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: $Zn(CO_2)_2/Fe_2[(CO_2)_2]_3/H_2O$ 1 : 1 mixing, H_2O evaporation, salts coprecipitation
Solid-solution mixing on atomic scale, filter, calcine in air

$$Zn(CO_2)_2 + Fe_2[(CO_2)_2]_3 \rightarrow ZnFe_2O_4 + 4CO + 4CO_2$$

Al_2O_3 Bayer Process

$$\begin{tikzcd}
\text{bauxite} \arrow[r, "\text{NaOH, p}"] & Al(OH)_4^- \arrow[r, "CO_2"] \arrow[d] & Al(OH)_3 \arrow[r, "1500\,^\circ C"] & \alpha\text{-}Al_2O_3 \\
 & Fe(OH)_3,\ TiO_2,\ SiO_2 & &
\end{tikzcd}$$

$BaTiO_3$

$$BaCl_2 + TiOCl_2 + 2\,H_2C_2O_4 + 4\,H_2O + \text{Ln dopants} \longrightarrow BaTiO(C_2O_4)_2.4H_2O + 4\,HCl$$

filtration, washing, drying, calcination @ 730 °C

Coprecipitation Method

Spinel

$Al(NO_3)_3 + Mg(NO_3)_2 + H_2O$ freeze-drying gives amorphous mixture, calcination @ 800 °C !!! low T

$$Mg(NO_3)_2 + 2\,Al(NO_3)_3 \longrightarrow \underset{\text{random}}{MgAl_2O_4} + 6\,NO_x + (10-3x)O_2$$

Ruby

Ion exchange

$$Al(NO_3)_3 + Cr(NO_3)_3 \longrightarrow Al(OH)_3 + Cr(OH)_3 \text{ sol}$$

freeze drying gives solid $(Al/Cr)(OH)_3$ @ LN_2 temperature, 5 Pa
anealing @ 950 °C for 2.5 h gives solid solution $Al_{2-x}Cr_xO_3$

Zirconia

$$ZrSiO_4\text{(zircon)} + NaOH \longrightarrow Na_2ZrO_3 + Na_2SiO_3 \xrightarrow{HCl}$$

$$ZrOCl_2 \xrightarrow{OH^-,\ YCl_3} Zr(OH)_4\ /\ Y(OH)_3 \xrightarrow[\text{calcination}]{\text{azeot. dist.}} \text{nano-}Y/ZrO_2$$

Coprecipitation Method

High-T_c Superconductors

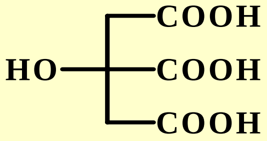
$$La^{3+} + Ba^{2+} + Cu^{2+} + H_2C_2O_4 \longrightarrow ppt \xrightarrow{1373\ K} La_{1.85}Ba_{0.15}CuO_4$$

Magnetic garnets, tunable magnetic materials

$$Y(NO_3)_3 + Gd(NO_3)_3 + FeCl_3 + NaOH \rightarrow Y_xGd_{3-x}Fe_5O_{12}$$

Firing @ 900 ^oC, 18-24 hrs, pellets, regrinding, repelletizing, repeated firings, removes $REFeO_3$ perovskite impurity
Isomorphous replacement of Y^{3+} for Gd^{3+} on dodecahedral sites, solid solution, similar rare earth ionic radii
complete family accessible, $0 < x < 3$, $2Fe^{3+}$ O_h sites, $3Fe^{3+}$ T_d sites, $3RE^{3+}$ 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

$BaTiO_3$
by conventional powder method at 1200 °C

Ba^{2+} + $Ti(O^iPr)_4$ + citric acid at 650 °C

$Sc_2O_3 + 6\ HCOOH \longrightarrow 2Sc(HCOO)_3 + 3\ H_2O$
$MnCO_3 + 2\ HCOOH \longrightarrow Mn(HCOO)_2 + CO_2 + H_2O$

added to citric acid, water removal, calcination @ 690 °C gives $ScMnO_3$
without citric acid only mixture of Sc_2O_3 and Mn_2O_3 is formed

Double Salt Precursors

Double salts of known and controlled stoichiometry such as:
$Ni_3Fe_6(CH_3COO)_{17}O_3(OH).12Py$

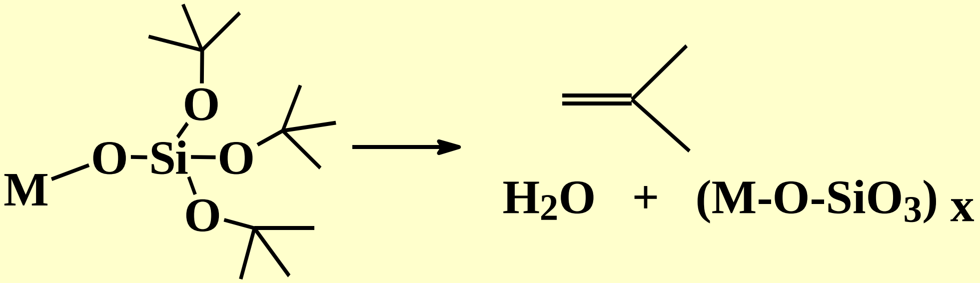
Burn off organics 200-300 ^oC, then 1000 ^oC in air for 2-3 days
Product highly crystalline phase pure $NiFe_2O_4$ spinel
Good way to make chromite spinels, important tunable magnetic materials
Juggling the electronic-magnetic properties of the O_h and T_d ions in the spinel lattice

Chromite spinel	Precursor	Ignition T, ^oC
$MgCr_2O_4$	$(NH_4)_2Mg(CrO_4)_2.6H_2O$	1100-1200
$NiCr_2O_4$	$(NH_4)_2Ni(CrO_4)_2.6H_2O$	1100
$MnCr_2O_4$	$MnCr_2O_7.4C_5H_5N$	1100
$CoCr_2O_4$	$CoCr_2O_7.4C_5H_5N$	1200
$CuCr_2O_4$	$(NH_4)_2Cu(CrO_4)_2.2NH_3$	700-800
$ZnCr_2O_4$	$(NH_4)_2Zn(CrO_4)_2. 2NH_3$	1400
$FeCr_2O_4$	$(NH_4)_2Fe(CrO_4)_2$	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

