LC/MS and ELSD Analytical Procedures for Ionic Liquids

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Introduction

Phosphonium ionic liquids (IL) are an important class of ionic liquids with enhanced stability with respect to degradation under various conditions and thermal stability.

In this report, we present an LC/MS procedure for the analysis and purity determination of mixtures of phosphonium IL. The method reported is a robust procedure providing excellent peak resolution and high detection sensitivity.

Since most cationic species of phosphonium type ionic IL are not sensitive to UV detection, this procedure utilizes two mass spec ionization techniques (Electrospray and APCI). A third HPLC detection technique (ELSD) is also evaluated.

Design of Experiment

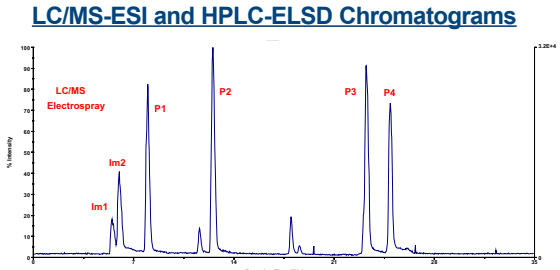
1. Selection of representative IL: four phosphonium IL (two low MW and two high MW) and two imidazolium.
2. Evaluation of the separation efficiency of HPLC column (column type, mobile phase, gradient conditions).
3. Selection of optimum HPLC conditions.
4. Comparison of LC/MS and LC/ELSD procedures: resolution and sensitivity.
5. Identification of anionic species from dimerized MS ion.
6. Analysis of residual chloride to 10ppm level.

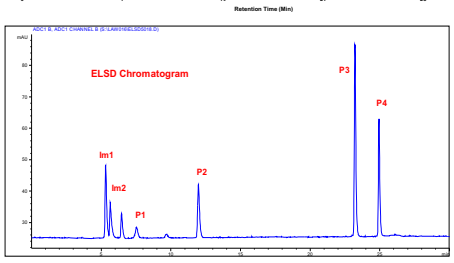
Conclusions

1. An LC/MS procedure is established for phosphonium type IL.
2. This procedure is also applicable for imidazolium type IL.
3. Sensitivity is 1 ppm (0.1% using 0.1% sample solutions).
4. LC/ELSD gives better peak resolution.
5. No LC/MS procedure specific for anionic species has been developed, however, anions can be identified from dimerized cluster ions.
6. IC can determine residual chloride in non-chloride IL to 10 ppm using 1% sample solutions.

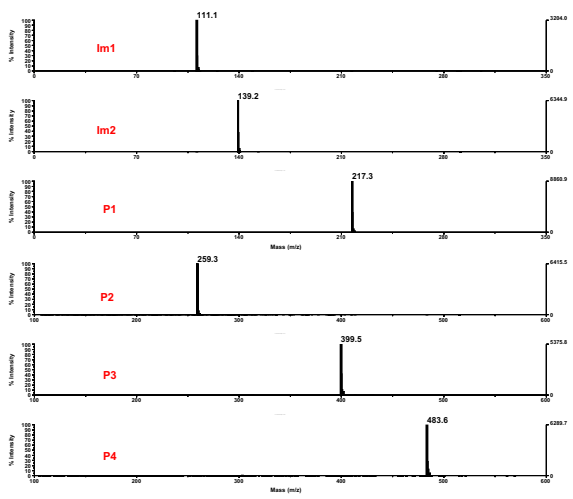
LC/MS and ELSD Procedures

LC/MS-ESI and HPLC-ELSD Chromatograms





Mass Spectra of IL Cationic Species



Observed Cations

P1	Triisobutyl(methyl)phosphonium, m/z = 217
P2	Tetrabutylphosphonium, m/z = 259
P3	Tributyl(tetradecyl)phosphonium, m/z = 399
P4	Trihexyl(tetradecyl)phosphonium, m/z = 483
Im1	1-Ethyl-3-methyl-1H-imidazolium, m/z = 111
Im2	3-Butyl-1-methyl-1H-imidazolium, m/z = 139

Relative Signal Response from Different Detectors

(normalized to P2)

Detector	P1	P2	P3	P4
APCI	0.42	1	1.57	1.67
Electrospray	0.85	1	0.86	0.67
ELSD	0.32	1	3.00	1.70

Analytical Procedure

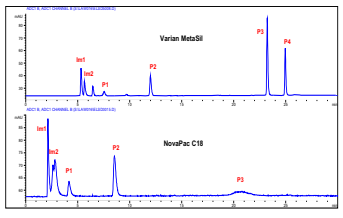
Mass Spectrometer: Applied Biosystems Mariner LC/MS system
Mass Spec ionization techniques: Electrospray and APCI

HPLC: Agilent HP 1100
HPLC detector: ELSD

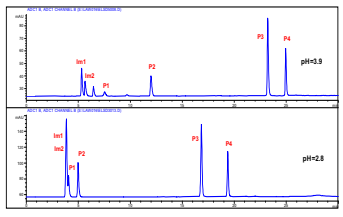
HPLC Conditions:
- Column: Varian MetaSil Basic, 250 x 4.6mm
- Aqueous mobile phase: 1% HAc, 0.2% NH_4Ac, pH = 3.9
  1% HAc only, pH = 2.8
- Organic mobile phase: Methanol
- Flow rate: 0.5 mL/min.
- Gradient: 50-100% MeOH (20min.) + 15 min.
- Column temperature: 30°C
- Sample size: 5 µL of 0.01% in MeOH

