## 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.

[A336][$BH_4$]/[$BO_2$]

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, $NaBH_4$, (0.378) added to the mixture. 10 ml of deionized $H_2O$ was added slowly, facilitating an emulsion and formation of some $H_2$ –bubbles according to the reaction scheme: $NaBH_4 + 2\ H_2O \rightarrow NaBO_2 + 4\ H_2$

A fine precipitate of 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% $H_2O$) 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, 8 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][$CH_3COO$]

0.01 mol (0.77 g) of Ammonium acetate, $CH_3COONH_4$, (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 $NH_4Cl$ (SEM/EDX) was left to sediment and 4 ml of extra dry acetone (Acros Organics, <0.005% $H_2O$) 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][$H_2PO_4$]

0.01 mol (0.88 g) of Sodium phosphate, $NaH_2PO_4$, (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][$HSO_4$]

0.01 mol (1.38 g) of sodium bisulfate, $NaHSO_4 \cdot H_2O$, (Merck, proanalysi) 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, $NH_4SCN$, (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 ($NH_4Cl$, 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][$NO_3$]

0.01 mol (0.85 g) of sodium nitrate, $NaNO_3$, (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, $CH_3CH=CHCOOH$, (m.p.70-73$^0$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][$PF_6$]

0.0094 mol of Aliquat 336® (Aldrich), as well as 0.01 mol of Sodium hexafluorophosphate, $NaPF_6$, (Aldrich, 98%) were dissolved in 5 ml and 10 ml of extra dry acetone (Acros Organics, <0.005% $H_2O$), 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, 800C, 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 hydrofobic IL was washed briefly with 20 ml of deionized $H_2O$ 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][$BF_4$]

0.0094 mol of Aliquat 336® (Aldrich) was dissolved in 5 ml of extra dry acetone (Acros Organics, <0.005% $H_2O$) and 0.01 mol (1.83 g) of $HBF_4$ (Aldrich, 48 wt-% in $H_2O$) 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][$HCO_3$]

0.0094 mol of Potassium bicarbonate, $KHCO_3$, (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][$(CF_3SO_2)_2N$]

0.0094 mol (2.87 g) of lithium (bistrifluoromethylsulfon)imide, $(CF_3SO_2)_2NLi$ (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% $H_2O$). 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)

## $[A336^+]\ [SO_2H^-]$

- TGA-analysis (Section IV)
  - Decomposition temperature: 157 $^oC$
  - Water content: 3,2 %
- DSC-analysis (Section V)
  - Melting point: -9,2 $^oC$
  - Freezing point: -4,9 $^oC$
- Solubility (T = 20 $^oC$)
  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 $^oC$) (Section I)
- FTIR: (Section II)
- NMR: (Section VI)
- Viscosity: ---
- $Cl^-$ content: contains chlorine (~60 mg/g; 1,7 mmol/g)

## $[A336^+]\ [BF_4^-]$

- TGA-analysis (Section IV)
  - Decomposition temperature: 294 $^oC$
  - Water content: 4,9 %
- DSC-analysis (Section V)
  - Melting point: 60 $^oC$
  - Freezing point: ----
  - Exothermic phase change: -9 $^oC$ (upon heating)
- Solubility (T = 20 $^oC$)
  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 $^oC$) (Section I)
- FTIR: (Section II)
- NMR: (Section VI)
- Viscosity: ---
- $Cl^-$ content: no chlorine detected

## $[A336^+]$ $[BH_4^-]/[B\ O_2^-]$

- TGA-analysis (Section IV)
  - Decomposition temperature: 144 $^oC$
  - Water content: 4,2 %
- DSC-analysis (Section V)
  - Melting point: -7,9 $^oC$
  - Freezing point: ---
  - Glass transition -7,4 $^oC$
- Solubility (T = 20 $^oC$)
  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 $^o$ C) (Section I)
- FTIR: (Section II)
- NMR: (Section VI)
- Viscosity: 2,76 Pa s (kg $m^{-1}$ $s^{-1}$) (T = 30 $^o$ C) (Section III)
- $Cl^-$ content: contains chlorine (~48,7 mg/g; 1,4 mmol/g)

## $[A336^+]$ $[croto^-]$

- TGA-analysis (Section IV)
  - Decomposition temperature: 183 $^oC$
  - Water content: 3,6 %
- DSC-analysis (Section V)
  - Melting point: 19,5 $^oC$
  - Freezing point: 15,7 $^oC$
  - Exothermic phase change: 28,4 $^oC$
- Solubility (T = 20 $^oC$)
  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 $^o$ C) (Section I)
- FTIR: (Section II)
- NMR: (Section VI)
- Viscosity: ---
- $Cl^-$ content: contains chlorine (~53,1 mg/g; 1,5 mmol/g)

## $[A336^+]\,[NO_3^-]$

- TGA-analysis (Section IV)
  - Decomposition temperature: 202 $^oC$
  - Water content: 3,1 %
- DSC-analysis (Section V)
  - Melting point: 5,5 $^oC$
  - Freezing point: 14,8 – 19,7 $^oC$
- Solubility (T = 20 $^oC$)
  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 $^o$ C) (Section I)
- FTIR: (Section II)
- NMR: (Section VI)
- Viscosity: 0,63 Pa s (kg $m^{-1}$ $s^{-1}$) (T = 50 $^o$ C) (Section III)
- $Cl^-$ content: contains chlorine (~5,6 mg/g; 0,2 mmol/g)

## $[A336^+]\,[H_2PO_4^-]$

- TGA-analysis (Section IV)
  - Decomposition temperature: 176 $^oC$
  - Water content: 0,4 % (straight after drying)
- DSC-analysis (Section V)
  - Melting point: -22 $^oC$
  - Freezing point: -24 $^oC$
- 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/$cm^3$ (50 $^oC$) (Section I)
- FTIR: (Section II)
- NMR: (Section VI)
- Viscosity: ---
- $Cl^-$ content: Reacts with $AgNO_3$, not possible to detect

## $[A336^+]$ $[HCO_3^-]$

- TGA-analysis (Section IV)
  - Decomposition temperature: 176 $^oC$
  - Water content: 0,1 % (straight after drying)
- DSC-analysis (Section V)
  - Melting point: -6 $^oC$
  - Freezing point: -7 $^oC$
  - Endothermic phase change: 22 $^oC$
  - Exothermic phase changes: -25 $^oC$, 8 $^oC$
- 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)

## $[A336^+]$ $[CH_3COO^-]$

- TGA-analysis (Section IV)
  - Decomposition temperature: 175 $^oC$
  - Water content: 0,9 % (straight after drying)
- DSC-analysis (Section V)
  - Melting point: -22 $^oC$
  - Freezing point: -23 $^oC$
- Solubility
  Acetone: +++
  Ethanol: +++ (at least 143,2 mg/ml)
  2-propanol:
  Ethyl acetate:
  Acetonitrile:
  Hexane:
  Toluene:
- Density: 0,873 g $cm^{-3}$ (50 $^oC$) (Section I)
- FTIR: (Section II)
- NMR: (Section VI)
- Viscosity: ---
- $Cl^-$ content: contains chlorine (~44,1 mg/g; 1,2 mmol/g)

## [$A336^+$] [$HSO_4^-$] (Microwave heating)

- TGA-analysis (Section IV)
  - Decomposition temperature: 196 $^oC$
  - Water content: 0,2 % (straight after drying)
- DSC-analysis (Appendix V)
  - Melting point: -19 $^oC$
  - Freezing point: -25 $^oC$
  - Endothermic phase change: 21 $^oC$
  - Exothermic phase change: 7 $^oC$
- Solubility
  Acetone: +++
  Ethanol: +++ (at least 117,4 mg/ml)
  2-propanol:
  Ethyl acetate:
  Acetonitrile:
  Hexane:
  Toluene:
- Density: 0,907 $cm^{-3}$ (50 $^oC$) (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 $^oC$
  - Water content: 0,4 % (directly after drying)
- DSC-analysis (Section V)
  - Melting point: 7 $^oC$
  - Freezing point: 1 $^oC$
  - Endothermic phase change: -44 $^oC$
  - Exothermic phase change: -25 $^oC$
- Solubility
  Acetone: +++
  Ethanol: +++ (at least 147,8 mg/ml)
  2-propanol:
  Ethyl acetate:
  Acetonitrile:
  Hexane:
  Toluene:
- Density: 0,878 g $cm^{-3}$ (50 $^oC$) (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 $^oC$
  - Water content: 0,5 %
- DSC-analysis (Section V)
  - Melting point: 51 $^oC$
  - Freezing point: 66 $^oC$
- Solubility
  Acetone: +++
  Ethanol: +++ (at least 101,4 mg/ml)
  2-propanol:
  Ethyl acetate:
  Acetonitrile:
  Hexane:
  Toluene:
- Density: too viscous below 70 $^oC$
- FTIR: (Section II)
- NMR: (Section VI)
- Viscosity: ---
- $Cl^-$ content: contains chlorine (~1,8mg/g; 51 μmol/g)

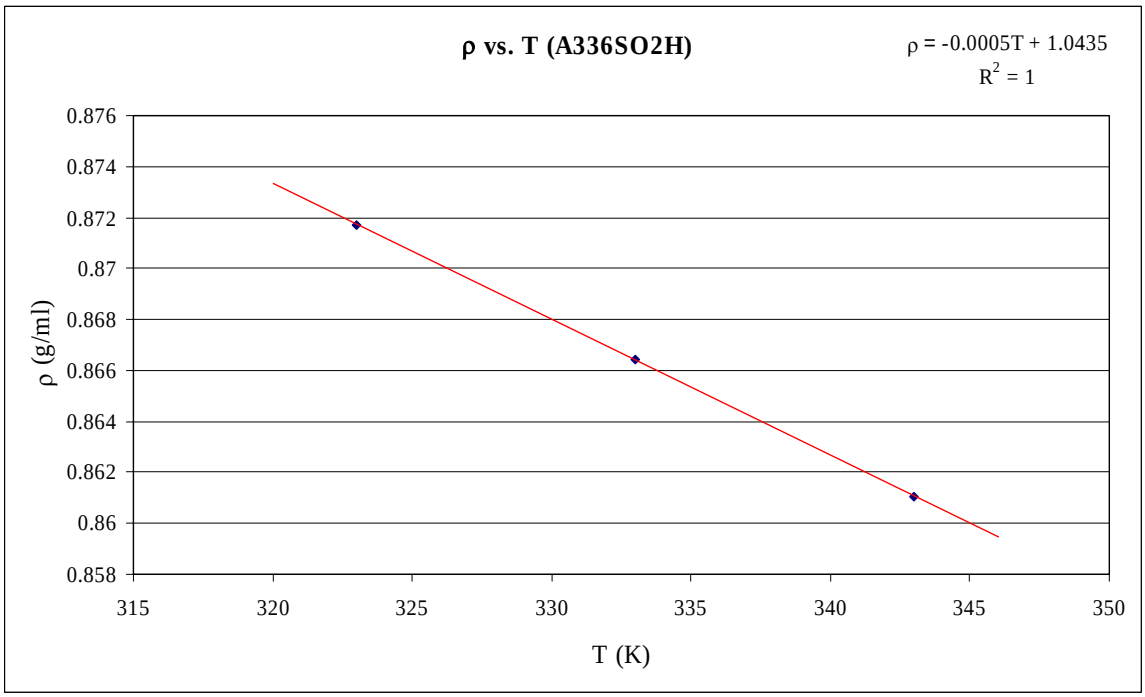
## $[A336^+]\,[(CF_3SO_2)_2N^-]$

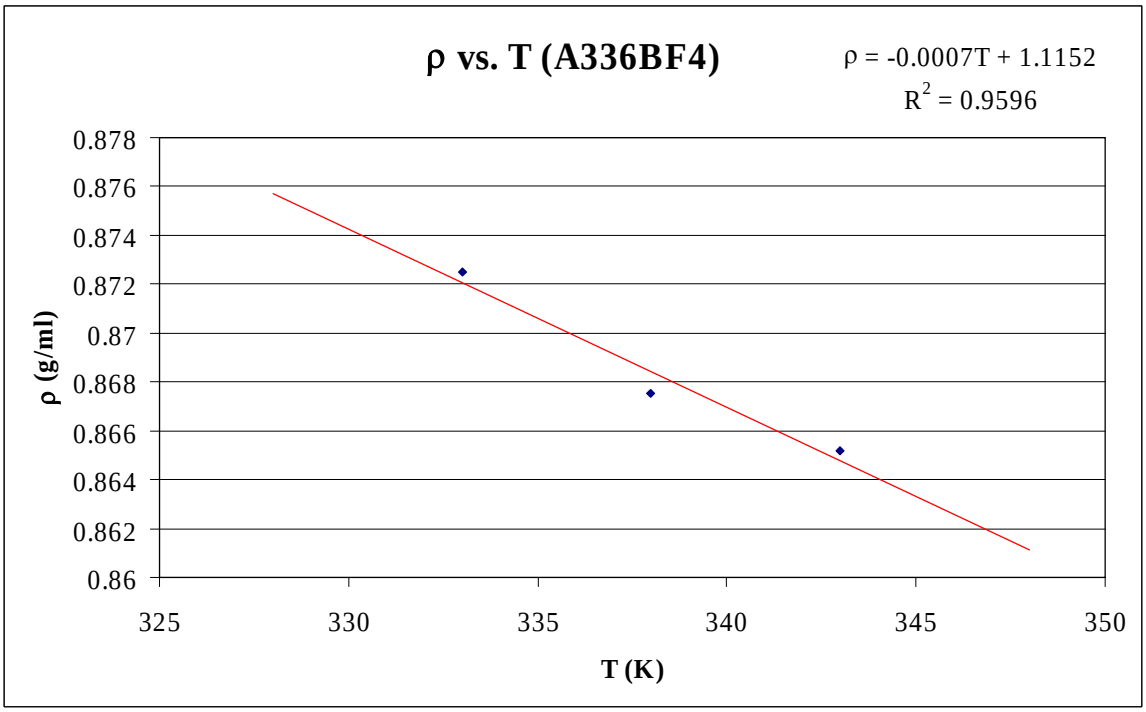
- TGA-analysis (Section IV)
  - Decomposition temperature: 367 $^oC$
  - Water content: 6,1 %
- DSC-analysis (Section V)
  - Melting point: -39 $^oC$
  - Freezing point: -39 $^oC$
  - Endothermic phase changes: -51 $^oC$, -12 $^oC$
- Solubility
  Acetone: +++
  Ethanol: +++ (at least 119,8 mg/ml)
  2-propanol:
  Ethyl acetate:
  Acetonitrile:
  Hexane:
  Toluene:
- Density: 1,060 g $cm^{-3}$ (50 $^oC$) (Section I)
- FTIR: (Section II)
- NMR: (Section VI)
- Viscosity: ---

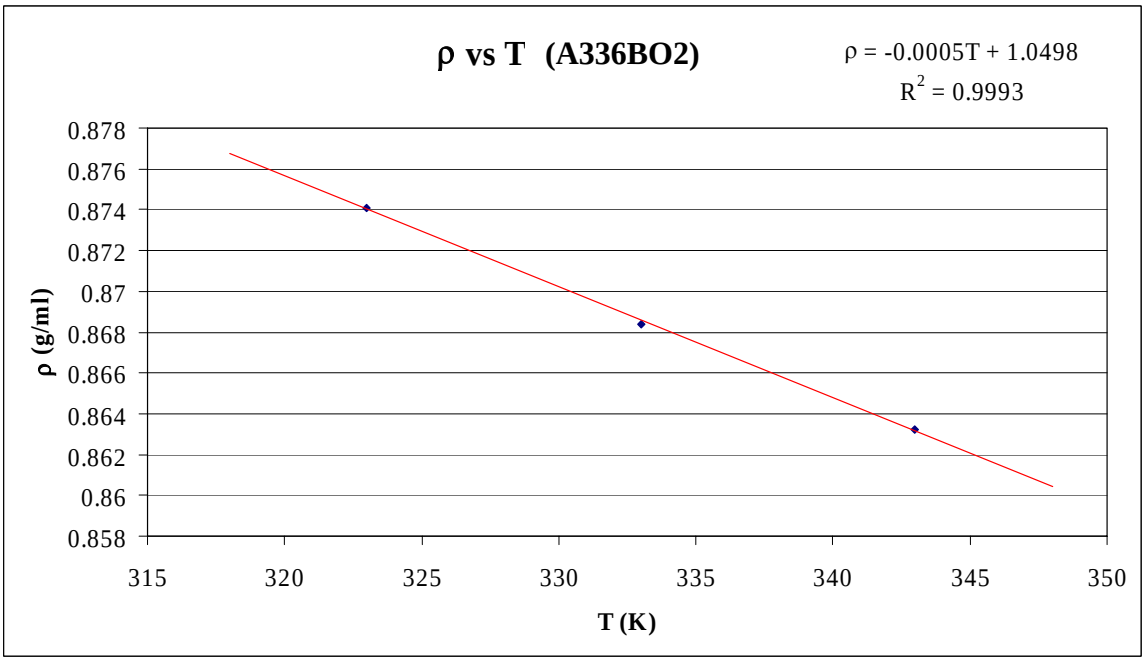
- $Cl^-$ content: no chlorine detected

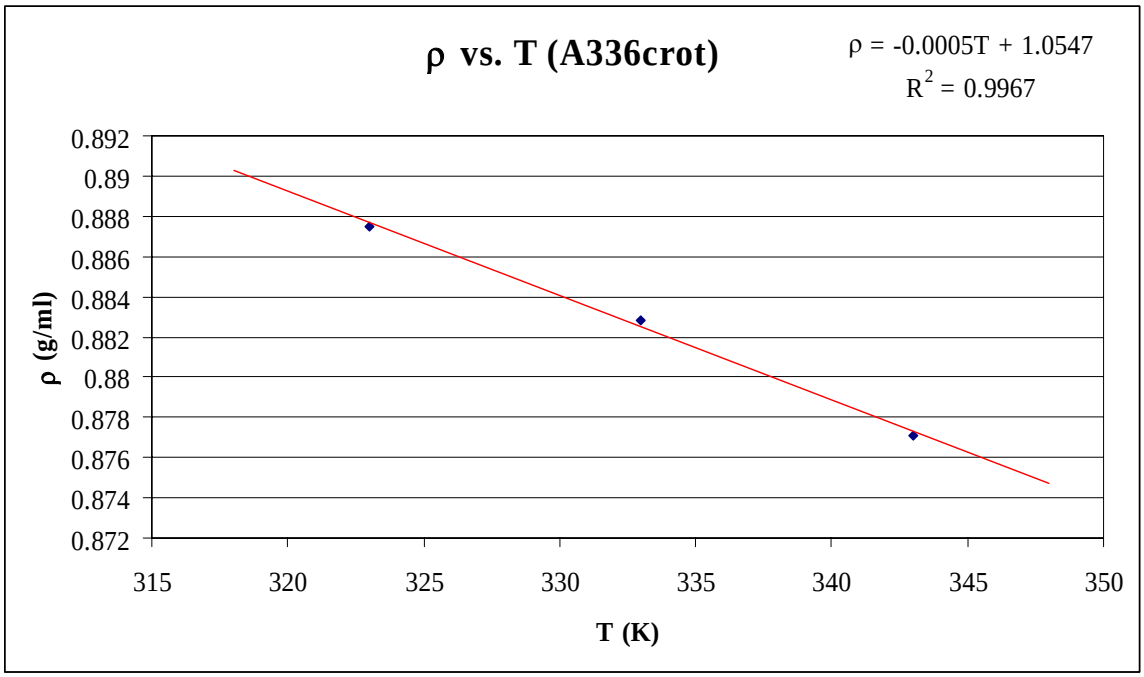
**Section I: Density vs. temperature graphs**

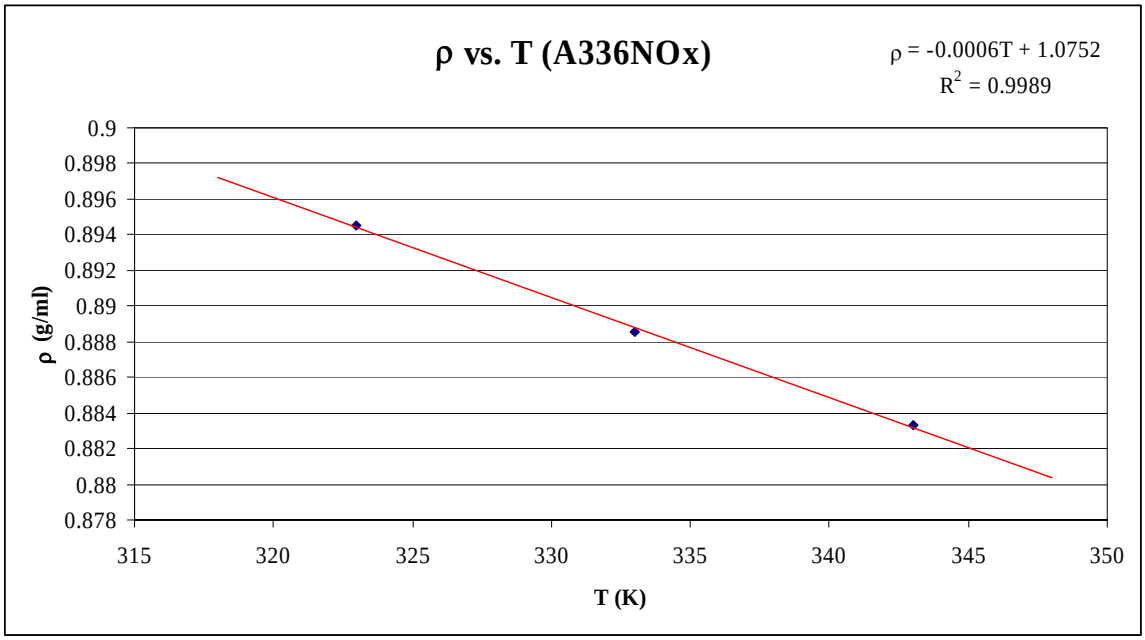
Density dependence of temperature: $\rho = A + BT$

