Part II: liquid- liquid extraction with ILs

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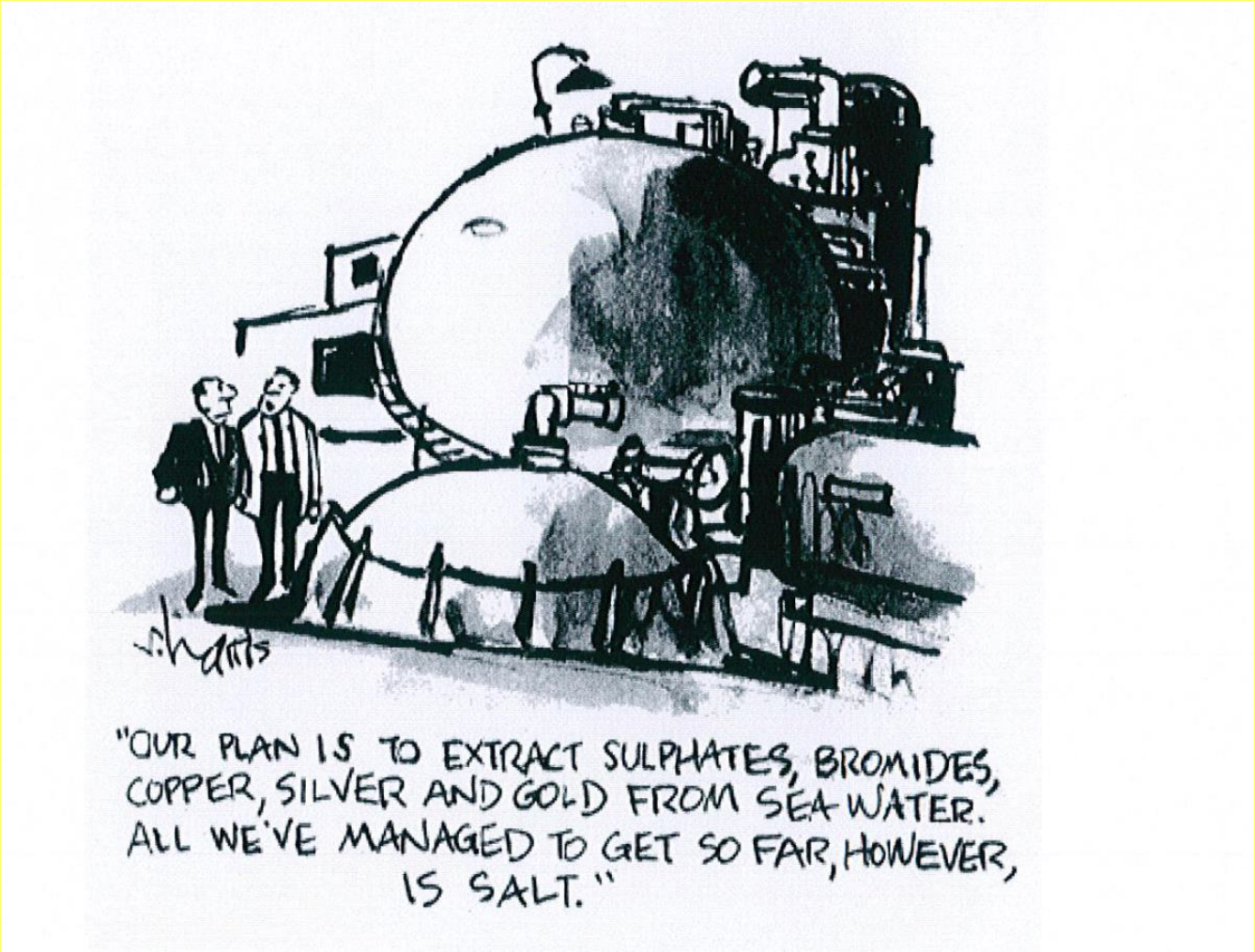
Do ILs bring something new ?



