Overview: industrial application of ionic liquids for liquid extraction

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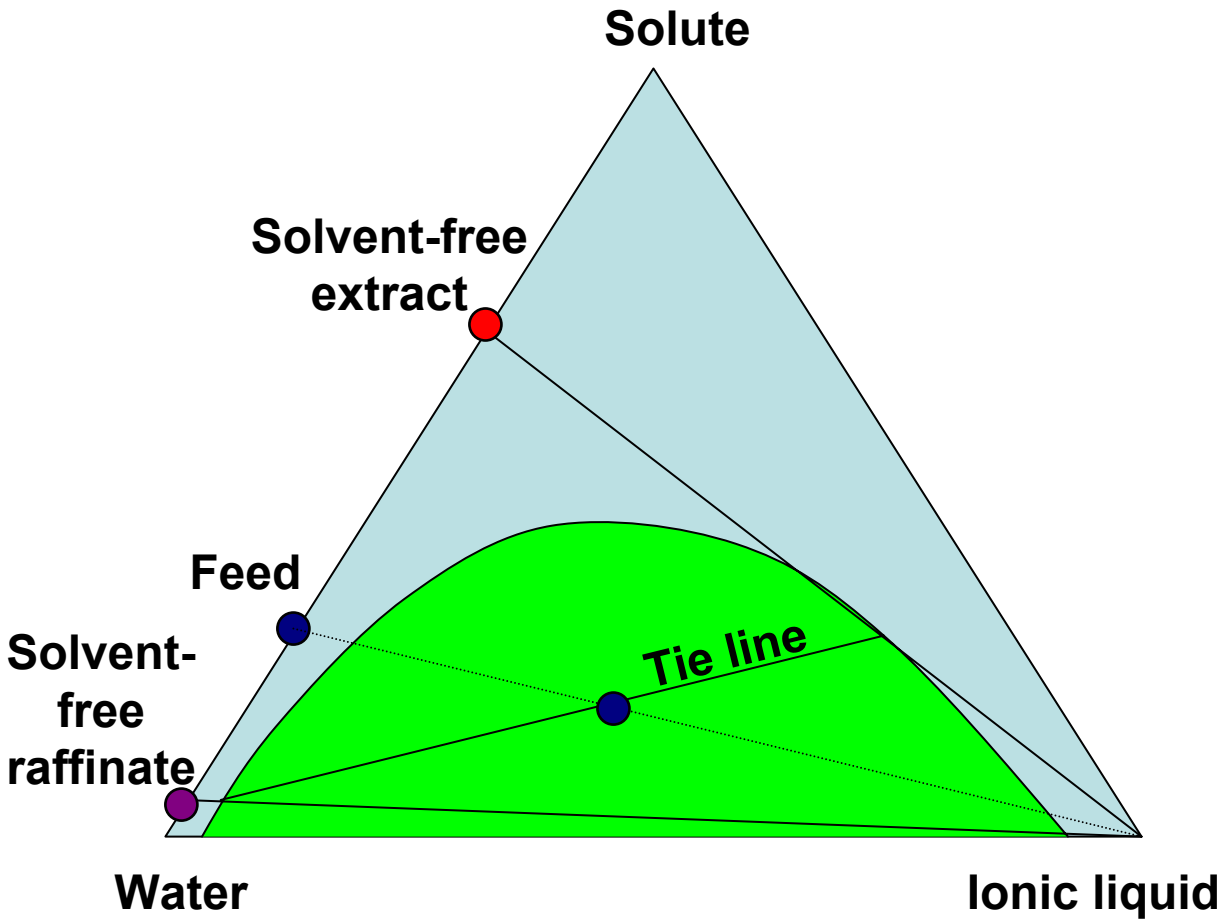
Solvent selection criteria for extraction according to Treybal (1963)

