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Synthesis and structural characterization of imidazolium-based dicationic ionic liquids †

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Abstract: Dicationic ionic liquids present a novel class of ionic liquids composed of dication and two monoanions, the latter have shown an increasing interest in recent years and they are used in many applications. Compared to conventional ionic liquids, the physicochemical properties of dicationic ionic liquids can be set by modifying the languor and the type of chaines linking the cationic heads as well as the type of cation. In this work, we present the synthesis of three dicationic ionic liquids based on imidazolium, with two steps, the first of which is a quaternization reaction leading to the formation of dicationic ionic liquids with the iodide ion. The characterization of these organic salts was carried out by magnetic resonance spectroscopy allowing a better identification of the products obtained.

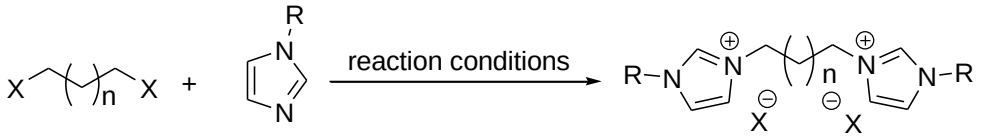
Keywords: Ionic liquids, dicationic ionic liquids, imidazolium, quaternization.

1. Introduction

Ionic liquids may be considered as a new and impressive class of solvents, or as a type of materials that possess a long and useful history [1]. Ionic liquids (ILs) are organic salts [2] comprised of organic cations in combination with organic and/or inorganic anions, which ewhibit a myriad of remarkable and interesting properties [3, 4]. The physicochemical properties of ILs such as their high thermal stability, their good electronic conductivity, their reasonable viscosity, their wide liquid range, their low vapor pressure, their high thermal conductivity, make them a very interesting reaction medium for green chemistry. allowing in particular to work at high temperature with good heat dispersion. [5] ILs are capable of dissolving a large number of organic or inorganic compounds [6], or organometallic compounds and provide a polar coordinating medium for transition metal catalysts. In this case, the ILs are used as inert solvents or co-catalysts. [7] The properties of ILs such as their very wide electro-activity range, their high conductivity, and their high thermal stability have made

these new media prime candidates in the search for new energy systems (photovoltaic cell, battery, etc.) [8,9]. They can also be used as battery electrolyte [10].

Recently, many researches have been focusing on the development of a new subclass of ILs known as dicationic ionic liquids (DILs), which typically comprise of two cationic head groups linked by a rigid or flexible spacer, associated with two counteranions [11]. Since the number of possible combinations of cations and anions in DILs is greater than that of monocationic LIs, greater variability in the properties of LIDs would be possible [12]. Compared to monocationic ILs, multicationic ones can have a higher melting point, surface tension, viscosity, wide liquid range, thermal stability and tenability of chemical and physical properties [13,14]. Therefore, they have good potential to be used in a wide range of applications including solar cells [15], DILs are studied in detail with improved photovoltaic properties for solar cells sensitized to dyes [16,17]. DILs are promoter catalysts for the esterification reaction. They have also been widely used in various scientific fields due to their high thermal stability, wide range of liquid state temperatures, and biological activities such as antiviral, antifungal and anticancer activities. [18]. DILs have proven to be essential in the fields of catalysis [19]. More recently, improving the isomerization degree of *n*-pentane and electrolytes for photo-harvesting [20-22]. However, they are also referred to as organic ionic plastic crystals due to their property of solid state electrolytes [23,24]. The property of being sufficiently stable at melting points above 200 ° C gives them superior lubricating properties, which allows them to be used in high temperature lubricants [25,26]. They have shown promising results in the separation of oils. aromatic fractions of the extracts, thereby replacing aromatic solvents [27]. In addition, they have been successfully studied in zeolite beta applications, which have given promising results [28-30]. Many researchers have described the synthesis of imidazolium-based LIDs by various methods with their advantages and disadvantages. After remarking various methods, the major limitation is the time spent on the synthesis and the tedious procedure. [31]. In 2007, Ding and coworkers synthesized an imidazolium-based DIL containing a substituted alkyl group 14 carbons long. where it had been synthesized by an elimination reaction of substituted quaternary ammonium salts where the synthesis process involves four consecutive steps. [32]. Recently, a series of dicationic imidazolium-based ionic liquids containing incorporated Br^-, BF_4^-, PF_6^-, NTf_2^- anions were synthesized by Zhang et al [33], in order to improve the thermal stability of these compounds and enhance the thermal storage density. More recently, Kuhn and his groupe [34] used the synthesized imidazolium-based dicarboxylate dicationic ionic liquids to study their thermal properties and showed that the dicarboxylate's spacer length has no effect on the melting point.



