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A Review on Dicationic Ionic Liquids: Classification and Application

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Abstract

Dicationic ionic liquids are attractive new group of ionic liquids that acquire higher melting point, wider liquid range and better thermal stability. However, the exploration made on the utilization of these dicationic ionic liquids in any application is still limited. To the best of the author's knowledge, this is the first review article that discuss about this new type of ionic liquids. This review describes about ionic liquids in general and gives a survey on the latest developments and progress concerning dicationic ionic liquids, from their classifications and properties to their employment in many applications.

Keywords: Dication; Ionic liquids; Geminal; Symmetrical; Asymmetrical; Heteroanionic; Synthesis

Introduction

Ionic liquids (ILs) are one of the most rapidly growing areas of chemistry research on new materials investigated in the last decade. Conventionally, ILs are entirely made by cation and anion that has melting point lower than 100°C. Therefore, they usually appear as liquid under ambient condition. They are alternatives to hazardous and volatile materials owing to their unique physicochemical properties such as higher thermal stability, simple recovery process and negligible vapour pressure that eliminate problem associated with volatility and flammability [1,2]. In addition, they are often labeled as "designer solvent", as their properties, such as polarity, hydrophobicity, solvating activity, density, melting point, viscosity and others, can be tuned to some extent by changing the cation, anion or alkyl substituents on the cation [3-5]. Figure 1 illustrates common cations and anions used to form ILs.

ILs have been widely explored in the various inter-disciplinary research areas in the field of organic synthesis, catalysis, biocatalysis, material science, separation process, sensoristics, chemical engineering, medicine, green chemistry and electrochemistry [6-10]. The synthesis of ILs can be split into two steps [11,12]: a) Formation of desired cation: The desired cation can be synthesized either through quaternization reactions of amine with a haloalkane, by the protonation of the amine by an acid or by formation of zwitterion. b) Direct combination or Anion exchange: I. Direct combination reaction can be performed by reacting a zwitterion carrying the desired cation with an acid carrying the desired anion. II. Anion exchange reactions can be carried out by either acid-base neutralization, anion metathesis or by treatment of halide salts with Lewis acids to form Lewis acid-based ILs. In some cases, only one step is necessary to synthesize the ILs.

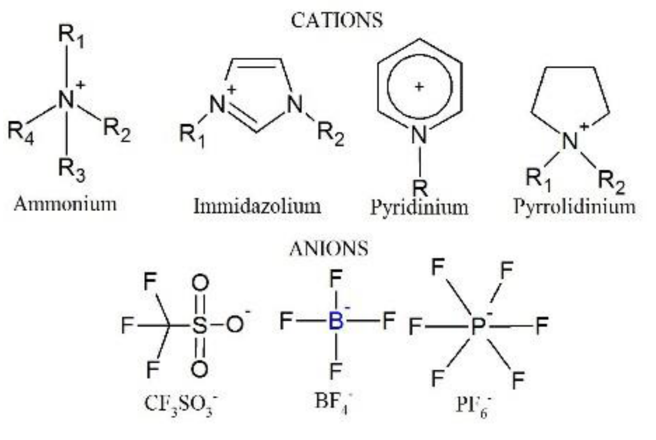

Figure 1: Common cations and anions used to form ILs.

Dicationic Ionic Liquids (DILS)

General ILs are composed of monocation and an anion. Recently, dicationic ionic liquids (DILs), a new category of ILs family, attracted great concern as it represents an interesting variation of the cationic partner. DILs can be classified as homoanionic dicationic ionic liquids and heteroanionic dicationic ionic liquids. These DILs can further be categorized as symmetrical and asymmetrical DILs for both homoanionic and heteroanionic DILs.

Homoanionic dicationic ionic liquids

Homoanionic dicationic ionic liquids are quintessential (typical) types of DILs which consist of a dication and two identical anions. The subsequent sections discuss about the symmetrical and asymmetrical homoanionic DILs.

