Ionic liquids

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http://www.iq.usp.br/wwwdocentes/rtorresi/index.htm

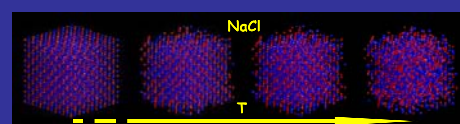
Outline

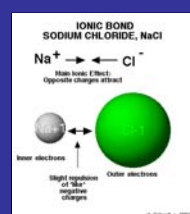
- Introduction
- Synthesis
- Some interesting Properties

What is an ionic liquid ?

An ionic liquid is a salt with melting point smaller that the boiling point of water.

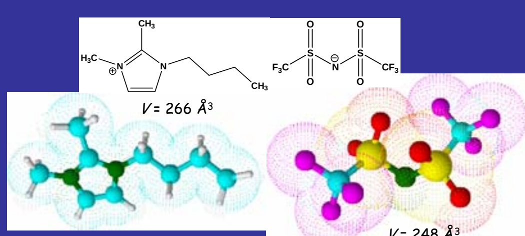
Why is an ionic liquid, a liquid ?





Phase at room temperature	Solid
Density	2.165 g/cm3
Melting point	801°C
Boiling point	1413°C

Why salts can be liquid at room temperature?



Weak interactions between ions

- Voluminous cations with delocalized charges
- Anions with delocalized charge

Why is an ionic liquid, a liquid ?

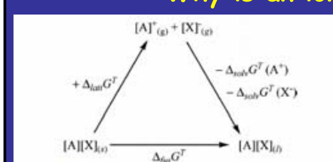


Figure 1. Born–Fajans–Haber cycle for the assessment of the melting (fusion) of a binary salt composed of complex ions ([A][X]), at temperature T, from lattice and solvation energies.

Table 1. Ion Volumes of Ions Found in ILs Investigated During This Study

cations	V_{ion} (nm^3)	anions	V_{ion} (nm^3)
$[EMIM]^+$	0.156 ± 0.018	$[BF_4]^-$	0.073 ± 0.009
$[C_3MIM]^+$	0.178 ± 0.028	$[PF_6]^-$	0.109 ± 0.008
$[BMIM]^+$	0.196 ± 0.021	$[TfO]^-$	0.131 ± 0.015
$[C_5MIM]^+$	0.219 ± 0.015	$[Tf_2N]^-$	0.232 ± 0.015
$[BMMIM]^+$	0.229 ± 0.012		
$[BPy]^+$	0.198 ± 0.013		
$[BMPyr]^+$	0.221 ± 0.015		
$[C_5MPyr]^+$	0.238 ± 0.018		
$[C_5NEt_3]^+$	0.268 ± 0.016		

It is not possible to calculate $\Delta_{fus}G$ *directly using simple methods,* but using an appropriate Born-Fajans-Haber cycle (Figure 1), $\Delta_{fus}G$ can be estimated using the recently developed principles of Volume-Based Thermodynamics (VBT) and simple quantum chemical calculations in combination with available experimental data.

I. Krossing, J. M. Slattery, C. Daguenet, P. J. Dyson, A. Oleinikova, H. Weingärtner - J. AM. CHEM. SOC. **2006**, 128, 13427.

Why is an ionic liquid, a liquid ?