Scheme 1. General synthesis of Dicationic Ionic liquids based on imidazolium

Here in we present the synthesis of three dicationic ionic liquids based on imidazolium. The synthesis takes places through two steps; the first one is a quaternization reaction where the first DIL was obtained with iodide ion. The second step would be an ion exchange, in order to obtain the two last

DILs. The characterization of the DILs was carried out by magnetic resonance spectroscopy allowing a better identification of the products obtained.

2. General experimental procedure

The synthesis of three different ionic liquids composed of 1,1-Bis(3-imadazoilum-1-yl) methane [$C_4(Mim)_2$] cation and three different anions were synthesized using the already reported approaches [35, 36]. Initially, Imidazole (0.1 mol) and diiodomethane (0.05 mol) were charged into round bottom flask contain acetonitrile (10 mL) and was stirred for 6 h at 50°C. The synthesized white crystalline intermediate, 1,1-Bis(imadazoilum-1-yl) methylene iodide ([$C_1(Mim)_2$]2I), was washed with ethyl acetate and toluene to remove unreactive residues. In the second step, [$C_1(Mim)_2$][2I] (0.025 mol) was dissolved in water (20 mL) and then respective acid (0.05 mol) were added dropwise under the cooling condition for 30 min. After dropwise addition, the temperature of the mixture was increased to 50 °C and stir for 12 h. The desired ILs were washed with water and toluene to remove the unreacted materials.

3. Results and discussion

NMR ^{1}H and NMR ^{13}C (Bruker 300MHz spectrometer) spectra were used to confirm the structure of synthesized dicationic ILs using methanol (CH_3OH) as internal solvent.

4. Conclusion

In summary, we have synthesized three dicationic ILs based on imidazolium composed of 1,1-Bis(3-imadazoilum-1-yl) methane dication and three different anions through two steps, the first is a quaternization reaction or the first dicationic IL was obtained with iodide ion. The characterization of the dicationic ILs was carried out by magnetic resonance spectroscopy allowing a better identification of the products obtained.

