

## Ionic Liquids

# Synthesis of High-Purity Imidazolium Tetrafluoroborates and **Bis(oxalato)borates**

Paulo Schmitz,<sup>[a, b]</sup> Rene Jakelski,<sup>[a, b]</sup> Kirsi Jalkanen,<sup>[a, b]</sup> Martin Winter,<sup>[a, b, c]</sup> and Peter Bieker\*<sup>[a, b]</sup>

Abstract: The synthesis and purification of imidazoliumbased ionic liquids (ILs) with boron-containing anions is reported. The scope was the optimization of the meta thesis reaction and on the purification of the synthesized ILs. It was possible to reduce the reaction and purification times, to avoid the use of acetonitrile as processing solvent, and to increase the yield compared to the known procedure for [BOB]<sup>-</sup> anion-containing ILs. Furthermore, to the best of our knowledge the flashpoints of the ILs could be determined for the first time by the continuously closed-cup flashpoint (CCCFP) method.

lonic liquids (ILs), and especially room-temperature ionic liquids (RTILs), have been intensively investigated during the last decade.<sup>[1]</sup> They often consist of organic cations and organic or inorganic fluorine-containing anions, both with delocalized charges.<sup>[2]</sup>

Depending on the detailed chemistry of the respective IL, they show favorable physical properties, such as miscibility with organic solvents, negligible vapor pressure also at elevated temperatures, chemical and thermal stability, recyclability, wide electrochemical stability windows, and high conductivities.<sup>[3]</sup>

As an additional major benefit, ILs are easily tunable to meet special requirements, as cations and anions can be combined and varied in different ways corresponding to the desired application. Thus various properties, such as for example the melting point, the viscosity, or the solubility can be customtailored in the desired way.<sup>[4]</sup>

[a]	P. Schmitz, R. Jakelski, Dr. K. Jalkanen, Prof. M. Winter, Dr. P. Bieker
	Institute for Physical Chemistry
	University Münster
	Corrensstrasse 28/30, 48149 Münster (Germany)
	E-mail: peter.bieker@uni-muenster.de

- [b] P. Schmitz, R. Jakelski, Dr. K. Jalkanen, Prof. M. Winter, Dr. P. Bieker MEET Battery Research Center University Münster Corrensstrasse 46, 48149 Münster (Germany)
- [c] Prof. M. Winter Helmholtz Institute Münster, IEK-12, Forschungszentrum Jülich GmbH Corrensstrasse 46, 48149 Münster (Germany)
- Supporting information for this article can be found under: http://dx.doi.org/10.1002/chem.201604461.

On account of these characteristics, ILs are utilized in numerous research and application fields, such as in synthesis,<sup>[3c, 5]</sup> catalysis,<sup>[6]</sup> separation processes,<sup>[7]</sup> energy storage,<sup>[1a,8]</sup> or lubrication<sup>[9]</sup> and metal deposition.<sup>[10]</sup> However, depending on the application, there are various purity requirements on the ILs. It is for instance inevitable to use strictly pure ILs for application in electrochemical energy storage systems,<sup>[11]</sup> for example, in lithium metal, lithium-ion, and dual-ion batteries.<sup>[12]</sup>

In general, ILs can be synthesized via two different routes: The first is a direct synthesis, while the alternative follows an anion metathesis.<sup>[13]</sup> Halide-free ILs, for example, can be produced by a direct alkylation reaction of an amine with an alkyl nitrate.<sup>[13a]</sup> As the variety of ILs that can be prepared by the route of direct alkylation route is limited, most ILs are synthesized in two steps. First an organic halide salt is formed through an alkylation of a base by a haloalkane, after which an anion exchange by metathesis or an acid-base reaction is performed.<sup>[14]</sup> Scheme 1 shows the two-step synthesis routes for ILs based on 1-methylimidazole.

Herein we focused on the synthesis and purification of 1-ethyl-3-methylimidazolium ([C2MIm]) and 1-butyl-3methylimidazolium ([C4MIm]) cations in combination with bis(oxalato)borate ( $BOB^-$ ) and tetrafluoroborate ( $BF_4^-$ ) anions. The metathesis reaction was carried out both in the melt and in suspension to obtain highly pure products, while optimizing the reaction time, yield, and cost efficiency compared to the reported procedure for BOB<sup>-</sup> anion-containing ILs.<sup>[3c]</sup> The method investigated herein reduces the reaction and purification times by two days, avoids the use of hazardous acetonitrile, and increases the yield for more than 15%. Additionally, the synthesized ILs were characterized with flashpoint and refractive-index measurements, differential scanning calori metry (DSC), and thermogravimetric analysis (TGA). To the best of our knowledge this is the first time the flashpoints of the respective ILs could be exactly determined by using the continuously closed-cup flashpoint (CCCFP) method.

