic liquids (RTILs) viz. 1-butyl-3-methylimidazolium tetrafluoroborate [C₄mim][BF₄], 1-butyl-2,3-dimethylimidazolium tetrafluoroborate [C₄mmim][BF₄] and 1-butyl-3-methylimidazolium octylsulfate [C₄mim][C₈OSO₃] with 1,2-propanediol have been prepared. Different, assorted techniques like ¹H NMR, FTIR have been used to analyze the microscopic behavior of all the binary mixtures on whole composition range. The data obtained analyzed to different interactions determine the effect of (i) cation and (ii) anion of ionic liquid. These techniques have been used to scrutinize the molecular level interactions between the binary mixtures and very valuable to spot the influence on the structural alterations in the ionic liquid.

Keywords: Ionic liquids, 1,2-propanediol, Binary mixtures, FTIR, ¹H NMR.

I. Introduction

The class of compounds which are liquids at or near room temperatures and excellent solvents for both polar and non-polar organic substances also known as room temperature ionic liquids (RTILs) gaining interest in the field of scientific investigations day by day. These molten salts composed of anions and cations [1], exhibit many interesting properties such as negligible vapor pressure, low melting point, suitable viscosity, stability up to high temperature, high electrical conductivity and non-volatile [2-5]. Moreover, their properties can be altered by varying the anion or cation in the compound and which is the cause to call them as "Designer solvents". As RTILs have many unique properties these are thought to be future replacements for the common harmful organic liquids, for carrying greener and environment friendly industrial processes. Further, addition of a suitable co-solvent to an IL can amend the physicochemical properties, thereby enlarging the array of application and usefulness of these fluids. Therefore, understanding of mixing behavior, thermodynamic properties and molecular level interactions in the binary mixtures of room temperature ionic liquids in the organic solvents are of significance both for understanding their solution behavior and providing accurate data for various industrial applications. Thermodynamic studies on binary mixtures of RTILs in organic solvents [6-21] are gaining importance day by day for a potential substitute to the mixtures of conventional volatile organic liquids used in different chemical processes. However, the physicochemical behavior of ethylene glycol derivatives in the room temperature ionic liquids is scarcely examined [22-26]. On the other hand, 1,2-propanediol is an important commodity with industrial applications such as in food additives, pharmaceuticals, cosmetics, and de-icers because of its physical properties and low toxicity [27]. 1, 2-Propanediol (1,2-PD) has similar properties like ethylene glycol (EG) but less-toxic in nature. Binary mixtures of RTILs and 1, 2-PD can serve as materials with enhanced heat-transfer properties than that of individual components, and can be used in a variety of chemical processes. Such systems need to be meticulously investigated for their bulk and molecular scale behavior.

We have found from our earlier investigations that various types of interactions exist in the binary mixtures of ILs and organic solvents. Hence, only thermodynamic studies are not adequate to understand the precise nature of solute-solvent interactions [28-30]. In order to achieve our goal, we have examined the interactions of binary mixtures at molecular level over the whole composition range using spectroscopic techniques such as Fourier transform infrared spectroscopy FTIR and ¹H NMR. Vibrational spectroscopy, particularly, Fourier Transform spectroscopy (FTIR), which is an important tool and in turn is very responsive to small changes in the dipole moment, or rather the polarizability [31-32]. ¹H NMR spectroscopy, which is a direct molecular approach, has also been used for determining the specific interactions between ILs and 1,2-PD molecules at molecular level. It is shown that ILs forms hydrogen bonds of varying strengths with 1,2-PD molecules whose relative strength depends on the structure of ILs (mono, di-substituted or the nature of anion) has been used to determine the intermolecular interactions in binary mixtures of ILs with organic solvents.

In short, the aim of the present article is to shed light on bulk and molecular scale interactions between RTILs 1-butyl-3-methylimidazolium tetrafluoroborate [C₄mim][BF₄], 1-butyl-2,3-dimethylimidazolium tetrafluoroborate [C₄mmim][BF₄]. It is well known that ionic liquids, obtained by coupling imidazolium cation with fluorinated organic anions, such as BF₄⁻, CF₃SO₃⁻ and (CF₃SO₂)₂N⁻ (TFSI⁻), have low melting points and high ionic conductivity [33]. 1-butyl-3-methylimidazolium octylsulfate [C₄mim][C₈OSO₃] and 1,2-propanediol (1,2-PD) in a systematic way using spectroscopic techniques. The RTILs used here are completely miscible with 1,2-PD under ambient conditions, and offer a comparison of changes in molecular level interactions with the structural variation in ILs.

