Green Chemistry

Ionic liquids: not always innocent solvents for cellulose

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Electronic Supplementary Information

1. General laboratory procedures

All reactions requiring an inert atmosphere were performed under a blanket of nitrogen gas, which was dried through a column of phosphorus pentoxide. All commercially acquired chemicals were obtained from Sigma-Aldrich, and were used without further purification unless otherwise stated. NMR spectra were recorded on Bruker Avance-400 (^{1}H NMR (400 MHz), ^{13}C (100 MHz), ^{7}Li (156 MHz)) NMR spectrometers. Chemical shifts are reported in ppm (relative to the DMSO-d6 residual peak). IR spectra were recorded on a Perkin Elmer spectrum 100 FTIR using an ATR inset with a diamond crystal. LSIMS mass spectrometry was performed on a Micromass AutoSpec Premier mass spectrometer. Melting point measurements were carried out on a Stanford Research Systems 'OptiMelt' automated melting point system, with a heating rate of 1 °C min^{-1}. Melting point values are uncorrected. Elemental analysis experiments were performed by London Metropolitan University.

2. Synthesis of ionic liquid and molten salt compounds

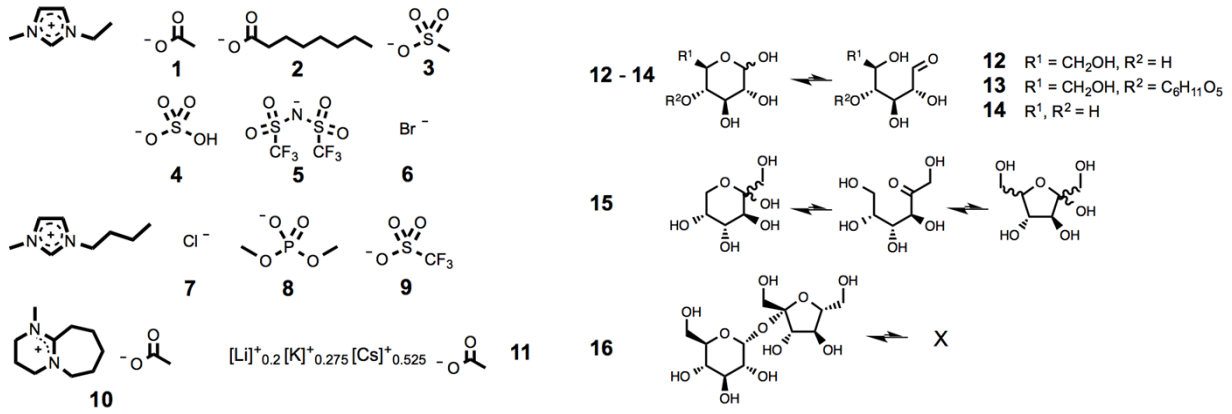


Fig. E1 Investigated ionic liquids (**1**-**10**), mixed inorganic eutectic salt, **11**, and carbohydrate model compounds (**12**-**16**).

1-Ethyl-3-methylimidazolium hydroxide aqueous solution. To a large sintered glass funnel was added 'Ambersep® 900 hydroxide form' ion exchange resin (8 kg, equivalent to 9.6 mol of [OH]$^{-}$). A 5 L dropping funnel was positioned above the sintered glass funnel, and charged with deionized water. Deionized water was passed through the resin and collected into a waste container, until the eluent had become neutral (pH 7). Subsequently, an aqueous ionic liquid solution was prepared by mixing 1-ethyl-3-methylimidazolium ethyl sulfate (1.70 Kg, 7.19 mol) with deionized water (1.7 L), in the dropping funnel. This solution was passed through the ion exchange column, collecting all alkaline material in three aliquots of ca. 5 L. Purities and crude concentrations of the aliquots were determined using HPLC. The second and third aliquots were found to contain impurities, and were discarded. In order to determine accurate concentrations of the first aliquot, titrations were performed against 1M aqueous HCl, neat acetic acid, and neat methanesulfonic acid. The concentration was found to be 0.33 mol dm^{-3}. This fraction contained aqueous 1-ethyl-3-methylimidazolium hydroxide (1.8 mol, 25%), as a pale yellow / colourless solution.

1-Ethyl-3-methylimidazolium acetate (**1a**). Aqueous 1-ethyl-3-methylimidazolium hydroxide (0.33 mol dm^{-3}, 3.00 Kg, 0.97 mol) was neutralized by careful addition of acetic acid (55.5 ml, 0.97 mol). The water was removed by rotary evaporation to yield 1-ethyl-3-methylimidazolium acetate (157 g, 95%) as a yellow viscous liquid. Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 9.96 (1H, s), 7.87 (1H, t, J = 2 Hz), 7.78 (1H, t, J = 2 Hz), 4.21 (2H, q, J = 7 Hz), 3.87 (3H, s), 1.57 (3H, s), 1.39 (3H, t, J = 7 Hz). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): δ 172.3, 136.7, 123.5, 121.9, 44.1, 35.6, 26.4, 15.2. *m/z* (LSIMS^{+}): 111 (100%) [C_2C_1im]$^{+}$, 69 (11%) [H_2im]$^{+}$, 83 (8%) [C_1Him]$^{+}$. *m/z* (LSIMS^{-}): 59 (100%) [OAc]$^{-}$, 230 (37%) {[C_2C_1im][OAc]$_2$}$^{-}$. Calc. for $C_8H_{14}N_2O_2$: C, 56.45; H, 8.29; N, 16.46%. Found: C, 56.32; H, 8.41; N, 16.38%.

1-Ethyl-3-methylimidazolium acetate (**1b**). The ionic liquid was acquired from BASF 'Basionics' as an orange viscous liquid, and was used as received. Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 9.96 (1H, s), 7.85 (1H, t, J = 2 Hz), 7.76 (1H, t, J = 2 Hz), 4.21 (2H, q, J = 8 Hz), 3.86 (3H, s), 1.55 (3H, s), 1.40 (3H, t, J = 8 Hz). *ν*(neat)/cm^{-1} 3141 3034 (aromatic C-H stretch, w), 2975 (aliphatic C-H stretch, m), 1559 (C=O stretch, s).

1-Ethyl-3-methylimidazolium octanoate (**2**). The ionic liquid was acquired from BASF 'Basionics' as a yellow viscous liquid, and was used as received. Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 9.81 (1H, s), 7.82 (1H, t, J = 2 Hz), 7.73 (1H, t, J = 2 Hz), 4.21 (2H, q, J = 7 Hz), 3.86 (3H, s), 1.76 (2H, t, J = 7 Hz), 1.43-1.33 (5H, m), 1.28-1.15 (8H, m), 0.85 (3H, t, J = 7 Hz). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): δ 175.1, 137.2, 123.5, 121.9, 44.0, 35.5, 31.4, 29.6, 28.9, 26.8, 22.1, 15.2, 14.0.