Symmetrical (geminal) dicationic ionic liquids: Symmetrical or geminal dicationic ILs can be synthesized joining two same cation candidates such as imidazolium or pyrrolidinium, which may contain cyclic or aliphatic chain, via either a rigid or a flexible spacer. Common spacer is an alkyl chain. Then, it is followed by second step of reaction of anion exchange. Some examples of symmetrical dicationic ILs are shown in Figure 2. They represent several advantages over the traditional monocationic ILs in term of thermal stability and volatility, as well as tenability of physical and chemical properties [13]. Therefore, they have good potential to be used as lubricants, solvents for high-temperature uses, gas chromatography stationary phases, separation media and catalyst for esterification and transesterification reactions [14,15].

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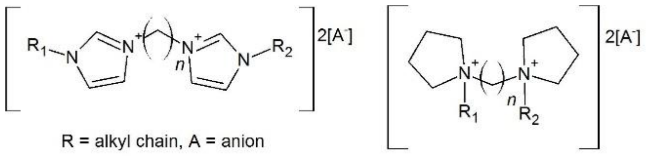


R = alkyl chain, A = anion

Figure 2: Examples of symmetrical dicationic ILs.

In 2005, Armstrong and co-workers [16] studied structure and properties relationship by synthesizing 39 imidazolium-based and pyrrolidinium-based dicationic ILs. The head groups were linked with an alkyl chain (from 3 to 12 carbons long) and hence reacted with four different traditional anions (Br, NTf_2, BF_4, and PF_6). The thermal stability of these ILs in the range of -4 to >400°C, are found to be greater than those of most traditional monocationic ILs. Besides that, a decrease in melting point was observed when longer alkyl chains were used as spacer, which might be due to an increase in the number of closely related configurational states and possibly crystalline polymorphs for these ILs. In contrast, the density of the ILs decreased with increasing alkyl chain. However, the length of the alkyl chain did not give a significant effect on surface tension of the ILs. Instead, the increase of length of the substituted alkyl group on the imidazolium rings resulted to a decrease of the surface tension of the ILs. While the solubility of these dicationic ILs in water and heptane tend to be similar to those of the monocationic ILs, except for one case in which the dication was very hydrophobic.

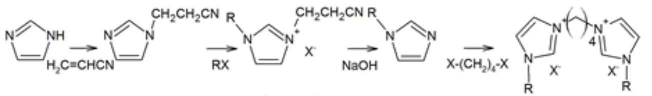
In 2007, Zhang and co-workers [17] synthesized 17 ammonium-based symmetrical dicationic ILs by reacting tetramethylethylenediamine, tetramethylpropylenediamine or tetramethylhexylenediamine with 3 equivalent mole of 1-alkylbromide by using acetone as solvent in an ice bath for 24 h. It was then followed by anion exchange with $LiNTf_2$ at room temperature for 24 h to form dication ILs containing double NTf_2 anions. The compound was precipitated as solid or phase separated as liquid, depending on the compound species. All the prepared dicationic ILs were found to be miscible in dichloromethane, in 99.7% ethanol (w/w) and in acetone. But, they were immiscible in diethyl ether and water. These dicationic ILs exhibited five different types of phase transition behaviour on heating, but they showed one stage decomposition behaviour, at a decomposition temperature range of 340-420°C. Besides that, these dicationic ILs undergo exothermic decomposition, opposed from traditional ammonium-based monocationic ILs that undergo endothermic decomposition.

In 2011, Shirota and co-workers [18] compared the properties of imidazolium-based monocationic and dicationic ILs with four anions (NTf_2, NPf_2, BF_4, and NO_3). The properties are liquid density, shear viscosity, surface tension and thermal properties such as melting point, glass transition temperature and decomposition temperature. By using the same type of anion and cation with the corresponding alkylene linker/alkyl group, the noticeable features of physical properties of the dicationic ILs compared to those of monocationic ILs are: higher density, higher glass transition temperature and melting point, higher thermal stability, larger surface tension and higher shear viscosity. In the same study, the properties of the ILs were also compared with the reference alcohols. Throughout the study, they found that the alkyl-chain-length effect on the liquids density and surface tension in the dicationic ILs were qualitatively similar to that in the alkanediols, except for the shear viscosity.

