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ARTICLE TYPE

A microwave assisted one pot synthesis of novel ammonium based dicationic ionic liquids

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An efficient one pot synthesis of novel ammonium based dicationic ionic liquids (DILs) under microwave (MW) condition is carried out. The synthesized DILs are characterized by ¹H NMR, ¹³C NMR, mass spectrometry and elemental analysis. The thermal properties of DILs are studied using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) methods. The decomposition of synthesized DILs falls between 209-266 °C. All synthesized DILs are soluble in polar solvents and insoluble in non polar solvents. The MW irradiation method provides significant quantitative yields and less time than conventional method.

Introduction

Ionic liquids (ILs) are the class of quaternary organic salts composed of moderately large organic cations and inorganic or organic anions. ILs have been recognized as a potential green alternate to the conventional organic solvents in various applications such as organic synthesis,¹ catalysis,² electrochemistry³ and chemical separation.^{4,5} They are further characterized by their inherent physicochemical properties such as negligible vapor pressure, non-flammability, high thermal stability, capability to dissolve organic, inorganic and polymeric materials, wide electrochemical window, intrinsic electric conductivity.⁵⁻¹⁰ Moreover, the physicochemical and solvation properties of ILs can be easily tuned by simple alteration of the substituent groups encompassing the cation and/or anion.

Despite the noteworthy developments in the utility of ILs, the applications of ILs in the industry are limited owing to their high cost and less availability. In order to facilitate the universal acceptance, these issues are indispensable to be addressed. A great deal of attention has been given to imidazolium based ILs in the recent past. However, major drawbacks associated with this class of ILs are complex synthesis procedures, high cost and toxicity.^{11,12} In contrast, ammonium based ILs are easy to prepare, cost-competitive and less toxic.¹³ Due to these salient features, ammonium based ILs are of great interest among researchers worldwide.¹⁴⁻¹⁷ This class of ILs is reported to act promisingly as surfactants, lubricants, extracting

agents, acid catalysts, solvents and CO₂ capturing agents.¹⁸⁻²⁴

Despite of such advantages, surprisingly these quaternary ammonium (QA) based ILs lack enough attention till date. Hence, a systematic study of this class of ILs is essential in order to explore their potential applications in various fields.

Nowadays, the DILs are receiving much attention due to their distinctive characteristics such as improved lubricity, electrolytic properties, reduced surface tension and higher thermal stability compared to monocationic ILs and other conventional solvents.²⁵⁻²⁸ Such ILs contains two monocations combined into a dication and linked by a rigid or flexible organic spacer (alkyl/aryl groups). Their tunability can be tailored by simple alteration of cationic/anionic group and chain length of the organic spacer. They are found suitable in various applications such as dye-sensitized solar cells, organic synthesis, extractions and lubricants.²⁹⁻³¹

Microwave heating has emerged as a powerful technique to promote variety of chemical reactions.³² The advantages of MW irradiation lead to considerably reduce reaction time, improves reaction yield, lower environmental impact, and also increases atom economy.³² Although, number of studies on microwave assisted synthesis of imidazolium ILs under solvent-free conditions³³ and aqueous media³⁴ have been reported, less than a handful reports are available on the synthesis of quaternary ammonium based ILs using MW irradiation.³⁵

In this context, present research work demonstrates microwave assisted novel one pot synthesis of QA based

dicationic ILs. The thermal properties and solubility of DILs are also carried out for their potential applications in various fields such as higher temperature organic reactions, lubricants, surfactants and extracting agents, etc.

5 Experimental

Materials

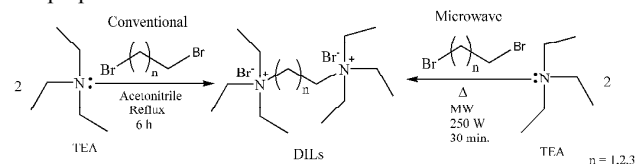
1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, triethylamine (TEA) and trioctylamine (TOA) were purchased from Sigma Aldrich, India. Acetonitrile (MeCN), methanol (MeOH), dimethyl sulfoxide (DMSO), trichloromethane (CHCl₃), propanone (Me₂CO), hexane, ethyl acetate (EtoAc), ethoxyethane (Et₂O) and oxolane (THF) were purchased from Labort, India. All chemicals were purchased from a commercial supplier and used as received unless otherwise stated.

