Extraction and separation of metals using (as less as possible) ionic liquids

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Hydromet seminar, Norway, march 2017

Context in liquid/liquid extraction of metals

- H_2O+acid//molecular solvent+ligand
  - Toxicity concerns (solvent, ligand)
  - Cost (ligand)
- H_2O+acid//**hydrophobic ionic liquid**+ligand
  - Toxicity concerns (ligand + IL)
  - Loss of IL by ion exchange mechanism
  - Cost (IL and ligand)
- H_2O+acid//hydrophobic ionic liquid
  - Toxicity concerns reduced **(no ligand)**
  - Loss of IL by ion exchange mechanism
  - Cost reduced (no ligand)

  Rh(III) extraction with Cyphos 101 and 102
- ABS H_2O+salt+**fluorine-free hydrophilic IL**
  - Toxicity is low
  - Cost reduced
  - Metal hydrolysis unmanageable
- **ABS H_2O+acid+fluorine-free hydrophilic IL**
  - Manageable metal hydrolysis
  - Cost reduced

  ABS with acid

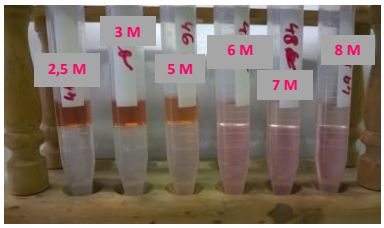
Metal extraction by pure hydrophobic IL phases

Rh(III) extraction from acidic aqueous phases by pure ILs

(Rh(III)] = 250 mgL^{-1}; [HCl] from 0.5 M to 8 M
$P_{66614}Cl$ and $P_{66614}Br$ used as pure IL phases. Room temperature.
Identical volumes of aqueous and IL phases

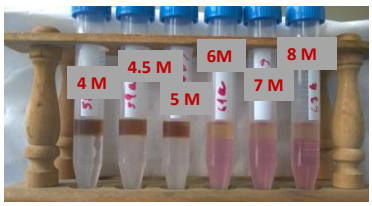
Cyphos 101

$P_{66614}Cl$ D =73 at 1M HCl
D drops to <0.05 M above 4 M HCl



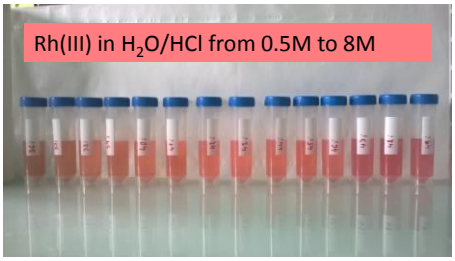
Cyphos 102

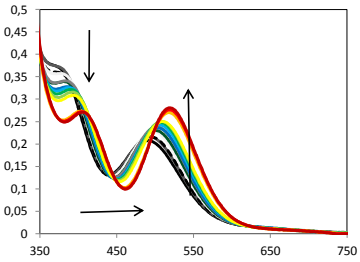
$P_{66614}Br$ D = 258 at 1M HCl
D drops below 0.32 above 5.5 M HCl



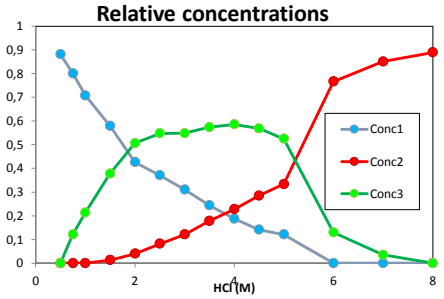
L. Svecova, N. Papaiconomou, I. Billard, Dalton Trans. 45(2016)15162

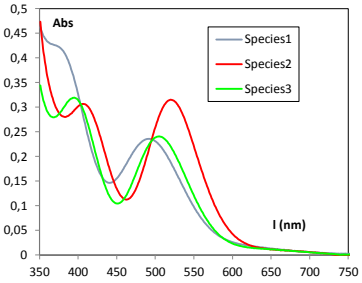
Aqueous Rh(III) speciation is one of the lever arms of extraction