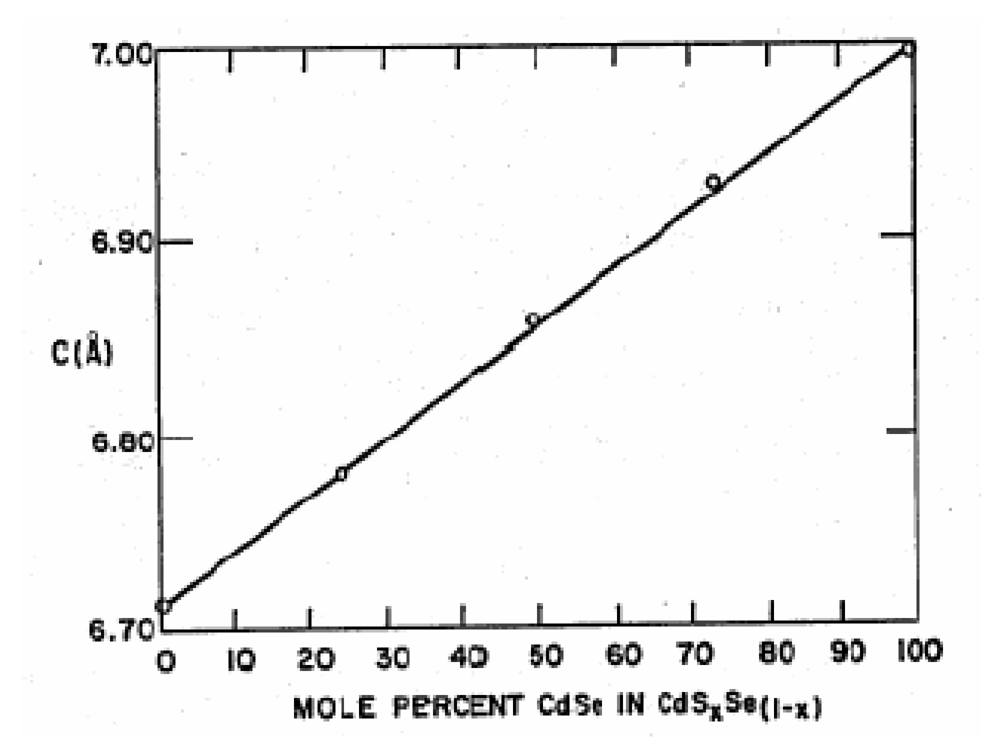
The composition of the $A_{1-x}B_x$ alloy can be calculated from Vegard’s law

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

$$c(CdSe_{1-x}S_x) = x\ c(CdS) + (1-x)\ c(CdSe)$$

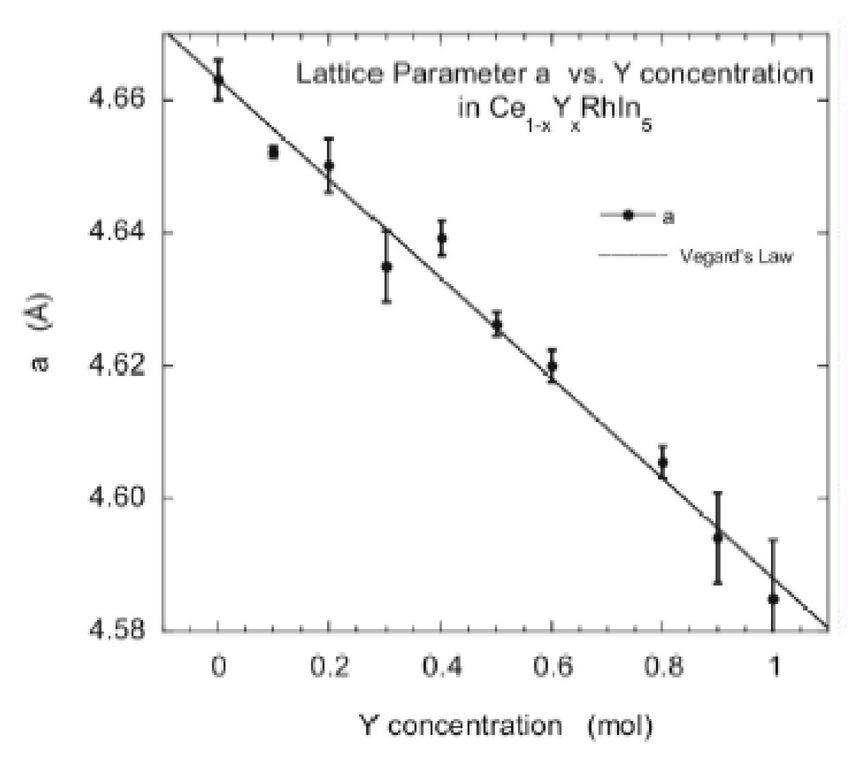


Vegard’s Law

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

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:

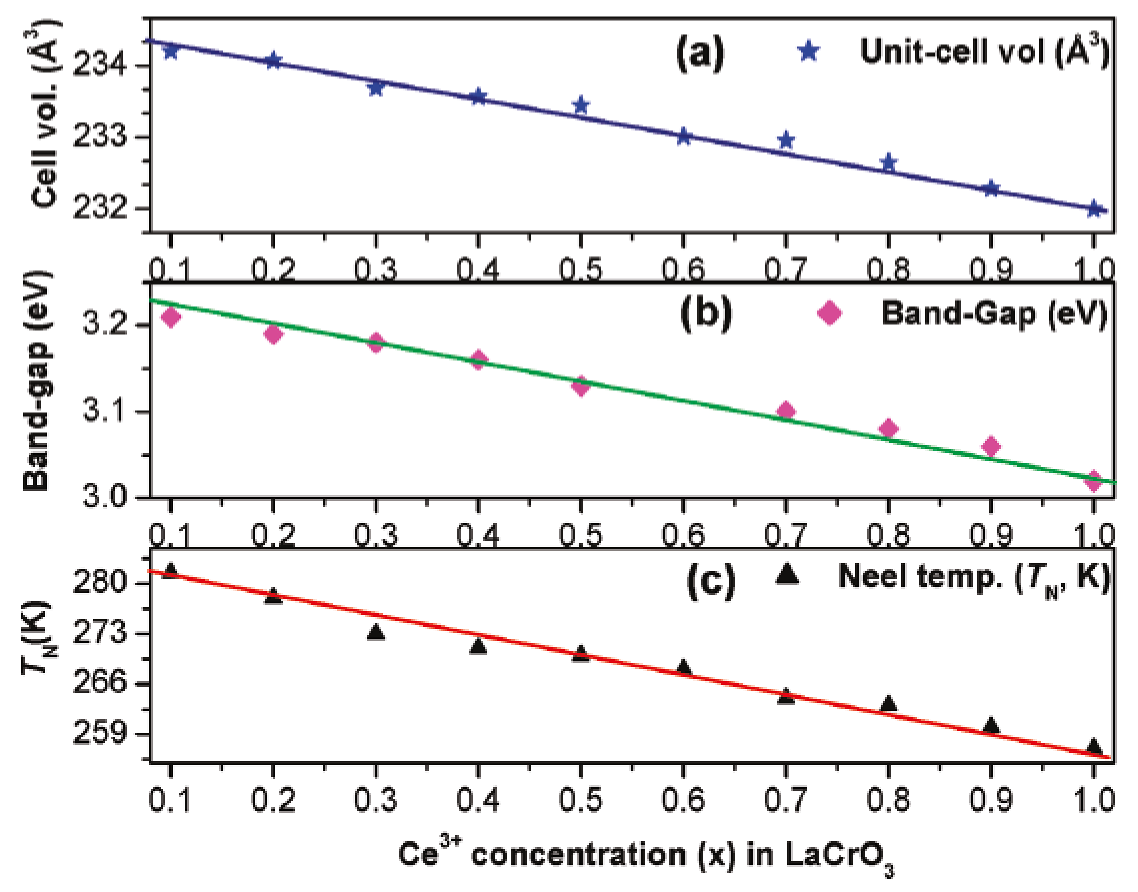
$$P\,(Y_xGd_{3-x}Fe_5O_{12}) = x/3\;P\,(Y_3Fe_5O_{12}) + (3-x)/3\;P\,(Gd_3Fe_5O_{12})$$

