Electronic Supplementary Information

Extended dissolution studies of cellulose in imidazolium based ionic liquids

Jürgen Vitz,[a,b] Tina Erdmenger,[a,b] Claudia Haensch,[a,b] Stephanie Hornig[#] and Ulrich S. Schubert*[a,b,c]

[a] Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology, P. O. Box 513, NL-5600 MB Eindhoven, The Netherlands, Tel.: +31 40 247 5303, Fax: +31 40 247 4186;
E-mail: u.s.schubert@tue.nl, www.schubert-group.com
[b] Dutch Polymer Institute (DPI), P.O. Box 902, NL-5600 AX Eindhoven, The Netherlands, Tel.: +31 40 247 56 29, Fax: +31 40 247 2462;
[c] Laboratory of Organic and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Humboldtstr. 10, D-07743 Jena, Germany,
Tel.: +49(0) 3641 9482 00, Fax:+49(0) 3641 9482 02;
E-mail: ulrich.schubert@uni-jena.de
[#] Current address: Kompetenzzentrum Polysaccharidforschung, Friedrich-Schiller-University Jena, Humboldtstr. 10, 07743 Jena, Germany

Content

1 Analytical data

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury spectrometer (400 MHz) or on a Varian Gemini spectrometer (300 MHz). Chemical shifts are given in ppm downfield from TMS.

IR spectra were recorded on a Perkin Elmer 1600 FT-IR ATR spectrometer. Also a Bruker TENSOR 37™ equipped with a HTS-XT (High Throughput Screening eXTension) compartment and a HYPERION™ 3000 microscope was used.

^{1}H NMR: chemical shift (multiplicity, number of protons, assignment, coupling constant).

[C_2MIM]F 1-ethyl-3-methylimidazolium fluoride:

^{1}H NMR: δ_H(300 MHz, DMSO) 1.37 (t, 3H, *J* = 7.2 Hz), 3.81 (s, 3H), 4.14 (q, 2H, *J* = 7.2 Hz), 7.65 (bs, 2H), 10.14 (bs, 1H).

[C_2MIM]Br 1-ethyl-3-methylimidazolium bromide:

^{1}H NMR: δ_H(300 MHz, DMSO) 1.39 (t, 3H, *J* = 7.4 Hz), 3.83 (s, 3H), 4.18 (q, 2H, *J* = 7.4 Hz), 7.69 (s, 1H), 7.78 (s, 1H), 9.15 (s, 1H). FT-IR: ν_{max}/cm^{-1} 3420 (H_2O), 3144, 3071, 2983, 1628, 1570, 1452, 1336, 1167, 1089, 829, 753.

[C_3MIM]Br 1-methyl-3-propylimidazolium bromide:

^{1}H NMR: δ_H(300 MHz, DMSO) 0.84 (t, 3H, *J* = 7.4 Hz), 1.79 (dd, 3H, *J* = 7.3, 14.4 Hz), 3.86 (s, 3H), 4.14 (t, 2H, *J* = 7.1 Hz), 7.74 (s, 1H), 7.81 (s, 1H), 9.23 (s, 1H). FT-IR: ν_{max}/cm^{-1} 3137, 3058, 2964, 2876, 1568, 1458, 1386, 1336, 1169, 1090, 753.

[C_4MIM]Br 1-butyl-3-methylimidazolium bromide: ^{1}H NMR: δ_H(300 MHz, DMSO) 0.89 (t, 3H, *J* = 7.3 Hz), 1.25 (m, 2H), 1.76 (m, 2H), 3.86 (d, 3H, *J* = 1.7 Hz), 4.18 (t, 2H, *J* = 7.2 Hz), 7.74 (s, 1H), 7.82 (s, 1H), 9.25 (s, 1H).

[C_5MIM]Br 1-methyl-3-pentylimidazolium bromide:

^{1}H NMR: δ_H(300 MHz, $CDCl_3$) 0.74 (bs, 3H), 1.20 (s, 4H), 1.78 (d, 2H, *J* = 6.8 Hz), 4.00 (s, 3H), 4.20 (t, 2H, *J* = 7.3 Hz), 7.47 (s, 1H), 7.62 (s, 1H), 10.18 (s, 1H).

