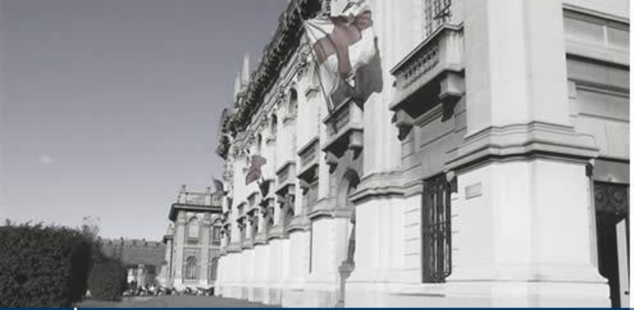


School of Industrial and Information Engineering

Course 096125 (095857)

Introduction to Green and Sustainable Chemistry

POLITECNICO DI MILANO

Ionic Liquids and Polymeric Solvents.

Prof. Attilio Citterio
Dipartimento CMIC “Giulio Natta”
https://iscamapweb.chem.polimi.it/citterio/it/education/course-topics/

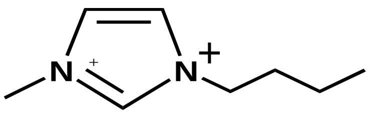
Ionic Liquids (LI) – Room-Temperature Ionic Liquids (RTIL).

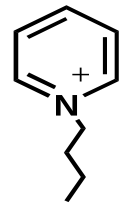
<u>Charged substance </u>mixtures <u>that form a liquid </u>at ambient temperatures.

- \+ Unusual solvent properties (for a wide range of organic, inorganic and polymeric compounds)
- \+ Typically consist of bulky, poorly coordinating ions
- \+ Negligible vapor pressure – attractive alternative to VOCs
- \+ Most Ionic Liquids are thermally stable at temp. > 200 ºC
- \+ Wide liquid phase range (300°C)
- \+ Very solvating, but weakly coordinating
- \+ Immiscible with many organic solvents
- \- Moderate to high viscosity
- \- Frequently expensive, easy of separation uncertain
- \- Some react with water and nucleophiles
- \- Not necessarily innocuous.

Ionic Liquids – Structure.

imidazolium **pyridinium** **ammonium** **fosfonium**





$Ph\text{-}N^{+}(CH_3)_3$ $R\text{-}P^{+}(R')_3$

Cations

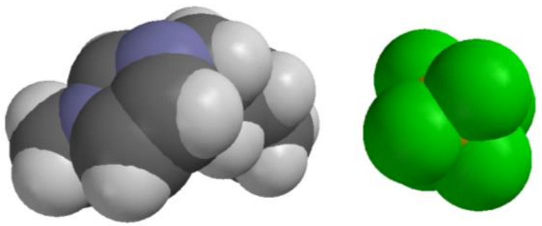
tetrafluoroborate **hexafluorophosphate** **heptachloroalluminate** **nonaflate**