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 $Y_xGd_{3-x}Fe_5O_{12}$
3 T_d Fe^{3+} sites, 5 UPEs
2 O_h Fe^{3+} sites, 5UPEs
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 x 5 - 2 x 5 = 5UPEs
Counting spins $Gd_3Fe_5O_{12}$ ferrimagnetic at low T: 3 x 7 - 3 x 5 + 2 x 5 = 16 UPEs
$Y_xGd_{3-x}Fe_5O_{12}$ 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

$La_{1-x}Ce_xCrO_3$



Flux Method

Molten salts (inert or reactive), oxides, metals
MNO_3, MOH, (M = alkali metal)
FLINAK: LiF-NaF-KF
M_2Q_x (M = alkali metal, Q = S, Se, Te)

molten salts ionic, low mp, eutectics, completely ionized
act as solvents or reactants, T = 250-550 °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

$$A + OB \longrightarrow AO + B$$

$$Zr(SO_4)_2 + \text{eut. } (Li/K)NO_3 \xrightarrow{700\ K} ZrO_2$$

$$Zr(SO_4)_2 + \text{eut. } (Li/K)NO_2 \xrightarrow{540\ K} ZrO_2$$

$$ZrOCl_2 + \text{eut. } (Na/K)NO_3 \xrightarrow{520\ K} ZrO_2 \text{ amorph.} \longrightarrow \text{t- } ZrO_2$$

$$ZrOCl_2 + YCl_3 + \text{eut. } (Na/K)NO_3 \xrightarrow{720\ K} ZrO_2$$

$$BaCO_3 + SrCO_3 + TiO_2 + \text{eut. } (Na/K)OH$$

$$\xrightarrow{570\ K} \text{cubic-}Ba_{0.75}\,Sr_{0.25}TiO_3$$

Flux Method

fly ash (aluminosilicates)
NaOH, NH_4F, $NaNO_3$ $\longrightarrow$ zeolites (sodalite, cancrinite)

$NH_4H_2PO_4$ + $(Na/K)NO_3$ + $M(NO_3)_2$ $\longrightarrow$ $(Na/K)MPO_4$

4 $SrCO_3$ + Al_2O_3 + Ta_2O_5 $\longrightarrow$ Sr_2AlTaO_6
900 °C in $SrCl_2$ flux
1400 °C required for a direct reaction

K_2Te_x + Cu $\longrightarrow$ $K_2Cu_5Te_5$ K_2Te_x reactive flux, 350 °C

Flux Method

Electrolysis in molten salts

Reduction of TiO_2 pellets to Ti sponge in a $CaCl_2$ melt at 950 °C

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

insulating $TiO_2 \rightarrow TiO_{2-x}$ conductive

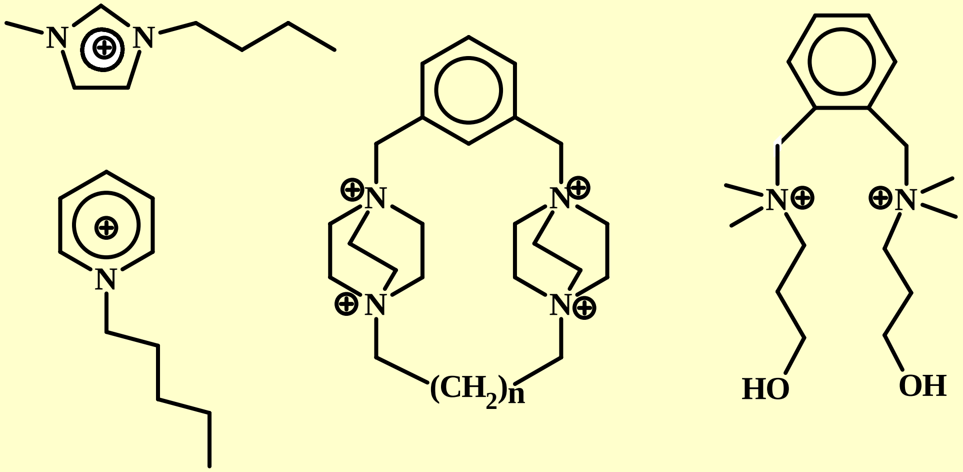
graphite anode
anodic oxidation $2\ O^{2-} \rightarrow O_2 + 4\ e^-$

cathode TiO_2 pellet
cathodic reduction $Ti^{4+} + 4\ e^- \rightarrow Ti$

Ionic Liquids

Organic cations (containing N, P)

Inorganic anions: Cl^-, $AlCl_4^-$, $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, PF_6^-, $SnCl_3^-$, BCl_3^-, BF_4^-, NO_3^-, $OSO_2CF_3^-$ (triflate), $CH_3C_6H_4SO_3^-$, $N(SO_2CF_3)_2^-$, PO_4^{3-}