The ILs 1-ethyl-3-methylimidazolium bis(oxalato)borate ([C2MIm]BOB), 1-butyl-3-me-thylimidazolium bis(oxalato)borate ([C4MIm]BOB), 1-ethyl-3-methylimidazolium tetrafluoroborate ([C2MIm]BF<sub>4</sub>), and 1-butyl-3-methylimidazolium tetrafluoroborate ([C4MIm]BF<sub>4</sub>) were synthesized both by a solvent-free method and with dichloromethane as a solvent. The methods were compared based on their yields. Furthermore, the purification step was investigated to obtain highly pure ILs, which fulfill the requirements for battery applications.<sup>[3b]</sup>

Chem. Eur. J. 2017, 23, 1-5

Wiley Online Library

1



Scheme 1. Two-step synthesis routes for ILs based on 1-methylimidazol.

Table 1 summarizes the results with regard to the yields, refractive indices, glass transition temperatures ( $T_g$ ), and flash-points of the synthesized ILs.

Considering the results from ion chromatography (IC) and Karl Fischer titration, purities higher than 99.9% were est imated for all of the synthesized ILs. The detected impurity contents were below 20 ppm for chloride, 2 ppm for lithium, and 10 ppm for water. In particular, low contents of chloride and water are important for the quality of the ILs, since these impurities have been found to influence their physical properties.<sup>[15]</sup> These results show that, except for [C2MIm]BF<sub>4</sub>, all ILs could be synthesized in higher yields by the solvent-free approach. This trend was more pronounced for the [C4MIm]-based ILs, as their yields were higher compared to the

Table 1. Yields, refractive indices, glass transition temperatures, and flash- points of the ILs synthesized by suspension or melt.							
IL	Synthetic approach	Yield [%]	Refractive index	Τ <sub>g</sub> [°C]	Flashpoint [°C]		
[C2MIm]BF <sub>4</sub> [C2MIm]BF <sub>4</sub> [C2MIm]BOB [C2MIm]BOB [C4MIm]BF <sub>4</sub> [C4MIm]BF <sub>4</sub> [C4MIm]BOB	suspension melt suspension melt suspension melt	70 50 80 82 80 95 87	1.408 1.408 - - 1.417 1.417 1.475	-93 -93 -23 -23 -85 -85 -85 -30	373 374 236 237 363 364 236		

[C2MIm]-based ILs. Thus the solvent-free synthesis route in combination with the used purification method can be stated as suitable for [C4MIm]BOB and [C4MIm]BF<sub>4</sub> (yield = 95%). For these ILs the solvent-based reaction route also delivered acceptable yields (ca. 80%). For [C2MIm]BOB, yields up to 82% were achieved by the solvent-free method. In contrast, for [C2MIm]BF<sub>4</sub> significantly lower yields were obtained (yield<sub>melt</sub>= 50%, yield<sub>suspension</sub> = 70%), because there was a much higher product loss during the purification process compared to the [C4MIm] ILs. This indicated that silica was not an optimal column material in particular for [C2MIm]BF<sub>4</sub>, because the less voluminous IL strongly adhered to the column material and could also not be extracted from the column with an excess amount of solvent. The smaller the ions and the lower the asymmetry of the cation, the higher the loss inside the column material. The yields of the synthesized ILs decreased in the following sequence: [C4MIm]BOB ([C4MIm]BOB>[C4MIm]BF<sub>4</sub> > [C2MIm]BOB > [C2MIm]BF<sub>4</sub>).

The refractive indices were measured for all the other ILs except for the [C2MIm]BOB, as it exists in a solid form at the measurement temperature of 20 °C. It can be seen that the synthesis route, as expected, had no influence on the refractive index. The indices for the  $BF_4^-$  containing ILs were almost equal: A longer alkyl side chain in [C4MIm]BF<sub>4</sub> led to a slight increase of the refractive index in comparison to [C2MIm]BF<sub>4</sub>. The BOB<sup>-</sup> anion showed a higher refraction compared to the  $BF_4^-$  anion ([C4MIm]BOB 1.475, [C4MIm]BF<sub>4</sub> 1.417).