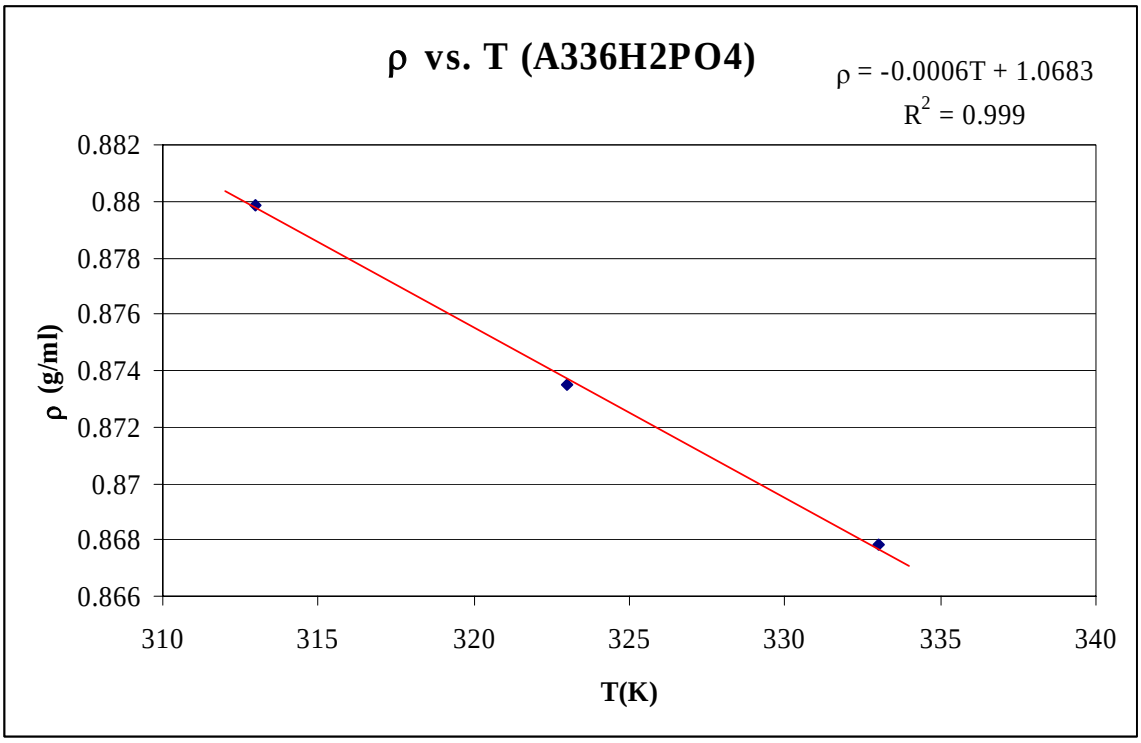


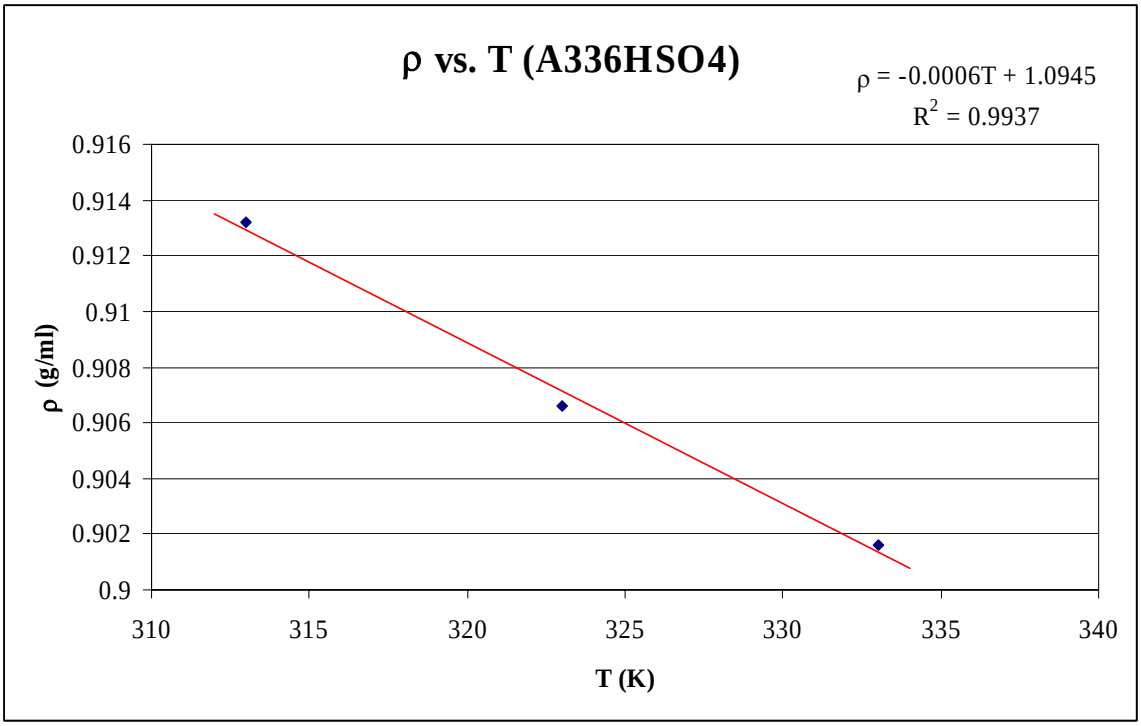



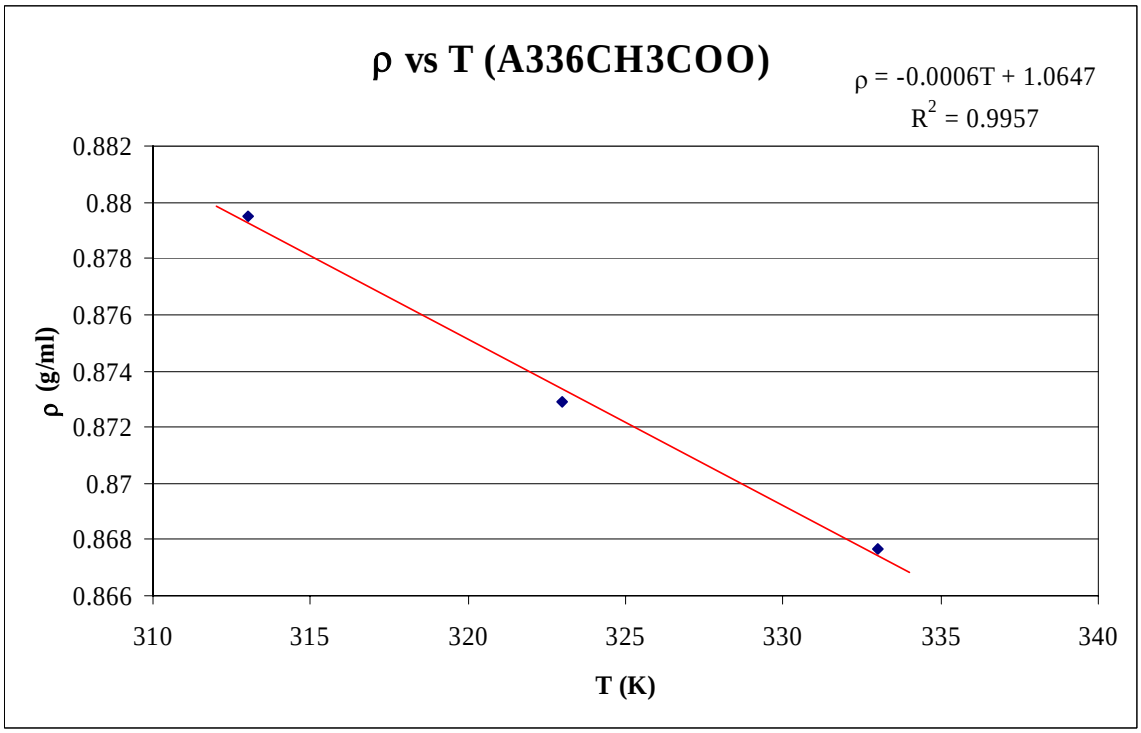

ρ vs T (A336BO2)
ρ = -0.0005T + 1.0498
R2 = 0.9993
ρ (g/ml)
0.878
0.876
0.874
0.872
0.87
0.868
0.866
0.864
0.862
0.86
0.858
315
320
325
330
335
340
345
350
T (K)

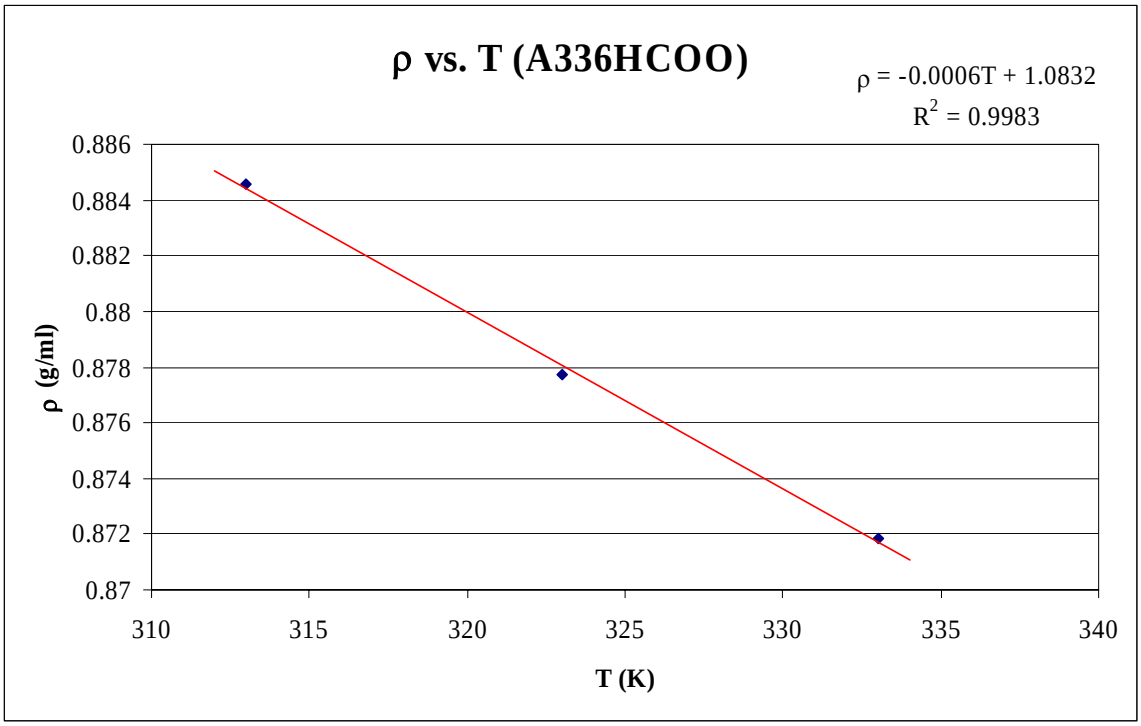

ρ vs. T (A336crot)
ρ = -0.0005T + 1.0547
R2 = 0.9967
ρ (g/ml)
0.892
0.89
0.888
0.886
0.884
0.882
0.88
0.878
0.876
0.874
0.872
315
320
325
330
335
340
345
350
T (K)

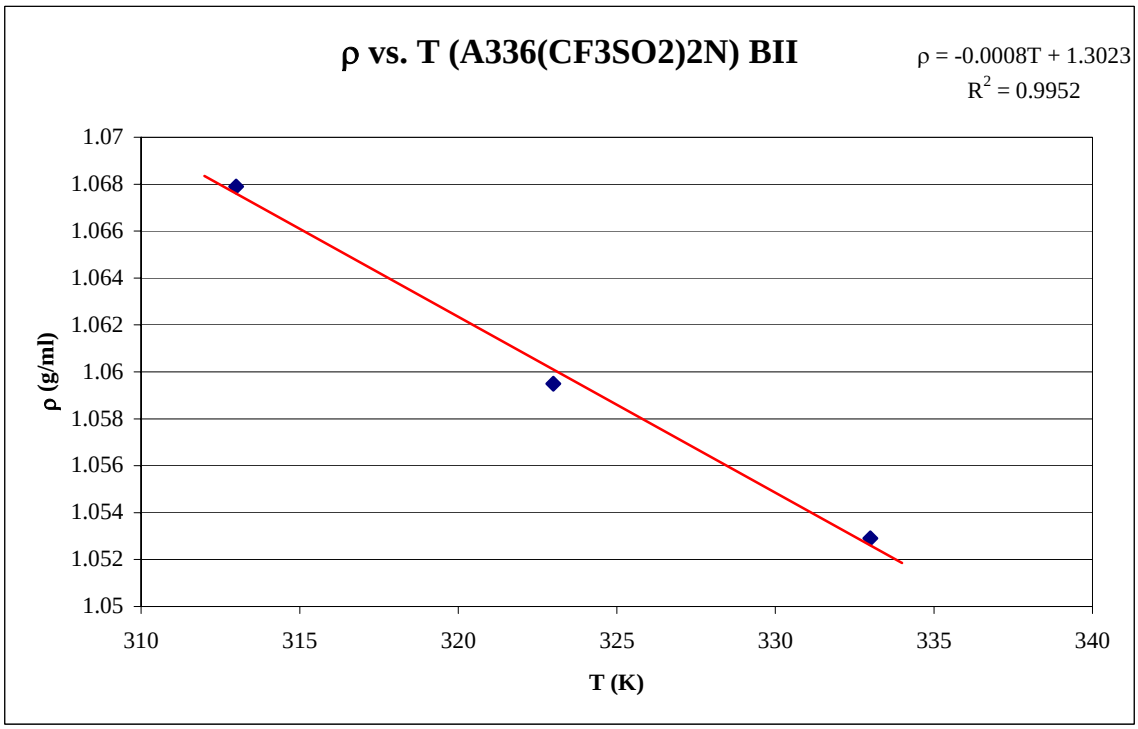

ρ vs. T (A336NOx)
ρ = -0.0006T + 1.0752
R2 = 0.9989
ρ (g/ml)
0.9
0.898
0.896
0.894
0.892
0.89
0.888
0.886
0.884
0.882
0.88
0.878
315
320
325
330
335
340
345
350
T (K)


ρ vs. T (A336H2PO4)
ρ = -0.0006T + 1.0683
R2 = 0.999
ρ (g/ml)
0.882
0.88
0.878
0.876
0.874
0.872
0.87
0.868
0.866
310
315
320
325
330
335
340
T(K)

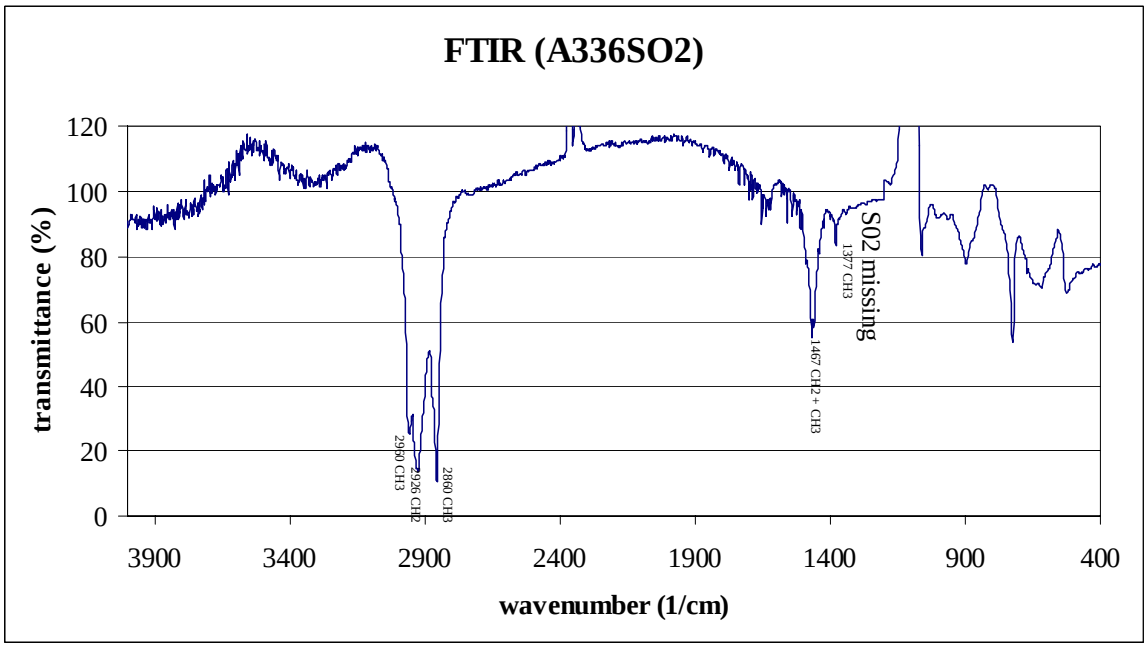

ρ vs. T (A336HSO4)
ρ = -0.0006T + 1.0945
R2 = 0.9937
0.916
0.914
0.912
0.91
0.908
0.906
0.904
0.902
0.9
ρ (g/ml)
310
315
320
325
330
335
340
T (K)

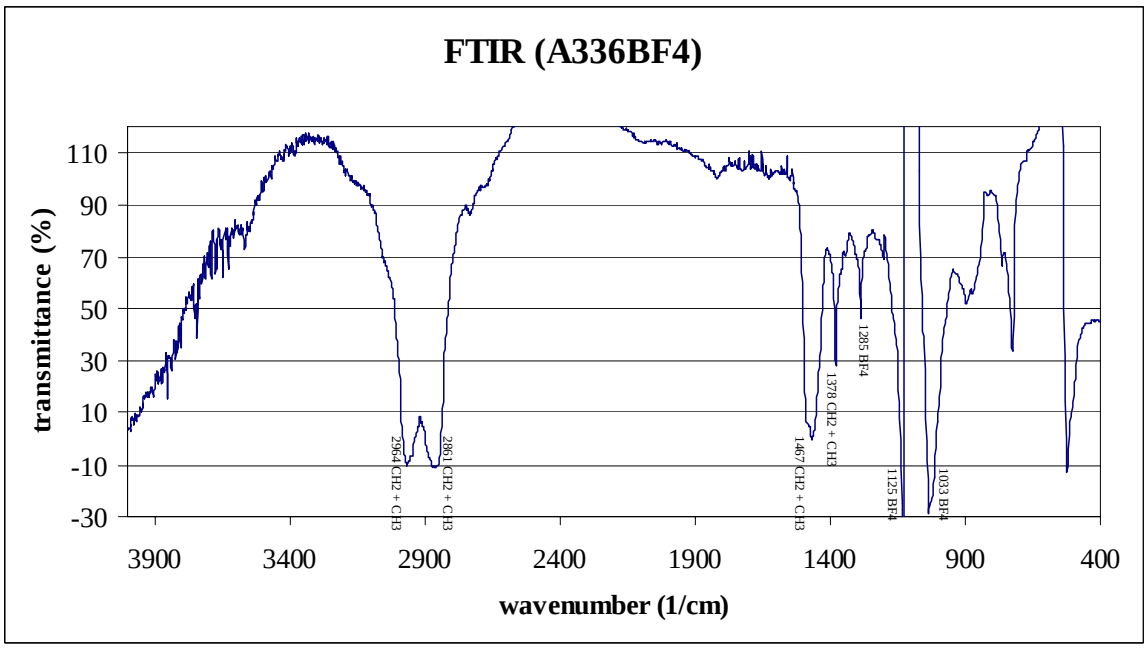

ρ vs T (A336CH3COO)
ρ = -0.0006T + 1.0647
R2 = 0.9957
0.882
0.88
0.878
0.876
0.874
0.872
0.87
0.868
0.866
ρ (g/ml)
310
315
320
325
330
335
340
T (K)

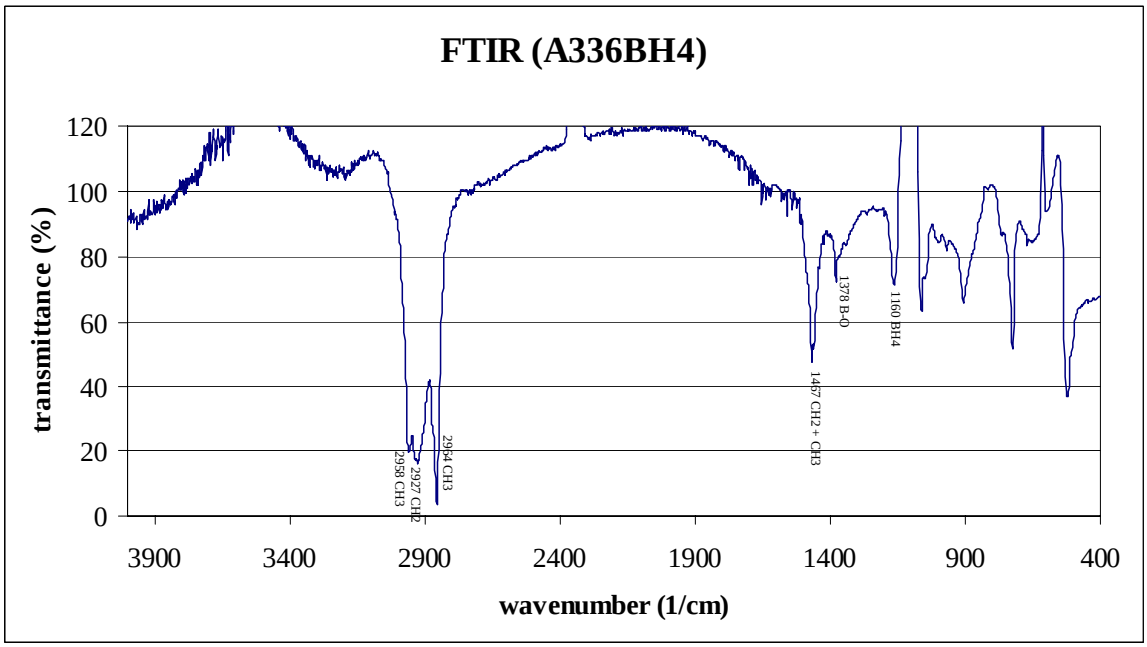

ρ vs. T (A336HCOO)
ρ = -0.0006T + 1.0832
R2 = 0.9983
0.886
0.884
0.882
0.88
0.878
0.876
0.874
0.872
0.87
ρ (g/ml)
310
315
320
325
330
335
340
T (K)