BF_4^- PF_6^- $Al_2Cl_7^-$ $(CF_3SO_2)_2N^-$

Anions

Principle is to use large, not-symmetrical ions

– Lower lattice energy



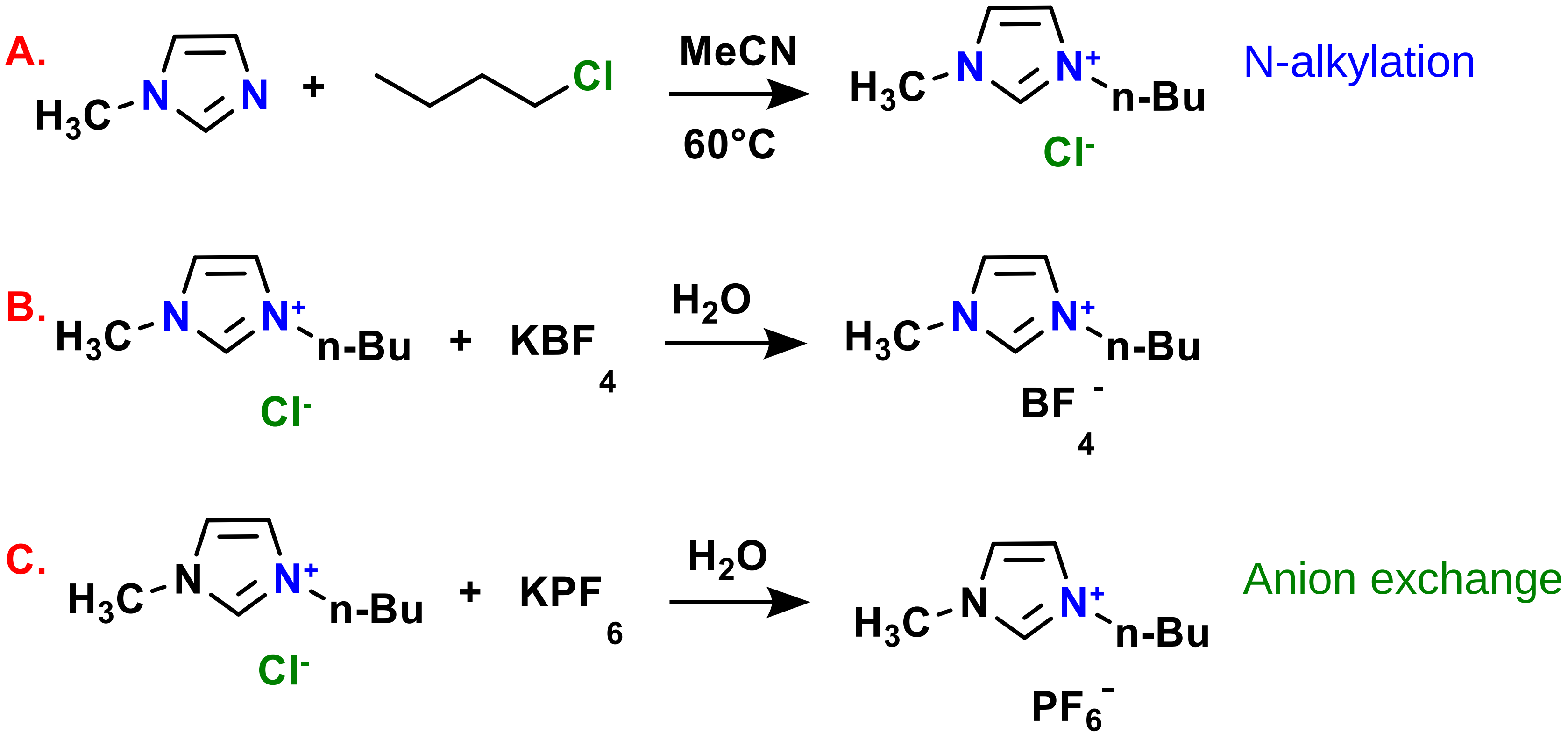
$BMIM^+$ PF_6^-

General Properties of Ionic Liquids.

- Choice of cation and anion determine physical properties (i.e. melting point, density, water solubility, …);
- Cations are typically big, bulky and asymmetric accounting for the low melting points;
- The anion contributes more to the overall characteristics of the LI and determines the air and water stability;
- Melting points can be easily changed by structural variation of one of the ions or combining different ions;
- LI have low or negligible vapor pressure at 20-150°C;
- Designer solvents: changing anion, the ionic liquid can adapt to specific applications.

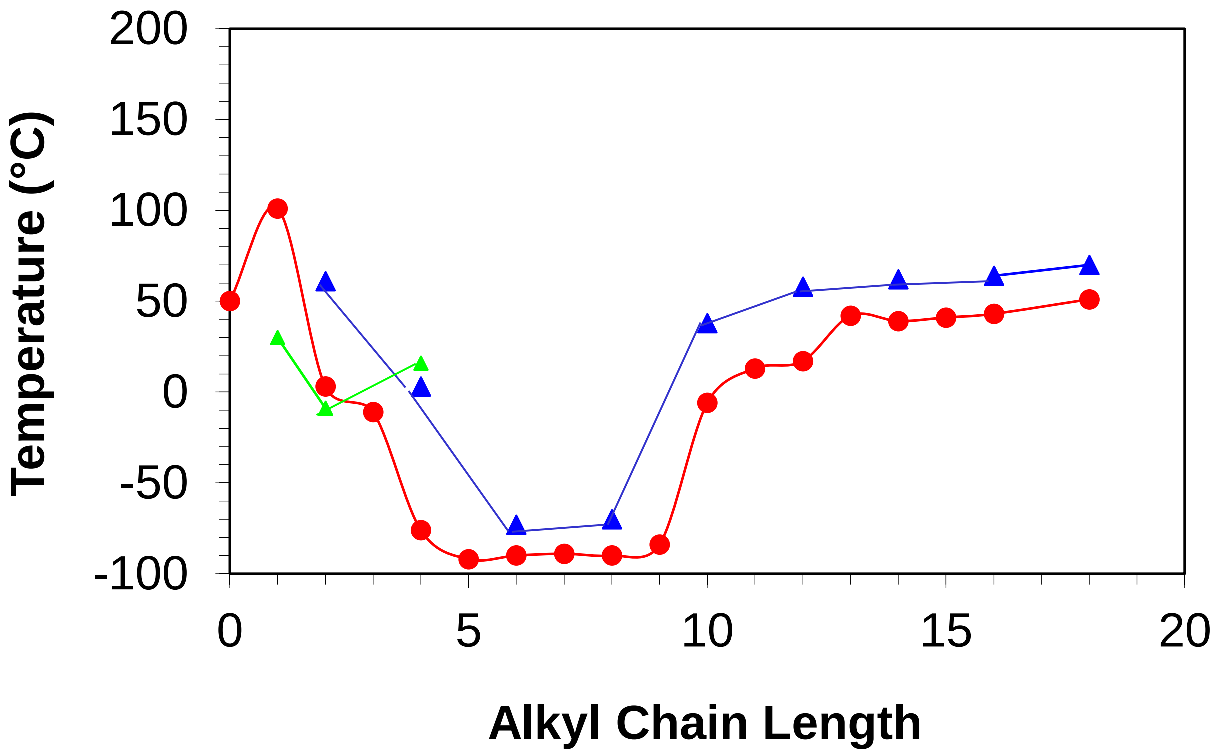
Rogers R.D. ***Chem. Comm.*** **1998. 1765-1766.**

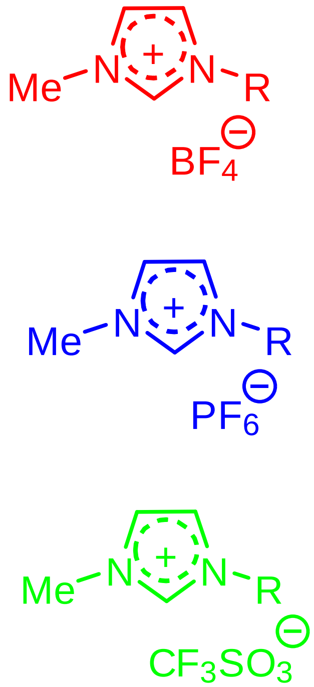
Synthesis of Ionic Liquids.



Huddlestone G.J., Rogers R.D., ***Green Chemistry 2001, 3, 156-164.***

Effect of Alkyl Chain Length on the Melting Point of Liquid Salts [RMIM][X].





Holbrey J:D:, Seddon, K.R. *J. Chem. Dalton Trans* **1998**,

Thermal Properties of Imidazolium Ionic Liquids.