The thermal behavior of the ILs was investigated by DSC. For the chosen settings only the [C2MIm]BF<sub>4</sub> showed a cold crystallization ( $T_{cc} = -44$  °C) and a melting point ( $T_m = 15$  °C) along with the glass transition  $(T_q)$ . No differences between the synthetic approaches were observed either in the DSC measurements. The BF<sub>4</sub><sup>-</sup> containing ILs showed much lower glass transition temperatures than the BOB<sup>-</sup> anion including ones. Considering the difference in glass transition temperatures, it can be concluded that an increasing alkyl chain length at the imidazolium ring leads to an increase in the  $T_{q}$  of the BF<sub>4</sub><sup>-</sup> ILs and to a decrease in the  $T_{g}$  of the BOB<sup>-</sup> ILs. Considering the glass transition temperatures of the synthesized ILs, the observed temperatures (Table 1) fit well to the literature values for [C2MIm]BF<sub>4</sub> (-92 °C), [C4MIm]BF<sub>4</sub> (-85 °C), and [C4MIm]BOB (-29°C).<sup>[3c,16]</sup> For [C2MIm]BOB no reference value could be found.

Furthermore, the thermal stability was measured by TGA. No influence of the synthesis route on the thermal stability was observed. Figure 1 shows the TGA results for each IL.

These results display that [C2MIm]BF<sub>4</sub> and [C4MIm]BF<sub>4</sub> are thermally stable up to more than 350 °C, whereas [C2MIm]BOB and [C4MIm]BOB decomposes below 300 °C. Thus it can be concluded that with the BOB<sup>-</sup> anion it is thermally less stable than with the BF<sub>4</sub><sup>-</sup> anion.

Finally, the flashpoints were determined according to CCCFP. The flashpoints are in line with the TGA results: For the BOB<sup>-</sup> containing ILs, flashpoints of about 235 °C were observed, whereas the BF<sub>4</sub><sup>-</sup> ILs showed flashpoints higher than 360 °C. The BF<sub>4</sub><sup>-</sup> ILs also showed a decreasing flashpoint with an increasing alkyl chain length on the nitrogen substituent. This

Chem. Eur. J. 2017, 23, 1-5

www.chemeurj.org

2

#### © 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

**KK** These are not the final page numbers!



Figure 1. TGA measurements of the synthesized ILs.

was to the best of our knowledge the first time the flashpoints of the shown imidazolium-based ILs could be measured. The flashpoint of [C4MIm]BF<sub>4</sub> was only estimated, based on TGA data by Fox et al. in 2008.<sup>[17]</sup> The results shown herein further refute the hypothesis that is often stated that ILs would be nonflammable.<sup>[18]</sup> It can be noted that the synthesized ILs are thermally stable and non-combustible at the operating temperatures of room-temperature lithium batteries, but elevated temperatures, which could be reached during a battery thermal runaway, would lead to decomposition and also

#### combustibility.

To conclude, the described procedure offers a viable way to synthesize highly pure imidazolium tetrafluoroborates and bis(oxalato)borates. In particular for the BOB<sup>-</sup> containing ILs, high yields were achieved, and the commonly used procedure could be significantly improved regarding time, yield, and cost. Nevertheless, the purification step is an important issue, and it has to be investigated and optimized separately for each single IL. Furthermore, the thermal properties, refractive indices, and flashpoints of the ILs were determined. In this work the flashpoints of [C2MIm]BF<sub>4</sub>, [C4MIm]BF<sub>4</sub>, [C2MIm]BOB, and [C4MIm]BOB were measured according to ASTM D6450-CCCFP for the first time.

#### **Experimental Section**

General synthetic procedure for the metathesis reaction:

a) Melt synthesis: The 1-butyl-3-methyl-imidazolium chloride was gently heated to 80  $^{\circ}$ C (melting point: ca. 73  $^{\circ}$ C) and the lithium salt of the desired anion was added to the melt. The mixture was stirred for 24 h. Afterwards the raw product was dissolved in dichloromethane (DCM) and the workup was carried out.

b) Solvent-based synthesis: Using a second reaction path with DCM, the reaction was carried out in a suspension. The 1-butyl-3-methyl-imidazolium chloride was suspended in the DCM before the lithium salt was added. After refluxing the suspension at 60 °C for 24 h, the workup was performed.

