Ionic Liquids

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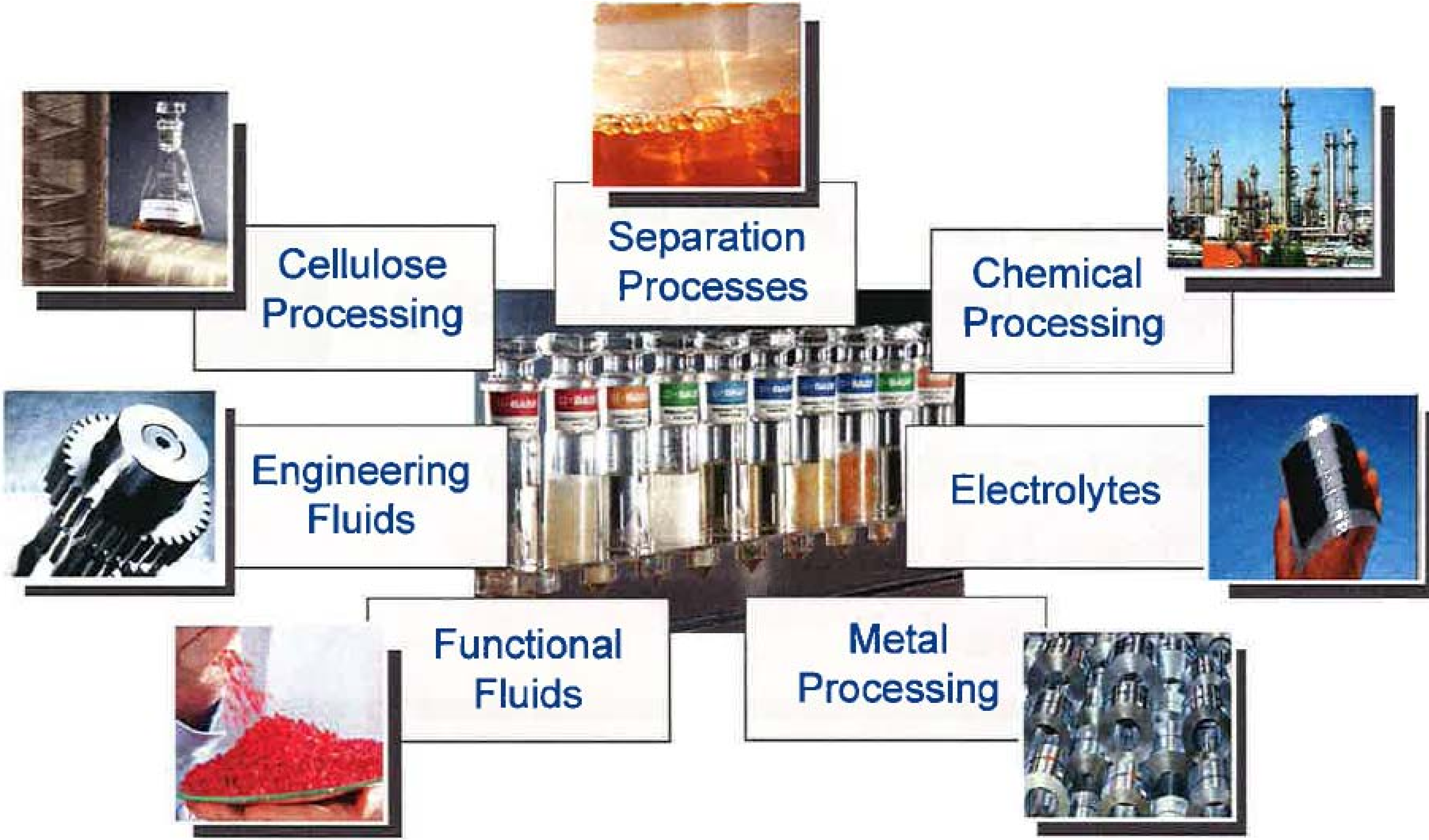
03-23-2011

