Investigation of PEG-6000 bridged -N-SO₃H functionalized geminal dicationic ionic liquids for catalytic conversion of fructose to 5-hydroxymethylfurfural

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Abstract. Eight new members of two series of PEG-6000-bridged geminal dicationic ionic liquids based on diphenylammonium/imidazolium cation were synthesized by the change of four anions CF₃COO[−], CCl₃COO[−], AcO[−] and HSO₄[−]. They were investigated as reusable acidic catalysts for dehydration of fructose to 5-hydroxymethylfurfural in polar aprotic solvent. The characterizations of dicationic ionic liquids were done using ¹H NMR, ¹³C NMR, IR and TGA analyses. Irrespective of Hammett acidity strength of the eight ILs, they displayed single peak selectivity for the 5-hydroxymethyl furfural intermediate in HPLC analysis.

Keywords. PEG-6000 linker; dicationic ionic liquid; dehydration of fructose; reusable catalyst.

1. Introduction

The chemistry of multi-charged ionic liquids has been recognized as a growing field for the generation of structurally diverse organic salts, either by change of charged heads or spacers separating them, with unique physicochemical properties, especially the wide temperature window to exist in liquid state (e.g., −4 °C to 400 °C) and greater thermal stability over monocationic ionic salts.^{1–5} Imidazolium and ammonium-based geminal dicationic ionic liquids (DILs) with different bridging groups have been utilized as high-temperature reaction media^{1,6} and lubricants,⁷ ultrastable separation phases,^{8,9} extraction processes¹⁰ and mass spectrometry.^{11–13} Polyethylene glycol can be considered as an identical linker for the preparation of geminal DILs with a variety of lengths, polymer architectures and charged groups. The polyethylene glycol (PEG) based materials possess several distinctive properties including temperature dependent phase behavior in solution, environment-friendliness, water miscibility, non-volatility and thermal stability. The various molecular weight PEG backbones are appropriate for immobilization of catalyst and reagents applicable in organic

synthesis.^{14,15} The combination of polyethylene glycol spacers and functionalized ionic liquids incorporates various attractive physical properties of the linkers and ionic liquids to the modified supported material.^{16–18} The transfer of unique ‘critical solution temperature’ (CST) of PEG to PEG-functionalized DILs was observed as temperature-dependent biphasic material in an organic solvent and thus further studied as tunable phase separable catalysts in organic reactions.^{19–24} As the solvent, they dissolve carbohydrates and polymers,²⁵ stabilize and activate protein or enzyme,²⁶ separate inorganic salts from aqueous solutions,²⁷ function as reductant and stabilizer for nanoparticle synthesis.²⁸ The attachment of one or more acidic sites to the charged heads may facilitate Brønsted acidic properties to them. The literature search finds some examples of the Brønsted acidic PEG-based DILs with an acidic proton in the anion and also from N-alkylsulfonic group or N-sulfonic group in the cation.^{29–31} Eshghi *et al.*,²⁹ reported only the direct N-sulfonic group containing benzimidazolium DIL as a reusable acidic catalyst for one-pot synthesis of α-amino phosphonates derivatives in solvent-free condition. Herein, we determined the structure of eight new members of -N-SO₃H functionalized PEG-6000 linked

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imidazolium/diphenylammonium dicationic geminal ionic liquids using NMR and FT-IR analyses (Scheme 1). Their utility were examined as a homogeneous recyclable catalyst in solutions for conversion of fructose to 5-hydroxymethyl furfural (HMF) (Scheme 2) by HPLC analysis. HMF is a reactive chemical intermediate for the synthesis of value-added chemical products in the context of sustainable development process.^{32,33}

Biomass is an alternative substitute of fossil fuel to produce liquid fuels and chemical intermediates for the synthesis of chemical products in industry.^{34–36} The biomass conversion methods include reactions like pyrolysis,³⁷ gasification,³⁸ transesterification,³⁹ and hydrolysis,⁴⁰ etc. The acid-catalyzed hydrolysis of carbohydrates occur at elevated temperature in water with many side products^{41,42} while the selective enzyme-catalyzed reactions prefer lower temperature because of limited thermal stability of enzymes with a slower rate.⁴³ Rogers *et al.*, in 2002, observed dissolution and decrystallization of cellulose in 1-butyl-3-methyl imidazolium chloride IL⁴⁴ and later on this was accounted for the depolymerization of carbohydrates in ILs for disruption of intermolecular H-bonds between different cellulose chains.^{45,46} A major amount of degradation products of carbohydrates in [BMIM][Cl] using mineral acid catalysts are furfural, 5-hydroxymethyl furfural (HMF) and other side products.^{47,48}