1-Ethyl-3-methylimidazolium methanesulfonate (**3**). Aqueous 1-ethyl-3-methylimidazolium hydroxide (0.33 mol dm^{-3}, 2.00 Kg, 0.66 mol) was neutralized by careful addition of methanesulfonic acid (43 ml, 0.66 mol). The water was removed by rotary evaporation, followed by thin-film evaporation, to yield 1-ethyl-3-methylimidazolium methanesulfonate (109 g, 80%) as a pale yellow viscous liquid. The water content was measured as 0.16 wt% by Karl Fischer titration. Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 9.15 (1H, s), 7.79 (1H, t, J = 2 Hz), 7.71 (1H, t, J = 2 Hz), 4.19 (2H, q, J = 7 Hz), 3.85 (3H, s), 2.31 (3H, s), 1.41 (3H, t, J = 7 Hz). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): δ 136.3, 123.6, 122.0, 44.1, 39.8, 35.7, 15.1. *m/z* (LSIMS^{+}): 111 (100%) $[C_2C_1im]^{+}$, 69 (10%) $[H_2im]^{+}$, 83 (7%) $[C_1Him]^{+}$. *m/z* (LSIMS^{-}): 95 (100%) $[CH_3SO_3]^{-}$. Calc. for $C_7H_{14}N_2O_3S$: C, 40.76; H, 6.84; N, 13.58%. Found: C, 40.69; H, 6.91; N, 13.52%.

$[Li]_{0.2}[K]_{0.275}[Cs]_{0.525}[OAc]$ (**11**). Lithium acetate (2.62 g, 39.7 mmol), potassium acetate (5.36 g, 54.6 mmol) and cesium acetate (20.00 g, 104.2 mmol) were carefully weighed under an inert atmosphere into a 100 ml three-necked round-bottomed flask, fitted with a nitrogen inlet, stopper, and rubber septum. The solid salt compounds were mixed vigorously. The mixture was induced to melt by heating to 170 °C for 15 minutes under a nitrogen atmosphere, to yield the eutectic lithium potassium cesium acetate (27.98 g, 100%) as a colourless, glassy liquid. Upon gradual cooling, the compound solidified into a colourless, glassy solid. Found: m.p. 116.0 - 118.0 °C (lit. 119 °C).[1] ^{1}H NMR (400 MHz, DMSO-d6): δ 1.54 (3H, s). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): 109.5, 26.2. ^{7}Li NMR (156 MHz, DMSO-d6): δ -0.47. *m/z* (LSIMS^{+}): 133 (Cs^{+}, 100%), 84 ({$KHCO_2$}$^{+}$, 55%), 39 (K^{+}, 19%), 7 (Li^{+}, 12%). *m/z* (LSIMS^{-}): 103 ({[OAc]-CO_2}$^{-}$, 100%).

1-Ethyl-2-(hydroxymethyl)-3-methylimidazolium acetate (**17**). 1-Ethyl-3-methylimidazolium acetate (5.00 g, 29 mmol) and paraformaldehyde (0.84 g, equivalent to 28 mmol formaldehyde) were carefully weighed into a 100 ml round-bottomed flask, fitted with a nitrogen bubbler. The mixture was heated at 80 ºC for 24 hours, and then allowed to cool to room temperature. The water was removed by rotary evaporation to yield 1-ethyl-2-(hydroxymethyl)-3-methylimidazolium acetate (4.69 g, 84%) as a pale yellow highly viscous liquid. The water content was measured as 1.25 wt% by Karl Fischer titration. Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 7.72 (1H, d, J = 2 Hz), 7.66 (1H, d, J = 2 Hz), 4.79 (2H, s), 4.27 (2H, q, J = 7 Hz), 3.87 (3H, s), 1.55 (3H, s), 1.36 (3H, t, J = 7 Hz). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): δ 173.4, 146.1, 122.8, 120.7, 50.0, 42.9, 34.7, 25.5, 15.5. *m/z* (LSIMS^{+}): 141 (100%) $[C_2C_1(HO)C_1^2im]^{+}$, 111 (20%) $[C_2C_1im]^{+}$, 281 (4%) {$[C_2C_1(HO)C_1^2im]_2$ - H}$^{+}$. *m/z* (LSIMS^{-}): 59 (100%) $[OAc]^{-}$, 230 (62%) {$[C_2C_1im][OAc]_2$}$^{-}$. Calc. for $C_9H_{16}N_2O_3$: C, 53.99; H, 8.05; N, 13.99%. Found: C, 53.92; H, 8.15; N, 13.86%.

3. Ionic liquid / sugar mixing procedures

*1-Ethyl-3-methylimidazolium acetate, **1a**, + D-(+)-glucose, **12** (4:1 w/w):*
Ionic liquid / sugar mixtures (4:1 w/w) were prepared by the addition of an aqueous sugar solution (2.50 ± 0.01 g in 12.5 ml deionized water) to a portion of the ionic liquid (10.0 ± 0.1 g) in a 50 ml round-bottomed flask, whereby the two liquids were readily miscible. Water was then removed by rotary evaporation for one hour; a pressure of 8 mbar was employed, and the water bath was set to a temperature of 70 °C. The sample was analysed by Karl Fischer titration, in order to confirm the water content was < 5 wt%. In addition, an HPLC spectrum was obtained, to confirm that no substantial decomposition had occurred prior to the primary heating period. Subsequently, the round-bottomed flask was fitted with an adaptor for an oil bubbler. The flask was partially submerged into an oil bath with integrated thermostat and magnetic stirrer, set at a constant temperature (120 or 100 °C). The mixture was maintained at this temperature for 24 hours under a gentle flow of nitrogen gas, with a stirring rate of 150 rpm. Small aliquots (0.06 ± 0.02 g) of the sample were extracted at regular intervals ('t_x', where x = 0, 0.25, 0.5, 1, 1.5, 2, 3, 4, 6 and 24 hours) for preparation of vials for HPLC analysis. The temperature of the oil bath was observed to fluctuate by ± 2 °C throughout the course of the experiment. ^{1}NMR spectra were recorded after the 24-hour heating period, and otherwise as required. In addition, the water content was measured at the end of the 24 hour heating period.

*1-Ethyl-3-methylimidazolium acetate, **1a**, + D-(+)-glucose, **12** (1:1 mol/mol):*
1-Ethyl-3-methylimidazolium acetate (5.0 g, 29 mmol) was added to an aqueous solution of D-(+)-Glucose (5.29 g, 29 mmol, in 25 ml deionized water) in a 100 ml round-bottomed flask, whereby the two liquids were readily miscible. Water was then removed by rotary evaporation for one hour; a pressure of 8 mbar was employed, and the water bath was set to a temperature of 70 °C. The sample was analyzed by Karl Fischer titration, in order to confirm the water content was < 5 wt%. In addition, an HPLC spectrum was obtained, to confirm that no decomposition had occurred prior to the primary heating period. Subsequently, the round-bottomed flask was fitted with an adaptor for an oil bubbler. The flask was partially submerged into an oil bath with integrated thermostat and magnetic stirrer, set at a constant temperature. The mixture was maintained at this temperature for 24 hours under a gentle flow of nitrogen gas, with a stirring rate of 300 rpm. Small aliquots (0.06 ± 0.02 g) of the sample were removed at regular intervals for HPLC analysis. ^{1}H / ^{13}C NMR spectra were taken as required.

