Electronic Supporting Information:

Cellulose solubilities in carboxylate-based ionic liquids

Bin Zhao, Lasse Greiner,*a,b and Walter Leitner*a,c

Table 1  The water content of ionic liquids before dissolving cellulose

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* They are solid, no water content.
* No water content, due to the high viscosity.

Table 2  Appearance of synthesized carboxylate-based structures

Experimental details and characterisation of carboxylate-based structures:

To get the intermediate 1,3-dimethylimidazolium-2-carboxylate, a few modifications was made according to the literature[ J. D. Holbrey, W. M. Reichert, I. Tkatchenko, E. Bouajila, O. Walter, I. Tommasi, R. D. Rogers, Chemical Communications 2003, 28.]. 10 mL 1,3-dimethylimidazole, 15 mL dimethylcarbonate and 20 mL methanol were added into a 75 mL autoclave, then heated up to 373 K for 24 h. After removing low boiling point compounds in vacuum and washing with acetone, 10.5 g the pure intermediate 1,3-dimethylimidazolium-2-carboxylate was obtained, yield: 59.7 %. Generally, 2.8 g intermediate was dissolved with 20 mL water or ethanol-water (10 mL-10 mL) as solvent, then 20 mmol carboxylic acid was added. At 343 K, the solution was stirred over 3 hours. After removal of the solvent, pure product was obtained quantitatively.

1,3-Dimethylimidazolium-2-carboxylate

^H-NMR(400 MHz; D2O; δ/ppm): 3.97 (s, 6H, NCH3), 7.35 (s, 2H, NCHN). It conforms the literature.

1,3-Dimethylimidazolium formate 1a: ^1H-NMR(400 MHz; DMSO-d6; δ/ppm): 3.86 (s, 6H, NCH3), 7.79 (d, 3J(H,H)=1.6 Hz, 2H, NCHN), 8.60 (s, 1H, HCOO), 9.70 (s, 1H, NCHN)
13C-NMR (100 MHz; DMSO-d$_6$; δ/ppm): 35.43 (NCH$_2$), 123.38 (NCHCHN), 137.76 (NCHN), 165.47 (HCOO).

1,3-Dimethylimidazolium acetate 1b: $^1$H-NMR (400 MHz; DMSO-d$_6$; δ/ppm): 1.57 (s, 3H, OOCCH$_3$), 3.83 (s, 6H, NCH$_3$), 7.80 (d, 3J(H,H)=1.6 Hz, 2H, NCHCHN), 10.02 (1H, s, NCHN).

13C-NMR (100 MHz; DMSO-d$_6$; δ/ppm): 26.23 (OOCCH$_3$), 35.35 (NCH$_3$), 123.34 (NCHCHN), 138.27 (NCHN), 173.08 (CH$_2$COO).

1,3-Dimethylimidazolium propionate 1c: $^1$H-NMR (400 MHz; DMSO-d$_6$; δ/ppm): 0.87 (q, 3J(H,H)=1.1 Hz, 2H, CH$_2$CH$_3$), 1.82 (q, 3J(H,H)=7.2 Hz, 3J=11.1 Hz, 2H, CH$_2$CH$_3$), 3.87 (s, 6H, NCH$_3$), 7.84 (s, 2H, NCHCHN), 10.17 (1H, s, NCHN).

13C-NMR (100 MHz; DMSO-d$_6$; δ/ppm): 11.49 (CH$_2$CH$_3$), 31.67 (CH$_2$CH$_3$), 35.30 (NCH$_3$), 123.34 (NCHCHN), 138.45 (NCHN), 176.42 (CH$_2$COO).

1,3-Dimethylimidazolium butyrate 1d: $^1$H-NMR (400 MHz; DMSO-d$_6$; δ/ppm): 0.79 (t, 3J(H,H)=7.2 Hz, 3H, CH$_2$CH$_3$), 1.40 (m, 2H, CH$_2$CH$_3$), 1.79 (t, 3J(H,H)=7.2 Hz, 2H, CH$_2$CH$_3$), 3.87 (s, 6H, NCH$_3$), 7.76 (d, 3J(H,H)=1.6 Hz, 2H, NCHCHN), 10.14 (1H, s, NCHN).

13C-NMR (100 MHz; DMSO-d$_6$; δ/ppm): 14.56 (CH$_2$CH$_3$), 19.87 (CH$_2$CH$_3$), 35.40 (NCH$_3$), 41.35 (OOCCH$_3$), 123.32 (NCHCHN), 138.22 (NCHN), 175.29 (CH$_2$COO).

