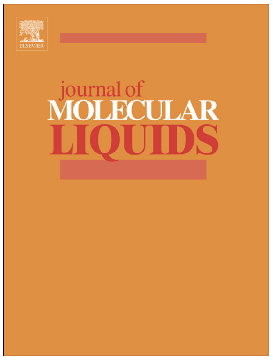

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How do isomeric ortho, meta and para dicationic ionic liquids give impact to the production of 5-hydroxymethylfurfural?

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Abstract

This research involves the investigation on how the dicationic ionic liquids (ILs) that differ in ortho, meta and para position influence the catalytic activity of production of 5-hydroxymethylfurfural (HMF). The development of this research was started with synthesizing new dicationic ILs with simple procedure then followed by characterization and measuring the acidity properties by using Hammet method. Throughout the screening process, the results exposed that substituent on three different position (ortho, meta and para) in cationic site give a remarkably effect on the overall catalytic performance. Highly efficient and selective dehydration of D-fructose to HMF was obtained by Br$_{ø}$nsted IL at ortho position with fructose conversion of 95.7% and yielding 90.5% of HMF in 60 min at 100 °C. From the results, it revealed that the geometry shape behaviour of the isomer ILs influenced the yield of HMF. The effects of reaction time, temperature, catalyst concentration and reusability of the dicationic ILs are also studied in this work.

Keywords: dicationic ionic liquids, ortho-meta-para position, fructose, 5-hydroxymethylfurfural

1. Introduction

It is something noteworthy to find a way to make fuels and chemicals from renewable sources that is promising alternatives for future energy supply. Recently, biomass-derived

HMF has become one of the prominent subjects as important platform to meet the needs of chemicals with important applications such as solvent or fuel and monomers for plastics[1]. In general, high conversion and yield of sugar to HMF can be manipulated in the aspects of catalyst, solvent, substrate, reaction time and also temperature. Thus, the used of green solvent (ILs) is the best candidate in development of environmentally route and related technologies for producing chemicals and fuel from non-fossil carbon sources [2].

Ionic liquids (ILs) have gained overwhelming interest as they offer some unique properties such as excellent thermal stability, negligible volatility and flammability[3] and can be recycled after accomplishing a task specific reaction[4-6]. ILs have great potential applications in wide area including, carbon capture [7, 8], nuclear fuel reprocessing[9], biomass processing[10], as catalysts in catalytic reaction [11-13], pharmaceutical [14] waste recycling [15-17], and batteries[18-21] due to the large number of possible combinations of cations and anions that give dramatic impact towards the properties.

To date, various modifications have been made to ILs according to the needs and desire application. Dicationic ILs has been reported to be more effective and more versatile in various types of reaction than conventional monocationic ILs [22]. The effectiveness of dicationic ILs can be highlighted when they contribute in higher intra and intermolecular interactions, that give significant impact towards the results of application area[23, 24]. Studied by Chinnappan *et al.*[25] have reported that dicationic ILs showed an excellent catalytic activity especially from the point where they provide a great extensive hydrogen bonding which in turns promote enormous dissolution of the substrate in the reaction. Therefore, in the context of employment ILs as a catalyst, we believe that dicationic ILs can serve a great medium for reaction to happen while tuning anion part to be acidic.

Our research is mainly devoted to design and synthesis simple dicationic ILs which differ in their position and their catalytic ability for dehydration of fructose to 5-hydroxymethylfurfural (HMF).Three important points that has been emphasized by Stahlberg *et al.*[26] that make a great impact in this study are, pertaining on the physicochemical properties of ILs, influence of both the cation and anion of the ILs on the reaction outcome, and examination of the mechanism and the interaction ILs with fructose. Studied by Kotadia and Soni[27] demonstrated that symmetrical and asymmetrical ionic liquids do have great impact in their physicochemical characters that eventually give promising results in catalytic application. Other than that, Jadhav *et al.*[28], illustrated that their longer chain dicationic ILs showed higher catalytic activity compared with the shorter ones. Therefore, it is our interest to expend and explore the geometry shape behaviour when the isomer ILs exists in ortho, meta and para position in terms of catalytic performance and a positive role in development of effective process for the dehydration.

2. Experimental

2.1. Materials

2,5-dichloro-para-xylene, α,α-dichloro-para-xylene, α,α-dichloro-ortho-xylene, α,α-dichloro-meta-xylene, benzyl-imidazole, acetonitrile, fructose, concentrated H_2SO_4, ethyl acetate, ethyl ether, 5-hydroxymethylfurfural were purchase from Sigma Aldrich and were used without further purification unless otherwise stated.

2.2. Instrumentation

^{1}H-NMR and ^{13}C-NMR were recorded by JEOL 399.0 MHz using CD_3OD and DMSO-D_6 as solvent. FT-IR spectra were recorded with Perkin Elmer with a universal ATR accessory .The Elemental analyses (CHN) were performed on a Pelkin-Elmer 2400 Series II Elemental Analyser. UV-vis spectra were recorded on UV-160A spectrophotometer (Shimadzu Corporation, Japan) in water.

2.3. Analysis

The amount of HMF in dehydration reaction was calculated using an external standard at 25 °C using an HPLC apparatus equipped with C18 reverse column (250 mm x 4.6 mm, particle size 5 μm) hypersil gold, Thermo Science USA, SPD-M20A diode array detector, SIL -20AHT auto sampler and CTO-10ASVP column oven. The mobile phase was a mixture of methanol and water (40:60 v/v). The flow rate was set at 1.0 mL min^{-1}, and detection wavelength was at 283 nm. The amount of fructose was calculated using external standard analysed using Waters HPLC system with ELS detector. Separation was achieved on Phenomenex Luna 5u NH_2 100A column (250 mm x 4.60 mm, 5 micron). The mobile phase consisted of acetonitrile : water (80:20 v/v) was degassed by ultrasonic bath before used. The flow rate was 1.0 mL min^{-1} and aliquot 20 μL of sample solution was injected into the HPLC-ELSD system. All samples were filtered through 0.45 μm Milipore membrane before use. The fructose conversion, product yield and selectivity are calculated based on previous reported works[25].

2.4. Synthesis of New Dicationic Ionic Liquids

Dicationic ionic liquids were prepared by using the following methods. The A-orthoCl, B-paraCl, and C-metaCl were obtained by reacting (2.801 g, 0.016 mol) of dichloro-o-xylene or dichloro-p-xylene or dichloro-m-xylene with (5.206 g, 0.033 mol) of benzyl imidazolium in 10 mL acetonitrile at 80 °C and stirred for 18 hours respectively. Each of the resulted products was then washed repeatedly with ethyl acetate to remove any non-ionic residues, and vacuum dried at 80 °C.

The obtained chloride based ILs was used as intermediates to synthesize A-orthoHSO_4, B-paraHSO_4, and C-metaHSO_4 by metathesis reaction. 2.4574 g, 0.005 mol of A-orthoCl, B-paraCl and C-metaCl respectively was mixed with 10 ml of acetonitrile and stirred at 0 °C for 1 hour. The stoichiometric amount of concentrated sulphuric acid (97%, 0.5330 mL) was added dropwise and the mixture was stirred for another 1 H at 0 °C before been stirred for 18 H at room temperature. The resulted Brønsted ionic liquid was washed repeatedly with diethyl-ether (2x5 mL) to remove non-ionic residues. The ILs was dried in vacuum for about 6 hours before being used.