*1-Ethyl-3-methylimidazolium acetate, **1a**, + D-(+)-xylose, **14** (1:1 mol/mol):*
1-Ethyl-3-methylimidazolium acetate (5.0 g, 29 mmol) was added to an aqueous solution of D-(+)-Xylose (4.41 g, 29 mmol, in 25 ml deionized water) in a 100 ml round-bottomed flask, whereby the two liquids were readily miscible. Water was then removed by rotary evaporation for one hour; a pressure of 8 mbar was employed, and the water bath was set to a temperature of 70 °C. The sample was analyzed by Karl Fischer titration, in order to confirm the water content was < 5 wt%. In addition, an HPLC spectrum was obtained, to confirm that no decomposition had occurred prior to the primary heating period. Subsequently, the round-bottomed flask was fitted with an adaptor for an oil bubbler. The flask was partially submerged into an oil bath with integrated thermostat and magnetic stirrer, set at a constant temperature. The mixture was maintained at this temperature for 24 hours under a gentle flow of nitrogen gas, with a stirring rate of 300 rpm. Small aliquots (0.06 ± 0.02 g) of the sample were removed at regular intervals for HPLC analysis. ^{1}H / ^{13}C NMR spectra were taken as required.

4. Data Tables: thermal decomposition of ionic liquid - carbohydrate mixtures

Table E1 (a) Experimental data for mixtures of ionic liquids (**1**-**10**) with 5 wt% *cellulose*, heated to 120 °C for 48 hours. (b) experimental data for mixtures of key selected ionic liquids (**1**, **2**, **3**, **7**, **8** and **11**) with sugar *model compounds*, heated for 24 hours.

(a)

With 5 wt% CELLULOSE

Ionic Liquid	Cellulose Conc. (wt%)	Temperature (± 2 °C)	H_2O wt% t_0	Novel ^1H NMR Peaks Observed? t_{48}
1a	5.0	120	0.20	✓
2	5.0	120	0.29	✓
3	5.0	120	0.19	✗
4	5.0	120	0.10	✗
5	5.0	120	0.05	✗
6	5.0	120	/	✗
7	5.0	120	/	✗
8	5.0	120	0.11	✓ (after 1 week)
9	5.0	120	0.05	✗
10	5.0	120	/	✗

(b)

	Exp.	Ionic Liquid	Sugar	Sugar Conc. (wt%)	Sugar Conc. (mol%)	Temperature (± 2 °C)	$[H^+]$ (mmol / Kg IL) t_0	$[H^+]$ (mmol / Kg IL) t_{24}	$\Delta[H^+]$	H_2O wt% t_0	H_2O wt% t_{24}	ΔH_2O wt%
Core	i	**1a**	**12**	10.0	9.5	120	/	787	/	3.76	4.17	0.41
	ii	**1a**	**12**	10.0	9.5	120	/	815	/	3.85	4.33	0.48
	iii	**1a**	**12**	10.0	9.5	120	/	783	/	4.31	4.47	0.16
Modify Sugar	iv	**1a**	**13**	10.0	5.0	120	/	739	/	4.56	4.71	0.15
	v	**1a**	**14**	10.0	11.3	120	/	807	/	3.73	3.85	0.12
	vi	**1a**	**15**	10.0	9.5	120	/	841	/	3.73	3.95	0.22
	vii	**1a**	**16**	10.0	5.0	120	/	147	/	4.34	3.95	-0.39
Modify Temp.	viii	**1a**	**12**	10.0	9.5	100	/	590	/	3.87	4.58	0.71
	ix	**1a**	**13**	10.0	5.0	100	/	543	/	4.84	5.23	0.39
Modify Acid Number	x	**1a**	**12**	10.0	9.5	120	110	895	785	4.83	4.52	-0.31
	xi	**1a**	**12**	10.0	9.5	120	145	855	710	5.00	4.73	-0.27
	xii	**1a**	**12**	10.0	9.5	120	235	946	711	4.53	4.56	0.03
	xiii	**1a**	**12**	10.0	9.5	120	271	1017	746	3.68	4.19	0.51
	xiv	**1a**	**12**	25.0	23.6	120	/	1590	/	2.79	4.13	1.34
Modify Ionic Liquid Cation and Anion	xv	**1b**	**12**	10.0	9.5	120	/	793	/	4.61	4.86	0.25
	xvi	**1b**	**13**	10.0	5.0	120	/	833	/	4.96	4.88	-0.08
	xvii	**2**	**12**	10.0	14.1	120	/	/	/	2.18	2.06	-0.12
	xviii	**3**	**12**	10.0	11.4	120	/	46	/	1.29	1.27	-0.02
	xix	**3**	**13**	10.0	6.0	120	/	26	/	1.60	1.36	-0.24
	xx	**3**	**12**	10.0	11.4	120	240	250	10	0.90	2.34	1.44
	xxi	**3**	**13**	10.0	6.0	120	279	267	-12	0.72	1.98	1.26
	xxii	**7**	**12**	10.0	9.7	120	/	/	/	3.74	2.68	-1.06
	xxiii	**8**	**12**	10.0	14.7	120	/	/	/	1.23	1.36	0.13
	xxiv	**11**	**12**	10.0	7.8	120	/	/	/	/	/	/

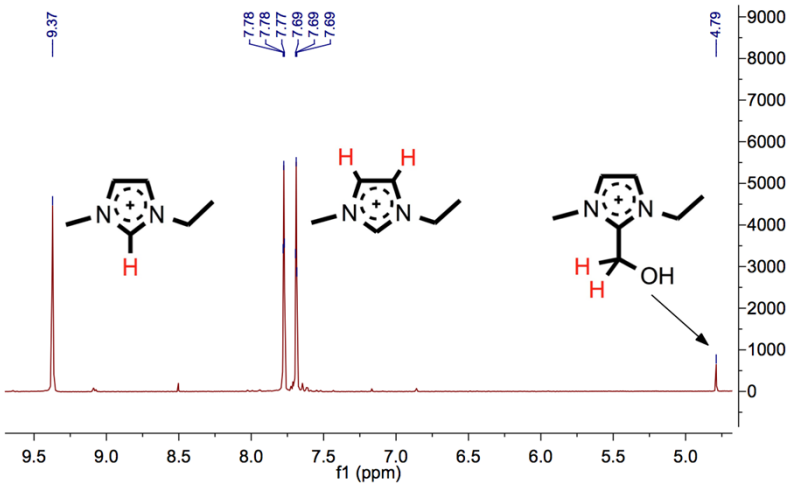


Fig. E2 Expanded region of the ^1H NMR spectrum of the mixture $[C_2C_1im][CH_3(CH_2)_6CO_2]$, **2**, with 5 wt% cellulose, heated to 120 °C for 48 hours. The new singlet peak at 4.79 ppm can (after model compound analysis) be retroactively assigned to the hydroxyalkyl methylene group of the 'C1' adduct cation, $[C_2C_1(HO)C_1{}^2im]^+$.