Workup: The solid lithium chloride was removed through column chromatography with silica as the stationary phase and DCM as the mobile phase. DCM was removed under reduced pressure. After predrying, the obtained ILs were dried using a High Cube 80 Eco turbomolecular pump (Pfeiffer Vacuum) at  $p \approx 10^{-7}$  mbar and

 $55\,^{\circ}$ C for two days. The water content of the final products was below 10 ppm as determined by Karl Fischer titration. The chloride content was below 20 ppm and the lithium content below 2 ppm, as measured by ion chromatography (IC).

For more experimental details, see the Supporting Information.

#### Acknowledgements

For financial support of this work within the research project "MEET Hi-EnD" (03X4634A) the authors wish to thank the Federal Ministry of Education and Research (BMBF).

**Keywords:** borates • flashpoints • ionic liquids • room-temperature molten salts • synthetic methods

- a) X. Cao, S. Röser, B. Rezaeirad, X. He, B. Streipert, M. Winter, I. Cekic-Laskovic, J. Inorg. Gen. Chem. 2015, 641, 2536–2542; b) P.-Y. Chen, J. Chin. Chem. Soc. 2006, 53, 1017–1026; c) S. Kuwabata, T. Tsuda, T. Torimoto, J. Phys. Chem. Lett. 2010, 1, 3177–3188.
- [2] a) T. Nishida, Y. Tashiro, M. Yamamoto, J. Fluorine Chem. 2003, 120, 135–141; b) C. Maton, N. D. Vos, C. V. Stevens, Chem. Soc. Rev. 2013, 42, 5963–5977; c) R. Hagiwara, Y. Ito, J. Fluorine Chem. 2000, 105, 221–227; d) M. Hirao, H. Sugimoto, H. Ohno, J. Electrochem. Soc. 2000, 147, 4168–4172; e) M. Chai, Y. Jin, S. Fang, L. Yang, S.-i. Hirano, K. Tachibana, J. Power Sources 2012, 216, 323–329.
- [3] a) Y. Huo, S. Xia, S. Yi, P. Ma, *Fluid Phase Equilib.* 2009, 276, 46–52; b) L. Larush, V. Borgel, E. Markevich, O. Haik, E. Zinigrad, D. Aurbach, G. Semrau, M. Schmidt, *J. Power Sources* 2009, 189, 217–223; c) W. Xu, L.-M. Wang, R. A. Nieman, C. A. Angell, *J. Phys. Chem. B* 2003, 107, 11749–11756; d) D. Zhao, Z. Fei, R. Scopelliti, P. J. Dyson, *Inorg. Chem.* 2004, 43, 2197–2205.
- [4] a) M. Yang, J.-N. Zhao, Q.-S. Liu, L.-X. Sun, P.-F. Yan, Z.-C. Tan, U. Welz-Biermann, *Phys. Chem. Chem. Phys.* **2011**, *13*, 199–206; b) J. H. Davis, Jr., *Chem. Lett.* **2004**, *33*, 1072–1077.
- [5] a) M. Amereller, T. Schedelbauer, D. Moosbauer, C. Schreiner, C. Stock, F. Wudy, S. Zugmann, H. Hammer, A. Maurer, R. M. Gschwind, H.-D. Wiemhöfer, M. Winter, *Prog. Solid State Chem.* **2014**, *42*, 39–56; b) C. Schreiner, M. Amereller, H. J. Gores, *Chem. Eur. J.* **2009**, *15*, 2270–2272; c) J. S. Yadav, B. V. S. Reddy, A. K. Basak, A. V. Narsaiah, *Tetrahedron Lett.* **2003**, *44*, 2217–2220.
- [6] P. Wasserscheid, in Handb. Green Chem. Vol. 6 (Ed.: W.-V. V. G. Co), Weinheim, 2010, pp. 65–91.
- [7] A. E. Visser, J. D. Holbrey, R. D. Rogers, Chem. Commun. 2001, 2484– 2485.
- [8] a) K. Xu, Chem. Rev. 2004, 104, 4303-4417; b) J. Reiter, E. Paillard, L. Grande, M. Winter, S. Passerini, *Electrochim. Acta* 2013, *91*, 101-107; c) M. Wetjen, G.-T. Kim, M. Joost, G. B. Appetecchi, M. Winter, S. Passerini, *J. Power Sources* 2014, 246, 846-857.
- [9] A. Westerholt, M. Weschta, A. Bösmann, S. Tremmel, Y. Korth, M. Wolf, E. Schlücker, N. Wehrum, A. Lennert, M. Uerdingen, W. Holweger, S. Wartzack, P. Wasserscheid, ACS Sustainable Chem. Eng. 2015, 3, 797–808.
- [10] S. Caporali, P. Marcantelli, C. Chiappe, C. S. Pomelli, Surf. Coat. Technol. 2015, 264, 23–31.
- [11] F. Wu, Q. Zhu, R. Chen, N. Chen, Y. Chen, L. Li, R. Soc. Chem. 2015, 6, 7274-7283.
- [12] a) R.-S. Kühnel, M. Lübke, M. Winter, S. Passerini, A. Balducci, *J. Power Sources* 2012, *214*, 178–184; b) M. Kunze, S. Jeong, E. Paillard, M. Winter, S. Passerini, *J. Phys. Chem. C* 2010, *114*, 12364–12369; c) T. Placke, O. Fromm, S. F. Lux, P. Bieker, S. Rothermel, H.-W. Meyer, S. Passerini, M. Winter, *J. Electrochem. Soc.* 2012, *159*, A1755–A1765; d) B. Rupp, M. Schmuck, A. Balducci, M. Winter, W. Kern, *Eur. Polym. J.* 2008, *44*, 2986–2990.
- [13] a) H. Srour, H. Rouault, C. C. Santini, Y. Chauvin, Green Chem. 2013, 15, 1341–1347; b) P. Wasserscheid, W. Keim, Angew. Chem. 2000, 112, 3926–3945.