Technological Applications

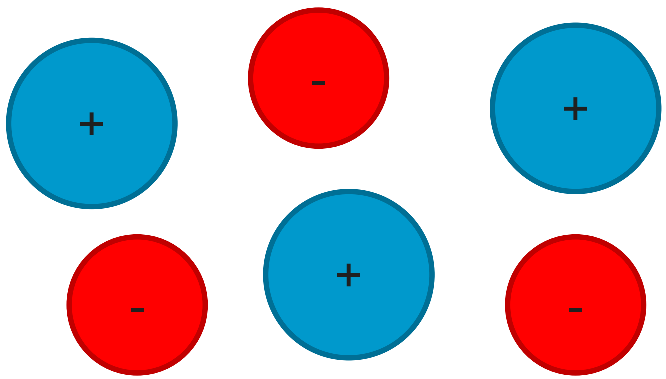


[4]DECHEMA-Meeting, February 2011, Erlangen

What are Ionic Liquids?

“The term ionic liquids refers to compounds consisting entirely of ions and existing in the liquid state below 100°C.”[1]

Entirely of ions:



Salts
e.g. NaCl

Liquid state below 100°C: NaCl liquid at 801°C
Binding Energy determines melting point

[1] “Electrodeposition from Ionic Liquds”, Endres, Abbott, MacFarlane, WILEY-VCH 2008

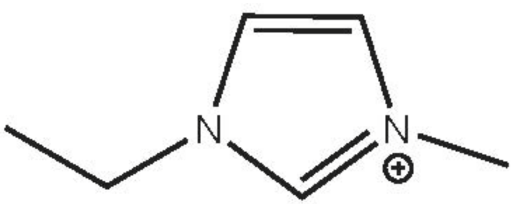
"Room-temperature molten salts"

Binding Energy due to Coulomb attraction

$$E_C = \frac{q_1 q_2}{4\pi\varepsilon_0 (r_+ + r_-)}$$

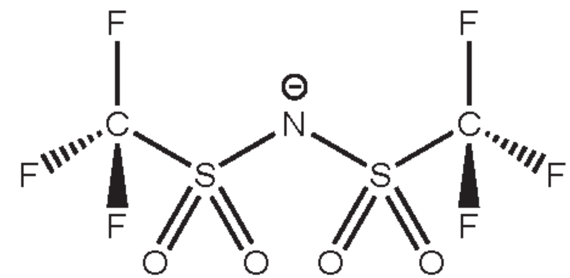
Increase in ion size → decrease in binding energy