General rules using molecular solvents

First tips

- initial aqueous phase contains the metallic ion(s) and a mineral acid
- Water, acid and metallic ions are not soluble in the organic phase
- The organic phase is poorly soluble in the acidic aqueous phase

An extractant is absolutely needed in the organic phase

Results

- The extractant is poorly soluble in the aqueous phase
- It extracts part of the acid and eventually water
- Extracted species are neutral

Distribution coefficient D: $D_M = [M]_{org}/[M]_{aq}$

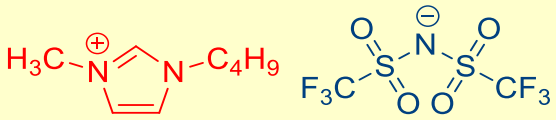
- D < 0,1 no significant extraction
- 0,1 < D < 1 low extraction efficiency
- D > 1 significant extraction
- D should not be too large !

Notations

ILs and salts are noted: $[Cat^+][Ani^-]$

imidazolium ILs as: $[C_nC_mim^+][Ani^-]$

Cat^+ Ani^-:



$C_1C_4im^+$ Tf_2N^-

Biphasic systems noted:

$M(n.o)/[H^+][X^-]/Solv1//E/Solv2$

Top phase on the left; compounds in their main initial phase (before extraction)

$Ni(II)/[H^+][Cl^-]/H_2O//Org/Cyanex$

Ideas for ILs and extraction

- ILs remplace the organic phase
  - Simple idea, surprising results
- ILs are additives to the organic phase
  - Very original idea
- ILs act as new extractants
  - Ideas of organic chemists
- ILs replace both phases
  - Very recent idea, potential application ?
- ILs as the ultimate solution (?)
  - Delete the organic phase !

Outline of presentation

- ILs as replacement of mol. solvents
- ILs as additives to organic phase
- Deleting the organic phase
- Conclusions and perspectives

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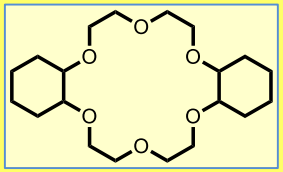
IL is used as the organic solvent

Sr(II)/pH=4.1/H_2O//DCH18C6/[Cat^+][Ani^-]