2.4.1. 3, 3'-(1,2-phenylenebis(methylene))bis(1-benzyl-1H-imidazol-3-ium) dichloride

A-orthoCl : ^{1}H-NMR (400MHz, CD_3OD) δ (ppm) = 9.38(s, 1H, NCHN), 7.59,7.51(s, 2H, NCHCHN), 7.43-7.53 (m, 7H, aromatic) ,5.74(s, 2H, HCH), 5.48(s, 2H), ^{13}C-NMR(400MHz, CD_3OD) 136.46,133.96,132.29, 130.37, 129.24, 128.77, 122.91, 122.69, 53.00 ; FT-IR(500-4000cm^{-1}) : 3352, 3055, 1829, 1650,1557,1453, 1357, 1153, 733.21

Anal. calcd.(%) for $C_{28}H_{28}C_{l2}N_4$: C, 68.430 ; H, 5.740 ; N, 11.400 Found: C, 67.337 ; H, 5.867 ; N, 11.698

2.4.2. 3, 3'-(1,4-phenylenebis(methylene))bis(1-benzyl-1H-imidazol-3-ium) dichloride

B-paraCl:^{1}H-NMR (400MHz, CD_3OD) δ(ppm) = 8.49(s, 1H, NCHN) , 6.86(s, 2H, NCHCHN) , 4.67 (s, 2H, HCH), 4.64 (s, 2H, HCH), ^{13}C-NMR (400MHz, CD_3OD) 137.30, 136.13, 134.94, 130.41, 130.16, 129.44, 123.85, 53.96, 53.33; FT-IR (500-4000cm^{-1}) : 3383.77, 3016.46, 1821.02, 1649.85, 1556.20, 1446.19,1352.36, 1150.27, 727.05, 705.99

Anal. calcd.(%) for $C_{28}H_{28}C_{l2}N_4$: C, 68.430 ; H, 5.740 ; N, 11.400 Found: C, 69.630 ; H, 5.918 ; N, 12.012

2.4.3. 3, 3'-(1,3-phenylenebis(methylene))bis(1-benzyl-1H-imidazol-3-ium) dichloride

C-metaCl : ^{1}H-NMR (400MHz, CD_3OD) δ (ppm) =9.38(s, 1H, NCHN), 7.51,7.62 (s, 2H,NCHCHN), 7.15, 7.37 (m, 7H, aromatic), 5.21 (s, 2H, HCH), ^{13}C-NMR (400MHz, CD_3OD) 139.12, 135.19, 133.98, 133.98, 133.10, 130.10, 129.31, 129.98, 129.31, 128.56, 122.79, 52.80, 52.29; FT-IR(500-4000cm^{-1}) 3378.62, 3060.10, 1878.90, 1661, 1557.39, 1453.60, 1355.05, 1148.47, 753.00,731.33

Anal. calcd.(%) for $C_{28}H_{28}C_{l2}N_4$: C, 68.430 ; H, 5.740 ; N, 11.400 Found: C, 67.862 ; H, 6.267 ; N, 12.698

2.4.4. 3,3'-(1,2-phenylenebis(methylene))bis(1-benzyl-1H-imidazol-3-ium) hydrogen sulfate

A-orthoHSO$_4$: ^{1}H-NMR (400MHz, CD_3OD) δ (ppm) = 10.39(s, 1H, NCHN) , 8.53,8.56(m, 7H,aromatic), 6.82(s, 2H, HCH) , 6.59 (s,2H, HCH) ^{13}C-NMR (400MHz, CD_3OD) 137.74, 135.15, 133.51, 131.47, 130.31, 129.87, 124.05, 123.79, 54.11, 51.01 ; FT-IR(500-4000cm^{-1}) 3134.75, 3066.62, 1559.09, 1497.43, 1451.96, 1228.97, 1149.76, 1000.88, 851.97, 746.54, 711.53, 567.25

Anal. calcd.(%) for $C_{28}H_{30}N_4O_8S_2$: C, 54.710 ; H, 4.920 ; N, 9.110 Found: C, 55.062 ; H, 2.267 ; N, 10.198

2.4.5. 3,3'-(1,4-phenylenebis(methylene))bis(1-benzyl-1H-imidazol-3-ium) hydrogen sulfate

B-paraHSO_4: ^{1}H-NMR (400MHz, CD_3OD) δ (ppm) = 9.55(s,1H, NCHN), 7.81 (s, 2H, NCHCHN), 7.18- 7.46 (m, 7H, aromatic), 5.40 (s,1H, HCH), 5.41 (s, 1H,HCH) ^{13}C-NMR (400MHz, CD_3OD) 145.67, 144.65, 144.07, 138.28, 137.71, 132.18, 132.14,61.27, 60.79; FT-IR (500-4000cm^{-1}) 3139.78, 3056.40, 1555.42, , 1233.95, 1168.81, 1142.62, 1025.58, 841.84, 726.67, 710.27, 581.00

Anal. calcd.(%) for $C_{28}H_{30}N_4O_8S_2$: C, 54.710 ; H, 4.920 ; N, 9.110 Found: C, 53.962 ; H, 5.160 ; N, 10.971

2.4.6. 3,3'-(1,3-phenylenebis(methylene))bis(1-benzyl-1H-imidazol-3-ium) hydrogen sulfate

C-metaHSO_4 : ^{1}H-NMR (400MHz, CD_3OD) δ (ppm) = 10.56 (s, 1H, NCHN), 8.54-8.65 (m, 7H, aromatic) , 6.66 (s, 1H, HCH), 6.62 (s, 1H, HCH) ^{13}C-NMR (400MHz, CD_3OD) 137.25,136.36,135.16,131.13,130.43, 130.43, 130.16, 130.13, 129.71, 123.88, 123.75, 123.05, 121.21, 53.87,53.37; FT-IR(500-4000cm^{-1}) 3136.88, 3066.62, 1559.09, 1497.43, 1451.96, 1206.89, 1145.87, 1029.13, 850.47, 824.81, 730.41, 709.01, 570.93

Anal. calcd.(%) for $C_{28}H_{30}N_4O_8S_2$: C, 54.710 ; H, 4.920 ; N, 9.110 Found: C, 55.902 ; H, 5.407 ; N, 10.008

2.5. Dehydration reaction for fructose

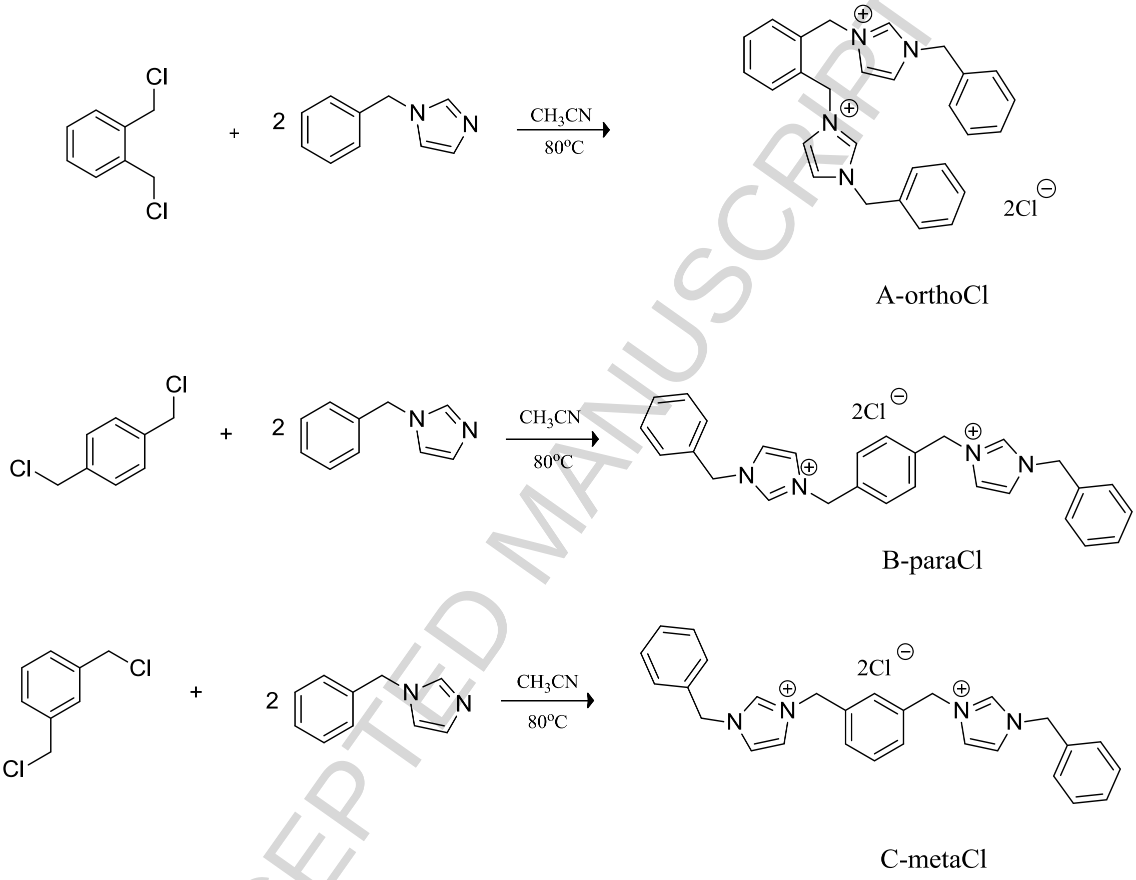
In a typical reaction, a 50 mL round bottle flask was charged with fructose 1.0 g and a given amount of catalyst was added into 10 mL DMSO and heated up. After reaction complete, the sample was diluted with ultrapure water (18.6 mΩcm^{-1}) before analysis by HPLC equipped with UV and ELS detector.