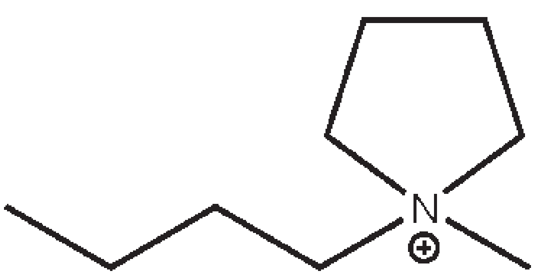
→ lower melting point



1-Ethyl-3-methylimidazolium
$[EMIm]^+$

Bis(trifluoromethylsulfonyl)imide
$[NTF]^-$



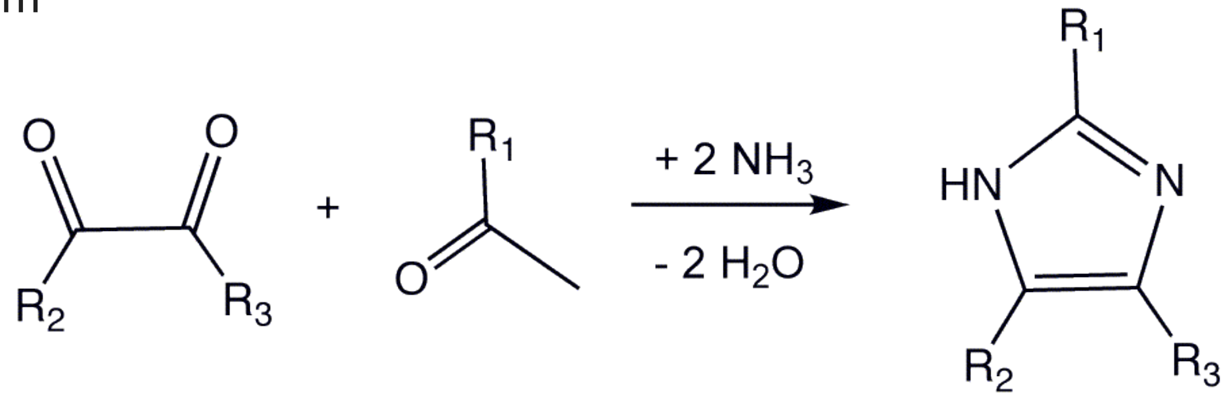


1-Butyl-1-methylpyrrolidinium
$[BMPyrr]^+$

Synthesis

Example: Imidazolium

1) Synthesis of aromatic system



Glyoxal Formaldehyde Imidazole

2) Alkylation

R'-X → + + X^-

3) Anion exchange

[EMIm]X $\xrightarrow{H_2O}$ [EMIm]OH $\xrightarrow{HY}$ [EMIm]Y + H_2O

electrodialysis

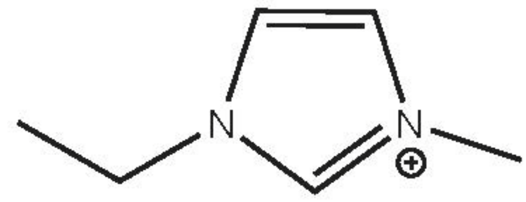
Melting points in °C

	Cl^- 181pm	Br^- 196pm	I^- 220pm	BF_4^- 229pm	$(CF_3SO_2)_2N^-$ 325pm
Na^+ 102pm	808	747	662	384	-
Cs^+ 167pm	645	636	621	-	-
$[EMIm]^+$ 304pm	87	77	78	11	-15

[1] "Electrodeposition from Ionic Liquds", Endres, Abbott, MacFarlane, WILEY-VCH 2008

[2]http://en.wikipedia.org/

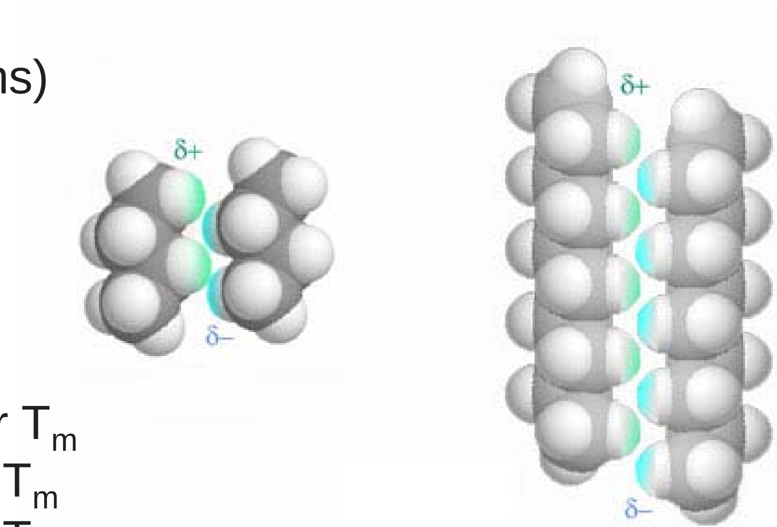
Other Influences on melting point



- Effect of cation structure
  - Delocalized charges lower electrostatic interaction

➡ Aromatic systems show lower melting points

- Effect of side chain length
  - Van der Waals force (dipole dipole interactions) between parallel side chain areas
  - 3D Orientation of molecules
  - Cation symmetry



[3]

Longer side chains lead to

- greater Van der Waals forces ➡ higher T_m
- more asymmetric molecules ➡ lower T_m
- more complex 3D orientation ➡ lower T_m

Interacting effects ➡ reasonable alkyl chain length 2 to 8 C atoms

- Analog aspects for anion

[2]http://en.wikipedia.org/

More physical properties

Decomposition Temperature: ~250°C to 450°C

[3] compound	T_{onset}/°C
[bmim][Cl]	264
[bmim][Br]	273
[bmim][dca]	300
[bmim][BF_4]	361
[bmim][methide]	413
[bmim][triflate]	392
[bmim][Tf_2N]	422
[bmmim][PF_6]	373
[bmmim][BF_4]	380
[pmmim][Tf_2N]	462

Vapor pressure:

- Substantially zero under ambient conditions
  → Comparable to solids
  No particles in gas phase
- Can be evaporated at higher temperatures under vacuum (decomposition)

[3]“Thermophysical Properties of Imidazolium-Based Ionic Liquids”, Fredlake, 2004

More physical properties

Viscosity: Several magnitudes higher than water
Great range depending on cation/anion combination

Compund	Viscosity in cP	Ref.
Water	0.89	[1]
$[BMIm][PF_6]$	207	[4]
$[BMIm](CF_3SO_2)_2N$	52	[4]
Engine oil	10-100	[2]

1cP = 1 Centipoise = 0,001 Pa*s

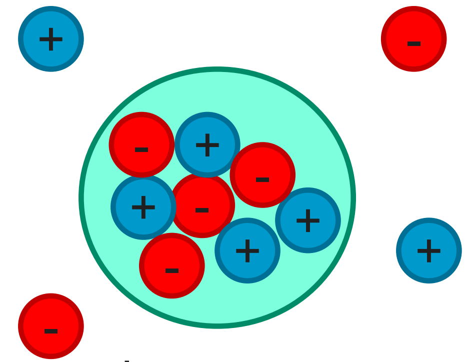
In general more viscous due to
- Longer side chains
- more aromatic/hydrophobic parts
- larger anion size

$$\eta = \eta_0 \cdot \exp\left(\frac{E_a}{k_B T}\right)$$

[2]http://en.wikipedia.org/
[4]DECHEMA-Meeting, February 2011, Erlangen

More physical properties

Conductivity: Walden equation $\eta \cdot \Lambda = const$



→ indirect proportional to viscosity

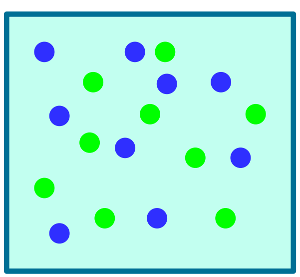
Ion clustering in Ionic Liquids

→ Smaller effective number of free charge carriers

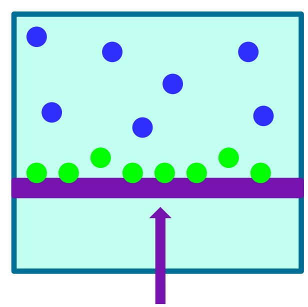
Solubility: Metal salts are well soluble ($AlCl_3$, $ZnCl_2$, …)

→ necessary for metal electro-deposition

Gas solubility $PH_3 >> H_2O > CO_2 > C_2H_6 > O_2 > Ar > N_2 > H_2$ [4]