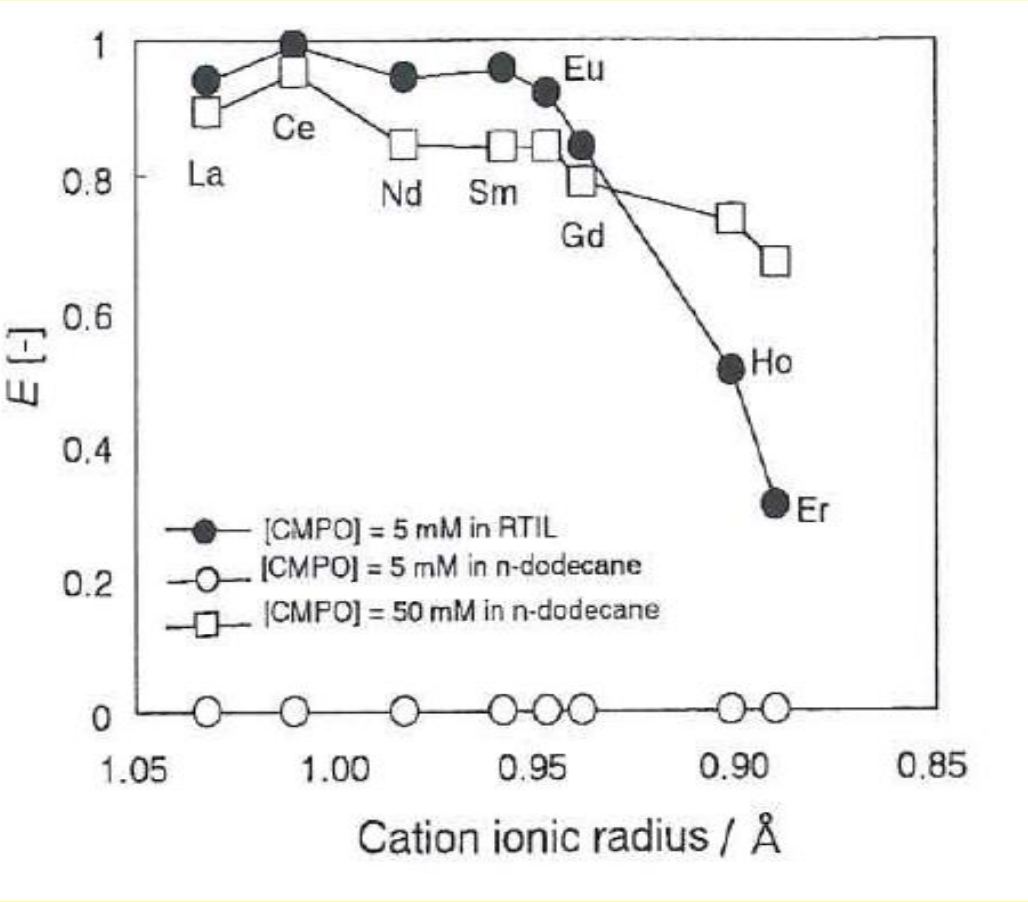
solvent	D without EC	D with EC
$C_4C_1C_1imPF_6$	0.67	4.2
$C_4C_1imPF_6$	0.89	24
$C_2C_1C_1imTf_2N$	0.81	4500
$C_2C_1imTf_2N$	0.64	11000
$C_3C_1C_1imTf_2N$	0.47	1800
$C_3C_1imTf_2N$	0.35	5400
$C_6H_5CH_3$	0	0.76
$CHCl_3$	0	0.77

It's a miracle ?!

Dai et al., J. Chem. Soc. Dalton Trans, (1999)1201

Is there a benefit ?

CMPO in $[C_1C_4im^+][PF_6^-]$ is ca. 10 times more efficient than in dodecane



Costly extractants can be saved thanks to costly solvents…

Ion exchange mechanism occurs, thus the IL amount needed is much lower than what is actually present !

Can we do better ?

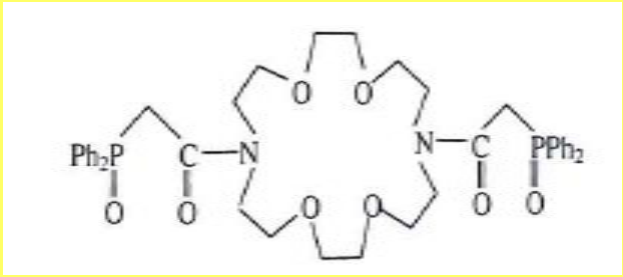
Nakashima et al., Anal. Sci. 19(2003)1097

