

Organic co-solvents mediated variation in anion-water hydrogen bonding in [Bmim][BF₄] ionic liquid through FTIR spectroscopy

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ABSTRACT: FTIR spectroscopy has been employed to investigate the variation of anion-water hydrogen bonding in 1-butyl 3-methyl imidazolium tetrafluoroborate ([Bmim][BF₄]) ionic liquid caused by addition of organic co-solvents with various polarities. The variation was estimated by probing band shape and intensity of the OH stretching vibration of trace water present in ionic liquid at 3400-3800 cm⁻¹. The presence of polar aprotic co-solvent in ionic liquid dramatically reduces the absorptivity of the OH stretch band, indicating that the co-solvent changes the nature of anion-water hydrogen bond drastically, which might be responsible for the reduction of the viscosity of ionic liquid in the presence of the co-solvent.

For the last two decades ionic liquids have drawn significant attentions of the scientific and industrial community for possessing characteristics like low vapor pressure, wide solubility range, large electrochemical window, low flammability, extensive liquid range, and inertness etc., which are desirable properties in synthesizing the chemical product efficiently by emphasizing on toxicity reduction as well as waste minimization.¹⁻⁴ Ionic liquids remain liquid at room temperature and are composed of organic cations and inorganic or organic anions.^{1,4} Built in molecular asymmetry in the structure of ionic liquids diminishes the extent as well as the range of Coulombic interactions among the constituent ions, resulting in properties more akin to normal liquids.³ Moreover, existence of hydrogen bonding network in the midst of cations and anions persuades *co-operative* effect and structural directionality (entropic effect) in the ionic liquids.^{5,6}

Though ionic liquids possess most of characteristics propagated in 'green chemistry', still wide spread applicability of ionic liquids in the realm of chemical synthesis at large scale is limited due to its high viscosity which retards the chemical reactions by slowing the dynamics or movement of the reactants.⁷ This challenge has been overcome by introducing co-solvents which help to reduce viscosity of the ionic liquids keeping other properties least altered to widen its applicability.⁸ However, the molecular origin of the process by which these co-solvents reduce viscosity of ionic liquids is still illusive. All these ionic liquids possess some water which is practically impossible to remove.² Presence of water at its various forms i.e. bonded or isolated has been established both experimentally as well as theoretically.^{2,4} Cammarata et. al. has established through ATR-IR spectroscopy that water molecule mainly form hydrogen bond with

the anions of ionic liquids.⁹ The quantity of water present in ionic liquids affect many characteristics like polarity, hydrogen bonding interactions among cations and anions, and viscosity etc.^{2,3}

FTIR spectroscopy has been applied as a very sensitive technique to probe molecular state of water dissolved in molecular solvent, polymer, and organic materials etc.^{10,11} Here FTIR technique was used to identify the molecular state of water and its interactions with the ionic environment by probing the position and intensity of vibrational modes of H₂O present in ionic liquid. Particularly in the O-H stretching region, i.e. 3200-3800 cm⁻¹, the appearance of two isolated IR bands implies that a few water molecules in ionic liquids remain free or isolated rather than participating in hydrogen bonding with other water molecules.⁹ Most of the properties of ionic liquid depend on the characteristics of constituent anion. The IR band is significantly modified by the variation of anions rather than cations of the ionic liquids. The band position and its shape are the function of stretching vibration of hydrogen bond evolved due to formation of 'anion...HOH...anion' hydrogen bond.⁹ We have concentrated on this specific region of IR spectra of water in ionic liquids since alteration of the position and intensity of these OH stretching region would imply change in the strength of hydrogen bond between anion and water.

Experimental section:

Chemicals: 98.9% [Bmim][BF₄] ionic liquid and spectroscopic-grade solvents were used as purchased from Sigma Aldrich Co.

Experimental Procedure: Sample had been prepared by mixing 20 μl of each organic solvent in 500 μl of [Bmim][BF₄]. Each mixture has been stirred and kept for 30 min to reach equilibrium. The equilibrated sample was then loaded into a 30 μm gas-tight sample cell with CaF₂ windows and FTIR spectra were collected. All the experiments have been done under at ambient temperature and pressure condition.

Results and discussion:

In order to confirm that the IR-bands observed in the range from 3500 cm⁻¹ to 3700 cm⁻¹ are due to the presence of minute amount of water in [Bmim][BF₄], we obtained FTIR spectra of only ionic liquid upon varying quantity of water in it. Figure 1 shows that the intensity of the O-H stretching bands at 3638cm⁻¹ and 3562 cm⁻¹ increases from dry [Bmim][BF₄] to [Bmim][BF₄] with added water. The symmetric (3562 cm⁻¹) and antisymmetric (3638 cm⁻¹) stretching modes of H₂O are highly sensitive to the change in the environment.^{9,11} The positions of two bands remain unchanged in three samples, indicating that the variation is the quantity of water only.