Storage



Compression

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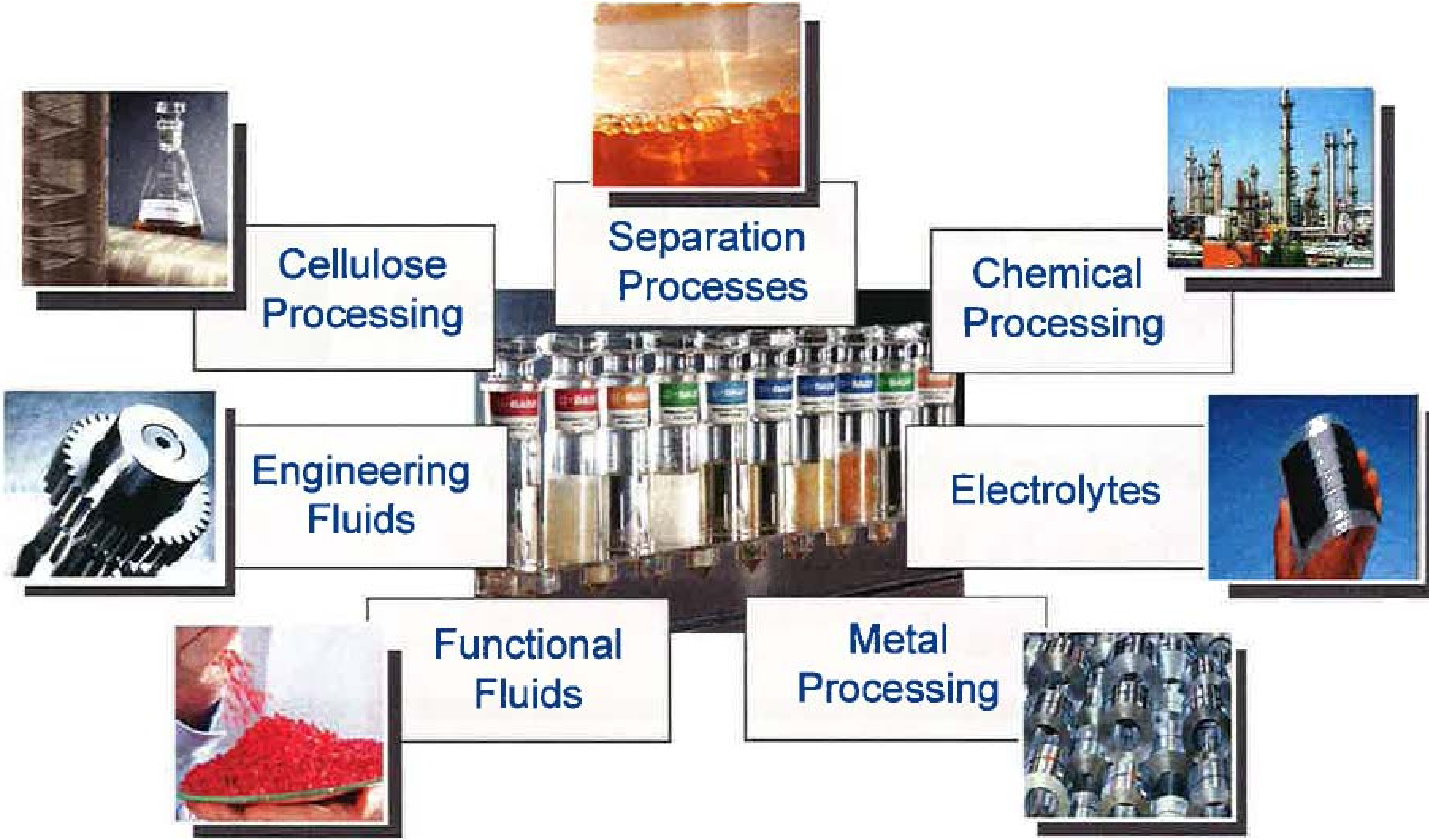
Where to use Ionic Liquids?



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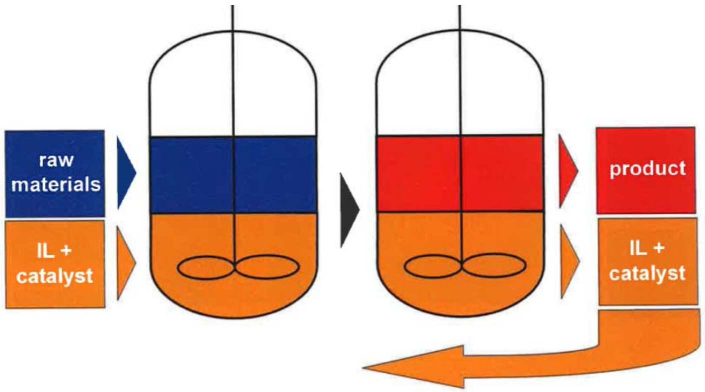
Chemical Processing

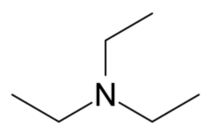
BASF's BASIL Process

Biphasic Acid Scavenging utilizing Ionic Liquids



+HCl $\rightleftharpoons$ [ ]Cl

- No suspensions (triethylamine)



- Liquid salt
- Easy to separate
- Higher reaction kinetics due to Ionic Liquid

First dedicated industrial-scale Ionic Liquid based process

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Ionic Liquids as Lubricants

[5]

Tribology: Study of Interacting surfaces in motion

A lot of lubricants are derived from petroleum
- Environment
- Resources
- Not applicable to all conditions

