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Utilisation of Ionic Liquids to Remove Harmful M^{2+} Contaminants from Hydrocarbon Streams

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Electronic Supplementary Information

1. General Laboratory Procedures

All reactions requiring an inert atmosphere were performed under standard Schlenk techniques using dry nitrogen. All commercially acquired chemicals were obtained from Sigma-Aldrich, and were used without further purification unless otherwise stated. Anhydrous solvents were dried through an HPLC column on an Innovative Technology Inc. solvent purification system. NMR spectra were recorded on Bruker Avance-400 (1H NMR (400 MHz), 13C (101 MHz)) NMR spectrometers. Chemical shifts are reported in ppm (relative to the DMSO-d6 residual peak). 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 ^{o}C min^{-1}. Melting point values are uncorrected. Elemental analysis experiments were carried out by the London Metropolitan University service.

2. Synthesis of Ionic Liquid Compounds

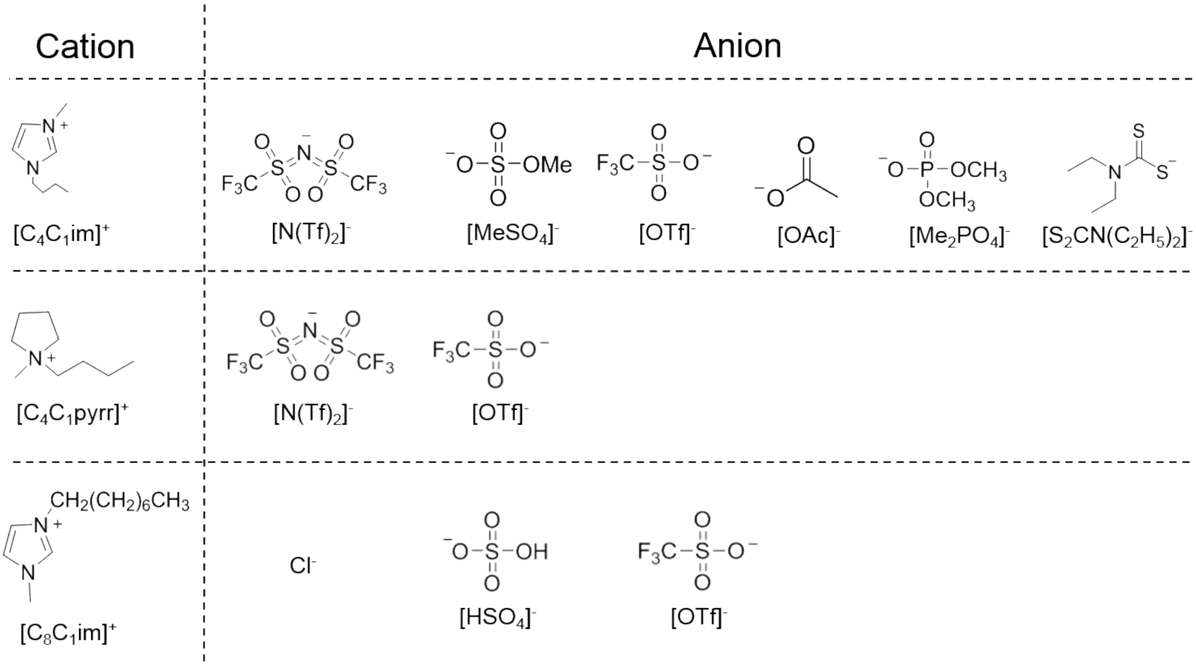


Fig E1. Range of ILs synthesised for use in this study 1) $[C_4C_1im][N(Tf)_2]$, 2) $[C_4C_1im][MeSO_4]$, 3) $[C_4C_1im][OTf]$, 4) $[C_4C_1im][OAc]$, 5) $[C_4C_1im][Me_2PO_4]$, 6) $[C_4C_1im][S_2CN(C_2H_5)_2]$, 7) $[C_4C_1pyrr][N(Tf)_2]$, 8) $[C_4C_1pyrr][OTf]$, 9) $[C_8C_1im]Cl$, 10) $[C_8C_1im][HSO_4]$, 11) $[C_8C_1im][HSO_4]$