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References

1. P. Wasserscheild and T. Welton. Ionic Liquids in Synthesis.*Org. Proc. Res. Dev.* **2003**, *7*, 2, 223-224. doi.org/10.1021/op0340210
2. Matthew A.Gebbie, Alexander M. Smith Howard A. Dobbs, Alpha A.Lee, Gregory G.Warr, Xavier Banquy, Markus Valtiner, Mark W.Rutland, Jacob N.Israelachvili, Susan Perkin and Rob Atkin, Long range electrostatic forces in ionic liquids, Chem. Commun, **2017**, 53, 1214-1224. doi.org/10.1039/C6CC08820A
3. Vekariya, R. L. A review of ionic liquids: Applications towards catalytic organic transformations. Journal of Molecular Liquids. **2017**, 227, 44–60. doi:10.1016/j.molliq.2016.11.123
4. Parveen, M., Azaz, S., Malla, A. M., Ahmad, F., Pereira da Silva, P. S., & Ramos Silva, M. *Solvent-free, [Et3NH][HSO4] catalyzed facile synthesis of hydrazone derivatives. New Journal of Chemistry,* **2015** *39(1), 469–481.* doi:10.1039/c4nj01666a
5. Mofaddel, N., Krajian, H., Villemin, D., & Desbène, P. L. *New ionic liquid for inorganic cations analysis by capillary electrophoresis: 2-hydroxy-N,N,N-trimethyl-1-phenylethanaminium bis(trifluoromethylsulfonyl)imide (phenylcholine NTf2). Analytical and Bioanalytical Chemistry*, **2009**, *393(5), 1545–1554*. doi:10.1007/s00216-008-2582-y
6. Pandey, A., Ekka, M. K., Ranjan, S., Maiti, S., & Sachidanandan, C. *Teratogenic, cardiotoxic and hepatotoxic properties of related ionic liquids reveal the biological importance of anionic components. RSC Advances,* **2017**, *7(37), 22927–22935.* doi:10.1039/c7ra01520h
7. H.Zhao,S.M.Malhorta, Application of ionic liquids in organic synthesis, AldrichimicaActa.35,No.3.**2002**, 75-83
8. Plechkova, N. V., & Seddon, K. R. *Applications of ionic liquids in the chemical industry. Chem. Soc. Rev.* **2008**, *37(1), 123–150.* doi:10.1039/b006677j
9. A.E.Visser, R.P.Swatloski, W.M.Reichert, S.T.Griffin, R.D.Rogers, Traditional Extractants in Nontraditional Solvents: Groups 1 and 2 Extraction by Crown Ethers in Room-Temperature Ionic Liquids, Ind. Eng. Chem. Res, 39, **2000**, 3596-3604. doi:10.1021/ie000426m
10. Niedermeyer, H., Hallett, J. P., Villar-Garcia, I. J., Hunt, P. A., & Welton, T. (2012). *Mixtures of ionic liquids. Chemical Society Reviews, 41(23), 7780.* doi:10.1039/c2cs35177c
11. Talebi, M., Patil, R. A., & Armstrong, D. W. *Physicochemical properties of branched-chain dicationic ionic liquids. Journal of Molecular Liquids,* **2018**, *256, 247–255.* doi:10.1016/j.molliq.2018.02.016
12. Shirota, H., Mandai, T., Fukazawa, H., & Kato, T. *Comparison between Dicationic and Monocationic Ionic Liquids: Liquid Density, Thermal Properties, Surface Tension, and Shear Viscosity. Journal of Chemical & Engineering Data,* **2011**, *56(5), 2453–2459.* doi:10.1021/je2000183
13. Steudte, S., Bemowsky, S., Mahrova, M., Bottin-Weber, U., Tojo-Suarez, E., Stepnowski, P., & Stolte, S. *Toxicity and biodegradability of dicationic ionic liquids. RSC Advances,* **2014**, *4(10), 5198.* doi:10.1039/c3ra45675g
14. Masri, A. N., Abdul Mutalib, M. I., Aminuddin, N. F., & Lévêque, J. Novel SO 3 H-functionalized dicationic ionic liquids – A comparative study for esterification reaction by ultrasound cavitation and mechanical stirring for biodiesel production. Separation and Purification Technology, **2018**, 196, 106–114. doi:10.1016/j.seppur.2017.08.061
15. Brennan, L. J., Barwich, S. T., Satti, A., Faure, A., & Gun'ko, Y. K. *Graphene–ionic liquid electrolytes for dye sensitised solar cells. Journal of Materials Chemistry A,* **2013**, *1(29), 8379.* doi:10.1039/c3ta11609c
16. Gorlov, M., & Kloo, L. *Ionic liquid electrolytes for dye-sensitized solar cells. Dalton Transactions,* **2008**, *(20), 2655.* doi:10.1039/b716419j
17. Hwang, D., Kim, D. Y., Jo, S. M., Armel, V., MacFarlane, D. R., Kim, D., & Jang, S.-Y. *Highly Efficient Plastic Crystal Ionic Conductors for Solid-state Dye-sensitized Solar Cells. Scientific Reports,* **2013**, *3(1).* doi:10.1038/srep03520
18. Moumene, T., Belarbi, E. H., Haddad, B., Villemin, D., Abbas, O., Khelifa, B., & Bresson, S. *Study of imidazolium dicationic ionic liquids by Raman and FTIR spectroscopies: The effect of the nature of the anion. Journal of Molecular Structure,* **2015**, *1083, 179–186.* doi:10.1016/j.molstruc.2014.11.061
19. Muskawar, P. N., Thenmozhi, K., Gajbhiye, J. M., & Bhagat, P. R. *Facile esterification of carboxylic acid using amide functionalized benzimidazolium dicationic ionic liquids. Applied Catalysis A: General,* **2014**, *482, 214–220.* doi:10.1016/j.apcata.2014.06.004