2. Experimental

2.1 General information

The chemicals were purchased in pure state from Tokyo Chemical Industry Co. Ltd. Japan, Merck India and Sisco Research Laboratory Pvt. Ltd. India. NMR spectra of the DILs were found using JEOL 400 MHz spectrometer in a DMSO- d_6 solvent. Perkin Elmer FT-IR spectrometer was employed to take FT-IR spectra. The acidity of DILs was done in UV 2550 spectrophotometer *via* determination of Hammett acidity plots. Shimadzu TGA 50 instrument was employed for observation of thermal stabilities of the dried ILs at 50 °C under vacuum condition. The HMF formation was measured quantitatively by Water 2489 High-Performance Liquid Chromatography instrument. The spectral data and soft copies of ^1H NMR and ^{13}C NMR spectra of **IL 1–8** are included in the supporting document.

2.2 General procedure for the synthesis of PEG₆₀₀₀-DILs

The preparation method of PEG-6000 bridged geminal DILs was sub-divided in three steps as follows:

Step I: Synthesis of oligo(ethylene glycol)dichloride (Intermediate A):

In a three-necked 100 mL round-bottomed flask equipped with a condenser, magnetic stirrer and N_2 inlet, a mixture of 12 g (2 mmol) of PEG ($M_n = 6000$ g/mol) and 0.871 mL (12 mmol) of SOCl_2 in 50 mL of freshly dried toluene was refluxed for 48 h fitted with a CaCl_2 guard tube in presence of 0.967 mL (12 mmol) of pyridine with continuous stirring in a fume hood. The solvent was evaporated under reduced pressure and the resulting solid washed with diethyl ether to yield intermediate **A** in the analytically pure state.

Step II: Synthesis of $-\text{SO}_3\text{H}$ functionalized PEG₆₀₀₀-DIL (Intermediate D/E):

At first, an equimolar mixture of 2-methylimidazole/diphenylamine (1 mmol) and sodium ethoxide (1 mmol) was stirred in ethanol (95%) (30 mL) at room temperature for 8 h. After that, the solvent was removed under reduced pressure, washed the residue with diethyl ether for three times and dried in vacuum to isolate the sodium salt of 2-methylimidazole/diphenylamine. Subsequently, the salt was treated with 2.962 g (0.5 mmol) of oligo(ethylene glycol) dichloride by dissolving it in ethanol (50 mL) and the mixture was refluxed for 10 h and filtered. The filtrate was washed with ether for three times and then evaporated under reduced pressure to get the respective intermediate **B/C** as brown solid. In the next step, ClSO_3H (3 mmol) was added dropwise into the solution of intermediate **B/C** in dry toluene (20 mL) in 30 min and the reaction mixture was stirred for 8 h. The solvent was removed under vacuum and the remaining part was washed three times (3×5 mL) with dry toluene to yield the intermediate **D/E**.

Step III: Metathesis reaction of intermediate D/E:

In the final step, $\text{CF}_3\text{COOH}/\text{CCl}_3\text{COOH}/\text{CH}_3\text{COOH}/\text{H}_2\text{SO}_4$ (3 mmol) was added dropwise in dry toluene within 30 min at ambient temperature. The final solution was stirred at 50 °C for another 8 h and evaporated under reduced pressure to get PEG₆₀₀₀-DIL as a viscous light yellow/brown liquid. The crude samples were again dried in vacuum oven at 25 °C for analysis of FT-IR, ^1H NMR and ^{13}C NMR spectra. For thermogravimetric studies, the DIL samples were pre-dried in a vacuum oven at 50 °C for 2 h.