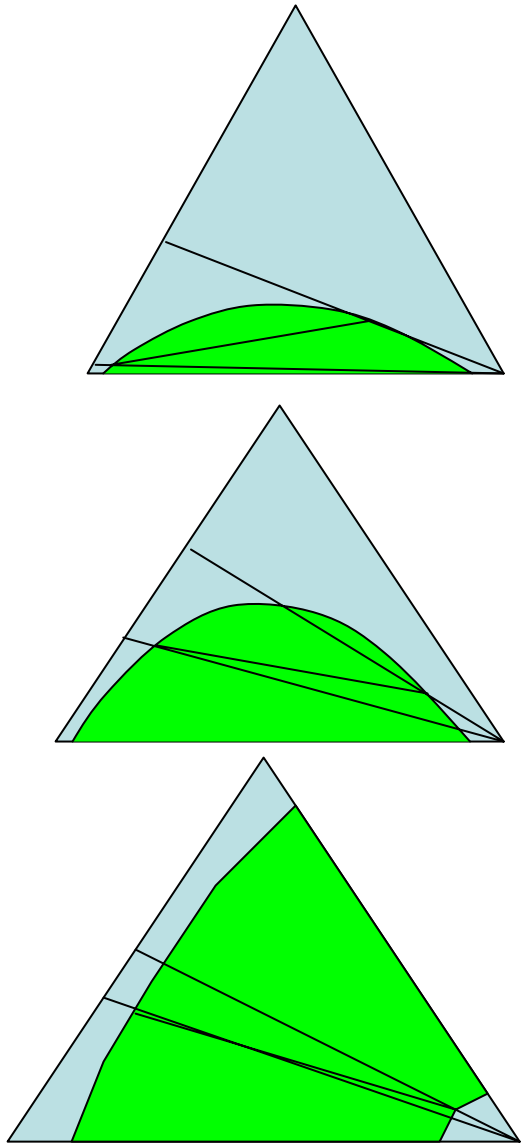
1. Selectivity
2. Distribution coefficients
3. Solvent loading
4. Toxicity
5. Corrosiveness
6. Cost and availability
7. Reactivity

   Thermal stability
8. Viscosity
9. Interfacial tension
10. Density Difference
11. Liquid range
12. Miscibility
13. Solvent recovery
14. Vapor pressure
15. Flammability
16. Intellectual property

1. Selectivity

This is the first property typically examined for extraction.





2. Distribution coefficients

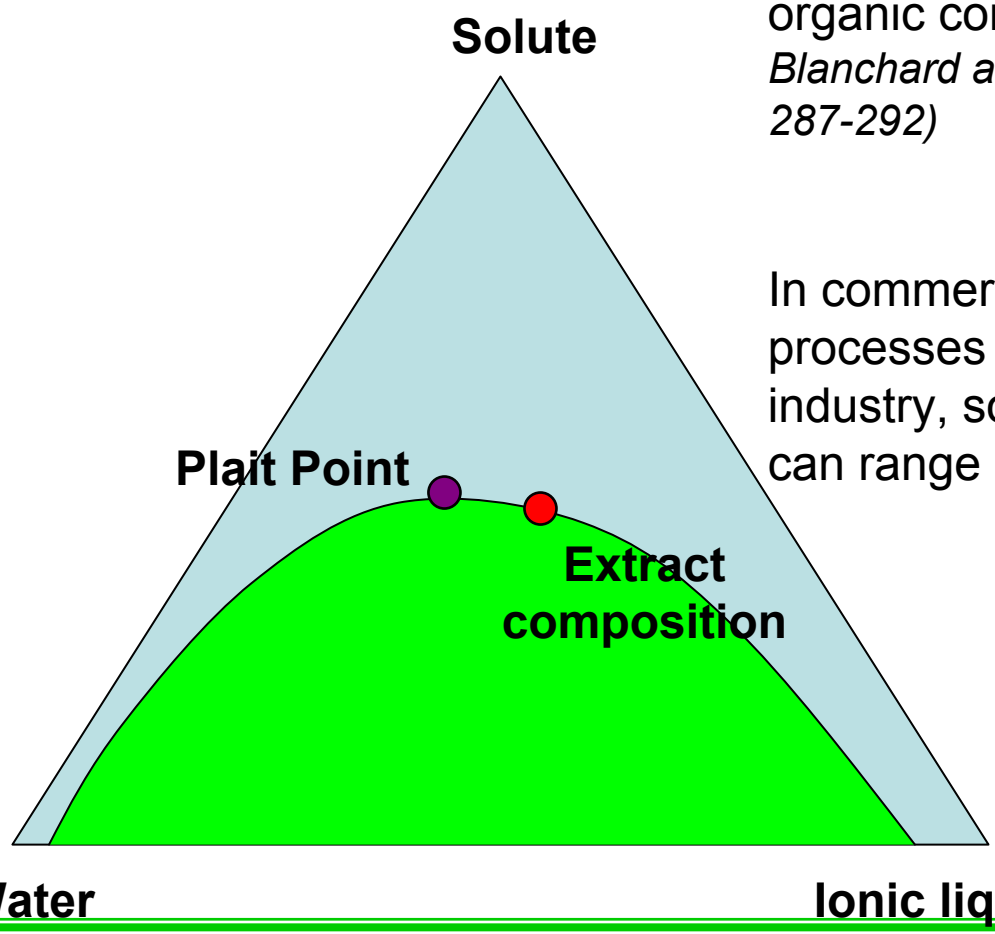
Partition coefficient data for substituted benzene derivatives between water and [BMIM][PF_6]. *(Chem. Commun., 1998, 1765-1766).*

