Electronic Supplementary Information

ALIQUAT 336® – A VERSATILE AND AFFORDABLE CATION SOURCE FOR AN ENTIRELY NEW FAMILY OF HYDROFOBIC IONIC LIQUIDS

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Part A. The preparation of ionic liquids

Note: the molar weight of 432 g/mol was used for Aliquat 336® instead of 404 g/mol frequently stated in various sources.

\([\text{A336}][\text{BH}_4]/[\text{BO}_2]\]

0.0094 mol (4.04 g) of A336 (Aldrich) was diluted with the addition of 10 ml of absolute ethanol (Primalco Oy) under magnetic stirring and heating (323 K). The heating was turned off and 0.01 mol of Sodium borohydride, \(\text{NaBH}_4\), (0.378) added to the mixture. 10 ml of deionized \(\text{H}_2\text{O}\) was added slowly, facilitating an emulsion and formation of some \(\text{H}_2\) –bubbles according to the reaction scheme:

\(\text{NaBH}_4 + 2 \text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4 \text{H}_2\)

A fine precipitate of \(\text{NaCl}\) (SEM/EDX) was formed until no more hydrogen evolvement could be observed, indicating the completed ion-exchange or reaction to sodium metaborate. The resulting IL was diluted with 60 ml of absolute ethanol, stirring turned off and the precipitate was left to sediment in a beaker covered with a plastic foil to minimize the adsorption of humidity from air. The resulting salt was filtered with a Millipore Millex 0.45 µm filter and placed into a rotavapor at 353 K and under vacuum (9 mbar, 250 min) for removal of the organic phase. Then the resulting IL was again diluted with 10 ml extra dry acetone (Acros Organics, <0.005% \(\text{H}_2\text{O}\)) upon which a few precipitate crystals still formed. The mixture was let to sediment and filtrated as above, followed by vacuum treatment in rotavapor (353 K,
9 mbar, 250 min). The resulting IL with comparable viscosity to the starting material was colourless oil, unoptimized yield: 61%. However, upon storage the liquid turned slightly brown-yellowish, indicating instability of the new compound.

[A336][OCN], recipe A

0.01 mol (0.65 g) of Sodium cyanate, NaOCN, (Fluka, 96%) was dissolved under vigorous magnetic stirring into 0.0094 mol (4.0415 g) of heated (373 K) Aliquat 336® (Aldrich) for 30 min. The formation of fine white sediment (NaCl, SEM/EDX) was taking place, allowed to sediment and the hot IL filtrated through a Millipore Millex 0.45 µm filter, followed by a vacuum treatment in a rotavapor (353 K, 7 mbar, 60 min) to remove excess moisture and rendered a clear, colourless, hydrophobic oil that is very viscous at room temperature. Unoptimized yield: 74%.

[A336][CH₃COO]

0.01 mol (0.77 g) of Ammonium acetate, CH₃COONH₄, (Merck, >98%) was added slowly into 0.0094 mol (4.0415 g) of (373 K) Aliquat 336® (Aldrich) under vigorous magnetic stirring. A white precipitate of NH₄Cl (SEM/EDX) was left to sediment and 4 ml of extra dry acetone (Acros Organics, <0.005% H₂O) was added to the mixture. The resulting IL was filtered through a Millipore Millex 0.45 µm filter, followed by a vacuum treatment in a rotavapor (353 K, 7 mbar, 16 h). The originally clear, viscous oil turned to golden colour with prolonged time under heating, possibly due to ammonium residues in the IL. Unoptimized yield: 73%.

[A336][OCN], recipe B

0.01 mol (0.81 g) of Potassium cyanate, KOCN, (Aldrich, 97%) was dissolved into 70 ml of warm methanol. 0.0094 mol (4.0415 g) of Aliquat 336® (Aldrich) was dissolved in 5 ml of methanol and added dropwise to the alcoholic solution of KOCN under vigorous magnetic stirring. The formation of fine white sediment (KCl, SEM/EDX) was taking place and allowed to sediment. The solution was filtrated through a Millipore Millex 0.45 µm filter, followed by a vacuum treatment in a rotavapor (353 K, 8 mbar, 60 min) to remove the volatiles. Further formation of white precipitate was observed and a portion of 7 ml of extra dry acetone (Acros Organics, <0.005% H₂O) was used to dilute the IL before 2nd filtration, followed by a vacuum treatment in a rotavapor (353 K, 8 mbar, 60 min) to remove volatiles. Completely clear, colourless,
hydrophobic oil that is very viscous at room temperature was formed. However, after prolonged storage (couple of weeks), yellowish color emerged. Unoptimized yield: 58%.