Until now, all the discussed symmetrical or geminal ILs contained short or intermediate length of substituted alkyl group on the head group in the range of 0 to 8 carbons long. The dications were simply prepared by reacting the alkyl chain (spacer candidate) with double equivalent mole of the head groups. In 2007, Ding and co-workers [19] synthesized an imidazolium-based dicationic IL containing substituted alkyl group of 14 carbons long. The synthesis process was different from the previous discussed study, where it was synthesized by elimination reaction of substituted quaternary ammonium salts. The synthesis process involves four consecutives steps as shown in Figure 3. The properties of the dicationic ILs was then compared with that of monocationic ILs with similar length of substituted alkyl group. It was found that the dicationic IL possessed higher thermal stability, lower critical micelle concentration (CMC) values and larger d-spacing of crystal structure than that of monocationic ILs. The solubility of both monocationic and dicationic ILs in nine different solvents were also investigated. It was found that both compounds were immiscible with low polarity solvents, such as toluene, cyclohexane, ethyl acetate and petroleum ether, but miscible in methanol, acetonitrile and chloroform. However, dicationic IL has lower solubility in acetone and water compared to that of monocationic IL. This might be due to more hydrophobic nature of dicationic IL.

Asymmetrical dicationic ionic liquids: Besides symmetrical or geminal dicationic ILs, asymmetrical dicationic ILs are another type of dicationic ILs which consist of different head groups of cation which are also attached via a spacer such as alkyl chain. This asymmetrical ILs can be said to have dual functionality as they have two different head groups. In 2008, Zhang and co-workers [20] synthesized two asymmetrical dicationic ILs based on both imidazolium and aliphatic ammonium as potential electrolyte additives applied to lithium secondary batteries. The asymmetrical dicationic ILs were synthesized by reacting methyl imidazole with either bromoethyl tri methyl ammonium bromide or bromopentyltrimethylammonium bromide, followed by anion exchange reaction with Li NTf_2 to get 1-(3-methylimidazolium-1-yl)ethane-(trimethylammonum) bi[bis(trifluoromethanesulfonyl)imide], MIC2N111-$(NTf_2)_2$ in a form of white solid and 1-(3-methylimidazolium-1-yl)pentane (trimethyl ammonium) bi[bis(trifluoromethanesulfonyl)imide], MIC5N111-$(NTf_2)_2$ in a form of light yellow liquid. The structure of the ILs are shown in Figure 4, with n=2,5. The thermal properties were studied and MIC2N111-$(NTf_2)_2$ shows solid-solid transition characteristics, while MIC5N111-$(NTf_2)_2$ has one of the lowest solid-liquid transformation temperature among analogues, and thus belongs to the greatest thermally stable ILs [20].

In 2010, Chang and co-workers [21] synthesized seven various



R = $C_{14}H_{29}$, X = Br

Figure 3: Synthesis process of 1,4-bis(3-tetradecylimidazolium-1-yl) butane bromide (Ding, Zha et al. [18]).

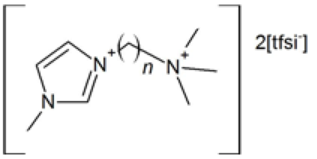


Figure 4: Structure of asymmetrical imidazolium and ammonium-based dicationic ILs (Zhang, Zhou et al. [19]).

symmetrical and asymmetrical dicationic ILs which contain (μ-oxo) bis[trichloroferrate(III)] anions, and characterized with regards to their solubility in solvents, crystal structures, and thermal properties. All synthesized ILs were in a form of yellow solid at ambient temperature. The ILs were found to be soluble in polar solvents such as water and methanol. The dication affected the melting point of these ILs by following the order of triphenylphosphinium > pyridinium > imidazolium dications and symmetrical > asymmetrical dicationic ILs. Dicationic ILs with a ring-type head group would have higher melting points attributed to the added π-π stacking, while symmetrical ILs have higher melting points due to easier packing. Besides that, the anion exists in either a linear or a bent form, depending on the dications [22]. In the following year, Chang and co-workers [23] again synthesized various symmetrical and asymmetrical dicationic ILs, but contained tetrachlorocobaltate (II) or tetrachloromanganate (II) anions. The ILs containing tetrachlorocobaltate (II) anions were in the form of blue solid, while the ILs containing tetrachloromanganate (II) anions were in the form of white solids. In the study, same trend was found for dicationic effect on melting point and also the solubility of the ILs in methanol and water [23].