II. Experimental

2.1 Materials

Ionic liquids (ILs), 1-butyl-3-methylimidazolium tetrafluoroborate [C₄mim][BF₄] (>0.98), 1-butyl-3-methylimidazolium octylsulfate [C₄mim][C₈OSO₃] (>0.98), were purchased from Merck and, 1-butyl-2,3-dimethylimidazolium tetrafluoroborate [C₄mmim][BF₄] (>0.998), was purchased from Sigma-Aldrich. IL[C₄mmim][BF₄] received from the commercial source was further purified according to the procedures described elsewhere [33]. Structures of ILs and 1,2-PD used in this study are given in Scheme 1. Prior to the mixture preparation, the ILs were dried and degassed under vacuum at 70 °C for 48 hrs to remove moisture. Karl-Fisher analysis of the samples indicated that the water content was reduced to less than 350 ppm in each IL. 1,2-propanediol (>0.99) was obtained from Acros Organics, USA. 1,2-propanediol was used after drying over the 0.4 nm molecular sieves and under vacuum at ambient conditions. Binary mixtures of ILs and 1,2-PD were prepared by mass using an A&D company limited electronic balance (Japan, Model GR-202) with precision of ± 0.01 mg and kept in airtight glass bottles to minimize the absorption of atmospheric moisture and CO₂.

2.2 Methods

2.2.1. FT-IR measurements

FT-IR spectra of the pure components and that of various binary mixtures over the complete composition range at room temperature were recorded using ABB (MB 3000) spectrometer. For sampling, a drop of sample has placed in the trough for collecting data. The sample must be in intimate contact with the sampling area for the ATR (PIKE Miracle) evanescent wave to provide the highest signal. Resolution better than 4 cm⁻¹. Maximum signal-to-noise ratio (root-mean-square, 60s, 4 cm⁻¹, at peak response): 50,000: 1. Beam splitter material ZnSe (non-hygroscopic).

2.2.2. ¹H NMR measurements

The ¹H NMR spectra of the ILs–1,2-PD mixtures over the whole composition range were recorded using a Bruker 200 MHz spectrometer at 298 K. The proton chemical shifts were referenced with respect to external standard TMS (δ=0.000 ppm) in C₆D₆ (deuterated benzene). The chemical shifts of the peaks of interest were determined using peak pick facility.

III. Results And Discussion

3.1 FT-IR studies

3.3.1. –OH stretching vibration of 1,2-PD: Fig. 1 shows the enlarged FT-IR spectra in the range 3000 to 3650 cm⁻¹ recorded for 1,2-PD–[C₄mim][BF₄] mixtures as representative. For other systems, the FTIR spectra are given in the Supporting Information (Figs. S1 and S2). In general, the absorption intensity of broad O–H stretching band of 1,2-PD decreases with increasing ILs mole fraction for all the investigated binary mixtures, thus reflecting the quantitative nature of spontaneous IR absorption.