- **Most LI salts are liquid at sub-ambient temperatures.**
- **Are glass at low temperatures and show minimal vapour pressures until to thermal decomposition temperature (> 400°C), but some IL can be distilled at very low pressure.**
- **Thermal decomposition is endothermic with inorganic anions and exothermic with organic anions**
- **Imidazolium cations are thermally more stable than tetraalkyl ammonium cations; the same is true for tetraalkyl phosphonium cations.**
- **Phosphonium cations are thermally more stable than the corresponding ammonium cations.**

Ngo H.L. *Thermochimica Acta.* 2000, 357-358, 97-102.

Using Molecular Simulations.

- **Detailed Geometric and Energetic model**
- **Adjustment of Force Field -**
  Inter and Intermolecular Potential Functions

$$V_{total} = 1/2 \sum_{ij} \left[4\sigma_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right\} + \frac{q_i q_j}{r_{ij}} \right] + v(\phi)$$

I

$$v(\phi) = v_3 + \frac{v_1}{2}\left(1+\cos(\phi)\right) + \frac{v_2}{2}\left(1-\cos(2\phi)\right) + \frac{v_3}{2}\left(1+\cos(3\phi)\right)$$

I = Lennard Jones Plot (includes both dispersive and electrostatic force)

Shah. K.J, Brennecke. F.J, Magnin. E.J., ***Green Chemistry***, 2002, 4, 112-116.

Low Volume Expansivity of IL.

Volume Expansivity (K^{-1})	Ionic Liquid	Toluene (Molecular Solvent)	Water
α_p	$5\text{-}6 \times 10^{-4}$	$8\text{-}11 \times 10^{-4}$	$2.57\text{-}5.84 \times 10^{-4}$

- **IL do not expand on heating as normal liquids**
- **Strong coulomb interactions**
- **IL with long alkyl chains are more compressible**
- **Results were confirmed with the tait equation, i.e.**

$$\frac{\rho - \rho_0}{\rho} = C \ln\left(\frac{B + p}{B + p_0}\right)$$

Which is useful for high pressure correlation.

Brennecke F.J., Gu J., *J. Chem. Eng. Data* **2002,** 47, 339-345.

Estimation of Solution Thermodynamics.

Comparison of Henry's Constant, γ^{∞} water in ionic liquid and conventional solvents.

P_{sat} = 0.031 *bar*, Temperature = 25 °C

Comp.	$[C_8min][BF_4]$	$[bmin][PF_6]$	$[C_8min][PF_6]$	Benzene	CCl_4	Ethanol
H_1	0.033	0.09	0.11	10	37	0.10
γ^{∞}	2.65	6.94	8.62	323	1194	3.23

(IL) Water Solutions.

- **Affinity for water is greater for anions such as $[BF_4]^-$ than $[PF_6]^-$**
- **Water affinity decreases with increase in alkyl length**
- **Entropy and Enthalpy are similar like dissolution of water in short chain alcohols**
- **Mutual solubility's increase with increase in temperature**
- **Contamination of water creates a waste water problem - activated carbon may be the answer.**

Anthony J.L., Magnin J.E., Brennecke F.J. *J.Phys.Chem. B*. **2001**,*105*,10942-10949.

Effect of Gas Solubility.

From solubility tests of nine different gases in [bmim][PF_6] was concluded:

- **Carbon Dioxide: highest solubility followed by ethylene and ethane**
- **Argon and Oxygen showed very low solubility**
- **Solubility decreases with increase in temperature**
- **Enthalpy and Entropy changes also indicate strong molecular interactions for carbon dioxide.**

Comparison of Henry's Constants (Bar)

	[Bmim][PF_6]	Heptane	Benzene	Ethanol	Acetone
H_2O	0.17	-	10[33]	0.1[34]	0.3[34]
CO_2	53.4	84.3	104.1	159.2	54.7
C_2H_4	173	44.2	82.2	166	92.9
C_2H_6	355	31.7	68.1	148.2	105.2
CH_4	1690	293.4	487.8	791.6	552.2

Magnin J.E., Anthony J.L., Brennecke J.F. *J. Phy. Chem. B*. **2002**, *106*,7315-7320.

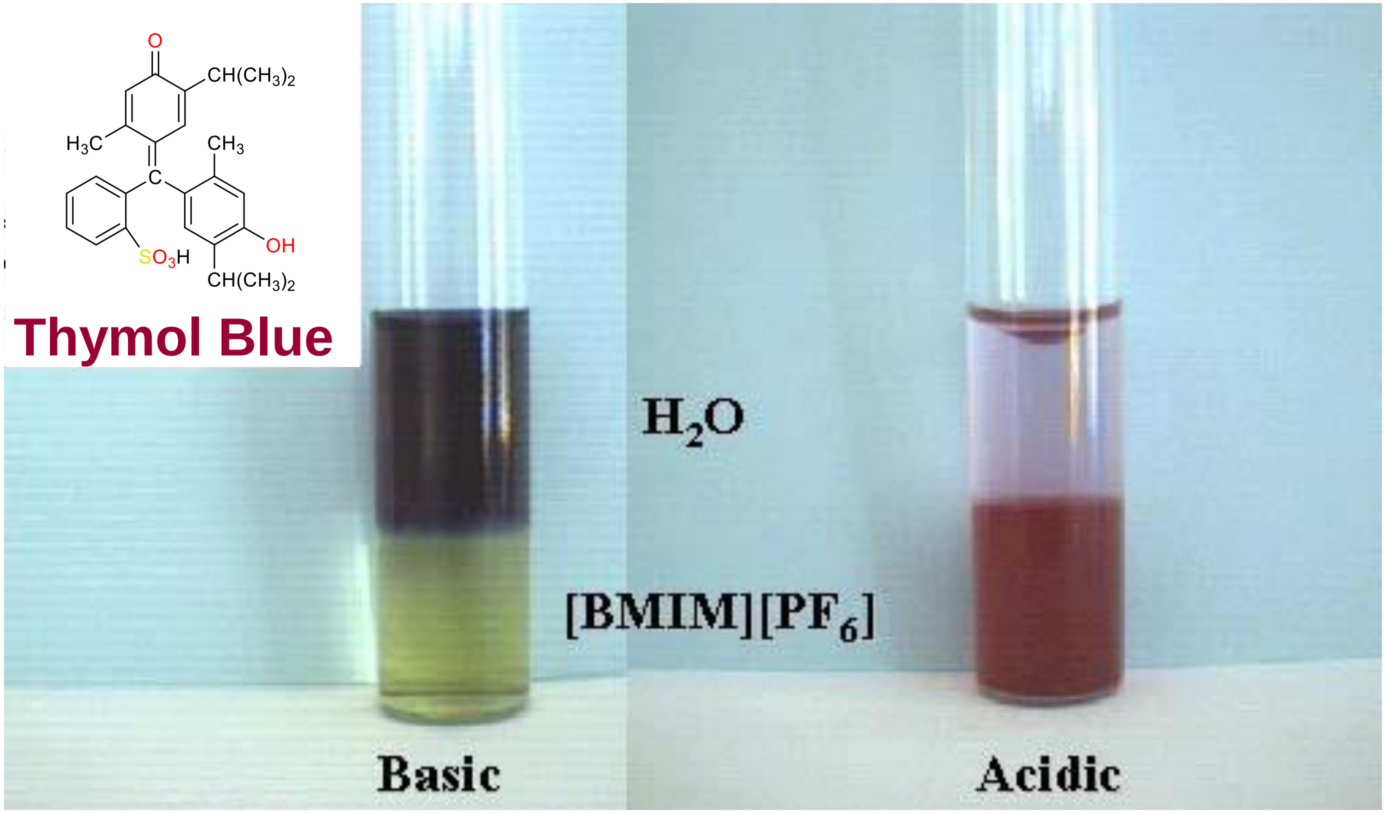
Polarity.