Instruments

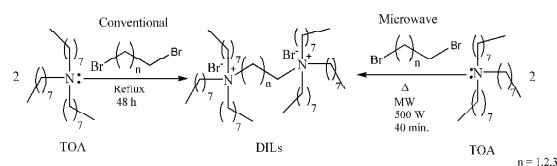
The ¹H and ¹³C NMR spectra were recorded on Avance-II (Bruker) spectrometer at 400 MHz and 100 MHz, respectively using CDCl₃ as a solvent and calibrated with tetramethylsilane (TMS) as the internal reference. Mass spectra were recorded on Waters Micromass Q-ToF Micro. Thermal analyses (TG-DSC) of ILs were conducted in the temperature range of 25 to 600 °C (SDT Q 600, TA) and at a heating rate of 10 °C/min (the T_d was the temperature corresponding to 10 % weight loss). Elemental analyses were carried out with Thermo Scientific CHN Elemental Analyser (FLASH 2000).

General procedure for the one pot synthesis of ammonium based DILs

In a typical procedure, a mixture of different dibromo alkane (1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane) and triethylamine (TEA) or trioctylamine (TOA) in 1:2 ratio was irradiated under RotoSYNTH microwave reactor (Milestone) at certain temperature and time mentioned in Table 1. The resultant product was washed with hexane to remove any unreacted reactants, followed by filtration to afford final products. The final products were dried in a vacuum oven at 60 °C under reduced pressure for 24 h. The synthesized DILs were confirmed by ¹H NMR, ¹³C NMR, mass spectrometry and elemental analysis. The preparation conditions of above DILs are compared with conventional heating method and results are represented in Table 1. The general procedure for the synthesis of all prepared DILs is shown in scheme 1 and 2.



Scheme 1. Synthetic route of TEA based DILs.



Scheme 2. Synthetic route of TOA based DILs.

N,N,N,N',N',N'-hexaethyl-ethane-1,2-diammonium dibromide (1a):

Reagents: Triethylamine (10.77 g, 106.43 mmol), 1,2-dibromo ethane (10 g, 53.23 mmol). Reaction time and temperature: 30 min. and 75 °C. Yield: (19.73 g, 95 %).

¹H NMR (400 MHz, CDCl₃-d₆/ TMS): δ = 1.43 (9H, t, CH₃), 3.19 (6H, q, CH₂), ¹³C NMR (100 MHz, CDCl₃-d₆/TMS): δ= 8.56, 46.47, 53.97. M.W. 390.24, ESIMS: *m/z*: 391.24 [M+1]; Elemental analysis: Anal. Cal. for C₁₄H₃₄Br₂N₂: C, 43.09; H, 8.78; N, 7.18. Found: C, 43.06; H, 8.80; N, 7.20.

N,N,N,N',N',N'-hexaethyl-propane-1,3-diammonium dibromide (1b):

Reagents: Triethylamine (10.02 g, 99.06 mmol), 1,3-dibromo propane (10 g, 49.53 mmol). Reaction time and temperature: 30 min. and 75 °C. Yield: (18.42 g, 92 %).

¹H NMR (400 MHz, CDCl₃-d₆/ TMS): δ = 1.45 (9H, t, CH₃), 3.17 (6H, q, CH₂), δ = 2.15 (2H, m, CH₂) ¹³C NMR (100 MHz, CDCl₃-d₆/TMS): δ= 8.58, 17.56, 46.44, 53.94. M.W. 404.27, ESIMS: *m/z*: 408.8 [M+4]; Elemental analysis: Anal. Cal. for C₁₅H₃₆Br₂N₂: C, 44.56; H, 8.98; N, 6.93. Found: C, 44.53; H, 8.95; N, 6.96.

N,N,N,N',N',N'-hexaethyl-butane-1,4-diammonium dibromide (1c):

Reagents: Triethylamine (9.37 g, 92.60 mmol), 1,4-dibromo butane (10 g, 46.31 mmol). Reaction time and temperature: 30 min. and 75 °C. Yield: (17.43 g, 90 %).

¹H NMR (400 MHz, CDCl₃-d₆/ TMS): δ = 1.41 (9H, t, CH₃), 3.20 (6H, q, CH₂), δ = 3.22 (2H, m, CH₂), δ = 1.77 (2H, m, CH₂) ¹³C NMR (100 MHz, CDCl₃-d₆/TMS): δ= 8.53, 22.30, 46.42, 53.99, 60.25. M.W. 418.29, ESIMS: *m/z*: 415.8 [M-3]; Elemental analysis: Anal. Cal. for C₁₆H₃₈Br₂N₂: C, 45.94; H, 9.16; N, 6.70. Found: C, 45.91; H, 9.18; N, 6.73.