5. Graphs representing wt% of $[C_2C_1im]^+$ and $[C_2C_1(HO)C_1^2im]^+$

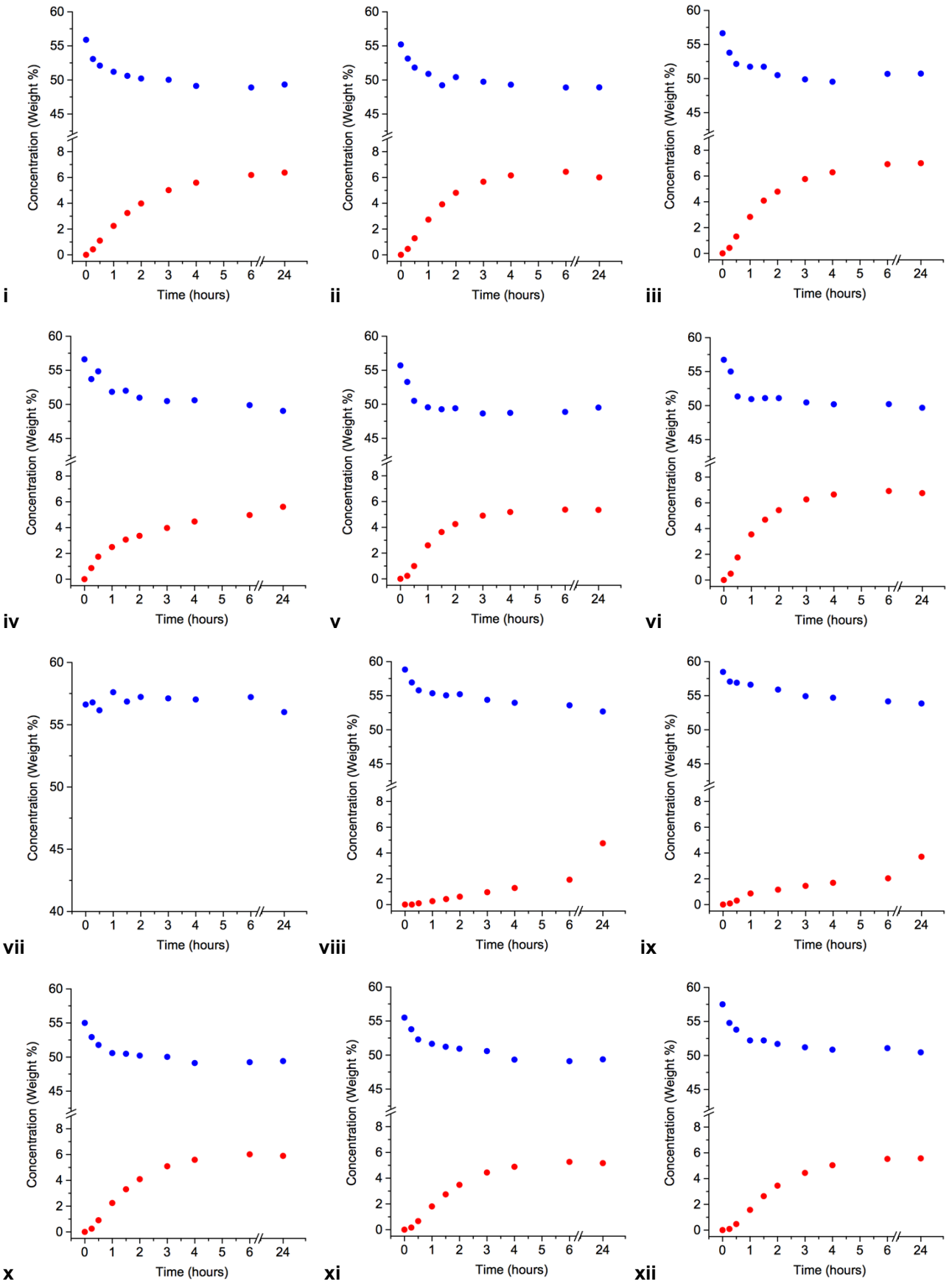


Fig. E3
Wt% concentrations of ionic liquid cations, $[C_2C_1im]^+$ (blue circles) or $[C_4C_1im]^+$ (blue triangles), and the 'C1' adduct cations, $[C_2C_1(HO)C_1^2im]^+$ (red circles) or $[C_4C_1(HO)C_1^2im]^+$ (red triangles), where observed, as a function of the heating time. The numerals, i-xxiii, refer to the experiments outlined in Table E1b.