[A336][H2PO4]

0.01 mol (0.88 g) of Sodium phosphate, NaH2PO4, (Merck, >98%) was added slowly into 0.0094 mol (4.0415 g) of (373 K) Aliquat 336® (Aldrich) under vigorous magnetic stirring. The mixture was stirred for 2 hours under which time a white precipitate (NaCl, SEM/EDX) was formed. After addition of 10 ml of extra dry acetone (Acros Organics, <0.005% H2O), the mixture was allowed to sediment and filtrated through a Millipore Millex 0.45 µm filter. A vacuum treatment in a rotavapor (353 K, 9 mbar, 60 min) was applied to remove volatiles. A viscous, colourless oil was obtained. Unoptimized yield: 73%.

*Even phosphor detected which might be due to IL contamination on the crystals.

[A336][HSO4]

0.01 mol (1.38 g) of sodium bisulfate, NaHSO4 · H2O, (Merck, proanalyti) was added slowly into 0.0094 mol (4.0415 g) of (373 - 400 K) Aliquat 336® (Aldrich) under vigorous magnetic stirring. The mixture was stirred for 15 min. Alternatively, 5 pulses (20+10+10+10+10 s) of microwave irradiation (250 W, Panasonic NN-Q543W inverter domestic MW oven) with intermediate mixing was applied. After this 10 ml of extra dry acetone (Acros Organics, <0.005% H2O), the precipitate was allowed to sediment and filtrated through a Millipore Millex 0.45 µm filter. A vacuum treatment in a rotavapor (353 K, 9 mbar, 60 min) yielded a clear, slightly yellowish, viscous oil. Unoptimized yield (traditional heating): 81%. Unoptimized yield (MW heating): 66%.

[A336][SCN]

0.01 mol (0.76 g) of ammonium thiocyanate, NH4SCN, (Merck, >99%) was dissolved in 20 ml of hot ethyl alcohol and added dropwise into a mixture of 0.0094 mol (4.0415 g) of (373 K) Aliquat 336® (Aldrich) and 20 ml of hot ethyl alcohol (Primalco) under vigorous magnetic stirring. The mixture was stirred for 2 hours under which time a white precipitate (NH4Cl, SEM/EDX) was formed. After sedimentation (30 min) and subsequent filtration through a Millipore Millex 0.45 µm
filter, vacuum was applied in a rotavapor (353 K, 9 mbar, 60 min). The filtration-vacuum-treatment was repeated twice using extra dry acetone as the intermediate diluting solvent upon filtrations. After the last vacuum treatment, a clear, slightly yellowish liquid was obtained. Unoptimized yield: 60%

[A336][NO₃]
0.01 mol (0.85 g) of sodium nitrate, NaNO₃, (Sigma, >99%) was dissolved in 2 ml of deionized water into which 5 ml acetone was added. 0.0094 mol (4.0415 g) of (373 K) Aliquat 336® (Aldrich) was dissolved in 5 ml of extra dry acetone and added dropwise into the aqueous-acetone mixture of sodium nitrate under vigorous magnetic stirring. The mixture was stirred for 1 hour and left to settle. After a while, an aqueous layer forms at the bottom. The mixture was poured into a vacuum rotavapor (353 K, 20 mbar, 30 min), facilitating the formation of white precipitate and 5 ml extra dry acetone was added. After sedimentation and subsequent filtration through a Millipore Millex 0.45 µm filter, vacuum was applied in a rotavapor (353 K, 19 mbar, 60 min). A clear, slightly yellowish liquid was obtained. Unoptimized yield: 61%.