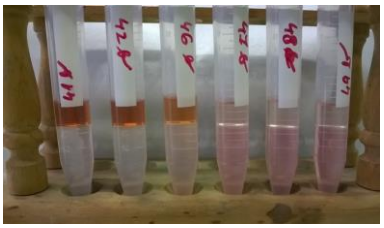


PCA-MCR-LS analysis of 14 UV-vis spectra

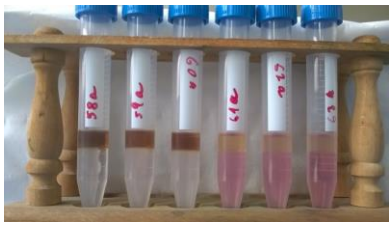




Metal speciation in IL phase is also a way to tune extraction



Cl-based IL



Br-based IL

$2\ P_{66614}^{+} + [RhCl_5(H_2O)]^{2-} \rightleftharpoons \overline{[P_{66614}]_2[RhCl_5(H_2O)]}$

$3\ P_{66614}^{+} + [RhCl_6]^{3-} \rightleftharpoons \overline{[P_{66614}]_3[RhCl_6]}$

$2\ P_{66614}^{+} + [RhCl_5(H_2O)]^{2-} + 6\ \overline{Br^-} \rightleftharpoons \overline{[P_{66614}]_2[RhBr_6]^-} + 5\ \overline{Cl^-} + H_2O$

Exact stoichiometry of the Rh species in IL phase is still unknown

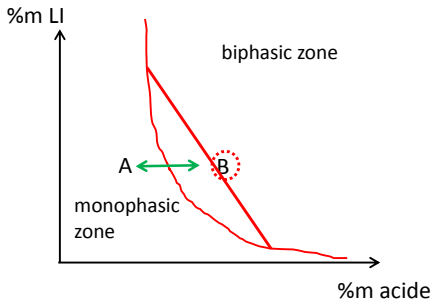
Envisioned application : recovery of PGM from automotive catalysts (Pt, Pd, Rh + Ir)
See : Chem. Sel. 1(2016)3892; Dalton Trans, 44(2015)20131; RSC Advances, 4(2014)48260-48266.

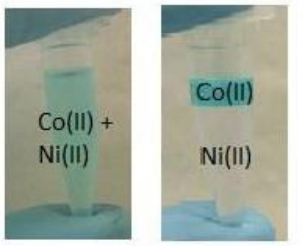
Metal separation with less (IL): Aqueous biphasic acidic systems

Principle of ABS for metal extraction/separation

Aqueous Biphasic Systems : H_2O + salt + IL

H_2O (55wt%) + NaCl (5wt%) + $P_{44414}Cl$ (40w%t), T of change mono/biphasic = 24°C





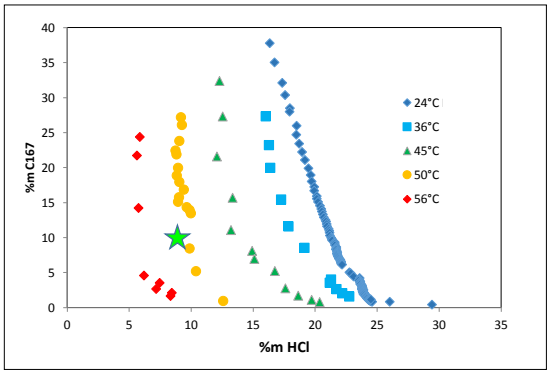
SF from 10 to 500 for NaCl from 5wt% to 11wt%, IL at 40wt%

At fixed T, change in composition flips from mono to biphasic
At fixed composition, change in T flips from mono to biphasic
Metallic ions partition between the two phases
System is easily reversible (especially with T stimulus)