1,3-Dimethylimidazolium iso-butyrate 1e: $^1$H-NMR (400 MHz; DMSO-d$_6$; δ/ppm): 0.90 (d, 3J(H,H)=6.8 Hz, 6H, CH(CH$_3$)$_2$), 1.97 (septet, 3J(H,H)=6.8 Hz, 1H, CHCOO), 3.87 (s, 6H, NCH$_3$), 7.80 (d, 3J(H,H)=1.6 Hz, 2H, NCHCHN), 10.14 (1H, s, NCHN).

13C-NMR (100 MHz; DMSO-d$_6$; δ/ppm): 20.98 (CH(CH$_3$)$_2$), 35.35 (NCH$_3$), 36.80 (CH$_3$CH$_2$CH$_2$), 123.33 (NCHCHN), 138.46 (NCHN), 179.02 (CHCOO).

1,3-Dimethylimidazolium mono-maleate 1f: $^1$H-NMR (400 MHz; DMSO-d$_6$; δ/ppm): 3.85 (s, 6H, NCH$_3$), 6.02 (s, 2H, CHCH), 7.68 (s, 2H, NCHCHN), 9.05 (s, 1H, NCHN).

13C-NMR (100 MHz; DMSO-d$_6$; δ/ppm): 35.66 (NCH$_3$), 123.45 (NCHCHN), 136.17 (CHCH), 137.07 (NCHN), 167.21 (CHCOO).

Bis(1,3-dimethylimidazolium) maleate 1g: $^1$H-NMR (400 MHz; DMSO-d$_6$; δ/ppm): 3.89 (s, 12H, NCH$_3$), 5.46 (s, 2H, CHCH), 7.72 (s, 4H, NCHCHN), 9.98 (s, 2H, NCHN).

13C-NMR (100 MHz; DMSO-d$_6$; δ/ppm): 35.41 (NCH$_3$), 123.10 (NCHCHN), 130.56 (CHCH), 139.12 (NCHN), 171.18 (CHCOO).

1,3-Dimethylimidazolium mono-succinate 1h: $^1$H-NMR (400 MHz; DMSO-d$_6$; δ/ppm): 2.23 (s, 4H, CH$_2$CH$_3$), 3.85 (s, 6H, NCH$_3$), 7.69 (s, 2H, NCHCHN), 9.08 (s, 1H, NCHN).

13C-NMR (100 MHz; DMSO-d$_6$; δ/ppm): 32.91 (CH$_2$CH$_3$), 35.65 (NCH$_3$), 123.45 (NCHCHN), 137.11 (NCHN), 175.38 (CH$_2$COO).

Bis(1,3-dimethylimidazolium) succinate 1i: $^1$H-NMR (400 MHz; DMSO-d$_6$; δ/ppm): 1.97 (s, 4H, CH$_2$CH$_3$), 3.87 (s, 12H, NCH$_3$), 7.75 (s, 4H, NCHCHN), 9.99 (s, 2H, NCHN).

13C-NMR (100 MHz; DMSO-d$_6$; δ/ppm): 35.45 (NCH$_3$), 37.00 (CH$_2$CH$_3$), 123.32 (NCHCHN), 138.42 (NCHN), 176.81 (CH$_2$COO).

According to the method of synthesizing 1,3-dimethylimidazolium carboxylate and the literature[ C. Rijksen, R. D. Rogers, The Journal of Organic Chemistry 2008, 73, 5582 & B. Bantu, G. M. Pawar, K. Wurst, U. Decker, A. M. Schmidt, M. R. Buchmeiser, European Journal of Inorganic Chemistry 2009, 2009, 1970], 1-ethyl-3-methylimidazolium carbonate was prepared. The procedure is: 10 mL 1-ethylmethylcarboxylate, 20 mL dimethylcarbonate, and 20 mL methanol were added into a 75 mL autoclave. Then the solution was heated up to 393 K for 24 hours. After reaction, the solvent was removed with reduced pressure (keep it less than 40 °C). After washing with acetone (10 mL ×3), the intermediate 1-ethyl-3-methylimidazolium-2-carboxylate was obtained, 8.1 g, yield: 50.5 %. Then 3.08 g intermediate pressure and washing with acetone, pure product 1-ethyl-3-methylimidazolium hydrogen carbonate was obtained.

1,3-Dimethylimidazolium formate 2a: $^1$H-NMR (400 MHz; DMSO-d$_6$; δ/ppm): 1.39 (t, 3J(H,H)=7.2 Hz, 3H, CH$_2$CH$_3$), 3.87 (s, 3H, NCH$_3$), 4.21 (q, 3J(H,H)=7.2 Hz, 2H, CH$_2$CH$_3$), 7.82 (s, 1H, NCH), 7.92 (s, 1H, NCH), 8.63 (s, 1H, HCOO), 9.86 (s, 1H, NCHN).