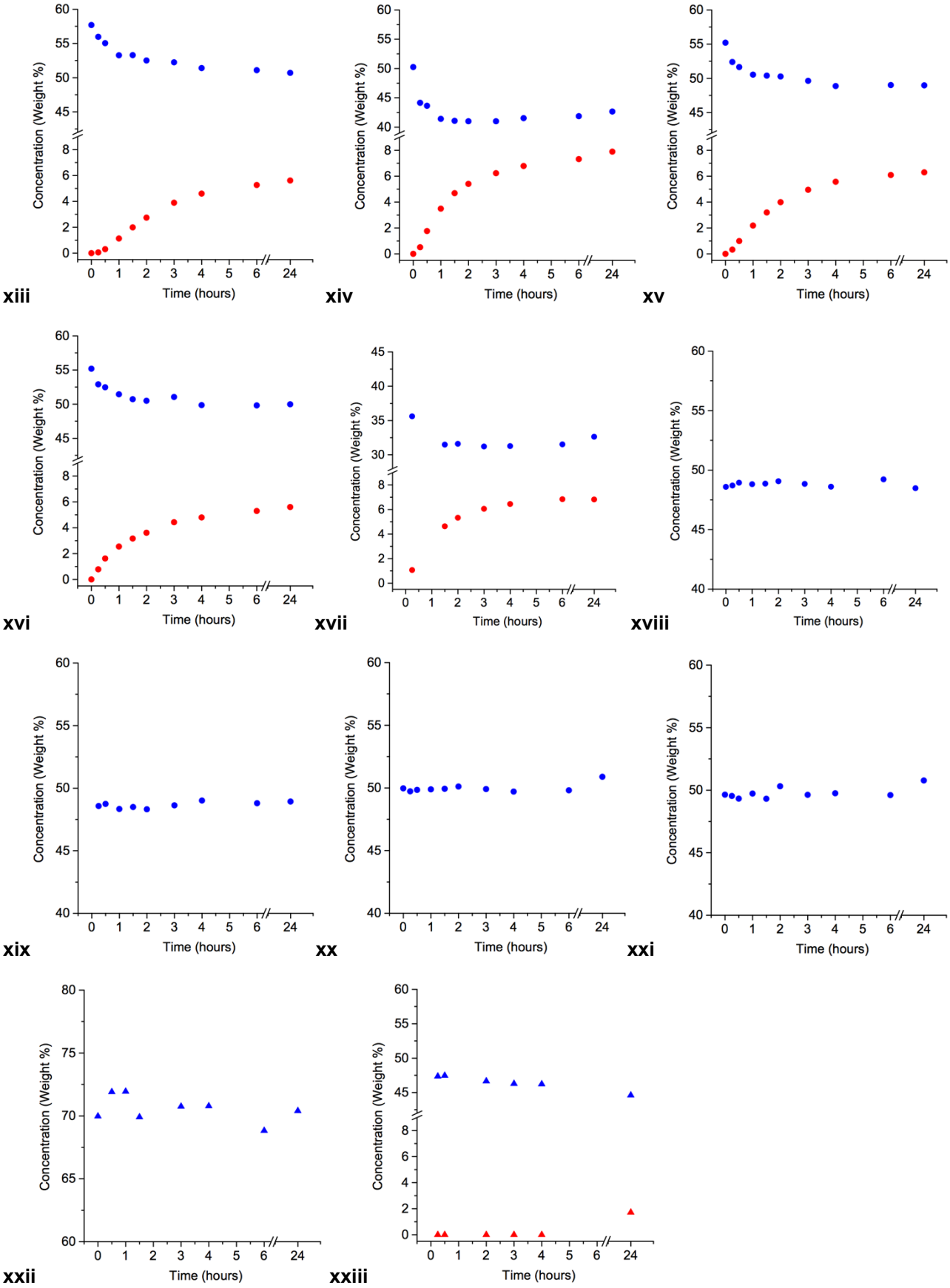


Fig. E3 *continued*
Wt% concentrations of ionic liquid cations, $[C_2C_1im]^+$ (blue circles) or $[C_4C_1im]^+$ (blue triangles), and the 'C1' adduct cations, $[C_2C_1(HO)C_1^2im]^+$ (red circles) or $[C_4C_1(HO)C_1^2im]^+$ (red triangles), where observed, as a function of the heating time. The numerals, i-xxiii, refer to the experiments outlined in Table E1b.

6. Intermediate adduct concentrations for temperature-modified experiments

The graphs below represent differences in rate of formation / depletion of the observed intermediate C6, C4, C3 and C2 adducts, for mixtures of 1-ethyl-3-methylimidazolium acetate, [C_2C_1im][OAc], **1a** + 10 wt% D-(+)-glucose, **12**, heated to temperatures of 120 °C (exp. i, Table E1b) and 100 °C (exp. viii, Table E1b).

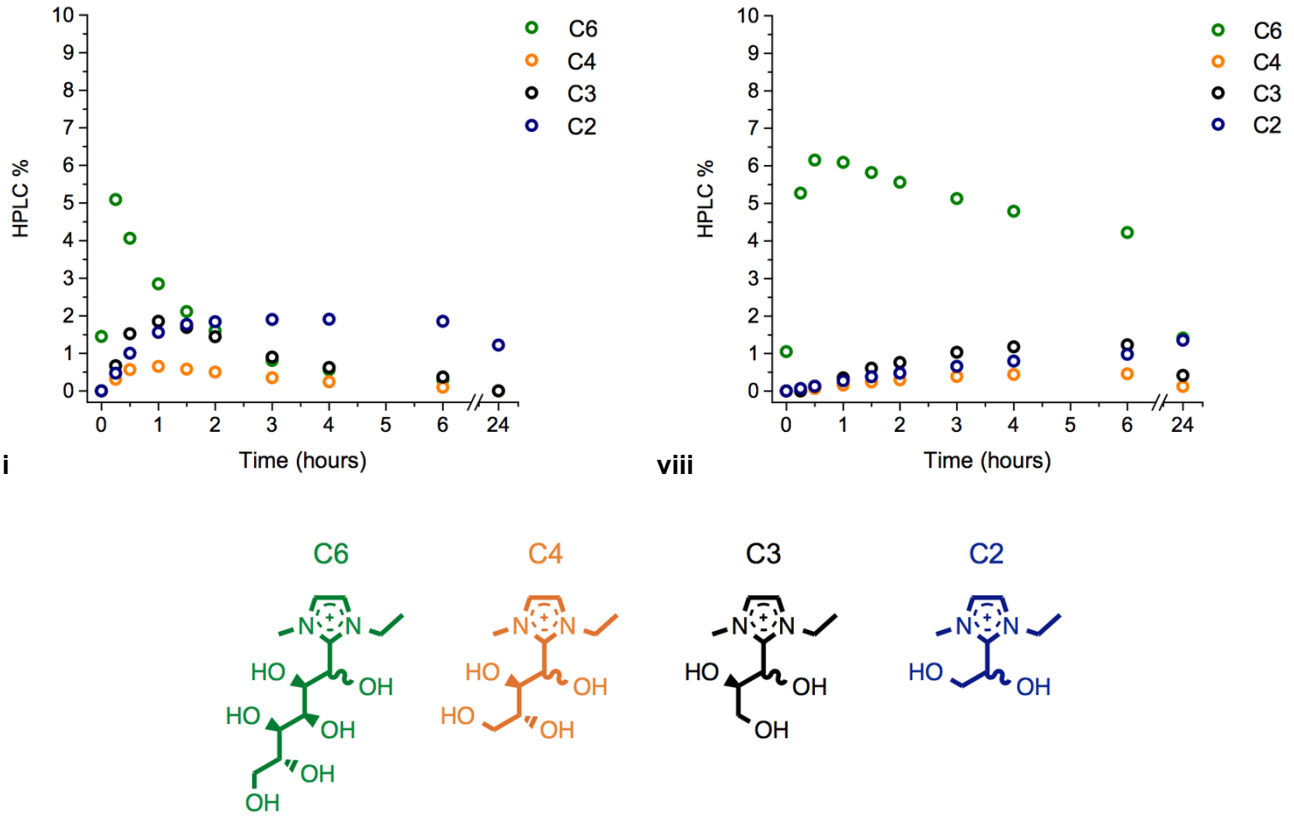
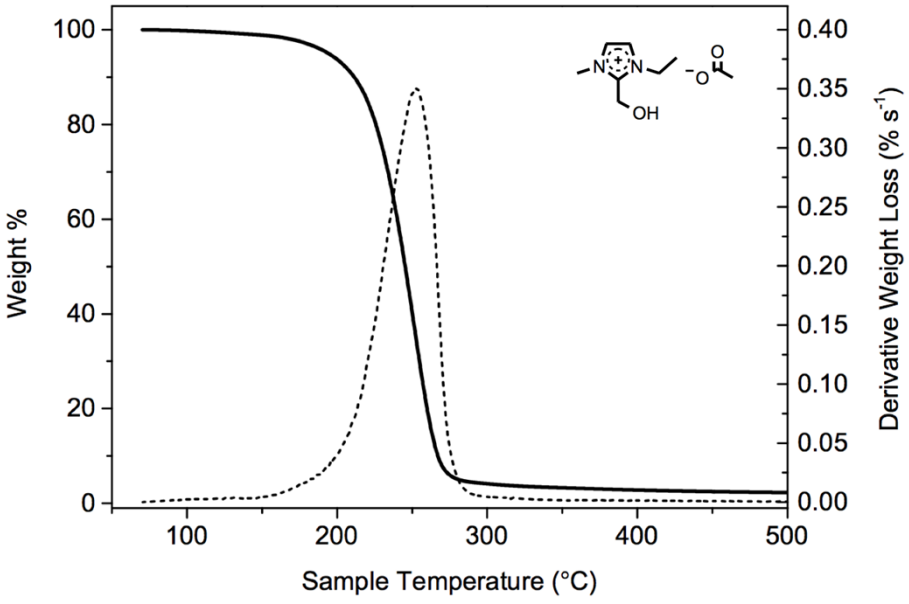