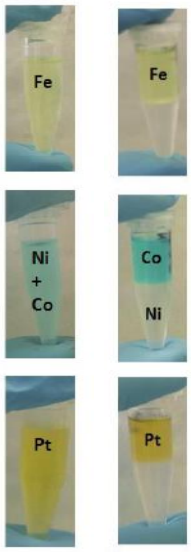
B. Onghena, T. Opsomer, K. Binnemans, Chem. Comm, (2015)15932;
'Ionic-liquid based aqueous biphasic systems : fundamentals and applications''
M. G. Freire, ed., Chapitre 9, pages 183-220, book series Green chemistry and sustainable technology, Springer, 2016

Aqueous Biphasic Acidic Systems (ABAS)

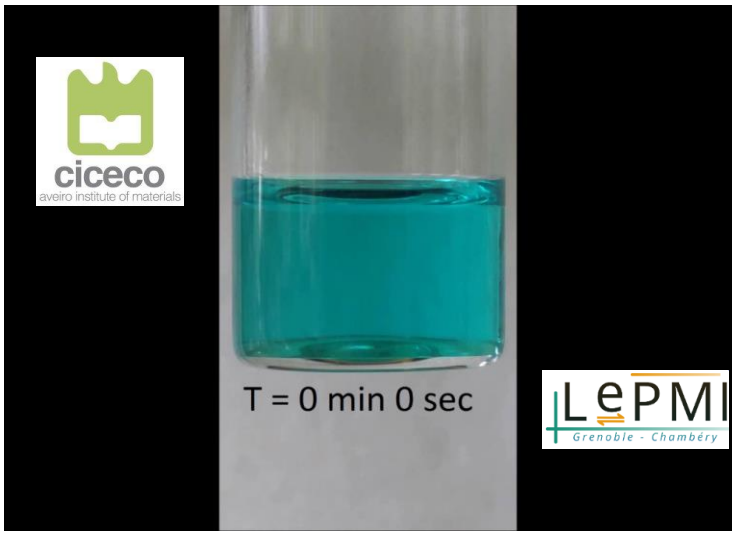
H_2O + **HCl** + $P_{44414}Cl$



T = 24°C



Advantages are :
Handling of metallic ions under very acidic conditions
State change at high water content:
10wt% HCl; 10 wt% IL corresponds to 80 wt% H_2O



FR-16-60999, N. Papaiconomou, M. Gras , J. Countinho, I. Billard, (14/11/2016)

Conclusion and perspectives

Pure IL phases

Although chemical composition is simple (simpler), tuning of extraction/separation is feasible through metal speciation in both phases

Aqueous biphasic acidic systems

They extend the use to samples for which acid is mandatory, (e.g. acidic sludges from steel pickling, ore management etc.)

ILs can do a lot but they do not brew coffee

A mix of classical hydrometallurgical means and IL-based process is probably the best way.

People

Joao Coutinho

Lenka Svecova

Helena Passos

Vijetha Mogilireddy

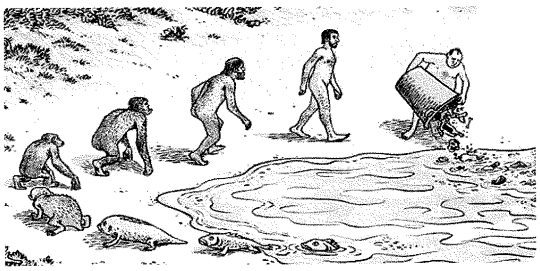
Fundings of the BATER-ARES project

Projet details:
European funding ERAMIN-I
French management by ADEME
Portuguese management by FCT

Partners :
LEPMI, CICECO, GSCOP, Recupyl

Scientific objectives
Recycling of all metals in NiMH batteries by use of ILs and ABS

Budget and duration
533 + 74 k€
36 months
Starting date 21rst April 2016



Thank you for your attention !