N,N,N,N',N',N'-hexaoctyl-ethane-1,2-diammonium dibromide (2a):

Reagents: Trioctylamine (36.65 g, 103.63 mmol), 1,2-dibromo ethane (10 g, 53.23 mmol). Reaction time and temperature: 40 min. and 120 °C. Yield: (45.74 g, 96 %)

¹H NMR (400 MHz, CDCl₃-d₆/ TMS): δ = 0.85 (3H, t, CH₃), 1.25-1.44 (11H, m, CH₂), 1.88-1.96 (2H, m, CH₂), 2.92-2.99 (2H, t, CH₂); ¹³C NMR (100 MHz, CDCl₃-d₆/TMS): δ= 13.99, 22.53, 25.75, 26.87, 28.99, 29.09, 31.61, 31.67, 47.74. M.W. 895.20, ESIMS: *m/z*: 891.3 [M-4]; Elemental analysis: Anal. Cal. for C₅₀H₁₀₆Br₂N₂: C, 67.08; H, 11.93; N, 3.13.

Found: C, 67.10; H, 11.94; N, 3.12.

N,N,N,N',N',N'-hexaethyl-propane-1,3-diammonium dibromide (2b):

Reagents: Trioctylamine (35.01 g, 98.99 mmol), 1,3-dibromo propane (10 g, 49.53 mmol). Reaction time and temperature: 40 min. and 150 °C. Yield: (41.88 g, 93 %).

¹H NMR (400 MHz, CDCl₃-d₆/ TMS): δ = 0.84 (3H, t, CH₃), 1.23-1.46 (11H, m, CH₂), 1.89-1.95 (3H, m, CH₂), 2.94-2.98 (2H, t, CH₂); ¹³C NMR (100 MHz, CDCl₃-d₆/TMS): δ = 13.98, 22.57, 25.77, 26.90, 28.95, 29.11, 31.65, 31.63, 47.71. M.W. 909.22, ESIMS: *m/z*: 906.3 [M-3]; Elemental analysis: Anal. Cal. for C₅₁H₁₀₈Br₂N₂: C, 67.37; H, 11.97; N, 3.08. Found: C, 67.34; H, 11.95; N, 3.10.

N,N,N,N',N',N'-hexaethyl-butane-1,4-diammonium dibromide (2c):

Reagents: Trioctylamine (32.75 g, 92.60 mmol), 1, 4-dibromo butane (10 g, 46.31 mmol). Reaction time and temperature: 40 min. and 180 °C. Yield: (38.91 g, 91 %).

Yield: 92%, ¹H NMR (400 MHz, CDCl₃-d₆/ TMS): δ = 0.86 (3H, t, CH₃), 1.22-1.43 (11H, m, CH₂), 1.86-1.98 (4H, m, CH₂), 2.93-2.98 (2H, t, CH₂); ¹³C NMR (100 MHz, CDCl₃-d₆/TMS): δ = 13.97, 22.55, 25.78, 26.83, 28.97, 29.10, 31.63, 31.65, 47.78. M.W. 923.25, ESIMS: *m/z*: 925.3 [M+2]; Elemental analysis: Anal. Cal. for C₅₂H₁₁₀Br₂N₂: C, 67.65; H, 12.01; N, 3.03. Found: C, 67.68; H, 12.03; N, 3.01.

Results and discussion

The aim of our study is to emphasize the potential coupling of solvent free reaction with focused MW irradiation for the synthesis of new ammonium based DILs. All the synthesized DILs were prepared in a single step as outlined in scheme 1 and 2. The comparison of reaction conditions of MW irradiation with conventional method is presented in Table 1. It reveals that the MW irradiation method significantly reduces the reaction time and increases the yield of DILs compared to conventional method.

Table 1. Comparison of reaction conditions between two synthetic methods.