[A336][Croto]
0.01 mol (0.86 g) of crotonic acid, CH₃CH=CHCOOH, (m.p.70-73°C) was slowly added to a 0.0094 mol of heated (353 K) and stirred Aliquat 336® (Aldrich) followed by stirring with an equal volume of added deionized water, facilitating HCl (g) formation. In a few hours most of the water had evaporated and 5 ml of acetone was added. Vacuum treatment in rotavapor (353 K, 19 mbar, 60 min), followed by another washing with 70 ml of deionized water and subsequent vacuum rotavapor treatment (353 K, 18 mbar, 60 min). Unoptimized yield: 86%.

[A336][PF₆]
0.0094 mol of Aliquat 336® (Aldrich), as well as 0.01 mol of Sodium hexafluorophosphate, NaPF₆, (Aldrich, 98%) were dissolved in 5 ml and 10 ml of extra dry acetone (Acros Organics, <0.005% H₂O), respectively. The latter solution was added dropwise to a stirred solution of Aliquat 336® (Aldrich), at room temperature, upon which the precipitate of NaCl crystals (SEM/EDX) immediately formed due to the insolubility of NaCl. The solution was decanted, filtered through a Millipore Millex 0.45 µm filter and heated under vacuum (rotavapor, 800°C, 8 mbar,
30 min) to remove acetone. Some more sediment was formed since the synthesis was carried out under normal atmosphere and the IL was dissolved in another portion of 5 ml acetone. The decanting-filtration-vacuum treatment procedure was repeated and, again, dissolved in 5 ml absolute ethyl alcohol (Primalco Oy). After yet another decanting-filtration-vacuum treatment procedure, the hydrophobic IL was washed briefly with 20 ml of deionized H₂O and placed in a rotavapor for drying of the excess moisture (343 K, 8 mbar, 2 h). The resulting ionic liquid, [A336][PF6], is a clear, colourless liquid with a relatively high melting point (too viscous below 343 K). Unoptimized yield: 70%.

[A336][BF₄]
0.0094 mol of Aliquat 336® (Aldrich) was dissolved in 5 ml of extra dry acetone (Acros Organics, <0.005% H₂O) and 0.01 mol (1.83 g) of HBF₄ (Aldrich, 48 wt-% in H₂O) was mixed with 5 ml of acetone as well. The tetrafluoroboric acid solution was added dropwise to the vigorously stirred alcoholic Aliquat 336® (Aldrich). After vacuum rotavapor (353 K, 20 mbar, 20 hours) and twice repeated dissolution-filtration-vacuum (353 K, 20 mbar, 1 hour) procedure, a slightly yellowish liquid with relatively low viscosity was obtained. Unoptimized yield: 36%.

[A336][HCO₃]
0.0094 mol of Potassium bicarbonate, KHCO₃, (1.0g) was dissolved in 0.01 mol of Aliquat 336® (Aldrich) under vigorous magnetic stirring and 10x10 sec pulses of microwave irradiation (250 W, Panasonic NN-Q543W inverter domestic MW oven) with intermediate mixing was applied. The white precipitate, KCl (SEM/EDX), was filtrated through a Millipore Millex 0.45 µm filter. Subsequent vacuum rotavapor treatment (353 K, 9 mbar, 30 min) was applied. The obtained colourless oil solidified upon cooling to the ambient temperature. Unoptimized yield: 71%.

[A336][(CF₃SO₂)₂N]
0.0094 mol (2.87 g) of lithium (bistrifluoromethylsulfon)imide, (CF₃SO₂)₂NLi (Fluka, >99%) was dissolved in 5 ml of deionized water. 0.01 mol of Aliquat 336® (Aldrich) was dissolved in 5 ml of extra dry acetone (Acros Organics, <0.005% H₂O). The
aqueous solution of lithium (bistrifluoromethylsulfon)imide was added dropwise under vigorous magnetic stirring to the mixture of Aliquat 336® and acetone. The milky solution was stirred at ambient temperature for 2 hours and allowed to separate. The colourless IL formed the bottom layer (note: Aliquat 336 is lighter than water) and the aqueous LiCl the top. The solution was washed with ample amount of water, and placed in vacuum rotavapor (353 K, 13 mbar, 30 min). The low-viscous, colourless oil was dissolved in 7 ml of extra dry acetone, followed by a filtration through a Millipore Millex 0.45 µm filter and subsequent vacuum rotavapor treatment (353 K, 13 mbar, 5 hours). Unoptimized yield: 66%.