Ionic Liquids

Oldest known (1914) : $EtNH_3^+NO_3^-$ mp 12 °C

➔Liquids at room temperature or low mp

➔Thermal operating range from –40 °C to 400 °C

➔Higly polar, noncoordinating, completely ionized

➔Nonvolatile – no detectable vapor pressure

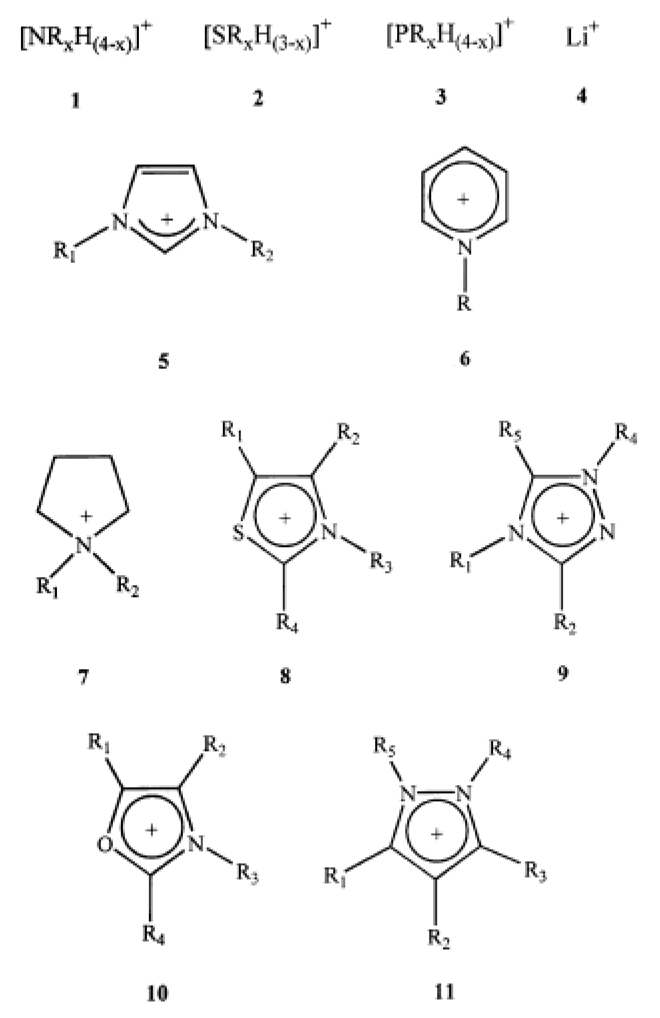
➔Nonflamable, nonexplosive, nonoxidizing, high thermal stability

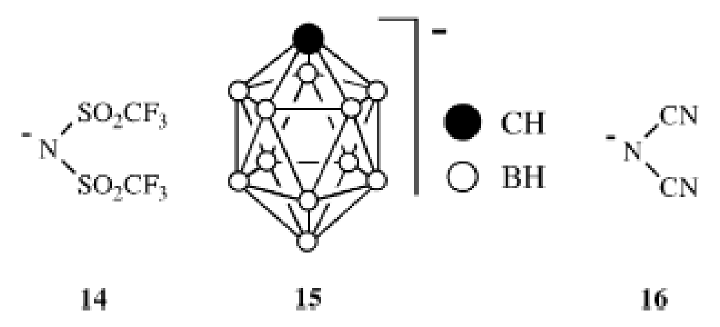
➔Electrochemical window > 4V (not oxidized or reduced)

➔Immiscible with organic solvents

➔Hydrophobic IL immiscible with water

Ionic Liquids





Synthesis of Ionic Liquids

$NR_3 + RCl \rightarrow [NR_4]^+ Cl^-$

Aluminates
$[NR_4]^+ Cl^- + AlCl_3 \rightarrow [NR_4]^+ [AlCl_4]^-$

Metal halide elimination
$[NR_4]^+ Cl^- + MA \rightarrow MCl + [NR_4]^+ A^-$

Reaction with an acid
$[NR_4]^+ Cl^- + HA \rightarrow HCl + [NR_4]^+ A^-$

Ion exchange
$[NR_4]^+ Cl^- + \text{Ion exchanger A} \rightarrow [NR_4]^+ A^-$

Halogenoaluminate(III) Ionic Liquids

The most widely studied class of IL

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

$RCl + AlCl_3 \rightleftarrows R^+ [AlCl_4]^-$

$2 [AlCl_4]^- \rightleftarrows [Al_2Cl_7]^- + Cl^-$ **autosolvolysis** $K_{eq} = 10^{-16}$ **to** 10^{-17} **at 40** ^{o}C

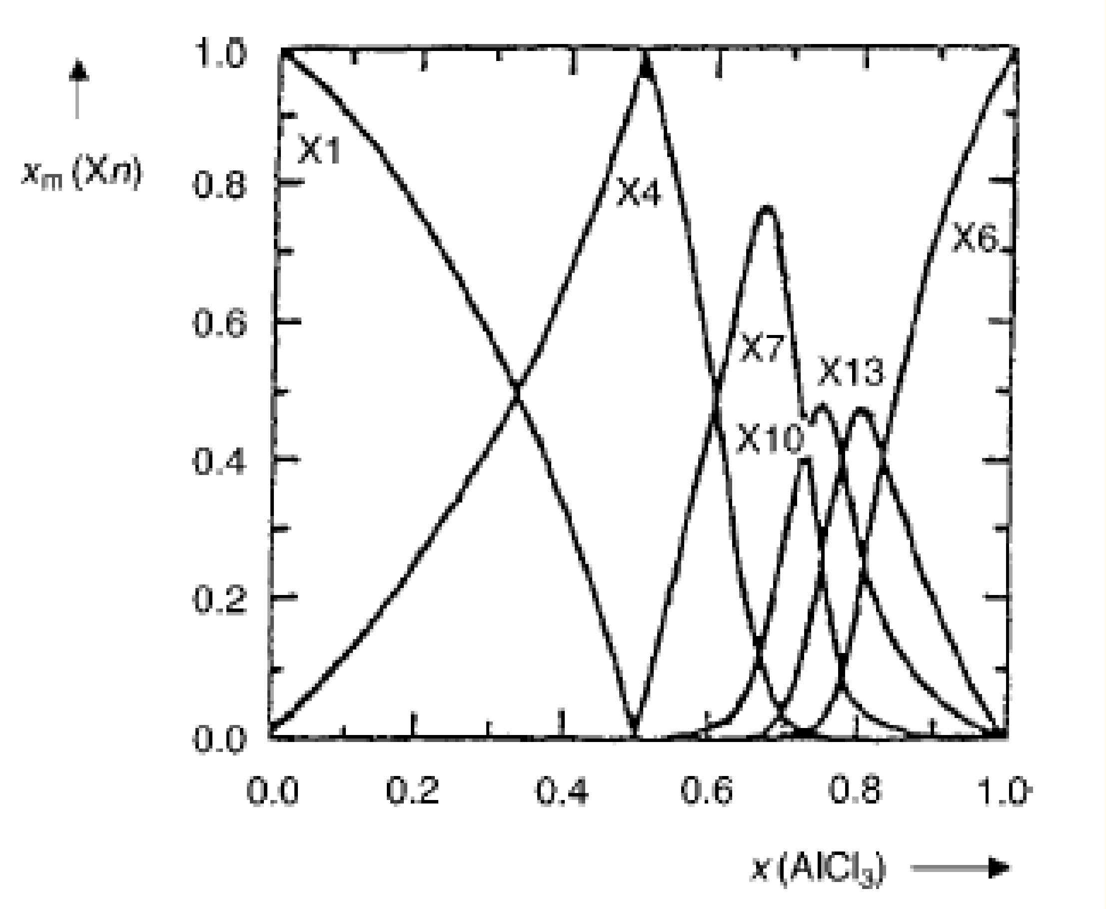
$2 [Al_2Cl_7]^- \rightleftarrows [Al_3Cl_{10}]^- + [AlCl_4]^-$