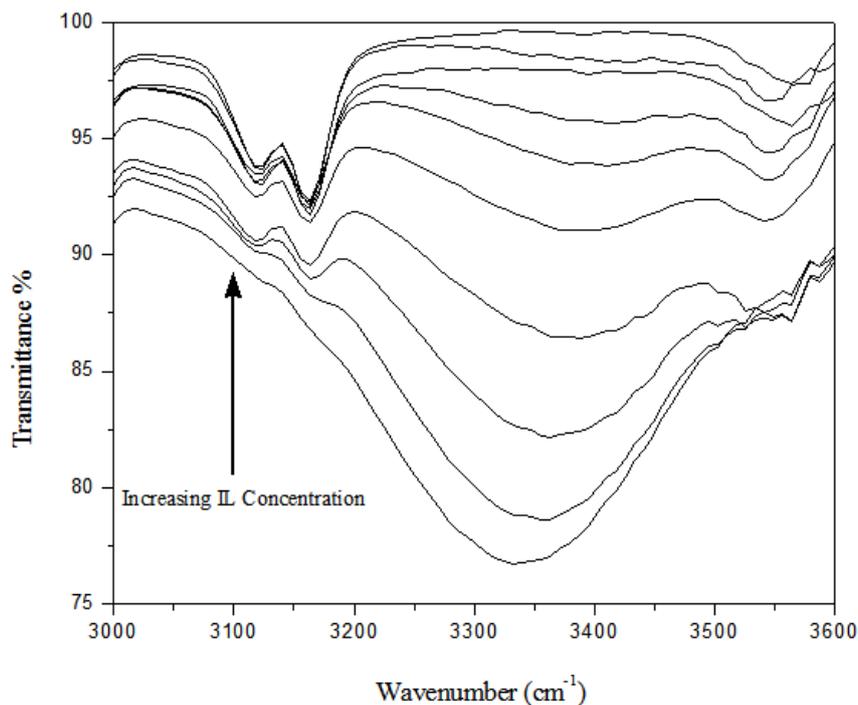


Fig. 1. Normalized FTIR spectra of 1,2-PD-[C₄mim][BF₄] binary mixture in the range 3000–3600 cm⁻¹.

The variation of –OH stretching band frequency in various IL-1,2-PD binary mixtures as a function of IL concentration have shown in Fig.2. A significant blue shifting in the band position of O–H stretch band of 1,2-PD is observed with the addition of [C₄mim][C₈OSO₃] whereas such shifting is less for the [C₄mim][BF₄] and [C₄mmim][BF₄] as can be seen from Fig. 2. The magnitude of peak shifting is indicative of changes in intermolecular hydrogen bonding between 1,2-PD and ILs depending on the nature of cation or anion. Presumably, the frequency changes are induced by the formation of hydrogen bonds between hydroxyl group of 1,2-PD and constituent ions of the ILs and the breaking of inter- and intramolecular hydrogen bonding in 1,2-PD. Blue shift in O–H stretching frequencies follow the order: 1,2-PD–[C₄mim][C₈OSO₃] > 1,2-PD–[C₄mmim][BF₄] > 1,2-PD–[C₄mim][BF₄].

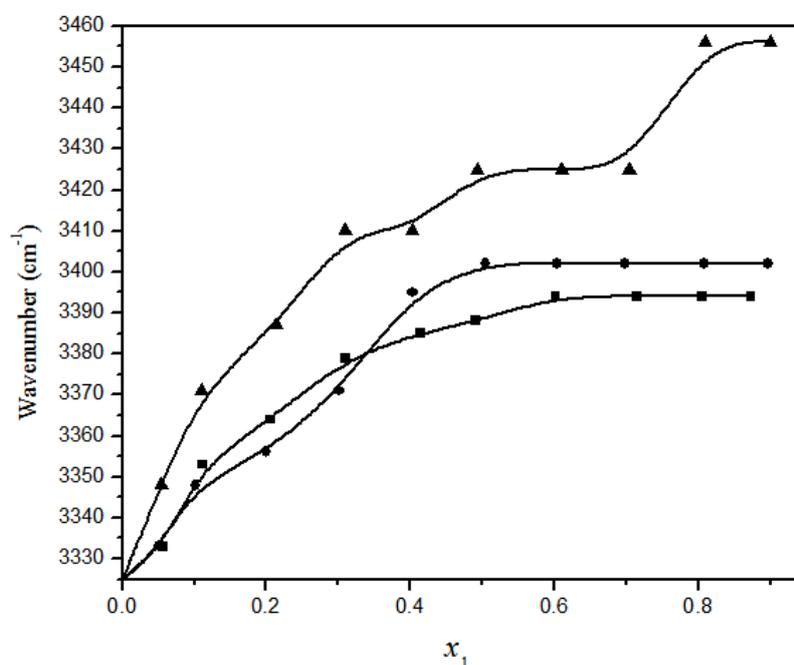


Fig. 2. Frequency shift for O–H stretch as a function of ILs concentration in (■)[C₄mim][BF₄]; (●)[C₄mmim][BF₄]; and (▲) [C₄mim][C₈OSO₃].

The order reflects both the effect of cation and anion on the interaction of IL with 1,2-PD. But, in case of 1,2-PD-[C₄mim][C₈OSO₃] the anion part of the IL shows greater affinity for hydrogen bonding when we compare ILs having same cation i.e. [C₄mim].