1-Butyl-3-methylimidazolium chloride – Freshly distilled 1-chlorobutane (102.85 g, 1.11 mol) was added dropwise (slowly) to a mixture of freshly distilled 1-methylimidazole (82.92 g, 1.01 mol) and ethyl acetate (100 mL) at RT. The temperature was increased to 45 ^{o}C for three days and once a biphasic mixture had formed the temperature was increased to 75 ^{o}C and stirred for a further 4 days. The colourless biphasic mixture was placed in a freezer overnight, a white precipitate formed and the solvent was removed via Schlenk techniques. The remaining white crystals were washed with ethyl acetate and then recrystallised in acetonitrile. The residual solution was carefully decanted off, and the solid was dried *in vacuo* to yield 1-butyl-3-methylimidazolium chloride (88.21 g, 50 %) as a white crystalline solid. Found: m.p. 69-72 ^{o}C,^{1}H NMR (400 MHz, DMSO-d6): δ 9.37 (s, 1H), 7.84 (t, *J* = 1.9 Hz, 1H), 7.76 (t, *J* = 1.7 Hz, 1H), 4.19 (t, *J* = 7.2 Hz, 2H), 3.87 (s, 3H), 1.77 (p, *J* = 7.4 Hz, 2H), 1.26 (h, *J* = 7.4 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO): δ 137.14, 128.78, 124.07, 122.74, 48.90, 36.19, 31.84, 19.24, 13.76. m/z (LSIMS$^+$): 139 (100%) $[C_4C_1im]^+$. m/z (LSIMS-): 35 (100%) $[^{35}Cl]^-$, 37 (19%) $[^{37}Cl]^-$. Calc. for $C_8H_{15}ClN_2$: C, 55.01; H, 8.66; N, 16.04%. Found: C, 55.04; H, 8.76; N, 15.89%.

1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (1) - A solution of lithium bis(trifluoromethylsulfonyl)imide (54.55 g, 0.19 mol) in water (50 mL) was added to a solution of 1-butyl-3-methylimidazolium chloride (29.69 g, 0.17 mol) in dichloromethane (100 mL) and stirred vigorously at room temperature for 8 hours. The lower phase from the biphasic mixture was collected and washed repeatedly with water (10 x 100 mL) until no chloride traces remained in the washings (test with silver nitrate solution). The ionic liquid in dichloromethane was purified through a short alumina column topped with a thin layer of activated charcoal (ca < 5 mm). The solvent was then removed *in vacuo* (24 hours) giving 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (71.29 g, 89 %) as a colourless viscous liquid. Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 8.01 (s, 1H), 6.94 – 6.88 (m, 1H), 6.83 (t, *J* = 1.7 Hz, 1H), 3.61 (t, *J* = 7.4 Hz, 2H), 1.35 – 1.22 (m, 2H), 0.77 (h, *J* = 7.4 Hz, 2H), 0.33 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR in progress. m/z (LSIMS^{+}): 139 (100%) [C$_4$C$_1$im]$^{+}$. m/z (LSIMS^{-}): 280 (100%) [NTf$_2$]$^{-}$. Calc. for $C_{10}H_{15}F_6N_3O_4S_2$: C, 28.64; H, 3.61; N, 10.02%. Found: C, 28.69; H, 3.50; N, 10.16%.

1-Butyl-3-methylimidazolium methyl sulphate (2) – Dimethyl sulphate (54.23 g. 0.43 mol) was added dropwise (slowly) to mixture of 1-butylimidazole (48.43 g, 0.39 mol) and toluene (100 ml) cooled by an ice bath with stirring. After one hour at RT the upper layer was removed via Schlenk techniques and the lower layer was washed three times with 50 ml of toluene. The solvent was removed *in vacuo* (24 hours) giving 1-Butyl-3-methylimidazolium methyl sulphate (89.81 g, 92 %) as a colourless viscous liquid. Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 8.55 (s, 1H), 7.27 (s, 1H), 7.18 (s, 1H), 3.67 (t, *J* = 7.3 Hz, 2H), 2.95 (s, 3H), 1.21 (p, *J* = 7.2 Hz, 2H), 0.63 (h, *J* = 7.3 Hz, 2H), 0.19 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d6): δ 136.66, 123.12, 121.93, 53.12, 48.40, 35.14, 31.26, 18.54, 12.50. m/z (LSIMS^{+}): 139 (100%) [C$_4$C$_1$im]$^{+}$, 83 (59%). m/z (LSIMS^{-}): 111 (100%) [MeSO4]$^{-}$. Calc. for $C_9H_{18}N_2O_4S$: C, 43.19; H, 7.25; N, 11.19%. Found: C, 42.99; H, 7.17; N, 11.05%.