[C_6MIM]Br 1-hexyl-3-methylimidazolium bromide:

^{1}H NMR: δ_H(300 MHz, DMSO) 0.85 (s, 3H), 1.25 (s, 6H), 1.76 (s, 2H), 3.85 (d, 3H, *J* = 4.0 Hz), 4.16 (s, 2H), 7.72 (s, 1H), 7.79 (s, 1H), 9.19 (s, 1H).

[C_7MIM]Br 1-heptyl-3-methylimidazolium bromide:
^{1}H NMR: δ_H(300 MHz, DMSO) 0.84 (bs, 3H), 1.24 (s, 8H), 1.77 (s, 2H), 3.85 (s, 3H), 4.16 (t, 2H, J = 7.2 Hz), 7.73 (s, 1H), 7.80 (s, 1H), 9.20 (s, 1H).

[C_8MIM]Br 1-methyl-3-octylimidazolium bromide: ^{1}H NMR: δ_H(300 MHz, DMSO) 0.84 (t, 3H, J = 6.7 Hz), 1.24 (s, 10H), 1.76 (s, 2H), 3.84 (s, 3H), 4.15 (t, 2H, J = 7.2 Hz), 7.72 (d, 1H, J = 1.7 Hz), 7.78 (d, 1H, J = 1.7 Hz), 9.17 (s, 1H).

[C_9MIM]Br 1-methyl-3-nonylimidazolium bromide:
^{1}H NMR: δ_H(300 MHz, DMSO) 0.84 (t, 3H, J = 6.7 Hz), 1.23 (s, 12H), 1.76 (s, 2H), 3.84 (s, 3H), 4.15 (t, 2H, J = 7.2 Hz), 7.72 (d, 1H, J = 1.7 Hz), 7.79 (t, 1H, J = 1.8 Hz), 9.19 (s, 1H).

[C_{10}MIM]Br 1-decyl-3-methylimidazolium bromide:
^{1}H NMR: δ_H(300 MHz, DMSO) 0.83 (s, 3H), 1.23 (s, 14H), 1.76 (s, 2H), 3.85 (s, 2H), 4.15 (s, 3H), 7.72 (s, 1H), 7.79 (s, 1H), 9.20 (s, 1H).

[AllylMIM]Br 1-allyl-3-methylimidazolium bromide:
^{1}H NMR δ_H(300 MHz, $CDCl_3$) 4.08 (s, 3H), 4.98 (d, 2H, J = 6.3 Hz), 5.43 (t, 2H, J = 13.0 Hz), 5.99 (d, 1H, J = 6.5 Hz), 7.48 (s, 1H), 7.67 (s, 1H), 10.19 (s, 1H). FT-IR: ν_{max}/cm^{-1} 3050, 2959, 2934, 2874, 1568, 1465, 1382, 1253, 1170, 742, 657.

[DiMIM]I 1,3-dimethylimidazolium iodide: ^{1}H NMR δ_H(400 MHz, DMSO) 3.84 (s, 6H), 7.66 (s, 2H), 9.02 (s, 1H).

[C_4MIM]I 1-butyl-3-methylimidazolium iodide:
^{1}H NMR: δ_H(300 MHz, $CDCl_3$) 0.91 (t, 3H, J = 8.2 Hz), 1.43–1.27 (m, 2H), 1.83–1.93 (m, 2H), 4.05 (s, 3H), 4.30 (pt, 2H, J = 7.4), 7.51 (pt, 1H, J = 1.7 Hz), 7.59 (pt, 1H, J = 1.7 Hz), 9.92 (s, 1H). FT-IR: ν_{max}/cm^{-1} 3468 (H_2O), 3140, 3077, 2958, 2933, 2872, 1568, 1462, 1382, 1337, 1165, 820, 749.

[DiMIM]Me_2PO_4 1,3-dimethylimidazolium dimethyl-phosphate: ^{1}H NMR: δ_H(400 MHz, $CDCl_3$) 3.24 (s, 3H), 3.26 (s, 3H), 3.83 (s, 6H), 7.70 (d, 2H, J = 1.6 Hz), 9.31 (s, 1H). FT-IR: ν_{max}/cm^{-1} 3153, 3068, 2945, 2838, 1575, 1462, 1241, 1179, 1091, 1036, 850, 770, 731.