2.3 General procedure for the synthesis of 5-hydroxymethyl furfural

In a typical reaction procedure, fructose (1 mmol), PEG₆₀₀₀-DIL (15 mol% with reference to the molecular weight of fructose) and solvent (5 mL) were added into a 50 mL round-bottomed flask. The reaction mixture was stirred vigorously and refluxed in an oil bath for a specific time (Tables 3 and 4). Reaction aliquots (0.1 mL) were collected after a definite time interval and they were diluted to 2 mL using ultrapure water as the diluent. The reaction mixtures were analyzed by HPLC to determine the percentage yield of HMF.

2.4 Analytical methods

Quantitative analyses of HMF were performed by HPLC using a C₁₈-reverse phased column (200 mm × 4.6 mm) equipped with a UV detector ($\lambda_{HMF} = 284$ nm) (Waters 2489). For the detection of HMF, a 10:90 (v/v) mixture of acetonitrile and water was used as the mobile phase at a flow rate of 0.6 mL/min. The column temperature was maintained at 25 °C. The volume of each injection was 20 μ L. HMF in the samples was identified by retention time determined using pure samples. The concentration of HMF in the samples was

determined from a standard curve obtained with samples of HMF of known concentrations (10, 20, 30, 40 and 50 ppm).

The yield of HMF was calculated as follows:

Mass of HMF (mg) = [HMF concentration on sample (mg/mL)] × [Volume of the reaction mixture (V_{RM})] × [dilution factor (DF)]

Where $V_{RM} = 0.1$ mL, DF = 20

HMF yield (wt %) = [mass of HMF (mg) / mass of fructose (mg)] × 100

Scheme 1. Preparation of PEG-6000 bridged DILs.

Scheme 2. Conversion of fructose into HMF in presence of PEG-6000 bridged DIL as a catalyst.

3. Results and Discussion

At first, the eight new members (**IL 1–8**) of two types of PEG-6000 bridged dicationic ionic liquids (DILs) were prepared containing $-N-SO_3H$ functionalized 2-methylimidazolium or diphenylammonium as a cation in association with four different anions namely CF_3COO^- , CCl_3COO^- , OAc^- and HSO_4^- according to the reaction Scheme 1. Each ionic liquid was carefully characterized by FT-IR, 1H and ^{13}C NMR, TGA and UV-Vis spectroscopy. The Brønsted acidities of these DILs were determined via the Hammett plots. The catalytic efficiencies of these ILs were explored as reusable acidic catalysts for the conversion of fructose to 5-hydroxymethylfurfural (HMF) in three different solvents, such as EtOAc, THF and CH_3CN using HPLC technique (Scheme 2).

3.1 Preliminary spectral analysis

FT-IR spectra of the two series of dicationic ILs are illustrated in Figure S1 (Supplementary Information) and their assignments of various frequencies are listed in Table S1 and Table S2 (Supplementary Information). The eight ILs possess strong O-H stretching vibrations around $3416\text{--}3446\text{ cm}^{-1}$ for the $-SO_3H$ group and also for physisorbed water. The C-H stretching frequencies of methyl and methylene groups present in these ILs appear as strong, medium or weak intensities at 2925 cm^{-1} . The C-H bending vibrations of both methyl and methylene groups show a peak at $1458\text{--}1469\text{ cm}^{-1}$ with a variation of intensities. Another C-H bending vibration of $-CH_3$ group is observed around $1355\text{--}1367\text{ cm}^{-1}$ possessing different intensity peaks for the eight ILs. The carboxylate anions of imidazolium ionic liquids **IL 1** to **IL 3** display $C=O$ stretching vibration at $1725\text{--}1786\text{ cm}^{-1}$ as strong to medium intensity band. This $C=O$ peak is observed as medium intensity around $1755\text{--}1776\text{ cm}^{-1}$ for the diphenyl ammonium based ionic liquids **IL 5** to **IL 8**. The four imidazolium ILs give medium intensities $C=C$ vibrations at $1633\text{--}1644\text{ cm}^{-1}$ which are also overlapped by $C=N$ stretching frequencies of imidazole ring along with

