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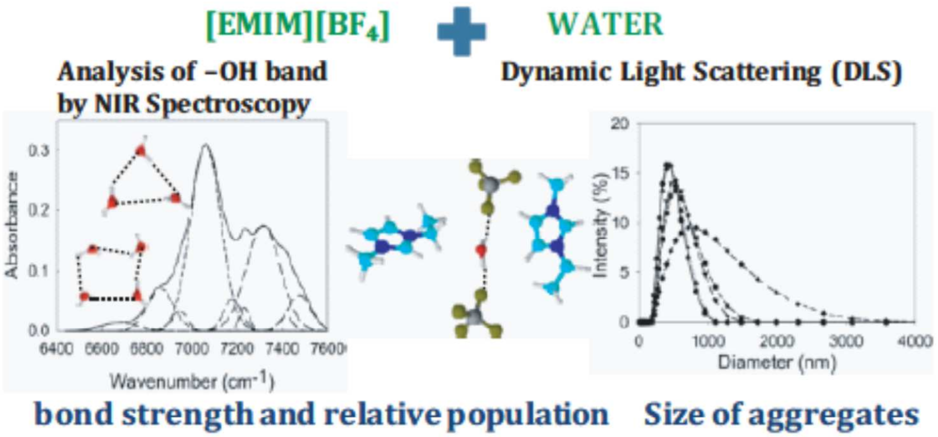

Molecular level interactions in binary mixtures of 1-ethyl 3-methylimidazolium tetrafluoroborate and water

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NIR spectroscopic analysis and DLS measurements have been done to study hydrogen bonding and aggregation in ionic liquid-water binary mixtures.

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ABSTRACT:

In this study, structures of different water species present in binary mixtures of an ionic liquid (IL), 1-ethyl 3-methylimidazolium tetrafluoroborate ([EMIM][BF_4]) and water of varying compositions have been investigated by near-infrared (NIR) spectroscopy and for the first time aggregation behavior and interactions between different species in the system have been inferred from the analyses of combination bands of NIR spectra. Relative population of different water species as well as the strength of hydrogen bonding were obtained from the analyses of peak area and peak positions of the deconvoluted –OH band of water, respectively. The ratio of population of associated water to the population of water species bonded to IL increases sharply with increasing mole fraction of IL at $X_{IL} > 0.4$. Consequently, excess molar volume of the mixtures passes through a maximum. For the water species bonded to IL, analysis of the peak position showed that the strength of hydrogen bonding shows a maximum suggesting the formation of two different types of aggregates of IL below and above $X_{IL} \approx 0.26$. The DLS measurements show that at the water-rich region of the binary systems, aggregates with hydrodynamic diameter of 354~590 nm are formed. The size of the aggregates has been found to increase with increasing amount of IL and decrease with increasing temperature. Finally, the properties of IL-water binary mixtures have been found to be governed by the strength of IL-water bonds and population of IL-IL and water-water clusters.

1. Introduction

Ionic liquids (IL) have emerged as one of the most promising materials in the field of modern science due to their unique properties such as negligible vapor pressure, non-flammability, high ionic conductivity and high thermal, chemical and electrochemical stability[1]. These remarkable properties have allowed ILs for use as solvent in organic, inorganic and polymer syntheses and enzymatic reactions as well as for the design of novel functional materials. They can also be used as electrolytes for energy devices such as lithium secondary batteries, electric double layer capacitors, supercapacitors, dye-sensitized solar cells (DSSC), fuel cells, actuators and as a medium for electrodeposition[2-15]. Due to the environmentally benign nature and recyclability, ILs are considered as possible alternative of hazardous conventional molecular solvents used in many important industrial processes. For task specific applications in multidisciplinary areas, IL-based mixed solvent systems have the potential to offer a novel route for tuning the properties of these designer solvents. Optimization of the properties to desirable chemistry can be achieved by varying the compositions of the binary systems. However, the high viscosity and considerably low conductivity of pure ILs make them inadequate for use as electrolytes in commercial electrochemical devices. These can be overcome by addition of polar solvents which lowers the viscosity and increases the conductivity significantly.[16-18]. In fact, specific reaction media with controlled reaction dynamics can be designed by tuning the polarity of IL-based binary systems by suitable choice of polar solvents .[19-23]