Partition coefficient data for strontium nitrate by crown ethers with IL *(J. Chem. Soc., Dalton Trans., 1999, 1201-1202)*

Task-specific ionic liquids for metal ion extraction from aqueous solutions *(Chem. Commun., 2001, 135-136)*

pH dependent partitioning of thymol blue *(Green Chemistry, Feb 2000 1-4)*

3. Solvent loading



Solubilities of a systematic group of organic compounds in [BMIM][PF_6] - *Blanchard and Brennecke (I&ECR 2001, 40 287-292)*

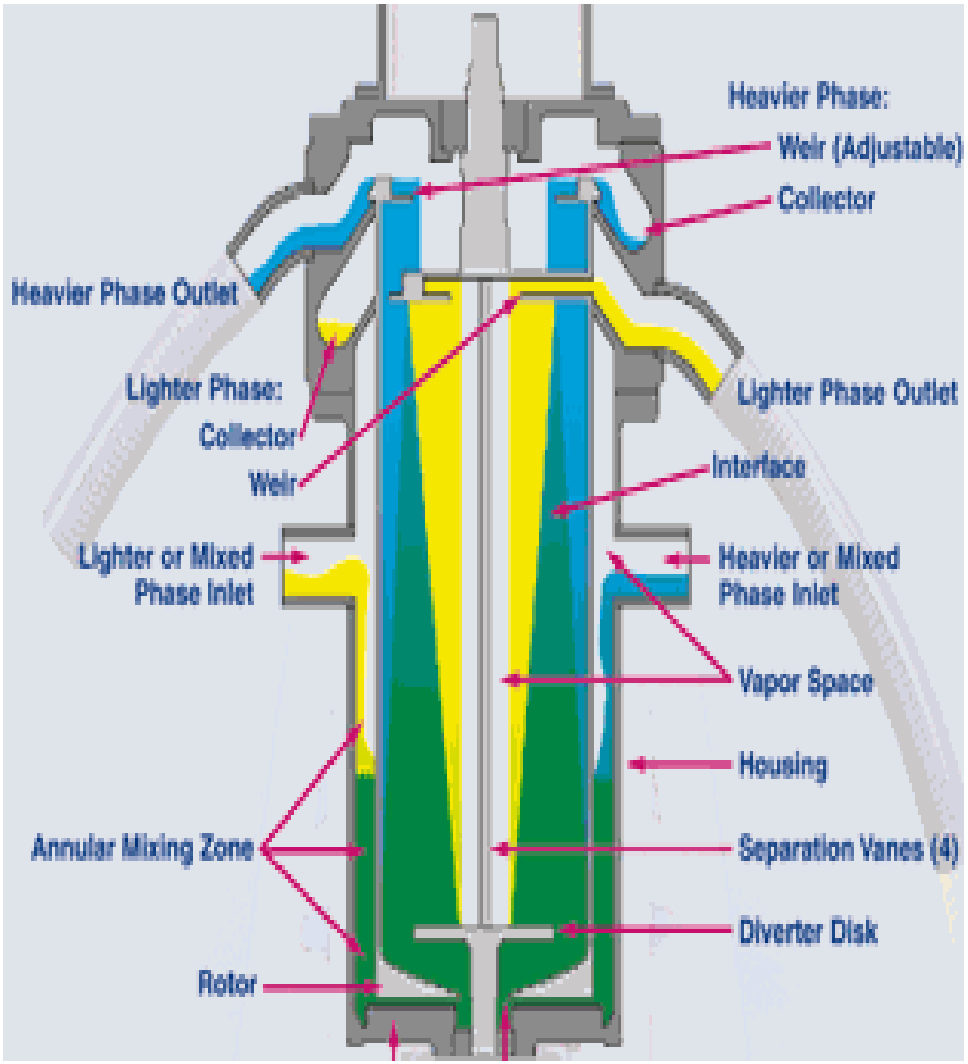
In commercial liquid extraction processes typical in the petrochemical industry, solvent loadings in the extract can range up to 50 wt%.