1-Butyl-3-methylimidazolium trifluoromethanesulfonate (3) - Lithium trifluoromethanesulfonate (54.60 g, 0.35 mol) was added to a mixture of 1-butyl-3-methylimidazolium chloride (55.96 g, 0.32 mol) and dichloromethane. The solution was stirred for 48 hours at RT. Upon completion the reaction mixture was filtered and washed with dichloromethane (2x30 mL). The organic extracts were combined and product extraction was carried out in a liquid-liquid extractor (water/DCM) system over 4 days. The organic phase was separated and the solvent was removed *in vacuo* (24 hours) giving 1-Butyl-3-methylimidazolium trifluoromethanesulfonate (50.03 g, 54.19 %) as a colourless viscous liquid. Found ^{1}H NMR (400 MHz, DMSO-d6): δ 8.34 (s, 1H), 7.10 (s, 1H), 7.03 (s, 1H), 3.63 (t, *J* = 7.3 Hz, 2H), 1.24 (p, *J* = 7.4 Hz, 2H), 0.69 (h, *J* = 7.3 Hz, 2H), 0.26 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d6): δ 136.22, 125.06, 122.91, 121.88, 121.69, 118.69, 115.51, 48.57, 35.01, 31.03, 18.37, 18.30, 12.12, 12.00. m/z (LSIMS^{+}): 139 (100%) [C$_4$C$_1$im]$^{+}$, 83 (59%). m/z (LSIMS^{-}): 149 (100%) [CF$_3$SO$_3$]$^{-}$. Calc. for $C_9H_{18}N_2O_4S$: C, 37.50; H, 5.24; N, 9.72%. Found: C, 37.61; H, 5.19; N, 9.93%.

1-Butyl-3-methylimidazolium acetate (4a) - Barium hydroxide octahydrate (141.88 g, 0.50 mol) was added to deionized water (10 ml per 1 g of barium hydroxide octahydrate), and the solution was heated at 70 ^{o}C for 1 hour. Separately, 1-butyl-3-methylimidazolium hydrogen sulphate (106.27 g, 0.45 mol) was diluted with an equal volume of deionized water and added dropwise to the hot aqueous barium hydroxide solution over ten minutes, whereupon a white precipitate formed. The mixture was then heated at 70 ^{o}C for a further hour, cooled to room temperature and refrigerated for a minimum of 30 minutes, to encourage all barium sulphate to precipitate out. The cold solution was filtered, generating an aqueous solution of 1-butyl-3-methylimidazolium hydroxide **(8).**

The basic aqueous solution of 1-butyl-3-methylimidazolium hydroxide was treated with the conjugate carboxylic acid H[A] (1 equiv.), until the pH of the solution had reached ca. 7. The water was removed by rotary evaporation and the ionic liquid was filtered to remove small quantities of solid material. The ionic liquid was dried *in vacuo* (24 hours) giving 1-butyl-3-methylimidazolium acetate (56.32 g, 63.13 %) a colourless viscous liquid. Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 9.17 – 9.11 (m, 1H), 7.43 (s, 1H), 7.34 (s, 1H), 3.75 (t, *J* = 7.2 Hz, 2H), 3.45 (s, 3H), 1.19 (d, *J* = 10.0 Hz, 5H), 0.64 (h, *J* = 7.4 Hz, 2H), 0.20 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d6): δ 176.22, 136.83, 123.50, 122.27, 48.40, 35.32, 31.55, 24.24, 24.21, 18.57, 12.66. m/z (LSIMS^{+}): 139 (100%) [C$_4$C$_1$im]$^{+}$. m/z (LSIMS^{-}): 59 (100%) [OAc]$^{-}$. Calc. for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15; N, 14.13%. Found: C, 60.55; H, 9.33; N, 13.99%.