Heteroanionic dicationic ionic liquids

Heteroanionic dicationic ILs are symmetrical or asymmetrical (head groups) dicationic ILs that have one dication with 2 different anions. In 2010, Chang and co-workers [22] synthesized a series of heteroanionic asymmetrical dicationic ILs by bridging pyridine group with aromatic or aliphatic compounds via alkyl chain of 3 carbons long. The dianions were either PF6-/Br- or NTf2-/Br. The synthesis of these dicationic ILs involves three steps which are: addition of alkyl chain spacer by reacting pyridine with 1,3-dibromopropane, anion exchange with KPF_6 or $LiNTf_2$, and, addition of second aromatic or aliphatic head group. For this heteroanionic-condition study, pyridine was chosen as one of the cation head group candidates instead of stronger nucleophiles such as imidazole because stronger nucleophiles tend to replace both of the bromide anions during the anion exchange process.

Then, these heteroanionic dicationic ILs were characterized in term of solubility and thermal stability. These dicationic ILs were found to be miscible with water, methanol and ethanol, but immiscible with acetone, ethyl acetate, tetrahydrofuran, diethyl ether, chloroform and hexane. Besides that, these dicationic ILs are miscible with methanol/diethyl ether and methanol/ethyl acetate co-solvents. For thermal properties, the thermal stability of these dicationic ILs affected by different second head groups follow the increasing order of the following; ammonium < piperidinium < imidazolium < pyrrolidinium. While for the anion effect, the dicationic ILs containing PF_6-/Br- has higher thermal stability than NTf_2-/Br-, which is in contrast with previous homoanionic dicationic ILs finding. This might be due to higher nucleophilicity of bromide anion to attack electrophilic S=O double bond in NTf_2- anion in initial weight loss step at elevated temperature [22,24,25].

Application

Currently, dicationic ILs are extensively investigated as potential candidates in many application and used as separation material and catalyst candidates. The following sections discuss about their application.

Separation material

Carbon dioxide, CO2, is a part of natural gas and is produced as fossil fuel and coal gasification product. The concentrated amount of CO_2 will lead to pipeline corrosion, decrease in calorific value of the natural gas streams and thus contribute to global warming and climate change. Several methods of CO_2 separation was explored including chemical looping, chemical and physical absorption, solid adsorption, cryogenic separation and membrane separation. Among all method, membrane separation technology possesses attractive features such as high energy efficiency, low capital cost, ability to be applied offshore, ease in development of membrane modules and environmental friendly. However, the conventional supported liquid membrane method face several drawbacks such as liquid evaporation, unstable selectivity and flux through membrane. Thus, ionic liquids which has negligible volatility become the main focus as an alternative for supported liquid membrane technology. From [26,27] Studies the application of monocationic imidazolium based supported ionic liquid membrane, SILM, and got high CO_2/CH_4 selectivity of 25-45 and 100-120, respectively. Shahkaramipour [28] applied dicationic imidazolium based SILM for CO_2/CH_4 separation and compared with monocationic imidazolium based SILM as reference. The results shows that the dicationic based SILM show lower values for CO_2/CH_4 permeability and selectivity than monocationic based SILM due to their higher viscosity. For this separation application, viscosity of the ILs are dominant factor compare to number of cation. Hence, in order to investigate the effect of number of cation, lower viscous dicationic ILs could be used such as PEG-functionalized dicationic ILs.

Catalyst

Hydrolysis: Hydrogen has high potential as energy carrier, with an energy density of three times higher than that of petroleum. It releases energy with high efficiency through electro-oxidation reaction in fuel cells, which allows an environmental friendly energy source as an alternative to toxic materials such as cadmium and nickel [29]. It can be stored in a form of molecular hydrogen in tanks and vessels, in a form of atomic hydrogen or in a form of hydride ion in protide compounds such as borohydrides. Sodium borohydride has attracted huge attention as potential hydrogen storage material as it is stable in dry air and easily handled [30]. The hydrolysis of sodium borohydride to form hydrogen could be executed through a catalytic decomposition as shown in Equation 1.