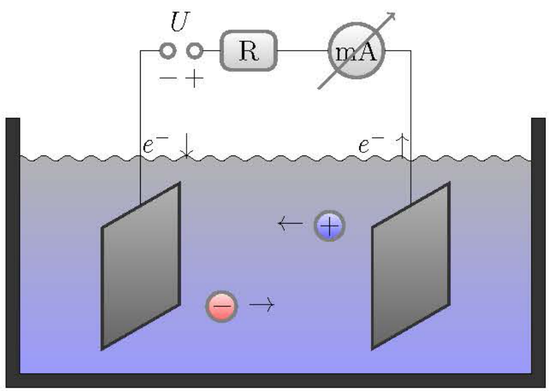
Ionic Liquids
- Less loss due to higher material wear lifetimes
- Stable at higher temperatures
- Working under vacuum due to negligible vapor pressure
- Surface Interactions to protect material
- Lubricants for more reactive light weight alloys (Al, Mg)
- As additives to improve existing lubricants

- Corrosion is a problem

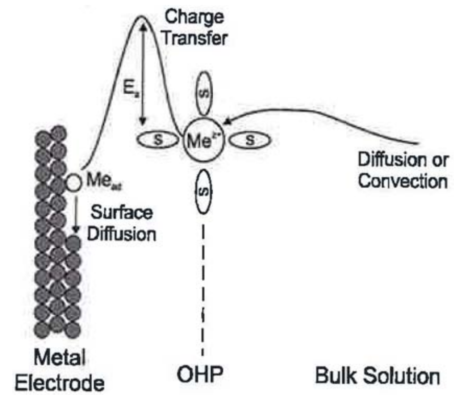
“Ionic Liquids as Advanced Lubricant Fluids”, Bermudez, Molecules 2009, 14, 2888-2908
[5]http://www.paul-langrock.de/docs/offshore_siemens.htm

Metal-Deposition

Electro-Chemistry



Metal-Deposition

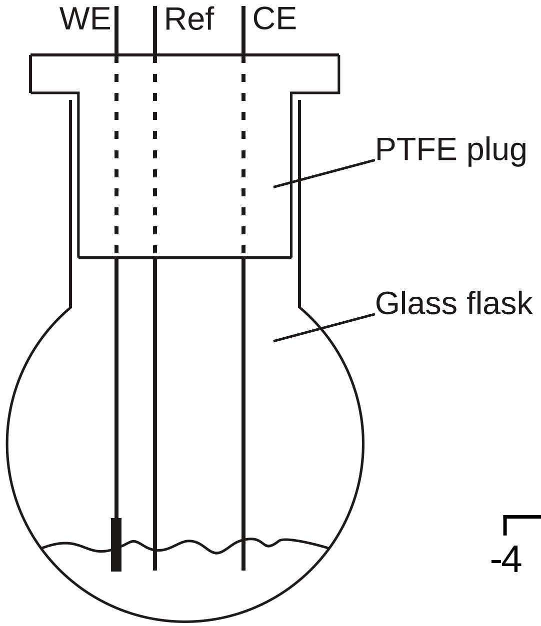


[4]DECHEMA-Meeting, February 2011, Erlangen

Why use electro-deposition?

- Complex geometries possible (not like vaporization)
- Decorative purposes (gold, silver)
- Improve Surface (friction, wear lifetime)
- Corrosion protection (reactiveness)
- Electrode purification (dissolve, deposit)

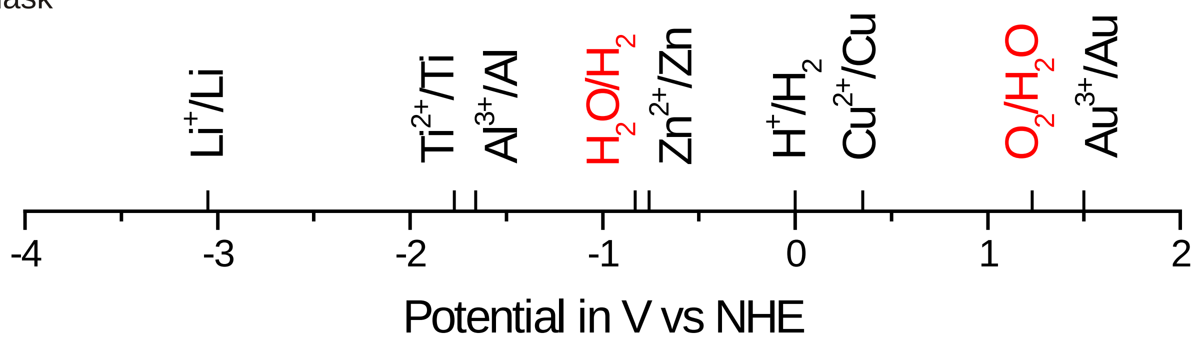
Aqueous Electrolytes



3 Electrode Setup:

Current influence on Potential (charge transfer, …)