2.6. Separation procedure for HMF

After the dehydration process, the reaction mixture was transferred into a flask. 30 mL of water was added to the mixture. The organic layer was extracted with ethyl-acetate (20 mL x 5) and distilled under reduced pressure.

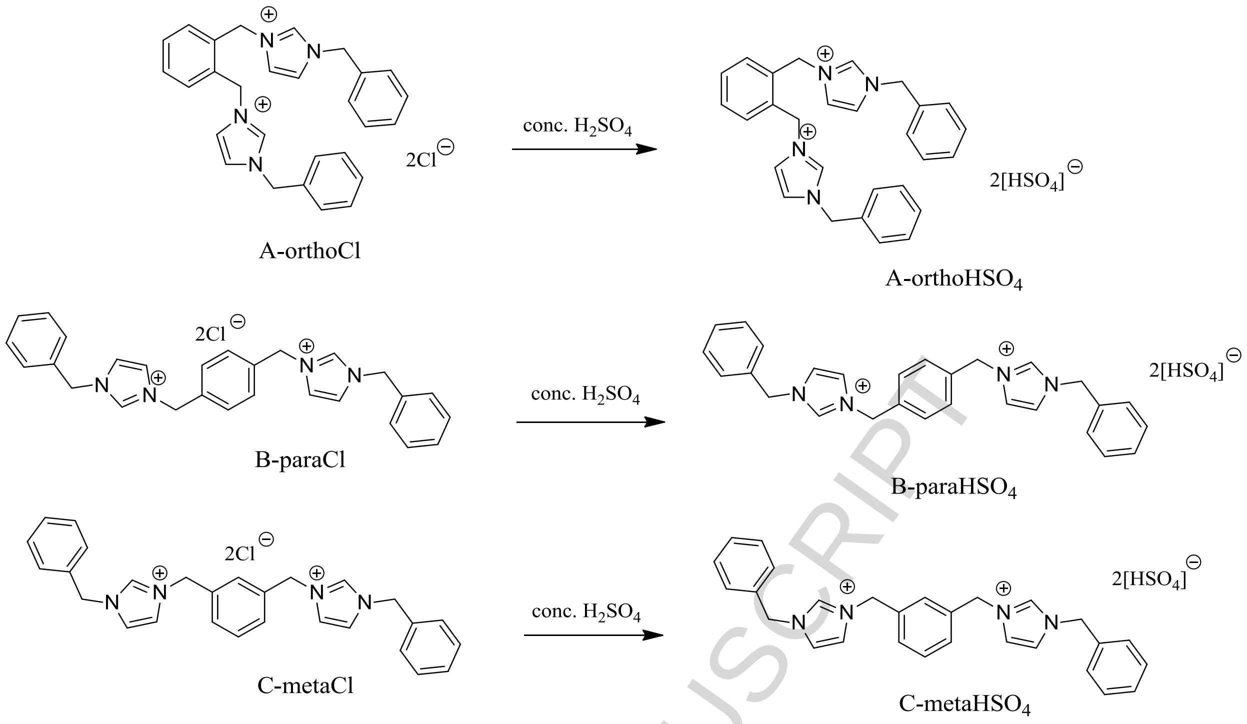
3. Results and Discussion

Scheme 1 illustrates that the synthetic route for ILs, **A-orthoCl, B-paraCl, C-metaCl** by using benzyl-imidazole and dichloro-xylene. The choice of the counter ion made this method convenient for preparation of imidazolium based ILs in good yield. In this experiment, different position of dichloro-xylene (ortho, meta and para) were used to develop new isomeric dicationic ionic liquids.



Scheme 1. Synthesis of dicationic ionic liquids

Further, **Scheme 2** shows the synthesis route of the anion was exchange by using metathesis reaction to produce **A-orthoHSO_4, B-paraHSO_4** and **C-metaHSO_4**. HSO_4 anion was reported to give the best catalytic activity [29] and therefore was chosen to promote the acidic properties to these ILs.



Scheme 2. Metathesis reaction

The acid properties were measured by using Hammet acidity function (H_o). The value of H_o was calculated based on intrinsic pK_a of the indicator (4-nitroaniline) in water and the molar ratio of protonated and unprotonated dye [I]/[IH$^+$] using following equation, which similar to the method used in the previous work [29]

$$Ho = pK(I)a + \log([I]/[IH^+]) \qquad (1)$$

The noticeable change in the absorption of curve of p-nitroaniline in the wavelength region of 350 to 400 nm are presented in **Figure 1** upon the addition of ILs where obviously the ILs with strong acidic anion, HSO$_4^-$ protonate the p-aniline more and give lower value of Ho. Overall, the corresponding Ho values order from highest to the lowest were in the order of**B-paraCl> C-metaCl> A-orthoCl> B-paraHSO$_4$> C-metaHSO$_4$> A-metaHSO$_4$.** Result in **Table 1** indicates that the acidity of A-orthoHSO$_4$ was the strongest among these ILs. The result reveals that the position of dichloro-xylene (ortho, meta and para) influence the acid properties of ILs.

