

Precursor Methods

Goals – decrease diffusion paths, shorten reaction times and temperatures

Intimate mixing of components in solution, precipitation, filtration, washing, drying, calcination

- * **High degree of homogenization**
- * **Large contact area**
- * **Reduction of diffusion distances**
- * **Faster reaction rates**
- * **Lower reaction temperatures**
- * **Metastable phases, smaller grain size, larger surface area**

Coprecipitation Method

Coprecipitation applicable to nitrates, acetates, oxalates, hydroxides, alkoxides, beta-diketonates

Requires: **similar salt solubilities**
 similar precipitation rates
 no supersaturation

Washing: **water, organic solvents**

Drying: **evaporation**
 azeotropic distillation
 freeze-drying

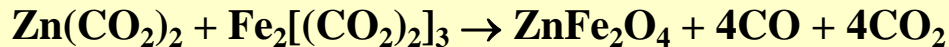
Disadvantage: difficult to prepare high purity, accurate stoichiometric phases if solubilities do not match

Coprecipitation Method

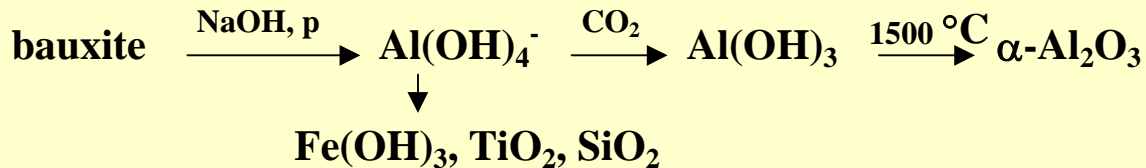
Spinels

oxalates: $\text{Zn}(\text{CO}_2)_2/\text{Fe}_2[(\text{CO}_2)_2]_3/\text{H}_2\text{O}$ 1 : 1 mixing, H_2O evaporation, salts coprecipitation

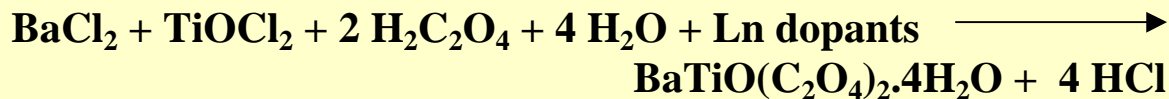
Solid-solution mixing on atomic scale, filter, calcine in air



Al_2O_3 Bayer Process



BaTiO_3

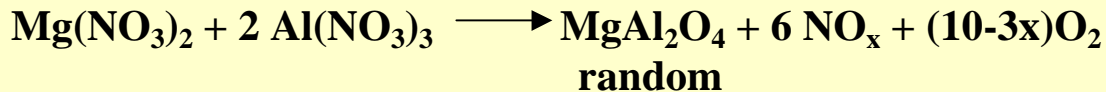


filtration, washing, drying, calcination @ 730°C

Coprecipitation Method

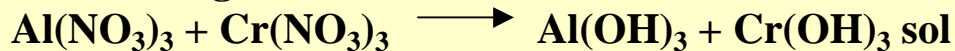
Spinel

$\text{Al}(\text{NO}_3)_3 + \text{Mg}(\text{NO}_3)_2 + \text{H}_2\text{O}$ freeze-drying gives amorphous mixture, calcination @ 800 °C !!! low T



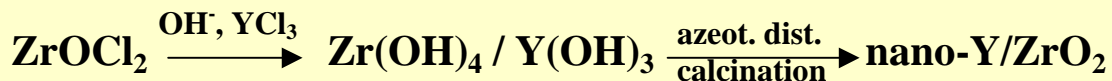
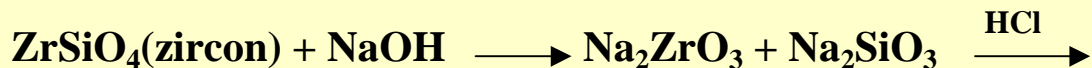
Ruby

Ion exchange



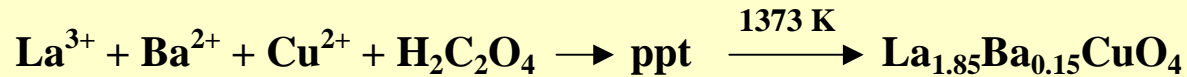
freeze drying gives solid $(\text{Al}/\text{Cr})(\text{OH})_3$ @ LN₂ temperature, 5 Pa
annealing @ 950 °C for 2.5 h gives solid solution $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$

Zirconia

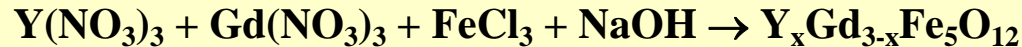


Coprecipitation Method

High- T_c Superconductors



Magnetic garnets, tunable magnetic materials



Firing @ 900 °C, 18-24 hrs, pellets, regrinding, repelletizing, repeated firings, removes REFeO₃ perovskite impurity

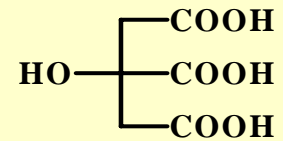
Isomorphous replacement of Y³⁺ for Gd³⁺ on dodecahedral sites, solid solution, similar rare earth ionic radii

complete family accessible, 0 < x < 3, 2Fe³⁺ O_h sites, 3Fe³⁺ T_d sites, 3RE³⁺ dodecahedral sites

Pechini and Citrate Gel Method

Aqueous solution of metal ions

Chelate formation with citric acid



Polyesterification with polyfunctional alcohol on heating

**Further heating leads to resin, transparent glassy gel
calcination provides oxide powder**

Control of stoichiometry by initial reagent ratio

Complex compositions, mixture of metal ions

Good homogeneity, mixing at the molecular level

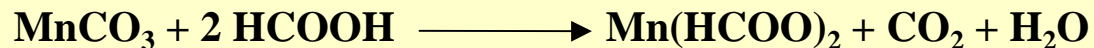
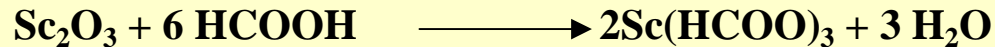
Low firing temperatures

Pechini and Citrate Gel Method

BaTiO₃

by conventional powder method at 1200 °C

Ba²⁺ + Ti(OⁱPr)₄ + citric acid at 650 °C



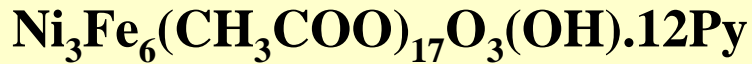
added to citric acid, water removal, calcination @ 690 °C gives

ScMnO₃

without citric acid only mixture of Sc₂O₃ and Mn₂O₃ is formed

Double Salt Precursors

Double salts of known and controlled stoichiometry such as:



Burn off organics 200-300 °C, then 1000 °C in air for 2-3 days

Product highly crystalline phase pure NiFe_2O_4 spinel

Good way to make chromite spinels, important tunable magnetic materials

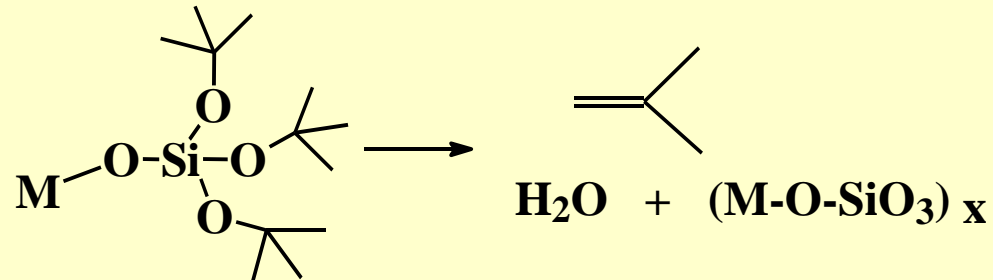
Juggling the electronic-magnetic properties of the O_h and T_d ions in the spinel lattice

Chromite spinel	Precursor	Ignition T, °C
MgCr_2O_4	$(\text{NH}_4)_2\text{Mg}(\text{CrO}_4)_2\cdot 6\text{H}_2\text{O}$	1100-1200
NiCr_2O_4	$(\text{NH}_4)_2\text{Ni}(\text{CrO}_4)_2\cdot 6\text{H}_2\text{O}$	1100
MnCr_2O_4	$\text{MnCr}_2\text{O}_7\cdot 4\text{C}_5\text{H}_5\text{N}$	1100
CoCr_2O_4	$\text{CoCr}_2\text{O}_7\cdot 4\text{C}_5\text{H}_5\text{N}$	1200
CuCr_2O_4	$(\text{NH}_4)_2\text{Cu}(\text{CrO}_4)_2\cdot 2\text{NH}_3$	700-800
ZnCr_2O_4	$(\text{NH}_4)_2\text{Zn}(\text{CrO}_4)_2\cdot 2\text{NH}_3$	1400
FeCr_2O_4	$(\text{NH}_4)_2\text{Fe}(\text{CrO}_4)_2$	1150

Single Source Precursor

Compounds containing desired elements in a proper stoichiometric ratio

Easy chemical pathway for ligand removal



Vegard's Law

Vegard law behavior:

Any property P of a solid-solution member is the atom fraction weighted average of the end-members

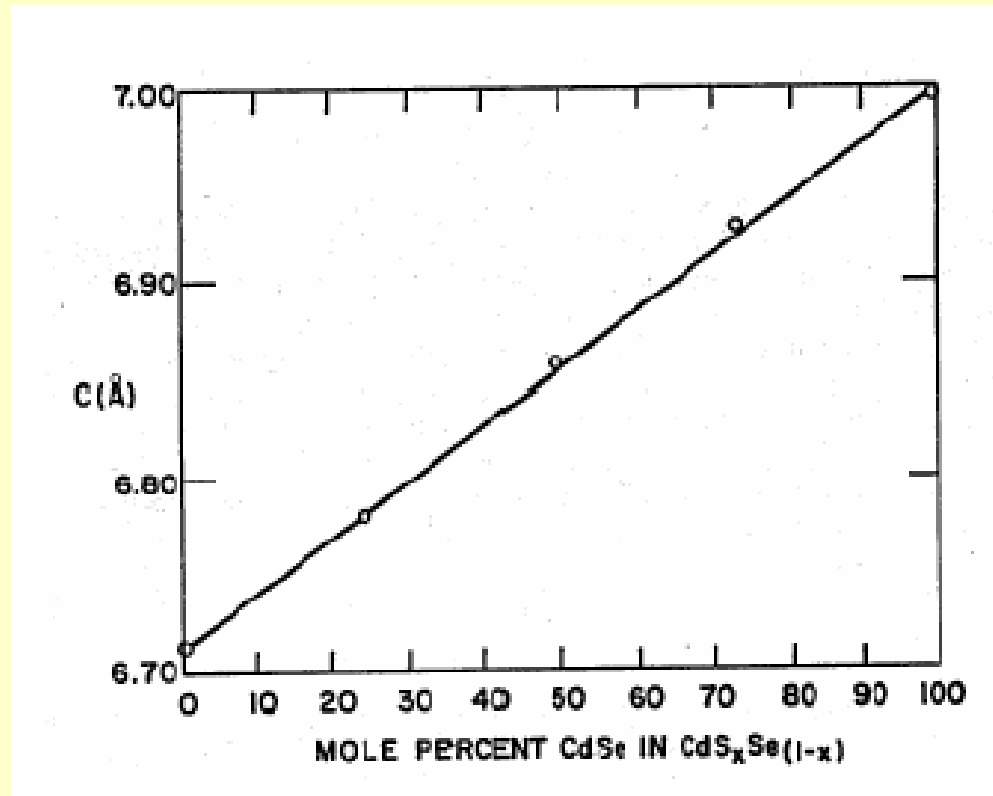
The composition of the $A_{1-x}B_x$ alloy can be calculated from Vegard's law

The lattice parameter of a solid solution alloy will be given by a linear dependence of lattice parameter on composition:

$$a(A_{1-x}B_x) = x a(B) + (1-x) a(A)$$

Vegard's Law

$$c(\text{CdSe}_{1-x}\text{S}_x) = x c(\text{CdS}) + (1-x) c(\text{CdSe})$$

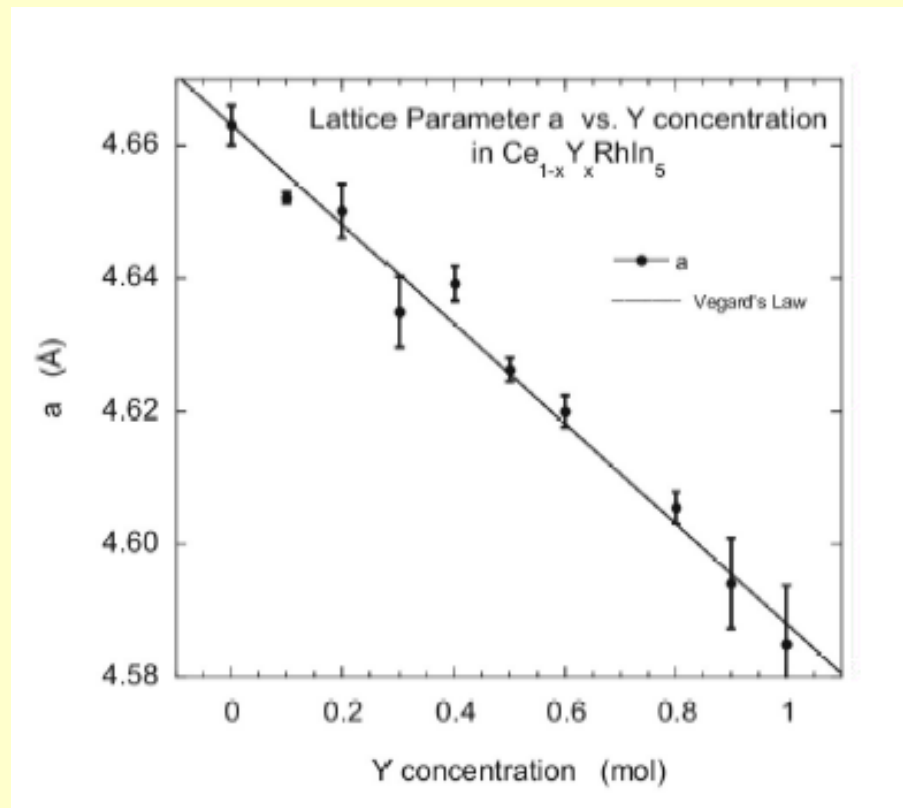


Vegard's Law

$$P(Y_xCe_{1-x}RhIn_5) = x P(Y_xCe_{1-x}RhIn_5) + (1-x) P(Y_xCe_{1-x}RhIn_5)$$

Any property P of a solid-solution member is the atom fraction weighted average of the end-members