H-O-H bending vibrations of water at 1641 cm^{-1} .⁴⁹ The attachment of $-SO_3H$ group with the imidazolium cation is evidenced through observation of $S=O$ symmetric stretching at $1162\text{--}1233\text{ cm}^{-1}$ and asymmetric stretching around $1058\text{--}1100\text{ cm}^{-1}$ in addition to strong intensity bending vibration in the range of $577\text{--}588\text{ cm}^{-1}$ for the **IL 1** to **IL 4**. The position of $C-C$ stretching and $C-F$ asymmetric stretching of CF_3COO^- group are also located in the same region of $S=O$ symmetric stretching frequencies. The characteristic $C-O/C-N$ stretch are also observed in the same range of $S=O$ asymmetric vibrations for $-O-CH_2-CH_2-O-$ bridging group attached with the N-atom of imidazolium/diphenyl ammonium cations. The typical $C-O-C$ stretching for the $O-CH_2-CH_2-O$ bridging group is observed at $998\text{--}1018\text{ cm}^{-1}$.⁵⁰ The eight ILs have unique N-S stretching vibrations around $843\text{--}897\text{ cm}^{-1}$ with weak to medium intensities. The aromatic C-H out of plane bending vibrations was observed at $678\text{--}698\text{ cm}^{-1}$. The C-Cl stretching peak for CCl_3 group of trichloroacetate anion in **IL 2** and **IL 6** was observed at 855 cm^{-1} and 835 cm^{-1} respectively.

The structures of these ILs were also confirmed by analyzing their 1H and ^{13}C NMR spectra as included in the supporting document. As a representative example, the presence of acetate anion in **IL 3** was supported from the $-CH_3$ peak of $-OAc$ at 1.85 ppm in 1H NMR spectrum and also from the $C=O$ peak at 172.6 ppm in the ^{13}C NMR spectrum of this IL. The repeating unit of PEG chain $-OCH_2-CH_2O-$ displays one broad singlet in its proton NMR spectrum at 6.67 ppm for the two methylene group protons and a peak at 70.2 ppm in the ^{13}C NMR spectrum. The chemical shift positions of two doublets for four protons at 7.46 and 7.11 ppm in the aromatic region support the presence of two imidazole rings on the geminal positions of the PEG-chain. Likewise, the protons of PEG-linker of diphenylammonium based ionic liquid **IL 8** was observed at 5.05–5.14 ppm and their ^{13}C NMR peak at 72.3 ppm. Furthermore, we found a significant amount of water peak in the proton NMR spectra of these ILs in DMSO- d_6 solvent. Study express that approximate two water molecules are bound to every repeating unit of PEG at room temperature.^{51–53} For our case, the two $-SO_3H$ groups attached at each end of these PEG bridged dicationic imidazolium/diphenyl ammonium ILs can be accounted for formation of some amount of self-organized PEG chains involving physisorbed water through interconnection of weak, reversible physical forces such as van der Waals, hydrogen bonding, ionic or hydrophobic interactions, etc. The stability of self-organized hydrated structures is often disturbed by the change of temperature and solvents.⁵⁴ Since the NMR spectra were taken using a

Figure 1. TGA profiles of the DILs.

Figure 2. Hammett plots of DILs as absorbance vs wavelength.

vacuum-dried sample at room temperature. Therefore, some of the PEG-bound water may release from the polymeric chain and hydrogels after disturbance of the physical interactions for the self-aggregation in presence of a polar DMSO- d_6 solvent during NMR analysis. This again could be the reason for the presence of water peak in ^1H NMR spectra of the DILs.

The analysis of proton NMR spectra of the eight ILs also represents broad NMR signals of bridged $-\text{OCH}_2 - \text{CH}_2 - \text{O}-$ linkages with varied chemical shift values against the four different counter anions (e.g., CF_3CO_2^- and $\text{CCl}_3\text{CO}_2^-$, CH_3CO_2^- and HSO_4^-). The broad signals of $-\text{OCH}_2 - \text{CH}_2 - \text{O}-$ group evidence some amount of self-aggregated structures of the polymeric chains in the NMR solution which restrict the motion of certain segments of the polymeric backbone and thus express unequal distribution of dipolar interactions with broadening of NMR lines.⁵⁵ The structural analysis of self-aggregated polymeric material by NMR spectra provides valuable information on the nature of intermolecular interactions, the values of critical concentration, the individual motional behavior or

other thermodynamic parameters associated with the formation of aggregated structures.^{56–58} Here we limit our study for predicting the exact mechanism for variation of chemical shift values of the DILs involving complex aggregated structures.