3.3.2. Stretching vibrations of imidazolium ring protons: Fig.3 (a) and (b) shows the variation in stretching frequency for the C(2)-H and C(4,5)-H stretch of the imidazolium cation of IL. The characteristic individual peaks around 3120 cm⁻¹ and 3160 cm⁻¹ are assigned to C(2)-H and C(4,5)-H stretching bands respectively [34-36]. Figure 3a shows the changes in C(2)-H stretching frequency over the whole composition range for all the binary mixtures investigated except that of [C₄mmim][BF₄] which have -CH₃ group instead of -H at C(2) position. With the increase in concentration of 1,2-PD in binary mixtures, C(2)-H frequency is blue shifted for [C₄mim][C₈OSO₃]. Blue shifting does not occur until x₁=0.60, and then the frequency shifts sharply in the IL-dilute region after that no change has been seen in the vibrational spectra of the mixture.

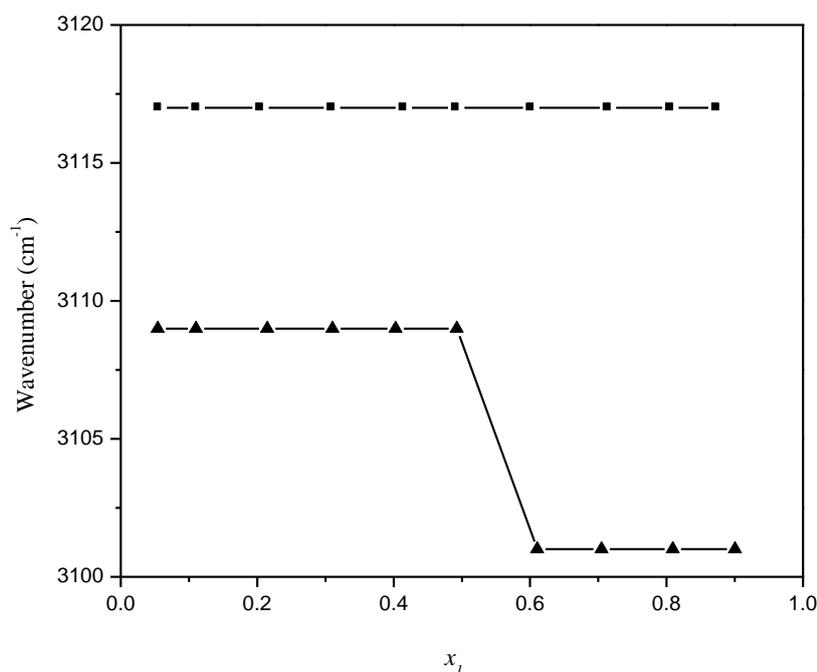


Fig. 3(a). Peak shift for absorption frequency of C(2)-H stretch for various 1,2-PD-IL binary mixtures as a function of IL concentration (■)[C₄mim][BF₄]; and (▲)[C₄mim][C₈OSO₃].

Blue shifting is the consequence of an increase of the force constant due to shortening (strengthening) of the C-H bond resulting from weak electrostatic interaction of the lone-pair electrons of the oxygen atom in 1,2-PD with C(2)-H of the IL cation. The presence of methyl group at position C-2 of the imidazolium ring in [C₄mmim][BF₄] as compared to proton in case of [C₄mim][BF₄] reflects itself an interaction of ILs with 1,2-PD where [C₄mmim][BF₄] is least effective in modifying the hydrogen-bonded network of 1,2-PD.