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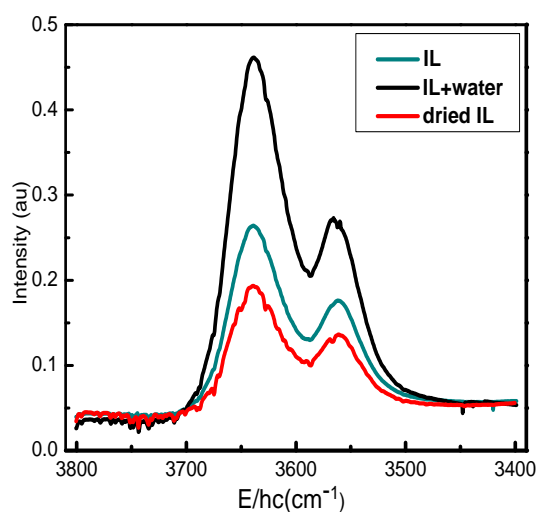


Figure 1: The O–H stretching band with varying water quantity in [Bmim][BF₄].

To understand the effect of organic molecular solvents on the hydrogen bonding among anion and water i.e. $BF_4^- \cdots HOH \cdots BF_4^-$, we obtained FTIR spectra of each mixture of ionic liquid and organic solvent and showed in figure 2.

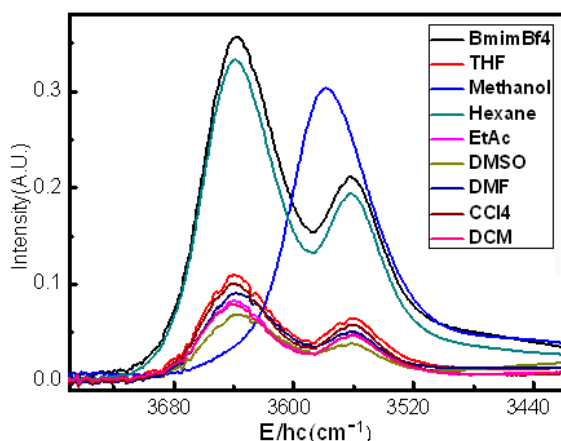


Figure 2. The OH stretching band upon introduction of organic molecular solvent in [Bmim][BF₄]

The shape and intensity of the O–H stretching modes vary due to the presence of foreign molecular solvents in ionic liquids. The band shape remains to be the same in hexane and aprotic co-solvent but the two bands merged to one in methanol co-solvent. The band position in methanol co-solvent suggests that H₂O is hydrogen bonded with methanol. The intensity of the bands was obtained by fitting them to Gaussian functions. As shown in Table 1, although the band intensity in hexane co-solvent is almost the same as in ionic liquid alone, the band intensity decreases dramatically upon addition of the polar aprotic solvents. The fact that there is no other O–H band except the observed one, implies that the absorptivity of the band decreases in aprotic co-solvent. The molecular nature for the reduction of the absorptivity is not clear yet.

The band intensity does not show any regular trend with respect to

polarity index of the added co-solvent. However, polar protic and aprotic natures of the co-solvents change the intensity as well as shape of the IR-band. Clearly introduction of organic co-solvents can alter the nature of hydrogen bonding between anion and isolated water or the absorptivity of the isolated water in ionic liquid.

Table 1. The intensity of the O–H stretching vibration as a consequence of adding organic co-solvent with various polarities.

Co-solvent	Polarity Index ¹³	Band Intensity
Hexane	0.0	26
CCl ₄	1.6	8.1
DCM	3.1	7.8
THF	4.0	8.9
Ethyl Acetate	4.4	6.4
Methanol	5.1	16
DMF	6.4	4.8
DMSO	7.2	4.8

Little change was observed when nonpolar hexane solvent was added but a significant reduction of the band intensity of the O–H stretching modes in [Bmim][BF₄] was observed upon introduction of only 4% by volume of polar aprotic solvents in ionic liquid. Introduction of polar protic solvent i.e. methanol in ionic liquid transforms the nature of hydrogen bonding from isolated to bulk.

In all the cases presented above, it was found that, irrespective of polarity of the co-solvent, the addition of modest amount of co-solvent in ionic liquids decreases the magnitude hydrogen bonding between inherent water and constituent anion of the ionic liquid. The reduction of the extent of hydrogen bonding in presence of the co-solvents may be responsible for decrease in viscosity of ionic liquids upon addition of co-solvents because hydrogen bonding in ionic liquid is the signature of co-operative effect as well structural directionality which indirectly contributes to the viscosity of ionic liquids.^{5, 6} However, further investigations are required to explore role of co-solvents during reduction of viscosity of ionic liquids.

KEYWORDS: Ionic liquid, FTIR, Co-solvent

Received August 28, 2015; Accepted September 7, 2015

ACKNOWLEDGEMENT

This work was supported by a 2-Year Research Grant of Pusan National University.

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