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

X1 = Cl^-
X4 = $[AlCl_4]^-$
X7 = $[Al_2Cl_7]^-$
X10 = $[Al_3Cl_{10}]^-$
X13 = $[Al_4Cl_{13}]^-$
X6 = Al_2Cl_6



Halogenoaluminate(III) Ionic Liquids

$2\ [AlCl_4]^- \leftrightharpoons [Al_2Cl_7]^- + Cl^-$ autosolvolysis $K_{eq} = 10^{-16}$ to 10^{-17} at 40 ºC

Acidic IL with an excess of $AlCl_3$

$HCl + [Al_2Cl_7]^- \leftrightharpoons H^+ + 2\ [AlCl_4]^-$

Proton extremely poorly solvated = high reactivity

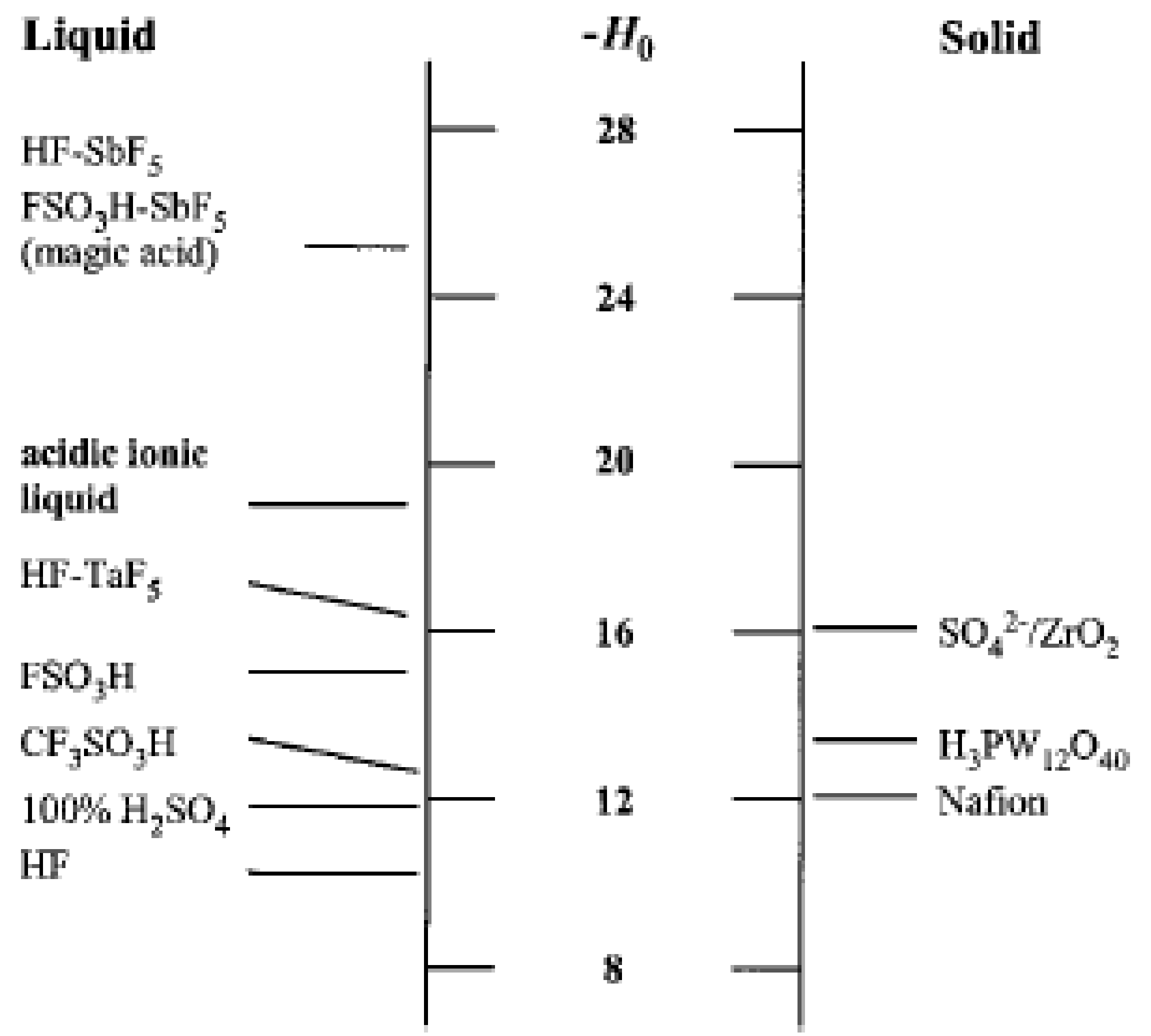
Superacid [EMIM]Cl/$AlCl_3$/HCl $H_0 = -19$ (HSO_3F: $H_0 = -15$)