*The preparation was also performed as a metathesis version upon which white crystals precipitated. When the precipitate was left for a while exposed to ambient air, it readily melted indicating the formation of very hygroscopic LiCl.
Part B. Characterization of A336 Ionic Liquids (A336 = tricaprylmethylammonium)

\[\text{[A336}^+\text{][SO}_2\text{H}^-]\]

- TGA-analysis (Section IV)
  - Decomposition temperature: 157 °C
  - Water content: 3,2 %
- DSC-analysis (Section V)
  - Melting point: -9,2 °C
  - Freezing point: -4,9 °C
- Solubility (T = 20 °C)
  - Acetone: +++
  - Ethanol: +++ (at least 83,2 mg/ml)
  - 2-propanol: +++ (at least 110,0 mg/ml)
  - Ethyl acetate: +++ (at least 55,0 mg/ml)
  - Acetonitrile: ++ (~40 mg/ml)
  - Hexane: + (~11 mg/ml)
  - Toluene: +++ (at least 56,2 mg/ml)
- Density: 0,872 g cm\(^{-3}\) (T = 50 °C) (Section I)
- FTIR: (Section II)
- NMR: (Section VI)
- Viscosity: ---
- Cl\(^-\) content: contains chlorine (~60 mg/g; 1,7 mmol/g)

\[\text{[A336}^+\text{][BF}_4^-]\]

- TGA-analysis (Section IV)
  - Decomposition temperature: 294 °C
  - Water content: 4,9 %
- DSC-analysis (Section V)
  - Melting point: 60 °C
  - Freezing point: ----
    - Exothermic phase change: -9 °C (upon heating)
- Solubility (T = 20 °C)
  - Acetone: +++
  - Ethanol: +++ (at least 99,0 mg/ml)
  - 2-propanol: + (~94 mg/ml)
  - Ethyl acetate: +++ (at least 67,4 mg/ml)
  - Acetonitrile: +++ (at least 70,0 mg /ml)
  - Hexane: not soluble
  - Toluene: +++ (at least 67,6 mg /ml)
- Density: 0,873 (T = 60 °C) (Section I)
- FTIR: (Section II)
- NMR: (Section VI)
- Viscosity: ---
- Cl\(^-\) content: no chlorine detected
[\text{A336}^+] \ [\text{BH}_4^-]/[\text{B}_2\text{O}_2^-]$

- TGA-analysis (Section IV)
  - Decomposition temperature: 144 °C
  - Water content: 4.2 %
- DSC-analysis (Section V)
  - Melting point: -7.9 °C
  - Freezing point: ---
  - Glass transition -7.4 °C
- Solubility (T = 20 °C)
  - Acetone: +++
  - Ethanol: +++ (at least 141.2 mg/ml)
  - 2-propanol: +++ (at least 155.6 mg/ml)
  - Ethyl acetate: +++ (at least 102.2 mg/ml)
  - Acetonitrile: +++ (at least 102.0 mg/ml)
  - Hexane: ++ (~65 mg/ml)
  - Toluene: +++ (at least 196.0 mg/ml)
- Density: 0.874 g cm$^{-3}$ (T = 50 °C) (Section I)
- FTIR: (Section II)
- NMR: (Section VI)
- Viscosity: 2.76 Pa s (kg m$^{-1}$ s$^{-1}$) (T = 30 °C) (Section III)
- Cl$^-$ content: contains chlorine (~48.7 mg/g; 1.4 mmol/g)

[\text{A336}^+] \ [\text{croto}^-]$

- TGA-analysis (Section IV)
  - Decomposition temperature: 183 °C
  - Water content: 3.6 %
- DSC-analysis (Section V)
  - Melting point: 19.5 °C
  - Freezing point: 15.7 °C
  - Exothermic phase change: 28.4 °C
- Solubility (T = 20 °C)
  - Acetone: +++ (at least 89.4 mg/ml)
  - Ethanol: +++ (at least 62.8 mg/ml)
  - 2-propanol: +++ (at least 86.8 mg/ml)
  - Ethyl acetate: +++ (at least 21.3 mg/ml)
  - Acetonitrile: +++ (at least 46.4 mg/ml)
  - Hexane: + (~8 mg/ml)
  - Toluene: +++ (at least 113.0 mg/ml)
- Density: 0.874 g cm$^{-3}$ (T = 50 °C) (Section I)
- FTIR: (Section II)
- NMR: (Section VI)
- Viscosity: ---
- Cl$^-$ content: contains chlorine (~53.1 mg/g; 1.5 mmol/g)
[A336⁺][NO₃⁻]