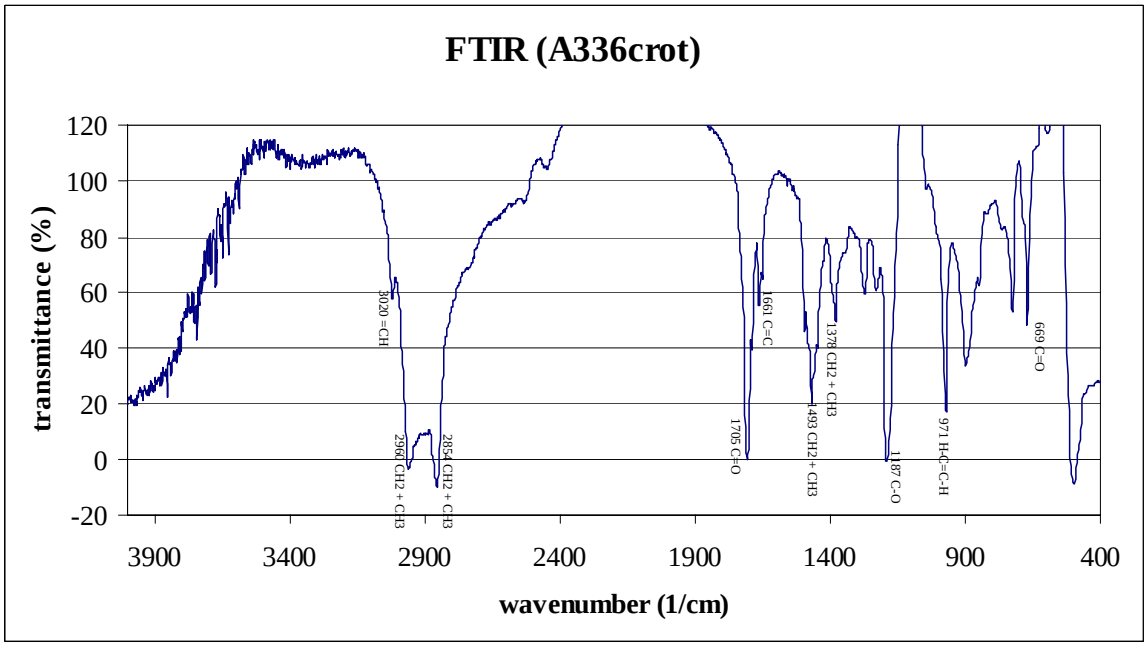

ρ vs. T (A336(CF3SO2)2N) BII
ρ = -0.0008T + 1.3023
R2 = 0.9952
1.07
1.068
1.066
1.064
1.062
1.06
1.058
1.056
1.054
1.052
1.05
ρ (g/ml)
310
315
320
325
330
335
340
T (K)

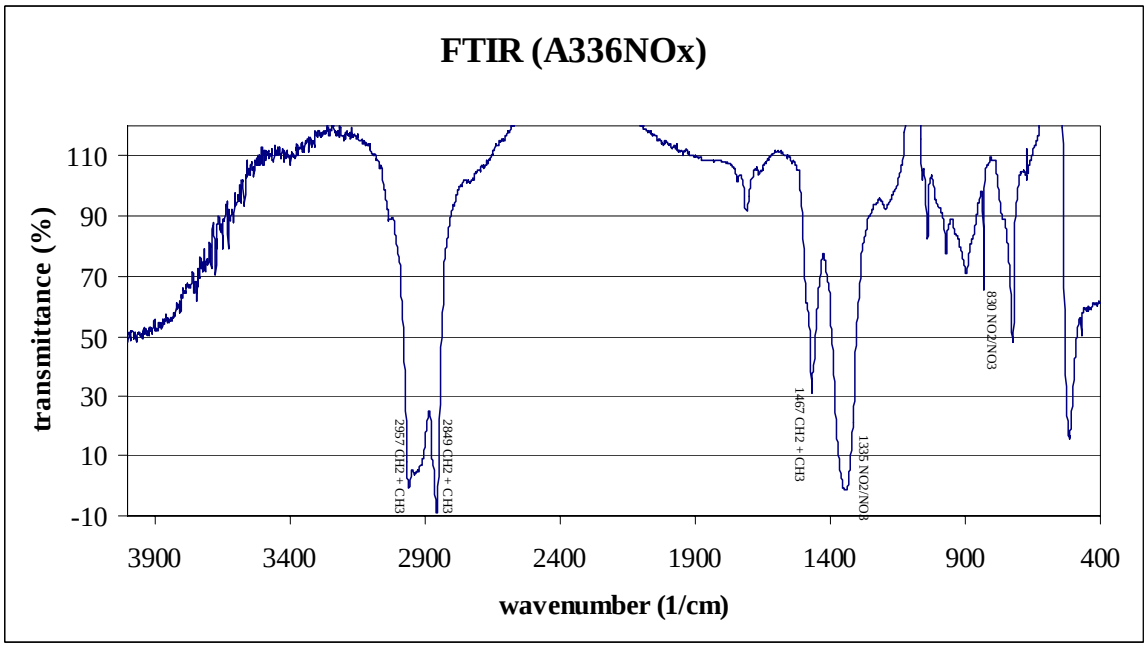
**Section II: FTIR-spectras**

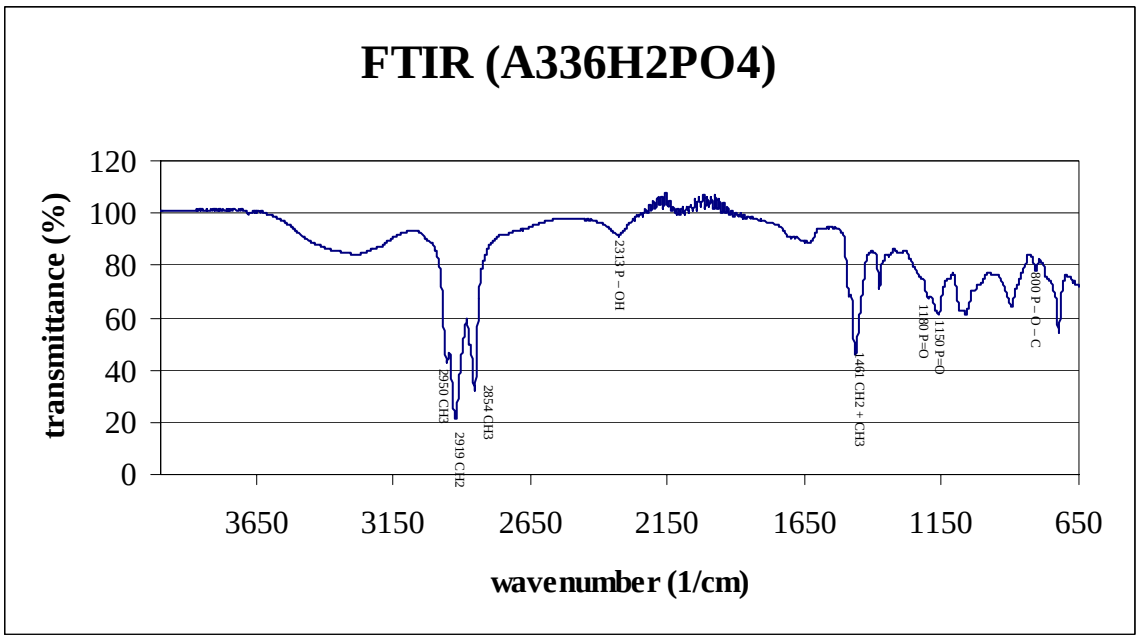


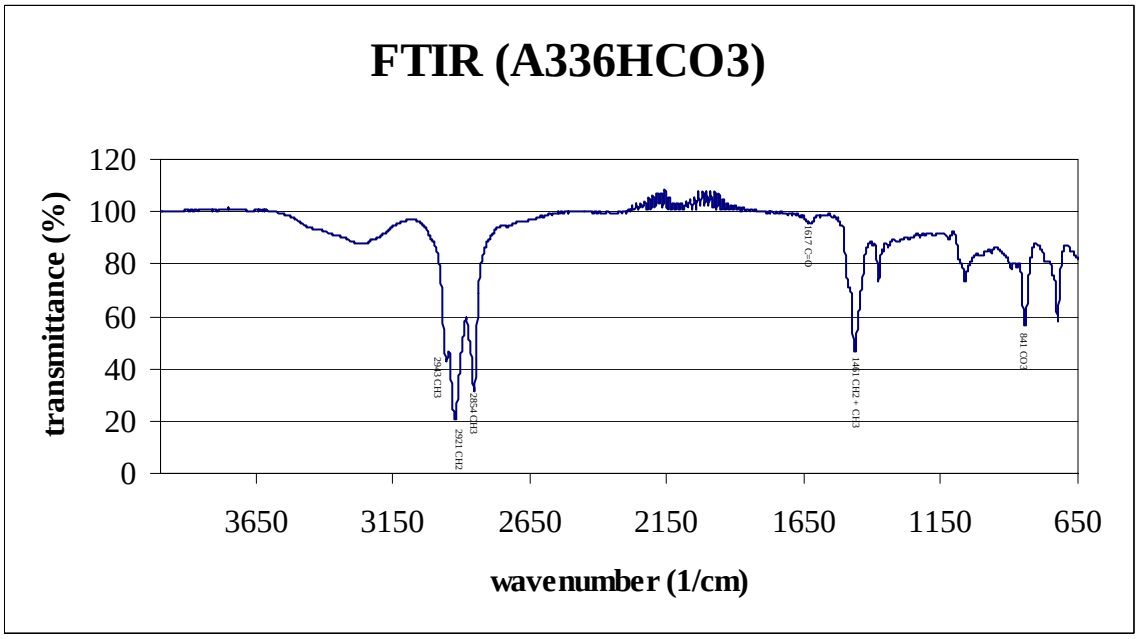



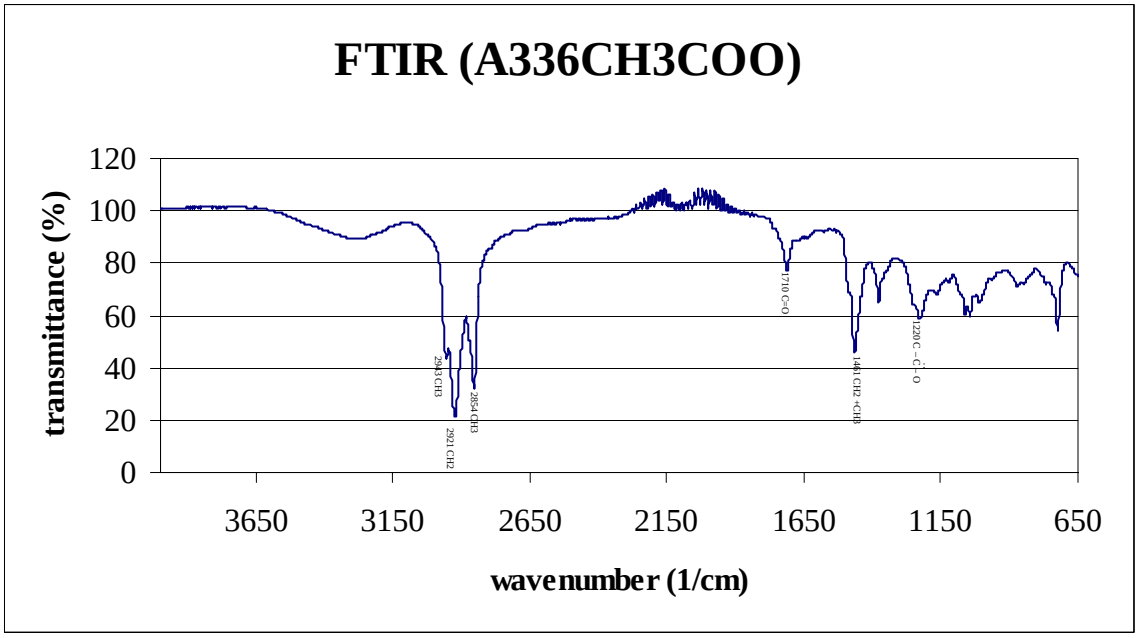

FTIR (A336BH4)
transmittance (%)
120
100
80
60
40
20
0
3900
3400
2900
2400
1900
1400
900
400
wavenumber (1/cm)
2958 CH3
2927 CH2
2854 CH3
1457 CH2 + CH3
1378 B-O
1160 BH4

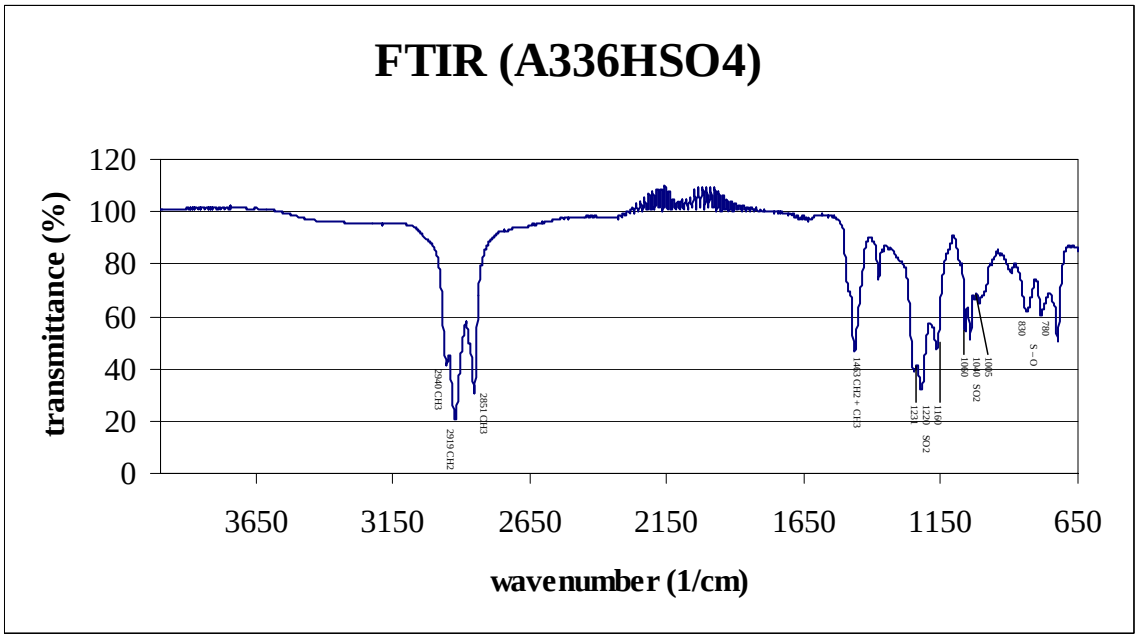

FTIR (A336crot)
transmittance (%)
120
100
80
60
40
20
0
-20
3900
3400
2900
2400
1900
1400
900
400
wavenumber (1/cm)
3020 =CH
2960 CH2 + CH3
2854 CH2 + CH3
1705 C=O
1661 C=C
1493 CH2 + CH3
1378 CH2 + CH3
1187 C-O
971 H-C=C-H
669 C=O

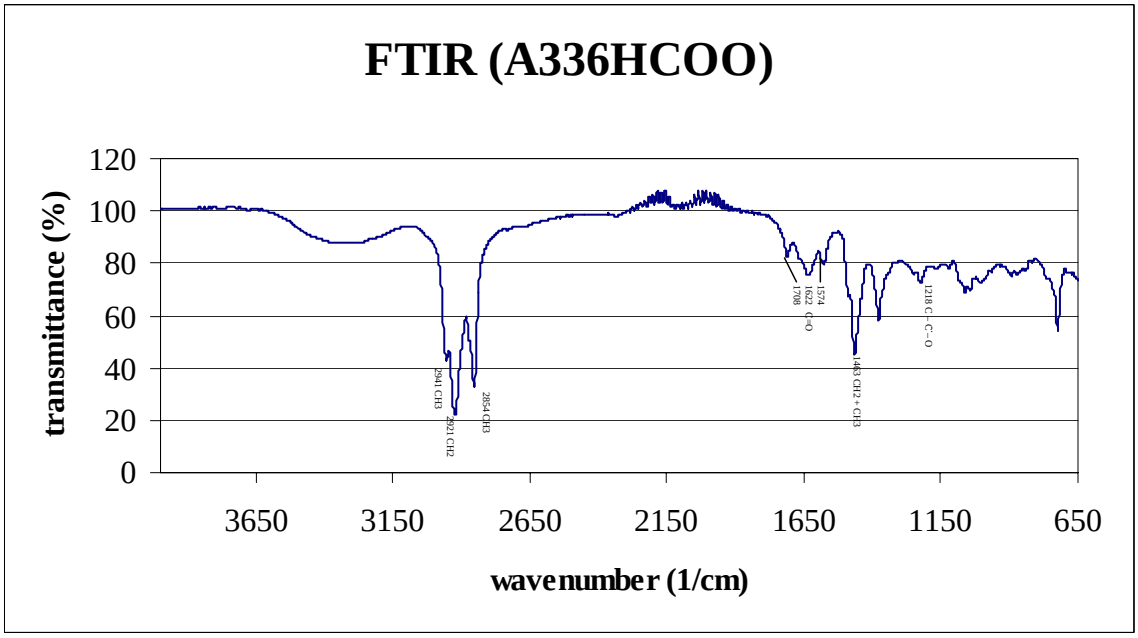

FTIR (A336NOx)
transmittance (%)
110
90
70
50
30
10
-10
3900
3400
2900
2400
1900
1400
900
400
wavenumber (1/cm)
2957 CH2 + CH3
2849 CH2 + CH3
1467 CH2 + CH3
1335 NO2/NO3
830 NO2/NO3

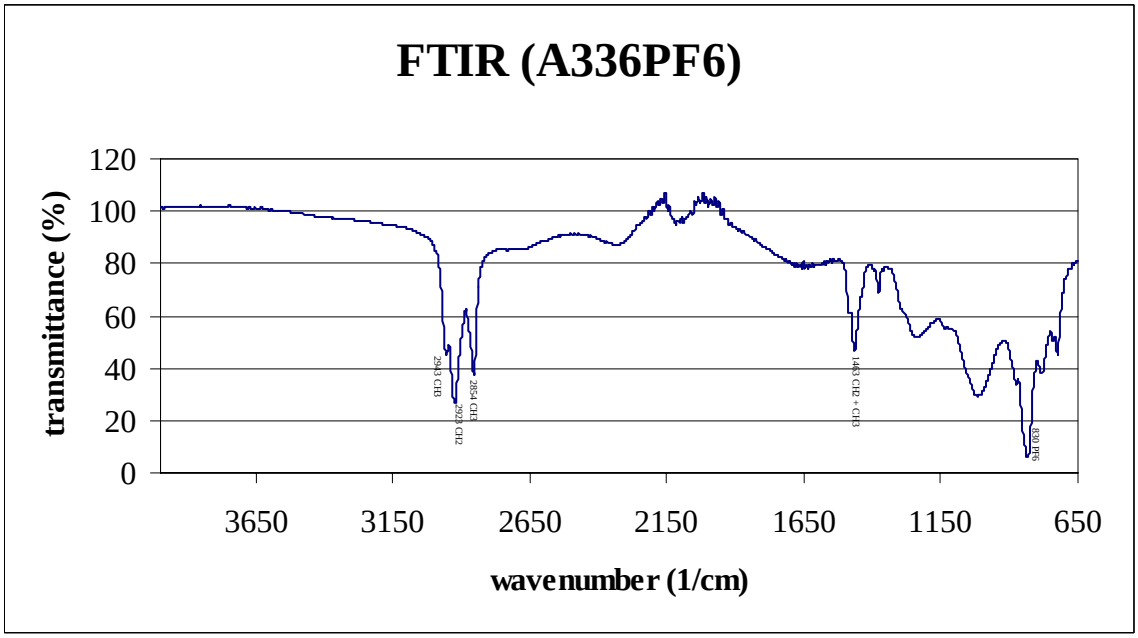

FTIR (A336H2PO4)
transmittance (%)
120
100
80
60
40
20
0
3650
3150
2650
2150
1650
1150
650
wavenumber (1/cm)
2950 CH3
2919 CH2
2854 CH3
2313 P – OH
1461 CH2 + CH3
1180 P=O
1150 P=O
1000 P – O – C

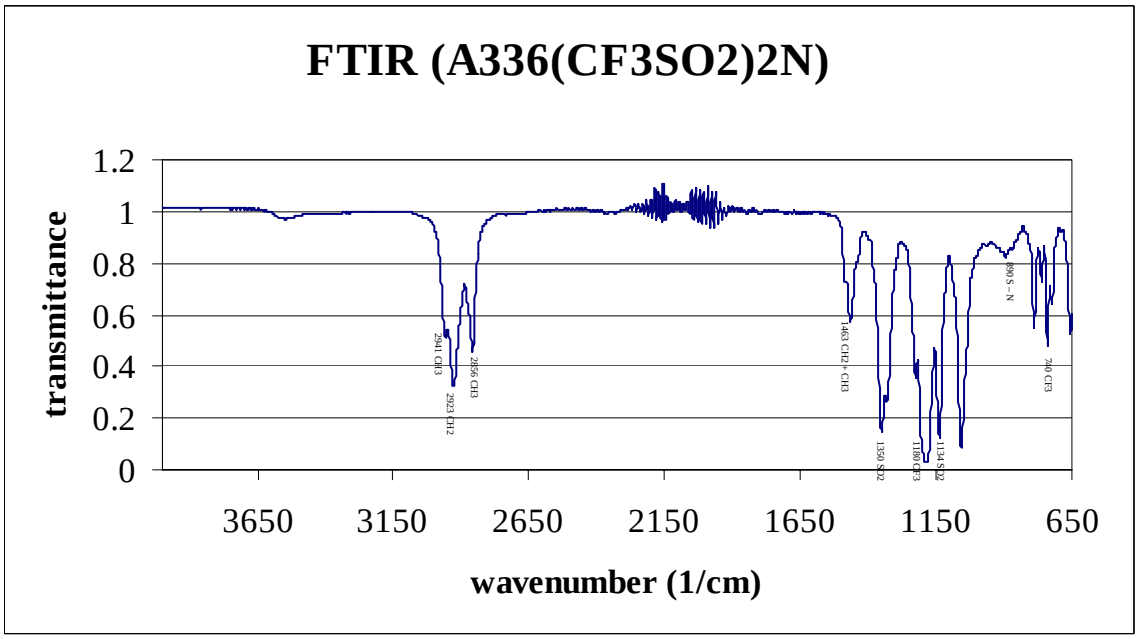

FTIR (A336HCO3)
transmittance (%)
120
100
80
60
40
20
0
3650
3150
2650
2150
1650
1150
650
wavenumber (1/cm)
2943 CH3
2921 CH2
2854 CH3
1617 C=O
1461 CH2 + CH3
841 CO3