1-Butyl-3-methylimidazolium acetate (4b) - 1-butyl-3-methylimidazolium chloride (16.42 g, 0.094 mol) and silver acetate (14.18 g, 0.085 mol) were carefully weighed into a 100 ml round-bottomed flask, and the flask was wrapped in aluminium foil to prevent photodegradation of the silver acetate. Deionized water (50 ml) was added, and the solution was stirred at room temperature for three days, during which time a white precipitate formed. The solution was then filtered and tested for the presence of excess Ag^+ or Cl^- as follows: one or two drops of the impure aqueous ionic liquid solution were added to two glass vials, and both were diluted with deionized water (1 ml). To the first vial was added a few drops of 1 M aqueous hydrochloric acid, and to the other a few drops of 1 M aqueous silver nitrate. The tests indicated that there was a slight excess of Ag+. Aqueous solutions of 1-butyl-3-methylimidazolium chloride and silver acetate were added dropwise to the acetate ionic liquid, alternately with stirring, until no further precipitate formation was observed. The opaque solution was filtered, giving a colourless solution, which tested negative with both 1 M aqueous hydrochloric acid and 1 M aqueous silver nitrate. The water was removed via rotary evaporation, and the product was dried *In vacuo*, to give 1-butyl-3-methylimidazolium acetate (14.71 g, 87.29 %) as a colourless viscous liquid. Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 10.19 (s, 1H), 8.09 (s, 1H), 7.94 (s, 1H), 5.26 (s, 1H), 3.95 – 3.87 (m, 2H), 1.28 (p, *J* = 7.3 Hz, 2H), 1.20 (s, 3H), 0.67 (h, *J* = 7.0 Hz, 2H), 0.26 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d6): δ 174.50, 174.45, 138.28, 123.78, 122.74, 48.06, 35.00, 31.77, 25.14, 18.69, 12.68, 12.64. m/z (LSIMS$^+$): 139 (100%) $[C_4C_1im]^+$. m/z (LSIMS$^-$): 59 (100%) $[OAc]^-$. Calc. for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15; N, 14.13%. Found: C, 60.55; H, 9.33; N, 13.99%.

1-Butyl-3-methylimidazolium dimethyl phosphate (5) - Trimethyl phosphate (157.4 g, 1.12 mol) was added dropwise to a cold mixture of 1-butylimidazole (126.9 g, 1.02 mol) and ethyl acetate (150 ml) with vigorous stirring. The reaction was stirred for 24 hours at 80 °C and then distilled water (60 ml) was added to produce a biphasic mixture. The IL phase was isolated and the solvent was removed via rotary evaporation to produce a colourless viscous liquid. The liquid was purified through a short alumina column topped with a thin layer of activated charcoal (ca < 5 mm) and dried in vacuo to give 1-butyl-3-methylimidazolium dimethyl phosphate (206.2 g 78.03 %) as a colourless viscous liquid. Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 9.39 (s, 1H), 7.70 (s, 1H), 7.54 (s, 1H), 4.29 (s, 2H), 3.78 (t, *J* = 6.6 Hz, 2H), 2.78 (d, *J* = 10.8 Hz, 6H), 1.18 (p, *J* = 7.3 Hz, 2H), 0.60 (h, *J* = 7.2 Hz, 2H), 0.17 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, DMSO_weak): δ 137.23, 123.54, 122.53, 51.05, 50.99, 48.12, 35.07, 31.67, 18.53, 12.54. m/z (LSIMS$^+$): 139 (100%) $[C_4C_1im]^+$. m/z (LSIMS$^-$): 125 (100%) $[Me_2PO_4]^-$. Calc. for $C_{10}H_{21}N_2O_4P$: C, 45.45; H, 8.01; N, 10.60%. Found: C, 45.39; H, 8.09; N, 10.47%.

1-butyl-3-methylimidazolium diethyldithiocarbamate (6) - An ion exchange column was prepared using Amberlite® IRA-400 chloride form (267.27 g, 1.4 eq/L, 0.782 mol). The resin was soaked overnight in distilled water and then flushed though with additional distilled water until the solution ran colourless. A solution of sodium diethyldithiocarbamate (528.58 g, 2.346 mol) and distilled water was prepared and run through the column (flow rate 1ml/min).Ion exchange chromatography was carried out to ensure no chloride traces remained. A solution of 1-butyl-3-methylimidazolium chloride (92.73 g, 0.531 mol) in distilled water was prepared and run through the column (flow rate 1ml/min) to produce an orange solution. This was run through a C18 column and the solvent was removed in vacuo to produce a pale yellow viscous liquid, 1-butyl-3-methylimidazolium diethyldithiocarbamate (96.14 g, 62.98%). Found: 1H NMR (400 MHz, DMSO-d6) δ 9.73 (d, J = 2.2 Hz, 1H), 7.86 (t, J = 1.8 Hz, 1H), 7.78 (t, J = 1.8 Hz, 1H), 4.23 (t, J = 7.2 Hz, 2H), 4.00 (q, J = 7.0 Hz, 4H), 3.91 (s, 3H), 1.84 – 1.71 (m, 2H), 1.32 – 1.18 (m, 2H), 1.09 (t, J = 7.0 Hz, 6H), 0.88 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 212.58, 123.94, 122.75, 48.89, 46.50, 36.13, 31.99, 19.27, 13.77, 13.02. m/z (LSIMS$^+$): 139 (100%) [C4C1im]$^+$. m/z (LSIMS$^-$): 149 (100%) $[S_2CN(C_2H_5)_2]^-$. Calc. for $C_{13}H_{25}N_3S_2$: C, 54.31; H, 8.77; N, 14.62%. Found: C, 54.26; H, 8.79; N, 14.57%.

