

Ionic liquids

Ionic liquids are a category of salt which are in liquid state at room temperature and made up entirely of ions.

Properties:

- Ionic liquids are restricted to salts whose melting point is below 100 °C (212 °F).
- Any salt that melts without decomposing or vaporizing usually yields an ionic liquid.
- While ordinary liquids such as water is predominantly made of electrically neutral molecules, ionic liquids are largely made of ions and short-lived ion pairs.
- Ionic liquids are variously called liquid electrolytes, ionic melts, ionic fluids, fused salts, liquid salts, or ionic glasses.
- Ionic liquids are powerful solvents and can be used as electrolytes (electric battery).

Applications:

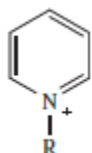
- ❖ Ionic liquids are good solvent for a range of polar and non-polar compounds.
- ❖ Ionic liquids are used as solvent to conduct Dies-Alder reactions and Friedel - Crafts reactions.
- ❖ Olefins are highly soluble, Aliphatic Compounds are sparingly soluble and aldehydes are miscible in ionic liquids.
- ❖ Ionic liquids are thermally stable (10K to 500 K), Low vapor pressure, Low Flammability and non Volatile.
- ❖ Ionic liquids have good solubility of CO₂, but less solubility of CO, Therefore Ionic liquids are used in separation of CO₂.
- ❖ Ionic liquids shows long liquid range (upto 400 °C), Therefore Ionic liquids are used in solubility of more number of compounds.

Examples:

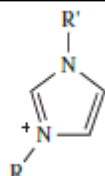
1. One of the earliest truly room temperature ionic liquid was **Ethylammonium Nitrate** ($\text{C}_2\text{H}_5\text{NH}_3^+ \cdot \text{NO}_3^-$) (m.p. 12 °C), reported in 1914 by Paul Walden
2. **Ethanolammonium nitrate**, $\text{C}_2\text{H}_5\text{NH}_3^+ \cdot \text{NO}_3^-$, (m.p. 52–55 °C) was reported in 1888 by S. Gabriel and J. Weiner.

Ionic Liquid System: Thousand numbers of ionic liquids are available by mixing salts of organic cation and organic/inorganic anion as follows

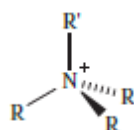
Organic cation	Organic/inorganic anion
Alkyl imidazolium	Tetra fluoro borate (BF_4^-)
Alkyl Pyridinium	Hexa fluoro phosphate (PF_6^-)
Alkyl Ammonium	Tosylate
Alkyl Phosphonium	Aluminium tetrachloride (AlCl_4^-)
	Sulphite (SO_3^-)



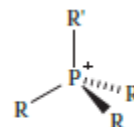
Alkyl Pyridinium



Alkyl imidazolium



Alkyl Ammonium

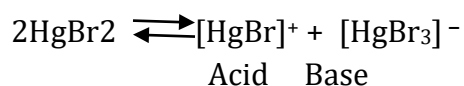


Alkyl Phosphonium

Molten salt (Ionic Liquid) solvent systems:

The solvent system of Ionic Liquid can be explained by taking NaCl system as an example. When an ionic salt such as NaCl melts, its ionic lattice will be collapsed, but some order is still retained which was evidenced by X-ray diffraction patterns. The coordination number will also decrease from 6 to 4. The internuclear distances are larger than for cation-anion separations. The solid-to-liquid transition is accompanied by an increase in volume of ~10–15%.

Other alkali metal halides behave in a similar manner to NaCl, but metal halides (e.g. Hg(II) halides) in which the bonding has a significant covalent contribution form melts as following reaction



In terms of non-aqueous solvent, above equation illustrates that, in molten HgBr_2 , species producing $[\text{HgBr}]^+$ ions may be considered to act as acids, and those providing $[\text{HgBr}_3]^-$ ions function as bases.

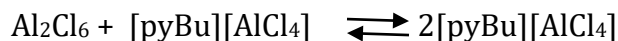
One more important molten salt with more convenient operating temperature is tetrachloroaluminate $[\text{AlCl}_4]^-$ ion.



The melting point of Al_2Cl_6 is 463K (at 2.5 bar), and its addition to NaCl (melting point, 1073 K) results $[\text{AlCl}_4]^-$ with a melting point of 446 K.