FTIR (A336CH3COO)
transmittance (%)
120
100
80
60
40
20
0
3650
3150
2650
2150
1650
1150
650
wavenumber (1/cm)
2943 CH3
2921 CH2
2854 CH3
1710 C=O
1461 CH2 +CH3
1220 C – C – O

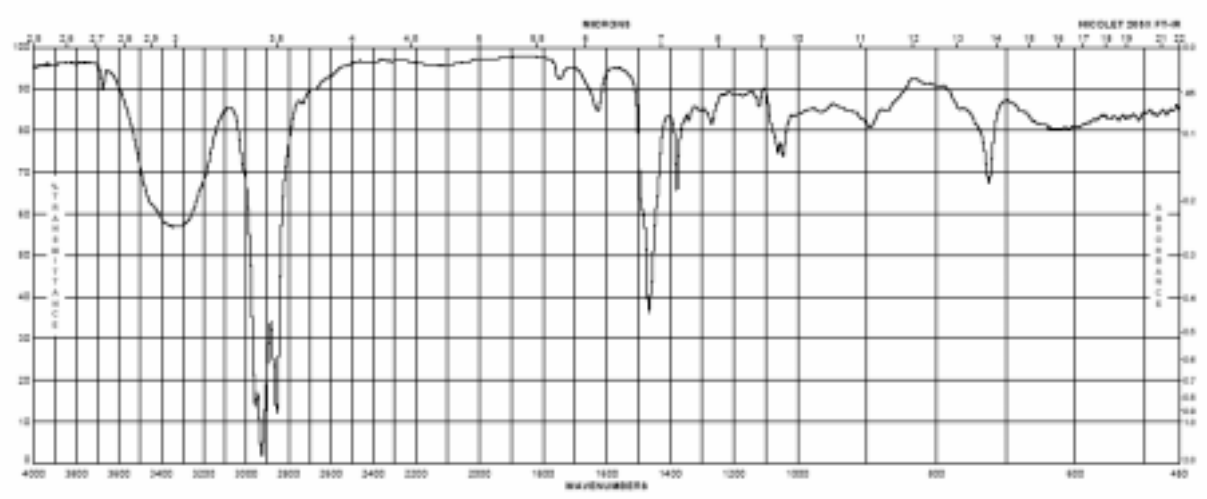

FTIR (A336HSO4)
transmittance (%)
120
100
80
60
40
20
0
3650
3150
2650
2150
1650
1150
650
wavenumber (1/cm)
2940 CH3
2919 CH2
2851 CH3
1463 CH2 + CH3
1231
1220
1169
SO2
1060
1005
SO2
830
780
S – O


FTIR (A336HCOO)
transmittance (%)
120
100
80
60
40
20
0
3650
3150
2650
2150
1650
1150
650
wavenumber (1/cm)
2941 CH3
2921 CH2
2854 CH3
1708
C=O
1574
1463 CH2 + CH3
1218 C – C – O


FTIR (A336PF6)
transmittance (%)
120
100
80
60
40
20
0
3650
3150
2650
2150
1650
1150
650
wavenumber (1/cm)
2943 CH3
2923 CH2
2854 CH3
1463 CH2 + CH3
830 PF6

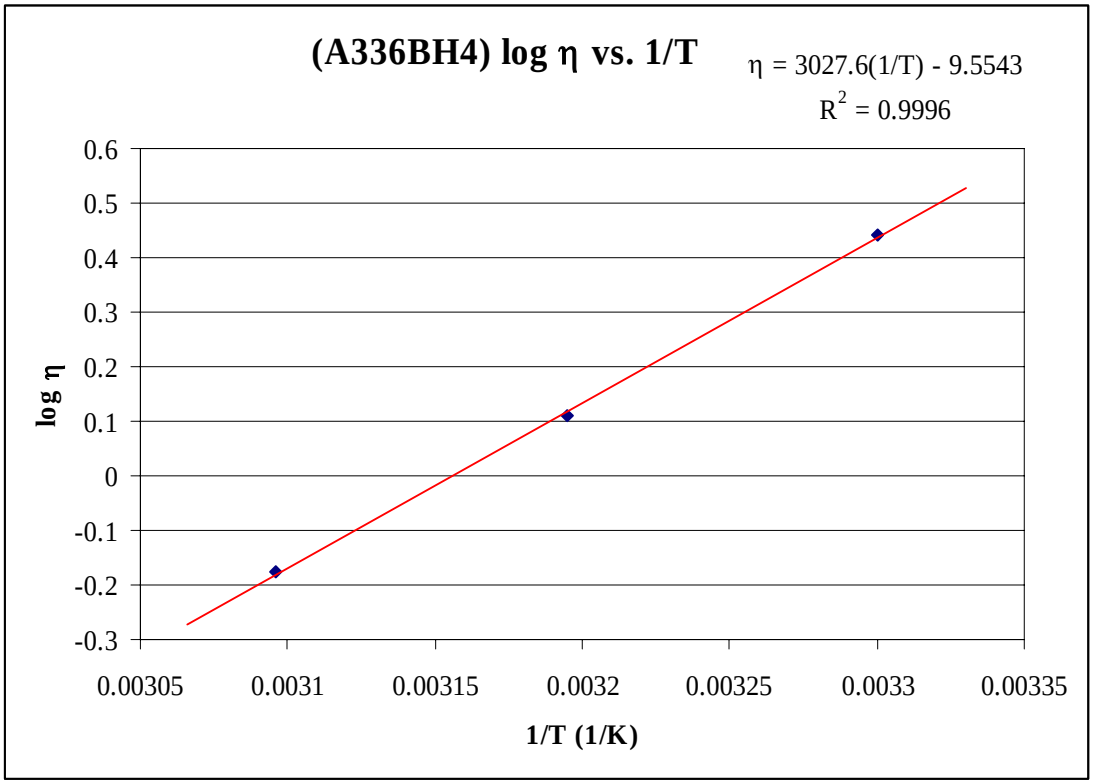

FTIR (A336(CF3SO2)2N)
transmittance
1.2
1
0.8
0.6
0.4
0.2
0
3650
3150
2650
2150
1650
1150
650
wavenumber (1/cm)
2941 CH3
2923 CH2
2856 CH3
1463 CH2+ CH3
1350 SO2
1180 CF3
1134 SO2
890 S – N
740 CF3

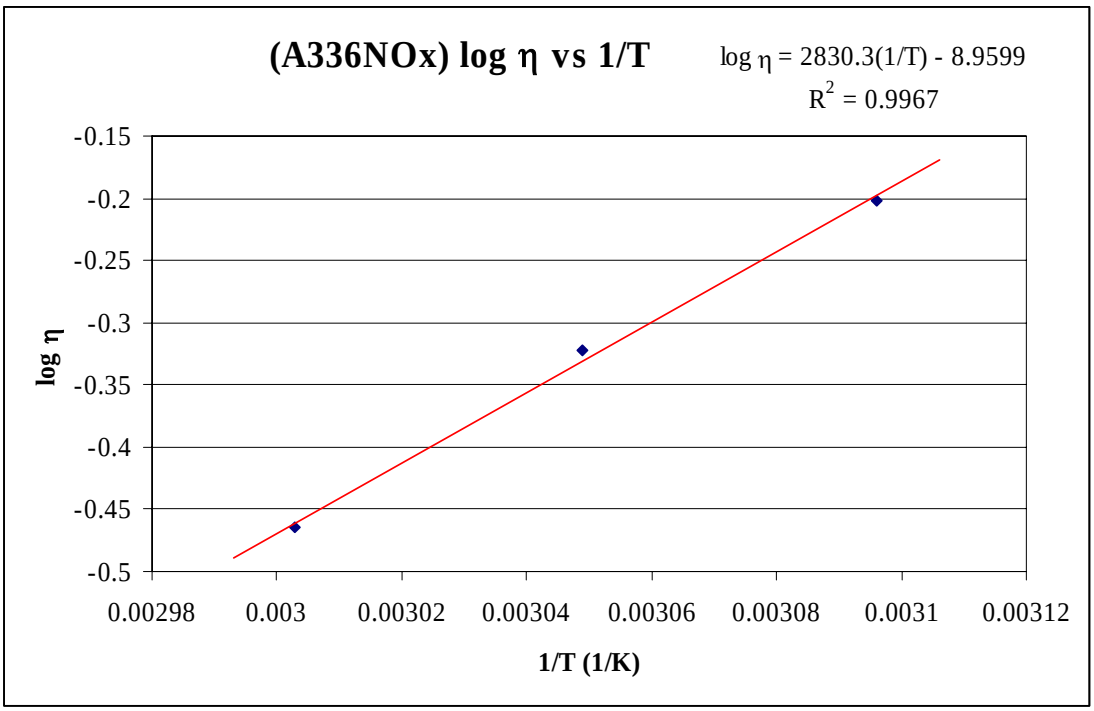
**FTIR (A336 Cl), from www.aldrich.com**



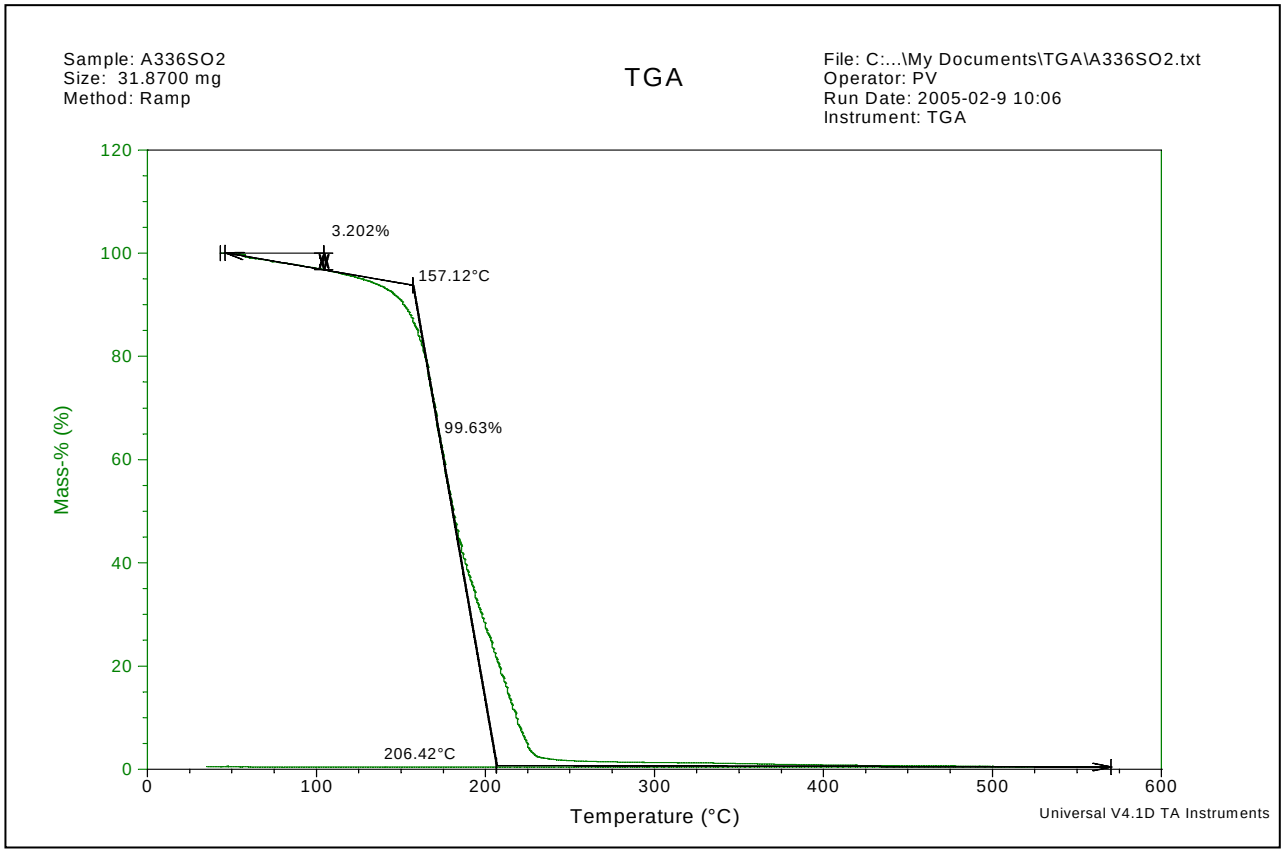
**Section III: Viscosity vs. temperature graphs**

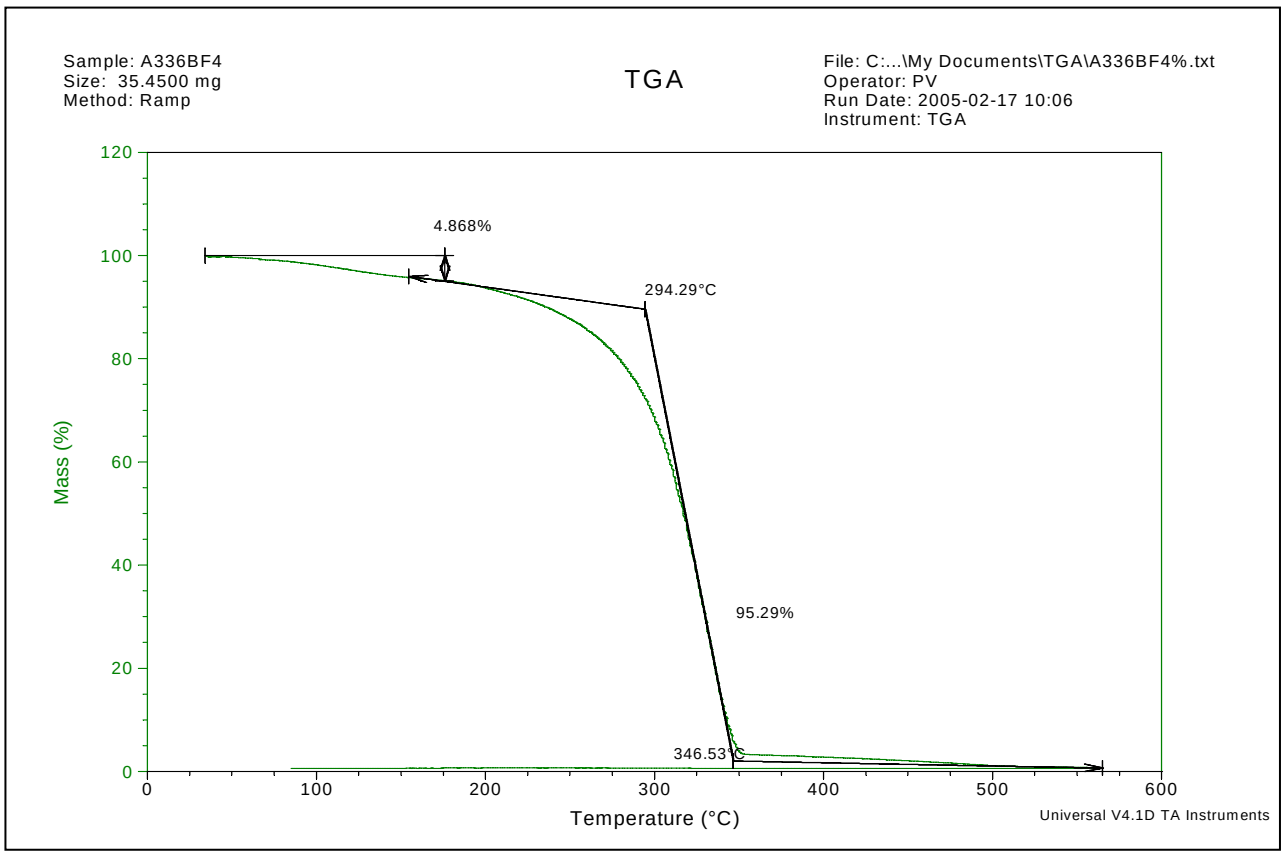
Viscosity dependence of temperature: $\log\eta = A + B \times \frac{1}{T}$