5 and 6. Corrosiveness and costs

Corrosion coupons need to be used with new ionic fluids as a function of temperature.

The IL should not be more corrosive than the solute or the carrier fluid.

The costs of IL can be reduced by using centrifugal extraction equipment.



7. Reactivity of ionic liquids

Reaction with water

For certain conditions with PF_6 ILs, hydrolysis can result in the presence of water of PF_6 to HF and other species *(Green Chemistry, 2001, 3, 156-164)*

"small amount of water impurity has a dramatic effect on the phase behavior of the IL [and CO_2]" *(I&ECR 2001 40, 287-292)*

Reaction with air

Air stability is not essential but is very advantageous.

Thermal degradation

Table of thermal stability and the impact of water concentration *(Green Chemistry, 2001, 3, 156-164)*

Halide ions reduced thermal stability.

8. Viscosity

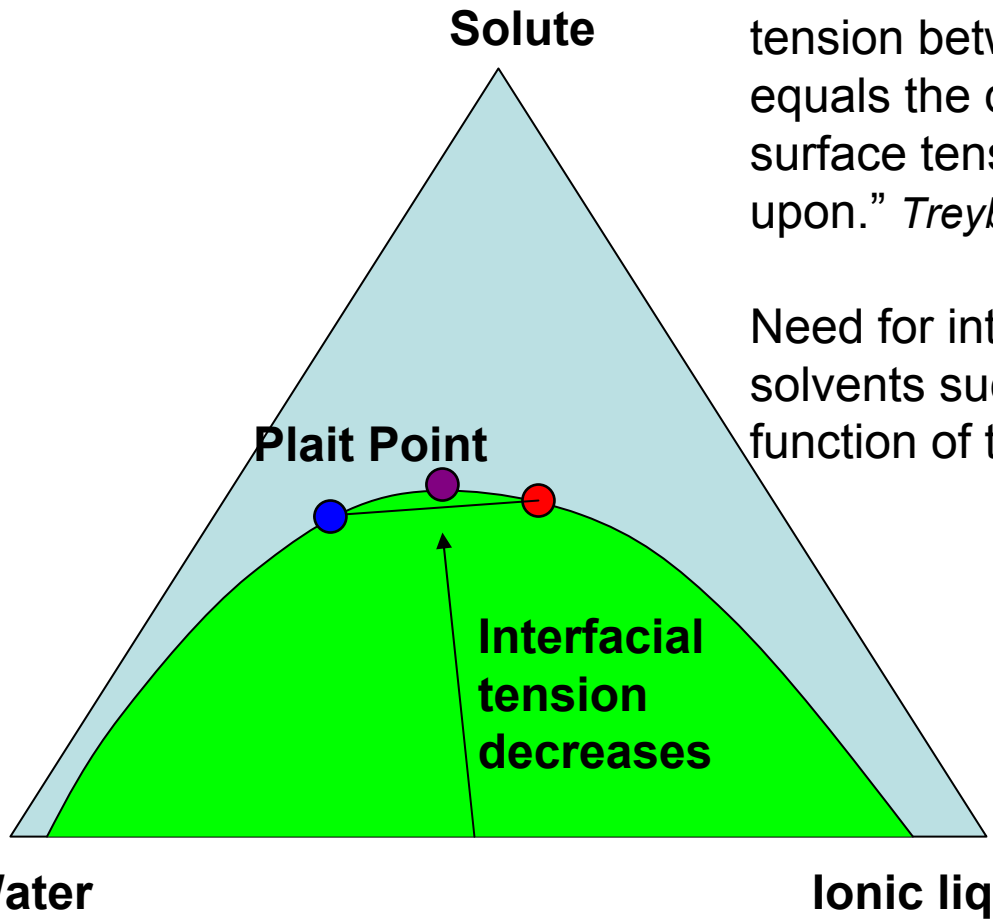
Viscosity at 20 - 25C ranged between 66 - 1110 cP for a variety of ionic liquids *(Green Chemistry 2001, 3, 156-164)*

"In our results, the viscosities in this type of RTILs are two or more orders of magnitude greater than that found for most traditional organic liquids (solvents)…" *(Green Chemistry 2001, 3, 156-164)*

IL impurities (water, NaCl, organic solvents) can have a significant impact on the IL viscosity.