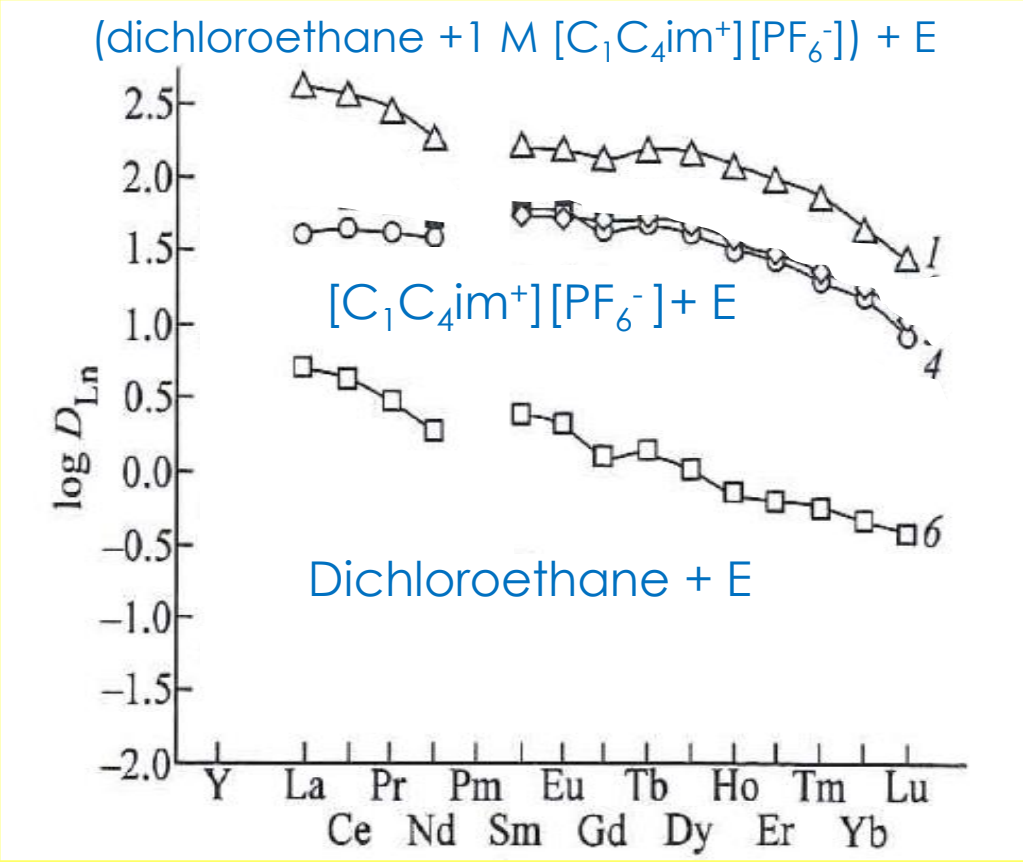
Outline of presentation

- ILs as replacement of mol. solvents
- **ILs as additives to organic phase**
- Deleting the organic phase
- Conclusions and perspectives

IL as an additive to a molecular solvent

Eu(III)/$[H^+][NO_3^-]/H_2O$//(E+$[C_1C_4im^+][Ani^-]$)/Mol





The amount of costly IL is reduced but this system is complicated and not « green ». Can we do better ?

E: organophosphorus compound

Turanov et al., Radiochem. 50(2008)266; Turanov et al., Solv. Ext. Ion Exch., 30(2012)244

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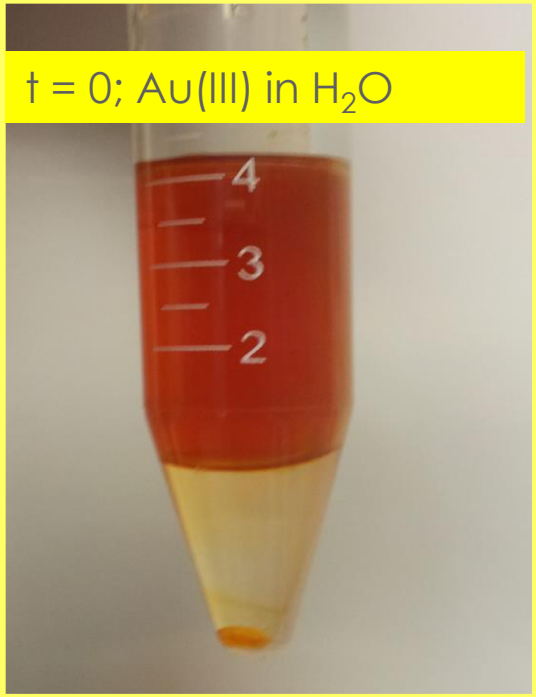
First, delete the extractant

Pure ILs do extract metallic ions. (cf. Dai et al.)