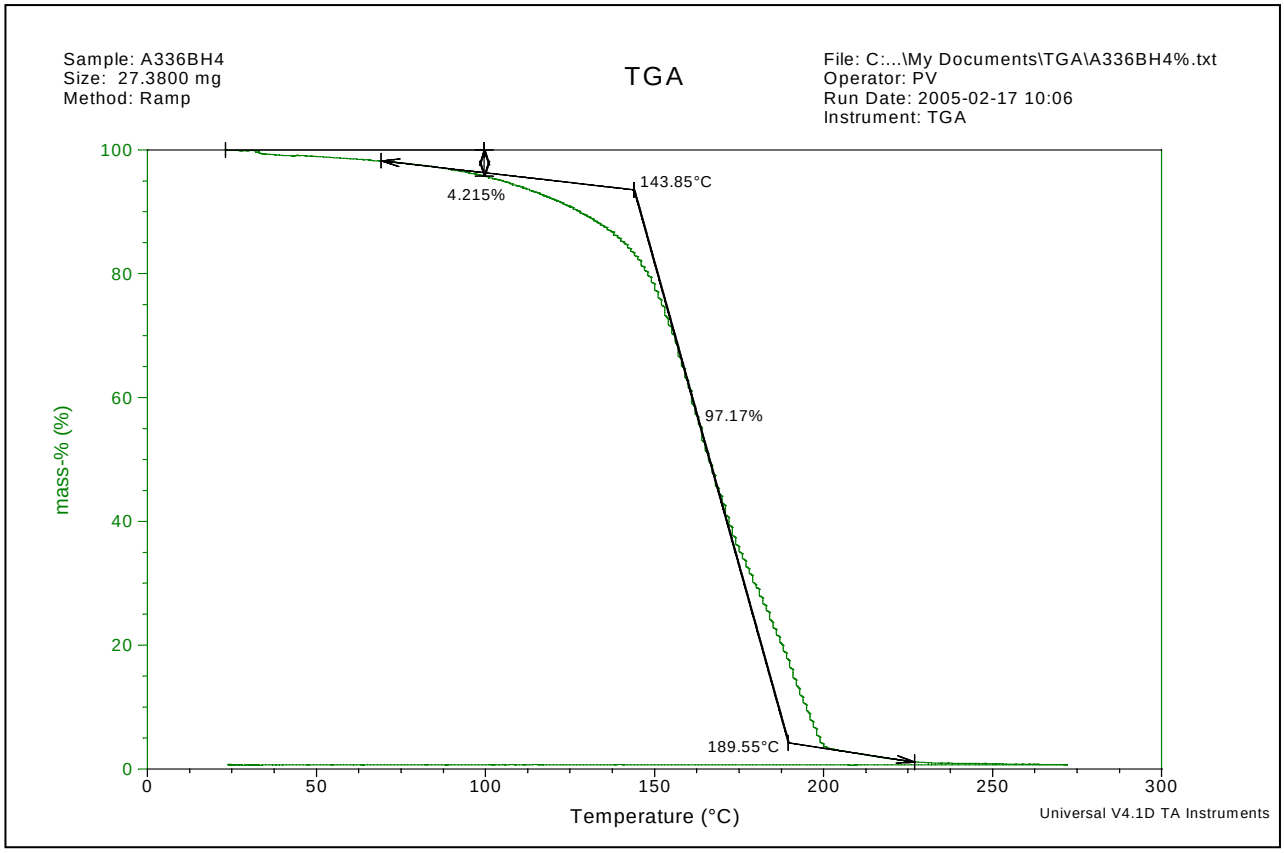


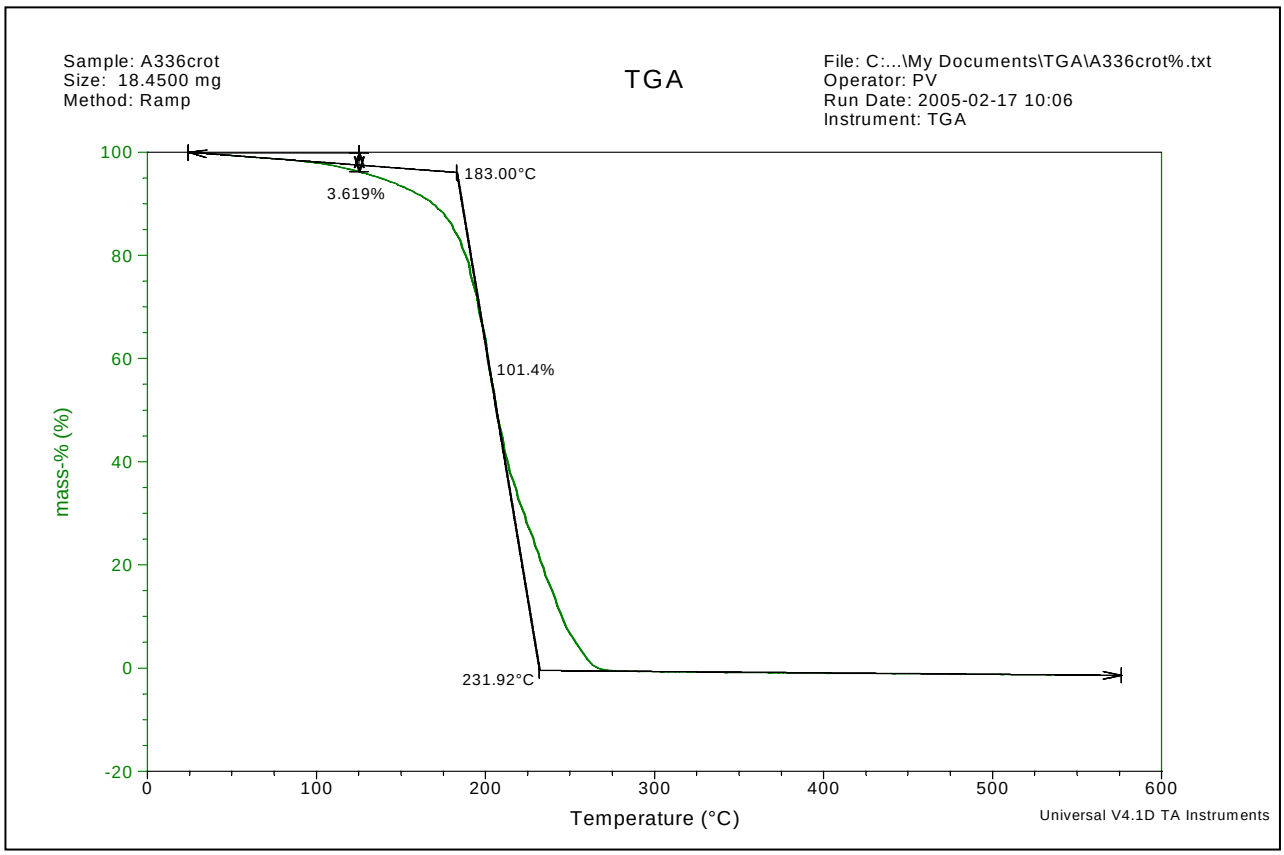



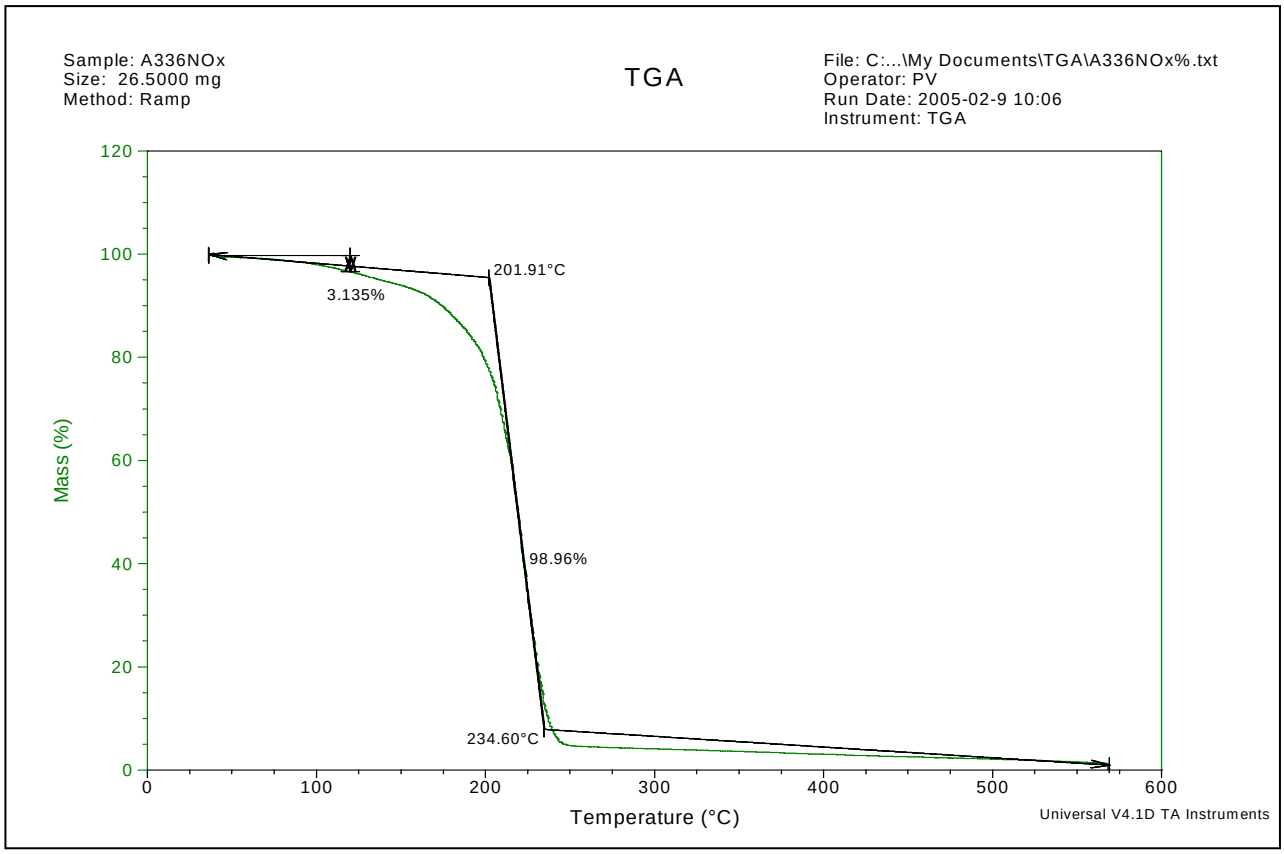
Section IV: TGA GRAFS

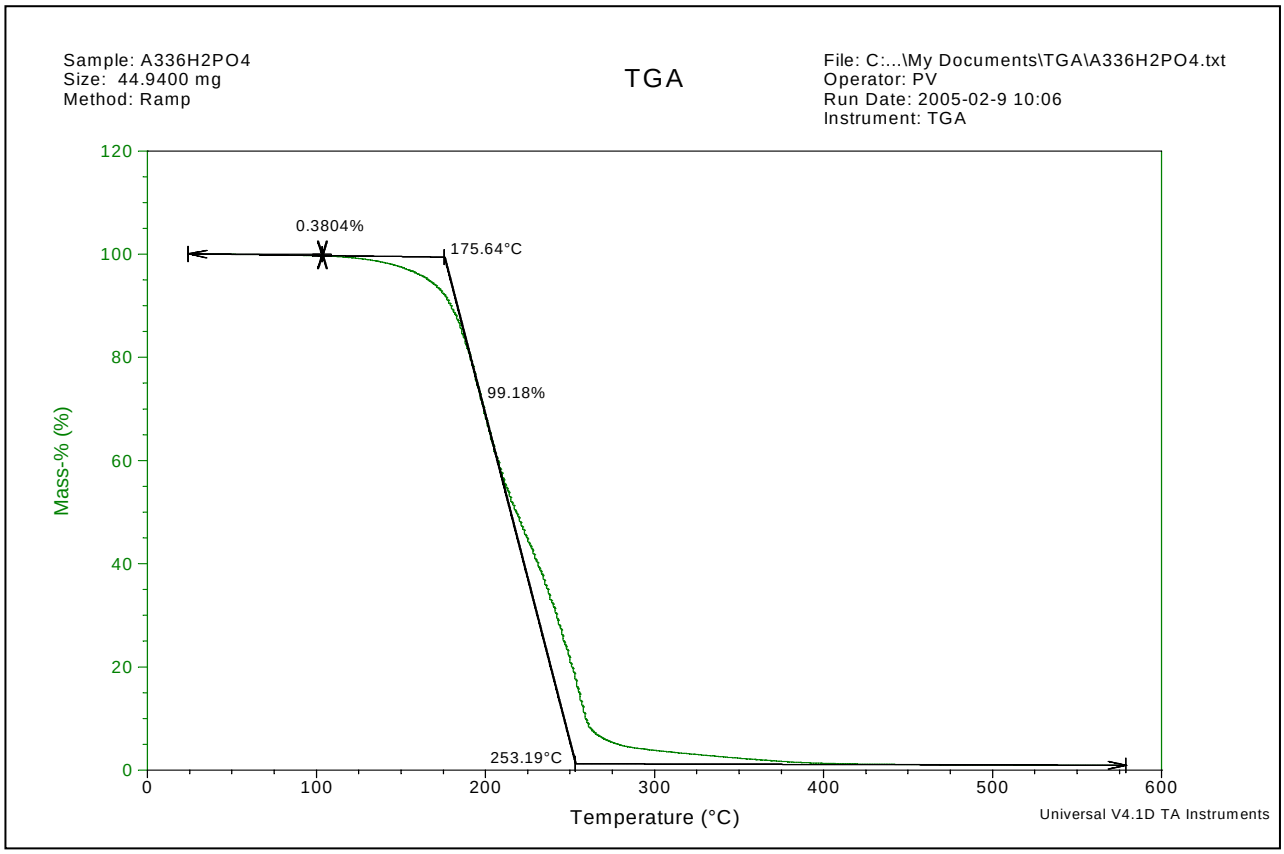


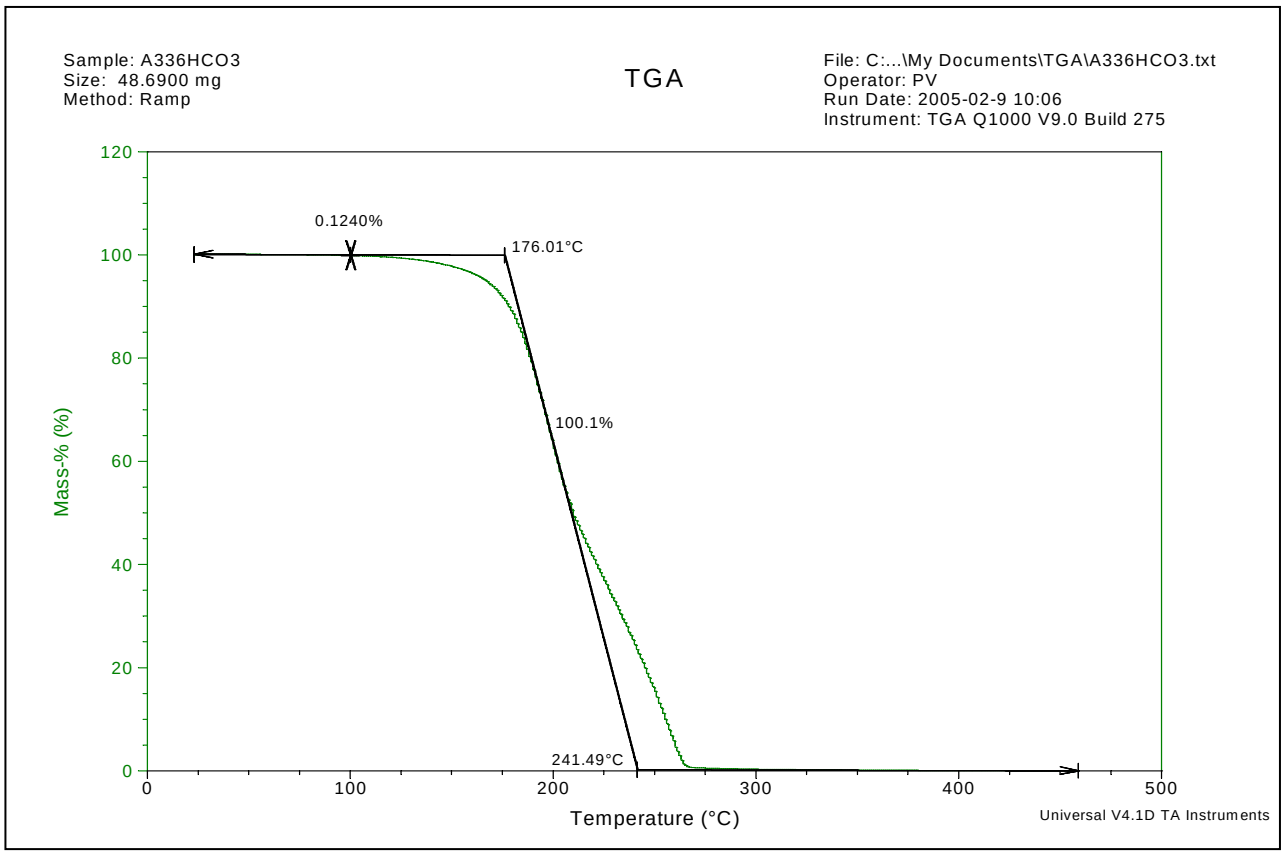



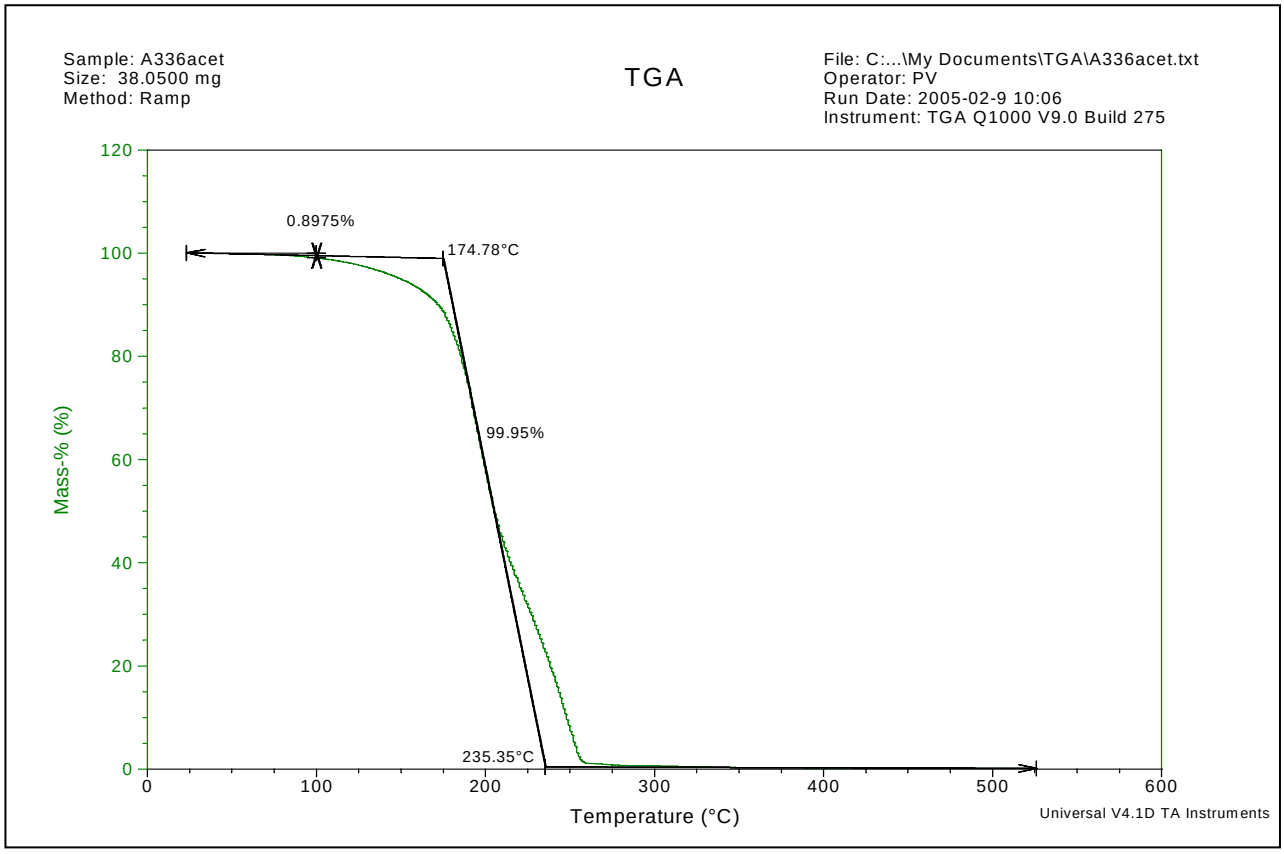

Sample: A336BH4
Size: 27.3800 mg
Method: Ramp
TGA
File: C:...\My Documents\TGA\A336BH4%.txt
Operator: PV
Run Date: 2005-02-17 10:06
Instrument: TGA
100
80
60
40
20
0
mass-% (%)
4.215%
143.85°C
97.17%
189.55°C
0
50
100
150
200
250
300
Temperature (°C)
Universal V4.1D TA Instruments

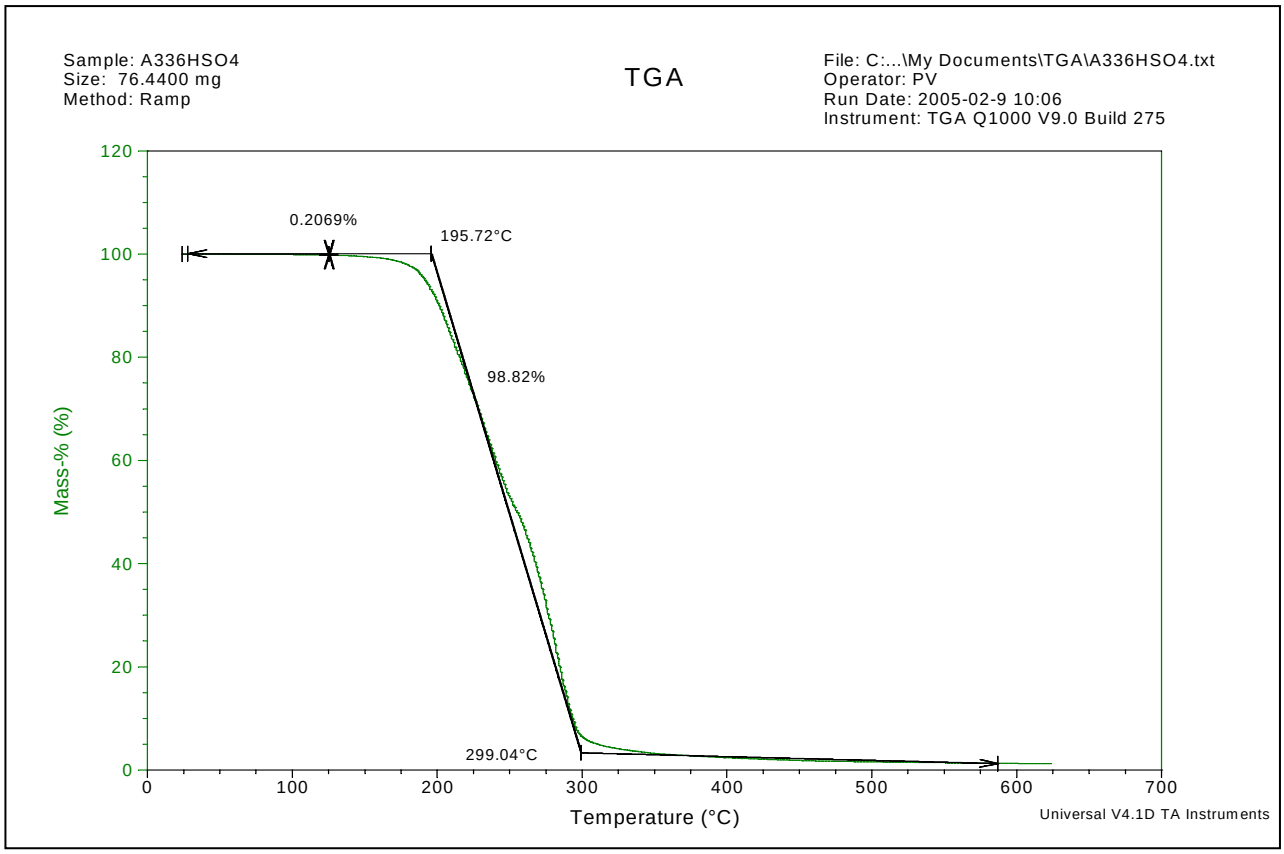

Sample: A336crot
Size: 18.4500 mg
Method: Ramp
TGA
File: C:...\My Documents\TGA\A336crot%.txt
Operator: PV
Run Date: 2005-02-17 10:06
Instrument: TGA
100
80
60
40
20
0
-20
mass-% (%)
3.619%
183.00°C
101.4%
231.92°C
0
100
200
300
400
500
600
Temperature (°C)
Universal V4.1D TA Instruments

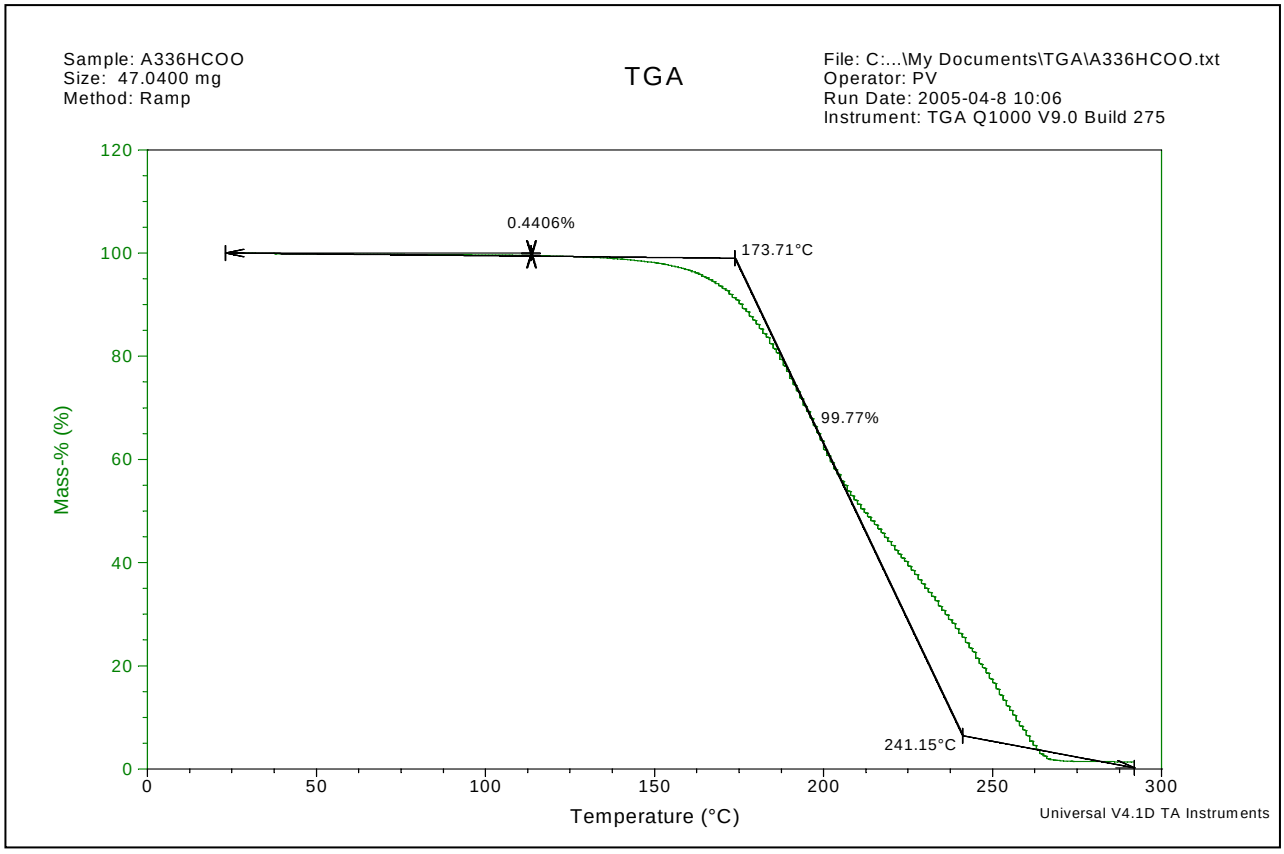

Sample: A336NOx
Size: 26.5000 mg
Method: Ramp
TGA
File: C:...\My Documents\TGA\A336NOx%.txt
Operator: PV
Run Date: 2005-02-9 10:06
Instrument: TGA
Mass (%)
Temperature (°C)
3.135%
201.91°C
98.96%
234.60°C
Universal V4.1D TA Instruments