$$NaBH_4+2(H_2O) \rightarrow NaBO_2+4(H_2) \qquad (1)$$

Chinnapan studied the application of pyridinium-based dicationic ILs, namely, 1,1'-hexane-1,6-diylbis (3-methylpyrdinium) tetrachloronickelate ($[C_6(Mpy)_2][NiCl_4]$, as catalyst. They started by screening between two types of metal halide anions which are $[NiCl_4]_2$- and $[CoCl_4]_2$- towards the hydrolysis reaction of sodium borohydride and compared with conventional nickel boron (NiB) [31]. They found that the newly synthesized ($[C_6(Mpy)_2][NiCl_4]$ generate higher amount of hydrogen eventhough the nickel content was 7 times lower than the conventional NiB catalyst. The catalyst could be reused at least five times and provides 5048 ml hydrogen generation over 23 h [32]. Using homogeneous catalyst for hydrolysis process is beneficial for continuous hydrogen production but face drawback in term of difficulty to stop the reaction for the hydrogen supply on demand [30]. Hence, Chinnapan further utilized the ($[C_6(Mpy)_2][NiCl_4]$ catalyst by fabricating various form heterogenous catalyst such as PVDF (poly(vinylidene fluoride))-IL nanofiber composites [33], PVDF(poly(vinylidene fluoride))-IL-PEG (polyethylene glycol)-EGDMA (ethylene glycol dimethacrylate) nanofiber composites [34], IL-MWCNT (multiwalled carbon nanotubes) [35] and rGO (reduced graphene oxide)-IL-CuO (copper oxide) nanocomposites [36]. All form of IL-incorporated heterogenous catalyst showed outstanding performance in generating hydrogen compared to naked ([$C_6(Mpy)_2$][$NiCl_4$] catalyst. Their activation energy in the range of 37.86-46.1 kJ/mol were significantly lower than that of ([$C_6(Mpy)_2$][$NiCl_4$] catalyst with activation energy of 67.81 kJ/mol. The activation energy of these heterogeneous catalyst are less than Cobalt (75 kJ/mol) and nickel (71 kJ/mol) [37], nickel powder (62.7 kJ/mol) [38], Ni-Co-B (62 kJ/mol) [39], Ru (56 kJ/mol) [2], Co_3O_4 (77.96 kJ/mol) [40], Pt/Li CoO_2 (70 kJ/mol) [41], Ru/Graphite (61 kJ/mol) [42], PAN/$CoCl_2$/CNTs (52.85 kJ/mol) [43] and Ni-Fe-B (57 kJ/mol) [44]. However, they are still higher than Pd-Ni-B (31.1 kJ/mol) [45], Ruthenium(0) nanoclusters (34.9 kJ/mol) [46] and Co-B-TiO_2 (30.93 kJ/mol) [47]. Apart from that, they are easily recovered and can be used multiple times, especially PVDF-IL-PEG-EGDMA nanofiber composites which can be reused at least 9 times with good catalytic activity.

Biodiesel production: Biodiesel is a fuel safe, renewable, non-toxic, biodegradable and much less contaminant for the environment than conventional diesel. The common synthetic route of biodiesel production is the transesterification of triglyceride (TG) and esterification of free fatty acid (FFA) with alcohol which is normally either methanol or ethanol. Generally, strong alkali and acid are the most widely used catalyst for the process due to their high catalytic activity. However, they faces several drawbacks where the acid and base processes are often related to decay, emulsification problem and also hazardous to environment. Therefore, the environmental friendly ionic liquids became a good substitute. More importantly, their miscibility and solvation properties can be adjusted by simply altering the cation and anion that results to different polarity [48]. Their conspicuous potential in biodiesel field is obvious as reviews regarding the role of ionic liquids as catalyst, co-catalyst, solvents and deep eutectic solvents (DES) for biodiesel production keep increasing by year [49-54].