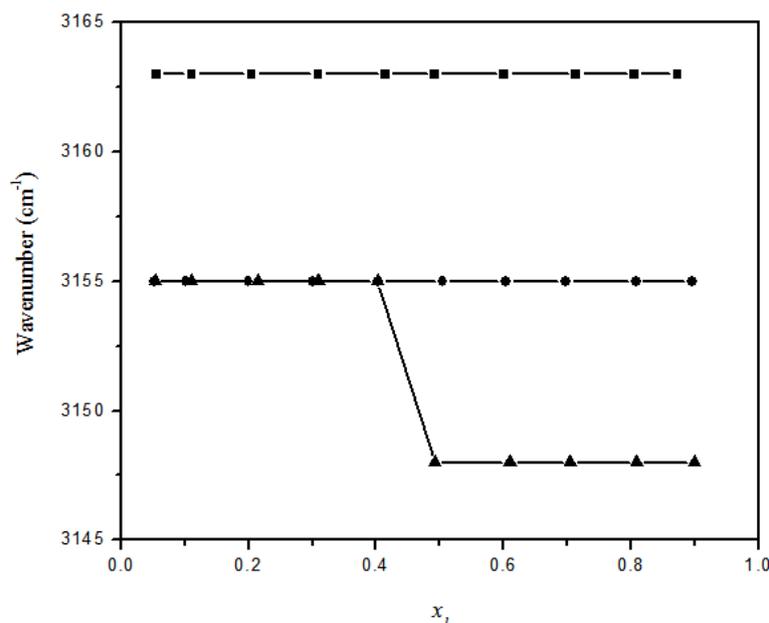


Fig. 3(b). Peak shift for absorption frequency of C(4,5)-H stretch for various 1,2-PD-IL binary mixtures as a function of IL concentration (■)[C₄mim][BF₄]; (●)[C₄mmim][BF₄]; and (▲) [C₄mim][C₈OSO₃].

In case of 1,2-PD-[C₄mim][BF₄], no shift is observed. This indicates the absence of hydrogen-bonding interactions between C(2)-H and 1,2-PD at least in FTIR measurements, which may be due to stronger C(2)-H-anion interactions, where 1,2-PD don't disrupt the interactions between cation and anion appreciably. The behaviour of C(4,5)-H stretch as a function of IL mole fraction is shown in Fig. 3(b). The behavior of C(4,5)-H stretching in the binary mixtures of 1,2-PD with [C₄mim][BF₄] and 1,2-PD with [C₄mmim][BF₄] is similar as no shift is observed, indicating the absence of hydrogen-bonding interactions between C(4,5)-H and 1,2-PD, which may be due to stronger C(4,5)-H-anion interactions in these ILs. In [C₄mim][C₈OSO₃]-1,2-PD mixtures, the C(4,5)-H stretching frequency remained almost constant until $x_1 > 0.60$, and then blue-shifted similarly to that observed for the C(2)-H stretching frequency in the IL-dilute region.

3.2¹H NMR studies

The 1-alkyl-3-methylimidazolium cation forms multiple hydrogen bonds from the various protons to even weak hydrogen bond acceptor anions. Competition for the interaction of various protons of the imidazolium salt for the anions and solvent molecules is expected when an IL is mixed in the organic liquid.

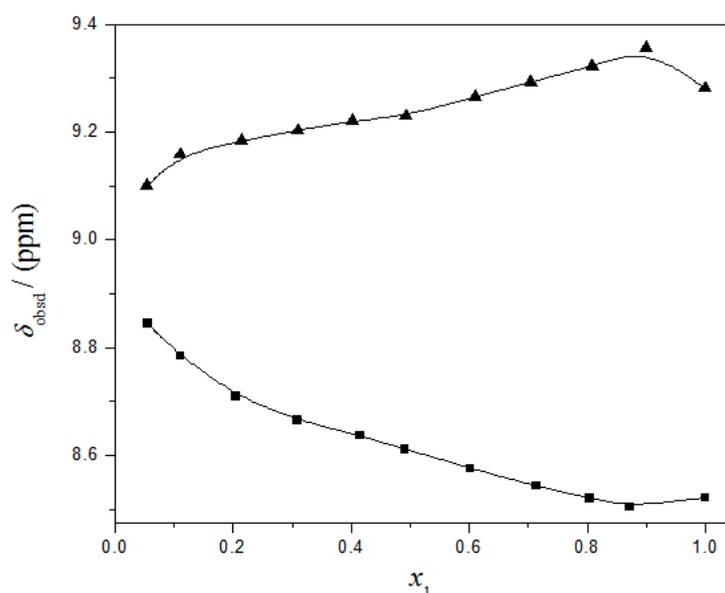


Fig. 4(a). Variation of δ_{obsd} for C(2)-H; imidazolium cation in 1,2-PD-IL mixtures as a function of IL concentration: (■)[C₄mim][BF₄]; and (▲) [C₄mim][C₈OSO₃].

