## Ionic liquids that form adducts with alcohols

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# **Electronic Supporting Information**

## Materials and general methods

Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich and used without further purifications.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance III 400 spectrometer (400 MHz). ESMS-mass spectroscopy measurements were carried out on a Waters LCT Premier instrument with an Advion TriVersa NanoMate injection system (cone voltage 50 V, source 120 °C). Both positive and negative ions were detected, with an m/z range of 50 to 1500. Samples were injected as dilute solutions in dry acetonitrile. Electronic absorption spectra were obtained using a Perkin Elmer Lamda 950 spectrophotometer using a cuvette with 1 cm path length. Head-space GC analysis was carried out using Perkin Elmer Clarus 500 Gas Chromatograph. FTIR spectra were obtained at room temperature on a PerkinElmer Spectrum 100 (ATR-IR).

**TGA**: The temperature of decomposition was measured on a TA instrument TGA Q5000 with a heating rate of 10°C.min 1 under dinitrogen atmosphere. The onset of the weight loss in each thermogram was used as a measure of the decomposition temperature.

**DSC**: Thermal profiles of the ionic liquids were obtained using a TA DSC Q2000 model with a TA Refrigerated Cooling System 90 (RCS), equipped with an auto-sampler. A cooling and heating ramp of 2 °C min-1 was used, ranging between -100°C and 120°C, depending on the ionic liquid system.

## Synthesis of ionic liquids

## 1-Ethyl-1-methyl-4-pyrrolidinone ethylsulfate (1a)

N-Mehylpyrrolidinone(3.39 g, 30 mM) and diethylsulfate (4.7g, 30.5 mM) were heated in a screw-cap tube at 50 °C for 24h. The viscous liquid product was washed with dry diethyl ether (2x10 ml) to remove excess starting materials. The resulting ionic liquid was dried under high vacuum to remove any trace amounts of solvents and water. Yield 7.6g, 95%

**NMR:** <sup>1</sup>H (CD<sub>3</sub>CN, 400 MHz); 3.84 (q, 2H, OCH<sub>2</sub>), 3.72(t, 4H, N<sup>+</sup>(CH<sub>2</sub>)<sub>2</sub>), 3.58(q, 2H, N<sup>+</sup>(CH<sub>2</sub>), 3.16(s, 3H, N<sup>+</sup>CH<sub>3</sub>), 2.78-2.62(m, 4H, CO(CH<sub>2</sub>)<sub>2</sub>), 1.36(tt, 3H, CH<sub>3</sub>), 1.16(t, 3H, CH<sub>3</sub>).

<sup>13</sup>C (CD<sub>3</sub>CN); 201.6, 63.2, 59.9, 59.4, 48.1, 35.8, 15.6, 8.35

ESMS: Cation; M<sup>+</sup>, calculated 142.1232, obtained 142.1226

Anion; M<sup>+</sup>, calculated 124.9909, obtained 124.9899

### 1-Ethyl-1-methyl-4-pyrrolidinone iodide (1b)

N-Mehylpyrrolidinone(3.39 g, 30 mM) and ethyl iodide (5.5 g, 35 mM) in dry acetonitrile (5 ml) were heated in a screw-cap tube at 50 °C for 24h. To the resulting mixture, dry diethyl ether (50 ml) was added and the precipitated pale yellow solid was filtered under suction and dried in a desiccator. Yield 7.7 g, 95%

**NMR:** <sup>1</sup>H (dmso-d<sub>6</sub>); 3.73(t, 4H, N<sup>+</sup>(**CH**<sub>2</sub>)<sub>2</sub>), 3.59(q, 2H, **CH**<sub>2</sub>CH<sub>3</sub>), 3.19(s, 3H, N<sup>+</sup>(**CH**<sub>3</sub>), 2.79-2.62(m, 4H, CO(CH<sub>2</sub>)<sub>2</sub>), 1.31(t, 3H, CH<sub>2</sub>**CH**<sub>3</sub>)

<sup>13</sup>C (dmso-d<sub>6</sub>); 201.8, 58.1, 57.7, 46.6, 34.9, 7.65

ESMS: Cation; M<sup>+</sup>, calculated 142.1232, obtained 142.1238

Anion; M<sup>+</sup>, calculated 126.9045, obtained 126.9034

1-Methyl-1-propyl-4-pyrrolidinone methylsulfate (1c) [not reported in the main manuscript]

This ionic liquid was synthesised employing a similar procedure, as for (1a), using N-propylpyrrolidinone and dimethylsulfate as starting materials. (1b) was obtained as a viscous liquid with 7.4g; 92% yield.