Water is a universal solvent which plays very important role in many chemical and biological processes. It has been reported that ILs are hygroscopic materials and even the hydrophobic ILs absorb a certain amount of water from atmosphere. [24-26]Addition of water and other polar solvents can bring significant changes in density, viscosity, conductivity and polarity of ILs.[18, 27-28]To explore the complete potential of IL-water binary systems as novel functional fluids, thorough understanding of IL-solvent interactions at molecular level is necessary. Despite various experimental as well as theoretical studies on IL-water binary systems, the fundamental knowledge of interactions between IL and water and their effect on physicochemical properties is still in the rudimentary stage. [26,29-36]An insight into the dissolution behavior of IL in water and interaction between IL and water relative to the interactions in pure ILs has been obtained from the thermodynamic studies and measurement of the physicochemical properties of binary systems of ILs [37-39]. Zhang *et al.* analyzed IL-water interactions from 2D correlation spectroscopic analysis and showed that with addition of water 3D network of IL is broken into smaller ionic clusters and IL-water bond gets stronger with weakening cohesion between cations and anions.[29] Presence of two water species have been indicated from the mid IR (MIR) spectra of 1-butyl 3-methylimidazolium tetrafluoroborate ([BMIM][BF_4])-water systems. Attenuated total reflectance (ATR)-IR and Raman spectroscopic studies on [BMIM][BF_4]-water binary mixtures have suggested that qualitative change in microscopic structure of water occurs at high water concentrations.[32-33] Wang *et al.* carried out ^{1}H NMR, dynamic light scattering (DLS) and ATR-IR spectroscopic studies to investigate the effect of concentration and temperature on microstructure of IL in binary mixtures of [BMIM][BF_4] and water and their results showed that with decrease in temperature, the interactions between cation and anion of the IL become stronger, but those between the IL and water weaken.[40]

Most of the research works conducted so far mainly involve the analysis of OH band in MIR region where bands for different water species are highly overlapped making the analysis difficult. The OH band of monomeric and polymeric water species are well separated in NIR than the MIR region. [41-43] The NIR region covers the overtone and combination transitions of the C–H, O– H, and N–H vibrations and NIR spectra more often show prominent shoulders for different types of water species. Simple deconvolution of combination bands can unveil significant information about the environment in the binary mixtures. It should be noted here that the absorption of free OH group in the fundamental region is very weak whereas it clearly appears in the NIR region.[42-47] In addition, cells of convenient path lengths can be used to have a suitable control over the absorption intensities for analysis. This makes NIR spectroscopy an effective tool for analysis of water structure in binary mixtures with very low water content as well as those with very high amount of water.

Regardless, studies on IL-water interactions by NIR spectroscopy has only been done in a limited scale. Tran *et al.* used NIR technique for the quantitative determination of the amount of absorbed water in ILs and Wu *et al.* compared the interactions in two different IL-water systems by analysis of spectral data from NIR spectroscopic measurements.[48-49] However, detailed NIR spectroscopic analyses of the relative population and strength of the hydrogen bonding in each type of water species in IL-rich as well as in water rich regions of the binary systems can reveal significant information about the molecular level interaction, but are yet to be reported. Furthermore, although the transport properties of ILs are governed by the aggregation or self-association of ILs in a solvent, fundamental understanding of the issue is not still clear.

In this work, NIR spectroscopy has been successfully employed to obtain both qualitative and quantitative idea about the interactions by studying different types of water species in 1-ethyl 3-methylimidazolium tetrafluoroborate ([EMIM][BF_4]) - water binary mixtures by deconvolution from the analysis of the combination band arising from symmetric and antisymmetric stretching mode of OH vibrations of water.[44] The variation of excess molar volumes of the binary mixtures with composition has been explained with the help of the observations from spectroscopic analysis. DLS measurements have been carried out to study the formation of aggregates and variation of its size with composition in water-rich binary systems. The information obtained from NIR spectroscopic analysis was correlated with the size of the aggregates at water-rich region to have an idea about the molecular level interaction in the binary systems. The ultimate goal has been to understand the aggregation behavior, water structure modification, and interactions in IL-water binary systems for the first time through systematic analysis of combination bands of NIR spectra and to correlate those with solution properties.

2.Experimental

2.1 Materials and sample preparation

The IL, [EMIM][BF_4] obtained from Sigma-Aldrich was HPLC grade with purity ≥ 99.0 % and was used without any further purification. Ultrapure water (σ= 0.059µS cm^{-1}, BOECO pure, model- BOE 8082060) was used to prepare binary mixtures. Determination of water content in pure [EMIM][BF_4] was carried out by Karl-Fischer titration (Metrohm- Titrando 890) and was found to be less than 0.5% (w/w) during preparation of samples and handling of the IL. All the binary mixtures were prepared gravimetrically by using an analytical balance (Unilab UB-110) with a precision of ± 0.0001 g. After preparation, all samples were sonicated (LU-2 Ultrasonic cleaner, Labnics Equipment) for 20 minutes to ensure homogeneous mixing.