13C-NMR (100 MHz; DMSO-d$_6$; δ/ppm): 15.19 (CH$_2$CH$_3$), 35.53 (NCH$_3$), 43.97 (NCH$_2$), 122.04 (NCH), 123.57 (NCH), 137.16 (NCHN), 165.49 (HCOO).
1-Ethyl-3-methylimidazolium acetate 2b: \(^1^H\)-NMR (400 MHz; DMSO-\(d_6\); \(\delta/ppm\)): 1.38 (t, \(J(H,H)=7.2\) Hz, 3H, CH\(_3\)CH\(_3\)), 1.58 (s, 3H, OOC\(CH_3\)), 3.89 (s, 3H, NCH\(_3\)), 4.23 (q, \(J(H,H)=7.2\) Hz, 2H, CH\(_2\)CH\(_3\)), 7.90 (d, \(J(H,H)=1.6\) Hz, 1H, NCH), 8.01 (d, \(J(H,H)=1.6\) Hz, 1H, NCH), 10.37 (s, 1H, NCHN).

\(^1^C\)-NMR (100 MHz; DMSO-\(d_6\); \(\delta/ppm\)): 15.27 (CH2CH3), 26.29 (OOC\(CH_3\)), 35.37 (NCH3), 43.85 (NCH2), 122.08 (NCH), 123.58 (NCH), 137.95 (NCHN), 173.42 (CH3COO).

1-Ethyl-3-methylimidazolium propionate 2c: \(^1^H\)-NMR (400 MHz; DMSO-\(d_6\); \(\delta/ppm\)): 0.87 (t, \(J(H,H)=7.6\) Hz, 3H, CH\(_2\)CH\(_3\)), 1.40 (t, \(J(H,H)=7.2\) Hz, 3H, NCH\(_3\)), 1.79 (q, \(J(H,H)=7.6\) Hz, 2H, OOC\(CH_3\)), 3.88 (s, 3H, NCH), 4.22 (q, \(J(H,H)=7.2\) Hz, 2H, CH\(_2\)CH\(_3\)), 7.78 (s, 1H, NCH), 7.88 (s, 1H, NCH), 10.11 (s, 1H, NCHN).

\(^1^C\)-NMR (100 MHz; DMSO-\(d_6\); \(\delta/ppm\)): 11.60 (CH\(_3\)CH\(_2\)), 15.27 (NCH\(_3\)), 31.75 (OOC\(CH_3\)), 35.47 (NCH\(_3\)), 43.91 (NCH\(_2\)), 121.92 (NCH), 123.47 (NCH), 137.60 (NCHN), 176.00 (CH\(_3\)COO).

1-Ethyl-3-methylimidazolium butyrate 2d: \(^1^H\)-NMR (400 MHz; DMSO-\(d_6\); \(\delta/ppm\)): 0.79 (t, \(J(H,H)=7.2\) Hz, 3H, CH\(_2\)CH\(_3\)), 1.40 (m, 5H, NCH\(_3\)CH\(_3\)), 1.79 (t, \(J(H,H)=7.2\) Hz, 2H, OOC\(CH_3\)), 3.88 (s, 3H, NCH), 4.22 (q, \(J(H,H)=7.2\) Hz, 2H, CH\(_2\)CH\(_3\)), 7.82 (s, 1H, NCH), 7.92 (s, 1H, NCH), 10.25 (s, 1H, NCHN).

\(^1^C\)-NMR (100 MHz; DMSO-\(d_6\); \(\delta/ppm\)): 14.59 (CH\(_2\)CH\(_2\)CH\(_3\)), 15.24 (NCH\(_3\)), 35.42 (NCH\(_3\)), 41.42 (OOC\(CH_3\)), 43.88 (NCH\(_2\)), 121.95 (NCH), 123.49 (NCH), 137.79 (NCHN), 175.44 (CH\(_3\)COO).

According to the literature [Z. Q. Zheng, J. Wang, T. H. Wu, X. P. Zhou, Advanced Synthesis & Catalysis 2007, 349, 1095], a few modifications were made to get pure product. Under argon protection, 7.0 g N,N-diethylammonium chloride (it was prepare by diethylamine with HCl gas, before use) was dissolved in 10 mL of water. After stirring overnight. After removing the low boiling point compounds under reduced pressure and washing with acetone, the pure intermediate was obtained.