Fig. E4
HPLC% concentrations of the intermediate 'C6', 'C4', 'C3' and 'C2' adduct cations. Experiments were performed with the ionic liquid [C_2C_1im][OAc], **1a**, and 10 wt% D-(+)-glucose, **12**, heated for 24 hours at 120 °C (i) and 100 °C (viii). The numerals, i and viii, refer to the experiments outlined in Table E1b. Identities of the intermediate adducts are given.

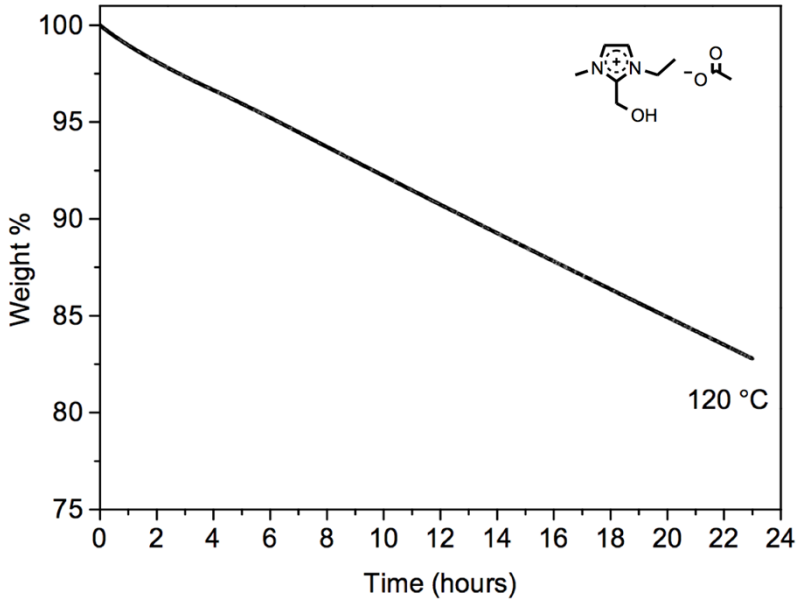
7. Thermogravimetric Analysis (TGA) investigation of C1 adduct

TGA Procedures

Thermogravimetric Analysis (TGA) spectra were obtained on a PerkinElmer 'Pyris 1 TGA' Thermogravimetric Analyzer, using platinum sample pans of 6 mm diameter. Temperature-ramped experiments were carried out for ionic liquids [C_2C_1im][OAc], **1b**, and [C_2C_1(HO)$C^2{}_1$im][OAc], **17**, in the range of 80 - 700 °C. Between 4 - 20 mg of the ionic liquid was measured into the platinum pan. Ionic liquids were dried thoroughly under high vacuum prior to TGA measurement. However, during the transferal of the hygroscopic ionic liquid into the TGA pan, a small quantity of water (≤ 5 wt%) would be absorbed from the atmosphere. A *drying procedure* was implemented: the ionic liquid was heated to 80 °C for 30 minutes in the TGA apparatus, in order to remove water.[2] A ramping rate of 10 °C min^{-1} and nitrogen flow of 20 ml min^{-1} were used for all experiments.



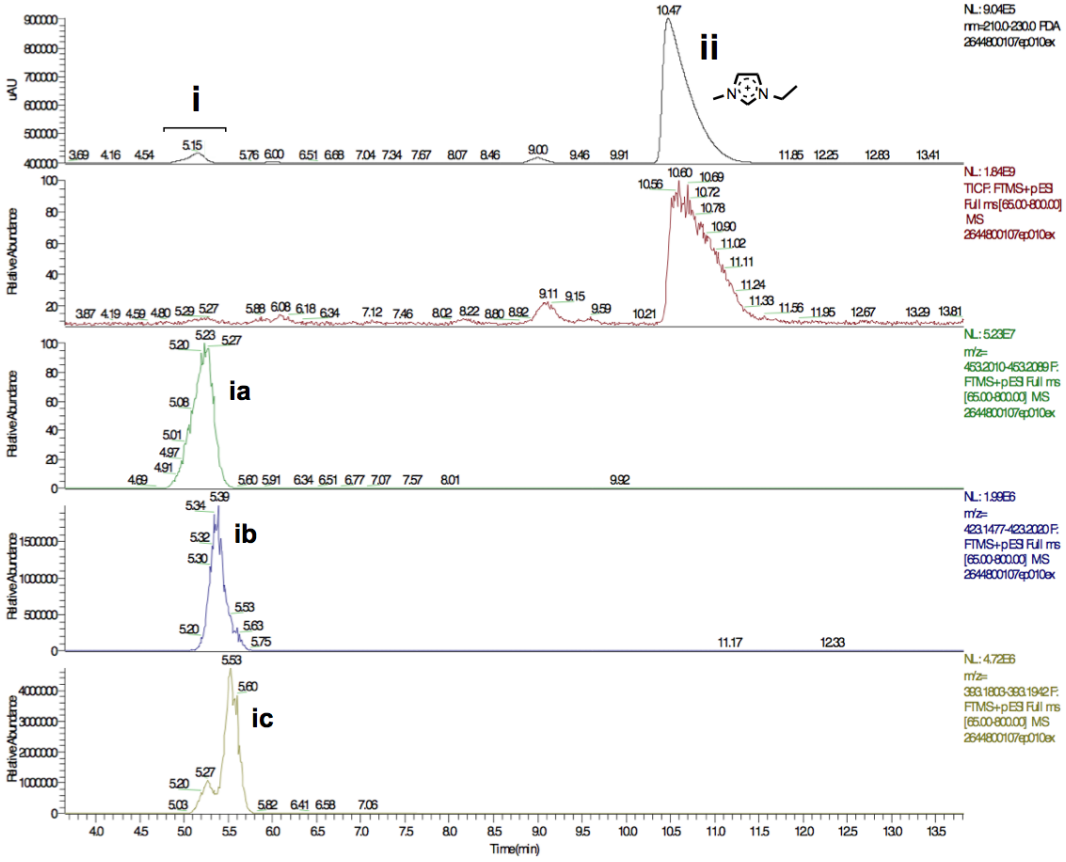
(a)