2.2 NIR spectroscopic analysis

NIR spectra were recorded by a Fourier transform spectrophotometer (PerkinElmer) in absorbance mode with 32 scans for each sample in the range 4000-12000 cm^{-1} at 4.0 cm^{-1} resolution. Rectangular quartz cells of path length 5.0 mm and 2.0 mm were used for measurement of binary mixtures with $X_{IL}> 0.05$ and $X_{IL} = 0.05$, respectively. Uncertainty is 1% for the measurements by this spectrophotometer. Raw spectra were smoothened and deconvoluted into Gaussian profiles. Each spectrum was subjected to baseline correction before deconvolution and co-efficient of determination (R^2) value of 0.9999 was reached for each peak fitting.

2.3 Density measurement

The densities of the binary mixtures were measured with Anton Paar (model DMA 4500) vibrating tube density meter. The accuracy of density data was 0.00005 gcm^{-3} with repeatability of 0.00001 gcm^{-3}.

2.4 Particle size analysis by DLS

Diameters of the aggregates of ILs in the binary mixtures were measured using a Zetasizer Nano ZS90 (ZEN3690, Malvern Instruments Ltd, UK) by dynamic light scattering method (DLS). A He-Ne laser of 632.8 nm wavelength was used as light source and the measurements were made at a fixed scattering angle of 90°. The scattering intensity data were analyzed to obtain the hydrodynamic diameter (D_h) of the aggregates formed in the binary mixtures with $X_{IL} \leq 0.079$.A measuring glass cell of 10 mm diameter was used. The accuracy of the D_h determined by DLS measurements has been ±2%. The temperature was controlled by using Peltier elements throughout the experiments.

3. Results and Discussion

Fig.1 shows the FT-NIR spectra of [EMIM][BF_4]-water binary mixtures of different compositions in the 6450-7650 cm^{-1} region where the combination band arising from the symmetric and antisymmetric stretching vibration of water molecules can be seen. Due to the overlapping of different combination bands in this region, the spectra has been deconvoluted into several Gaussian peaks for the analysis of different water species in the binary mixtures.

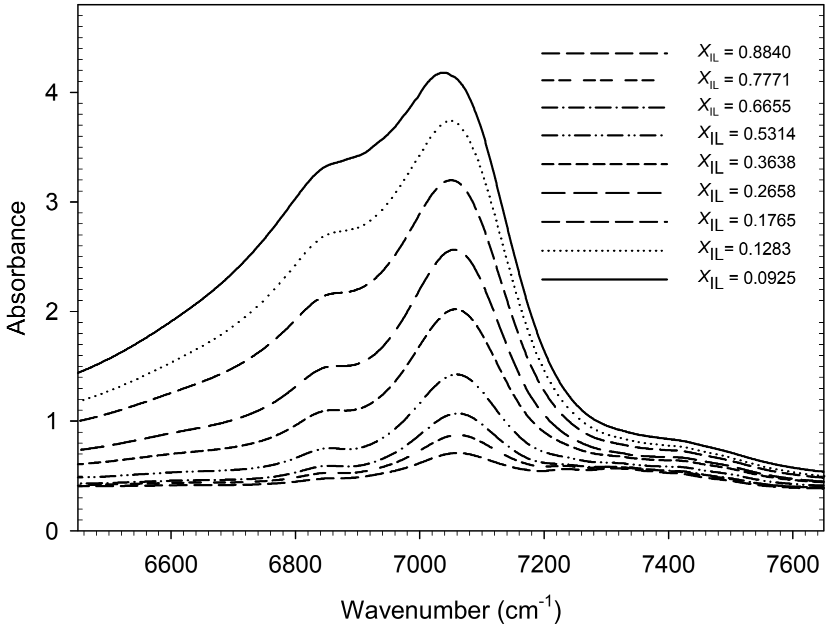

Fig. 1. NIR spectra of [EMIM][BF4]-water binary mixtures.

Fig. 2 shows the deconvoluted spectrum of [EMIM][BF$_4$]-water binary mixture with 0.88 mole fraction of IL where the broad band has been fitted to nine Gaussian peaks. The 7090-7600 cm^{-1} region of the spectra did not show any appreciable change with addition of water and hence the bands in this region were assumed to arise from the CH vibrations of imidazolium cation. [50]The band at 7060 cm^{-1} with is attributed to the combination band of –OH in water molecules bonded to the IL since the absorbance rises most significantly in this region with increasing amount of water at low concentrations. Previous studies have shown that water mainly remains in monomeric form in IL-rich region and interacts mainly with anions.[30] Therefore, the band centered around 7060 cm^{-1} can be assumed to arise from the water interacting with the anion of [EMIM][BF$_4$]. The smaller peaks at lower wavenumber region centered around 6678, 6860 and 6945 cm^{-1} have originated from the hydrogen bonded water clusters. The peaks for associated water appears at lower wavenumber region than the peak for water bonded to IL since the hydrogen bonds formed between the water molecules themselves are much stronger than the hydrogen bond between BF_4^- anion and water.[29] The spectra of all other binary systems have also been deconvoluted in similar manner (Figure not shown).