DILs	Watt. (W)	MW			Conventional		
		Time (min.)	Temperature (°C)	Yield (%)	Time (h)	Temperature (°C)	Yield (%)
1a	250	30	75	95	6	Reflux ^a	81
1b	250	30	75	92	6	Reflux ^a	78
1c	250	30	75	90	6	Reflux ^a	76
2a	500	40	120	96	48	Reflux ^b	85
2b	500	40	150	93	48	Reflux ^b	83
2c	500	40	180	91	48	Reflux ^b	80

^aReflux in acetonitrile solvent

^bReflux without solvent

Probable mechanism of synthesized DILs

The DIL 1a is selected as a representative IL to understand the probable mechanism of the synthesized DIL. As shown in Fig. 1, the nitrogen present in triethylamine has a lone pair of electron and act as a nucleophile. This lone pair of electron attacks the terminal methylene group of 1,2-dibromo ethane and simultaneously displacement of Br⁻ take place. Finally charge stabilization occurs and forms quaternized salt as N,N,N,N',N',N'-hexaethyl-ethane-1,2-diammonium dibromide DIL.

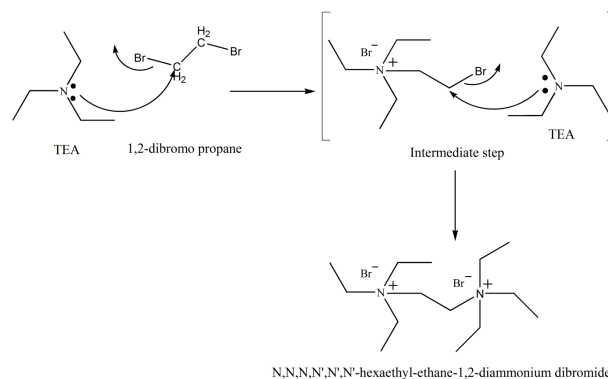


Fig. 1. Plausible mechanism of synthesized DIL.

Thermal stability

The thermal stability and melting point of the synthesized DILs are studied using TGA and DSC method. The TGA curves are presented in Fig. 2. The thermal decomposition temperature (*T_d*) as well as melting point (*T_m*) and corresponding enthalpies are shown in Table 2. The peak maximum is considered as melting point instead of an onset value in DSC (see SI). The manual selection of a tangent point leads to uncertainty in determining the degradation onset temperature in TGA. Thus, to shrink the uncertainty, the degradation onset values were determined using step tangents, that were set to points at a sample weight remained intact and showed 10 % weight loss, respectively.³⁶ As shown in Table 2, the thermal stability of DIL 1a to 1c and 2a to 2c progressively decreases with increase in alkyl chain length between the cations. This may be owing to increased stability of linear aliphatic carbo-cations and/or free radicals with their increasing chain length, which makes them as better leaving groups during the heating and, thus, endorsing the breakdown of the C-N bond.^{37,38} Comparing thermal stability data with the values reported in the literature, it is observed that thermal stability of 1a to 1c DILs are similar to different mono and dicationic QA bromides.³⁹⁻⁴¹ Whereas, 2a to 2c DILs show slight higher stability than reported dicationic QA and imidazolium di bromide ILs.⁴² In the case of 1a and 1c DILs, no phase-transitions were observed using DSC measurements before decomposition which started at temperatures 221 and 207 °C, respectively. The 1b, 2a, 2b and 2c DILs shows melting point at 84, 250, 219 and 213 °C, respectively and that also confirmed with melting point apparatus. ILs are generally defined as solvents which entirely consist of ions and have a melting point usually lower than 100 °C. Lower

melting points are usually preferred for ILs but that does not exclude applications of high melting ILs. Consequently, the trioctylamine salts can be considered as a high melting DILs, with melting points between 213 and 250 °C and triethylamine salts can be considered as a low melting DILs. Similar high melting ILs were synthesized and reported by many research groups of late where melting point of IL is far above 100 °C and they are considered as an IL.^{17,36,43-48} The melting points of DIL are strongly dependent on the alkyl spacer length between cations. As shown in Table 2, the melting point decreases with an increase in alkyl spacer chain length. The observed higher melting point of the synthesized 2a to 2c DILs as compared to imidazolium based ILs may be ascribed to the good degree of charge dispersion around the cation in case of imidazolium than that of triethylamine or trioctylamine.⁴⁹ Further, studied bromide anion has the most symmetrical sphere that increases the melting point of the ILs.⁵⁰

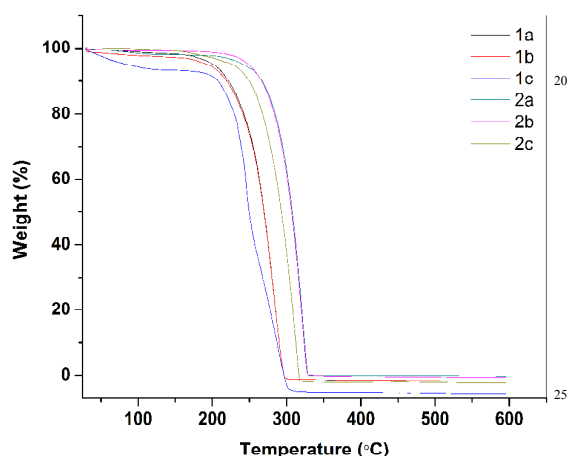


Fig. 2. TGA curves for synthesized DILs measured under nitrogen atmosphere at heating rate of 10 °C·min⁻¹.