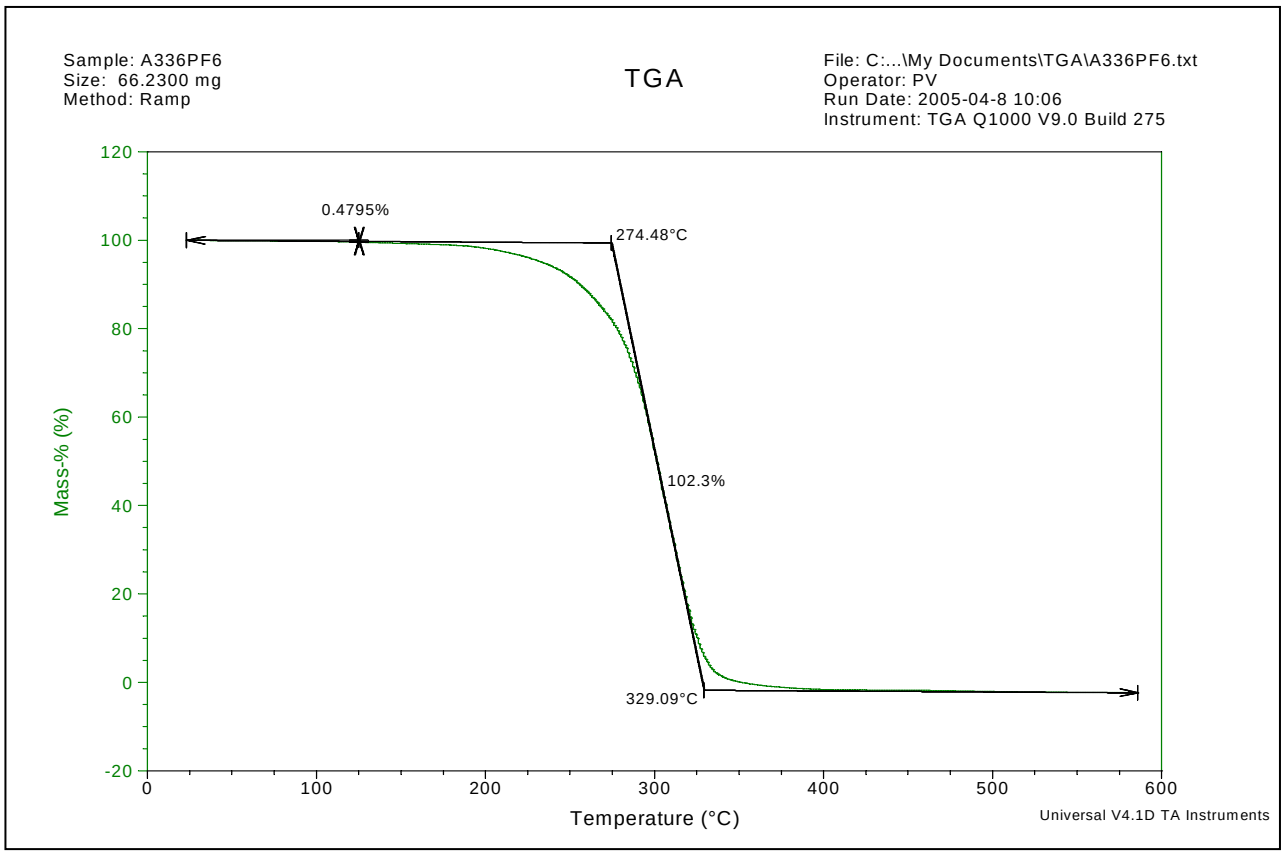

Sample: A336H2PO4
Size: 44.9400 mg
Method: Ramp
TGA
File: C:...\My Documents\TGA\A336H2PO4.txt
Operator: PV
Run Date: 2005-02-9 10:06
Instrument: TGA
Mass-% (%)
Temperature (°C)
0.3804%
175.64°C
99.18%
253.19°C
Universal V4.1D TA Instruments

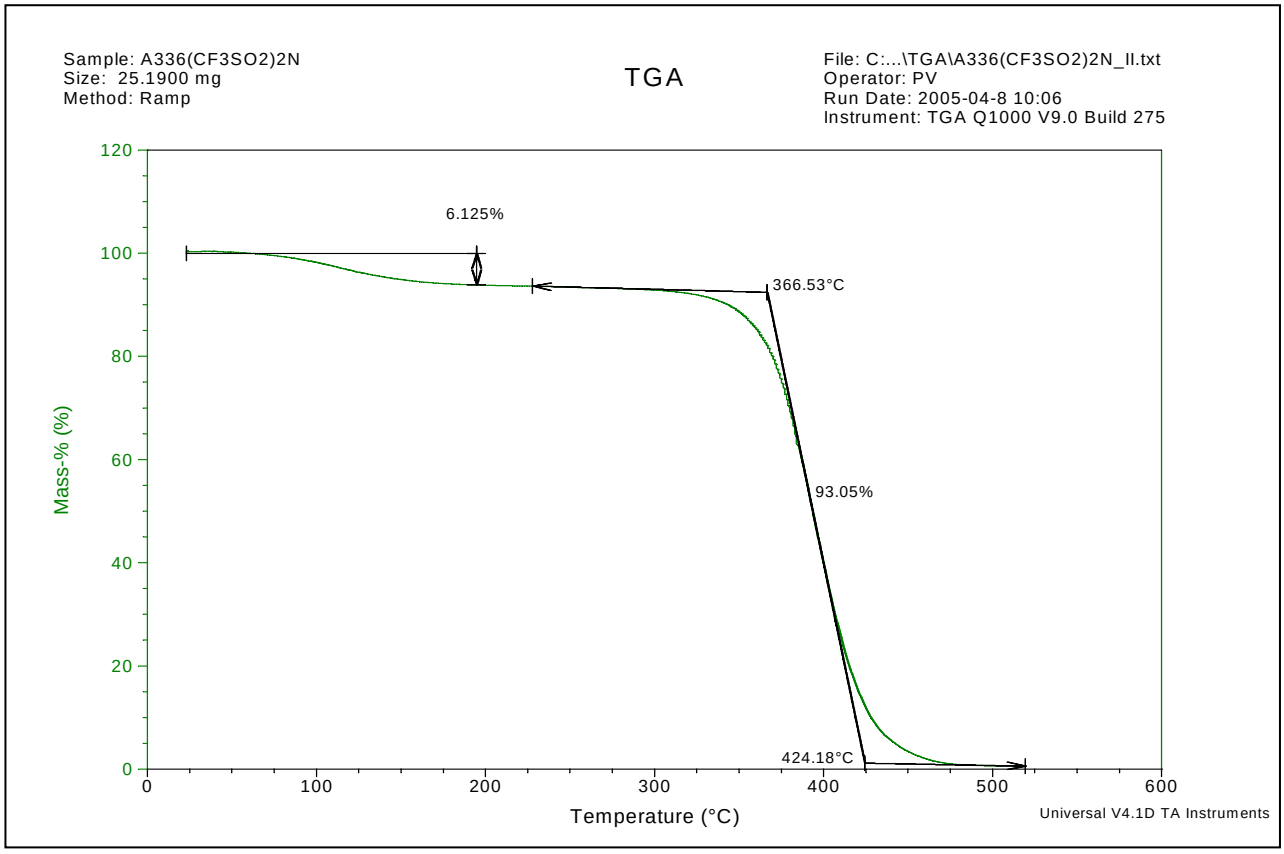

Sample: A336HCO3
Size: 48.6900 mg
Method: Ramp
TGA
File: C:...\My Documents\TGA\A336HCO3.txt
Operator: PV
Run Date: 2005-02-9 10:06
Instrument: TGA Q1000 V9.0 Build 275
0.1240%
176.01°C
100.1%
241.49°C
Mass-% (%)
Temperature (°C)
Universal V4.1D TA Instruments


Sample: A336acet
Size: 38.0500 mg
Method: Ramp
TGA
File: C:...\My Documents\TGA\A336acet.txt
Operator: PV
Run Date: 2005-02-9 10:06
Instrument: TGA Q1000 V9.0 Build 275
0.8975%
174.78°C
99.95%
235.35°C
Mass-% (%)
Temperature (°C)
Universal V4.1D TA Instruments

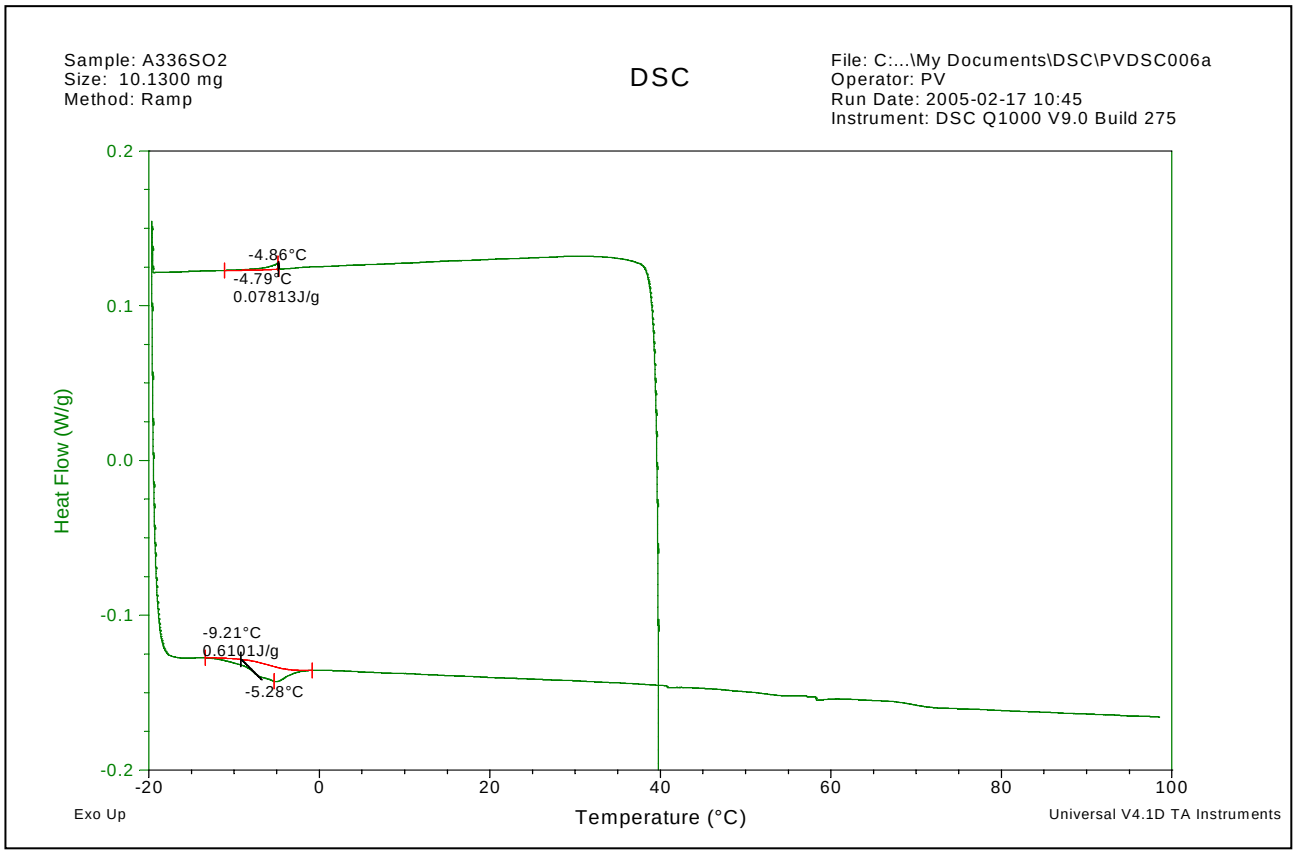

Sample: A336HSO4
Size: 76.4400 mg
Method: Ramp
TGA
File: C:...\My Documents\TGA\A336HSO4.txt
Operator: PV
Run Date: 2005-02-9 10:06
Instrument: TGA Q1000 V9.0 Build 275
0.2069%
195.72°C
98.82%
299.04°C
Mass-% (%)
Temperature (°C)
Universal V4.1D TA Instruments

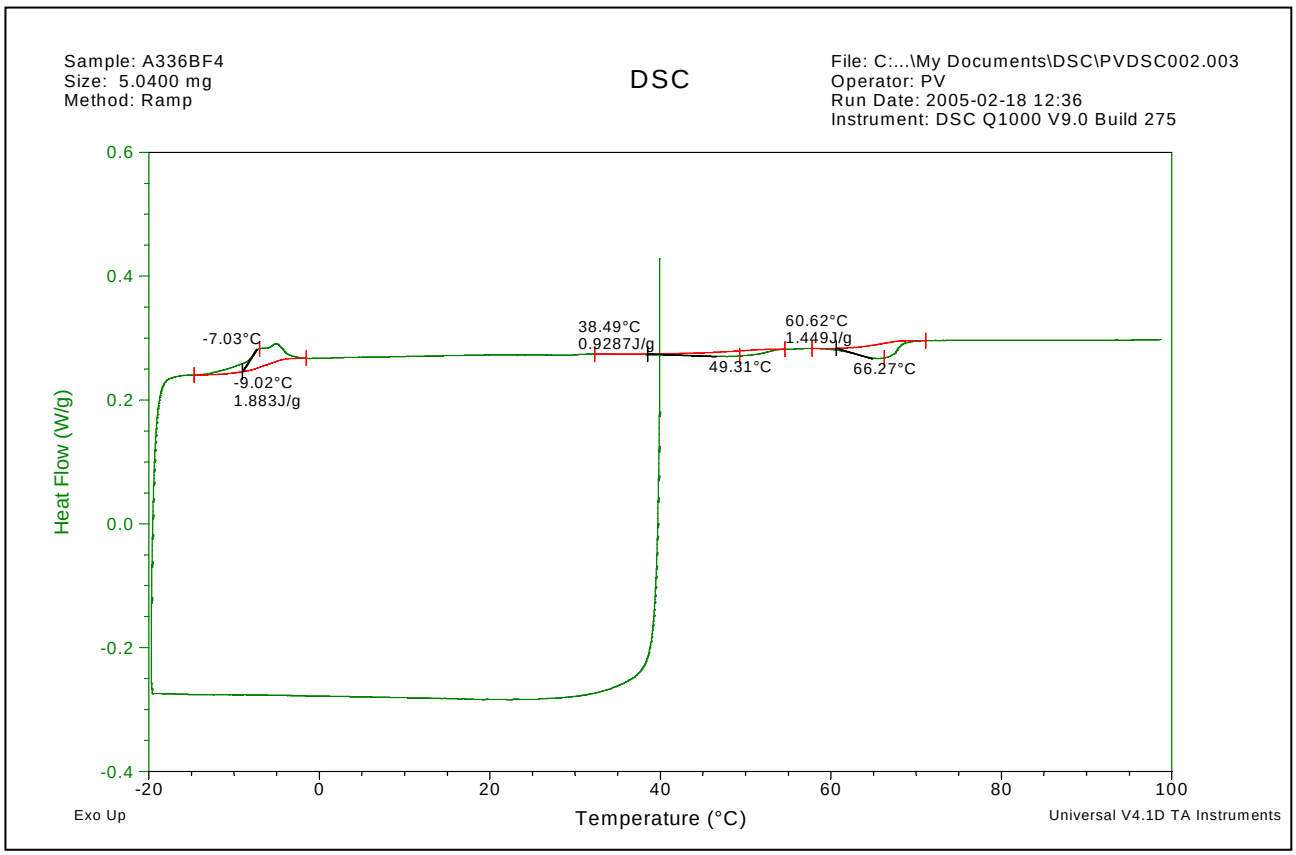

Sample: A336HCOO
Size: 47.0400 mg
Method: Ramp
TGA
File: C:...\My Documents\TGA\A336HCOO.txt
Operator: PV
Run Date: 2005-04-8 10:06
Instrument: TGA Q1000 V9.0 Build 275
0.4406%
173.71°C
99.77%
241.15°C
Mass-% (%)
Temperature (°C)
Universal V4.1D TA Instruments

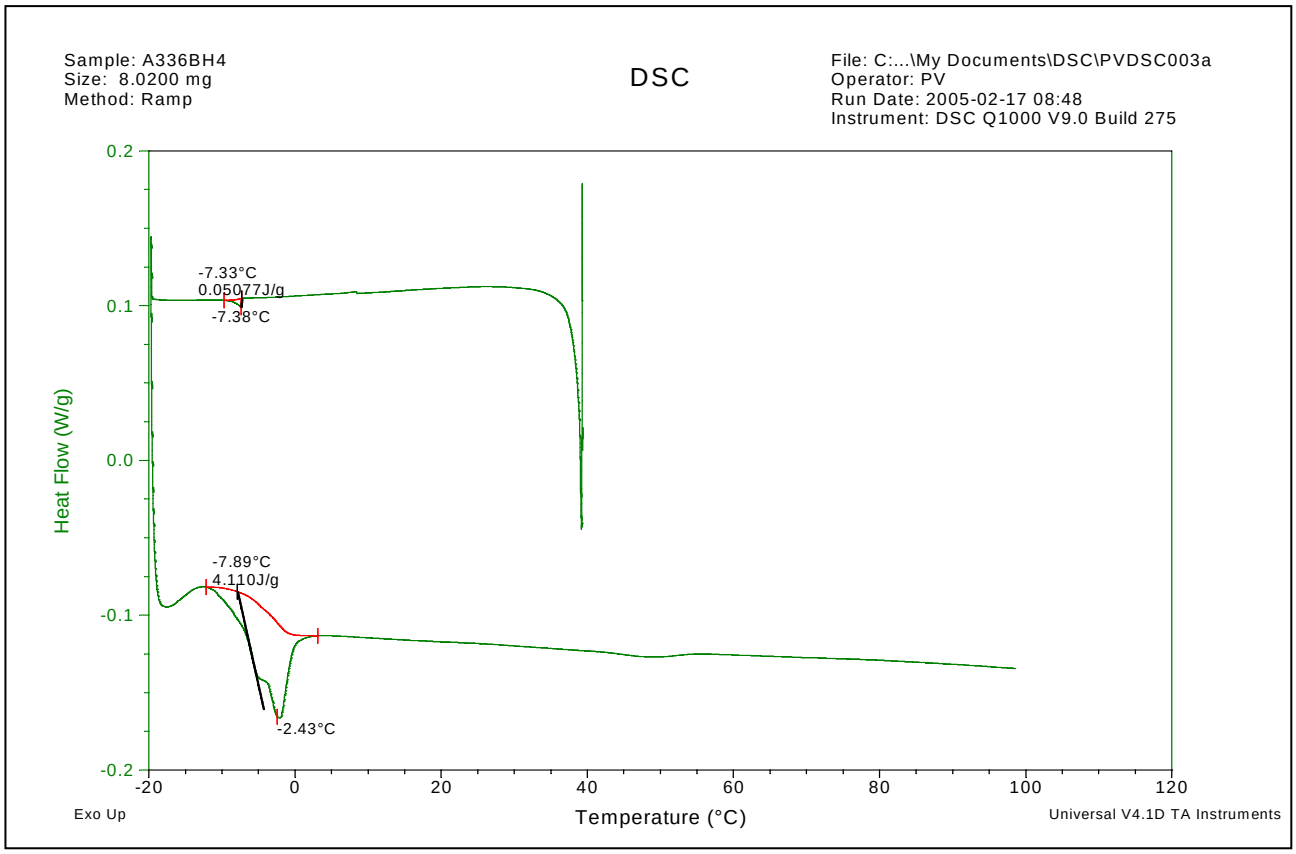

Sample: A336PF6
Size: 66.2300 mg
Method: Ramp
TGA
File: C:...\My Documents\TGA\A336PF6.txt
Operator: PV
Run Date: 2005-04-8 10:06
Instrument: TGA Q1000 V9.0 Build 275
0.4795%
274.48°C
102.3%
329.09°C
Mass-% (%)
Temperature (°C)
Universal V4.1D TA Instruments