- **TGA-analysis (Section IV)**
  - Decomposition temperature: 202 °C
  - Water content: 3.1%
- **DSC-analysis (Section V)**
  - Melting point: 5.5 °C
  - Freezing point: 14.8 – 19.7 °C
- **Solubility (T = 20 °C)**
  - Acetone: +++ (at least 139.4 mg/ml)
  - Ethanol: ++ (≤ 84 mg/ml)
  - 2-propanol: +++ (at least 74.0 mg/ml)
  - Ethyl acetate: +++ (at least 91.3 mg/ml)
  - Acetonitrile: +++ (at least 64.0 mg/ml)
  - Hexane: not soluble
  - Toluene: +++ (at least 99.8 mg/ml)
- **Density: 0.895 g cm⁻³ (T = 50 °C) (Section I)**
- **FTIR:**
- **NMR:**
- **Viscosity: 0.63 Pa s (kg m⁻¹ s⁻¹) (T = 50 °C) (Section III)**
- **Cl⁻ content: contains chlorine (~5.6 mg/g; 0.2 mmol/g)**

[A336⁺][H₂PO₄⁻]

- **TGA-analysis (Section IV)**
  - Decomposition temperature: 176 °C
  - Water content: 0.4% (straight after drying)
- **DSC-analysis (Section V)**
  - Melting point: -22 °C
  - Freezing point: -24 °C
- **Solubility**
  - Acetone: +++
  - Ethanol: +++ (119.6 mg/ml)
  - 2-propanol: +++ (87.6 mg/ml)
  - Ethyl acetate: +++ (at least 125.4 mg/ml)
  - Acetonitrile: + (~ 4.5 mg/ml)
  - Hexane: +++ (at least 88.8 mg/ml)
  - Toluene: +++ (at least 79.8 mg/ml)
- **Density: g cm⁻³ 0.874 g/cm³ (50 °C) (Section I)**
- **FTIR:**
- **NMR:**
- **Viscosity: ---**
- **Cl⁻ content: Reacts with AgNO₃, not possible to detect**
[A336⁺] [HCO₃⁻]

- TGA-analysis (Section IV)
  - Decomposition temperature: 176 °C
  - Water content: 0.1 % (straight after drying)
- DSC-analysis (Section V)
  - Melting point: -6 °C
  - Freezing point: -7 °C
  - Endothermic phase change: 22 °C
  - Exothermic phase changes: -25 °C, 8 °C
- Solubility
  - Acetone: +++
  - Ethanol: +++ (at least 79.4 mg/ml)
  - 2-propanol: +++ (at least 105.6 mg/ml)
  - Ethyl acetate: +++ (at least 86.6 mg/ml)
  - Acetonitrile: ++ (~ 46.4 mg/ml)
  - Hexane: +++ (at least 81.6 mg/ml)
  - Toluene: +++ (at least 85.0 mg/ml)
- Density: not enough sample
- FTIR: (Section II)
- NMR: (Section VI)
- Viscosity: ---
- Cl⁻ content: contains chlorine (~58.7 mg/g; 1.7 mmol/g)

[A336⁺] [CH₃COO⁻]

- TGA-analysis (Section IV)
  - Decomposition temperature: 175 °C
  - Water content: 0.9 % (straight after drying)
- DSC-analysis (Section V)
  - Melting point: -22 °C
  - Freezing point: -23 °C
- Solubility
  - Acetone: +++
  - Ethanol: +++ (at least 143.2 mg/ml)
  - 2-propanol:
  - Ethyl acetate:
  - Acetonitrile:
  - Hexane:
  - Toluene:
  - Density: 0.873 g cm⁻³ (50 °C) (Section I)
  - FTIR: (Section II)
  - NMR: (Section VI)
  - Viscosity: ---
  - Cl⁻ content: contains chlorine (~44.1 mg/g; 1.2 mmol/g)
[A336⁺][HSO₄⁻] (Microwave heating)