- Important property to determine its solvent strength:
- Betaine dye was used with the help of Fluorescent tubes (E_T).

Component		E_T (30)	Cost (€/kg)
[Bmim][PF_6]		52.39	260
[C_8mim][PF_6]		46.84	300
[BuPy][BF_4]		44.91	180
Acetonitrile		45.30	10
Methanol		55	0.8

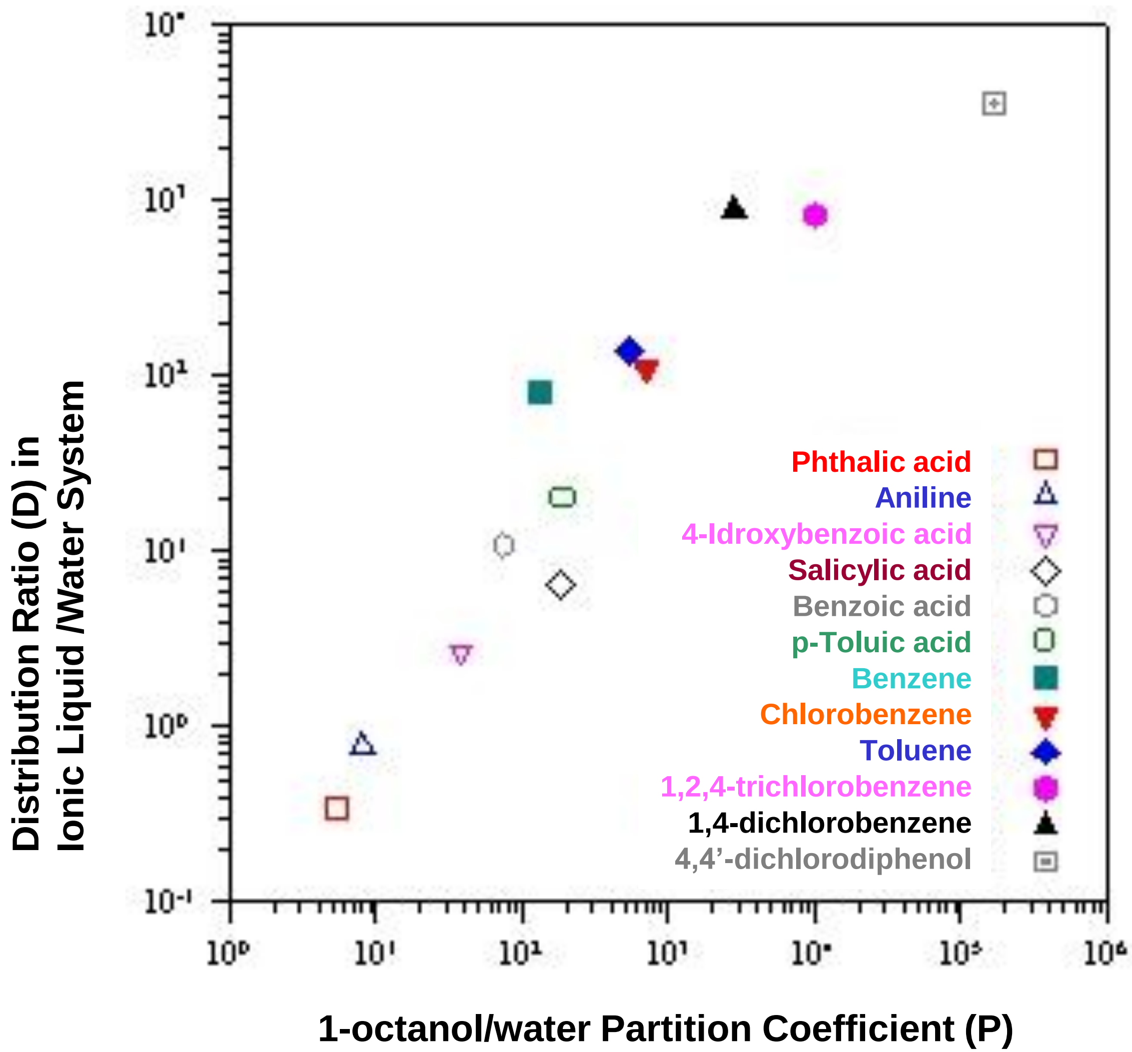
Samanta A., Brennecke F.J. *Chem. Comm.* **2001**, 413-414.