Latent acidity

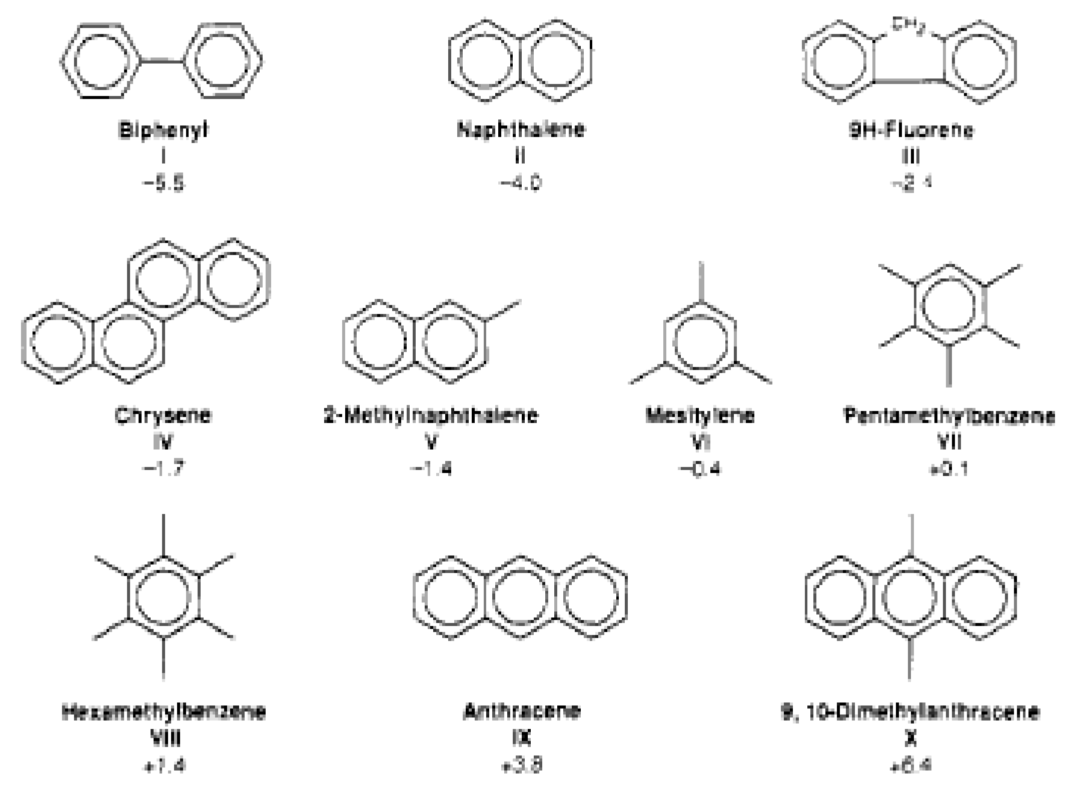
$MCl + [Al_2Cl_7]^- \leftrightharpoons M^+ + 2\ [AlCl_4]^-$ buffered IL

$B + M^+ + [AlCl_4]^- \leftrightharpoons MCl + B\text{-}AlCl_3$

Superacidity



Superacidic [EMIM]Cl/AlCl$_3$/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

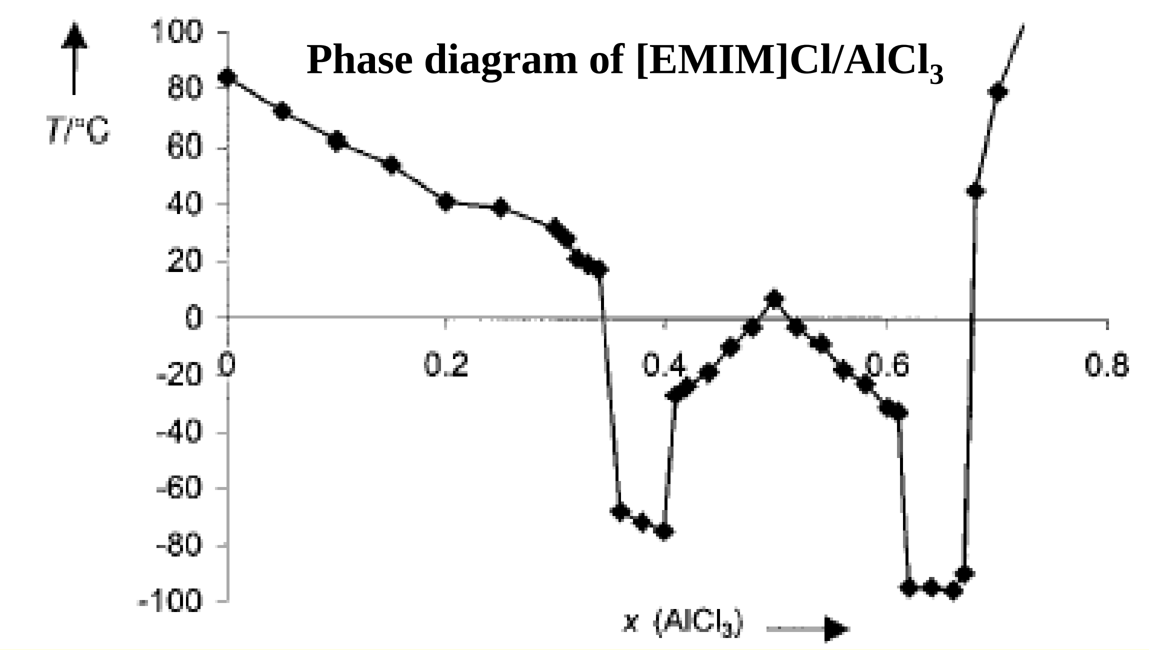
Completely inorganic ionic liquids

Compound	mp (K)	Compound	mp (K)
$Na_{13}[La(TiW_{11}O_{39})_2]$	253.0	$Na_{13}[Tm(TiW_{11}O_{39})_2]$	260.2
$Na_{13}[Ce(TiW_{11}O_{39})_2]$	263.0	$Na_{13}[Yb(TiW_{11}O_{39})_2]$	267.2
$Na_{13}[Pr(TiW_{11}O_{39})_2]$	253.0	$Na_5[CrTiW_{11}O_{39}]$	261.5
$Na_{13}[Sm(TiW_{11}O_{39})_2]$	256.0	$Na_5[MnTiW_{11}O_{39}]$	253.0
$Na_{13}[Gd(TiW_{11}O_{39})_2]$	265.1	$Na_5[FeTiW_{11}O_{39}]$	257.6
$Na_{13}[Dy(TiW_{11}O_{39})_2]$	265.2	$Na_6[ZnTiW_{11}O_{39}]$	257.4
$Na_{13}[Er(TiW_{11}O_{39})_2]$	261.0		