Table 2. Summary of Experimental and Thermodynamic Data

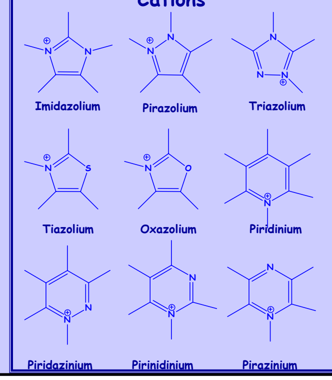
salt name	melting point (°C, ± 0.3)	dielectric constant (±0.3)	molecular volume (V_m/nm³)	$\Delta_{lat}H°$ (kJ mol⁻¹)	$\Delta_{lat}S°$ (kJ K⁻¹ mol⁻¹)	$\Delta_{lat}G°$ (kJ mol⁻¹)	$\Delta_{solv}G°$ (kJ mol⁻¹)	$\Delta_{sol}G°$ (kJ mol⁻¹)
[EMIM][BF$_4$][2,69]	15 to −1[a]	12.9	0.229 ± 0.027	492	0.324	395	−418	−23
[EMIM][TfO][2,64,70]	−9 to −15[a]	15.1	0.265 ± 0.033	464	0.339	363	−404	−41
[EMIM][Tf$_2$N]	−19	12.3	0.388 ± 0.033	425	0.370	320	−364	−44
[C$_3$MIM][Tf$_2$N]	not observed	11.8	0.410 ± 0.043	420	0.372	314	−359	−45
[BMIM][BF$_4$][60]	not observed	11.7[a]	0.269 ± 0.030	472	0.331	373	−409	−37
[BMIM][PF$_6$][60]	9	11.4[a]	0.305 ± 0.029	457	0.325	360	−385	−25
[BMIM][TfO]	13	13.2	0.327 ± 0.036	449	0.346	346	−395	−49
[BMIM][Tf$_2$N]	−5	11.6	0.428 ± 0.036	420	0.377	308	−358	−50
[BMMIM][Tf$_2$N]	not observed	11.5	0.461 ± 0.027	412	0.387	297	−349	−52
[C$_5$MIM][Tf$_2$N]	−10	11.4	0.451 ± 0.033	415	0.380	302	−357	−55
[BPy][Tf$_2$N]	23	11.5	0.430 ± 0.028	420	0.353	315	−358	−43
[BMPyr][Tf$_2$N]	−9	11.9	0.453 ± 0.030	414	0.345	311	−356	−45
[C$_5$MPyr][Tf$_2$N]	8	11.1	0.470 ± 0.033	411	0.352	306	−351	−45
[C$_3$NEt$_3$][Tf$_2$N]	0	10.0	0.500 ± 0.031	404	0.367	295	−337	−43

[a] Values not determined during this study; relevant references are indicated next to compound names.

I. Krossing, J. M. Slattery, C. Daguenet, P. J. Dyson, A. Oleinikova, H. Weingärtner - J. AM. CHEM. SOC. **2006**, 128, 13427.

Some ionic species

Cations



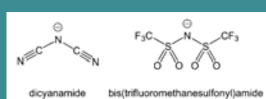
Some ionic species

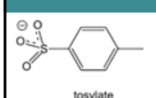
Anions

Cl^-, Br^-, I^-

$AlCl_4^-$

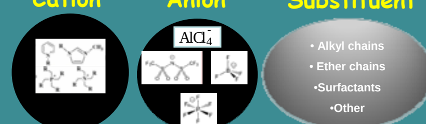
CF_3COO^-, $CF_3SO_2^-$





How many RTILs can be prepared?

Cation | Anion | Substituent



Cation 1 → Subst 1 → Anion 1, Anion 2, Anion 3
Cation 1 → Subst 2 → Anion 1, Anion 2, Anion 3
Cation 1 → Subst 3 → Anion 1, Anion 2, Anion 3

More than 1,000,000 possibilities

vs.

600 moleculars solvents

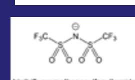
Properties

Ionic liquid
- Thermal stability
- Very low vapor pressure
- Ionic conductivity
- Tuning properties

- Electrochemical window → Cation → Negative potential limit; Anion → Positive potential limit
- Viscosity
- Hydrophobic degree → Mainly depends on the anion used
- Structural characteristics → Polar/non-polar characteristics of the substituents

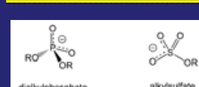
General classification

$AlCl_4^-$ — First generation of ionic liquids — Water instable



CF_3COO^-
$CF_3SO_2^-$

Second generation of ionic liquids — Water stable

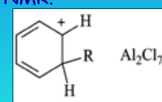


Third generation of ionic liquids — Non-toxic and biodegradable

A little bit about history

Room temperature ionic liquids: the casual beginning

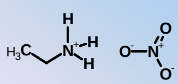
The first documented observation of an ionic liquid, it was during Friedel-Crafts reactions (19th century), by the formation of a red-oil liquid characterized some decades after by NMR.



A short history of ionic liquids—from molten salts to neoteric solvents - John S. Wilkes - *Green Chemistry*, 2002, **4**, 73-80.

Room temperature ionic liquids: recognized beginning

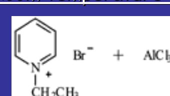
The accepted discovery of the first RTIL is related to a paper published in 1914, where the synthesis of $[EtNH_3]^+$ $[NO_3]^-$ was described.