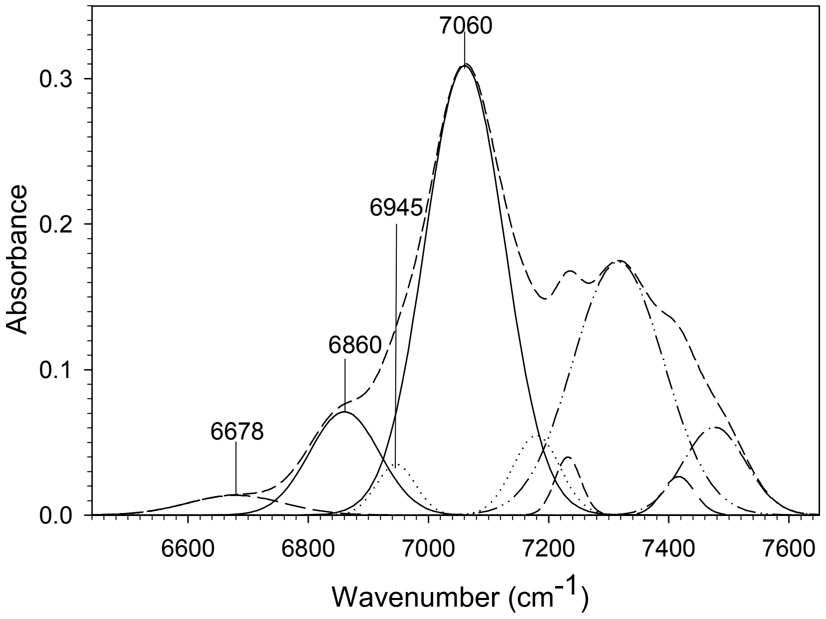

Fig. 2.Deconvoluted spectrum of [EMIM][BF4]-water binary mixture with X_{IL} = 0.88.

The peak area of each Gaussian band has been analyzed to quantitatively estimate the population of associated and free water in the mixtures. **Fig. 3** shows the ratio of the peak area of the associated water to that of the water bonded to IL plotted against the mole fraction of IL in the binary systems. Significant decrease could be observed in the ratio for increase in the mole fraction of IL for mixtures up to $X_{\mathrm{IL}} \approx 0.4$, above which the ratio becomes almost constant. In fact, for mixtures with $X_{\mathrm{IL}} > 0.4$ (from pure IL to $X_{\mathrm{IL}} \approx 0.4$), water mainly breaks the 3-D network of cations and anions into smaller ionic clusters. This makes sufficient number of sites in IL available for formation of hydrogen bonds with water molecules with weakening cohesion between cations and anions[29] for maintaining the ratio of the amount of associated water to the amount of water bonded to IL almost constant. However, at $X_{\mathrm{IL}} < 0.4$, added water molecules not only disrupts the network structure of cations and anions, but the excess water molecules have greater tendency to form hydrogen bonds among themselves after forming bond with IL in most of the available sites.

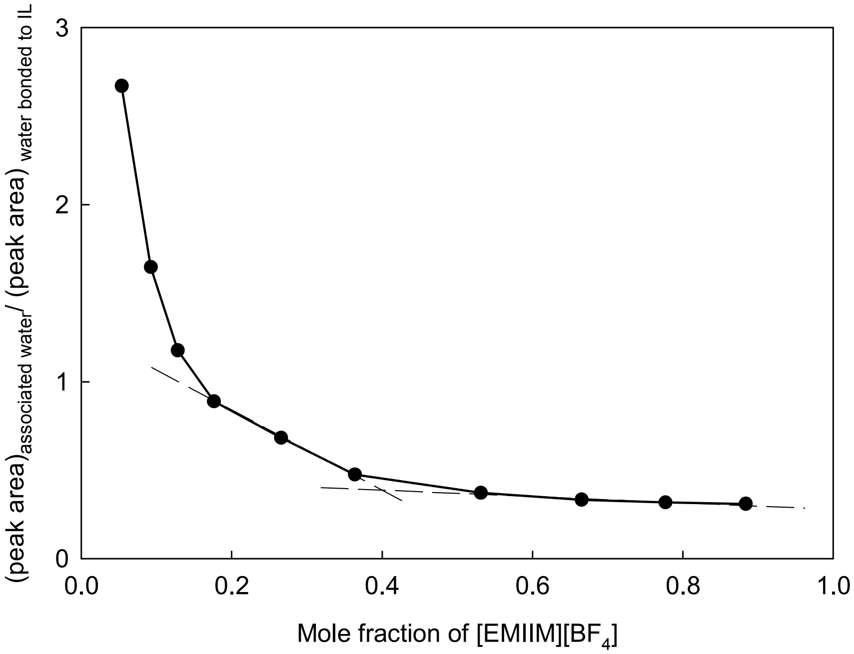

Fig. 3. Ratio of the peak areas of the –OH band from associated water to the peak area of –OH band of water boded to IL with variation of mole fraction of IL.