3.2 TGA analysis

The thermogravimetric analyses of the DILs are presented in Figure 1. Among the imidazolium-based four ILs, **IL 1** with trifluoroacetate anion was found to be more thermally stable than the ionic liquids possessing other anions such as CCl_3COO^- , AcO^- and HSO_4^- . All the four ILs of 2-methyl imidazolium cation seemed to be stable up to 150 °C. Out of the four anions varied, it is the CF_3COO^- anion which displayed strong interaction with its cation, while HSO_4^- anion was the most loosely bound. In case of diphenylamine based four ILs, **IL 6** with CCl_3COO^- anion was more stable up to 200 °C than the three other ILs. The TGA patterns of both series of DILs express no weight loss of physisorbed water near 100 °C. Here we expect that during the

pre-treatment process in a vacuum oven at 50 °C, the polymer-water interaction becomes less favorable and thus the amount of physisorbed water content decreases in TGA analysis.⁵⁴

3.3 Miscibility properties of the DILs with solvents

The solubility properties of DILs were investigated in water, polar and non-polar organic solvent at room temperature and the results are illustrated in Table S3 (Supplementary Information). It can be seen from the table that, owing to the capability of $-\text{SO}_3\text{H}$ groups of the ILs as well as the carboxylate anions to form hydrogen bonds or other secondary interactions with varying strengths, they tend to be more soluble in polar-protic and aprotic organic solvents.

3.4 Hammett acidity determination of the ILs

The acid strength of the $-\text{SO}_3\text{H}$ functionalized PEG-6000 bridged DILs were estimated *via* Hammett indicator method by following the standard procedure using 4-nitroaniline as the basic indicator.⁵⁹ The procedure required equal mixing of the indicator (5 M) and catalysts (equal amount of all) solution in ethanol. The absorbance of the basic indicator decreases with increasing acidic strength of the ILs. The maximum absorbance for the indicator was observed at 378 nm in ethanol (Figure 2). The highest acidity was observed for the two ILs of bisulfate anion such as **IL 4** of imidazolium cation and **IL 8** of diphenyl ammonium cation followed by the ILs of trifluoroacetate anion (**IL 1** and **IL 5**). The acetate anion bearing two ILs (**IL 3** and **IL 7**) showed the lowest acidic nature among the four anions for the two series of DILs. The acidity order found for the eight ILs in increasing order is (Table 1): **IL3** < **IL7** < **IL2** < **IL1** < **IL4** < **IL6** < **IL5** < **IL8**.

Table 1. Determination of Hammett acidity of the $-\text{SO}_3\text{H}$ functionalized dicationic ionic liquids.

Sample	A_{max}	[I]%	[IH]%	H°
Blank	0.376	100	0	—
IL1	0.183	48.67	51.33	0.967
IL2	0.187	49.73	50.27	0.985
IL3	0.184	48.93	51.07	1.340
IL4	0.176	46.80	53.2	0.934
IL5	0.113	30.05	69.95	0.623
IL6	0.115	30.59	69.41	0.634
IL7	0.260	69.15	30.85	0.971
IL8	0.104	27.66	72.34	0.572

3.5 Evaluation of catalytic dehydration of fructose into 5-hydroxymethyl furfural (HMF)

The catalytic efficiencies of the **IL 1-8** were evaluated for the fructose dehydration reaction under reflux temperature in different organic solvents. The quantitative analyses of HMF formation were monitored by HPLC method in presence of C-18 reverse phase column and UV-detector for identification of maximum λ_{HMF} at 284 nm. The concentration of HMF in each sample of the reaction mixture was calculated from a standard curve of HMF solutions of known concentrations (10, 20, 30, 40, and 50 ppm) in Figure S2 (Supplementary Information).

3.5a Influence of **IL 8 dosage on fructose dehydration:** In this study, the different dosage of most acidic diphenylamine based **IL 8** was initially screened for optimization of catalyst amount in acetonitrile under reflux for selective dehydration of fructose to HMF during 3.5 h included in Table 2.

Figure 3 shows the influence of **IL 8** dosages on selective dehydration of fructose to HMF in CH_3CN . The amounts of IL used were 5, 10, 15, 20 and 25 mol% of weight with reference to the molecular weight of fructose.