Above all, SO3H-functionalized acidic ILs shows excellent performance and high yield of biodiesel as the sulfonic group is the active site that supply H^+ for protonation of carboxylic group in the triglycerides or free fatty acids [55-58]. In 2011, Fang [59] synthesized a series of ammonium-based dicationic ILs with dialkylsulfonic group and HSO4- anion, and compare their performance as catalyst with monocationic ILs. The best dicationic IL was N,N,N',N'-tetramethyl-N,N'-dipropanesulfonic acid ethylenediammonium hydrogen sulfate. They found that using dicationic IL as catalyst results to 11% increase of conversion (dicationic IL: 95%, monocationic IL: 85%) at the condition of 70°C, 6 h, n(ethanol):n(oleic acid):n(IL)=1.8:1:0.2. After that, Chang [60] improved the performance by altering the structure of ILs synthesized by Fang. They added long alkyl chain (C_{12}) on the dication, resulting to 87% of conversion with 10 times lower amount of IL at a better reaction condition (60°C, 4 h, n(methanol):n(oleic acid):n(IL)=1.5:1:0.02). Changing the anion to p-$CH_3(C_6H_4)SO_3$- also increased the conversion to 93.5%. The addition of long alkyl chain and bulky anion structure helped to promote esterification because of a 'phase transfer' effect where micelle may formed. The formation of micelle facilitate mass transfer in the reaction system. The structures of these ammonium based dicationic IL by Fang et. Al and Chang are illustrated in Figure 5 for ease of understanding.

On the other hand, Aghabarari [1] utilized 4-sulfobenzyl imidazolium hydrogen sulfate dicationic IL as catalyst and get 95% conversion at the condition of 50°C, 6 h, n(methanol):n(oleic acid):n(IL)=2:1:0.075. On the other hand, Ghiaci [55] adopted a longer dicationic IL by the addition of sulfobenzyl group on both sides of the cation as shown in Figure 6. The addition of sulfobenzyl group doubled the active site for esterification reaction, which theoretically should improve the conversion of biodiesel. However, the esterification catalyzed by their dicationic ILs exhibit a slightly lower performance at higher temperature and higher amount of methanol and IL compared to Aghabarari et al. dicationic IL. The conversion was 94.6% at a condition of 60°C, 6 h, n(methanol):n(oil):n(IL)=9:1:0.1. These results shows that, besides the number of sulfonic group (active site), the way we alter the structure of cation and type of anion gave significant effect towards the performance of ILs as catalyst, such that the mass transfer for reaction may increase.

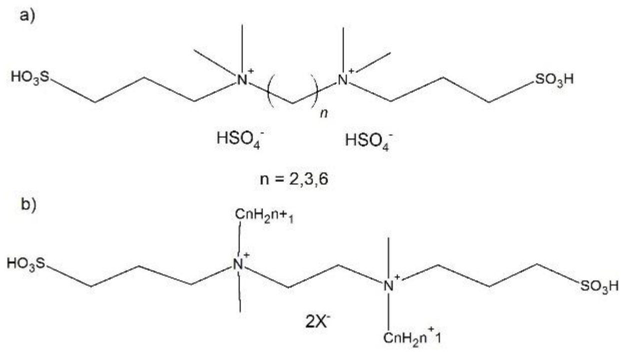


Figure 5: Structure of dicationic ILs by a) Fang et al. [58] b) Chang et al. [60].

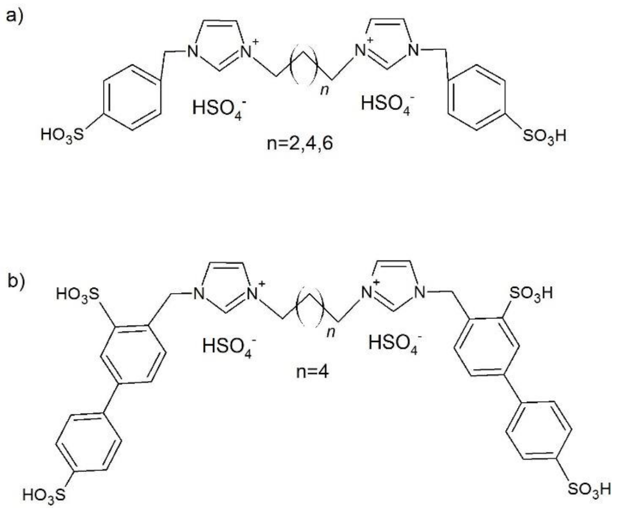


Figure 6: Structure of dicationic ILs by a) Aghabarari et al. [1] b) Ghiaci et al. [54.