- TGA-analysis (Section IV)
  - Decomposition temperature: 196 °C
  - Water content: 0.2 % (straight after drying)
- DSC-analysis (Appendix V)
  - Melting point: -19 °C
  - Freezing point: -25 °C
  - Endothermic phase change: 21 °C
  - Exothermic phase change: 7 °C
- Solubility
  - Acetone: +++
  - Ethanol: +++ (at least 117.4 mg/ml)
  - 2-propanol:
  - Ethyl acetate:
  - Acetonitrile:
  - Hexane:
  - Toluene:
- Density: 0.907 cm³ (50 °C) (Section I)
- FTIR: (Section II)
- NMR: (Section VI)
- Viscosity: ---
- Cl⁻ content: contains chlorine (~27 mg/g; 0.8 mmol/g)

[A336⁺][HCOO⁻]

- TGA-analysis (Section IV)
  - Decomposition temperature: 174 °C
  - Water content: 0.4 % (directly after drying)
- DSC-analysis (Section V)
  - Melting point: 7 °C
  - Freezing point: 1 °C
  - Endothermic phase change: -44 °C
  - Exothermic phase change: -25 °C
- Solubility
  - Acetone: +++
  - Ethanol: +++ (at least 147.8 mg/ml)
  - 2-propanol:
  - Ethyl acetate:
  - Acetonitrile:
  - Hexane:
  - Toluene:
- Density: 0.878 g cm⁻³ (50 °C) (Section I)
- FTIR: (Section II)
- NMR: (Section VI)
- Viscosity: ---
• Cl\(^{-}\) content: contains chlorine (~39 mg/g; 1,1 mmol/g)

\([A336^+][PF_6^-]\)

- TGA-analysis (Section IV)
  - Decomposition temperature: 274 °C
  - Water content: 0,5 %
- DSC-analysis (Section V)
  - Melting point: 51 °C
  - Freezing point: 66 °C
- Solubility
  - Acetone: +++
  - Ethanol: +++ (at least 101,4 mg/ml)
  - 2-propanol:
  - Ethyl acetate:
  - Acetonitrile:
  - Hexane:
  - Toluene:
- Density: too viscous below 70 °C
- FTIR: (Section II)
- NMR: (Section VI)
- Viscosity: ---
- Cl\(^{-}\) content: contains chlorine (~1,8mg/g; 51 µmol/g)

\([A336^+][(CF_3SO_2)_2N^-]\)

- TGA-analysis (Section IV)
  - Decomposition temperature: 367 °C
  - Water content: 6,1 %
- DSC-analysis (Section V)
  - Melting point: -39 °C
  - Freezing point: -39 °C
  - Endothermic phase changes: -51 °C, -12 °C
- Solubility
  - Acetone: +++
  - Ethanol: +++ (at least 119,8 mg/ml)
  - 2-propanol:
  - Ethyl acetate:
  - Acetonitrile:
  - Hexane:
  - Toluene:
- Density: 1,060 g cm\(^{-3}\) (50 °C) (Section I)
- FTIR: (Section II)
- NMR: (Section VI)
- Viscosity: ---
• Cl⁻ content: no chlorine detected
Section I: Density vs. temperature graphs

Density dependence of temperature: \( \rho = A + BT \)

**Graph 1:**

\[ \rho \text{ vs. } T \text{ (A336SO2H)} \]

\[ \rho = -0.0005T + 1.0435 \]

\[ R^2 = 1 \]

**Graph 2:**

\[ \rho \text{ vs. } T \text{ (A336BF4)} \]

\[ \rho = -0.0007T + 1.1152 \]

\[ R^2 = 0.9596 \]
\[ \rho = -0.0005 T + 1.0547 \]

\[ R^2 = 0.9967 \]

\[ \rho = -0.0005 T + 1.0498 \]

\[ R^2 = 0.9993 \]
\( \rho \) vs. T (A336NOx) 
\[ \rho = -0.0006T + 1.0752 \]
\[ R^2 = 0.9989 \]