1-Butyl-1-methylpyrrolidinium chloride – Freshly distilled N-methylpyrrolidine (311.65 g, 3.66 mol) was added dropwise to a mixture of freshly distilled 1-chlorobutane (309.18 g, 3.33 mol) and ethyl acetate (300 mL). The reaction was heated for 3 days at 75 ^{o}C and upon completion the solution was cooled to give a white precipitate. The mixture was placed in a freezer overnight to encourage precipitation and then the solvent was removed via Schlenk techniques. The remaining white crystals were washed with ethyl acetate and then recrystallised in acetonitrile. The residual solution was carefully decanted off, and the solid was dried *in vacuo* to yield 1-Butyl-1-methylpyrrolidinium chloride (356.66 g, 60.3 %) as a white crystalline solid. ^{1}H and ^{13}C NMR in progress. m/z (LSIMS$^+$): 142 (100%) $[C_4C_1py]^+$. m/z (LSIMS$^-$): 35 (100%) $[^{35}Cl]^-$, 37 (19%) $[^{37}Cl]^-$. Calc. for $C_9H_{20}ClN$: C, 60.83; H, 11.34; N, 7.88%. Found: C, 60.74; H, 11.42; N, 7.83%.

1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (7) - A mixture of 1-butyl-1-methylpyrrolidinium chloride (33.78 g, 0.19 mol) and dichloromethane (50 mL) was added to lithium bis-(trifluoromethylsulfonyl)imide (60.29 g, 0.21 mol) and stirred vigorously at room temperature for 24 hours. The mixture was filtered and washed repeatedly with deionized water (10 x 100 mL) until no chloride traces remained (test with silver nitrate solution). The ionic liquid in dichloromethane was purified through a short alumina column topped with a thin layer of activated charcoal (ca < 5 mm). The solvent was then removed *in vacuo* (24 hours) giving 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (71.29 g, 89 %) as a colourless viscous liquid. Found: ^{1}H NMR (400 MHz, DMSO-d6) δ 3.53 – 3.39 (m, 1H), 3.38 – 3.25 (m, 1H), 2.98 (s, 1H), 2.16 – 2.01 (m, 2H), 1.75 – 1.62 (m, 1H), 1.32 (h, J = 7.4 Hz, 1H), 0.94 (t, J = 7.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 124.76, 121.56, 118.37, 63.89, 63.39, 47.95, 40.62, 40.41, 40.20, 39.99, 39.78, 39.58, 39.36, 25.38, 21.53, 19.76, 13.88. m/z (LSIMS^{+}): 142 (100%) $[C_4C_1pyrr]^{+}$. m/z (LSIMS^{-}): 280 (100%) $[NTf_2]^{-}$. Calc. for $C_{11}H_{20}F_6N_2O_4S_2$: C, 31.28; H, 4.77; N, 6.63%. Found: C, 31.29 H, 4.80; N, 6.70%.

1-Butyl-1-methylpyrrolidinium trifluoromethanesulfonate (8) - A mixture of 1-butyl-1-methylpyrrolidinium chloride (67.88 g, 0.38 mol) and acetone (50 mL) was added to sodium trifluoromethanesulfonate (71.92 g 0.42 mol) and the reaction was stirred for 48 hours at room temperature. The resulting organic phase was filtered and washed with water until chloride tests proved negative (silver nitrate test). The solvent was then removed via rotary evaporation and the ionic liquid was passed through a short alumina column topped with a layer of activated charcoal (ca < 5 mm. The remaining liquid was dried *In vacuo* (24 hours) giving 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate (72.15 g, 65.18 %) a colourless viscous liquid. Found ^{1}H NMR (400 MHz, DMSO-d6) δ 3.53 – 3.37 (m, 3H), 3.39 – 3.25 (m, 2H), 2.98 (s, 3H), 2.08 (dqd, J = 4.9, 3.2, 1.9 Hz, 4H), 1.75 – 1.62 (m, 2H), 1.32 (h, J = 7.4 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 125.97, 122.76, 119.56, 63.90, 63.86, 63.38, 47.94, 25.38, 21.52, 19.75, 13.90. m/z (LSIMS^{+}): 142 (100%) $[C_4C_1pyrr]^{+}$. m/z (LSIMS^{-}): 149 (100%) $[CF_3SO_3]^{-}$. Calc. for $C_{10}H_{20}F_3NO_3S$: C, 41.23; H, 6.92; N, 4.81%. Found: C, 41.42; H, 7.09; N, 4.91%.