Tetragonal lattice constant a
as a function of
Y concentration x
for the $Ce_{1-x}Y_xRhIn_5$ system



Vegard's Law

A linear relationship exists between the concentration of the substitute element and the size of the lattice parameters

The direction of the linear relationship, increasing or decreasing, depends upon the system being analyzed

As the concentration of Y is increased, lattice constant a decreases, implying the cell is contracting along the a axis

Vegard's Law

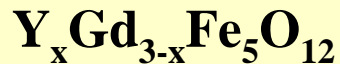
Vegard law behavior:

$$P(Y_xGd_{3-x}Fe_5O_{12}) = x/3 P(Y_3Fe_5O_{12}) + (3-x)/3 P(Gd_3Fe_5O_{12})$$

Any property P of a solid-solution member is the atom fraction weighted average of the end-members

Vegard's Law

Tunable magnetic properties by tuning the x value in the binary garnet



3 T_d Fe^{3+} sites, 5 UPEs

2 O_h Fe^{3+} sites, 5 UPEs

Ferrimagnetically coupled material, oppositely aligned electron spins on the T_d and O_h Fe^{3+} magnetic sublattices

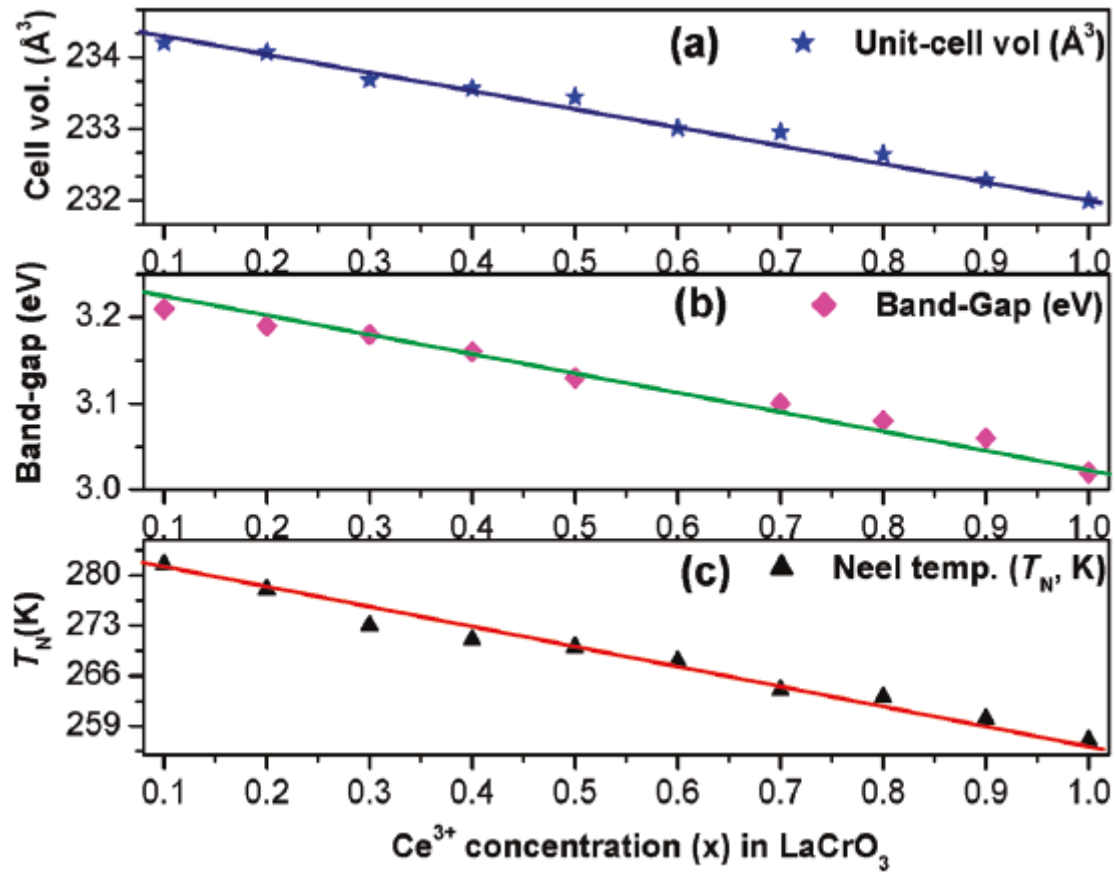
Counting spins $Y_3Fe_5O_{12}$ ferrimagnetic at low T: $3 \times 5 - 2 \times 5 = 5$ UPEs

Counting spins $Gd_3Fe_5O_{12}$ ferrimagnetic at low T: $3 \times 7 - 3 \times 5 + 2 \times 5 = 16$ UPEs

$Y_x Gd_{3-x} Fe_5 O_{12}$ creates a tunable magnetic garnet that is strongly temperature and composition dependent,

applications in permanent magnets, magnetic recording media, magnetic bubble memories and so forth, similar concepts apply to magnetic spinels

$\text{La}_{1-x}\text{Ce}_x\text{CrO}_3$



Flux Method

Molten salts (inert or reactive), oxides, metals

MNO_3 , MOH , ($M = \text{alkali metal}$)

FLINAK: $LiF-NaF-KF$

M_2Q_x ($M = \text{alkali metal}$, $Q = S, Se, Te$)

molten salts ionic, low mp, eutectics, completely ionized

act as solvents or reactants, $T = 250-550\text{ }^\circ\text{C}$

enhanced diffusion, reduced reaction temperatures in comparison with powder method

products finely divided solids, high surface area (SA)

slow cooling to grow crystals

separation of water insoluble product from a water soluble flux

incorporation of the molten salt ions in product prevented by using salts with ions of much different sizes than the ones in the product

($PbZrO_3$ in a B_2O_3 flux)