- Counter electrode for current
- High-ohmic Reference electrode for potential



$$Zn^{2+} + 2e^- \longrightarrow Zn$$

$$2\,H_2O + 2e^- \longrightarrow H_2 + 2\,OH^-$$

$$4\,H_2O \longrightarrow 2\,O_2 + 4\,H_3O^+ + 4e^-$$

[6]

[6]http://www.autosieger.de/images/articles/a-klasse_rohbaukarosserie_3.jpg

Why use Ionic Liquids?

Aqueous electro-deposition

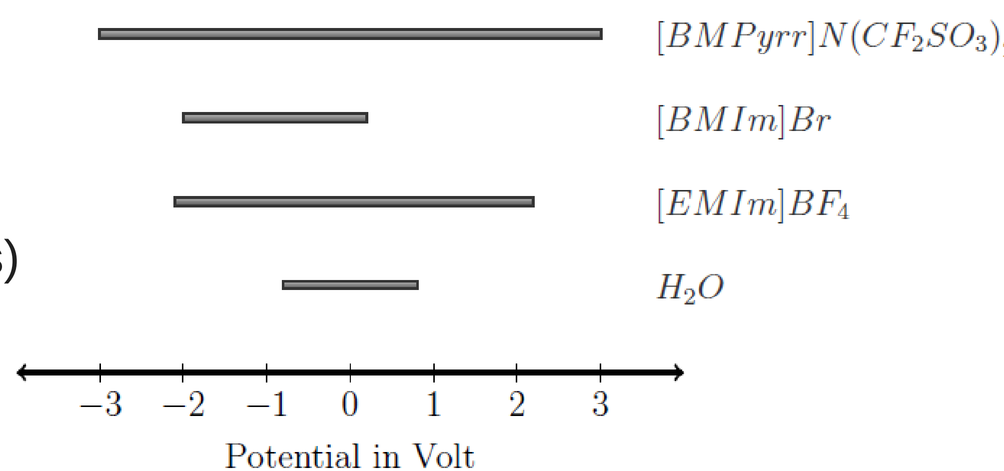
- Cheap
- Well understood
- Established processes

- Small electrochemical window
- Hydrogen evolution, Embrittlement
- Some metals are not depositable

Electro-deposition in Ionic Liquids

- Thermal stability
- Vapor pressure
- Non Volatile (unlike organic electrolytes)
- Wide electrochemical window

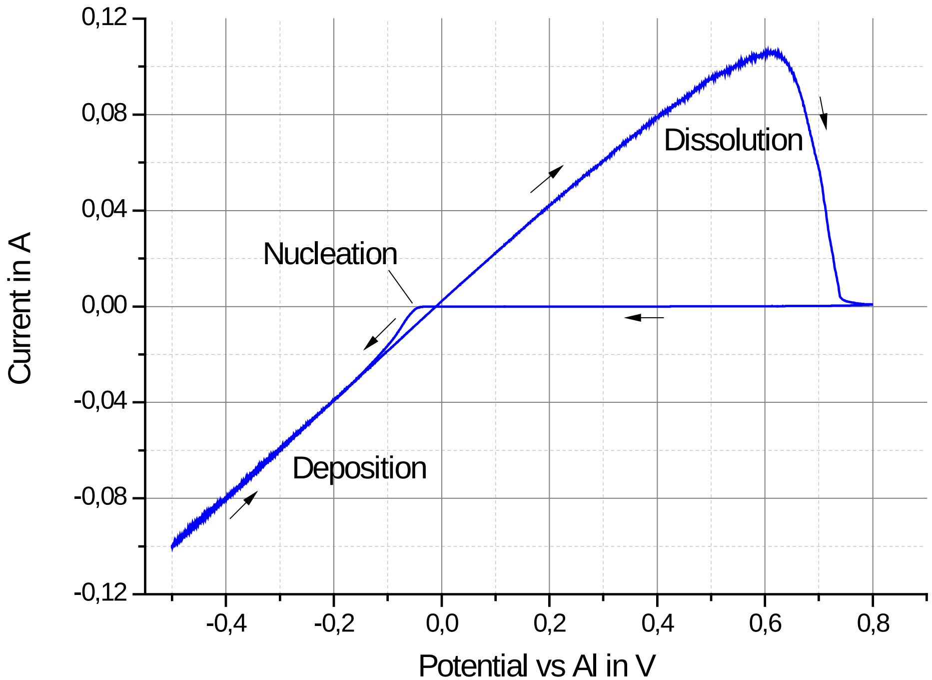
- Relatively high costs
- Hygroskopic, impurities
- Working in inert atmosphere required (Glovebox)