\(^1^H\)-NMR (100 MHz; DMSO-\(d_6\); \(\delta/ppm\)): 1.20 (t, \(J(H,H)=7.2\) Hz, 6H, CH\(_2\)CH\(_3\)), 2.99 (s, 6H, NCH\(_3\)), 3.34 (q, \(J(H,H)=7.2\) Hz, 4H, NCH\(_2\)), 8.58 (s, 1H, NCHN), 121.99 (NCH), 123.58 (NCH), 136.40 (NCHN), 175.47 (CH\(_3\)COO).

Bis(1-ethyl-3-methylimidazolium) succinate 2i: \(^1^H\)-NMR (400 MHz; DMSO-\(d_6\); \(\delta/ppm\)): 1.39 (t, \(J(H,H)=7.2\) Hz, 6H, NCH\(_3\)), 1.97 (s, 4H, CH\(_2\)CH\(_3\)), 3.88 (s, 6H, NCH\(_3\)), 4.23 (q, \(J(H,H)=7.2\) Hz, 4H, CH\(_2\)CH\(_3\)), 7.79 (s, 2H, NCH), 7.88 (s, 2H, NCH), 10.24 (s, 2H, NCHN).

\(^1^C\)-NMR (100 MHz; DMSO-\(d_6\); \(\delta/ppm\)): 15.26 (NCH\(_3\)), 35.44 (NCH\(_3\)), 37.25 (CH\(_2\)CH\(_3\)), 43.87 (NCH\(_2\)), 121.87 (NCH), 123.46 (NCH), 137.89 (NCHN), 176.96 (CH\(_3\)COO).

According to the literature [Z. Q. Zheng, J. Wang, T. H. Wu, X. P. Zhou, Advanced Synthesis & Catalysis 2007, 349, 1095], a few modifications were made to get pure product. Under argon protection, 7.0 g N,N-diethylammonium chloride (it was prepare by diethylamine with HCl gas, before use) was dissolved in 10 mL of water. After stirring overnight. After removing the low boiling point compounds under reduced pressure and washing with acetone, the pure intermediate N,N-diethyl-N,N-dimethylammonium chloride were obtained, 8.5 g, yield: 90.1%. Then the intermediate went through the anion exchange resin IRA-400 (OH), to get the corresponding hydroxide. The hydroxide was neutralized with stoichiometric acid. After removal of water under reduced pressure, the target molecule was obtained.
N,N-Diethyl-N,N-dimethylammonium acetate 3b: $^1$H-NMR (400 MHz; DMSO-$d_6$; $\delta$/ppm): 1.19 ($t$, $^3$J(H,H)=7.2 Hz, 6H, CH$_2$CH$_3$), 1.54 (s, 3H, OOCCH$_3$), 3.00 (s, 6H, NCH$_3$), 3.37 ($q$, $^3$J(H,H)=7.2 Hz, 4H, NCH$_2$).

$^{13}$C-NMR (100 MHz; DMSO-$d_6$; $\delta$/ppm): 7.74 (CH$_2$CH$_3$), 25.91 (OOCCH$_3$), 48.65 (NCH$_3$), 57.52 (NCH$_2$), 172.52 (CH$_2$COO).

N,N-Diethyl-N,N-dimethylammonium propionate 3c: $^1$H-NMR (400 MHz; DMSO-$d_6$; $\delta$/ppm): 0.85 ($t$, $^3$J(H,H)=7.6 Hz, 3H, CH$_2$CH$_3$), 1.20 ($t$, $^3$J(H,H)=7.2 Hz, 6H, NCH$_2$CH$_3$), 1.77 ($q$, $^3$J(H,H)=7.6 Hz, 2H, CH$_2$CH$_3$), 3.01 (s, 6H, NCH$_3$), 3.36 ($q$, $^3$J(H,H)=7.2 Hz, 4H, NCH$_2$).

$^{13}$C-NMR (100 MHz; DMSO-$d_6$; $\delta$/ppm): 7.74 (NCH$_2$CH$_3$), 11.55 (CH$_2$CH$_3$), 31.58 (CH$_2$CH$_3$), 48.66 (NCH$_3$), 57.55 (NCH$_2$), 175.50 (CH$_2$COO).

N,N-Diethyl-N,N-dimethylammonium butyrate 3d: $^1$H-NMR (400 MHz; DMSO-$d_6$; $\delta$/ppm): 0.78 ($t$, $^3$J(H,H)=7.2 Hz, 3H, CH$_2$CH$_2$CH$_3$), 1.20 ($t$, $^3$J(H,H)=7.2 Hz, 6H, NCH$_2$CH$_3$), 1.92 ($m$, $^3$J(H,H)=6.8 Hz, 1H, (CH$_2$)$_2$CH), 2.99 (s, 6H, NCH$_3$), 3.35 ($q$, $^3$J(H,H)=7.2 Hz, 4H, NCH$_2$).