1-Octyl-3-methylimidazolium chloride (9) – Freshly distilled 1-chlorooctane (258.69 g, 1.74 mol) was added dropwise to a cold mixture of freshly distilled 1-methylimidazole (129.72 g, 1.58 mol) and ethyl acetate (200 mL) with vigorous stirring. The reaction was continued for 1 week at 75 °C, cooled to room temperature and the solvent was removed via rotary evaporation. The remaining liquid was washed with ethyl acetate (3x200 ml) and removed by freezing the ionic liquid over dry ice and evacuating via a fritted filter. The product was dried *In vacuo* (24 hours) giving 1-octyl-3-methylimidazolium chloride (291.70 g, 80 %), a colourless viscous liquid. Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 9.27 (s, 1H), 7.81 (d, *J* = 2.0 Hz, 1H), 7.74 (t, *J* = 1.9 Hz, 1H), 4.17 (t, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 1.78 (p, *J* = 7.2 Hz, 2H), 1.26 (dh, *J* = 10.9, 6.6, 5.6 Hz, 11H), 0.90 – 0.82 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d6): δ 138.19, 127.64, 119.95, 48.50, 35.74, 32.81, 31.41, 31.22, 29.73, 28.64, 28.50, 25.62, 22.00, 13.37. m/z (LSIMS^{+}): 195 (100%) $[HC_8C_1im]^{+}$. m/z (LSIMS^{-}): 35 (100%) $[^{35}Cl]^{-}$, 37 (19%) $[^{37}Cl]^{-}$ Calc. for $C_{12}H_{23}ClN_2$: C, 62.45; H, 10.05; N, 12.14%. Found: C, 62.34; H, 10.13; N, 12.24%.

1-Octyl-3-methylimidazolium hydrogen sulphate (10) – A round-bottomed flask was fitted with two oil bubblers (1 M sodium hydroxide) and a dropping funnel. Sulfuric acid 98% (22.18 g, 0.23 mol) was added dropwise to a cold mixture of 1-octyl-3-methylimidazolium chloride (50.00 g 0.22 mol) and water (50 ml) over a period of one hour. The water was removed via rotary evaporation and the remaining liquid was dried in vacuo (24 hours) 1-octyl-3-methylimidazolium hydrogen sulphate (62.48 g, 97.1%) a colourless viscous liquid. Found: ^{1}H NMR (400 MHz, DMSO-d6): δ 11.25 (s, 2H), 8.56 (s, 1H), 7.12 (d, *J* = 18.6 Hz, 2H), 3.38 (s, 3H), 1.26 (s, 2H), 0.66 (s, 5H), 0.56 (s, 6H), 0.16 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d6): δ 136.24, 135.19, 123.22, 122.90, 121.88, 119.27, 48.87, 40.39, 40.18, 39.97, 39.76, 39.55, 35.58, 35.37, 31.18, 29.56, 29.45, 28.55, 28.44, 25.55, 21.97, 13.29. m/z (LSIMS^{+}): 195 (100%) $[C_8C_1im]^{+}$. m/z (LSIMS^{-}): 97 (100%) $[HSO_4]^{-}$. Calc. for $C_{12}H_{24}N_2O_4S$: C, 49.29; H, 8.27; N, 9.58%. Found: C, 49.14; H, 8.34; N, 9.57%.

1-octyl-3-methylimidazolium trifluoromethanesulfonate (11) - A mixture of 1-octyl-3-methylimidazolium chloride (66.93 g, 0.29 mol) and acetone (100 mL) was added to sodium trifluoromethanesulfonate (54.89 g, 0.31 mol) and the reaction was stirred for 48 hours at room temperature. The resulting organic phase was filtered and washed with water until chloride tests proved negative (silver nitrate test). The solvent was then removed via rotary evaporation and the remaining liquid was dried *In vacuo* (24 hours) giving 1-octyl-3-methylimidazolium trifluoromethanesulfonate (66.28 g, 66.2 %) a colourless viscous liquid. Found: ^{1}H NMR (400

MHz, DMSO-d6): δ 8.46 (s, 1H), 7.17 (s, 1H), 7.09 (s, 1H), 3.69 (t, *J* = 6.8 Hz, 2H), 1.34 (q, *J* = 6.9 Hz, 2H), 0.80 – 0.67 (m, 11H), 0.31 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO_weak): δ 137.64, 136.31, 127.92, 125.14, 123.03, 121.95, 121.77, 119.89, 118.77, 115.58, 48.95, 40.20, 39.99, 39.78, 35.13, 32.04, 31.06, 29.35, 28.36, 28.27, 25.40, 21.88, 13.09, 12.97. m/z (LSIMS$^+$): 195 (100%) $[C_8C_1im]^+$. m/z (LSIMS$^-$): 149 (100%) $[CF_3SO_3]^-$. Calc. for $C_{13}H_{23}F_3N_2O_3S$: C, 45.34; H, 6.73; N, 8.13%. Found: C, 45.45; H, 6.73; N, 8.23%.