Fig. 4 shows the variation of peak position of the band arising from water bonded to IL (centered around 7060 cm^{-1} in Figure 2) with mole fraction of IL. With increase in the mole fraction of IL, the wavenumber of the corresponding band decreases and passes through a minimum at $X_{\mathrm{IL}} \approx 0.26$ and slightly increases again. This suggests that, when network structures of IL get broken gradually with addition of water (from pure IL to $X_{\mathrm{IL}} \approx 0.26$) and the bonding between ions of IL gets weaker due to interaction with water molecules. Consequently, the bonding between IL and water gets is favored. When the mole fraction of IL decreases from $X_{\mathrm{IL}} \approx 0.26$ to pure water region, H-bonding between water and IL weakens due to stengthened coulombic interaction between hydrated cations and anions. Conductivity measurements have shown that with addition of IL in water, the conductivity of the IL-water binary mixtures increases and reaches a maximum at $0.1<X_{\mathrm{IL}}<0.2$ and then decreases again.[51-53]. The surface tension of the binary mixtures shows a marked fall up to $X_{\mathrm{IL}}\approx 0.2$ then becomes almost constant with further addition of IL in water.[54]. These indicate the formation of self-organized aggregates or clusters of IL for mixtures with $X_{\mathrm{IL}} > 0.2$, where interionic attractions gets stronger with increasing amount of IL in water to result in gradual weakening of H-bonding between IL and water due to enhanced interactions between the ions in IL. For mixtures with $X_{\mathrm{IL}} < 0.2$ no such structure exists and hence an opposite trend in IL-water bonding strength is observed as IL-water H-bonds become stronger with increasing amount of IL. So, it can be assumed that ILs form aggregates of two different type of structures in water-rich ($X_{\mathrm{IL}} < 0.26$) and IL-rich ($X_{\mathrm{IL}} > 0.26$) regions of the binary mixtures.

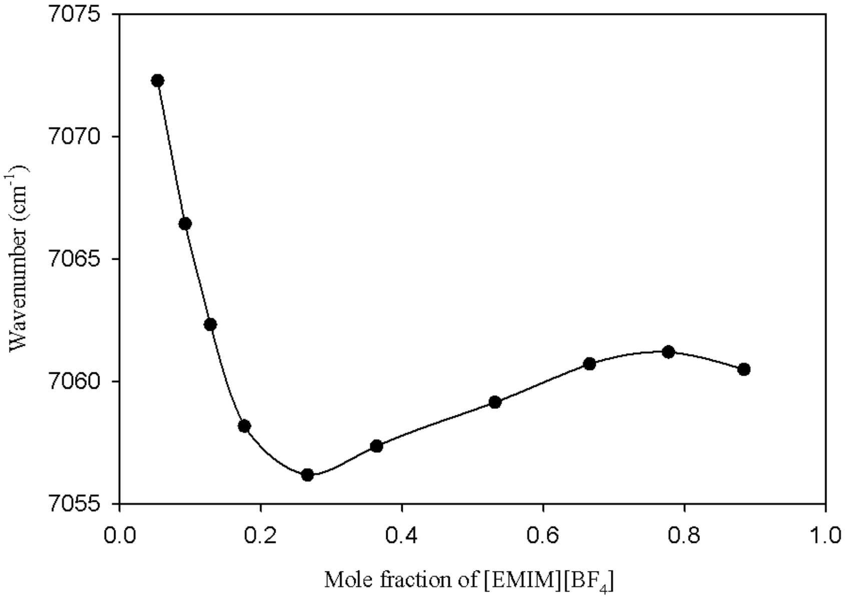

Fig. 4. Peak position of –OH combination band arising from water molecules bonded to [EMIM][BF_4] as a function of mole fraction of IL in the binary mixtures.