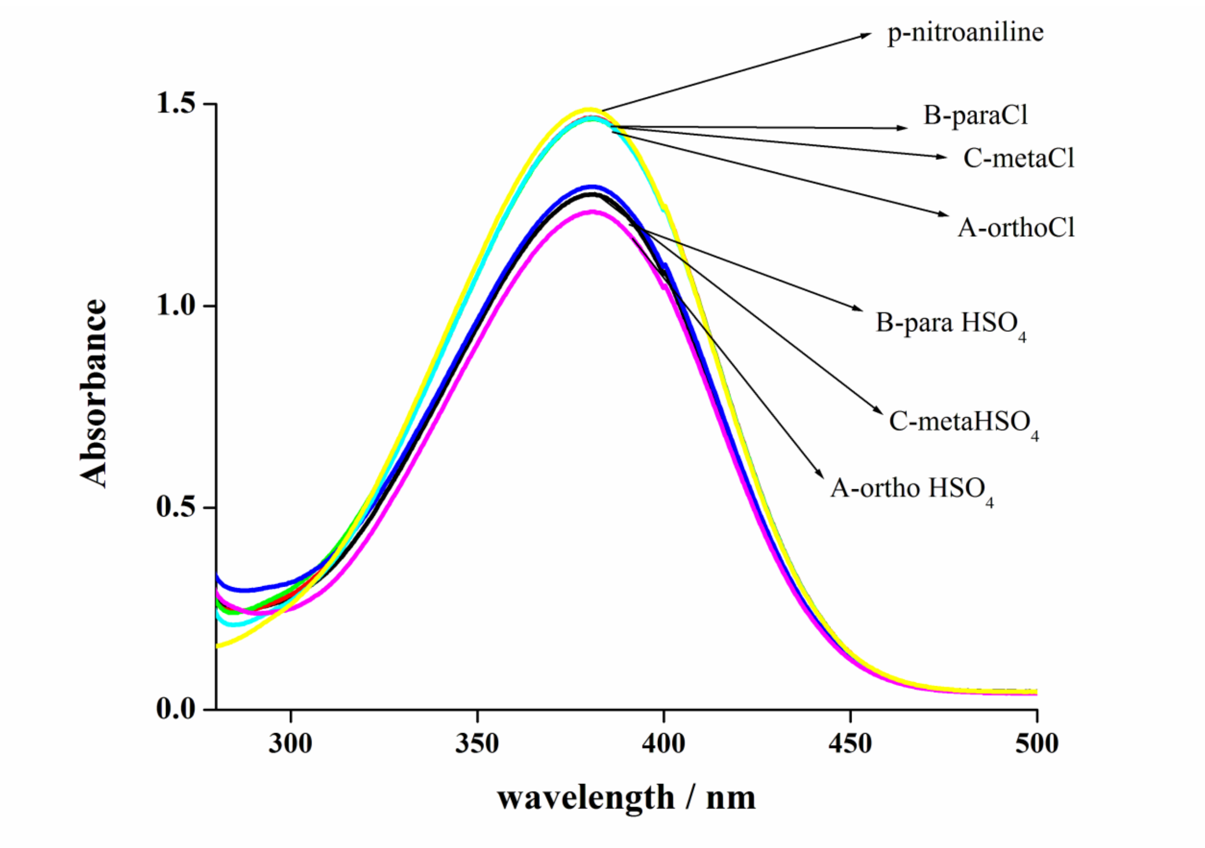


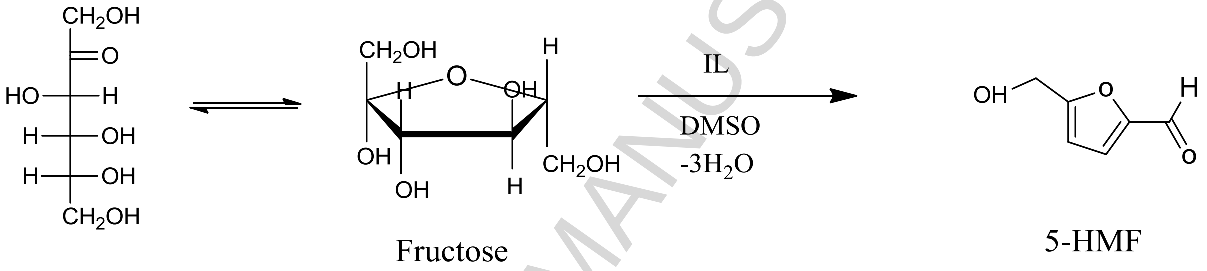
Fig.1. Absorbance of six ILs in protonated p-nitroaniline

Table 1. H_o value of six ILs. Reaction carried out at 25°C.

Ionic liquids	Absorbance	[I] [%]	[HI] [%]	H_o
p-nitroaniline	1.486	100	0	-
A-orthoCl	1.462	98.45	1.54	2.77
B-paraCl	1.466	98.38	1.61	2.85
C-metaCl	1.464	98.65	1.34	2.79
A-orthoHSO$_4$	1.232	82.91	17.08	1.67
B-paraHSO$_4$	1.295	87.08	12.91	1.81
C-metaHSO$_4$	1.276	85.81	14.18	1.77

3.1. Dehydration of fructose in dicationic ILs

To study the catalytic activity of the synthesized ILs, we have carried out the dehydration of fructose in DMSO at 100 °C for 60 minutes by using 0.20 g of ILs as illustrated on **scheme 3**.The ILs were dried under vacuum for two hours to reduce the effect of moisture in the reaction prior to the experiment. During the reaction, the colour of the reaction mixture was initially pale yellow however, when the reaction was continued at higher temperature and longer reaction time the colour was gradually changed to deep brown. This observation indicates that formation of side product such as humins other than HMF [27, 30]



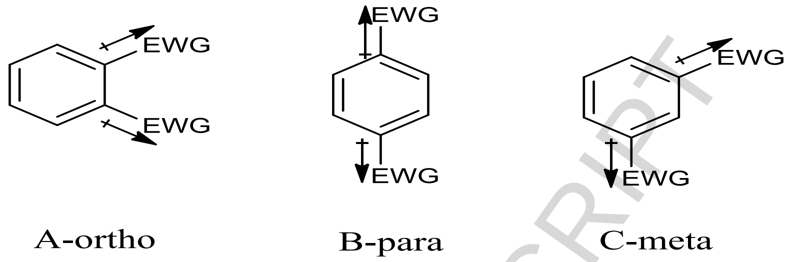
Scheme 3. Reaction process for dehydration of fructose

The analysis of fructose conversion and HMF yield by all six ILs were conducted using HPLC. The result from figure 4 showed that, A-orthoCl produced 82.8% fructose conversion and yielding 49.3% of HMF. On the other hand, the conversion percentage is slightly lower for C-metaCl which was 79.5% and the HMF yield was 47.0%. The B-paraCl achieved only 77.1% conversion and 34.3% HMF yield at a uniform reaction condition.

Similar trend was observed when ILs with HSO_4^- anion was used. The IL with ortho position led the reaction with 95.7% fructose conversion and 90.6% of HMF yield. In the presence of C-metaHSO_4 and B-paraHSO_4, fructose converted were 95.3% and 93.0% with 89.1% and 62.0% of HMF yield, respectively.

The percentage of selectivity was calculated based on the percentage of conversion and yield. It was found that, A-orthoHSO_4 showed the highest selectivity which was 95.0% while C-metaHSO_4 and B-paraHSO_4 recorded 93.0% and 66.7% respectively. While Cl^- based ILs gave much lower selectivity in which only 44.4% for B-paraCl, 59.0% for C-metaCl and 60.0% for A-orthoCl.

The catalytic performance of the ILs can be rationalized due to the different in dipole moment and polarity. **Scheme 4** illustrates the net resultant dipole moment (μ)



Scheme 4. Different dipole moment in ortho, meta and para.
EWG: Electro withdrawing group.

and can be explained by:

$$\mu_{ortho} = \sqrt{\mu^2{}_1 + \mu^2{}_2 + 2\mu_1\mu_2 cos60^\circ} = \sqrt{\mu^2{}_1 + \mu^2{}_2 + \mu_1\mu_2} \quad (2)$$

$$\mu_{meta} = \sqrt{\mu^2{}_1 + \mu^2{}_2 + 2\mu_1\mu_2 cos120^\circ} = \sqrt{\mu^2{}_1 + \mu^2{}_2 - \mu_1\mu_2} \quad (3)$$

$$\mu_{para} = \sqrt{\mu^2{}_1 + \mu^2{}_2 + 2\mu_1\mu_2 cos180^\circ} = \sqrt{\mu^2{}_1 + \mu^2{}_2 - 2\mu_1\mu_2} \quad (4)$$

From the above expression, when both substituents are electro withdrawing group, para position has the least dipole moment and ortho product has the highest. In general the trend of dipole moment is **ortho>meta>para** [31, 32]. Therefore, the polarity in cationic site absolutely gives a significant impact as it will reflect in the acidity of C2 proton (**Figure 2**) of imidazolium. In fact, in these dicationic ILs the delocalization system is more effective because of the support from three benzene ring that give rise in polarity of C2 proton which in turns led to alleviate the acidity strength [27, 33]. As a result, acidity behaviour of cationic will facilitate and contribute in solvation mechanism of dehydration process [25, 34]. In this scenario, the ortho position produced high conversion fructose and HMF yield compared to meta and para positions.