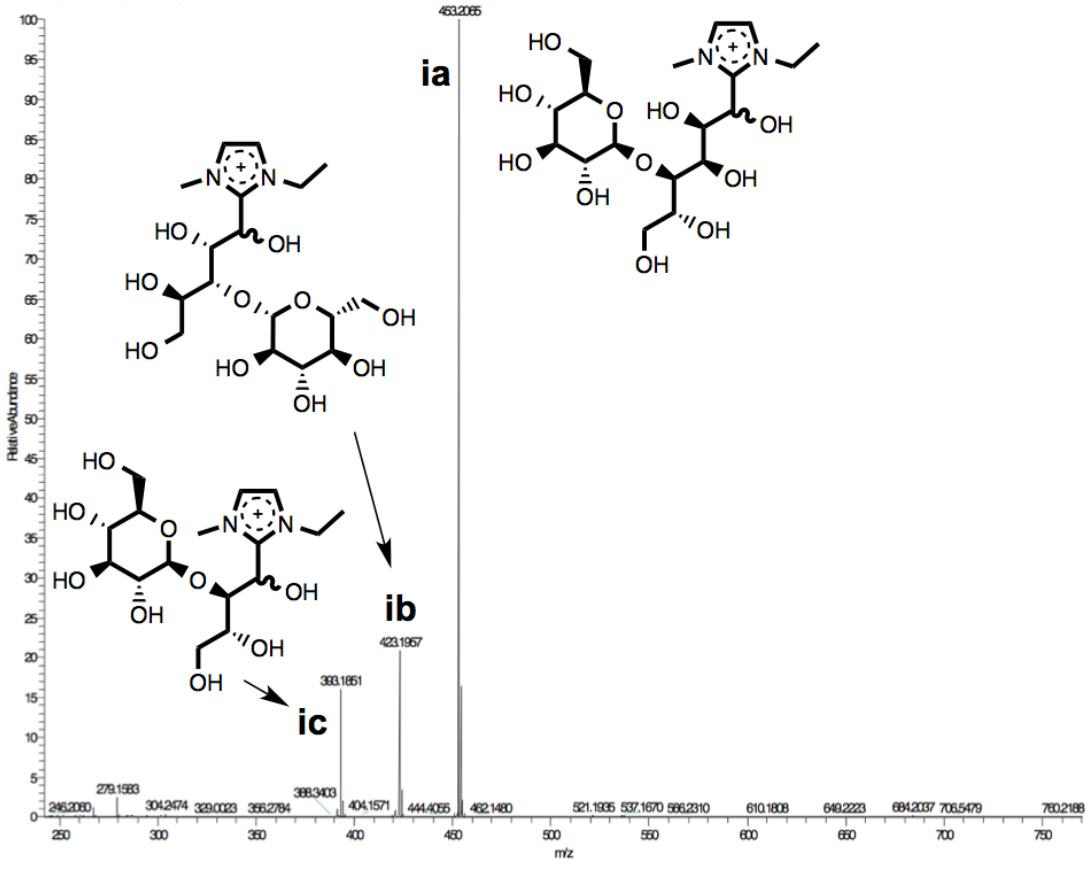
(b)

Fig. E5 (a) Temperature-ramped TGA investigation of the synthesised 'C1' adduct species, [C_2C_1(HO)$C^2{}_1$im][OAc], **17**. The solid line represents the thermograph, the dashed line represents the derivative weight. T_{onset} values of **17** and ionic liquid [C_2C_1im][OAc], **1b**, are very similar, at 221 and 216 °C, respectively.[2] The 'C1' adduct exhibits only one thermal decomposition step under inert (nitrogen) conditions, demonstrated by the single broad peak of the derivative weight; (b) Isothermal TGA thermograph of [C_2C_1(HO)$C^2{}_1$im][OAc], **17**, measured at 120 °C for 24 hours.

8. LCMS spectra and interpretation



(a)



(b)

Fig. E6 Liquid Chromatography - Mass Spectrometry (LCMS) analysis of adduct species formed from $[C_2C_1im][OAc]$, **1a**, and 10 wt% D-(+)-cellobiose, **13**, heated to 120 °C for 0.25 hours ($t_{0.25}$): (a) survey of peaks i, ii; (b) mass spectrum of i, showing peaks ia, ib and ic, representing the 'C12', 'C11' and 'C10' adducts, respectively. Peak ii represents $[C_2C_1im]^+$.