The results in **Fig. 4** contradicts with the MIR spectroscopic observations of Zhang *et al*. and Singh *et al.* where peak positions of OH fundamental band in raw spectra and deconvoluted spectra of IL-water binary mixtures, respectively have been analyzed. [29,34] It was reported that the peak position of OH band shifts to lower wavenumber with addition of water which implies the strengthening of IL-water hydrogen bond over the whole composition range. However, a change in the trend of variation of IL-water hydrogen bonding strength is expected as the environment varies from water-rich to IL-rich region of the mixtures which is reflected in the conductivity and surface tension measurements. Because of the well separation of associated and free water species in the NIR region the analysis of change of H-bonding between IL and water in the mixtures have been performed with more accuracy and correlated with the results of the previous studies on IL-water binary systems.

The presence of different additives in water can show structure breaking or making effect in the water clusters which causes spectral changes of bands arising from associated water similar to that of changing temperature.[44-45, 55-56].The structure breaking effect is similar to that of increasing temperature where the OH peak shifts to higher wavenumber due to the weakening of the hydrogen bonds between water molecules. Similarly, the structure making effect resembles to that of decreasing temperature where hydrogen bonds in water clusters become stronger. **Fig. 5** shows the change of peak position of the band centered around 6860 cm^{-1} originating from associated water in the binary mixtures. In pure water this band occurs at 6886 cm^{-1} and when IL is added to pure water the band shifts to lower wavenumber for mixtures with $X_{IL} < 0.68$ which indicates formation of stronger hydrogen bonds in water clusters. For mixtures where $X_{IL} \geq 0.68$, the hydrogen bonds in the water clusters gets weaker with addition of IL which indicates a structure breaking effect of IL. So,

[EMIM][BF_4] can be considered to have a structure making effect on water structure at water-rich region and a structure breaking effect at IL rich region of [EMIM][BF_4]-water binary mixtures.

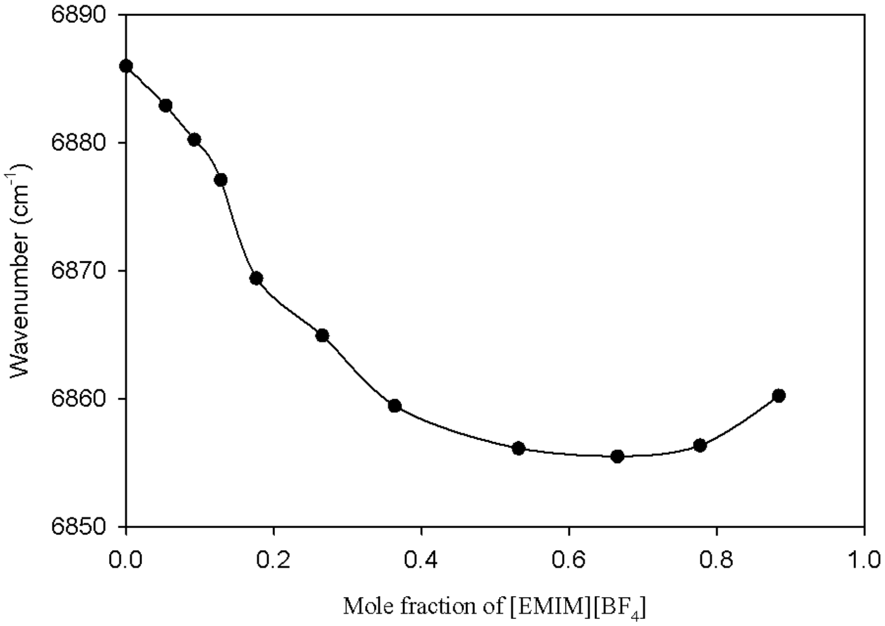

Fig. 5. Peak position of –OH combination band arising from associated water molecules as a function of mole fraction of IL in the binary mixtures.

Fig. S1 shows the change of excess molar volume with mole fraction of IL. The excess molar volume V_m^E shows a positive deviation from the ideal behavior over the whole composition range indicating the expansion of volume of the binary mixtures. The weaker interaction of IL-water than the interactions between cations and anions in pure [EMIM][BF_4] is responsible for the expansion of volume**.** **Fig. S1** shows that the V_m^E reaches a maximum value at $0.3<X_{IL}< 0.4$ then falls with further addition of water. Our results vary slightly from the literature value in the position of maximum of the excess molar volume profile.[38] The change in excess molar volume of the mixtures can be explained from **Fig. 3** where it is observed that the amount of associated water rises with addition of water in IL sharply for $X_{IL} < 0.4$. The positive deviation reaches a maximum mainly due to the breaking of 3-D network formed by the cations and anions of [EMIM][BF_4] and for $X_{IL}< 0.4$, the presence of considerable amount of strongly bonded associated water results in the lowering of V_m^E from this maximum value of deviation.