$AuCl_4^-/[H^+][Cl^-]\ /H_2O//\ [C_8C_1im^+][Tf_2N^-]$



Other examples with Pt(IV), Ir(IV), Pd(II), Rh(III).

N. Papaiconomou et al., Green Chem. 14(2012)2050
Papaiconomou et al., RSC Advances, 4(2014)48260-48266

Separation Co/Pt from real life sample

Proton Exchange Membrane Fuel Cells (PEMFC) are used for vehicules (and other applications). They contain two valuable metals: Pt and Co

PEMFC are dismantled

Active Co-Pt-C powder is collected

The powder is dissolved in HCl 12 M/H_2O_2

How to separate the two metals, without using an extractant ?

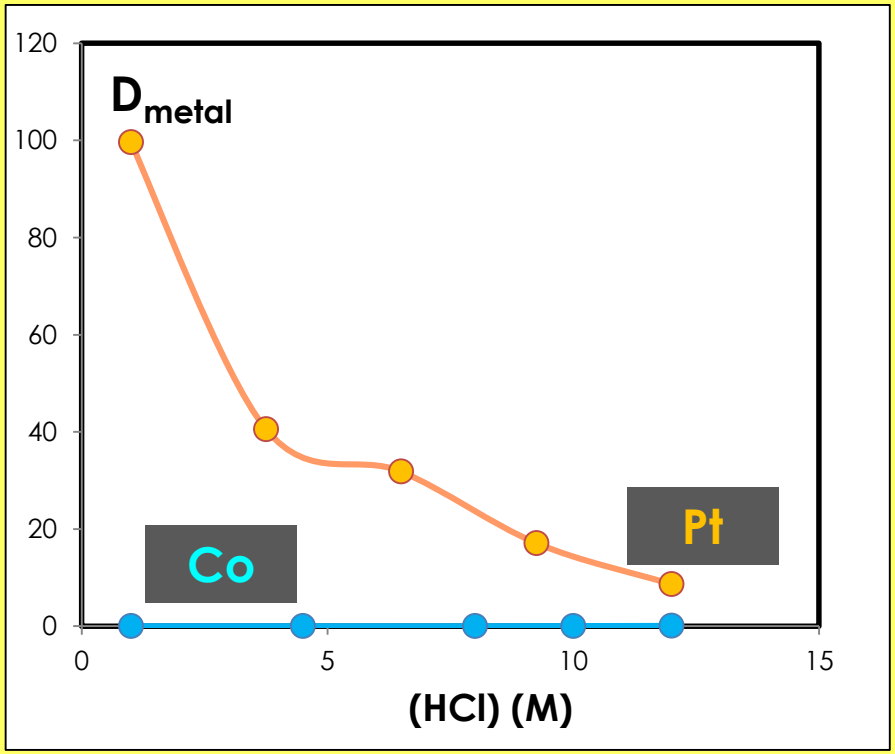
Separation Co/Pt using $[C_{14}pyr][Tf_2N]$, T = 40 °C

Step 1: individual extraction study

Co alone at $9x10^{-2}$ M in H_2O/HCl or Pt alone at 10^{-2} M in H_2O/HCl 12 M; Room T.

Step 2: mixtures Co/Pt arising from real PEMFC lixiviation

- (Co, Pt) at ($4.8x10^{-3}$ M/ $1.16x10^{-2}$M)
- (Co, Pt) at ($2.4x10^{-3}$ M/$5.8x10^{-2}$ M)