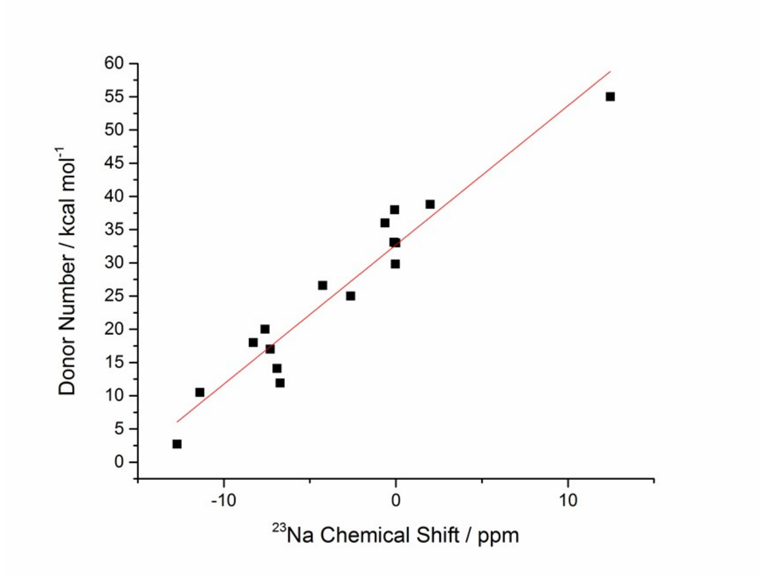
3. Donor Number assignments via ^{23}Na NMR

The recorded spectra were evaluated using MestReNova's NMR software and the DN values were assigned to the ILs by using a linear calibration line consisting of values for 16 different organic solvents as used in previous literature, the calibration line had a fit coefficient of around 0.95.

Table E1: ^{23}Na NMR data and corresponding DN for a range of solvents used in the production of a calibration line [1]

Solvent	Donor Number (kcal mol^{-1})	^{23}Na shift (ppm)
Nitromethane	2.7	-12.7184
Acetanhydride	10.5	-11.3866
Benzonitrile	11.9	-6.7318
Acetonitrile	14.1	-6.9038
Acetone	17	-7.2938
γ-butyrolactone	18	-8.2835
THF	20	-7.5993
n-Pentanol	25	-2.6268
DMF	26.6	-4.2517
DMSO	29.8	-0.0245
H_2O	33	0
Pyridin	33.1	-0.11
Isopropanol	36	-0.6233
t-Butanol	38	-0.0733
HMPA	38.8	2[a]
Ethylendiamine	55[b]	12.4618

[a] Popov
[b] Gutmann



$$DN\ (kcal\ mol^{-1}) = 32.7397712308 + 2.1061380895\ \times Na\ \delta\ 23\ (ppm)$$

Figure E2: Calibration line used for the assignment of Donor Numbers and equation used for the calculation of the DN from the chemical shift of the ^{23}Na signal [1]

4. NRTL Tau Parameters

Table E2 Tau Parameters for Zn^{2+} in both Fuel and IL phase.

Ionic Liquid	$\tau_{Zn\ Hex}$	$\tau_{Zn\ IL}$
$[C_4C_1im][N(Tf)_2]$	2.97	-4.34
$[C_4C_1im][OTf]$	3.15	-4.21
$[C_4C_1im][MeSO_4]$	4.56	-6.53
$[C_4C_1im][Me_2PO_4]$	9.78	-13.86
$[C_4C_1im][OAc]$	9.05	-7.67
$[C_4C_1im][S_2CN(C_2H_5)_2]$	-7.59	-8.49
$[C_4C_1pyr][N(Tf)_2]$	2.90	-12.71
$[C_4C_1pyr][OTf]$	2.75	-4.68
$[C_8C_1im][OTf]$	2.24	-2.86
$[(CH_3)_2NH_2][(CH_3)_2NCOO]$	-7.50	2.26

Table E3 Tau Parameters for Cu^{2+} in both Fuel and IL phase.