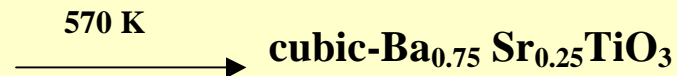
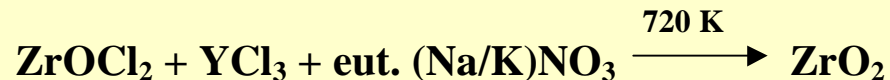
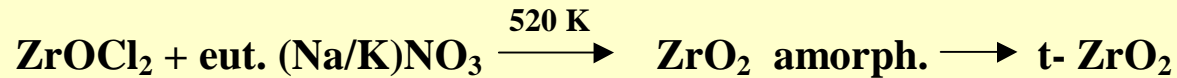
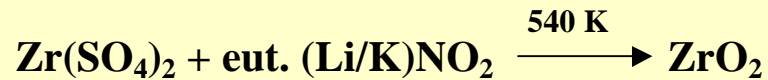
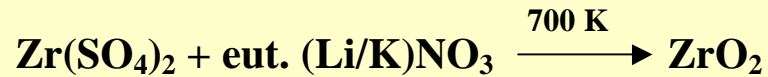
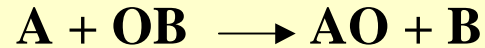
Flux Method

Lux-Flood formalism

oxide = strong base

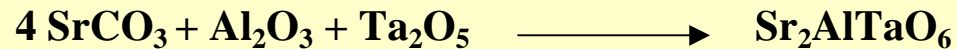
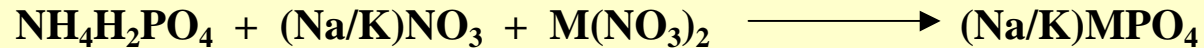
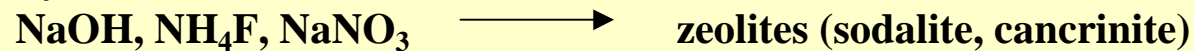
acid = oxide acceptor

base = oxide donor



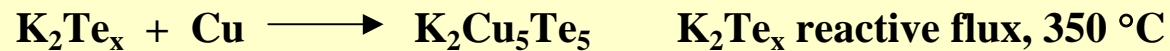
Flux Method

fly ash (aluminosilicates)



900 °C in SrCl₂ flux

1400 °C required for a direct reaction



Flux Method

Electrolysis in molten salts

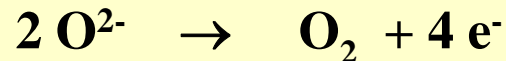
Reduction of TiO_2 pellets to Ti sponge in a CaCl_2 melt at $950\text{ }^\circ\text{C}$

O^{2-} dissolves in CaCl_2 , diffuses to the graphite anode

insulating TiO_2 \rightarrow TiO_{2-x} conductive

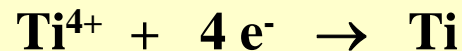
graphite anode

anodic oxidation



cathode TiO_2 pellet

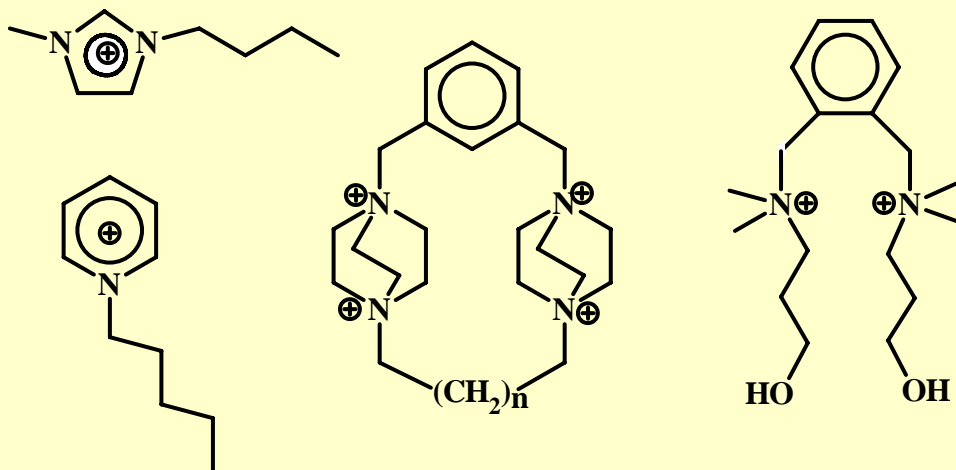
cathodic reduction



Ionic Liquids

Organic cations (containing N, P)

Inorganic anions: Cl^- , AlCl_4^- , Al_2Cl_7^- , $\text{Al}_3\text{Cl}_{10}^-$, PF_6^- , SnCl_3^- , BCl_3^- , BF_4^- , NO_3^- , $\text{OSO}_2\text{CF}_3^-$ (triflate), $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$, $\text{N}(\text{SO}_2\text{CF}_3)_2^-$, PO_4^{3-}

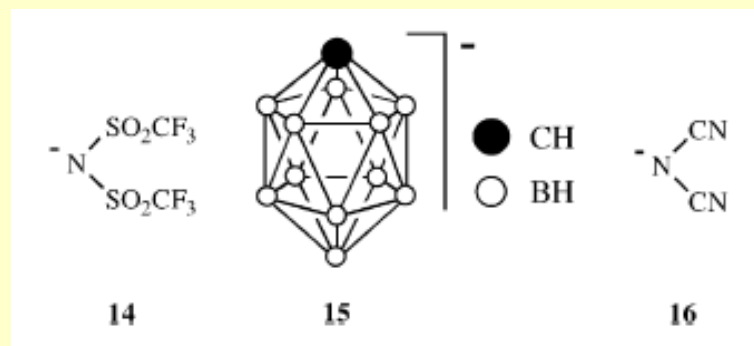
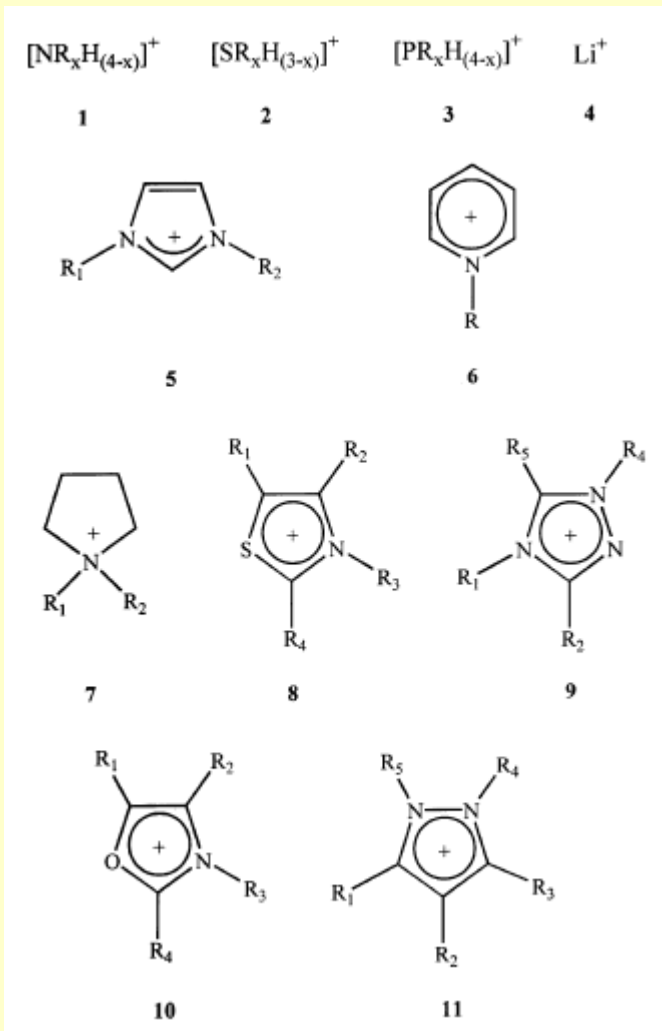