Acid and Base Solutions.



Reversible partitioning of Thymol Blue between water and IL.

Correlation Between Partitioning in IL/Water and 1-Octanol/water Biphasic Systems.



Ionic Liquids – Uses.

- Chemical Processing (solvents for catalysis)
- Pharmaceuticals
- Petroleum Refining (i.e. desulfurisation)
- Microelectronics
- Metal deposition (e.g. Aluminum)
- Organic Polymer Processing
- Pulp and Paper
- Nuclear Fuels
- Textiles
- Lubricants
- Anti-static agents
- Agents for the elimination of trace components.

Recent Applications of Ionic Liquids.

E. Beckman	sc CO_2 Stripping after extraction
P. Bonhote	Conductive IL
R. Carlin	Ionic Liquid - polymer gel electrolytes
J. Dupont	Catalytic hydrogenation Reactions
C. Hussey	Electrochemistry in IL
H. Oliver	Butene dimerization
B. Osteryoung	Benzene polymerization
R.D. Rogers	Two-phase separations
K. Seddon	Friedel-Crafts reactions; regioselective alkylat.
T. Welton	Organometallic syntheses.

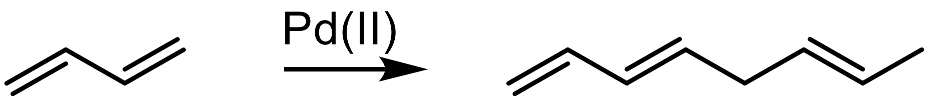
P. Wasserscheid, T. Welton *Ionic Liquid in Synthesis*, Wiley Ed. 2008

Industrial Processes with Ionic Liquids.

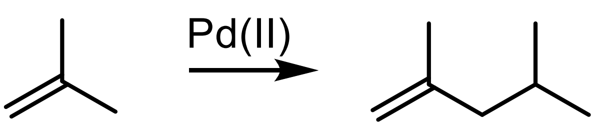
Company	Process	IL function	Scale
BASF	Acid Scavenging	Auxiliary	commercial
	Extractive distillation	Extractant	pilot
	Chlorination	Solvent	pilot
IFP	Olefin Dimerization	Solvent	commercial
Degussa	Hydrosilylation	Solvent	pilot
	Compatibilizer	Perform. additive	commercial
Arkema	Fluorination	Solvent	pilot
Chevron Philips	Olefin Oligomeriz.	Catalyst	pilot
Eastman	Rearrangement	Catalyst	commercial
Eli Lilly	Cleavage of Ether	Catalyst/Reagent	pilot
Air Products	Storage of gases	Liquid Support	commercial
Iolitec/Wandres	Cleaning Fluid	Perform. additive	commercial

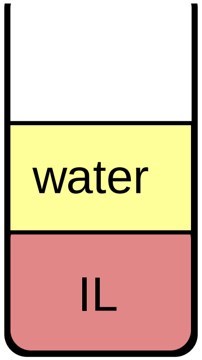
Examples of Reactions in IL.

Pd(II) Compounds in [bmim][BF_4] catalyze butadiene and butene hydrodimerization.



Dupont J. Et al. *Organometallics* **1998**, *17*, 815

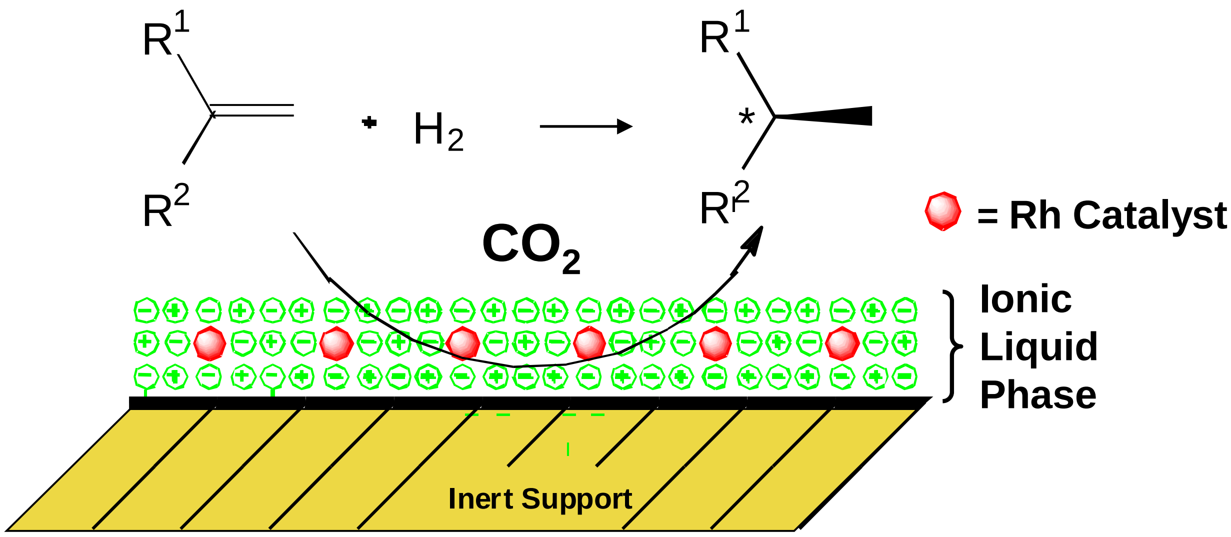




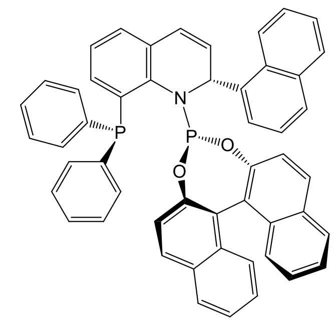
Product insoluble in Ionic Liquid

97% catalyst retained in IL phase

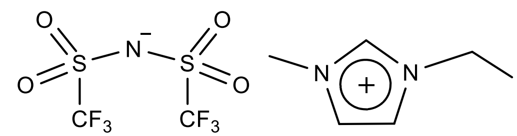
Asymmetric Catalytic Hydrogenation on Solid Support with Ionic Liquid.