Aluminum deposition

$[EMIm]Cl + 60mol\text{-}\%\ AlCl_3$
Cyclic Voltammetry on steel


[2]



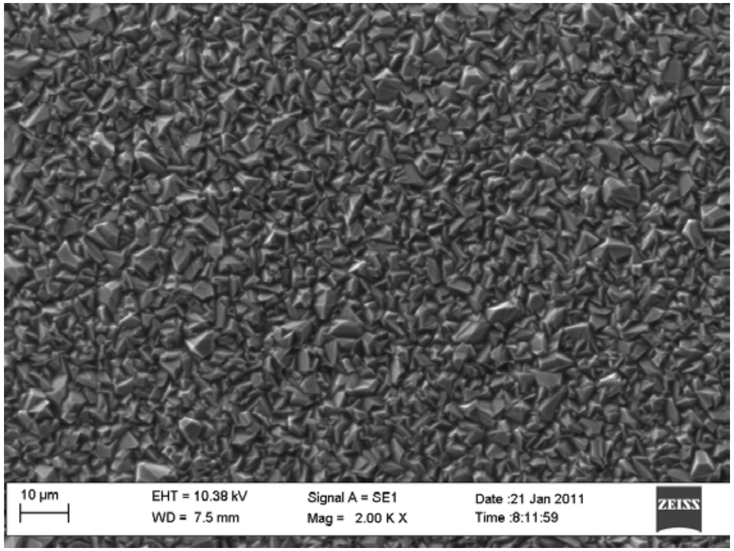
Parameters:

- Temperature
- Applied Potential
- $AlCl_3$ Concentration

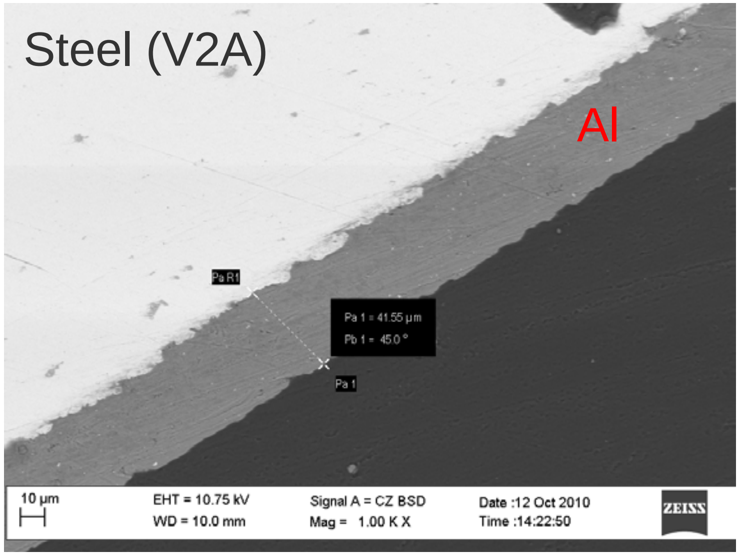
[2]http://en.wikipedia.org/

Aluminum deposition

Deposition on steel
-0,5V, 40 Coulomb, 35°C



Surface



Cross section

- Well adherent and dense Al layers
- Thickness adjustable through charge

Faraday's law $$n = \frac{Q}{zF}$$

Thank you for your attention