From Figure 3, it is evident that when only 5 mol% of **IL 8** was employed, 91.2% fructose conversion was achieved with 61.2% HMF yield. Further increasing amount of **IL 8** up to 15 mol% achieved 100% conversion of the fructose with 73% yield of HMF. However, above 15 mol% of the catalyst dosages as observed in Figure 3 both the fructose conversion and HMF yield decreased. This can be attributed for prevailing side reactions such as rehydration of HMF, aldol condensation, etc., in the presence of excess amount of acidic IL catalyst above the 15 mol% dose. Therefore, the best selective formation of HMF was achieved at 73% yield for 100% conversion fructose with 15 mol% of **IL 8**.

3.5b Effect of different solvents on fructose conversion: The above-optimized amount of **IL 8** was extended for evaluation of the catalytic activities of the eight DILs for the dehydration of fructose to HMF in three different polar aprotic solvents such as EtOAc, THF and CH_3CN under reflux condition (Figures 4 and 5). In this study, we avoided the use of a polar protic solvent for the possible greater extent of intermolecular H-bonding abilities with the catalyst, substrate and final product HMF, and then associated problems for separation of the HMF during workup steps. The results of solvent studies results are summarized in Tables 3 and 4 separately for diphenyl ammonium/imidazolium-based DILs. The acidities of the ILs showed significant

Table 2. Optimization of catalyst amount **IL 8** at 75 °C in CH₃CN.

Entry	IL8 (mol%) ^{a,b}	Time (h)	% Conversion of fructose	% Yield of HMF
1	5	3.5	91.2	61.2
2	10	3.5	94.5	65.4
3	15	3.5	100	73
4	20	3.5	95.4	63.2
5	25	3.5	89.2	60.7

^aWeight mol% of catalyst with reference to molecular weight of fructose;^bCalculated from the HPLC analysis. **Figure 3.** Influence of **IL 8** amount on fructose conversion and HMF yield.

influence on the fructose conversion to HMF. The nature of the anion also influences the catalytic activity of these ILs. The progress of the reactions was monitored *via* HPLC analysis. The HPLC profile of each catalytic systems displayed single peak formation of HMF during analysis.

From the screening, CH₃CN and EtOAc seem to be the best solvents for both the type of DILs, while **IL 3** in THF proves to be as mild reaction medium.

In the case of 2-methyl imidazolium-based ILs with varied anions, 100% conversion of fructose in ethyl acetate was observed within 6 h reaction for **IL 2** and 12 h reaction for **IL 3** (Table 3). It can be expected due to the weak ion-pair interaction of acetate anion with the cation of **IL 3**. Using acetonitrile as the reaction medium, the **IL 1** and **IL 4** showed 100% conversion of fructose during 12 h reaction in spite of their different Brönsted acidities as found in the Hammett plots.

For diphenyl ammonium-based DILs with varied anions, we observed best catalytic activity for **IL 8** in ethyl acetate and acetonitrile within 3–5 h reaction under reflux conditions (Table 4). Two other diphenyl ammonium ionic liquids **IL 6** and **IL 7** also expressed

Figure 4. Fructose conversion in different solvents with 15 mol% of **IL 4** as the catalyst. **Figure 5.** Fructose conversion in different solvents with 15 mol% of **IL 8** as catalyst.

good catalytic conversion for the dehydration of fructose to HMF during 4–5 h reaction in ethyl acetate. **IL 5** also showed 100% conversion of fructose to HMF for 4 h reaction in acetonitrile. We observed almost comparable catalytic activities of the **IL 5** and **IL 8** in acetonitrile containing HSO₄[−] and CF₃COO[−] anions respectively.

Out of the two series of DILs, the most acidic **IL 8** worked as the best catalytic activity in CH₃CN at

Table 3. Effect of different solvents on the catalytic activity of **IL 1–4** under reflux temperature.

Solvent	Time (h)	% Conversion ^a			
		IL 1	IL 2	IL 3	IL 4
EtOAc	3	4.6	76.5	45.6	17.9
	4	5.9	84.3	51.2	20.4
	6	—	100	—	—
	12	35.6	—	100	34.9
THF	3	10.1	3.9	3.5	22.2
	4	23.2	7.3	3.9	34.7
	12	64.2	58.4	56.2	67.6
CH ₃ CN	3	46.2	15.1	16.8	30.5
	4	56.3	20.5	27.2	47.7
	12	100	63.7	33	100

^aCalculated from HPLC analysis.**Table 4.** Effect of different solvents on the catalytic activity of **IL 5–8** under reflux temperature.