Ionic Liquid	$\tau_{\text{Cu Hex}}$	$\tau_{\text{Cu IL}}$
$[C_4C_1im][N(Tf)_2]$	-3.51	5.69
$[C_4C_1im][OTf]$	4.87	-11.06
$[C_4C_1im][MeSO_4]$	-3.32	0.59
$[C_4C_1im][Me_2PO_4]$	3.14	-3.63
$[C_4C_1im][OAc]$	-2.69	-6.94
$[C_4C_1pyr][N(Tf)_2]$	8.48	-7.06
$[C_4C_1pyr][OTf]$	-0.91	-1.88
$[C_8C_1im][OTf]$	-1.61	-4.18
$[C_8C_1im]Cl$	1.52	2.10
$[(CH_3)_2NH_2][(CH_3)_2NCOO]$	-1.22	6.95

5. Extraction Data

The data for the extractions are evaluated via partition coefficients due to the difficulty in achieving exact concentrations when preparing the fuel model. Table E3 displays an exemplar run though with each of the ILs displaying the maximum Zn^{2+} and Cu^{2+} extraction within the volume range and the concentration of the fuel model used.

Table E4 Peak Zn^{2+} Extraction data for ILs

Ionic Liquid	Peak Zn^{2+} Extraction (%)	Zn^{2+} Concentration in Model Fuel (mg L^{-1})
$[C_4C_1im][N(Tf)_2]$	54.5	1.59
$[C_4C_1im][OTf]$	39.3	1.66
$[C_4C_1im][MeSO_4]$	72.3	1.62
$[C_4C_1im][Me_2PO_4]$	99.6	1.62
$[C_4C_1im][OAc]$	99.4	2.67
$[C_4C_1im][S_2CN(C_2H_5)_2]$	99.3	1.62
$[C_4C_1pyrr][N(Tf)_2]$	54.4	1.59
$[C_4C_1pyrr][OTf]$	50.6	1.45
$[C_8C_1im][OTf]$	93.2	1.45
$[(CH_3)_2NH_2][(CH_3)_2NCOO]$	98.5	1.59

Table E5 Peak Cu^{2+} Extraction data for ILs

Ionic Liquid	**Peak Cu^{2+} Extraction (%)**	**Cu^{2+} Concentration in Model Fuel (mg L^{-1})**
$[C_4C_1im][N(Tf)_2]$	74.0	1.11
$[C_4C_1im][OTf]$	68.5	0.65
$[C_4C_1im][MeSO_4]$	90.6	1.18
$[C_4C_1im][Me_2PO_4]$	69.5	1.28
$[C_4C_1im][OAc]$	99.9	1.28
$[C_4C_1pyrr][N(Tf)_2]$	72.5	1.11
$[C_4C_1pyrr][OTf]$	57.0	0.65
$[C_8C_1im][OTf]$	99.2	0.65
$[C_8C_1im]Cl$	99.4	1.18
$[(CH_3)_2NH_2][(CH_3)_2NCOO]$	60.9	1.03

6. Mole Fractions for NRTL Data

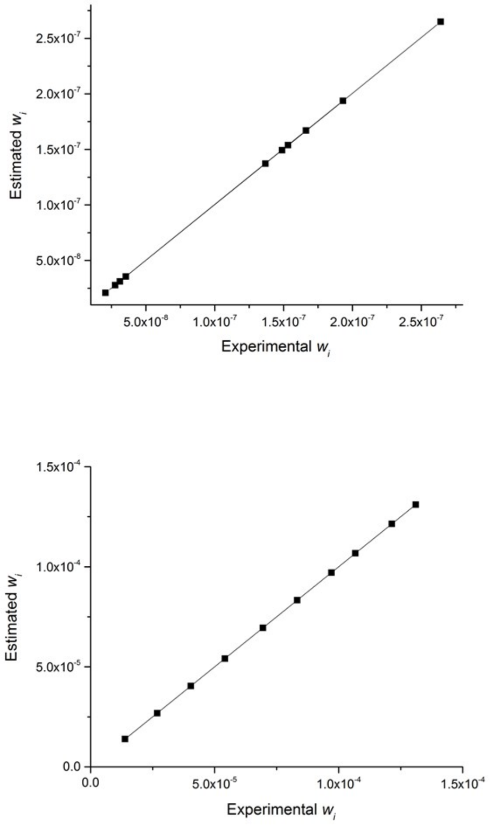


Fig E3. Experimental mole fraction (W_i) vs calculated for (a) Zn^{2+} in n-hexadecane and (b) Zn^{2+} in $[C_4C_1im][Me_2PO_4]$