Compare to acidic ionic liquids, basic ionic liquids are famous for being able to catalyzed transesterification reaction in a shorter time, even though with the requirement that the free fatty acids present in the feedstock should be as low as 0.5% to prevent saponification. For basic catalyzed reaction, OH^- anion is the active site as it will start attacking the methanol molecule by taking away H^+, resulting to formation of methoxide ion (CH_3O). This nucleophilic methoxide ion will then attack the carbonyl group to complete transesterification reaction. Several researchers synthesized imidazolium-based monocationic and dicationic basic ionic liquids as shown in Table 1 [5,14,61-66].

Based on the results in Table 1, the monocationic IL, 1-butyl-3-methylimidazolium hydroxide, BMImOH, were able to catalyzed transesterification reaction in a very short time (50-70 min) compared to monocationic acidic ILs (~6 h), except for reaction done by Zhou

No.	IL	Oil	Temperature (°C)	Time	MeOH:Oil ratio	IL amount (%)	Conversion (%)	Reusability	References
1	BMImOH	*Cornus Wilsoniana* fruit oil	60	70 min	6	0.9 mol%	96.4	6	Li [62]
2	BMImOH	Castor oil	40	60 min	6	1.0 mol%	95.0	6	Zhang [5]
3	BMImOH	Glycerol trioleate	120	8 h	9	Not reported	87.2	6	Zhou, Liu et al. [64]
4	BMImOH	Rapeseed oil	150	4 h	16	6.0 wt%	96.2	5	Han [60]
5	EMImOH	Cottonseed oil	55	50 min	6	3.5 mol%	90.0	6	Zhou [61]
6	$Et[MIm]_2[OH]_2$	Cottonseed oil	55	4 h	12	0.4 mol%	98.5	7	Liang, Ren et al. [13]
7	BMImIm	Soybean oil	60	1 h	6	8.0 wt%	95.8	Not reported	Li [63]
8	$Et[MIm]_2[Im]_2$	Soybean oil	60	2.5 h	15	4.0 wt%	99.6	5	Fan [65]

Table 1: Transesterification reaction by basic ILs.

No.	Author	Ionic Liquids	Carboxylic acid	Alkyl halide/alcohol	Temperature	Time	Yield	References
Monocationic Ionic Liquids								
1	Brinchi et al.	1,3-Dimethylimidazolium methanesulfonate	Acetic acid	Benzyl chloride	90°C	2 h	>95%	Brinchi [70]
2	Deng et al.	1-Butylpyridinium chloride-Aluminium(III) chloride	Acetic acid	Isopentanol	80°C	2 h	87%	Deng [69]
3	Chen et al.	1-Ethyl-2-methylbenzimidazolium tetrafluoroborate	Acetic acid	Ethanol	80°C	2 h	96%	Chen [71]
Dicationic Ionic Liquids								
4	Zhao et al.	1,1'-Propyl-1,3-diylbis(3-methylimidazolium) dihydrogensulfate	Acetic acid	Ethanol	25°C	2.5 h	93%	Zhao, Liu et al. [72]
5	Muskawar et al.	3,3'-(2,2'-(hexane-1,6-diylbis(azanediyl) bis(2-oxoethane-2,1-diyl)bis(1-propyl-1H-benzimidazolium) dichloride	Nitrobenzoic acid	1-Bromopropane	60°C	18 min	93%	Muskawar, Thenmozhi et al. [73]
6	Chinnappan and Kim	1,1'-Hexane-1,6-diylbis (3-methylpyridinium) dibromide	Nitrobenzoic acid	Benzyl chloride	72°C	20 min	91%	Chinnappan and Kim [32]

Table 2: Esterification of carboxylic acid by monocationic and dicationic ILs.

[65] and Han [61] that require 8 h and 4 h to get high conversion, respectively. It is worth to note that the two reactions were done at far higher temperature (120°C and 150°C) compare to others (40-60°C). The longer reaction time taken by BMImOH to catalyzed the reaction at high temperature could be explained by the instability of hydroxide basic ILs at high temperature.