\( \rho \) vs. T (A336H2PO4) 
\[ \rho = -0.0006T + 1.0683 \]
\[ R^2 = 0.999 \]
$\rho$ vs. $T$ (A336\text{HSO}_4)

$\rho = -0.0006T + 1.0945$

$R^2 = 0.9937$

$\rho$ vs. $T$ (A336\text{CH}_3\text{COO})

$\rho = -0.0006T + 1.0647$

$R^2 = 0.9957$
$\rho$ vs. $T$ (A336HCOO)

$\rho = -0.0006T + 1.0832$

$R^2 = 0.9983$

$\rho$ vs. $T$ (A336(CF$_3$SO$_2$)$_2$N) BII

$\rho = -0.0008T + 1.3023$

$R^2 = 0.9952$
Section II: FTIR-spectras

FTIR (A336SO2)

FTIR (A336BF4)
FTIR (A336NOx)

FTIR (A336H2PO4)
FTIR (A336HCO3)

FTIR (A336CH3COO)
FTIR (A336 Cl), from www.aldrich.com
Section III: Viscosity vs. temperature graphs

Viscosity dependence of temperature: \( \log \eta = A + B \times \frac{1}{T} \)

(A336BH4) \( \log \eta \) vs. 1/T

\( \eta = 3027.6(1/T) - 9.5543 \)

\( R^2 = 0.9996 \)

(A336NOx) \( \log \eta \) vs 1/T

\( \log \eta = 2830.3(1/T) - 8.9599 \)

\( R^2 = 0.9967 \)
Section IV: TGA GRAFS

- Sample: A336SO2
- Size: 31.8700 mg
- Method: Ramp
- File: C:\My Documents\TGA\A336SO2.txt
- Operator: PV
- Run Date: 2005-02-09 10:06
- Instrument: TGA

- Sample: A336BF4
- Size: 35.4500 mg
- Method: Ramp
- File: C:\My Documents\TGA\A336BF4%.txt
- Operator: PV
- Run Date: 2005-02-17 10:06
- Instrument: TGA
Sample: A336NOx
Size: 26.5000 mg
Method: Ramp

Sample: A336H2PO4
Size: 44.9400 mg
Method: Ramp
Sample: A336HCO3
Size: 48.6900 mg
Method: Ramp
Sample: A336acet
Size: 38.0500 mg
Method: Ramp
Section V: DSC GRAPHS

**Sample: A336SO2**
Size: 10.1300 mg
Method: Ramp

**Sample: A336BF4**
Size: 5.0400 mg
Method: Ramp
Sample: A336BH4
Size: 8.0200 mg
Method: Ramp

Sample: A336crot
Size: 6.7900 mg
Method: Ramp
Sample: A336H2PO4  
Size: 21.5400 mg  
Method: Ramp  

Sample: A336HCO3  
Size: 10.4500 mg  
Method: Ramp
Section VI: Results from $^1$H and $^{13}$C NMR

Table S1. $^1$H NMR chemical shifts of hydrogen atoms in the [A336$^+$] cation for different ionic liquids