Solvent	Time (h)	% Conversion ^a			
		IL 5	IL 6	IL 7	IL 8
EtOAc	3	6.2	86.4	78.9	65.3
	4	12.2	100	—	85.8
	5	—	—	100	100
	12	56.2	—	—	—
THF	3	47.2	43.2	2.5	47.6
	4	56.7	49.8	14.7	47.6
	12	80.4	78.2	61.3	2.7
CH ₃ CN	3	87.3	25.4	75.6	100
	4	100	36	96.5	—
	12	—	100	—	—

^aCalculated from HPLC analysis.

its reflux temperature. The percentage conversion of fructose obtained using different acidic strength ILs in these three solvents are not in accordance with the acidity order obtained from the Hammett plot. They are found to be slightly different, depending on the nature of solvents. However, in some cases 100% fructose conversion was achieved according to the same acidity order of the Hammett plot as presented in both the tables. At present, we didn't find any concrete reason for this variation. The ion-pair strength of IL and its interaction with the substrate fructose molecule in a particular solvent may be the key factor for catalytic activity of these ILs.

3.5c Effect of anions on the extraction of HMF from the reaction mixture: To know the effect of anions on percentage yield of HMF, **IL 5–8** was employed as catalysts. It is evident from the Figure 6 that the nature

Figure 6. Effect of the nature of anions on the extraction of HMF. **Figure 7.** Reusability profile of **IL 5**.

of anions indeed plays a part in the efficient extraction of HMF from the reaction mixture. The results suggest that anions with stronger hydrogen bond accepting ability have a stronger interaction with HMF and hence the separation of HMF became increasingly difficult. From this study, the formation abilities of hydrogen bonds of the anions with the –OH group of HMF were found to decrease in the order: CH₃COO⁻ > HSO₄⁻ > CCl₃COO⁻ > CF₃COO⁻.

3.5d Recycling of catalyst IL 5: To study the reusability of **IL 5**, HMF was extracted from the reaction mixture using water-EtOAc as the extraction phase. Figure 7 illustrates the reusability study of **IL 5**. After the first cycle of reaction in EtOAc was over, 10 mL of distilled water was added. Subsequently, HMF was separated from the reaction mixture by continuous extraction with small aliquots of EtOAc. The amount of extracted product was determined by HPLC. It demonstrated that 65–73% product extraction was possible with EtOAc. After extraction, the catalyst was dried in a vacuum oven to remove the water and residual EtOAc. The dried

IL could be reused for three more cycles with good reproducibility.

The decreasing catalytic activity of the IL with increasing cycle numbers may be attributed to the blocking of the catalytic sites by the residual HMF in the previous cycle. This inefficient extraction of the resulting product in the previous run strongly influences the results of the recycling test. Hence, efficient extraction of HMF from the reaction mixture will remain the topic of future studies.

4. Conclusions

In summary, two new series of PEG-6000 bridged geminal diphenyl ammonium/imidazolium-based DILs were developed as an acidic catalyst through variation of four anions CF_3COO^- , CCl_3COO^- , AcO^- and HSO_4^- for selective dehydration of fructose into HMF in a polar aprotic solvent. Their structures were established by ^1H NMR, ^{13}C NMR and FT-IR spectra. The Brönsted acidic strength of the ILs seemed to play a significant role in the outcome of the reaction. Though the ILs were strongly acidic in nature, they did not affect the selectivity of HMF in the reaction. Single peak indicating the presence of only HMF was evident from the HPLC analysis. The dosage of the catalyst also had an impact on the outcome of the reaction. The efficient extraction of HMF was strongly influenced by the nature of the anion used in the ILs. The anions with stronger hydrogen bonding formation ability had a negative impact on the extraction process. This factor also affected the recyclability test by blocking the active catalytic sites for further reaction.

Supplementary Information (SI)

The supporting information includes data and spectra (^1H NMR, ^{13}C NMR and IR) of eight ionic liquids **IL 1-8**, assignment of IR stretching frequencies (Table S1 and Table S2), solvent miscibility table of ionic liquids (Table S3) and the calibration graph of HMF concentration (Figure S2). Supplementary Information is available at www.ias.ac.in/chemsci.

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