Chem. Eur. J. **2017**, 23, 1–5

1-5 www.chemeurj.org

rg

© 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

These are not the final page numbers! **77** 



- [14] a) S. I. Lall-Ramnarine, A. Castano, G. Subramaniam, M. F. Thomas, J. F. Wishart, *Radiat. Phys. Chem.* 2009, *78*, 1120–1125; b) N. Madria, T. A. Arunkumar, N. G. Nair, A. Vadapalli, Y.-W. Huang, S. C. Jones, V. P. Reddy, *J. Power Sources* 2013, *234*, 277–284.
- [15] K. R. Seddon, A. Stark, M.-J. Torres, Pure Appl. Chem. 2000, 72, 2275– 2287.
- [16] a) Z. Zhang, X. Gao, L. Yang, *Chin. Sci. Bull.* 2005, *50*, 2005–2009; b) C. P. Fredlake, J. M. Crosthwaite, D. G. Hert, S. N. V. K. Aki, J. F. Brennecke, *J. Chem. Eng. Data* 2004, *49*, 954–964.
- [17] D. M. Fox, J. W. Gilman, A. B. Morgan, J. R. Shields, P. H. Maupin, R. E. Lyon, H. C. D. Long, P. C. Trulove, *Ind. Eng. Chem. Res.* 2008, 47, 6327–6332.
- [18] a) B. Dilasari, Y. Jung, J. Sohn, S. Kim, K. Kwon, Int. J. Electrochem. Sci. 2016, 11, 1482-1495; b) A. Eftekhari, Y. Liu, P. Chen, J. Power Sources

**2016**, *334*, 221–239; c) R. Hagiwara, J. S. Lee, *Electrochemistry* **2007**, *75*, 23–34; d) S. Keskin, D. Kayrak-Talay, U. Akman, Ö. Hortacsu, *J. Supercrit. Fluids* **2007**, *43*, 150–180; e) S. Seki, Y. Ohno, Y. Kobayashi, H. Miyashiro, A. Usami, Y. Mita, H. Tokuda, M. Watanabe, K. Hayamizu, S. Tsuzuki, M. Hattori, N. Terada, *J. Electrochem. Soc.* **2007**, *154*, A173–A177; f) O. A. El Seoud, A. Koschella, L. C. Fidale, S. Dorn, T. Heinze, *Biomacromolecules* **2007**, *8*, 2629–2647.

Manuscript received: September 21, 2016 Accepted Article published: January 9, 2017 Final Article published: **I**, 0000

urj.org



# COMMUNICATION

IL? Better! The synthesis and purification of imidazolium-based ionic liquids (ILs) with boron-containing anions is reported. It was possible to shorten the reaction and purification times, to avoid the use of acetonitrile as processing solvent, and to increase the yield compared to the known procedure for bis(oxalato)borate-containing ILs. Flashpoints of the ILs could be exactly determined by the continuously closed-cup flashpoint method.



### lonic Liquids

P. Schmitz, R. Jakelski, K. Jalkanen, M. Winter, P. Bieker\*



Synthesis of High-Purity Imidazolium 🖳 Tetrafluoroborates and Bis(oxalato)borates