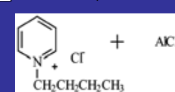


Melting point: 12 ºC

P. Walden*, *Bull. Acad. Sci. St. Petersburg 1914, 405-422

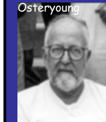
Room temperature ionic liquids: later on, in the 70´s



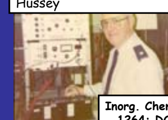


Problems:
1- Melting point for equimolar composition at 40 °C.
2- It is not stable in the presence of water
3- Very narrow electrochemical window (It is not enough for electrochemical reduction of Al).

Professor Robert Osteryoung



Professor Charles L. Hussey



J. Am. Chem. Soc.; 1975; *97*(11) pp 3264 - 3265; DOI: 10.1021/ja00844a081

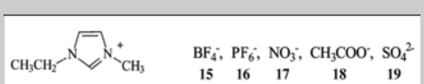
Inorg. Chem.; 1982; *21*(3) pp 1263 - 1264; DOI: 10.1021/ic00133a078

Room temperature ionic liquids: from the 90´s

Water-stable RTILs

J. S. Wilkes, M. J. Zaworotko, *Chemical Communications 1992, 965-*

P. A. Z. Suarez, J. E. LDullius, S. Einloft, R. F. De Souza, J. Dupont, *Polyhedron 1996, 15, 1217-1219.*



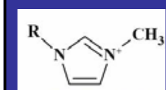
O u t l i n e

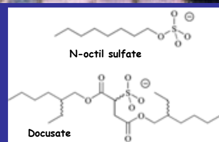
- Introduction
- Synthesis
- Some interesting Properties

Where to buy

EMPRESAS

- Solvent Innovation
- Cytec
- Sigma-Aldrich
- BASF
- Merck
- Dupont





More than 300 available

Problems

Costs: EMIM com Cl^-, PF_6^-, BF_4^-, $CF_3SO_3^-$

(Aldrich)

Cl^-: U$100/25 g

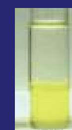
PF_6^-: U$86/5g

BF_4^-: U$127/5mL

$CF_3SO_3^-$: U$164/5mL

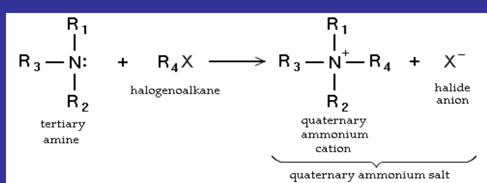
Purity: Not always appropriate

Especial needs

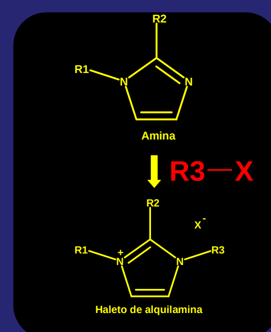


Synthesis: First step

Amines (P) alquilation



Synthesis: First step - quaternization



Synthesis: First step - quaternization

Preferential conditions of reactions

Reactivity ↑

R- I	Temperature lower than a 40 ºC	Inert atmosphere
R- Br	Temperature lower than a 60 ºC	Without solvent
R- Cl	Temperature ~ at 80 ºC	

Synthesis: Second step

NR_3

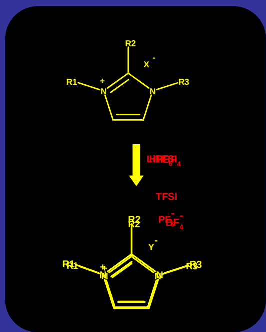
Step 1 — $R'X$

$[R'R_3N]^+ X^-$

Step 2a: + Lewis acid- MX_y → $[R'R_3N]^+ [MX_{y+1}]^-$ — Binary ionic liquids

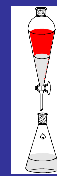
Step 2b: 1) Metallic salt- M^+X^- 2) Bronsted acid– H^+A^- → $[R'R_3N]^+ [A]^-$ — Pure ionic liquids

Synthesis: Ionic exchange



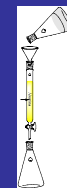
Purification of ionic liquids immiscible with water

washing



Active carbon

Filter column



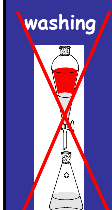
Fundamental characterizations

✓Elemental analysis
✓Spectroscopy (UV-Vis, FTIR, RMN)
✓Karl Fisher

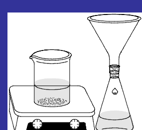
drying

Purification of ionic liquids miscible with water

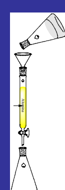
washing



Active carbon



Filter column



Fundamental characterizations

✓Elemental analysis
✓Spectroscopy (UV-Vis, FTIR, RMN)
✓Karl Fisher

drying

Ionic liquids distillation

Vol 439|16 February 2006|doi:10.1038/nature04451 nature

LETTERS

The distillation and volatility of ionic liquids

Martyn J. Earle[1], José M.S.S. Esperança[2], Manuela A. Gilea[1], José N. Canongia Lopes[2], Luís P.N. Rebelo[2], Joseph W. Magee[3], Kenneth R. Seddon[1] & Jason A. Widegren[3]

Purification without using VOCs!!!!!!