Ionic Liquids

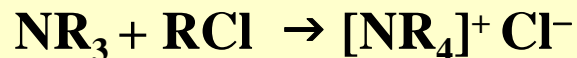
Oldest known (1914) : $\text{EtNH}_3^+\text{NO}_3^-$ mp 12 °C

- Liquids at room temperature or low mp**
- Thermal operating range from -40 °C to 400 °C**
- Highly polar, noncoordinating, completely ionized**
- Nonvolatile – no detectable vapor pressure**
- Nonflammable, nonexplosive, nonoxidizing, high thermal stability**
- Electrochemical window > 4V (not oxidized or reduced)**
- Immiscible with organic solvents**
- Hydrophobic IL immiscible with water**

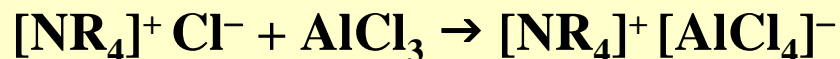
Ionic Liquids



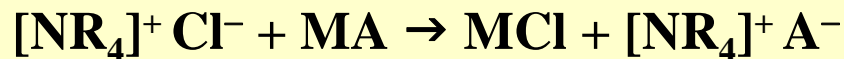
Synthesis of Ionic Liquids



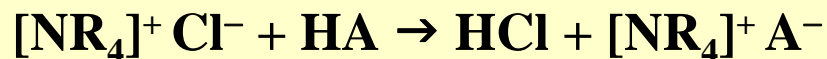
Aluminates



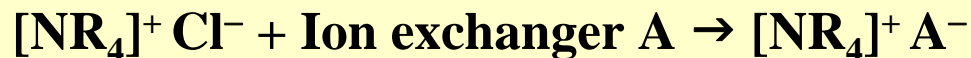
Metal halide elimination



Reaction with an acid



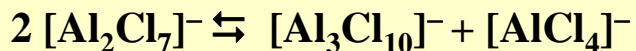
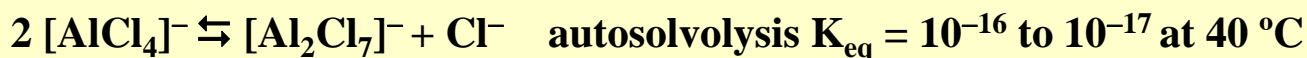
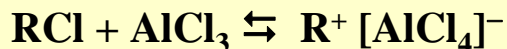
Ion exchange



Halogenoaluminate(III) Ionic Liquids

The most widely studied class of IL

High sensitivity to moisture – handling under vacuum
or inert atmosphere in glass/teflon



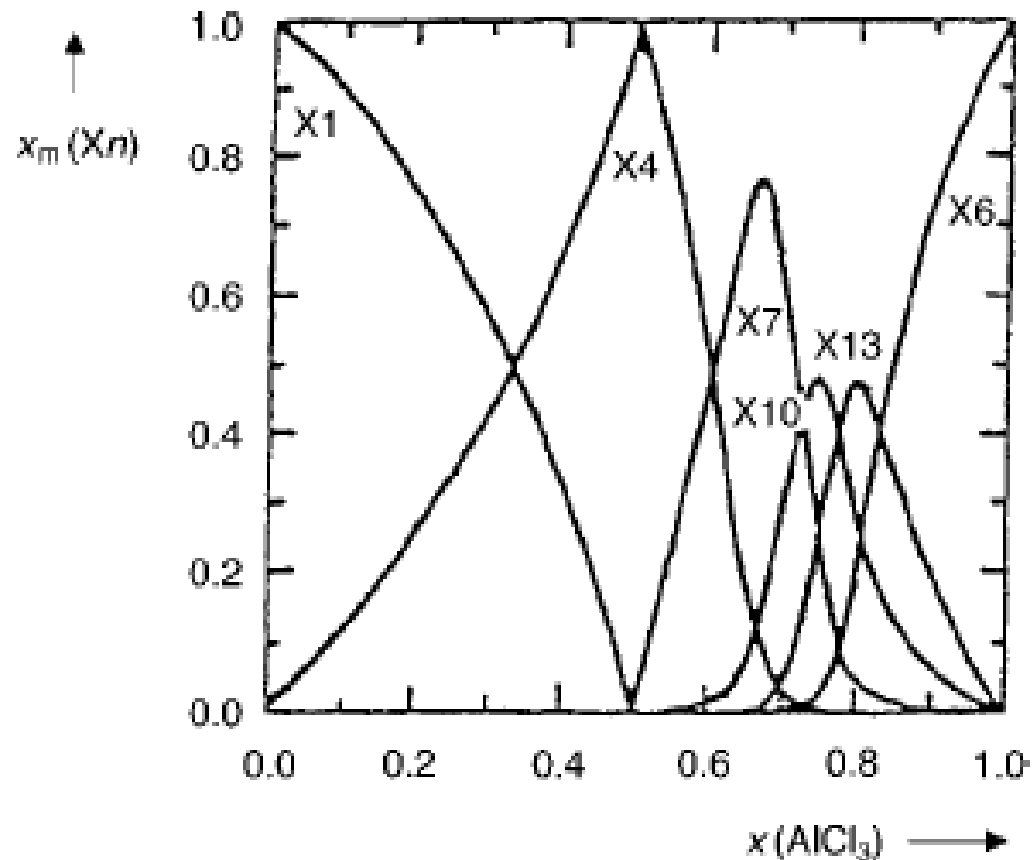
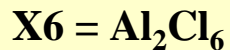
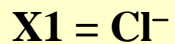
Acidic: excess of $AlCl_3$ as $[Al_2Cl_7]^-$ $x(AlCl_3) > 0.5$

Basic: excess of Cl^- $x(AlCl_3) < 0.5$

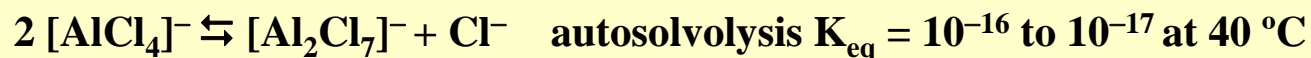
Neutral: $[AlCl_4]^-$ $x(AlCl_3) = 0.5$

Equilibria in Halogenoaluminate(III) IL

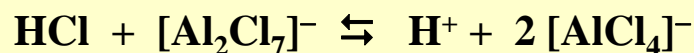
Equilibria in IL



Halogenoaluminate(III) Ionic Liquids



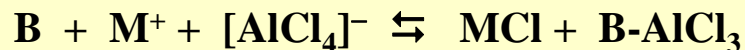
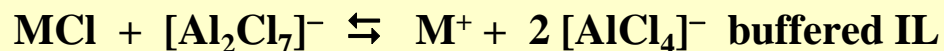
Acidic IL with an excess of AlCl_3