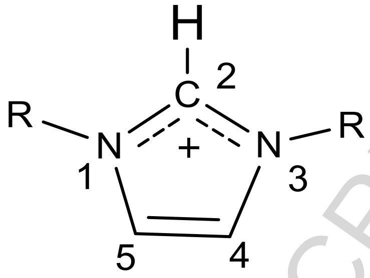


Fig. 2. The numbering of ring atoms in imidazolium.

Therefore A-orthoHSO_4 was chosen for further optimization of reaction residence time, temperature, catalyst loading and recyclability.

3.2. Reaction mechanism consideration

Figure 3 below shows a time-progression stacked of H-NMR spectra of fructose dehydration. This experiment was carried out to further investigate the selectivity of A-orthoHSO_4 for HMF formation.

Sudipta *et al.*[35] has suggested that the formation of HMF was initiated via a cyclic mechanism. The proton that generated during hydrolysis assisted the reaction and followed by nucleophile attack to get final product. On the other hand, according to mechanism proposed by Deepali *et al.* [27], the conversion of fructose to HMF was activated by their cationic that act as electrophile. Then the elimination of three water molecules was driven by anion and also facilitate by C2 imidazolium cation via hydrogen bonding. According to **Figure 3**, as the reaction time is increased from 5 min to 60 min at 100°C, the peaks characteristic of HMF (4.45 (s), 6.55 (d), 7.45 (d), and 9.51(s) ppm) gradually increase while fructose peaks (between 3.0 to 4.6 ppm) started to disappear. The transformation of fructose to HMF was assisted by DMSO which works more than just a medium but also as an electrophile [36]. The ^{1}H-NMR recorded after 60 min of reaction showed only HMF and H_2O (3.6 ppm) signals indicate that the fructose dehydration reaction in DMSO with A-orthoHSO_4 is selective for HMF formation.

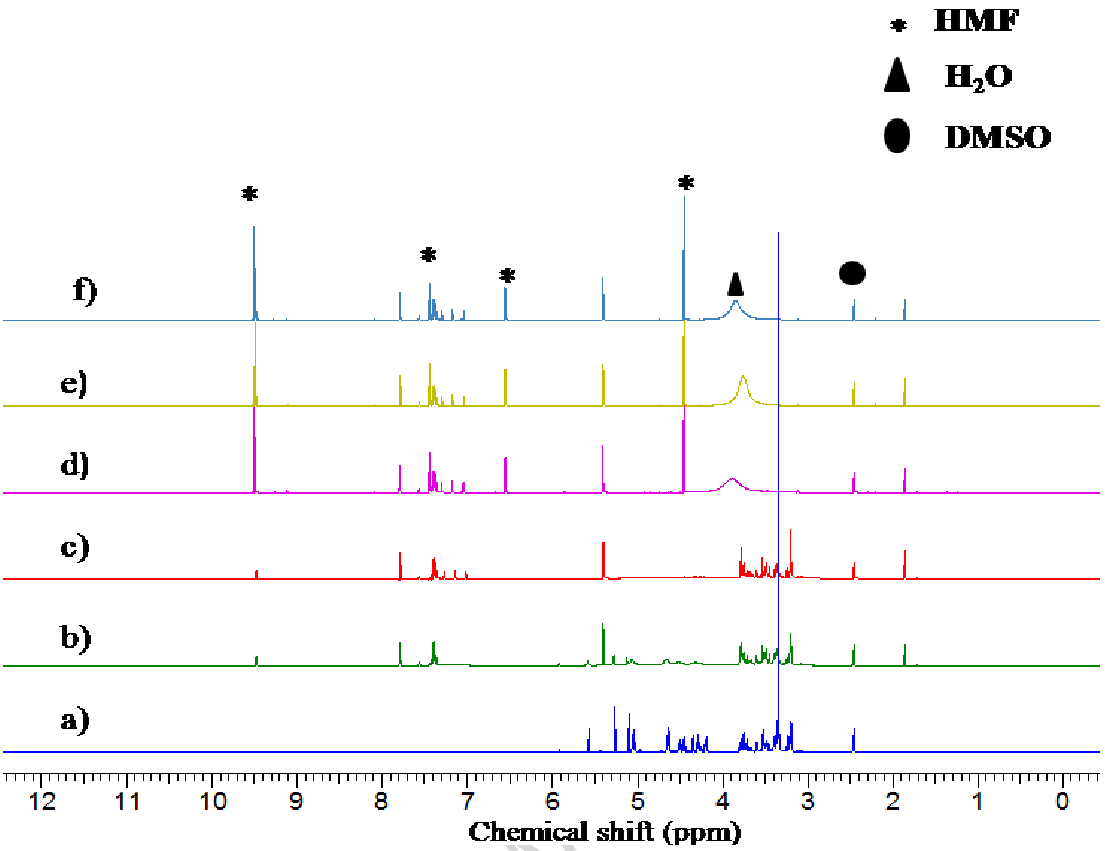


Fig. 3. ^{1}H-NMR spectra of a) 25mg fructose in DMSO-d_6 b) 25mg fructose in DMSO-d_6 in the presence of 17.5 mg of A-orthoHSO_4 (2:1 ratio) at 0 min b) reaction at 5 min c) reaction at 20 min, e) reaction at 40 min f) reaction at 60 min.

Figure 4 shows that the dehydration of fructose in DMSO without catalyst able to get fructose conversion about 16.6% and 1.2% of HMF yield in which supported our previous justification. Additionally, the line broadening from our ^{1}H-NMR spectra (3 to 5ppm) indicates that hydrogen bonding interaction between a –OH of fructose and the HSO_4^- give evidence that this anion was responsible to eliminate the water molecule from reaction and at same time promote fructose dissolution. The result from this study are consisted with Xinli & Yongdan [37].