Ionic liquids at ambient temperatures:

Ionic liquids show solvent properties at room temperature or below 100 °C (Ambient temperature). Another well-established and useful system consists of Al_2Cl_6 with an organic salt such as butylpyridinium chloride, $[\text{pyBu}]\text{Cl}$; occurs to give ionic liquid $[\text{pyBu}][\text{AlCl}_4]$,

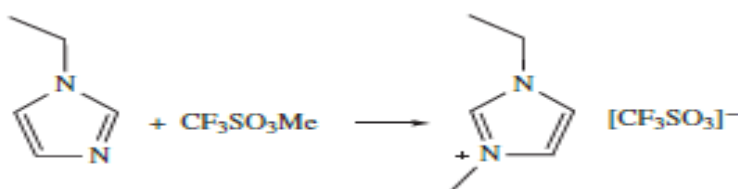


Applications of $2[\text{pyBu}][\text{AlCl}_4]$ are as follows:

1. It is a conducting liquid below 373 K.
2. It dissolves a wide range of inorganic and organic compounds
3. It has long liquid ranges, high thermal stabilities, negligible vapour pressures (this enables product separation by distillation), and the fact that they are non-flammable.
4. It replaces organic solvents from organic reactions like, Diels–Alder reactions, Friedel–Crafts alkylations and acylations, and Heck reactions.

Production of Ionic Liquids:

Direct Reaction: Some ionic liquids can be formed by the direct reaction of pyridine or alkylimidazole, with an appropriate alkylating agent.



Imidzolium

The range of compounds can be produced either by reaction with a Lewis acid (e.g. AlCl_3 , BCl_3 , CuCl , SnCl_2). Reactions with Lewis acids give species which may contain more than one anion (Table) depending on the ratio of $[\text{X}]\text{Cl}$: Lewis acid.

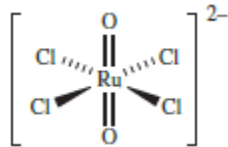
Reagents for ionic liquid formation	Anions present in the ionic liquid
$[\text{X}]\text{Cl} + \text{AlCl}_3$	Cl^- , $[\text{AlCl}_4]^-$, $[\text{Al}_2\text{Cl}_7]^-$, $[\text{Al}_3\text{Cl}_{10}]^-$
$[\text{X}]\text{Cl} + \text{BCl}_3$	Cl^- , $[\text{BCl}_4]^-$
$[\text{X}]\text{Cl} + \text{AlEtCl}_2$	$[\text{AlEtCl}_3]^-$, $[\text{Al}_2\text{Et}_2\text{Cl}_5]^-$
$[\text{X}]\text{Cl} + \text{CuCl}$	$[\text{CuCl}_2]^-$, $[\text{Cu}_2\text{Cl}_3]^-$, $[\text{Cu}_3\text{Cl}_4]^-$
$[\text{X}]\text{Cl} + \text{FeCl}_3$	$[\text{FeCl}_4]^-$, $[\text{Fe}_2\text{Cl}_7]^-$
$[\text{X}]\text{Cl} + \text{SnCl}_2$	$[\text{SnCl}_3]^-$, $[\text{Sn}_2\text{Cl}_5]^-$

Applications of molten salt/ionic liquid media:

1. **Isolation of Cations:** Some unusual cations have been isolated as products from reactions in molten salt media.

For example, the reaction of Bi and BiCl₃ in KCl–BiCl₃ solvent at 570K yields [Bi₉]₂[BiCl₅]₄[Bi₂Cl₈] which contains [Bi₉]⁺, [BiCl₅]²⁺ and [Bi₂Cl₈]²⁻

2. The Anionic d-block metal chloro complexes and organometallic compounds are unstable in some solvents but stable in ionic liquid [Al₂Cl₆-ethylpyridinium chloride]



d-block metal chloro complexes

3. [TiOCl₄]²⁻ are toxic nature, but this toxicity can be removed by addition of COCl₂
Reaction: [TiOCl₄]²⁻ + COCl₂ → [TiCl₆]²⁻ + CO₂

Supercritical fluids

At temperatures and pressures above the critical temperature and pressure (i.e. above the critical point), a substance becomes a supercritical fluid.