Chiral Quinaphos Ligand



Ionic Liquid



Supported Ionic Liquid Phase (SILP)

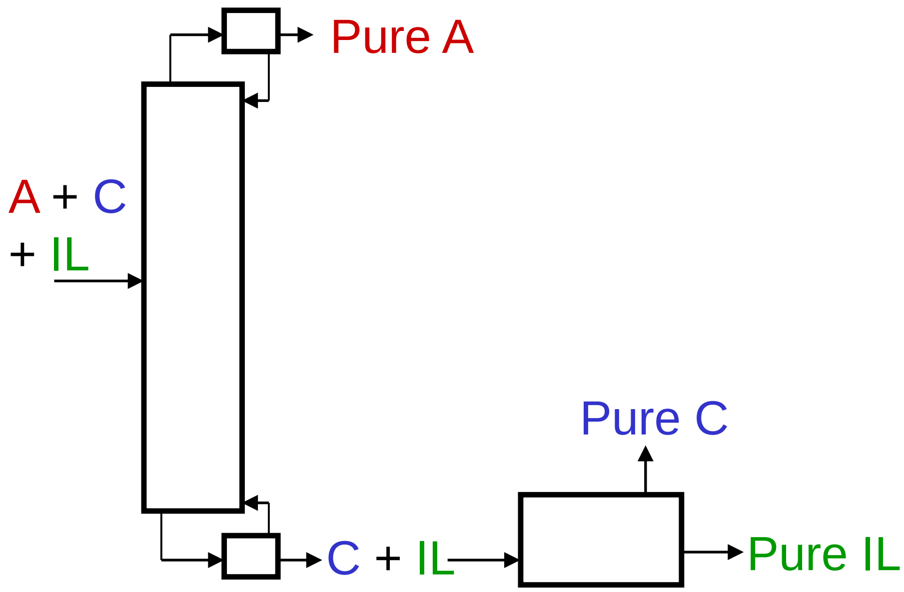
- Silica based support
- Catalyst is soluble in Ionic Liquid
- Ionic Liquid and Catalyst are fixed in the silica pores
- Diffusion pathway is reduced

Catalyst

- Rhodium (Rh) based
- Uses chiral Quinaphos Ligand
- More efficient when applied in continuous flow
- Deactivates with time

Extractive Distillation and Breaking Azeotropes.

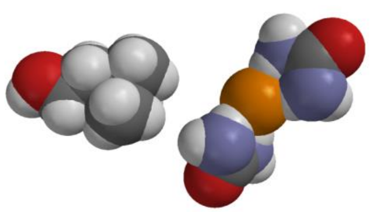
- IL have greater affinity for some components in a mixture.
- Results in a change in the activity coefficients that usually enhances separation.
- No IL in distillate.
- Arlt claims that virtually all azeotropes can be broken by the correct selection of an ionic liquid.



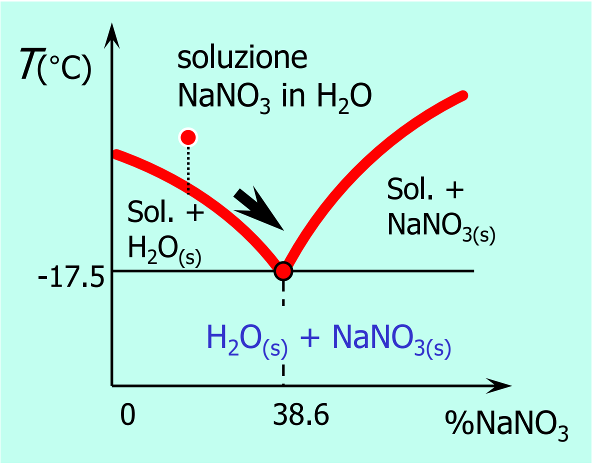
- Gmehling and Krummen, DE10154052
- Arlt et al., DE10136614/WO2002074718

Deep Eutectic Solvents (DES).

- DES is a fluid generally composed of two or three cheap and safe components that are capable of self-association, often through hydrogen bond interactions, to form a eutectic mixture with a melting point lower than that of each individual component. Complex formed between a quaternary ammonium salts and a hydrogen bond donor.
- Example: 2 $H_2NC(=O)NH_2$ / 1 $HOC_2H_4N^+(CH_3)_3$ (choline) or
- Example: $[Me_3NCH_2CH_2OH]\ I^-$ / Glycerol* or urea / ethylene glycol.
- **Versatile,** *economic, environmentally compatible*, **biodegradable.**



mixing 2 solids to make a liquid



*Jhong, H.R. et al. *Electroc. Comm*. **2009**, *11*, 209–211.