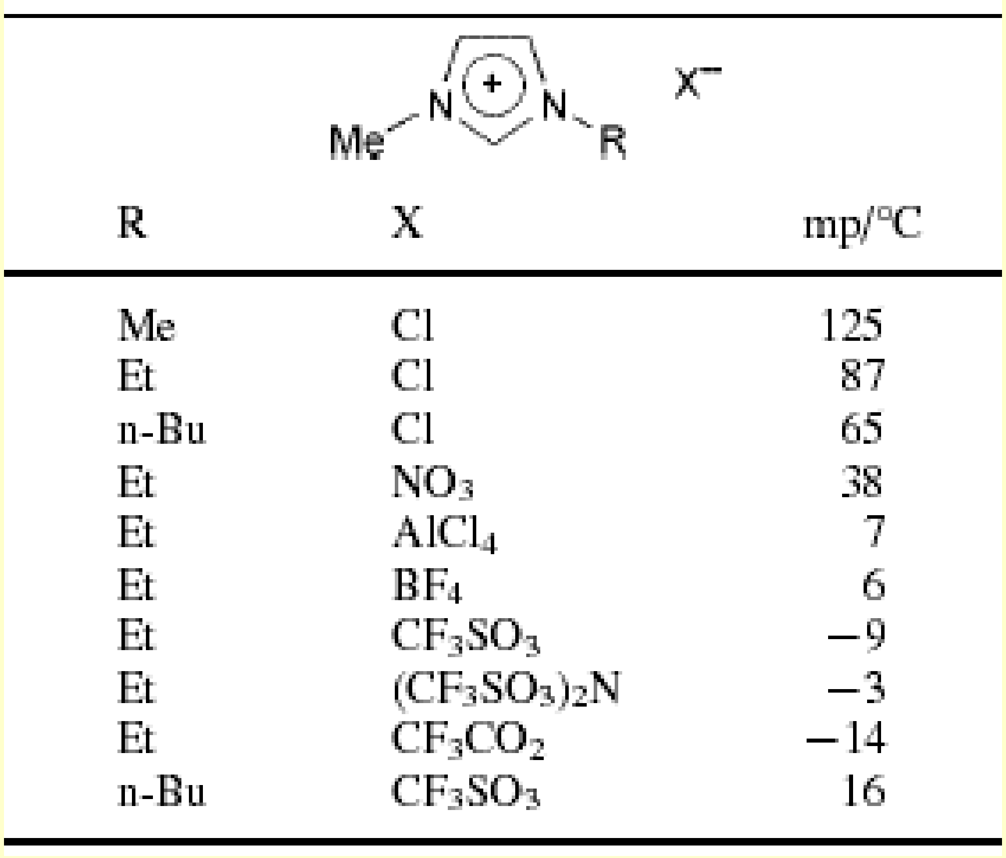
Melting Point of Ionic Liquids

Melting point is influenced by:

Cation – low symmetry, weak imtermolecular interactions, good distribution of charge
Anion – increasing size leads to lower mp
Composition – Phase diagram



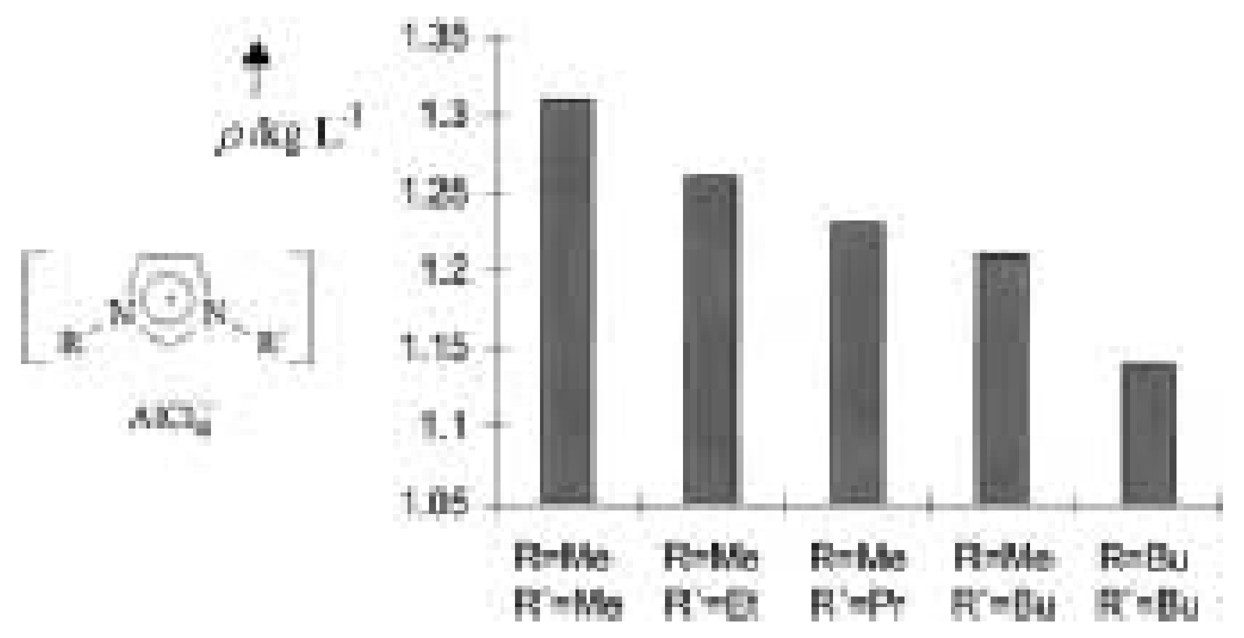
Melting Point of Ionic Liquids



R	X	mp/°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_3SO_3	−9
Et	$(CF_3SO_3)_2N$	−3
Et	CF_3CO_2	−14
n-Bu	CF_3SO_3	16