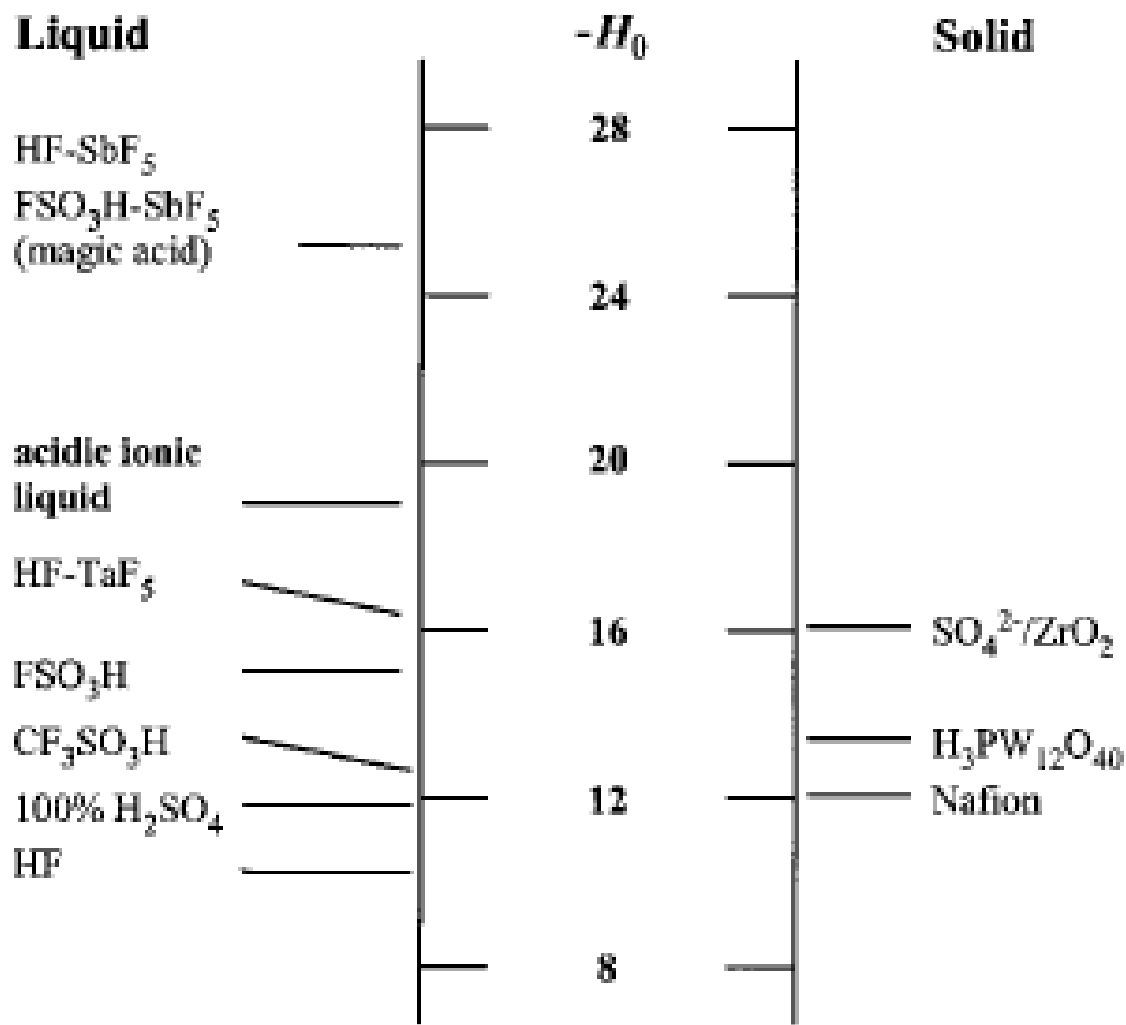
Proton extremely poorly solvated = high reactivity

Superacid $[\text{EMIM}]\text{Cl}/\text{AlCl}_3/\text{HCl}$ $H_0 = -19$ (HSO₃F: $H_0 = -15$)

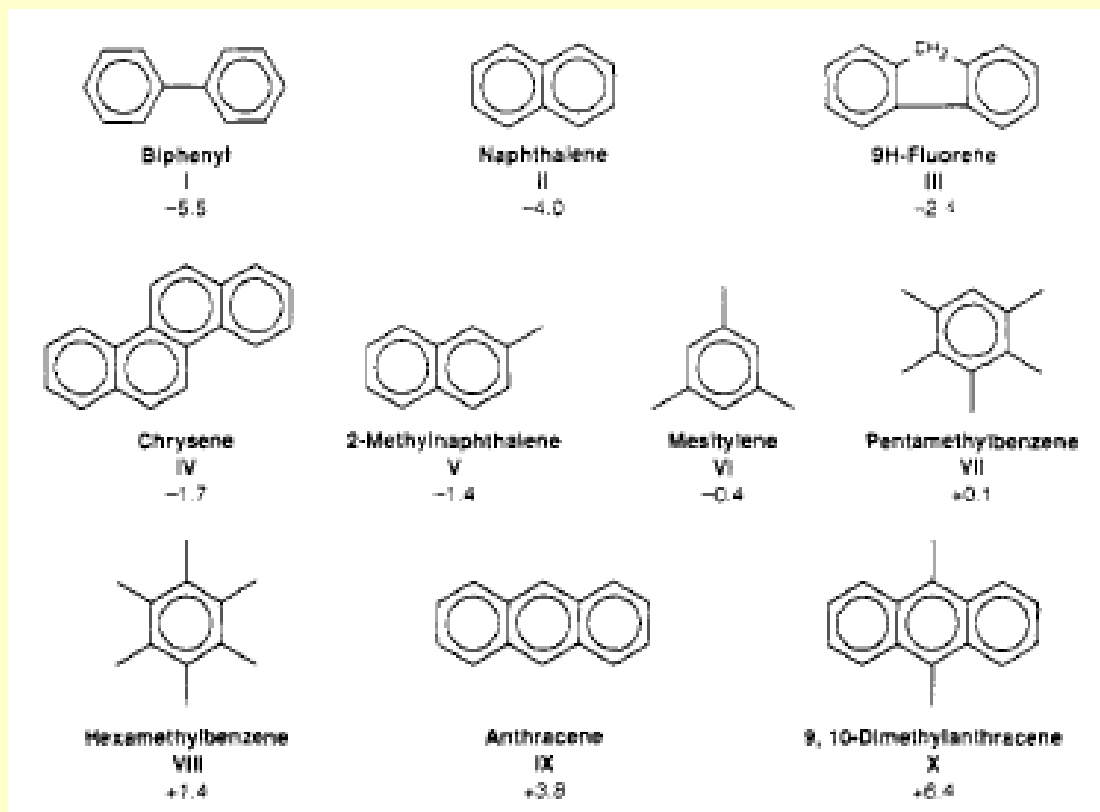
Latent acidity



Superacidity



Superacidic [EMIM]Cl/AlCl₃/HCl



I = not protonated
II = slightly protonated
III and IV = 10-20 %
V = 75-90%
VI-VIII = nearly completely
IX and X = completely