Viscosity impacts dispersed phase selection, equipment selection, and the mass transfer coefficient

9. Interfacial tension



"The well-known Antonoff rule, that interfacial tension between two saturated liquid phases equals the difference between their separated surface tensions with air, cannot be relied upon." *Treybal, p. 132*

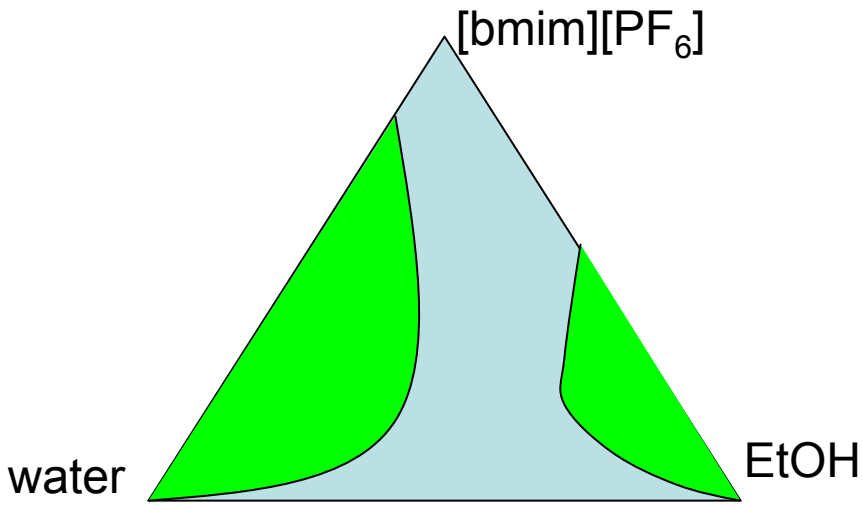
Need for interfacial tension data with key solvents such as water and hexane as a function of temperature.

12. Miscibility

With the exception of benzene and chlorobenzene, other substituted benzene compounds were miscible with [bmim][PF_6] while substituted hexane compounds were typically immiscible. *(I&ECR 2001, 40 287-292)*

The solvent strength of [bmim][PF_6] is in the region of methanol or ethanol. *(I&ECR 2001, 40 287-292)*

[bmim][PF_6] is immiscible with both water and ethanol at 25C *(Chem. Commun., 2001, 2070-2071)*



13. Solvent recovery

Recovery of organics from [bmim][PF_6] with $SCCO_2$ was demonstrated *(I&ECR, 2001, 40, 287-292)*

Extraction of the solute from the ionic liquid

Distillation/stripping of the solute from the ionic liquid (thermal stability of the ionic liquid is required for the reboiler)