Table 2. Thermal properties of DILs.

DILs	T _m and ΔH (°C, J/g)	T _d (°C)
1a	-	221.83
1b	84.97 (76.76)	219
1c	-	207
2a	250.28 (32.19)	266.91
2b	219.76 (14.38)	266.37
2c	213.75 (12.83)	249.63

T_m = melting temperature, ΔH = enthalpy of a transition (J/g),

T_d = decomposition temperature at which weight loss of 10 % is observed

Solubility

The solubility of DILs in organic solvents is an interesting property from application point of view. The solubility of DILs are measured at room temperature and corresponding results are presented in Table 3. The earlier research signified that the solubility behavior of geminal DILs were moderately similar to

that of monocationic ILs,^{30,42,47,51} i.e. the cation combines with Br⁻ anion is hydrophilic in nature and soluble in polar solvents and insoluble in non polar solvents. Without exception, all the synthesized DILs are completely soluble in highly polar MeCN solvent and absolutely insoluble in poorly polar Et₂O solvent. Table 3 indicates that all the investigated DILs are soluble in MeCN, MeOH, DMSO, CHCl₃ and Me₂CO, but not in EtoAc, Hexane, Et₂O and THF. The solubility of DILs in studied solvents seemed not to be affected by alkyl chain length on the cation except water. DIL having shorter alkyl chain length (1a to 1c) are soluble whereas those having longer alkyl chain length (2a to 2c) are found insoluble in water. This may be due to increase in hydrophobicity of the dication, which clearly overrules the coordinating nature of the bromide anion and thereby making DILs (2a to 2c) insoluble in water.⁴² This is a best example of tuning the properties of ILs by the individual effect of cations, anions and alkyl chain length.

Table 3. Solubility of DILs in different solvents. (+: soluble, -: insoluble)

Solvents	DILs					
	1a	1b	1c	2a	2b	2c
H ₂ O	+	+	+	-	-	-
MeCN	+	+	+	+	+	+
MeOH	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
CHCl ₃	+	+	+	+	+	+
Me ₂ CO	+	+	+	+	+	+
Hexane	-	-	-	-	-	-
EtoAc	-	-	-	-	-	-
Et ₂ O	-	-	-	-	-	-
THF	-	-	-	-	-	-

Conclusions

The ammonium based DILs are successfully synthesized using an expeditious MW assisted protocol. The DILs are soluble in MeCN, MeOH, DMSO, CHCl₃ and Me₂CO but not with hexane, EtoAc, Et₂O and THF. The DILs 1a to 1c are soluble in water, whereas 2a to 2c are insoluble in water owing to difference in alkyl chain length that makes them more hydrophobic. The good thermal stability of DILs may have many new perspectives in various fields of applications such as extracting agent, electrolytes, heat transfer fluids, high temperature solvents and lubricants etc. The development of MW assisted approaches with an advantages such as solvent free conditions, less time and significant yields compared to conventional methods meets the need of sustainable chemistry for synthesizing task specific ILs. Presently, the application of these DILs as extracting agent for extraction of hazardous organic pollutants is under investigation.

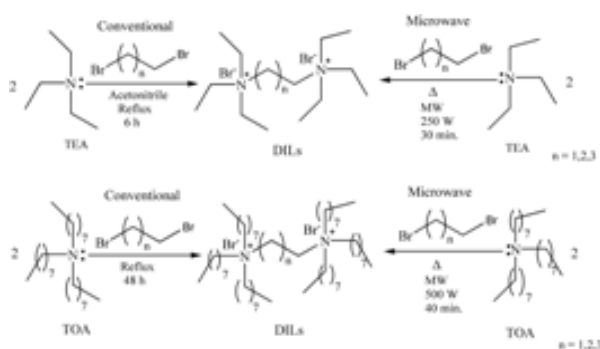
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TOC abstract



25 A greener one pot synthesis of ammonium based dicationic ionic liquids is carried out under microwave conditions. The present method provides better yield and less reaction time compared to conventional methods.