log K_b in HF

Ionic Liquids

Completely inorganic ionic liquids

Compound	mp (K)	Compound	mp (K)
$\text{Na}_{13}[\text{La}(\text{TiW}_{11}\text{O}_{39})_2]$	253.0	$\text{Na}_{13}[\text{Tm}(\text{TiW}_{11}\text{O}_{39})_2]$	260.2
$\text{Na}_{13}[\text{Ce}(\text{TiW}_{11}\text{O}_{39})_2]$	263.0	$\text{Na}_{13}[\text{Yb}(\text{TiW}_{11}\text{O}_{39})_2]$	267.2
$\text{Na}_{13}[\text{Pr}(\text{TiW}_{11}\text{O}_{39})_2]$	253.0	$\text{Na}_5[\text{CrTiW}_{11}\text{O}_{39}]$	261.5
$\text{Na}_{13}[\text{Sm}(\text{TiW}_{11}\text{O}_{39})_2]$	256.0	$\text{Na}_5[\text{MnTiW}_{11}\text{O}_{39}]$	253.0
$\text{Na}_{13}[\text{Gd}(\text{TiW}_{11}\text{O}_{39})_2]$	265.1	$\text{Na}_5[\text{FeTiW}_{11}\text{O}_{39}]$	257.6
$\text{Na}_{13}[\text{Dy}(\text{TiW}_{11}\text{O}_{39})_2]$	265.2	$\text{Na}_6[\text{ZnTiW}_{11}\text{O}_{39}]$	257.4
$\text{Na}_{13}[\text{Er}(\text{TiW}_{11}\text{O}_{39})_2]$	261.0		

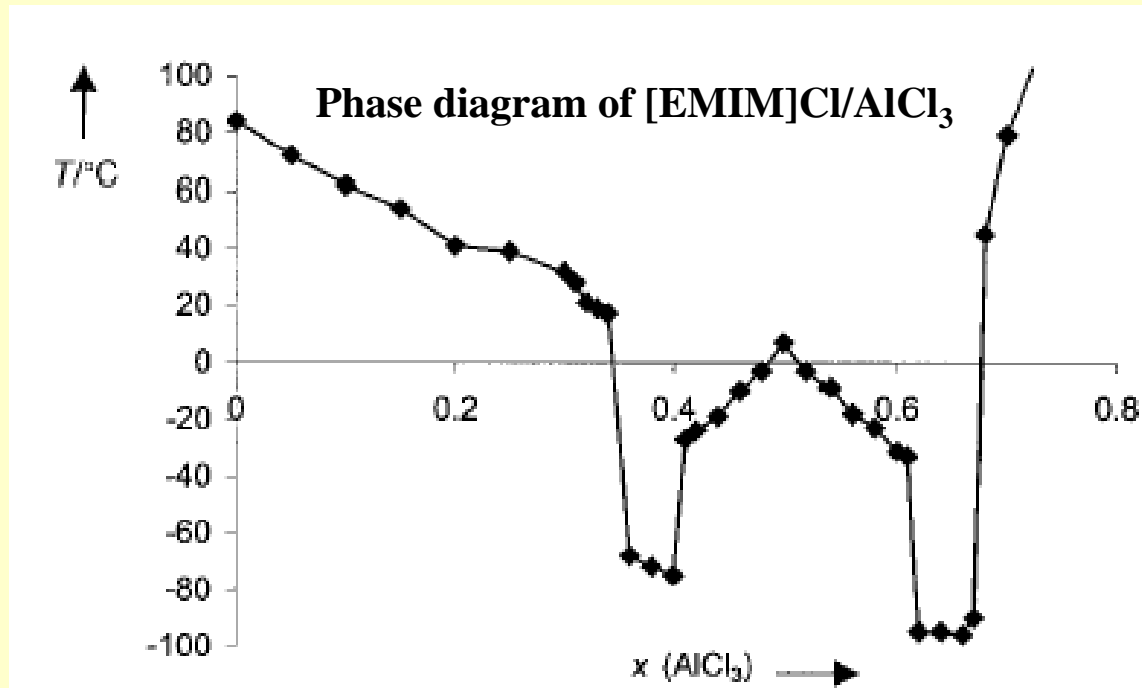
Melting Point of Ionic Liquids

Melting point is influenced by:

Cation – low symmetry, weak intermolecular interactions, good distribution of charge

Anion – increasing size leads to lower mp

Composition – Phase diagram



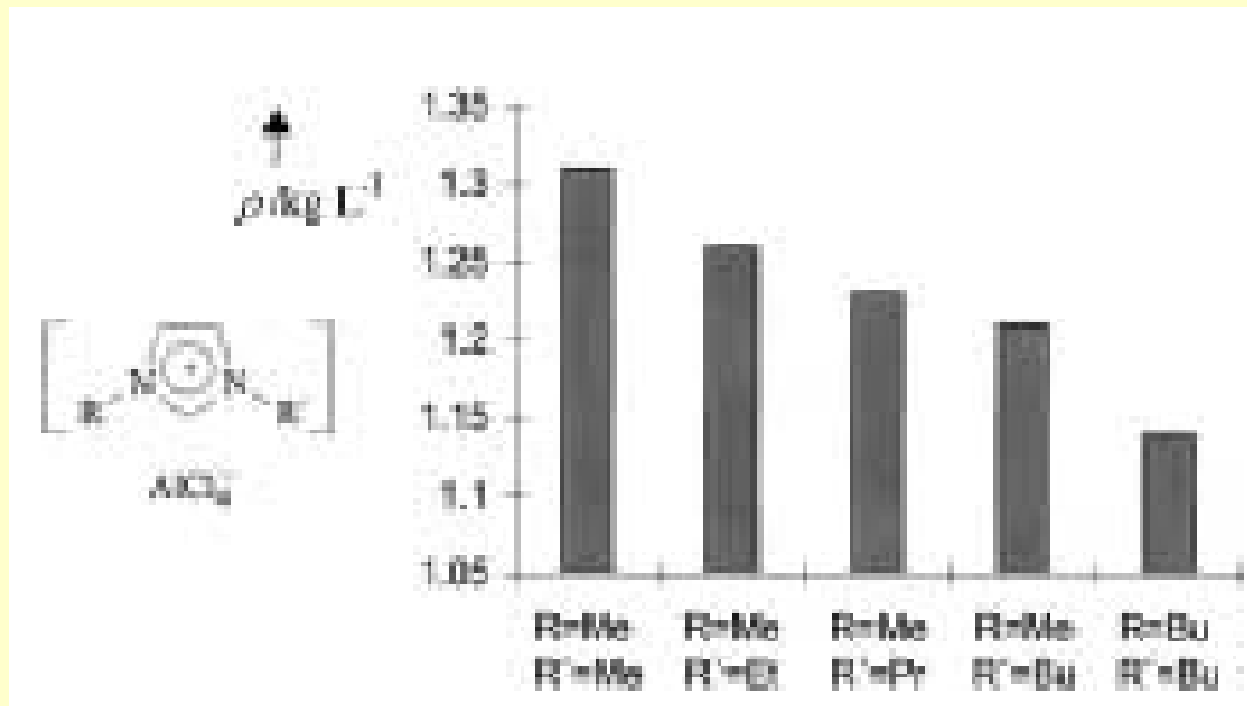
Melting Point of Ionic Liquids



R	X	mp/ ^o C
Me	Cl	125
Et	Cl	87
n-Bu	Cl	65
Et	NO ₃	38
Et	AlCl ₄	7
Et	BF ₄	6
Et	CF ₃ SO ₃	-9
Et	(CF ₃ SO ₃) ₂ N	-3
Et	CF ₃ CO ₂	-14
n-Bu	CF ₃ SO ₃	16