Evaluation Criteria

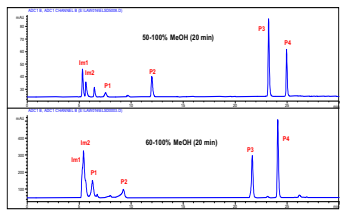
Selection of Column



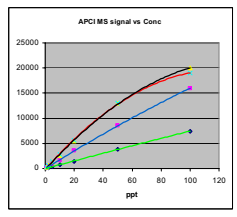
Effect of pH of Aqueous Phase



Effect of Gradient System

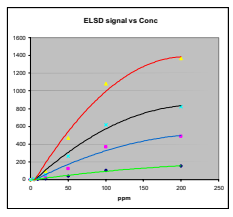


Linearity of LC/MS



P1: Green
P2: Blue

Linearity of ELSD



P3: Black
P4: Red

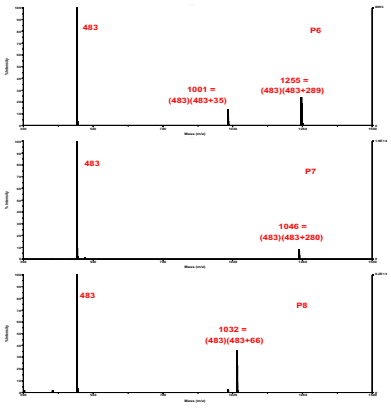
Results of Linearity Study

1. LC/MS has excellent sensitivity and linearity.
   - Sensitivity is 1 ppm.
   - Can detect 0.1% impurity with a 0.1% sample solution.
   - Linearity is 2 orders of magnitude.
2. ELSD gives better peak resolution.

Identification of Anions

MS CLUSTER IONS

Identification of Anionic Species using Dimerized Cluster Ion Three IL with the Same Cation, Different Anions



Identification of Anionic Species

All three IL have the same cation (m/z = 483)

Anion of P6 is confirmed as m/z = 289

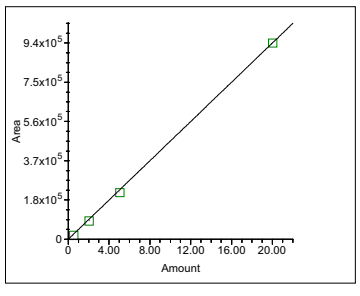
Anion of P7 is confirmed as m/z = 280

Anion of P8 is confirmed as m/z = 66

Impurity in P6 is chloride, m/z = 35

Ion Chromatography Linearity for Chloride

(Sensitivity: 0.1ppm = 10ppm in sample using 1% solution)



Residual Chloride in non-Chloride Ionic Liquids

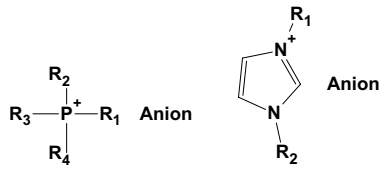
(using 1% solution)

IL abbr.	Residual Cl in sample
P1	80 ppm
P5	50
P6	160
P8	630
P9	890
P10	280
P11	540
P12	170
Im3	10
Py1	500

List of Analyzed Ionic Liquids

Ionic Liquids used in HPLC Study (LC/MS and ELSD)

P1	CYPHOS IL® 106	Triisobutyl(methyl)phosphonium tosylate
P2	CYPHOS IL 164	Tetrabutylphosphonium chloride
P3	CYPHOS IL 167	Tributyl(tetradecyl)phosphonium chloride
P4	CYPHOS IL 101	Trihexyl(tetradecyl)phosphonium chloride
Im1	1-Ethyl-3-methyl-1H-imidazolium chloride	
Im2	3-Butyl-1-methyl-1H-imidazolium chloride	



Phosphonium IL Imidazolium IL

Ionic Liquids used for Anion Study (MS and IC)

P5	CYPHOS IL® 163	Tetrabutylphosphonium bromide
P6	CYPHOS IL 104	Trihexyl(tetradecyl)phosphonium (ditrimethylpentyl)phosphinate
P7	CYPHOS IL 109	Trihexyl(tetradecyl)phosphonium bis(trifluoromethane)sulfonylamide
P8	CYPHOS IL 105	Trihexyl(tetradecyl)phosphonium dicyanamide
P9	CYPHOS IL 162	Tributyl(hexadecyl)phosphonium bromide
P10	CYPHOS IL 107	Tetrabutylphosphonium dibutylphosphate
P11	CYPHOS IL 102	Trihexyl(tetradecyl)phosphonium bromide
P12	CYPHOS IL 110	Trihexyl(tetradecyl)phosphonium hexafluorophosphate
Im3	1-Ethyl-3-methyl-1H-imidazoliumtrifluoromethanesulfonate	
Py1	Pyridinium p-toluenesulfonate	

References

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Acknowledgements

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