<table>
<thead>
<tr>
<th>compound</th>
<th>11 CH$_3$</th>
<th>1 CH$_2$</th>
<th>2 CH$_2$</th>
<th>3-7 (3-9) CH$_2$</th>
<th>8 (10) CH$_3$*</th>
</tr>
</thead>
<tbody>
<tr>
<td>[A336$^+$][Cl$^-$]</td>
<td>2.924</td>
<td>3.178</td>
<td>1.596</td>
<td>1.2 - 1.3</td>
<td>0.866</td>
</tr>
<tr>
<td>[A336$^+$][NO$_3^-$]</td>
<td>2.922</td>
<td>3.175</td>
<td>1.597</td>
<td>1.2 - 1.3</td>
<td>0.869</td>
</tr>
<tr>
<td>[A336$^+$][crot$^-$]</td>
<td>2.926</td>
<td>3.182</td>
<td>1.598</td>
<td>1.2 - 1.3</td>
<td>0.867</td>
</tr>
<tr>
<td>[A336$^+$][BF$_4^-$]</td>
<td>2.92</td>
<td>3.173</td>
<td>1.597</td>
<td>1.2 - 1.3</td>
<td>0.867</td>
</tr>
<tr>
<td>[A336$^+$][BH$_4^-$]</td>
<td>2.93</td>
<td>3.184</td>
<td>1.597</td>
<td>1.2 - 1.3</td>
<td>0.867</td>
</tr>
<tr>
<td>[A336$^+$][SO$_2^-$]</td>
<td>2.927</td>
<td>3.181</td>
<td>1.597</td>
<td>1.2 - 1.3</td>
<td>0.865</td>
</tr>
<tr>
<td>[A336$^+$][CH$_3$COO$^-$]</td>
<td>2.929</td>
<td>3.182</td>
<td>1.596</td>
<td>1.2 - 1.3</td>
<td>0.868</td>
</tr>
<tr>
<td>[A336$^+$][H$_2$PO$_4^-$]</td>
<td>2.907</td>
<td>3.16</td>
<td>1.583</td>
<td>1.2 - 1.3</td>
<td>0.854</td>
</tr>
<tr>
<td>[A336$^+$][HSO$_4^-$]</td>
<td>2.914</td>
<td>3.167</td>
<td>1.589</td>
<td>1.2 - 1.3</td>
<td>0.857</td>
</tr>
<tr>
<td>[A336$^+$][PF$_6^-$]</td>
<td>2.923</td>
<td>3.174</td>
<td>1.597</td>
<td>1.2 - 1.3</td>
<td>0.868</td>
</tr>
<tr>
<td>[A336$^+$][HCOO$^-$]</td>
<td>2.93</td>
<td>3.184</td>
<td>1.598</td>
<td>1.2 - 1.3</td>
<td>0.867</td>
</tr>
<tr>
<td>[A336$^+$][HCO$_3^-$]</td>
<td>2.932</td>
<td>3.185</td>
<td>1.597</td>
<td>1.2 - 1.3</td>
<td>0.866</td>
</tr>
<tr>
<td>[A336$^+$][(CF$_3$SO$_2$)$_2$N$^-$]</td>
<td>2.923</td>
<td>3.172</td>
<td>1.596</td>
<td>1.2 - 1.3</td>
<td>0.868</td>
</tr>
</tbody>
</table>

*The highest peak in a group of peaks between 0.8-0.9. In the table hydrogen atoms are numbered according to the carbon atom they are attached to. Numbers without brackets are for trioctyl methylammonium and those inside brackets are for tridecyl methylammonium except numbers 1, 2 and 11, which are for both of them. (see below)
Table S2. $^{13}$C NMR chemical shifts of carbon atoms in the [A336$^+$] cation for different ionic liquids.

<table>
<thead>
<tr>
<th>A336 Ionic liquids $^{13}$C-NMR chemical shifts (ppm)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>8 (10)</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>[A336$^+$][Cl$^-$]</td>
<td>60.547</td>
<td>60.737</td>
<td>21.280</td>
<td>21.312</td>
<td>25.731</td>
</tr>
<tr>
<td>[A336$^+$][BF$_4^-$]</td>
<td>60.566</td>
<td>21.294</td>
<td>21.325</td>
<td>25.742</td>
<td>25.780</td>
</tr>
<tr>
<td>[A336$^+$][BH$_4^-$]</td>
<td>60.52</td>
<td>60.781</td>
<td>21.315</td>
<td>21.351</td>
<td>25.756</td>
</tr>
<tr>
<td>[A336$^+$][HSO$_4^-$]</td>
<td>60.491</td>
<td>60.728</td>
<td>21.268</td>
<td>21.301</td>
<td>25.719</td>
</tr>
<tr>
<td>[A336$^+$][(CF$_3$SO$_2$)$_2$N$^-$]</td>
<td>60.481</td>
<td>60.700</td>
<td>21.258</td>
<td>21.291</td>
<td>25.708</td>
</tr>
</tbody>
</table>

In the table carbon atoms are numbered the same way as in table 1. Numbers without brackets are for trioctyl methylammonium and those inside brackets are for tridecyl methylammonium except numbers 1, 2, 3 and 11, which are for both of them. (see above)

The large number of peaks is due to the fact that the cation is a mixture of trioctyl and tridecyl methylammonium groups.