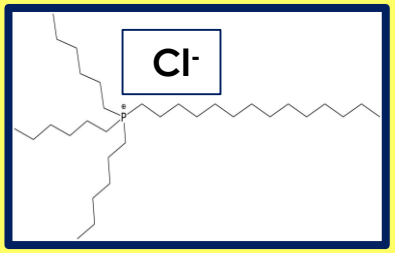
before

after

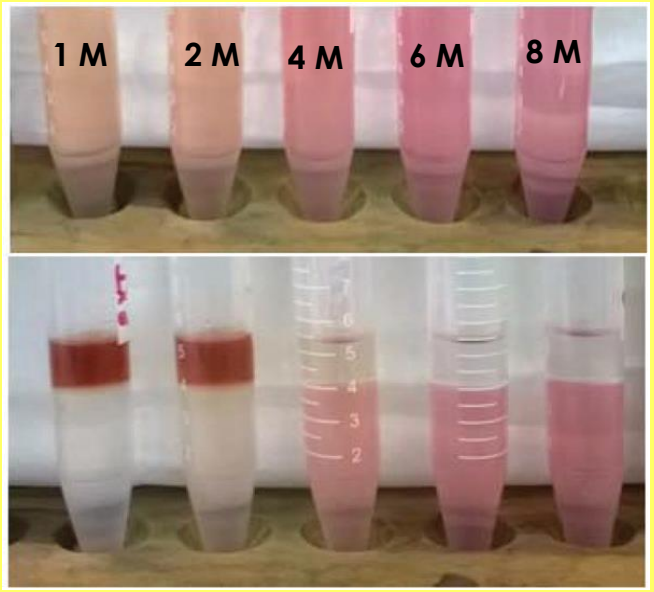
Dilution factor applied to the sample : 1 (i.e. HCl final value is 6 M)

Separation Pd(II) vs. Rh(III)

P_{66614} Cl //H_2O/HCl/Rh(III)/ Pd(II)