Addition of hydrogen-bond donors such as 1,2-PD can bring about significant changes in the magnitude of hydrogen-bonding interactions through formation of new hydrogen bonds or breaking/weakening of the existing hydrogen bonds in the pure ILs. The ^1H NMR chemical shift (δ), a measure of electron density about the probe nuclei, was used for the examination of electronic distribution and intra-molecular polarization of the molecules in the 1,2-PD-IL systems. To analyze the changes in the electronic environment of protons of various ILs as a consequence of 1,2-PD addition, we plotted the concentration dependence of the chemical shift of ring protons, C(2)-H (δ_{2H}), C(4)-H (δ_{4H}), C(5)-H (δ_{5H}) and the terminal alkyl chain proton, C(t)-H (δ_{tH}), of alkyl imidazolium cations (Figures 4 a-d). As can be seen from Figure 4 a, with the addition of 1,2-PD to the IL $[\text{C}_4\text{mim}][\text{BF}_4]$ δ_{2H} went downfield slowly (ca. 8.52 to 8.57 ppm) until $1 > x_1 > 0.6$, and then a sharp downfield shift was observed in the dilute IL region ($0.6 > x_1 > 0$). A similar pattern was observed in δ_{4H} and δ_{5H} for these systems (Figure 4b and 4c). Addition of 1,2-PD to $[\text{C}_4\text{mim}][\text{C}_8\text{OSO}_3]$ brought all the δ_{2H} , δ_{4H} and δ_{5H} upfield (ca. 9.28 to 9.10, 7.96 to 7.78, and 7.85 to 7.73 ppm, respectively) until $1 > x_1 > 0$. The chemical shift for the terminal protons, C(t)-H (δ_{tH}), went continuously downfield with the addition of 1,2-PD in all the investigated ILs over the whole composition range, with a maximum shift in $[\text{C}_4\text{mmim}][\text{BF}_4]$ and a minimum shift in $[\text{C}_4\text{mim}][\text{C}_8\text{OSO}_3]$ (ca. 0.65 to 1.14 and 0.89 to 1.15 ppm, respectively) (Figure 4d).

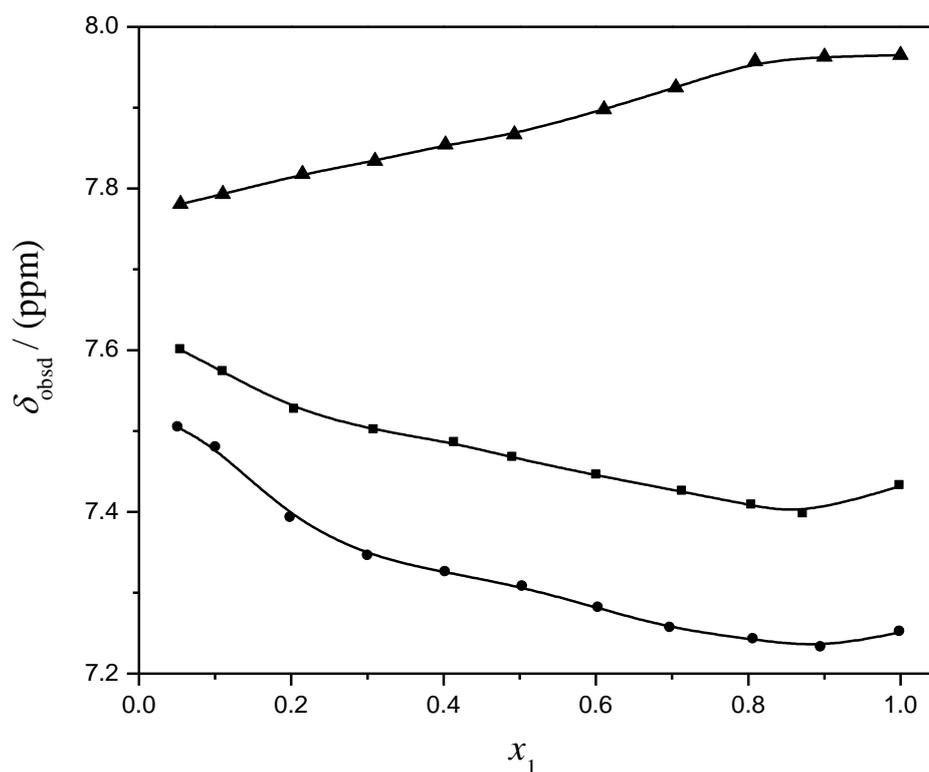


Fig. 4(b). Variation of δ_{obsd} for C(4)-H; imidazolium cation in 1,2-PD -IL mixtures as a function of IL concentration: (■) $[\text{C}_4\text{mim}][\text{BF}_4]$; (●) $[\text{C}_4\text{mmim}][\text{BF}_4]$; and (▲) $[\text{C}_4\text{mim}][\text{C}_8\text{OSO}_3]$.