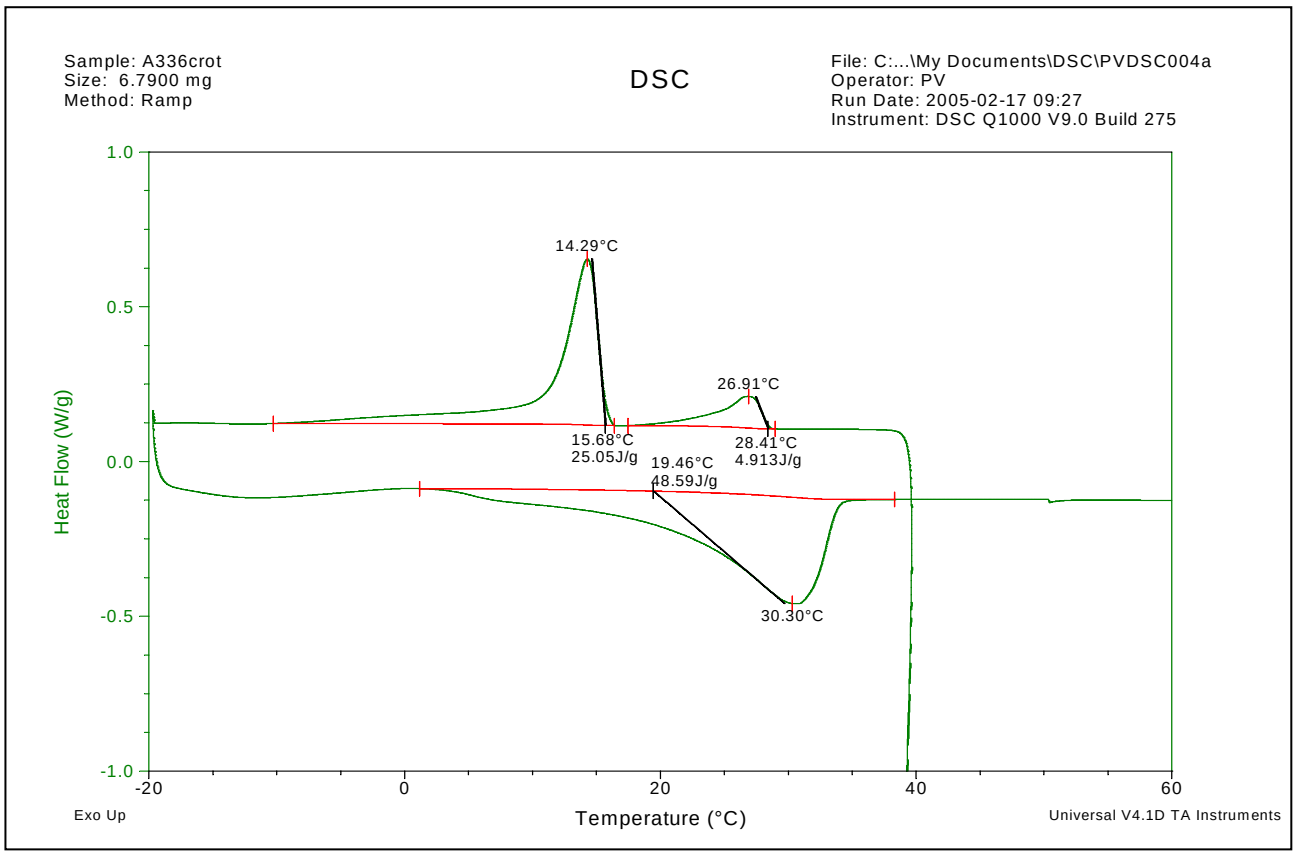

Sample: A336(CF3SO2)2N
Size: 25.1900 mg
Method: Ramp
TGA
File: C:...\TGA\A336(CF3SO2)2N_II.txt
Operator: PV
Run Date: 2005-04-8 10:06
Instrument: TGA Q1000 V9.0 Build 275
6.125%
366.53°C
93.05%
424.18°C
Mass-% (%)
Temperature (°C)
Universal V4.1D TA Instruments

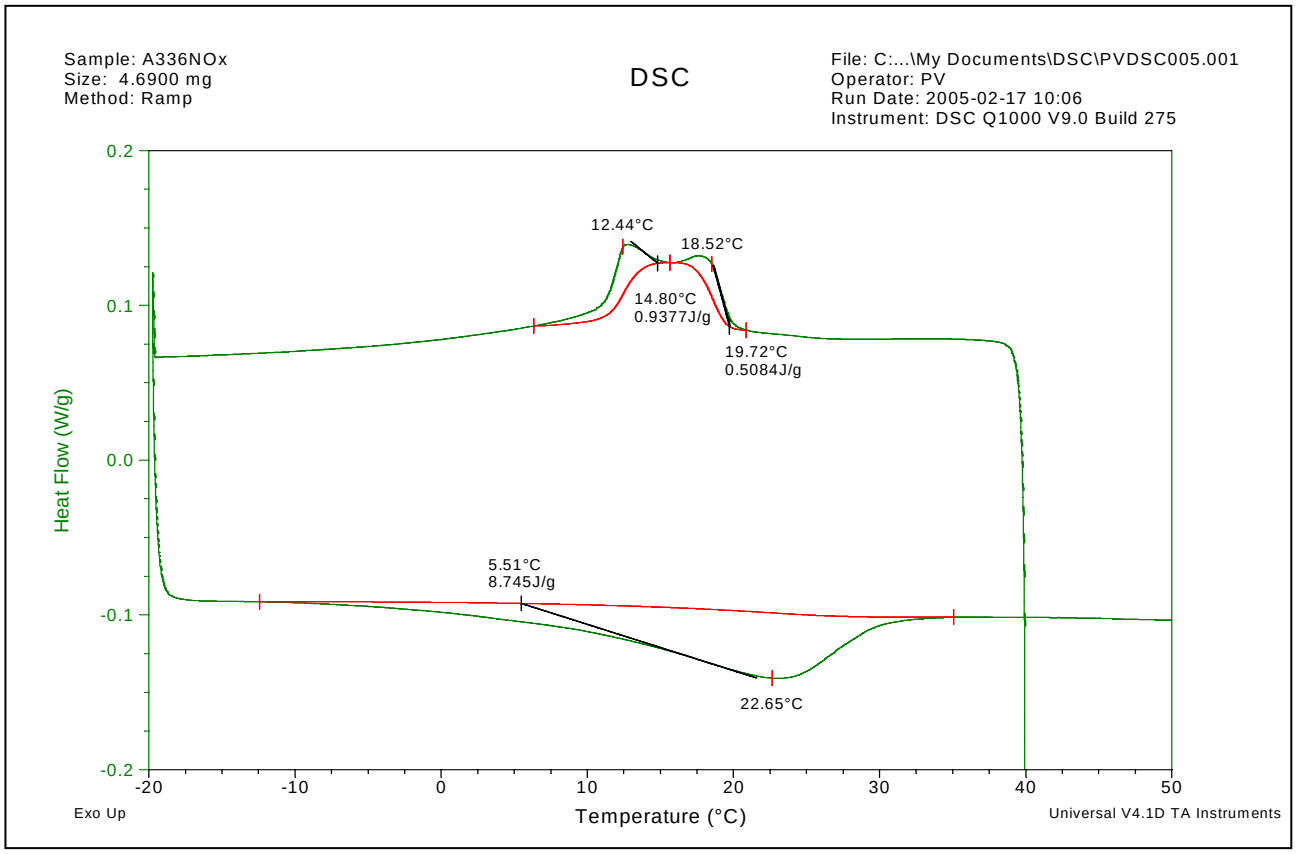
Section V: DSC GRAFS

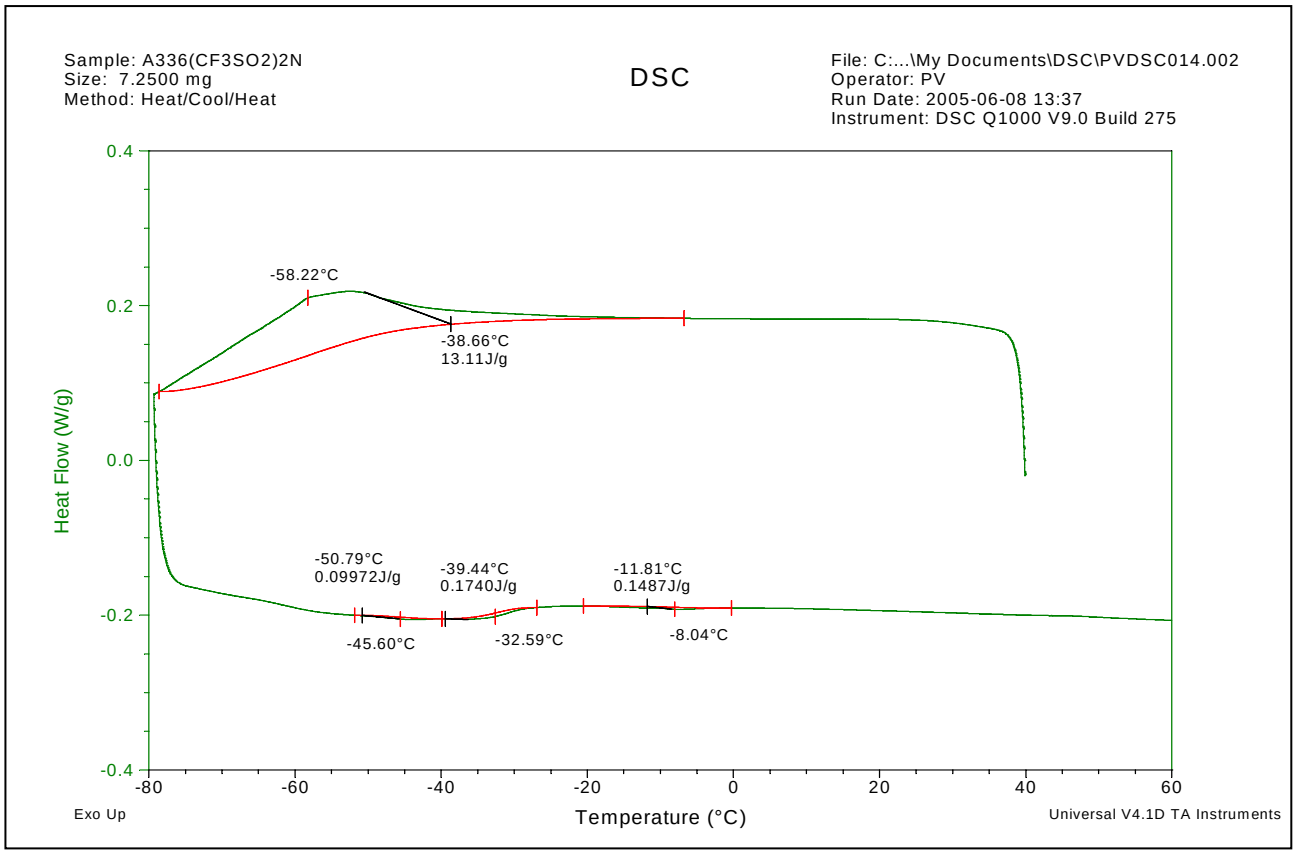


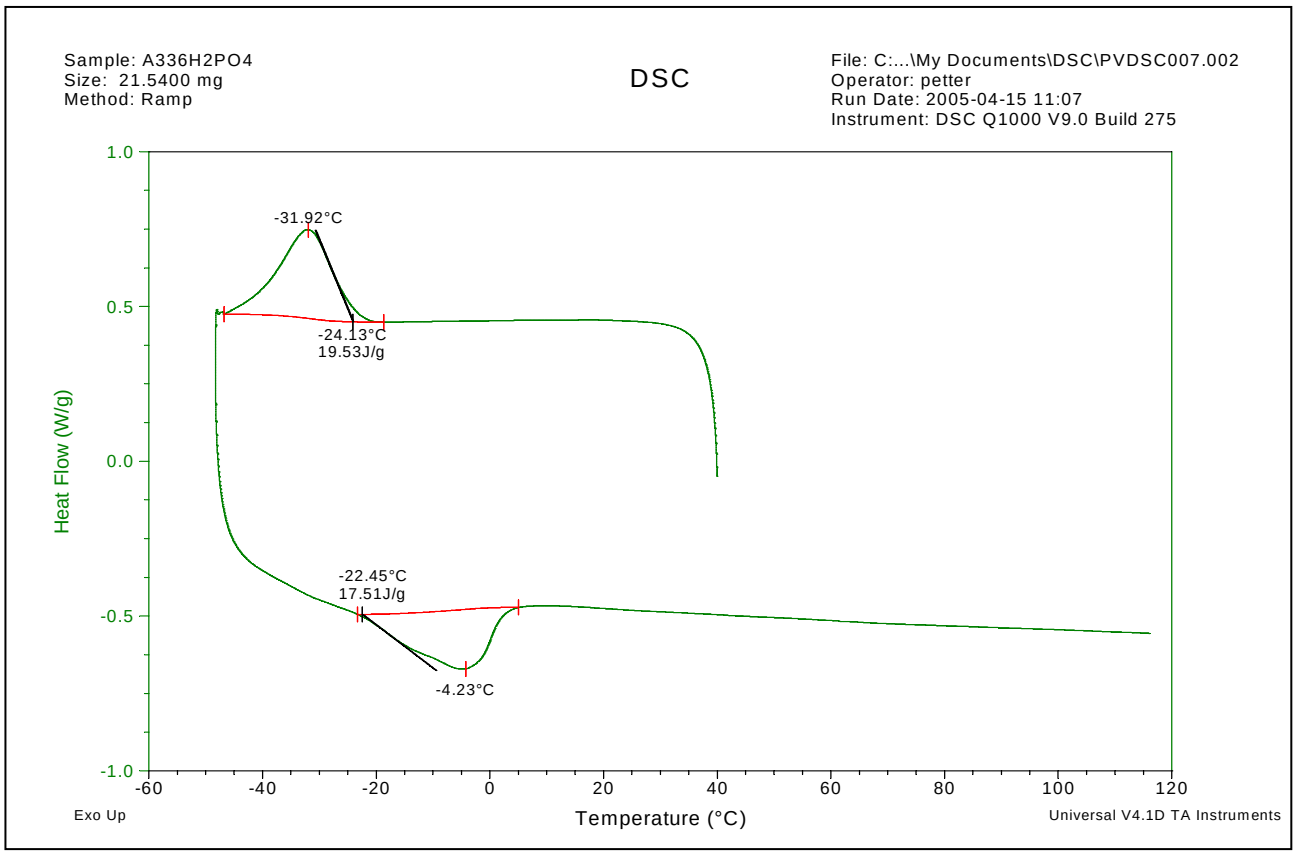



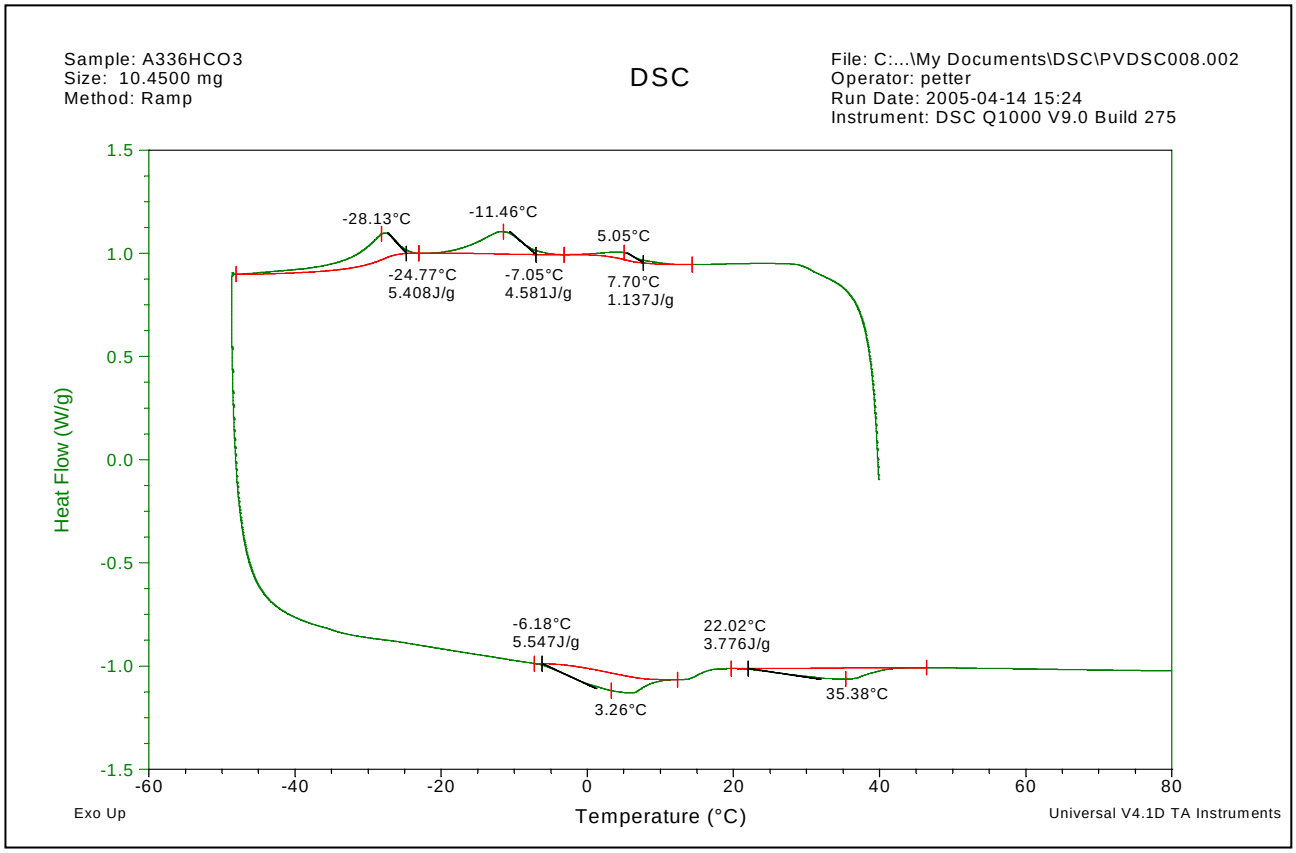

Sample: A336BH4
Size: 8.0200 mg
Method: Ramp
DSC
File: C:...\My Documents\DSC\PVDSC003a
Operator: PV
Run Date: 2005-02-17 08:48
Instrument: DSC Q1000 V9.0 Build 275
-7.33°C
0.05077J/g
-7.38°C
-7.89°C
4.110J/g
-2.43°C
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.1D TA Instruments

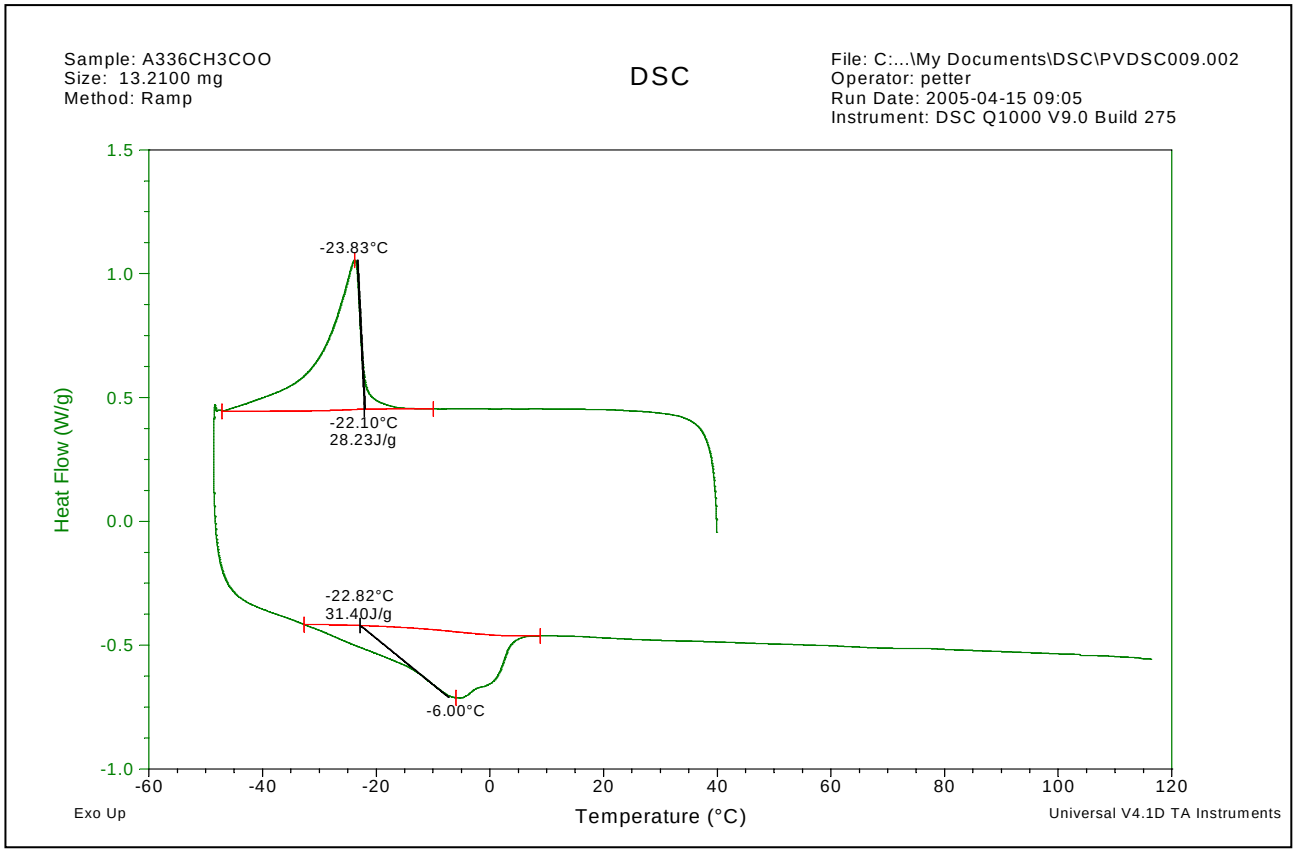

Sample: A336crot
Size: 6.7900 mg
Method: Ramp
DSC
File: C:...\My Documents\DSC\PVDSC004a
Operator: PV
Run Date: 2005-02-17 09:27
Instrument: DSC Q1000 V9.0 Build 275
14.29°C
15.68°C
25.05J/g
26.91°C
28.41°C
4.913J/g
19.46°C
48.59J/g
30.30°C
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.1D TA Instruments