[C_2MIM]Et_2PO_4 1-ethyl-3-methylimidazolium diethyl-phosphate: ^{1}H NMR: δ_H(400 MHz, DMSO) 1.04 (t, 6H, J = 7.1 Hz), 1.39 (t, 3H, J = 7.3 Hz), 3.59 (p, 4H, J = 7.0 Hz), 3.84 (s, 3H), 4.18 (q, 2H, J = 7.3 Hz), 7.71 (s, 1H), 7.80 (s, 1H), 9.38 (s, 1H). FT-IR:

ν_{max}/cm^{-1} 3375 (H_2O), 3073, 2974, 2934, 2893, 1572, 1232, 1173, 1107, 1082, 1043, 935, 779, 733.

[C_4MIM]Bu_2PO_4 1-butyl-3-methylimidazolium dibutyl-phosphate: ^{1}H NMR: δ_H(400 MHz, DMSO) 0.85 (m, 9H), 1.18–1.50 (m, 10H), 1.69–1.82 (m, 2H), 3.54–3.67 (m, 4H), 3.84 (s, 3H), 4.15 (t, 2H, *J* = 7.2 Hz), 7.71 (s, 1H), 7.78 (s, 1H), 9.36 (s, 1H). FT-IR: ν_{max}/cm^{-1} 3387 (H_2O), 3078, 2959, 2936, 2874, 1570, 1464, 1236, 1173, 1067, 1026, 1005, 974, 889, 820, 797, 733.

[C_2MIM]OAc 1-ethyl-3-methylimidazolium acetate:

^{1}H NMR: δ_H(400 MHz, DMSO) 1.39 (t, 5H, *J* = 7.3 Hz), 3.84 (s, 3H), 4.19 (q, 3H, *J* = 7.3 Hz), 7.72 (d, 1H, *J* = 1.6 Hz), 7.81 (s, 1H), 9.73–9.81 (m, 1H). FT-IR: ν_{max}/cm^{-1} 3362 (H_2O), 3073, 2981, 1562, 1451, 1427, 1384, 1331, 1172, 907, 759, 701, 667.

[C_4MIM]OAc 1-butyl-3-methylimidazolium acetate:

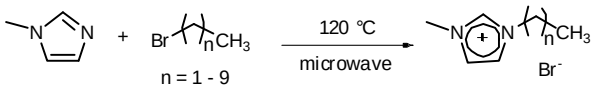
^{1}H NMR: δ_H(400 MHz, DMSO) 0.87 (t, 3H, *J* = 8.4 Hz), 1.23 (dq, 2H, *J* = 7.4, 14.7 Hz), 1.56 (s, 3H), 1.74 (dt, 2H, *J* = 7.4, 14.8 Hz), 3.85 (s, 4H), 4.11–4.23 (m, 2H), 7.73 (s, 1H), 7.79 (s, 1H), 9.72 (s, 1H).

[C_4MIM]NO_3 1-butyl-3-methylimidazolium nitrate: ^{1}H NMR: δ_H(300 MHz, DMSO) 0.90 (t, 3H, *J* = 7.3 Hz), 1.26 (dq, 2H, *J* = 7.3, 14.6 Hz), 1.66–1.84 (m, 2H), 3.85 (s, 3H), 4.16 (t, 2H, *J* = 7.2 Hz), 7.71 (pt, 1H, *J* = 1.7 Hz), 7.78 (pt, 1H, *J* = 1.8 Hz), 9.13 (s, 1H).

[C_4MIM]NTf_2 1-butyl-3-methylimidazolium bis(trifluoro-methylsulfonyl)imide: ^{1}H NMR: δ_H(400 MHz, DMSO) 0.78–0.96 (m, 3H), 1.23 (m, 2H), 1.75 (m, 2H), 3.82 (s, 3H), 4.14 (q, 2H, *J* = 3.6 Hz), 7.68 (s, 1H), 7.75 (s, 1H), 9.08 (s, 1H). FT-IR: ν_{max}/cm^{-1} 3457 (H_2O), 3017, 2971, 2946, 1738, 1729, 1456, 1435, 1365, 1353, 1229, 1217, 1204, 1183, 1132, 1053, 741, 654.