DLS measurements have been carried out in order to analyze the size of the aggregates formed in the water-rich binary mixtures. In the MD simulation studies on [EMIM][EtSO$_4$]-water systems carried out by Bernardes *et al.* formation of chain-like aggregates was indicated instead of self-organized structures at $X_{IL} = 0.05$.[35] No significant evidence of tail-tail aggregation was either found in the MD simulation study of [BMIM][BF$_4$]- water mixtures by Zhong *et al.* and the absence of self-organized aggregation was due to the small length of alkyl chain in the imidazolium ring in the above mentioned ILs.[36] However, Wu *et al.* have carried out SLS, DLS and TEM studies of aqueous solutions [BMIM][BF$_4$] and showed that in 1.0 molL^{-1}aqueous solution (X_{IL} = 0.018) IL form vesicle-like hollow spherical shape aggregates with hydrodynamic radius of 121.7 nm(diameter = 243.4 nm) in which water is bonded to BF_4^- anions surrounding the macrocations.[57] DLS measurements of [BMIM][BF4] in aqueous solutions (X_{IL}=0.0017) by Wang *et al.* showed that, when the system temperature is below the upper critical solution temperature (UCST) of the binary mixture at about 4◦C, the aggregate size of the IL is larger than 1000 nm.[40] In the present study DLS measurements show that (**Fig. 6** and **Table 1**), for mixtures with $0.020 \leq X_{IL} < 0.079$, aggregates with hydrodynamic diameter of 354~590 nm are formed. At low IL concentrations ($X_{IL} < 0.020$), the size distribution as shown in Figure 6 becomes narrower. However, replicate measurements show that the average size of the aggregates changes and it is somewhat random with number of measurements and time. The aggregates are not sufficiently stable and sizes change retaining the narrow distribution.

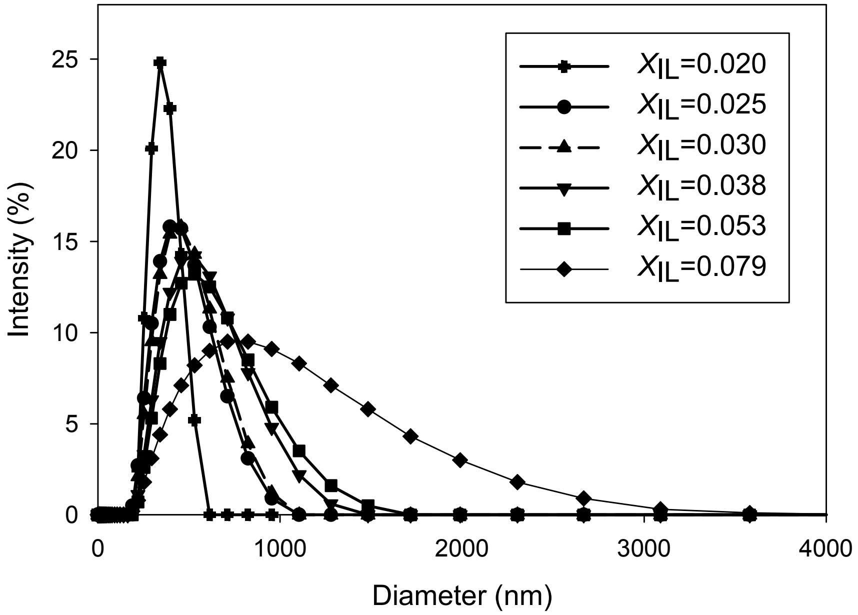

Fig.6. Size distribution of aggregates formed in [EMIM][BF$_4$]-water binary mixtures.

Table1. Variation of size of aggregates in [EMIM][BF$_4$]-water binary mixtures with mole fraction of [EMIM][BF$_4$]

Mole fraction of [EMIM][BF$_4$]	Hydrodynamic diameter (D_h nm)
0.020	354.1
0.025	452.9
0.030	468.5
0.038	549.5
0.053	585.0
0.079	897.2

The systematic increase in the size of the aggregates with addition of IL to water is observed for solutions with X_{IL}> 0.020 (Table 1). Since formation of vesicle-shape aggregates is rather unfeasible for ILs with ethyl side chain, it can be suggested that the aggregates formed in [EMIM][BF$_4$]- water systems mostly consists of chain-like structure.

In **Fig. 6**, it can be observed that with increasing amount of IL in water, the peak broadens indicating the presence of aggregates of various sizes. The increased polydispersity in the size of the aggregates may result from the association of the smaller aggregates with increasing amount of IL in the systems. From the analysis of the NIR band arising from the water bonded to IL in **Fig. 4**, it has been observed that for mixtures with $X_{\mathrm{IL}}< 0.261$, increasing the amount of IL makes the IL-water hydrogen bonds become stronger which reflects the weakening cohesion between cations and anion interactions. This may result in the higher dissociability of the ions in water and hence higher conductivity of the mixtures. From NIR and DLS measurements it can be suggested that, prior to self-organized structure formation at $X_{\mathrm{IL}} \approx 0.2$, the conductivity increases up to a maximum value due to high dissociability of these aggregates compared to the larger clusters formed even though addition of IL results in the formation of larger aggregates. In **Fig. 7** and **Table 2** the variation of the size of the aggregates with temperature has been shown.