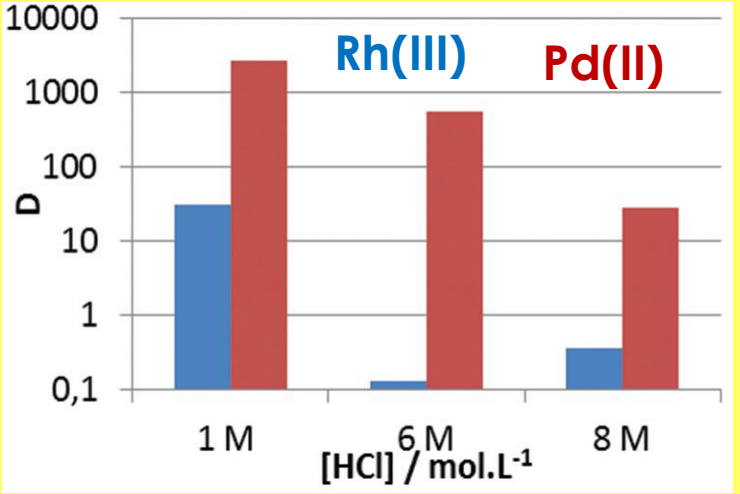


[Rh] = 250 mgL^{-1} ; [Pd] = 250 mgL^{-1}; V_{aq} / V_{IL} = 3,4



aqueous phases

After extraction

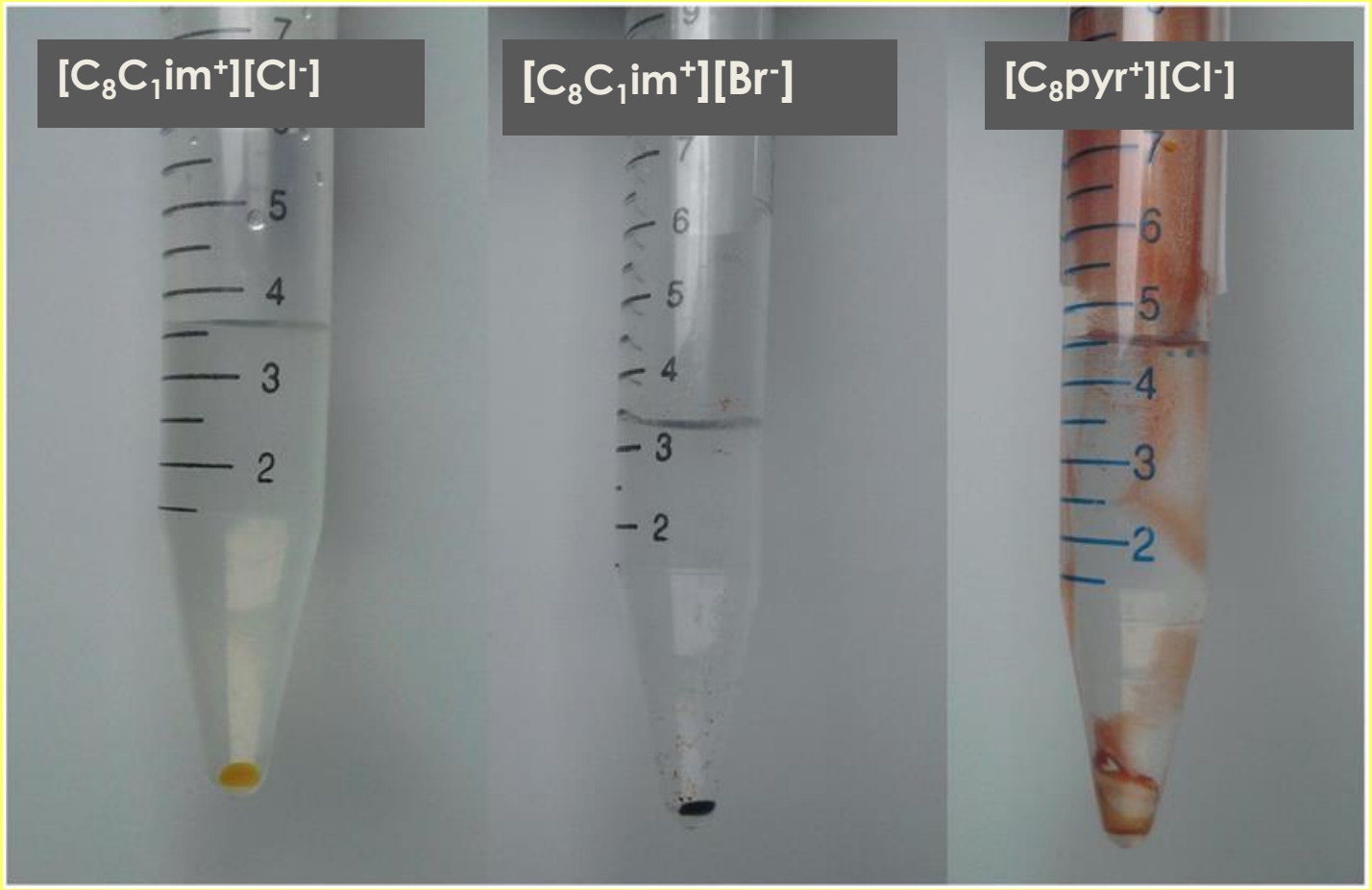


HCl ≥ 5 M: Pd in IL, Rh remains in water

Svecova et al. Dalton Trans, 45(2016)15162;

Second, delete the organic phase (almost do it…)

Au(III)/[H^+][Cl^-]/H_2O//[Cat^+][Ani^-]
[Cat^+][AuX_4^-] precipitates as a solid (or a liquid)