Estimates of deviations from ideality in the ^1H NMR chemical shift ($\Delta\delta$) from the additivity rule ($\Delta\delta = \delta - x_1\delta_1^\infty - x_2\delta_2^\infty$) have been made and provided the extent of solute-solvent interactions (see supporting information, Figure S3 a-d)[34,36]. $\Delta\delta$ is negative for all the imidazolium protons in all the mixtures except for 1,2-PD- $[\text{C}_4\text{mim}][\text{C}_8\text{OSO}_3]$ which is positive for ring protons (C(2)-H (δ_{2H}), C(4)-H (δ_{4H}), C(5)-H (δ_{5H})). The highest magnitude of chemical shift ($\Delta\delta$) is for C(t)-H protons and the lowest magnitude for the C(4)-H of the imidazolium alkyl chain. Also, when a comparison among individual ILs was made, we found the magnitude of interactions between C(2)-H in the order $[\text{C}_4\text{mim}][\text{BF}_4] > [\text{C}_4\text{mim}][\text{C}_8\text{OSO}_3]$. And for C(4)-H, C(5)-H protons and 1,2-PD in the order $[\text{C}_4\text{mmim}][\text{BF}_4] > [\text{C}_4\text{mim}][\text{BF}_4] > [\text{C}_4\text{mim}][\text{C}_8\text{OSO}_3]$, whereas the order of magnitude of interactions between terminal protons of the imidazolium alkyl chain and 1,2-PD was $[\text{C}_4\text{mmim}][\text{BF}_4] > [\text{C}_4\text{mim}][\text{C}_8\text{OSO}_3] > [\text{C}_4\text{mim}][\text{BF}_4]$.

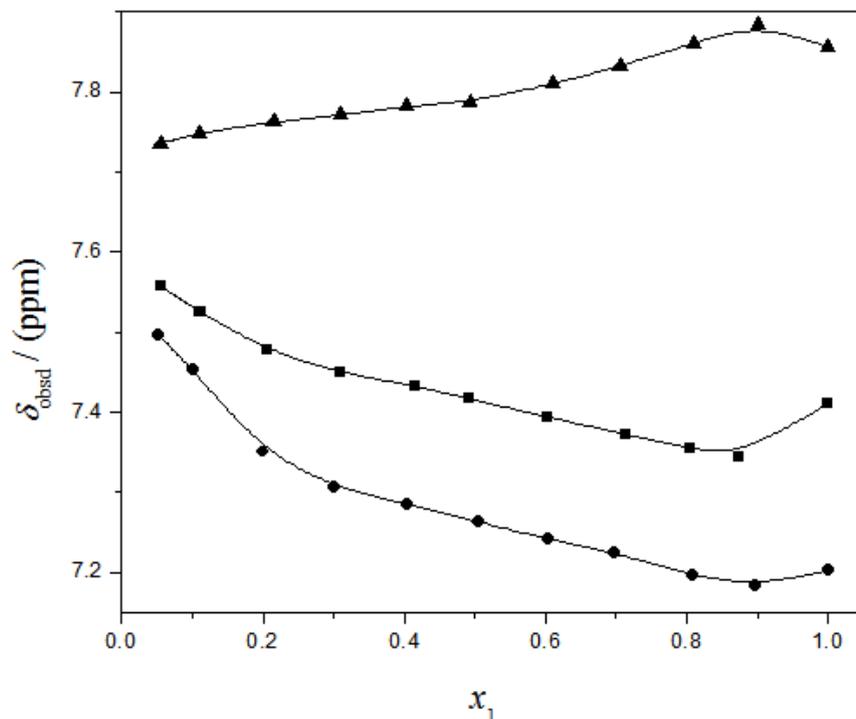


Fig. 4(c). Variation of δ_{obsd} for C(5)-H; imidazolium cation in 1,2-PD-IL mixtures as a function of IL concentration: (■)[C₄mim][BF₄]; (●)[C₄mmim][BF₄]; and (▲) [C₄mim][C₈OSO₃].

On comparing the NMR results for various binary mixtures, it is found that the extent of interaction of various protons of different ILs with 1,2-PD follows the order: C(2)H > C(5)-H > C(4)-H > C(t)-H(δ_{IH}) for 1,2-PD-[C₄mim][BF₄], for 1,2-PD-[C₄mmim][BF₄], it follows: C(t)-H(δ_{IH}) > C(5)-H > C(4)-H, and for 1,2-PD-[C₄mim][C₈OSO₃] it is as: C(t)-H(δ_{IH}) > C(4)H > C(5)-H > C(2)-H.