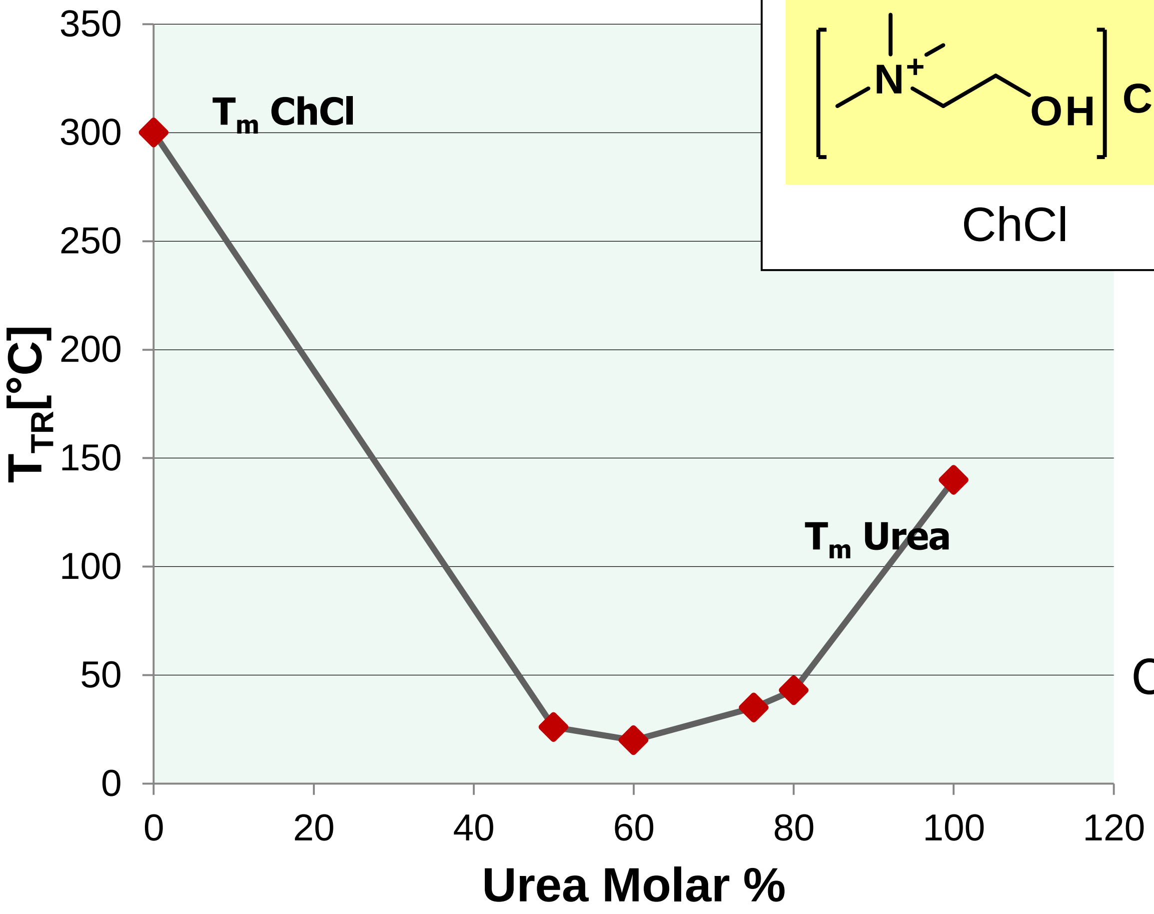
Uses of Deep Eutectic Solvents.

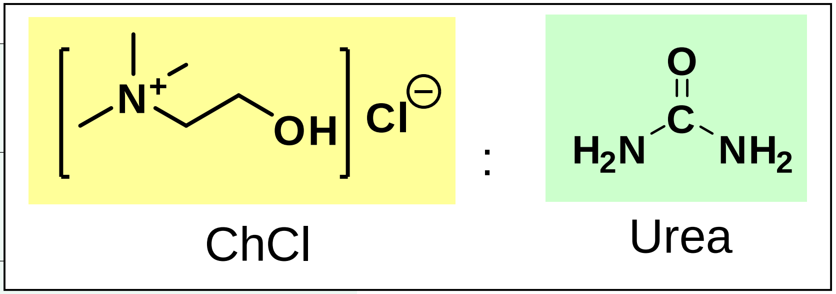
- Metal Deposition, e.g. Cr
- Electropolishing
- Ore reprocessing
- Catalysis

Wide range of solutes show high solubility e.g. metal oxides.

Q. Zhang, K. De Oliveira Vigier, S. Royera, F. Jérôme Deep eutectic solvents: syntheses, properties and applications, ***Chem. Soc. Rev.***, 2012,**41**, 7108-7146
Yan Shen, Xiaoxia He, and Francisco R. Hung, Structural and Dynamical Properties of a Deep Eutectic Solvent Confined Inside a Slit Pore, ***J. Phys. Chem.*** C 2015 119 (43), 24489-24500

Melting Points of Eutectic Liquid ChCl/Urea.