Papaiconomou et al., Green Chem. 14(2012)2050

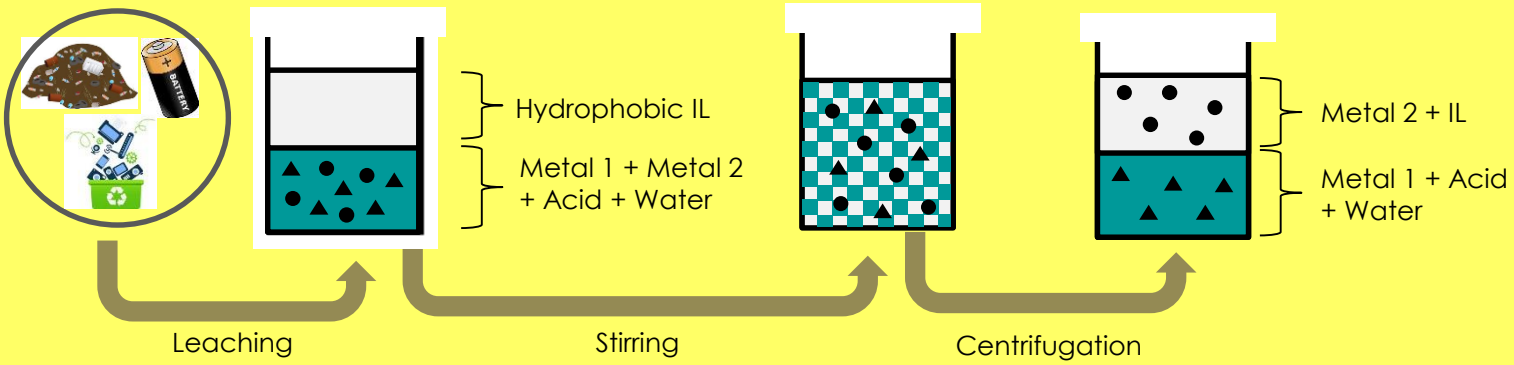
Delete the organic phase frankly

Another example

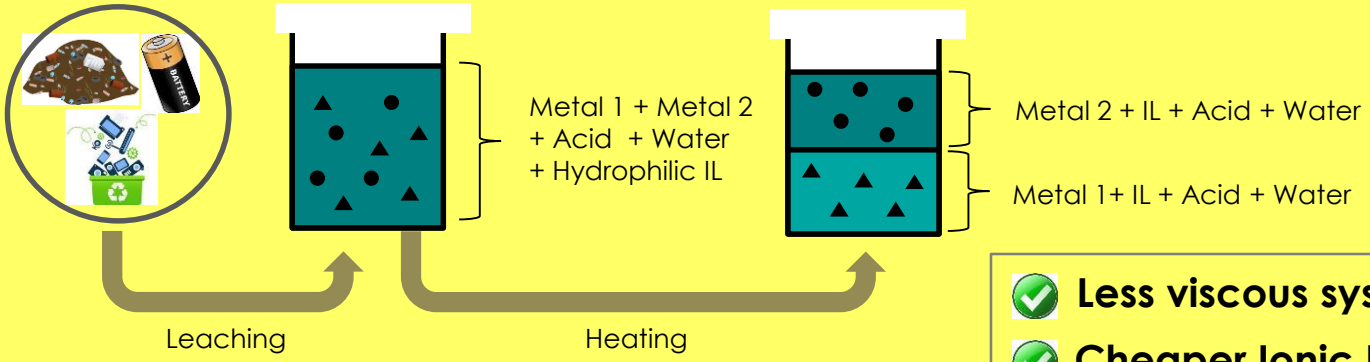
The system is composed of : mineral acid, metallic ion, water, an hydrophilic IL highly soluble in water.
Temperature makes the system change from monophasic to biphasic

AQUEOUS BIPHASIC SYSTEMS FOR METAL RECOVERY

- **Conventional liquid-liquid extraction**



- **Aqueous Biphasic Systems**



- **Less viscous systems**
- **Cheaper Ionic Liquids**
- **Less steps in the process**

Conclusions, perspectives

- **ILs impulse a new definition of solvent, solutes and biphasic systems for extraction**

- **ILs allow *different* extractions, which benefit has to be estimated**

- **Their unique solvation properties make them the best playground ever**

Thanks for your attention