NMR: <sup>1</sup>H (CD<sub>3</sub>CN, 400 MHz); 3.72(t, 4H, N<sup>+</sup>(CH<sub>2</sub>)<sub>2</sub>), 3.50 (s, 2H, OCH<sub>3</sub>), 3.43(m, 2H, N<sup>+</sup>CH<sub>2</sub>), 3.18(s, 3H, N<sup>+</sup>CH<sub>3</sub>), 3.71(brm, 4H, CO(CH<sub>2</sub>)<sub>2</sub>), 1.80(m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.0(t, 3H, CH<sub>3</sub>).

<sup>13</sup>C (CD<sub>3</sub>CN); 201.5, 65.5, 59.9, 54.1, 48.9, 35.8, 16.5, 10.8

ESMS: Cation; M<sup>+</sup>, calculated 156.1388, obtained 156.1379

Anion; M<sup>+</sup>, calculated 110.9752, obtained 110.9746

#### FTIR analysis and ESMS of mixtures of alcohols and ionic liquids

Ionic liquid **(1a)** was mixed with 4-fold excess of appropriate alcohols in screw-cap vials and sonicated for 10 min before FTIR analysis. Same samples were analysed by Electron Spray Mass Spectrometry (ESMS), diluted with dry acetonitrile, to show the adduct formation.

#### ESMS of mixtures of alcohols and ionic liquids



Figure 1: ESMS of a mixture of (1a) and 1-propanol (4-fold excess) in dry acetonitrile



Figure 2: ESMS of a mixture of (1a) and t-butanol (4-fold excess) in dry acetonitrile. In this case a peak corresponding to the adduct is not observed.



Figure 3: ESMS of a mixture of (1a) and 2-propanol (4-fold excess) in dry acetonitrile



Figure 4: ESMS of a mixture of (1a) and PhCH<sub>2</sub>CH<sub>2</sub>OH (4-fold excess) in dry acetonitrile



Figure 5: ESMS of a mixture of (1a) and MeOH (4-fold excess) in dry acetonitrile



Figure 6: ESMS of a mixture of (1a) and geraniol (4-fold excess) in dry acetonitrile

2.48e4

## <sup>1</sup>H and <sup>13</sup>C NMR spectra of ionic liquids



Figure 7: Partial <sup>1</sup>H NMR spectrum of 1-ethyl-1-methyl-4-pyrrolidinone ethylsulfate (1a) in CD<sub>3</sub>CN



Figure 8: Partial <sup>13</sup>C NMR spectrum of 1-ethyl-1-methyl-4-pyrrolidinone ethylsulfate (1a) in CD<sub>3</sub>CN



Figure 9: Partial <sup>1</sup>H NMR spectrum of 1-ethyl-1-methyl-4-pyrrolidinone iodide (1b) in dmso-d<sub>6</sub>



Figure 10: Partial <sup>13</sup>C NMR spectrum of 1-ethyl-1-methyl-4-pyrrolidinone iodide (1b) in dmso-d<sub>6</sub>



Figure 11: Partial <sup>1</sup>H NMR spectrum of 1-ethyl-1-propyl-4-pyrrolidinone methylsulfate (1c) in CD<sub>3</sub>CN



Figure 12: Partial <sup>13</sup>C NMR spectrum of 1-ethyl-1-propyl-4-pyrrolidinone methylsulfate (1c) in CD<sub>3</sub>CN

## Differential Scanning Colourimetry of ionic liquids

1-Ethyl-1-methyl-4-pyrrolidinone ethylsulfate (1a)



Figure 13: DSC (second cycle) of ionic liquid (1a) carried out with a scanning rate of 5 °C m<sup>-1</sup>



Figure 14: DSC (second cycle) of ionic liquid (1b) carried out with a scanning rate of 5 °C m<sup>-1</sup>



Figure 15: DSC (second cycle) of ionic liquid (1c) carried out with a scanning rate of 5 °C m<sup>-1</sup>



<sup>1</sup>H NMR spectrum of the regenerated (1b) after extraction process.

Figure 16: <sup>1</sup>H NMR spectrum of recovered 1-ethyl-1-methyl-4-pyrrolidinone iodide (1b) in CD<sub>3</sub>CN