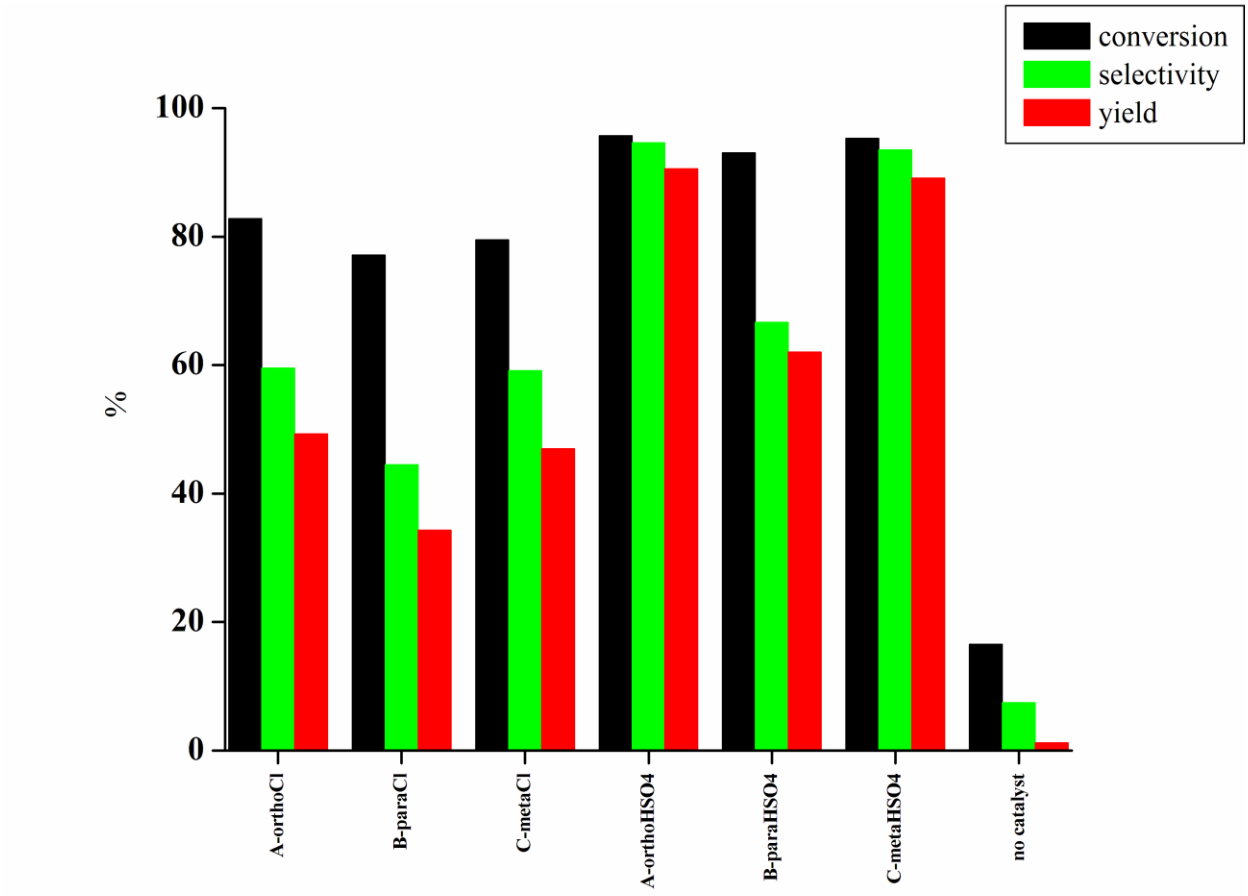


Fig. 4. Dehydration of fructose in the presence of six ILs as catalyst. Reaction condition (1.00 g fructose, 0.2 g IL, 10 mL DMSO, 100 °C, 60 min)

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3.3. Effect of reaction temperature

The dehydration reaction of fructose were studied at 40-160 °C in order to determine the efficiency of dicationic A-orthoHSO_4 as well as the effect of reaction temperature on the formation of HMF. As shown in **Figure 5** below, the reaction temperature plays important role in both fructose conversion and HMF yield. When the reaction temperature was 40 °C the conversion and yield were relatively low where only 56.4% and 32.0% respectively. The gradual increase was observed resulted 98.3% conversion and 95.1% yield at 130 °C. Meanwhile, at 160°C, the fructose conversion increase slightly higher but a decrease in the HMF yield was observed as well as the colour of the solution changed from light yellow to deep brown that indicate a formation of humins much more higher than HMF.

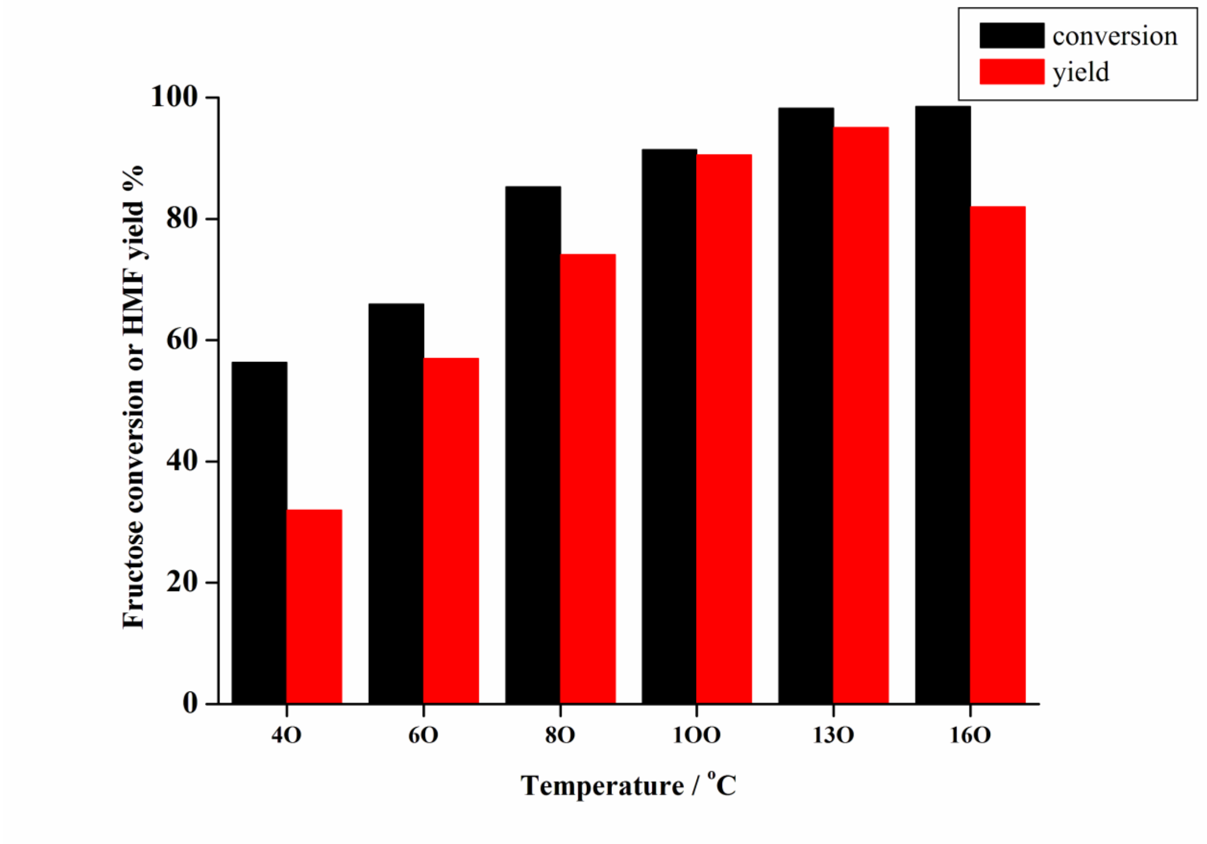

Fig. 5. Effect of temperature on HMF yield and conversion. Reaction of fructose was performed on a 1.0 0g scale (5.5 mmol) at six reaction temperatures in the presence of 0.20 g A-orthoHSO$_4$ in DMSO (10 mL), reaction time 60 min.

3.4. *Effect of reaction time*

The dehydration reaction time of fructose was varied to study the rate of HMF formation as a function of time. As plotted in **Figure 6**, the yield of HMF improved from 73.2% to 90.5% upon increasing the duration of reaction period from 30 min to 60 min at 100 °C. Further increase the reaction time to 120 min resulted in maximum HMF yield of 94.2% with 98.3% fructose conversion. Afterwards at 180 min the production of HMF started to drop up to 79.9%.