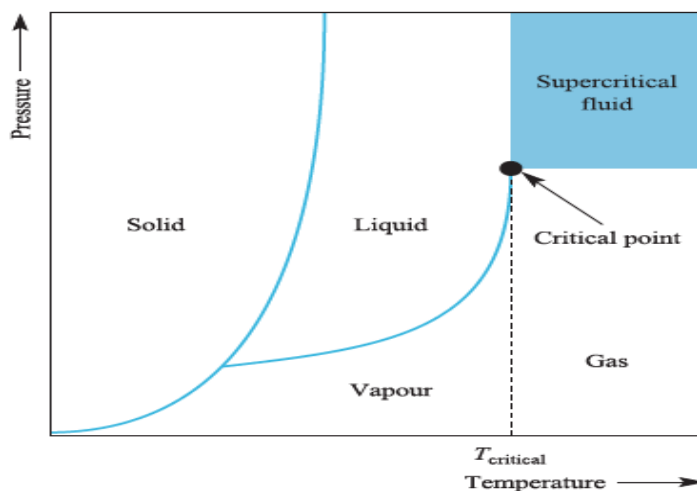
Properties:

- A supercritical fluid possesses non-polar-solvent properties that resemble those of a liquid, but also exhibits gas-like transport properties. Act as good solvent for polar-solutes and poor solvent for non-polar-solutes.
- Supercritical fluids are low cost, easy accessibility, low cost, non-toxicity, chemical inertness and non-inflammability, therefore used as a solvent, and in many commercial applications.
- Thus, not only can a supercritical fluid dissolve solutes, but it is also miscible with ordinary gases and can penetrate pores in solids.
- Supercritical fluids exhibit lower viscosities and higher diffusion coefficients than liquids.
- The density of a supercritical fluid increases as the pressure increases, and as the density increases, the solubility of a solute in the supercritical fluid increases dramatically.
- Supercritical fluids are used as green solvents to replace volatile organic solvents.
- Supercritical fluids used in the extraction of toxic metals present in the food.
- Critical temperatures and pressures of selected compounds with applications as supercritical fluids.

Compound	Critical temperature / K	Critical pressure / MPa
Xenon	289.8	5.12
Carbon dioxide	304.2	7.38
Ethane	305.4	4.88
Propane	369.8	4.25
Ammonia	405.6	11.28
Pentane	469.7	3.37
Ethanol	516.2	6.38
Water	647.3	22.05

Two other well-studied solvents are supercritical NH_3 and H_2O . The critical temperature and pressure of supercritical NH_3 are accessible, but it is chemically very reactive and is relatively hazardous for large-scale applications. Supercritical H_2O has a relatively high critical temperature and pressure which limit its uses. Even so, it has important applications as a solvent. At its critical point, the density of water is 0.32 g cm^3 ; the density of the supercritical phase can be controlled by varying the temperature and pressure. Unlike subcritical H_2O , supercritical H_2O behaves like a non-polar solvent. Thus, it is a poor solvent for inorganic salts, but dissolves nonpolar organic compounds. This is the basis for its use in supercritical water oxidation (or hydrothermal oxidation) of toxic and hazardous organic wastes. In the presence of a suitable oxidizing agent, liquid organic waste in scH_2O is converted to CO_2 , H_2O , N_2 and other gaseous products with efficiencies approaching 100%.

Phase diagram of Supercritical fluid

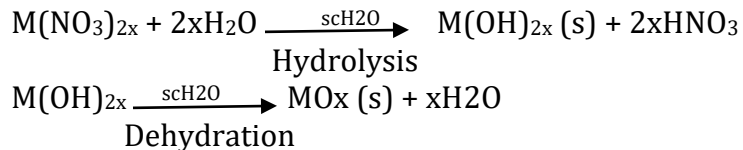


The solid lines represent the boundaries between the phases. The hashed line illustrates the distinction between a vapour and a gas; a vapour can be liquefied by increasing the pressure, while a gas cannot. Above the critical temperature, T_{critical} , the gas can no longer be liquefied, no matter how high the pressure is increased.

Supercritical fluids as media for inorganic chemistry:

In this section, the inorganic reactions that are carried out in supercritical water (scH₂O) and ammonia (scNH₃) were discussed. An important application of scH₂O is in the hydrothermal generation of metal oxides from metal salts (or supercritical hydrothermal crystallization).

where, for example, M=Fe(III), Co(II) or Ni(II).



Supercritical amines have been found to be useful solvents for the assembly of complex metal sulfides, including K₂Ag₆S₄, KAgSbS₄, Rb₂AgSbS₄, KAg₂SbS₄, KAg₂AsS₄ and RbAg₂SbS₄. Use of scNH₃ allows these solid state compounds to be prepared at lower temperatures than more traditional routes used to synthesize related compounds such as SrCu₂SnS₄.