$^{13}$C-NMR (100 MHz; DMSO-$d_6$; $\delta$/ppm): 7.74 (NCH$_2$CH$_3$), 14.66 (CH$_2$CH$_3$), 20.00 (OOCCH$_2$CH$_2$), 41.58 (OOCCH$_2$), 48.69 (NCH$_3$), 57.59 (NCH$_2$), 174.58 (CH$_2$COO).

N,N-Diethyl-N,N-dimethylammonium iso-butyrate 3e: $^1$H-NMR (400 MHz; DMSO-$d_6$; $\delta$/ppm): 0.87 ($d$, $^3$J(H,H)=6.8 Hz, 6H, CH(CH$_3$)$_2$), 1.20 ($t$, $^3$J(H,H)=7.2 Hz, 6H, NCH$_2$CH$_3$), 3.00 (s, 6H, NCH$_3$), 3.30 ($q$, $^3$J(H,H)=7.2 Hz, 4H, NCH$_2$), 6.04 (s, 2H, CHCH).

$^{13}$C-NMR (100 MHz; DMSO-$d_6$; $\delta$/ppm): 7.73 (CH$_2$CH$_3$), 21.05 (CH(CH$_3$)$_2$), 36.72 ((CH$_3$)$_2$CH), 48.70 (NCH$_3$), 57.61 (NCH$_2$), 178.20 (CHCOO).

N,N-Diethyl-N,N-dimethylammonium mono-maleate 3f: $^1$H-NMR (400 MHz; DMSO-$d_6$; $\delta$/ppm): 1.22 ($t$, $^3$J(H,H)=7.2 Hz, 6H, CH$_2$CH$_3$), 2.96 (s, 6H, NCH$_3$), 3.30 ($q$, $^3$J(H,H)=7.2 Hz, 4H, NCH$_2$), 6.04 (s, 1H, CHCH).

$^{13}$C-NMR (100 MHz; DMSO-$d_6$; $\delta$/ppm): 7.72 (CH$_2$CH$_3$), 48.86 (NCH$_3$), 57.93 (NCH$_2$), 136.04 (CHCH), 167.22 (CHCOO).

Bis(N-diethyl-N,N-dimethylammonium) maleate 3g: $^1$H-NMR (400 MHz; DMSO-$d_6$; $\delta$/ppm): 1.19 ($t$, $^3$J(H,H)=7.2 Hz, 12H, CH$_2$CH$_3$), 3.01 (s, 12H, NCH$_3$), 3.38 ($q$, $^3$J(H,H)=7.2 Hz, 8H, NCH$_2$), 5.27 (s, 2H, CHCH).

$^{13}$C-NMR (100 MHz; DMSO-$d_6$; $\delta$/ppm): 7.80 (CH$_2$CH$_3$), 48.71 (NCH$_3$), 57.45 (NCH$_2$), 130.18 (CHCH), 170.47 (CHCOO).

N,N-Diethyl-N,N-dimethylammonium mono-succinate 3h: $^1$H-NMR (400 MHz; DMSO-$d_6$; $\delta$/ppm): 1.22 ($t$, $^3$J(H,H)=7.2 Hz, 6H, CH$_2$CH$_3$), 2.96 (s, 6H, NCH$_3$), 3.30 ($q$, $^3$J(H,H)=7.2 Hz, 4H, NCH$_2$).

$^{13}$C-NMR (100 MHz; DMSO-$d_6$; $\delta$/ppm): 7.72 (CH$_2$CH$_3$), 33.03 (CH$_2$CH$_2$), 48.83 (NCH$_3$), 57.87 (NCH$_2$), 175.36 (CH$_2$COO).

Bis(N,N-diethyl-N,N-dimethylammonium) succinate 3i: $^1$H-NMR (400 MHz; DMSO-$d_6$; $\delta$/ppm): 1.19 ($t$, $^3$J(H,H)=7.2 Hz, 12H, CH$_2$CH$_3$), 1.86 (s, 8H, CH$_2$CH$_3$), 3.01 (12H, s, NCH$_3$), 3.37 ($q$, $^3$J(H,H)=7.2 Hz, 4H, NCH$_2$).

$^{13}$C-NMR (100 MHz; DMSO-$d_6$; $\delta$/ppm): 7.76 (CH$_2$CH$_3$), 37.62 (CH$_2$CH$_2$), 48.63 (NCH$_3$), 57.48 (NCH$_2$), 176.37 (CH$_2$COO).