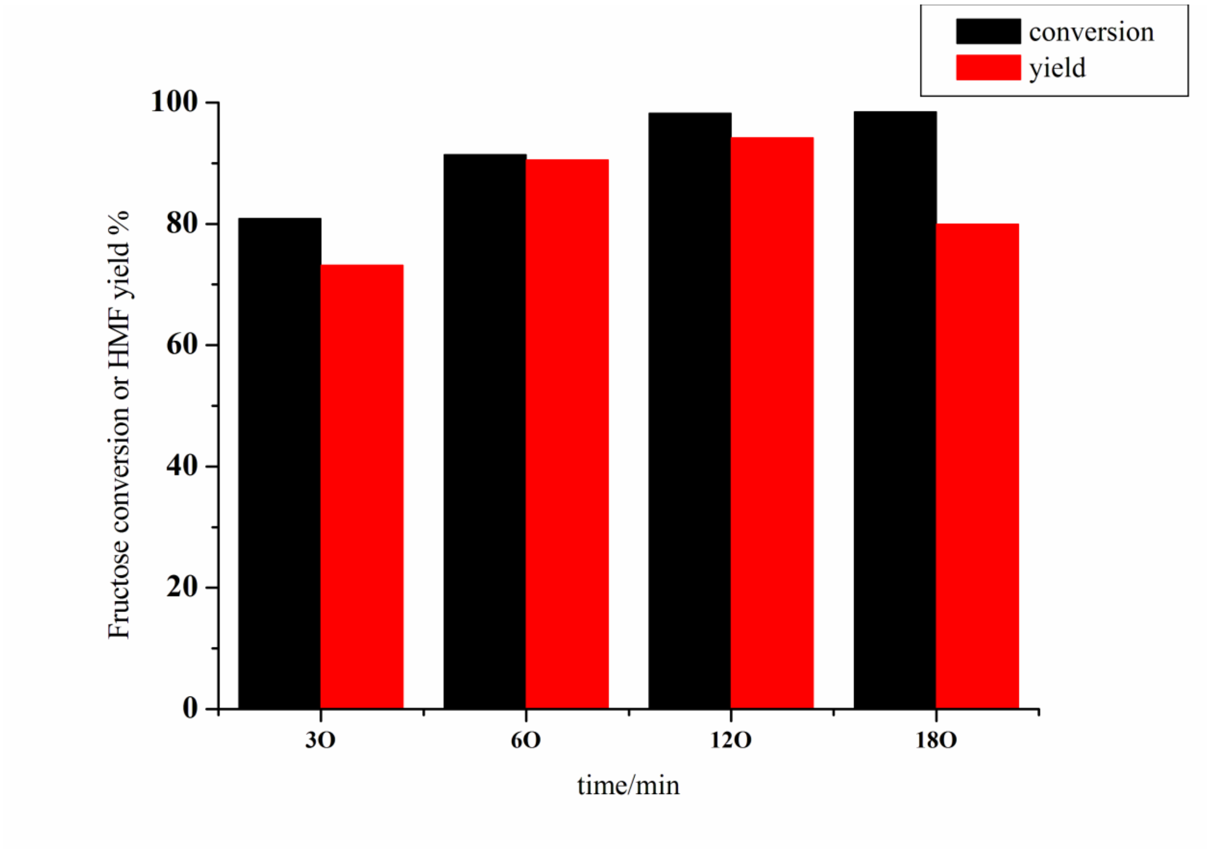

Fig. 6. Effect of temperature on HMF yield and fructose conversion. Reaction of fructose was performed on a 1.00g scale (5.5mmol) at four different reaction time in the presence of 0.20 g A-orthoHSO_4 in DMSO (10 mL), temperature at 100 °C.

3.5. Catalyst dosage

The dehydration reaction of fructose into HMF was studied at variable dosage of catalyst of A-orthoHSO_4 for optimizing the reaction condition and maximizing the HMF yield. The amount of catalyst was varied from 0.01 g to 1.00 g. As shown in **Figure 7** the yield of HMF increased from 32.9% to 90.6% with an increasing the catalyst from 0.01 g to 0.20 g. When the amount of catalyst further increase it shows that yield of HMF decrease until 24.5% with 98.7% fructose conversion.

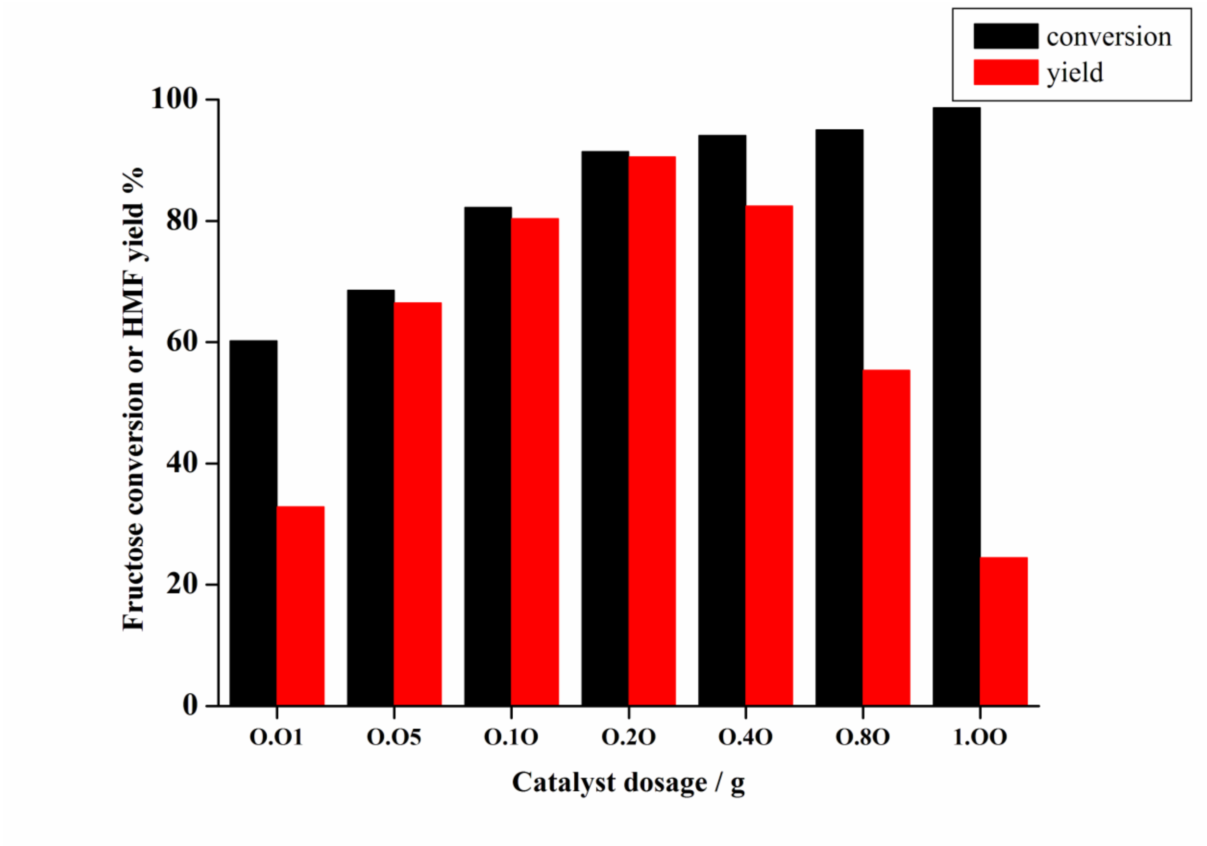

Fig. 7. Effect of catalyst loading on HMF yield and fructose conversion. Reaction of fructose was performed on a 1.00 g scale (5.5 mmol) at seven different catalyst dosages in DMSO (10 mL), reaction time 60 min and temperature at 100 °C.

3.6. The recycling of catalyst and solvent

The recycling of catalyst and the reuse of solvent were examined by at 100 °C for 60 min in the presence of 0.20 g A-orthoHSO_4. Prior to each reuse of the IL and solvent, they were extracted by using ethyl acetate where HMF sole mostly in the organic phase even though there still some will remain in aqueous [38] while IL and DMSO in aqueous medium. **Figure 8** shows that the lost of activity of the catalyst in terms of HMF yield is approximately around 10% in every cycle. Loss of activity of catalyst was related with loss of ILs that might occur during the extraction step.