2 Tables

Table 1 Synthesized imidazolium based ionic liquids with different side chain lengths.



Ionic liquid	Reaction time (min)	Conversion (%)	T_{decomp} [b] (°C)	T_m [c] (°C)
$[C_2MIM]Br$	20	>99[a]	279	65
$[C_3MIM]Br$	30	>99[a]	277	-[d]
$[C_4MIM]Br$	10	>99[a]	269	-[d]
$[C_5MIM]Br$	20	99	273	-[d]
$[C_6MIM]Br$	10	>99[a]	268	-[d]
$[C_7MIM]Br$	10	>99[a]	263	-[d]
$[C_8MIM]Br$	10	>99[a]	262	2
$[C_9MIM]Br$	10	>99[a]	259	1
$[C_{10}MIM]Br$	10	>99[a]	271	10

[a] No starting material detectable (determined by ^1H NMR). [b] Temperature of thermal decomposition. [c] Melting point. [d] Melting point could not be determined by DSC.

Table 2 DP of cellulose samples after processing in $[C_4MIM]Cl$ under microwave heating.

IL	Temperature (°C)	Time (min)	DP
Avicel PH-101	-	-	398[a]
$[C_4MIM]Cl$	100	30	172[b]
	100	60	255[b]
	100	90	300[b]
	100	120	230[b]

[a] Before processing, [b] after regeneration.

3 Figures

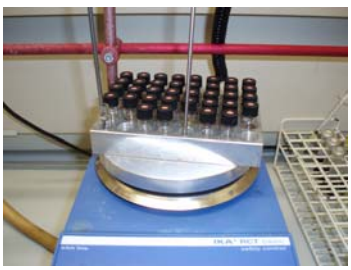


Fig. 1 Parallel setup to study the dissolution of cellulose.

Fig. 2 Dissolution of cellulose in [C_2MIM]Cl under microwave irradiation: a) 6 wt-% of cellulose, 100 °C, power between 60 and 140 W, b) 2 – 10 wt-% of cellulose, 140 °C, 80 W, 30 min, c) 2 – 10 wt-% of cellulose, 160 °C, 80 W, 30 min.

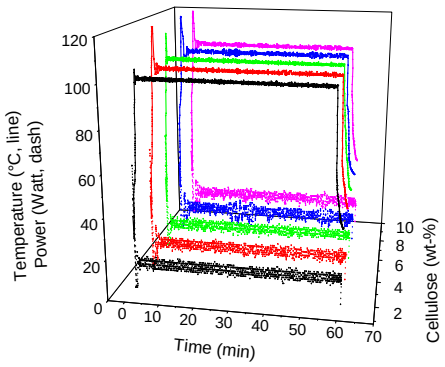
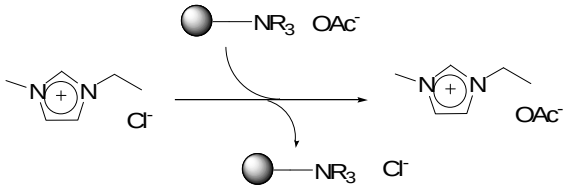
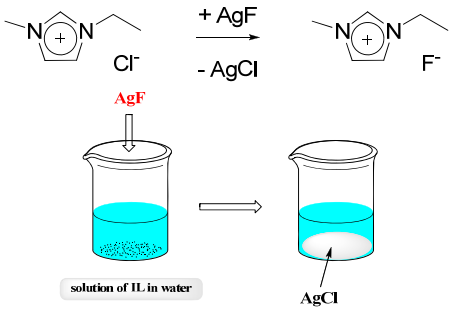


Fig. 3 Heating and power profiles for the dissolution of cellulose in [C_2MIM]Cl at different concentrations under microwave irradiation.

4 Schemes



Scheme 1 Schematic representation of the anion exchange with "Amberlite IRA-400".



Scheme 2 Schematic representation of the reaction scheme and schematic process of the anion exchange with AgF.