Density of Ionic Liquids

The density of IL decreases as the bulkiness of the organic cation increases:




Viscosity of Ionic Liquids

The viscosity of IL depends on:

van der Waals interactions

H-bonding

	Anion $[A]^-$	η [cP]
 $[A]^-$	$CF_3SO_3^-$	90
	$n-C_4F_9SO_3^-$	373
	CF_3COO^-	73
	$n-C_3F_7COO^-$	182
	$(CF_3SO_2)_2N^-$	52

Solubility in/of Ionic Liquids

Variation of the alkyl group

Increasing nonpolar character of the cation increases solubility of nonpolar solutes.

Water solubility depends on the anion

water-soluble [BMIM] Br, CF₃COO, CF₃SO₃

Water-immiscible [BMIM] PF₆ (CF₃SO₂)₂N

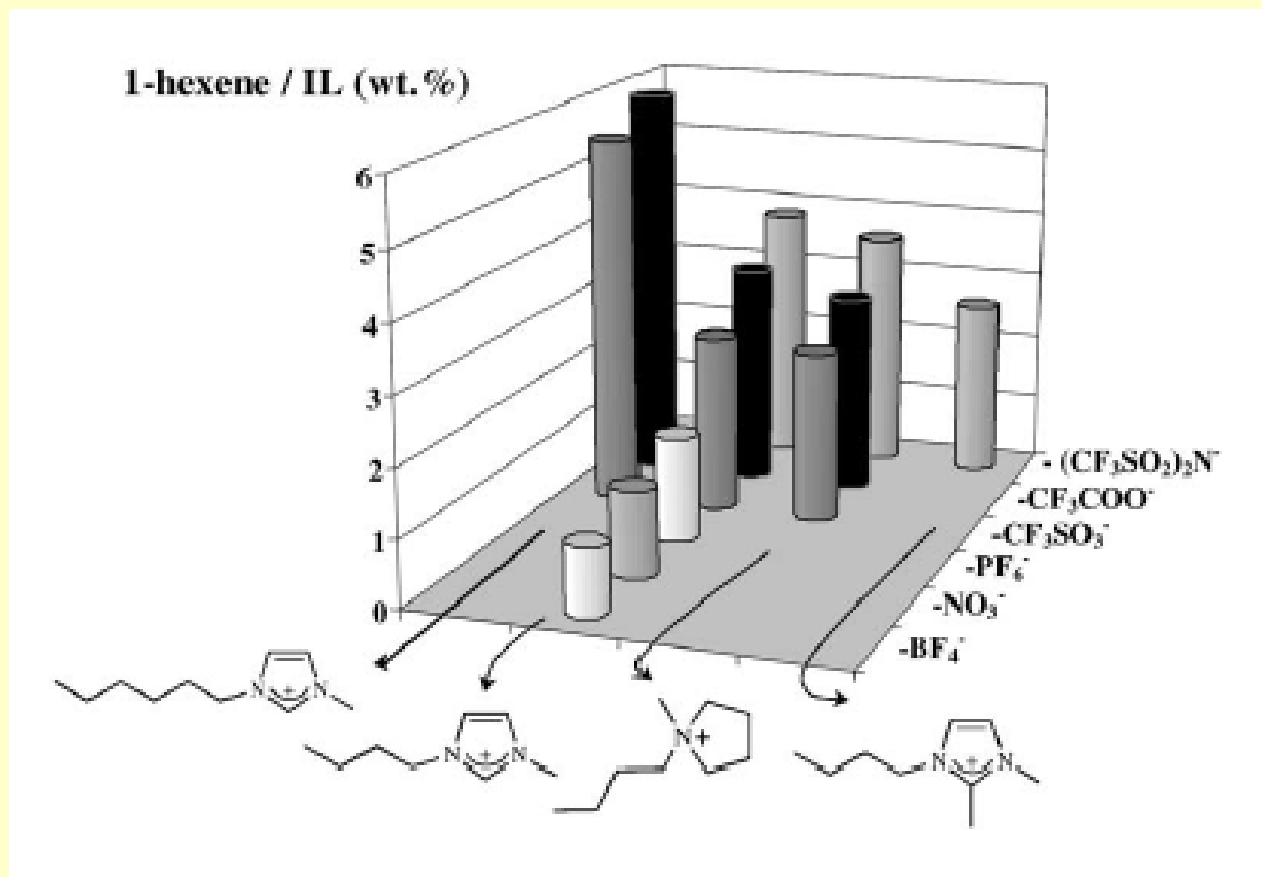
IL miscible with organic solvent IF their dielectric constant is above a certain limit given by the cation/anion combination

Polarity by E_(T)(30) scale

[EtNH₃][NO₃] 0.95 between CF₃CH₂OH and water

[BMIM] PF₆ as methanol

Solubility in/of Ionic Liquids



Applications of Ionic Liquids

Electrodeposition of metals and alloys (also nanoscopic)

Al, CoAl_x, CuAl_x, FeAl_x, AlTi_x

Semiconductors Si, Ge, GaAs, InSb, CdTe

Electrodeposition of a Bi-Sr-Ca-Cu alloy (precursor to SC oxides)

Melt of MeEtImCl at 120 °C

BiCl₃, SrCl₂, CaCl₂, CuCl₂ dissolve well

Constituent	BiCl₃	SrCl₂	CaCl₂	CuCl₂
Concentration (mol kg⁻¹ MeEtImCl)	0.068	0.50	0.18	0.050

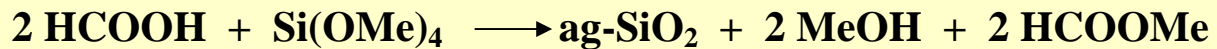
Substrate Al

-1.72 V vs the Ag/Ag⁺ reference electrode

Applications of Ionic Liquids

Biphasic solvent systems

Preparation of aerogels



Natural gas sweetening (H₂S, CO₂ removal)

Electrolytes in batteries or solar cells

Dissolving spent nuclear fuel (U⁴⁺ oxidized to U⁶⁺)

Extraction

Enzyme activity

Applications of Ionic Liquids

Olefin polymerization

Ethene + TiCl_4 + AlEtCl_2 in acidic IL

Ethene + Cp_2TiCl_2 + $\text{Al}_2\text{Me}_3\text{Cl}_3$ in acidic IL



Olefin hydrogenation

Cyclohexene + H_2 + $[\text{RhCl}(\text{PPh}_3)_3]$ (Wilkinson's catalyst)