Density of Ionic Liquids

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

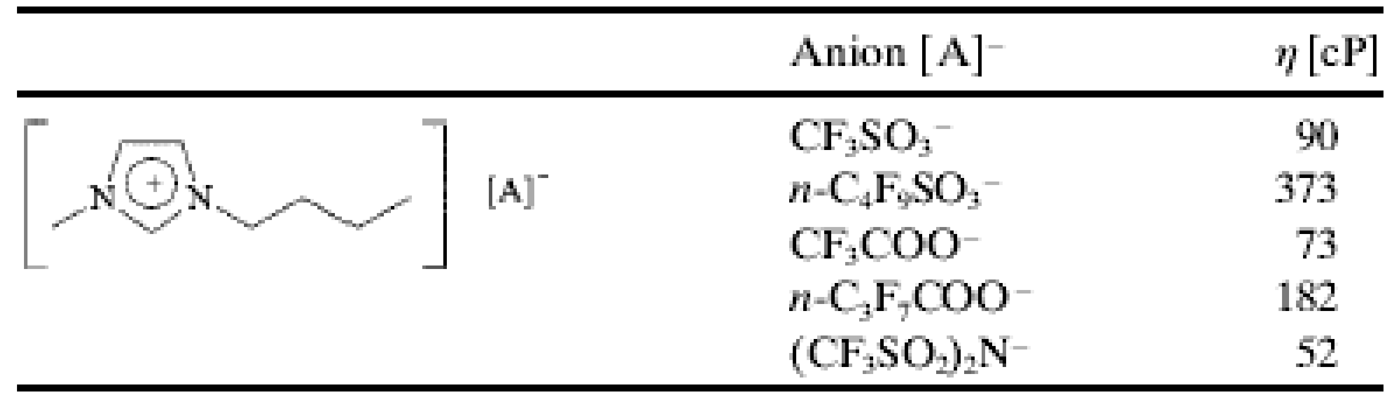


Viscosity of Ionic Liquids

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, CF_3COO, CF_3SO_3
Water-immiscilble [BMIM] PF_6 $(CF_3SO_2)_2N$

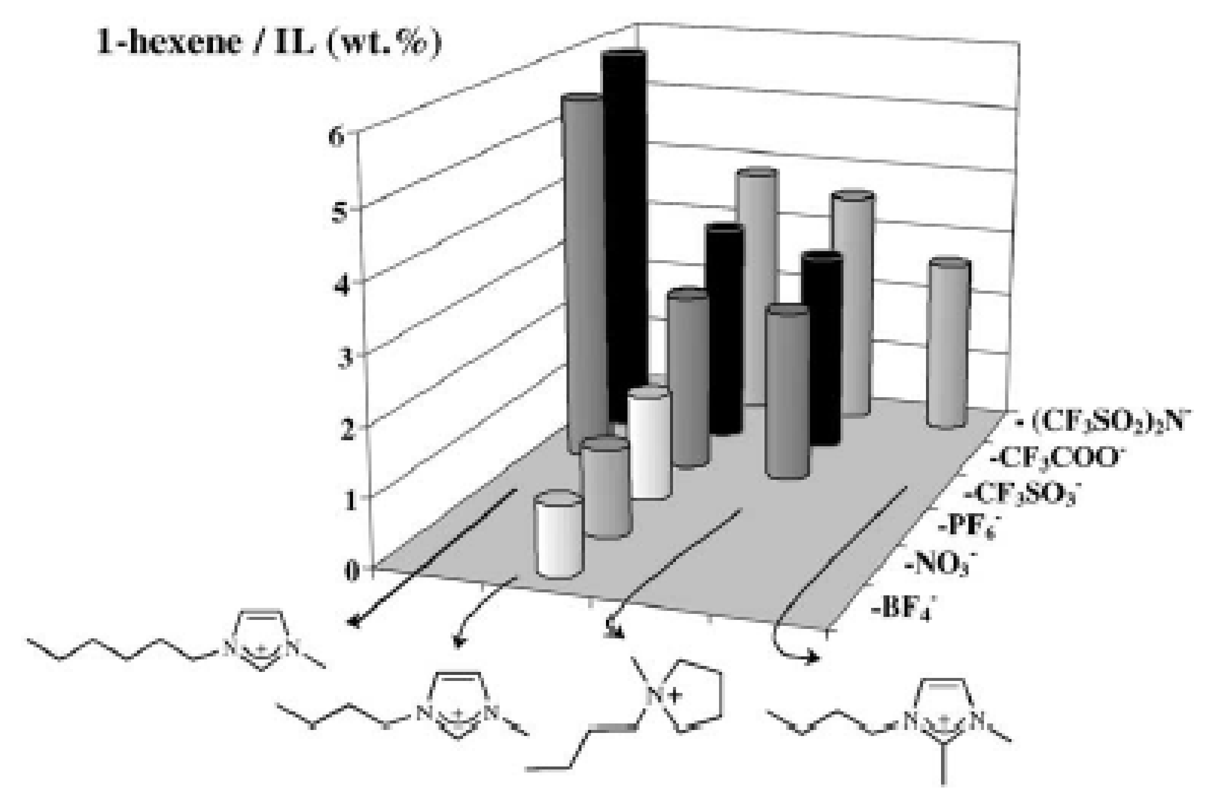
IL miscible with organic solvent IF their dielectric constant is above a certain limit given by the cation/anion combination

Polarity by $E_{(T)}(30)$ scale

$[EtNH_3][NO_3]$ 0.95 between CF_3CH_2OH and water

[BMIM] PF_6 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 ºC

$BiCl_3$, $SrCl_2$, $CaCl_2$, $CuCl_2$ dissolve well

Constituent	$BiCl_3$	$SrCl_2$	$CaCl_2$	$CuCl_2$
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

$2\ HCOOH + Si(OMe)_4 \longrightarrow ag\text{-}SiO_2 + 2\ MeOH + 2\ HCOOMe$

Natural gas sweetening (H_2S, CO_2 removal)

Electrolytes in batteries or solar cells

Dissolving spent nuclear fuel (U^{4+} oxidized to U^{6+})

Extraction

Enyzme activity

Applications of Ionic Liquids

Olefin polymerization
Ethene + $TiCl_4$ + $AlEtCl_2$ in acidic IL
Ethene + Cp_2TiCl_2 + $Al_2Me_3Cl_3$ in acidic IL

$$Cp_2TiCl_2 + [\text{cation}]^+[Al_2Cl_7]^- \leftrightarrows [Cp_2TiCl]^+ + [\text{cation}]^+ + 2\,[AlCl_4]^-$$

Olefin hydrogenation
Cyclohexene + H_2 + $[RhCl(PPh_3)_3]$ (Wilkinson’s catalyst)