20. Daneshvar, N., Nasiri, M., Shirzad, M., Safarpoor Nikoo Langarudi, M., Shirini, F., & Tajik, H. *The introduction of two new imidazole-based bis-dicationic Brönsted acidic ionic liquids and comparison of their catalytic activity in the synthesis of barbituric acid derivatives. New Journal of Chemistry,* **2018**, *42(12), 9744–9756.* doi:10.1039/c8nj01179f
21. Chen, J., Yang, L., Zhou, W., Zhu, L., Zhou, Y., Xiang, Y., & Xia, D. *Dicationic Ionic Liquid: A Novel Method for Improving the Isomerization Degree of n-Pentane. Energy & Fuels,* **2018**, *32(4), 5518–5526.* doi:10.1021/acs.energyfuels.8b00267
22. Dhar, A., Kumar, N. S., Asif, M., & Vekariya, R. L. *Pyridinium-clubbed dicationic ionic liquid electrolytes for efficient next-generation photo harvesting. New Journal of Chemistry,* **2018**, *42(9), 6990–6996.* doi:10.1039/c8nj00330k
23. Armel, V., Velayutham, D., Sun, J., Howlett, P. C., Forsyth, M., MacFarlane, D. R., & Pringle, J. M. *Ionic liquids and organic ionic plastic crystals utilizing small phosphonium cations. Journal of Materials Chemistry,* **2011**, *21(21), 7640.* doi:10.1039/c1jm10417a
24. Wang, Y. F., Zhang, J. M., Cui, X. R., Yang, P. C., & Zeng, J. H. *A novel organic ionic plastic crystal electrolyte for solid-state dye-sensitized solar cells. Electrochimica Acta,* **2013**, *112, 247–251.* doi:10.1016/j.electacta.2013.08.159
25. Somers, A., Howlett, P., MacFarlane, D., & Forsyth, M. *A Review of Ionic Liquid Lubricants. Lubricants,* **2013**, *1(1), 3–21.* doi:10.3390/lubricants1010003
26. Bermúdez, M.-D., Jiménez, A.-E., Sanes, J., & Carrión, F.-J. *Ionic Liquids as Advanced Lubricant Fluids. Molecules,* **2009**, *14(8), 2888–2908.* doi:10.3390/molecules14082888
27. Bahadur, I., Singh, P., Kumar, S., Moodley, K., Mabaso, M., & Redhi, G. *Separation of Aromatic Solvents from the Reformate Fraction of an Oil Refining Process using Extraction by a Designed Ionic Liquid. Separation Science and Technology,* **2014**, *49(12), 1883–1888.* doi:10.1080/01496395.2014.900568
28. Kore, R., Satpati, B., & Srivastava, R. *Synthesis of Dicationic Ionic Liquids and their Application in the Preparation of Hierarchical Zeolite Beta. Chemistry - A European Journal,* **2011**, *17(51), 14360–14365.* doi:10.1002/chem.201102946
29. Cooper, E. R., Andrews, C. D., Wheatley, P. S., Webb, P. B., Wormald, P., & Morris, R. E. *Ionic liquids and eutectic mixtures as solvent and template in synthesis of zeolite analogues. Nature,* **2004**, *430(7003), 1012–1016.* doi:10.1038/nature02860
30. Arya, K., Rawat, D. S., & Sasai, H. *Zeolite supported Brønsted-acid ionic liquids: an eco approach for synthesis of spiro[indole-pyrido[3,2-e]thiazine] in water under ultrasonication. Green Chemistry,* **2012**, *14(7), 1956.* doi:10.1039/c2gc35168d
31. Lee, M., Niu, Z., Slebodnick, C., & Gibson, H. W. *Structure and Properties ofN,N-Alkylene Bis(N'-Alkylimidazolium) Salts. The Journal of Physical Chemistry B,* **2010**, *114(21), 7312–7319.* doi:10.1021/jp102370j
32. Ding, Y.-S., Zha, M., Zhang, J., & Wang, S.-S. *Synthesis, characterization and properties of geminal imidazolium ionic liquids. Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **2007**, *298(3), 201–205.* doi:10.1016/j.colsurfa.2006.10.063
33. Zhang, H, Xu, W. Lui, J., & Yang, B. Thermophysical propertiez of dicationic imidazolium-based ionic compounds for thermal storage. *Journal of Molecular Liquids,* **2019**, 282, 474–483. doi: 10.1016/j.molliq.2019.03.012
34. Kuhn, B. L., Osmari, B. F., Heinen, T. M., Bonacorso, H. G., Zanatta, N., Nielsen, S. O.,Ranathunga, D. T. S., Villetti, M. A., Frizzo, C. P. *Dicationic imidazolium-based dicarboxylate ionic liquids: Thermophysical properties and solubility. Journal of Molecular Liquids,* **2020**. *112983.* doi:10.1016/j.molliq.2020.112983
35. M. Ao, P. Huang, G. Xu, X. Yang, Y. Wang, Aggregation and thermodynamic properties of ionic liquid-type gemini imidazolium surfactants with different spacer length, Colloid and Polymer Science, 287 (**2009**) 395-402. doi:10.1007/s00396-008-1976-x
36. Q.Q. Baltazar, J. Chandawalla, K. Sawyer, J.L. Anderson, Interfacial and micellar properties of imidazolium-based monocationic and dicationic ionic liquids, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 302 ,**2007**, 150-156. doi:10.1016/j.colsurfa.2007.02.012