In 2010, Liang [14] synthesized a series of dicationic hydroxide basic ILs for the production of biodiesel from Cottonseed oil, where bis-(3-methyl-1-imidazole)-ethylene dihydroxide ($Et[MIm]_2[OH]_2$) was found to be the best catalyst. At the first reaction executed for 2 h, the conversion achieved 91%, [14] which is almost similar to conversion of reaction catalyzed by monocationic basic IL, 1-ethyl-3-methyilimidazolium hydroxide in 50 min (90%) [62]. Eventhough the dicationic ILs take double the time taken by monocationic ILs to catalyzed the reaction for the same conversion, the monocationic ILs used was 9 times the dicationic ILs to get the result. The reaction was optimized to get 98.5% conversion in 4 h [14]. Therefore, the use of dicationic basic ILs as catalyst significantly improved the performance in converting cottonseed oil to biodiesel. Besides hydroxide basic ILs, imidazolide basic ILs were also chosen as basic ILs catalyst candidate for the transesterification reaction. Li [S] synthesized monocationic imidazolide basic IL, namely, 1-butyl-3-methylimidazolium imidazolide ([BMIm][Im]), for the production of biodiesel from soybean oil. 95.8% conversion was achieved after 1 h at mild condition (60°C). On the other hand, Fan [66] enhanced the reaction by utilizing dicationic imidazolide basic ILs to get a conversion as high as 99.6%, using half amount of IL at the same temperature. All monocationic and dicationic basic ILs could be recycled for 5-7 times without significant loss. During the recovery of catalyst, the number of catalytic active site reduced. This is because glycerol attached to the catalyst may not be completely detached and partially transformed to carbonaceous deposition due to high temperature distillation which covers the active sites [14].

In general, using dicationic ILs improved the conversion of feedstock to biodiesel as it provides more active site for the reaction to happen. In addition, the separation and recovery of dicationic ILs are easier than monocationic ILs as many of dicationic ILs are in solid form, while monocationic ILs are in liquid form.

Esterification of carboxylic acid: Esterification of carboxylic acid with alcohol or alkyl halides is one of the most fundamental and commonly employed reactions in chemistry. The esterification processes are extensively applied in industry for a variety of desired end-products such as fatty acids, paints, flavors, fragrances, monomers, polymers, plasticizers and medicinal agents [67]. Conventionally, esterification reaction are usually catalyzed by mineral acids, Bronsted acids, Lewis acids, ion exchange resins and zeolites. However, the traditional catalyst faces several drawbacks such as the mineral acids are extremely corrosive and require large effort in removal and neutralizing them with a huge amount of base at the end [68]. Besides that, the traditional catalyst are also costly, toxic, complex, hardly-acquired, volatile and difficult to be separated from products [69]. Therefore, the green ionic liquids received a great deal of attention as alternative catalyst. There are several researchers published papers regarding dicationic ILs as catalyst for esterification of carboxylic acid with alkyl halide or alcohol [70-73]. Table 2 (entries 4-6) simplify the results obtained by them. The table list the best ILs catalyst with the reaction conditions. However, they did not compare the performance of their dicationic ILs with monocationic ILs with the same head group. Therefore, performance of several monocationic ILs (with almost the same structure with the dicationic ILs) as catalyst are compared. In general, dicationic ILs could catalyzed the esterification reaction at lower temperature (25-72°C) in a shorter time (18 min to 2.5 h) with satisfactory yield (91-93%) as compared to monocationic ILs (temperature 80-90°, time 2 h, yield 87-96%).

Conclusion

Even though, the first dicationic ILs were synthesized over 10 years ago, the utilization of these dicationic ILs for any application are still very less. However, compared to conventional monocationic ILs, dicationic ILs possess higher melting point, wider liquid range, and better thermal stability. The structure of dicationic ILs also can be tuned to become either homoanionic or heteroanionic symmetrical or asymmetrical dicationic ILs. Therefore more type of ILs with more functional group can be synthesized for a wider application area or even improved current application. However, the performance of these dicationic ILs in all application should be compared with monocationic ILs with the same head or structure in order to evaluate and prove the enhancement made by the dicationic ILs. Besides that, since many of the chemical reaction and separation processes used in industry require the use of a large amount of ionic liquids, the study on toxicity of these dicationic ILs should be taken into account. The number of recyclability also should be done in maximum to reduce the cost of production as a whole.

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