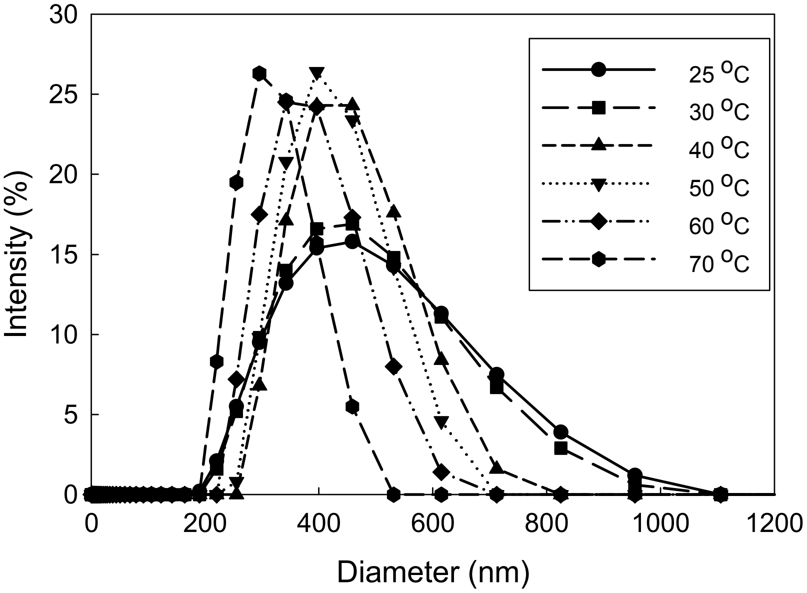

Fig.7. Size distribution of aggregates formed in [EMIM][BF$_4$]-water binary mixture with $X_{\mathrm{IL}} = 0.030$ at several temperatures from 25 °C to 70 °C.

Table 2. Variation of size of aggregates in [EMIM][BF_4]-water binary mixture with X_{IL} = 0.030 at different temperatures

Temperature (^oC)	Hydrodynamic diameter (D_h nm)
25	468.5
30	460.2
40	442.5
50	417.7
60	379.6
70	317.3

With increase in temperature, smaller aggregates are formed and above 50 ^oC the peak becomes significantly broader. These are in agreement with the observations of Wang *et al.* for [BMIM][BF_4]-water mixtures.[40] This indicates that, raising temperatures causes the breaking of larger aggregates into smaller ones of different sizes.

4. Conclusions

The properties of IL-water binary mixtures are mainly governed by two factors, the strength of IL-water bonds and population of IL-IL and water-water clusters. In this study, NIR spectroscopy has been successfully employed to have an idea about the strength of interaction between IL-water as well as different water species in [EMIM][BF_4]-water binary mixtures over the whole composition range. At IL-rich region, the ratio of the population of associated water species to free water species is almost constant and it implies that the changes in the physicochemical properties mainly arise from the breaking of clusters of IL where the ratio of different molecular states of water remains the same. Significant changes of different water species occur when the mole fraction of IL becomes less than 0.4. With increasing amount of water in the binary mixtures with $X_{IL} < 0.4$ there is a significant rise in the amount of associated water where the hydrogen bonding between the water molecules in the clusters becomes stronger and IL acts as a structure maker additive. The increase in the amount of associated water also explains the profile of the excess molar volume vs. X_{IL}. With addition of water to IL, the hydrogen bonding between IL and water becomes stronger up to $X_{\mathrm{IL}} \approx 0.26$ due to the breaking of IL clusters and weakening of cation-anion interactions. For mixtures with $X_{\mathrm{IL}} < 0.26$, the IL-water bond gets weaker with increasing amount of water in the mixtures. This results from the formation an aggregate of IL which is different than the clusters or network structure of IL formed in the IL-rich region. The size of these aggregates in the mixtures with $0.020 \leq X_{\mathrm{IL}} \leq 0.079$ was found to be about 354-590 nm. At higher concentrations of IL the solutions become highly polydisperse containing aggregates of larger size resulting from the association of smaller aggregates.

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Supplementary Information

Electronic Supplementary Information (ESI) available: Fig. S1. Excess molar volume of [EMIM][BF_4]-water binary mixtures as a function of mole fraction [EMIM][BF_4].

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