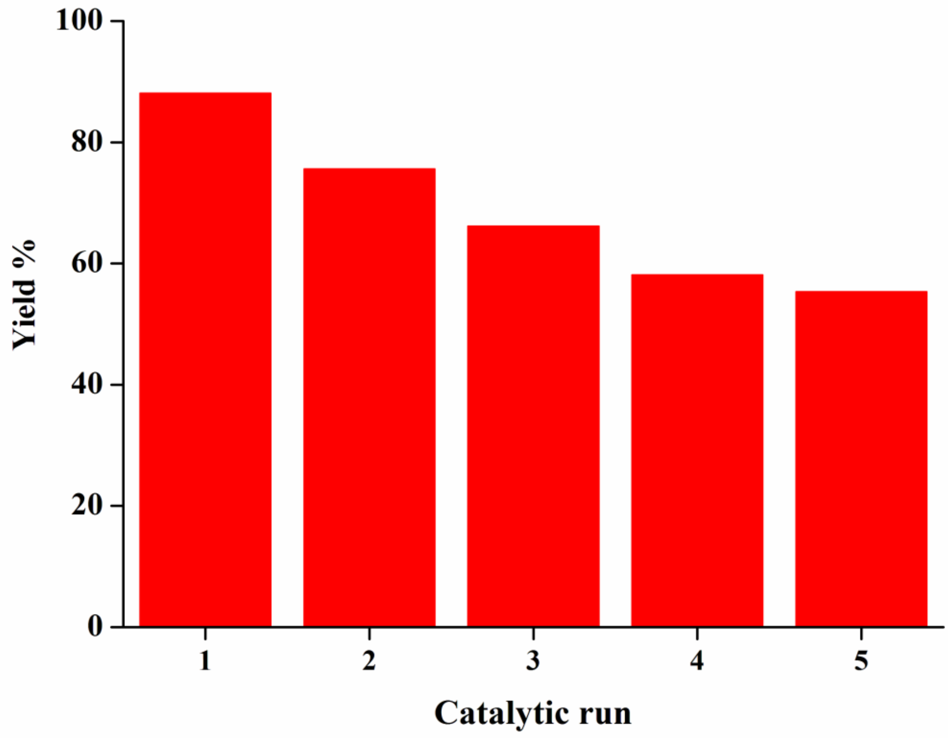

Fig. 8. Recycling of A-orthoHSO$_4$ and DMSO solvent for dehydration reaction. Reaction condition for each run: Fructose (1g, 5.5mmol), 0.20 g A-orthoHSO$_4$ (recycled), reaction time: 60 min, temperature: 100 °C.

Table 2. Comparison study of different catalyst in dehydration process.

Entry	Catalysed used	Solvent	T/ C	t/ min	HMF Yield%	reference
1	[DiEG(mim)$_2$][OMs]$_2$	-	120	40	69.8	[28]
2	[TriEG(mim)$_2$][OMs]$_2$	-	120	40	77.2	[28]
3	[TetraEG(mim)$_2$][OMs]$_2$	-	120	40	92.3	[28]
4	[C$_6$(mpy)2]$_2$Br	DMSO	110	60	91.0	[25]
5	[C$_{10}$(Epy)$_2$]$_2$Br	DMSO	110	60	83.0	[25]
6	A-ortho-HSO$_4$	DMSO	100	60	90.5	This work
7	B-para-HSO$_4$	DMSO	100	60	62.0	This work
8	C-meta-HSO$_4$	DMSO	100	60	89.1	This work
9	[NMP]$^+$[HSO$_4$]$^-$	DMSO	90	120	69.4	[37]
10	[Mim][HSO$_4$]	DMSO	90	120	23.6	[37]
11	[NMP]$^+$[CH$_3$SO$_3$]$^-$	DMSO	90	120	72.3	[37]
12	[PSMBIM]HSO$_4$	DMSO	80	60	72.8	[27]

The capability and effectiveness of our catalysts for the reaction was tabulated in **Table 2**. As shown in **Table 2**, the dehydration reaction in terms of reaction time, reaction temperature and HMF yield were remarkably improved by A-orthoHSO_4.

4. Conclusion

In summary, six new dicationic ILs A-orthoCl, B-paraCl, C-metaCl , A-orthoHSO_4, B-paraHSO_4, and C-metaHSO_4 have been effectively synthesized, characterized, and their Hammet acidity function was also have been measured. Among all, A-orthoHSO_4 shows very high acidity and catalytic activity for fructose dehydration and thus further used for optimisation of respect to different parameters such as reaction time and reaction temperature and catalyst loading on the HMF yield. From the above discussion it is clearly reveal that polarity of A-orthoHSO_4 ILs influenced the yield of HMF.

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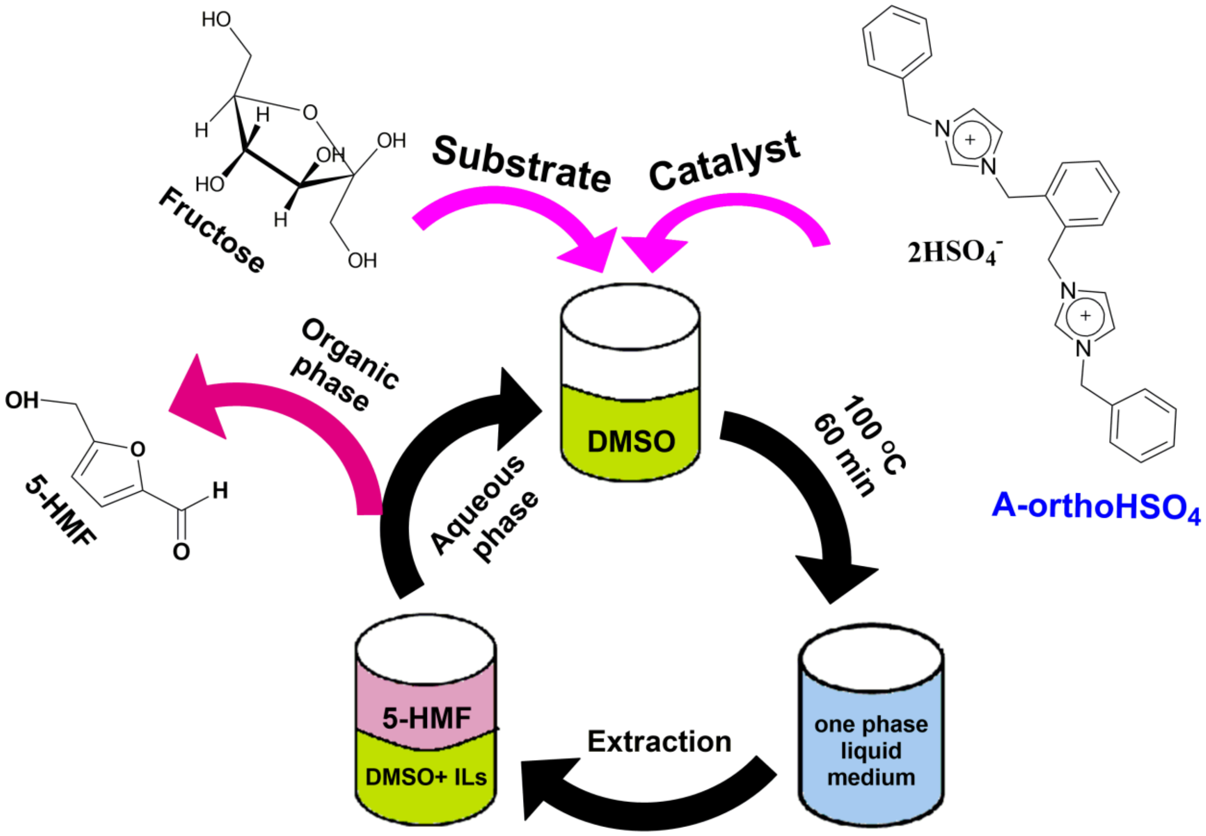

Graphical abstract

Highlight from this paper

- Six new dicationic ionic liquids were successfully synthesized and characterized
- These new ionic liquids have been used for the first time in dehydration process of fructose to 5-hydrxymethylfurfural.
- Hammet acidity function (H_o) illustrated the acidity properties of these six ILs.
- The different of polarity in ILs structure were discussed thoroughly
- Optimization parameter of reaction time, temperature and catalyst loading were investigated.