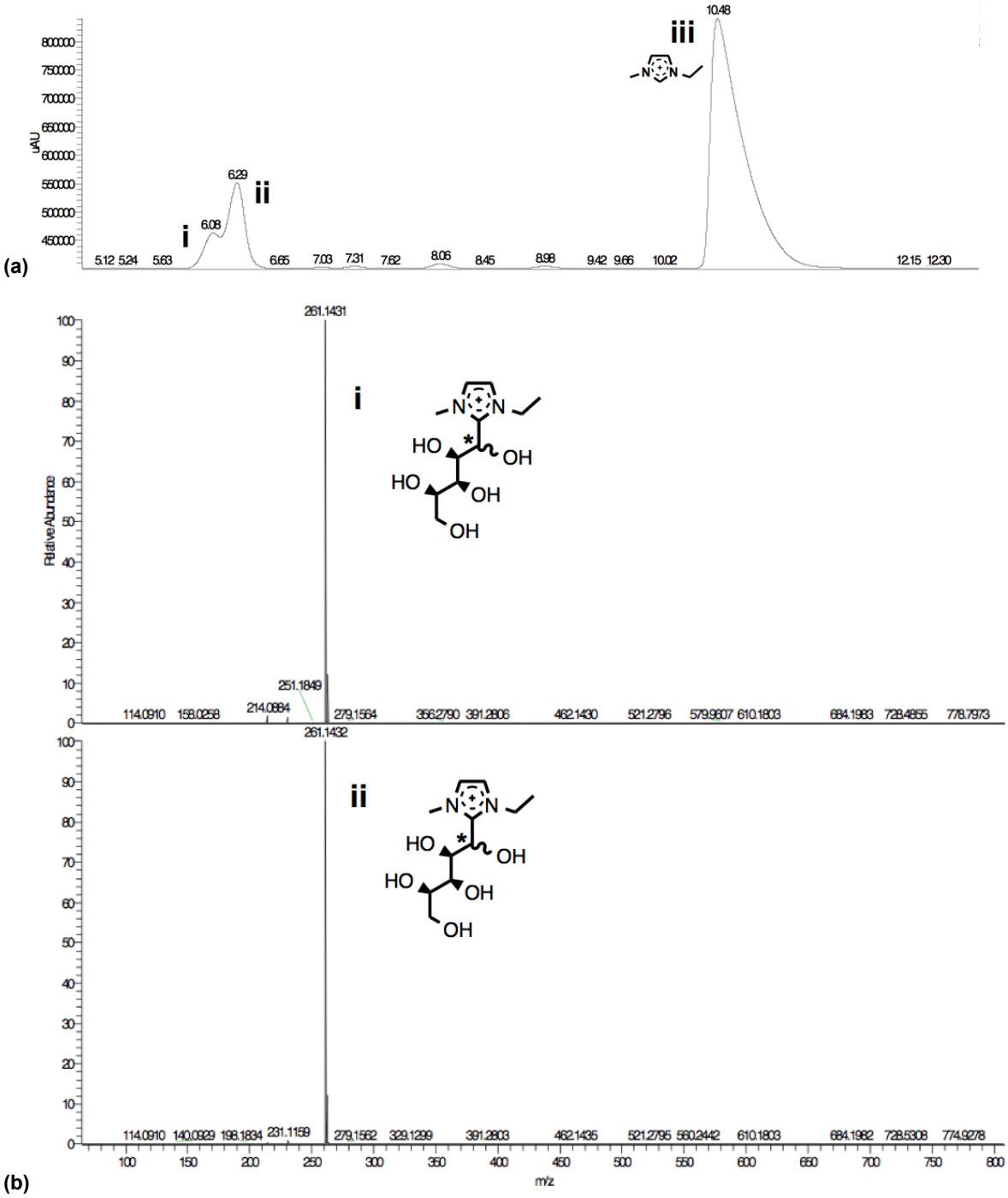


Fig. E7 Liquid Chromatography - Mass Spectrometry (LCMS) analysis of adduct species formed from $[C_2C_1im][OAc]$, **1a**, and 10 wt% D-(+)-xylose, **14**, heated to 120 °C for 0.25 hours ($t_{0.25}$): (a) survey of peaks i - iii; (b) mass spectra of peaks i, ii. Peaks i and ii each exhibit a single sharp peak at *m/z* 261, and were assigned as two diastereoisomers of the C5 adduct, arising from uncertain stereochemistry at the α carbon relative to the C^2 position (labelled *). Peak iii corresponds to $[C_2C_1im]^+$.

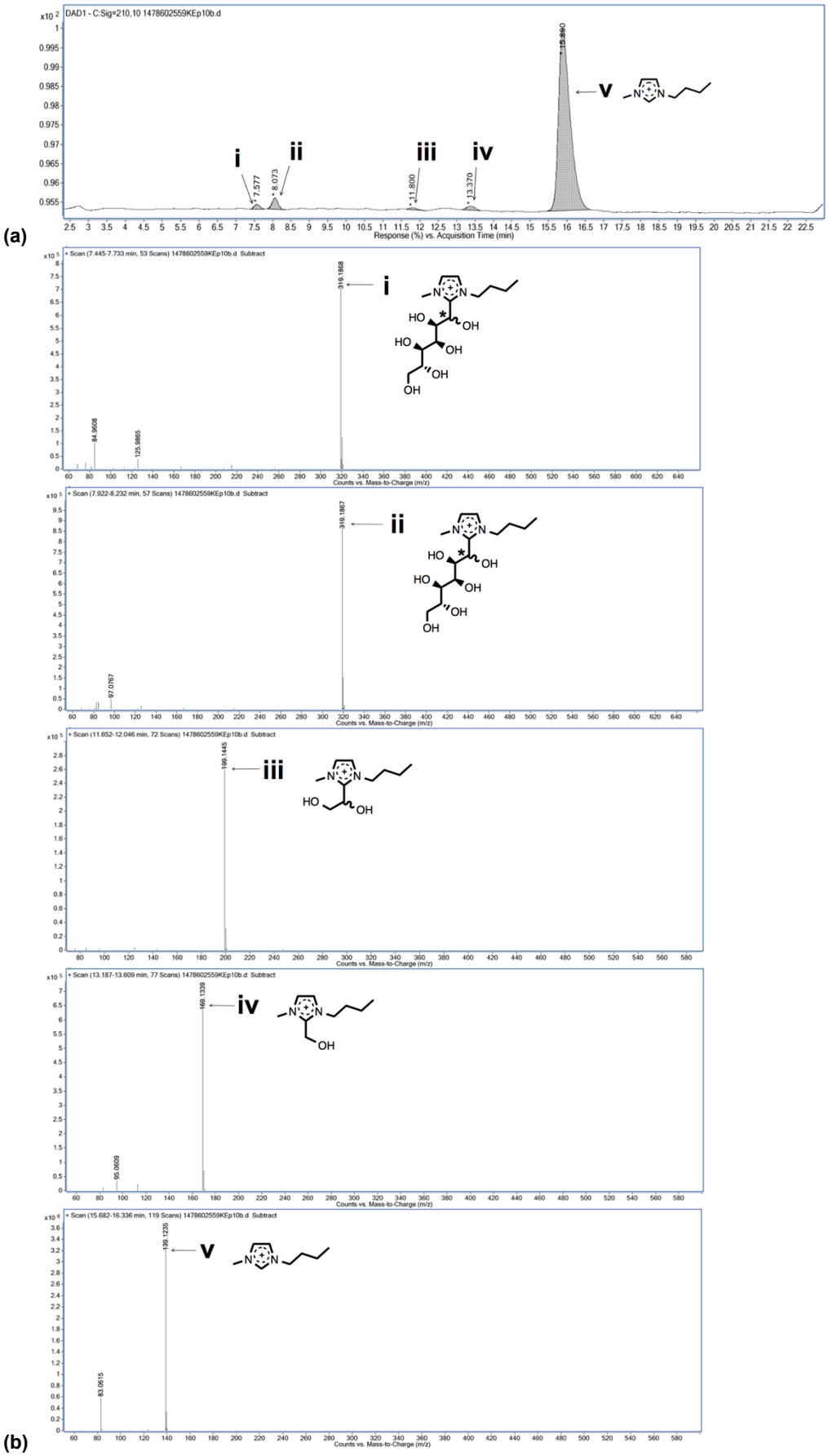


Fig. E8 Liquid Chromatography - Mass Spectrometry (LCMS) analysis of adducts formed from $[C_4C_1im][(CH_3)_2PO_4]$, **8**, and 10 wt% D-(+)-glucose, **12**, heated to 120 °C for 24 hours (t_{24}): survey of peaks i - v; (b) mass spectra of peaks i - v. Peaks i and ii each exhibit a strong singlet at *m/z* 319, and were assigned as two diastereoisomers of the C6 adduct, arising from uncertain stereochemistry at the α carbon relative to the C^2 position (labelled *). Peak v corresponds to $[C_4C_1im]^+$.

References

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