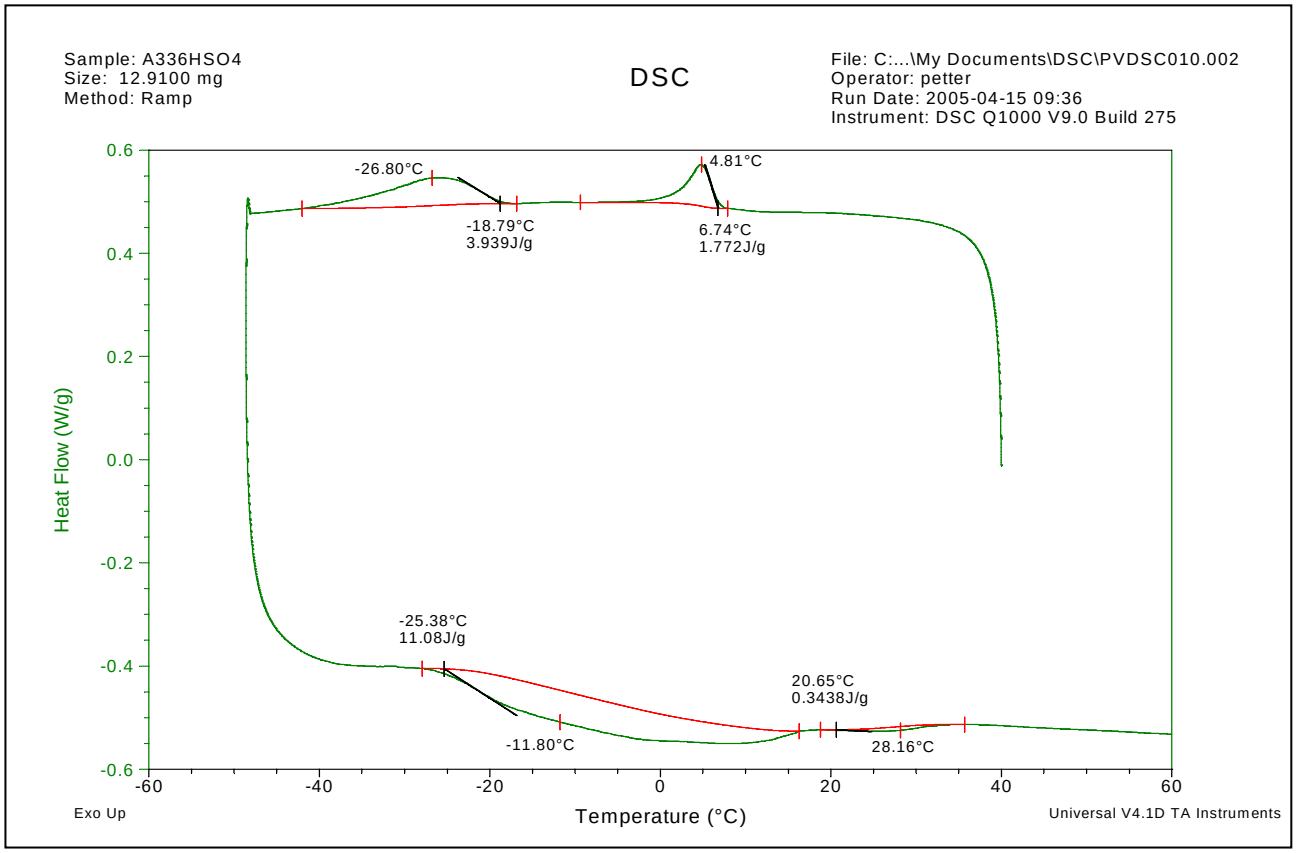

Sample: A336NOx
Size: 4.6900 mg
Method: Ramp
DSC
File: C:...\My Documents\DSC\PVDSC005.001
Operator: PV
Run Date: 2005-02-17 10:06
Instrument: DSC Q1000 V9.0 Build 275
12.44°C
18.52°C
14.80°C
0.9377J/g
19.72°C
0.5084J/g
5.51°C
8.745J/g
22.65°C
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.1D TA Instruments

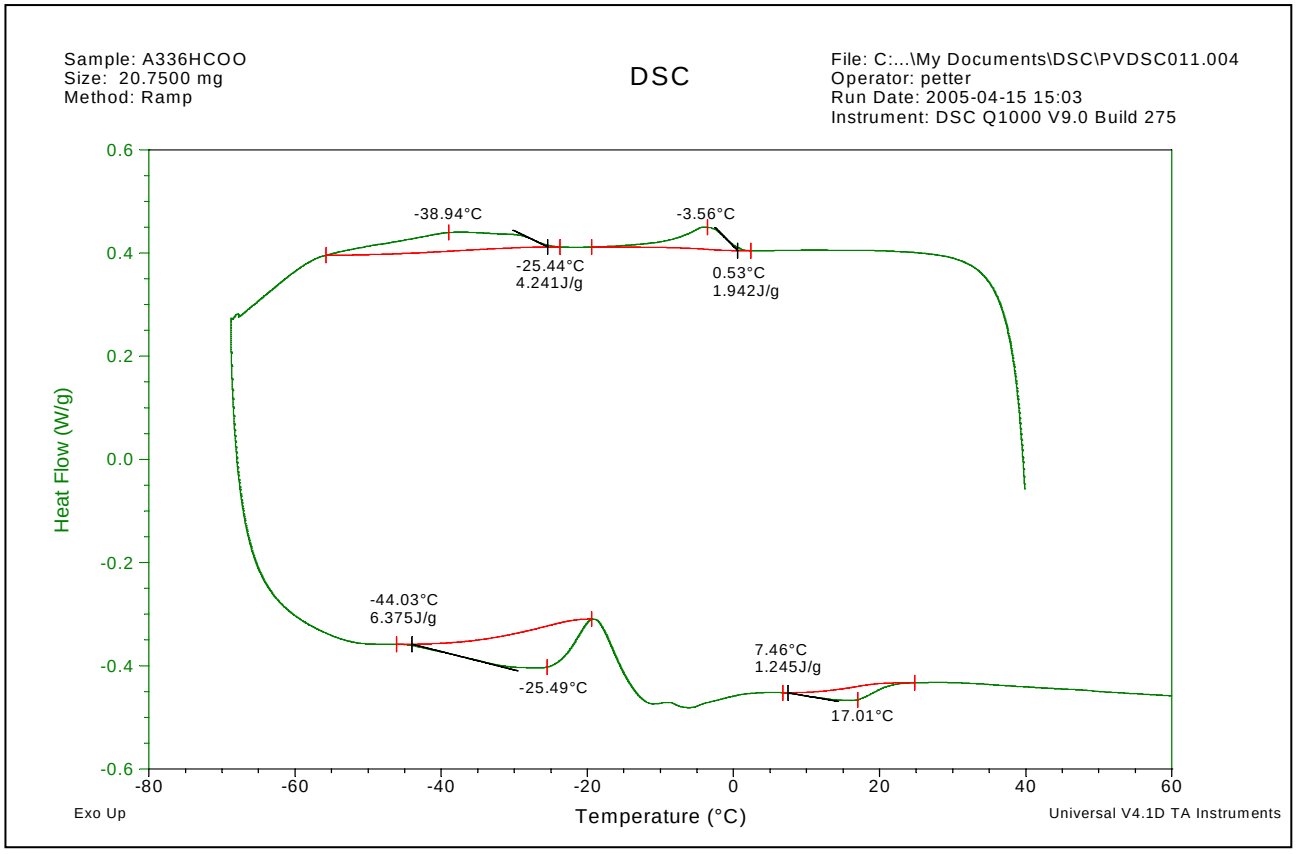

Sample: A336(CF3SO2)2N
Size: 7.2500 mg
Method: Heat/Cool/Heat
DSC
File: C:...\My Documents\DSC\PVDSC014.002
Operator: PV
Run Date: 2005-06-08 13:37
Instrument: DSC Q1000 V9.0 Build 275
-58.22°C
-38.66°C
13.11J/g
-50.79°C
0.09972J/g
-39.44°C
0.1740J/g
-11.81°C
0.1487J/g
-45.60°C
-32.59°C
-8.04°C
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.1D TA Instruments

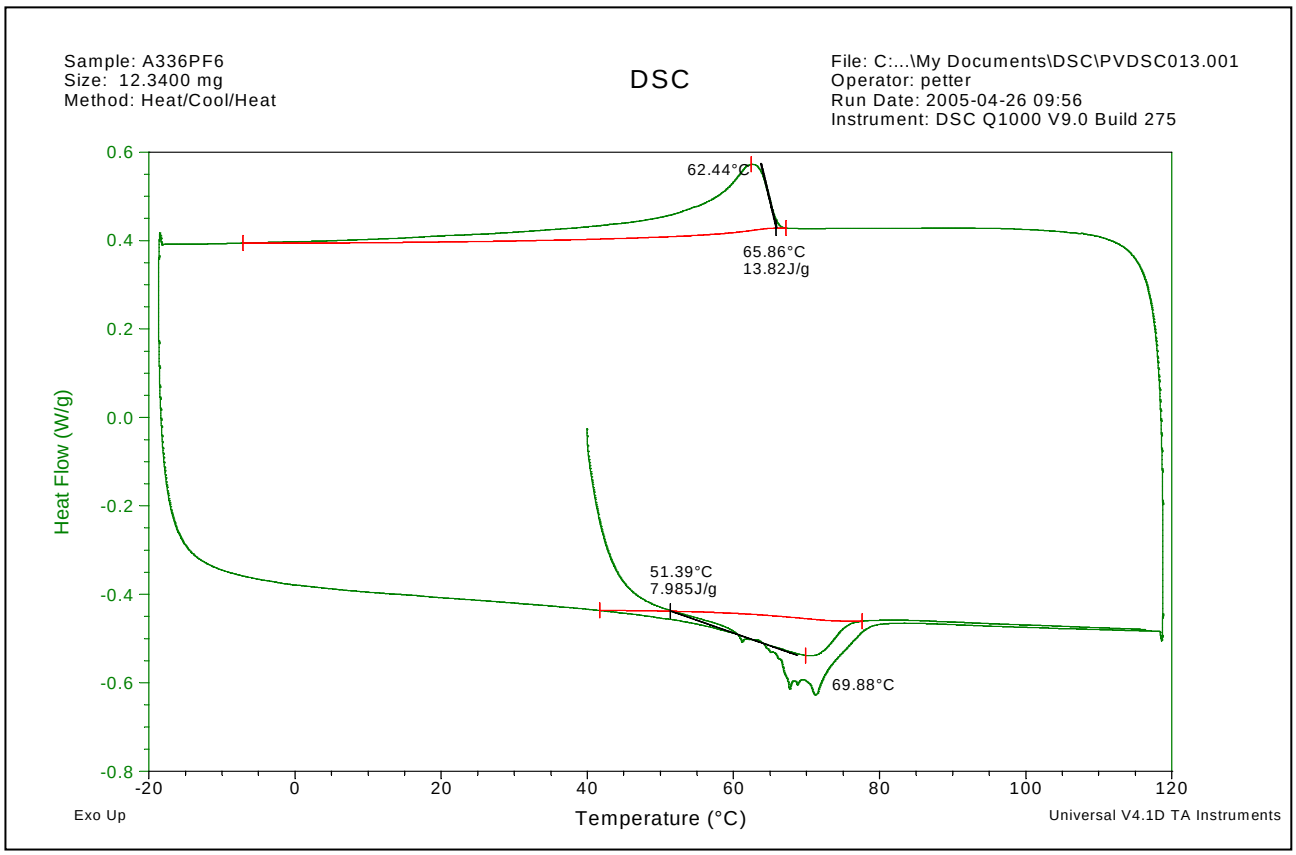

Sample: A336H2PO4
Size: 21.5400 mg
Method: Ramp
DSC
File: C:...\My Documents\DSC\PVDSC007.002
Operator: petter
Run Date: 2005-04-15 11:07
Instrument: DSC Q1000 V9.0 Build 275
-31.92°C
-24.13°C
19.53J/g
-22.45°C
17.51J/g
-4.23°C
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.1D TA Instruments


Sample: A336HCO3
Size: 10.4500 mg
Method: Ramp
DSC
File: C:...\My Documents\DSC\PVDSC008.002
Operator: petter
Run Date: 2005-04-14 15:24
Instrument: DSC Q1000 V9.0 Build 275
-28.13°C
-24.77°C
5.408J/g
-11.46°C
-7.05°C
4.581J/g
5.05°C
7.70°C
1.137J/g
-6.18°C
5.547J/g
3.26°C
22.02°C
3.776J/g
35.38°C
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.1D TA Instruments


Sample: A336CH3COO
Size: 13.2100 mg
Method: Ramp
DSC
File: C:...\My Documents\DSC\PVDSC009.002
Operator: petter
Run Date: 2005-04-15 09:05
Instrument: DSC Q1000 V9.0 Build 275
-23.83°C
-22.10°C
28.23J/g
-22.82°C
31.40J/g
-6.00°C
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.1D TA Instruments


Sample: A336HSO4
Size: 12.9100 mg
Method: Ramp
DSC
File: C:...\My Documents\DSC\PVDSC010.002
Operator: petter
Run Date: 2005-04-15 09:36
Instrument: DSC Q1000 V9.0 Build 275
-26.80°C
-18.79°C
3.939J/g
4.81°C
6.74°C
1.772J/g
-25.38°C
11.08J/g
-11.80°C
20.65°C
0.3438J/g
28.16°C
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.1D TA Instruments


Sample: A336HCOO
Size: 20.7500 mg
Method: Ramp
DSC
File: C:...\My Documents\DSC\PVDSC011.004
Operator: petter
Run Date: 2005-04-15 15:03
Instrument: DSC Q1000 V9.0 Build 275
-38.94°C
-25.44°C
4.241J/g
-3.56°C
0.53°C
1.942J/g
-44.03°C
6.375J/g
-25.49°C
7.46°C
1.245J/g
17.01°C
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.1D TA Instruments


Sample: A336PF6
Size: 12.3400 mg
Method: Heat/Cool/Heat
DSC
File: C:...\My Documents\DSC\PVDSC013.001
Operator: petter
Run Date: 2005-04-26 09:56
Instrument: DSC Q1000 V9.0 Build 275
62.44°C
65.86°C
13.82J/g
51.39°C
7.985J/g
69.88°C
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.1D TA Instruments

**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

| A336 Ionic liquids $^{1}H$-NMR chemical shifts (ppm) | | | | | |
|---|---|---|---|---|---|
| compound | 11 $CH_3$ | 1 $CH_2$ | 2 $CH_2$ | 3-7 (3-9) $CH_2$ | 8 (10) $CH_3$* |
| [$A336^{+}$][$Cl^{-}$] | 2.924 | 3.178 | 1.596 | 1.2 - 1.3 | 0.866 |
| [$A336^{+}$][$NO_3^{-}$] | 2.922 | 3.175 | 1.597 | 1.2 - 1.3 | 0.869 |
| [$A336^{+}$][$crot^{-}$] | 2.926 | 3.182 | 1.598 | 1.2 - 1.3 | 0.867 |
| [$A336^{+}$][$BF_4^{-}$] | 2.92 | 3.173 | 1.597 | 1.2 - 1.3 | 0.867 |
| [$A336^{+}$][$BH_4^{-}$] | 2.93 | 3.184 | 1.597 | 1.2 - 1.3 | 0.867 |
| [$A336^{+}$][$SO_2^{-}$] | 2.927 | 3.181 | 1.597 | 1.2 - 1.3 | 0.865 |
| [$A336^{+}$][$CH_3COO^{-}$] | 2.929 | 3.182 | 1.596 | 1.2 - 1.3 | 0.868 |
| [$A336^{+}$][$H_2PO_4^{-}$] | 2.907 | 3.16 | 1.583 | 1.2 - 1.3 | 0.854 |
| [$A336^{+}$][$HSO_4^{-}$] | 2.914 | 3.167 | 1.589 | 1.2 - 1.3 | 0.857 |
| [$A336^{+}$][$PF_6^{-}$] | 2.923 | 3.174 | 1.597 | 1.2 - 1.3 | 0.868 |
| [$A336^{+}$][$HCOO^{-}$] | 2.93 | 3.184 | 1.598 | 1.2 - 1.3 | 0.867 |
| [$A336^{+}$][$HCO_3^{-}$] | 2.932 | 3.185 | 1.597 | 1.2 - 1.3 | 0.866 |
| [$A336^{+}$][$(CF_3SO_2)_2N^{-}$] | 2.923 | 3.172 | 1.596 | 1.2 - 1.3 | 0.868 |

*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)

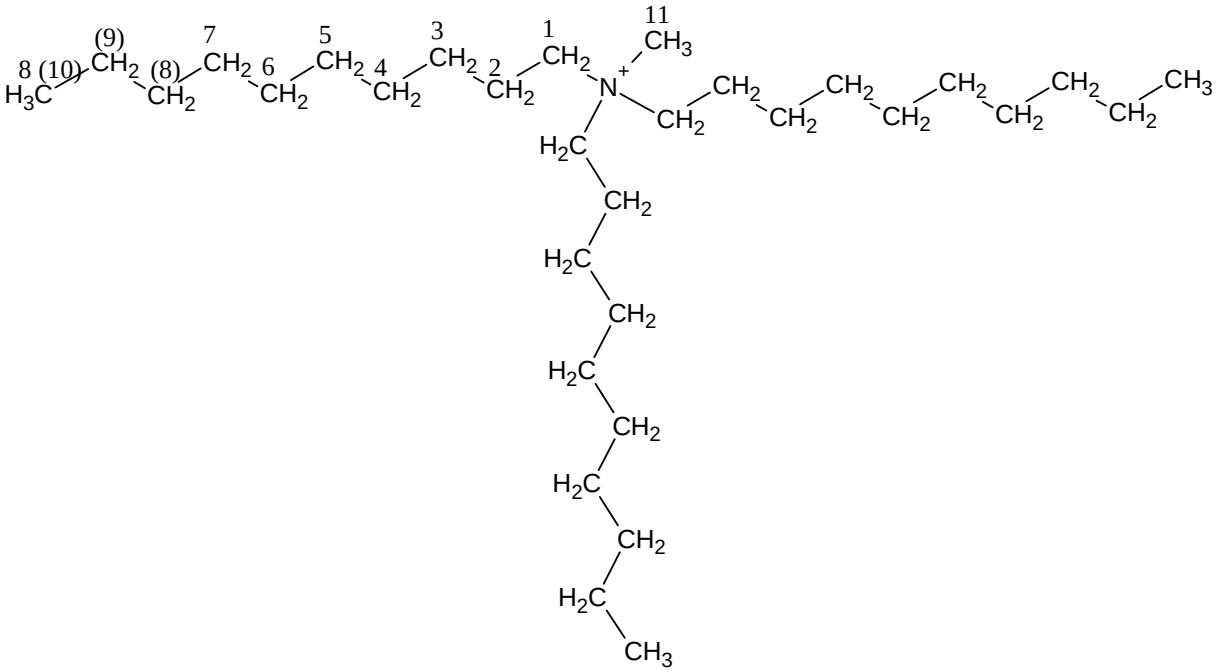


Table S2. $^{13}C$ NMR chemical shifts of carbon atoms in the [$A336^+$] cation for different ionic liquids.

| A336 Ionic liquids $^{13}C$-NMR chemical shifts (ppm) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| compound | 1 | | 2 | | 3 | | 8 (10) | 11 | |
| [$A336^+$][$Cl^-$] | 60.547 | 60.737 | 21.280 | 21.312 | 25.731 | 25.763 | 13.9 | 47.557 | |
| [$A336^+$][$NO_3^-$] | 60.499 | 60.690 | 21.220 | 21.254 | 25.666 | 25.700 | 13.923 | 47.462 | |
| [$A336^+$][$crot^-$] | 60.498 | 60.687 | 21.219 | 21.255 | 25.657 | 25.699 | 13.930 | 47.502 | |
| [$A336^+$][$BF_4^-$] | 60.566 | | 21.294 | 21.325 | 25.742 | 25.780 | 13.979 | 47.553 | |
| [$A336^+$][$BH_4^-$] | 60.52 | 60.781 | 21.315 | 21.351 | 25.756 | 25.793 | 13.992 | 47.564 | |
| [$A336^+$][$SO_2^-$] | 60.477 | 60.678 | | 21.35 | 25.768 | 25.817 | 13.993 | 47.477 | |
| [$A336^+$][$CH_3COO^-$] | 60.500 | 60.686 | 21.267 | 21.298 | 25.722 | 25.759 | 13.936 | 47.491 | |
| [$A336^+$][$H_2PO_4^-$] | 60.706 | 60.936 | 21.417 | 21.464 | | 25.894 | 14.125 | 47.727 | |
| [$A336^+$][$HSO_4^-$] | 60.647 | 60.837 | 21.362 | 21.392 | 25.797 | 25.833 | 14.055 | 47.631 | |
| [$A336^+$][$PF_6^-$] | 60.513 | | 21.258 | 21.293 | 25.714 | 25.749 | 13.936 | 47.521 | |
| [$A336^+$][$HCOO^-$] | 60.55 | | 21.267 | 21.298 | 25.732 | 25.769 | 13.964 | 47.504 | |
| [$A336^+$][$HCO_3^-$] | 60.491 | 60.728 | 21.268 | 21.301 | 25.719 | 25.758 | 13.935 | 47.518 | |
| [$A336^+$][$(CF_3SO_2)_2N^-$] | 60.481 | 60.700 | 21.258 | 21.291 | 25.708 | 25.748 | 13.939 | 47.53 | |
| | 7 / (9) | | in chain carbons 4 - 6 (4 - 8) | | | | | | |
| [$A336^+$][$Cl^-$] | 22.054 | 22.098 | 28.388 | 28.437 | 28.677 | 28.757 | 28.886 | 31.287 | 31.164 |
| [$A336^+$][$NO_3^-$] | 22.008 | 22.048 | 28.336 | 28.383 | 28.627 | 28.704 | 28.835 | 31.236 | 31.112 |
| [$A336^+$][$crot^-$] | 22.005 | 22.041 | 28.328 | 28.374 | 28.624 | 28.696 | 28.828 | 31.233 | 31.108 |
| [$A336^+$][$BF_4^-$] | 22.085 | 22.123 | 28.404 | 28.455 | 28.701 | 28.777 | 28.908 | 31.309 | 31.182 |
| [$A336^+$][$BH_4^-$] | 22.099 | 22.135 | 28.426 | 28.481 | 28.721 | 28.8 | 28.923 | 31.33 | 31.202 |
| [$A336^+$][$SO_2^-$] | 22.104 | 22.148 | 28.431 | 28.491 | 28.72 | 28.816 | 28.937 | 31.334 | 31.189 |
| [$A336^+$][$CH_3COO^-$] | 22.046 | 22.084 | 28.376 | 28.429 | 28.665 | 28.748 | 28.878 | 31.280 | 31.156 |
| [$A336^+$][$H_2PO_4^-$] | 22.210 | 22.269 | 28.528 | 28.585 | 28.825 | 28.898 | 29.03 | 31.444 | 31.313 |
| [$A336^+$][$HSO_4^-$] | 22.153 | 22.189 | 28.47 | 28.523 | 28.761 | 28.84 | 28.965 | 31.376 | 31.25 |
| [$A336^+$][$PF_6^-$] | 22.045 | 22.086 | 28.371 | 28.419 | 28.663 | 28.746 | 28.871 | 31.275 | 31.147 |
| [$A336^+$][$HCOO^-$] | 22.042 | 22.078 | 28.393 | 28.43 | 28.665 | 28.749 | 28.89 | 31.288 | 31.157 |
| [$A336^+$][$HCO_3^-$] | 22.046 | 22.083 | 28.376 | 28.424 | 28.664 | 28.746 | 28.875 | 31.315 | |
| [$A336^+$][$(CF_3SO_2)_2N^-$] | 22.043 | 22.089 | 28.372 | 28.431 | 28.663 | 28.744 | 28.864 | 31.317 | 31.175 |

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.