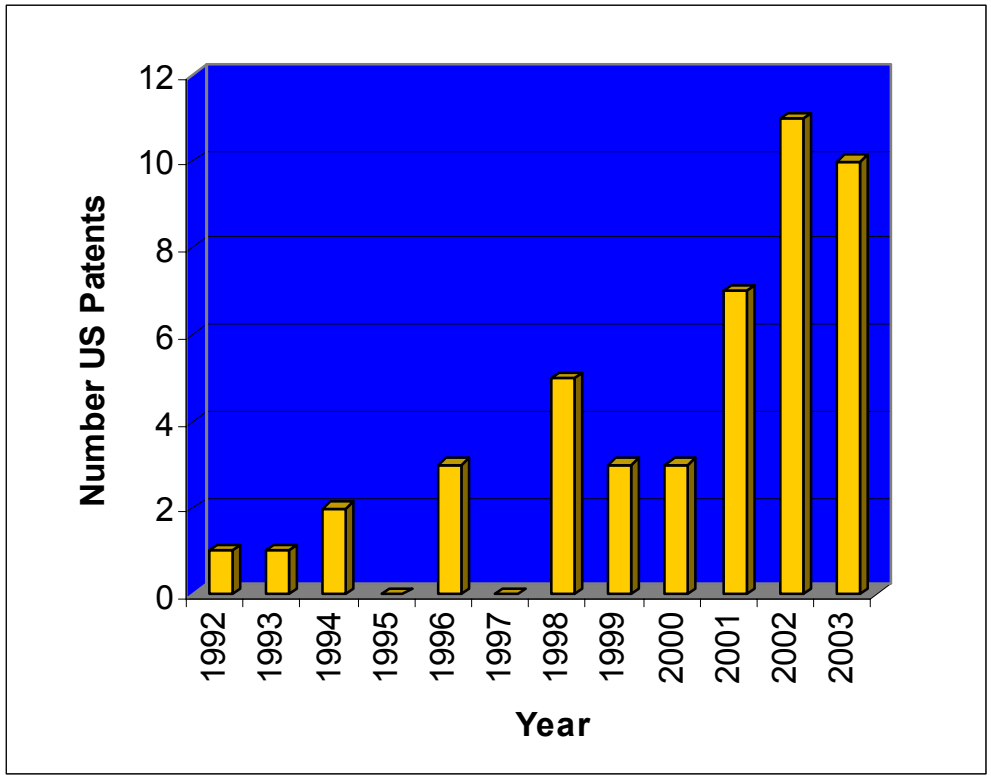
16. Intellectual property

Patents focus on:

- IL compositions
- Processes

Assignee companies:

- Exxon
- Chevron
- BP
- Celanese
- Akzo Nobel



USPTO search for “ionic liquid” in the claims

2003 data are through 9/1

Demonstrated biphasic reactions with ionic liquids

Butene oligomerization

Hydrodimerization of dienes

Alkylation of olefins

Hydrogenation (of cyclohexene, and chiral)

Hydroformylation (of 1-hexene and 1-octene)

Oxidation (epoxidation of 2,2 dimethyl chromene)

Alkoxycarbonylation (of styrene)

Hydrodimerizations/ Telomerizations (of 1,3 butadiene)

Beneficial characteristics:

No vapor pressure

Reasonable thermal stability

Good solubility for organic and organometallic compounds

Gas solubility (CO, O_2, H_2) is good

Can be immiscible with alkanes

Lipophilic RTIL can be used with aqueous biphasic systems

Hydroformylation: Potential application of RTIL

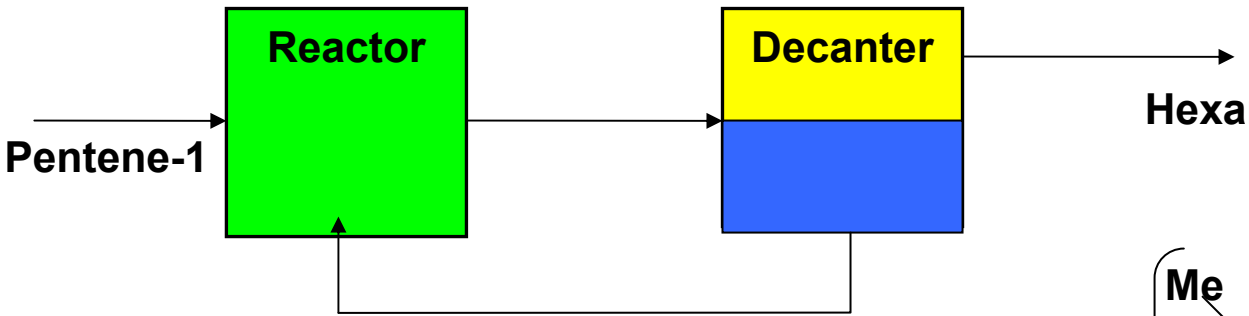
Hydroformylation is used for the production of OXO alcohols, > 2.6 billion #/yr US demand in 1998

Ruhrchemie's aqueous biphasic system

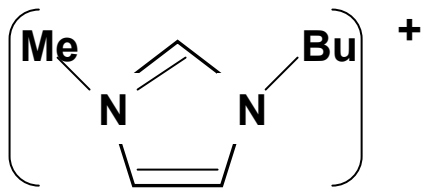
Water soluble rhodium catalyst

Decantation for catalyst/ product separation

Chauvin and coworkers at the Institut Francias du Petrolecatal



Rhodium catalyst with $[bmim]^+PF_6^-$



[bmim]+

Conclusions

1. Data are still needed for engineers to make good solvent selection courses.
2. The combination of reaction and extraction is heavily applied industrially with organic solvents, and IL show promise in this area.
3. Pilot-plant scale demonstration data are needed in the literature that address practical problems with IL
4. IL cleanup after extraction is a key area of need for further work