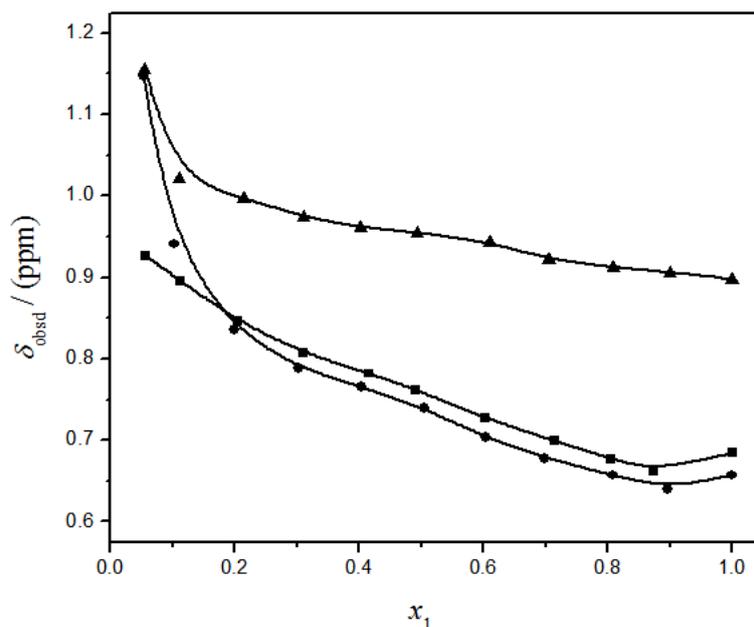


Fig. 4(d). Variation of δ_{obsd} terminal methyl group of imidazolium cation in 1,2-PD-IL mixtures as a function of IL concentration: (■)[C₄mim][BF₄]; (●)[C₄mmim][BF₄]; and (▲) [C₄mim][C₈OSO₃].

In the system 1,2-PD-[C₄mim][C₈OSO₃], the maximum interaction between C(t)-H(δ_{IH}) and 1,2-PD is indicative of strong interaction between aromatic ring protons and [C₈OSO₃] anion which weakens the interaction between ring protons and 1,2-PD.

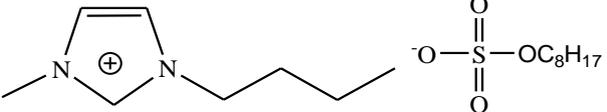
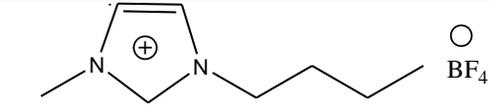
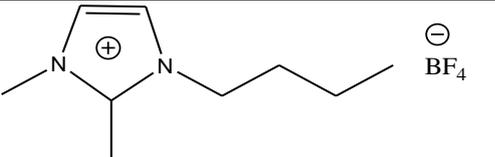
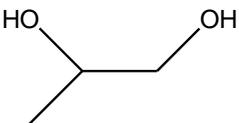
IV. Conclusions

The FTIR and ¹H NMR spectroscopic techniques provided information about the molecular scale interactions prevailing in these systems. Non bonding oxygen electron and hydroxyl protons of 1, 2-PD were found to interact strongly with the aromatic ring protons as compared to alkyl chain protons. Various ring protons shows different interactional preferences towards 1,2-PD depending upon the nature of cation or anion. [C₈OSO₃] anion interacts strongly with 1,2-PD as compared to other anions. FTIR and ¹H NMR results reveal the importance of nature of functional group present at C(2) position of imidazolium ring where the presence of -CH₃ group in place of -H modifies the interactions between cation and anion, consequently affecting the interactions of IL with 1,2-PD. Analysis of spectroscopic results show that the multiple hydrogen bonding interactions occurring in the investigated systems at microscopic level.

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Scheme 1. Schematic representation of various ILs and 1,2-propanediol used for study.

Sr. No.	Compound	Structure	Molecular Weight (g · mol ⁻¹)
1.	1-Butyl-3-methylimidazolium octylsulfate [C ₄ mim][C ₈ OSO ₃]		348.50
2.	1-Butyl-3-methylimidazolium tetrafluoroborate [C ₄ mim][BF ₄]		226.02
3.	1-Butyl-2,3-dimethylimidazolium tetrafluoroborate [C ₄ mmim][BF ₄]		240.05
4.	1,2-propanediol (1,2-PD)		76.09