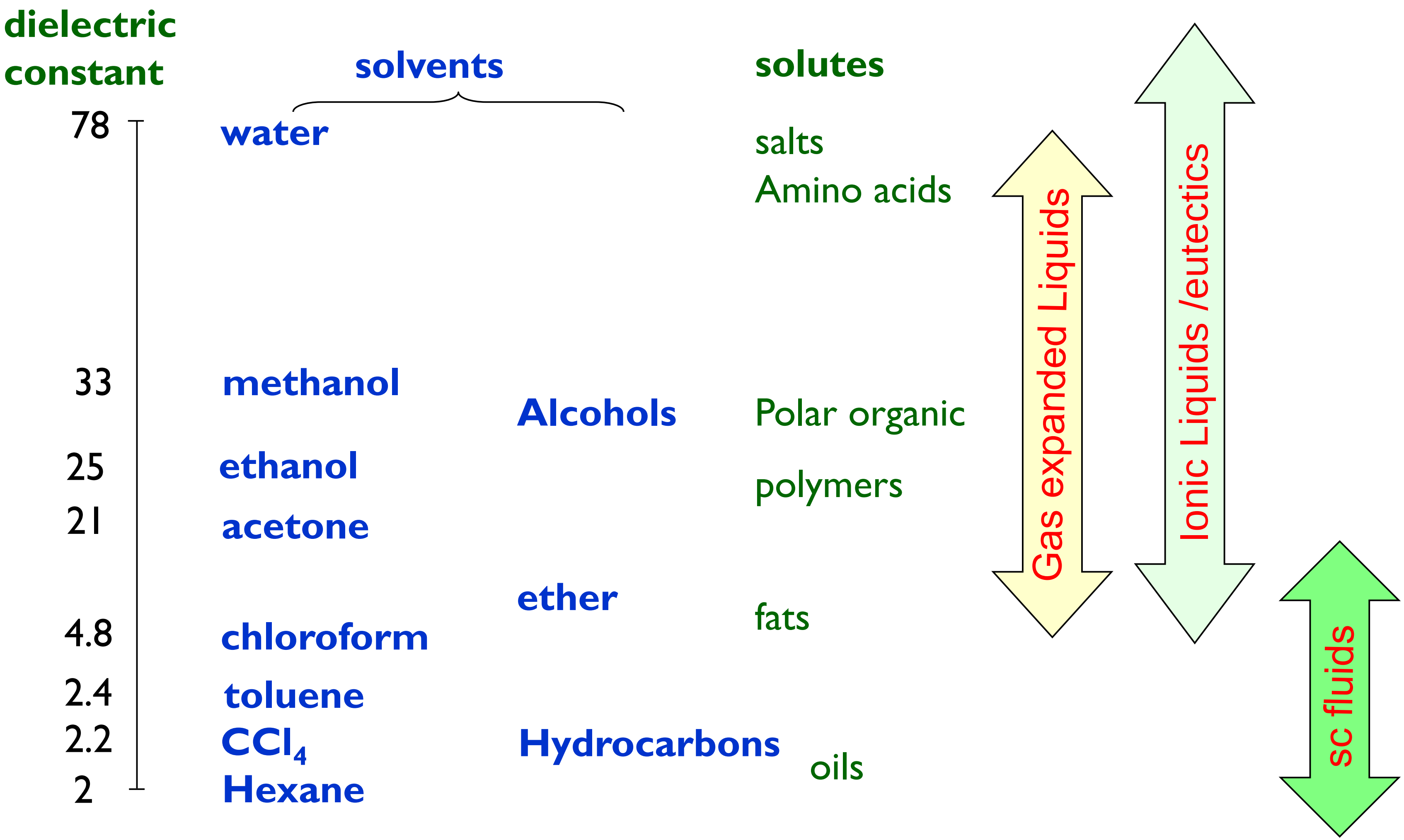




ChCl = Choline chloride

Rengstl D, Fischer V, Kunz W. ***Phys Chem Chem Phys***. 2014 Nov 7;16(41):22815-22

Comparison between Classical Solvents and Neoteric Solvents.



Solvent Formulations.

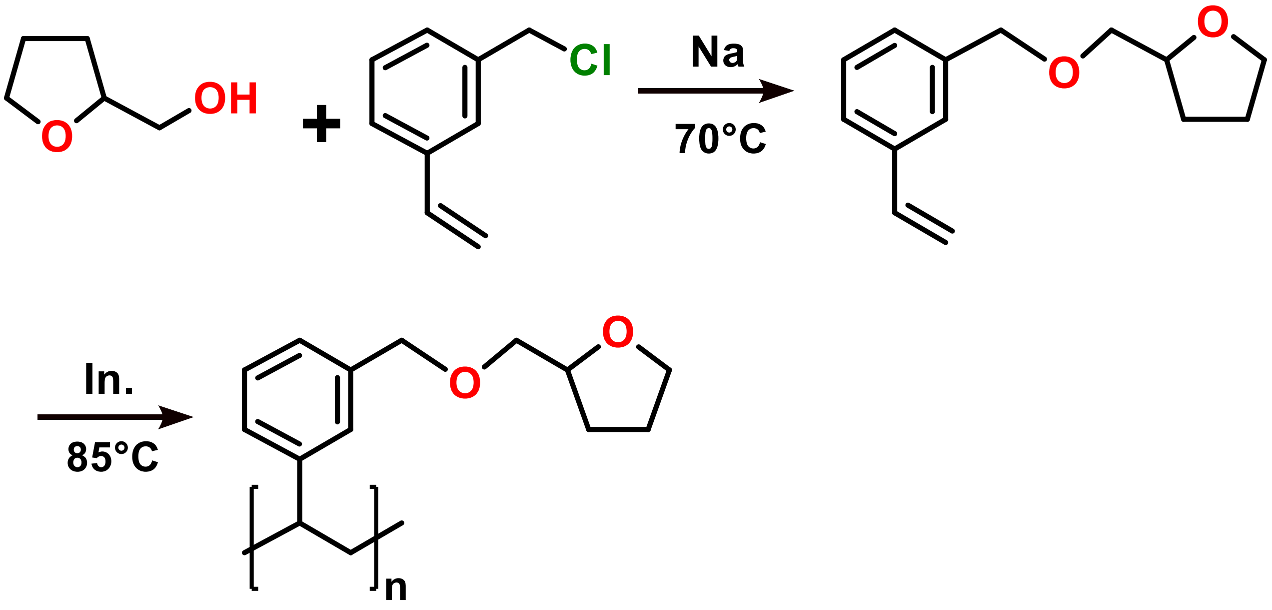
- The most appropriate solvent may contain a variety of components depending on the solute and the application
  - e.g. water, surfactants, alcohols, buffers, oils
- Formulation meets the operative functionality principle.

Polymeric /immobilized or derivatized Solvents.

- Solvents that are oligomeric, polymeric, or that are tethered to polymeric systems:
- Advantages:
  - Low volatility
  - No ozone depleting potential (ODP)
  - No global warming potential (GWP)
  - Possible ease of separation
- Disadvantages:
  - Expensive to manufacture
  - Life cycle impact uncertain
  - Possible separation difficulties

Polymeric – immobilized / derivatized Solvents.

Derivatized/Polymeric Solvent Replacement for THF:



How We can Select a Solvent.

- Solvent alternatives Guide

  clean.rti.org/

- Solvent data base

  solvdb.ncms.org/index.html

- Expert systems available on web

  www.epa.gov/greenchemistry/tools.htm

- Environmental fate data base

  esc.syrres.com/efdb.htm