Ionic liquids distillation

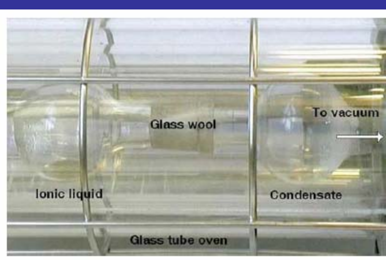


Figure 1 | Labelled photograph of the Kugelrohr oven and distillation apparatus. The central glassware rapidly rotates.

Ionic liquids distillation

Table 2 | Effects of distillation at 300 °C in the Kugelrohr apparatus

Ionic liquid	Conditions	Fraction of residue decomposed (%)	Fraction of distillate decomposed (%)
$[C_4mim][NTf_2]$	8 h, 6 mbar	2	2
$[C_4dmim][NTf_2]$	4 h, 6 mbar	1	1
$[C_8dbu][NTf_2]$	4 h, 6 mbar	3	3
$[NC_{2226}][NTf_2]$	4 h, 6 mbar	1	50
$[NC_{2222}][NTf_2]$	4 h, 6 mbar	1	2
$[C_4mpyrr][NTf_2]$	4 h, 6 mbar	1	1
$[PC_{66614}][NTf_2]$	4 h, 6 mbar	1	65
$[PC_{44416}][NTf_2]$	4 h, 6 mbar	1	60
$[C_{611}N(C_2H_4OH)][NTf_2]$	4 h, 6 mbar	15	85
$[C_2mim][OTf]$	4 h, 7 mbar	4	12
$[C_6mim][OTf]$	4 h, 6 mbar	1	50
$[C_2dbu][OTf]$	4 h, 8 mbar	1	1
$[C_4mim][PF_6]$	4 h, 6 mbar	1	1
$[C_4mim][FAP]$	18 h, 8 mbar	99	50
$[P(s\text{-}C_4)_3C_1][OTs]$	4 h, 6 mbar	5	5
$[C_2mim][OSO_3C_2H_5]$	5 h, 7 mbar	99	99
$[PC_{66614}]$[decanoate]	6 h, 7 mbar	98	95

$[C_nmpyrr]^+$ is 1-alkyl-1-methylpyrrolidinium; $[FAP]^-$ is trifluorotriperfluoroethylphosphate. A fraction of 1% represents the limit of our detection, and is thus an upper bound.

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Ionic liquids distillation

Table 4 | Distillation of approximately equimolar mixtures of ionic liquids

Ionic liquid A	Ionic liquid B	Composition ratios of the residue (A:B)	Composition ratios of the distillate (A:B)	Fraction of distillate decomposed (%)
[C_2mim][NTf_2]†‡	[C_{10}mim][NTf_2]	24:76	76:24	<1
[C_2mim][NTf_2]§	[C_6mim][NTf_2]	51:49	59:41	<1
[C_4mpyr][NTf_2]‡	[NC_{2222}][NTf_2]	47:53	53:47	<1
[C_4mim][NTf_2]§	[C_4mim][PF_6]	52:48	98:2	<1
[C_2mim][OTf]‡	[NC_{2222}][NTf_2]	[illegible]	[illegible]	<1

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O u t l i n e

- Introduction
- Synthesis
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Some Properties

- Good thermal stability
- Very low vapor pressure
- Non flammable
- Good ionic conductivity
- Very good electrochemical stability
- Excellent solvent with low or strong coordinating properties
- Solvent with organized structure

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Needs

- ✓ Toxicological information
- ✓ Developing new ionic liquids
- ✓ Data base with all properties
- ✓ Real comparison between traditional solvents and ionic liquids
- ✓ Methods of synthesis less expensive
- ✓ Easier availability

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Departamento de Química Fundamental
Laboratório de Materiais Eletroativos

Professor: Roberto Manuel Torresi

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Under-graduated students: Alisson Barros, Lucas L. de Carvalho, Tatiana C. Penna

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Prof. Aldo Zarbin - DQ - UFPr

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