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M. Sc. Chemistry

Semester II (CBCS)

C 204 Analytical chemistry

Green chemistry-

Green solvents used in the organic synthesis

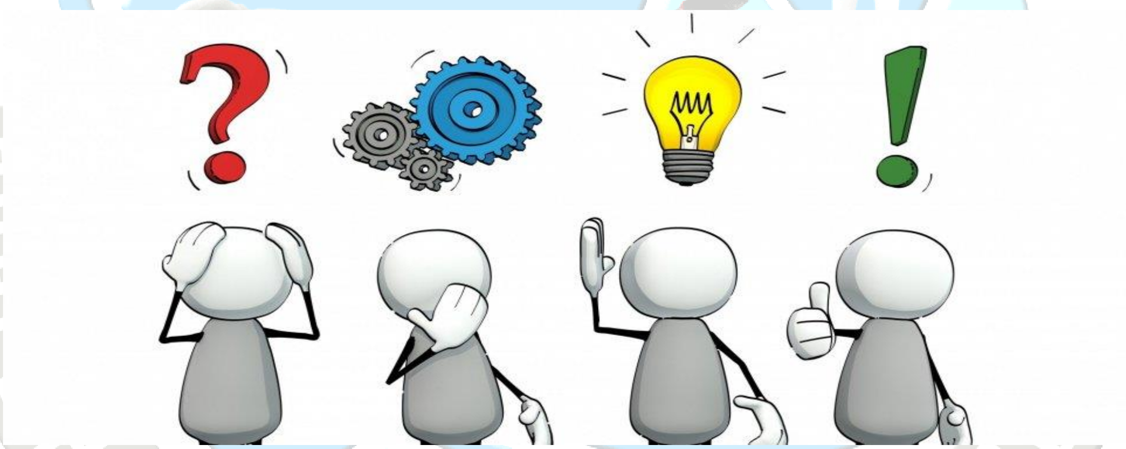
Prepared by;

Rahul Talaviya

What is solvent?

A solvent is the component of a solution that is present in the greatest amount. It is the substance in which the solute is dissolved. Usually, a solvent is a liquid.

- The conventional solvents used in chemical, pharmaceutical, biomedical and separation processes represent a great challenge to green chemistry because of their toxicity and flammability.
- Since the beginning of "the 12 Principles of Green Chemistry" in 1998, a general effort has been made to replace conventional solvents with environmentally benign substitutes.
- Water has been the most popular choice so far, followed by ionic liquids, surfactant, supercritical fluids, fluorous solvents, liquid polymers, bio-solvents and switchable solvent systems.
- Green chemistry is getting extended in many researches and industry areas due to its advantages such as decreasing of waste and cost.



The idea of "green" solvents expresses the goal to minimize the environmental impact resulting from the use of solvents in chemical production. Here the question is raised of how to measure how "green" a solvent is.

What is a green solvent?

Green solvent or also known as bio-solvent is typically an alternative to the conventional solvents available in the market.

It is an innovative idea of reducing the environmental impact resulting from the use of solvents in chemical production.

How is a green solvent produced?

Currently, there are four methods of producing a green solvent namely:

- Substitution of hazardous solvents with ones that show better environmental, health and safety properties.
    - **(Example: Ability to biodegrade or ability to reduce ozone depletion.)**
- Production of solvents using renewable resources.
    - **(Example: Fermentation of agricultural waste to produce ethanol.)**
- Substitution of organic solvents with environmentally harmless supercritical fluids.
    - **(Example: Usage of supercritical CO2 instead of CFC.)**
- Substitution of organic solvents with ionic liquids of low volatility.
    - **(Example: Lowering emission of volatile com-pounds to the atmosphere.)**

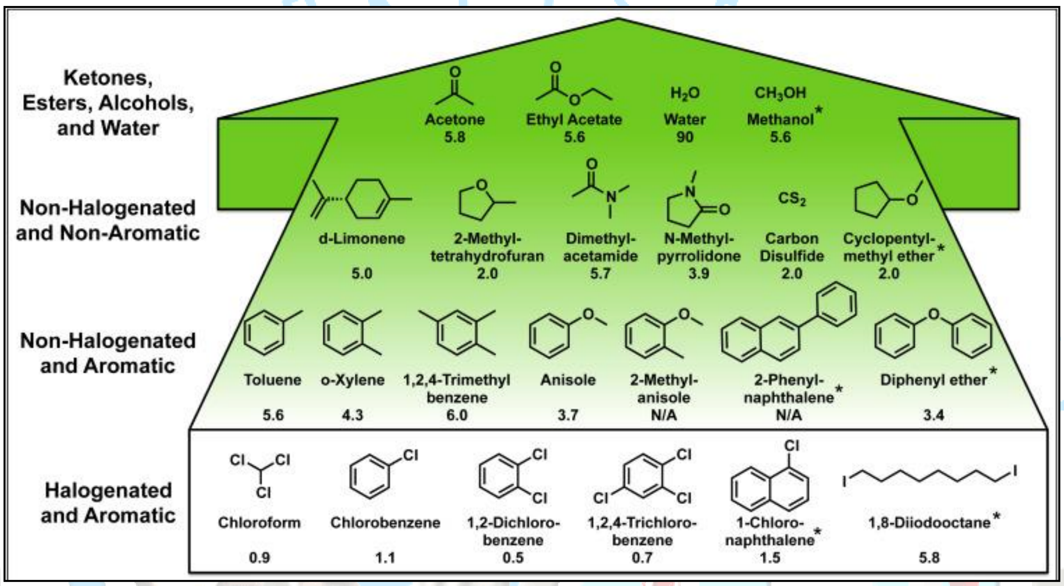
Why is green solvent better?

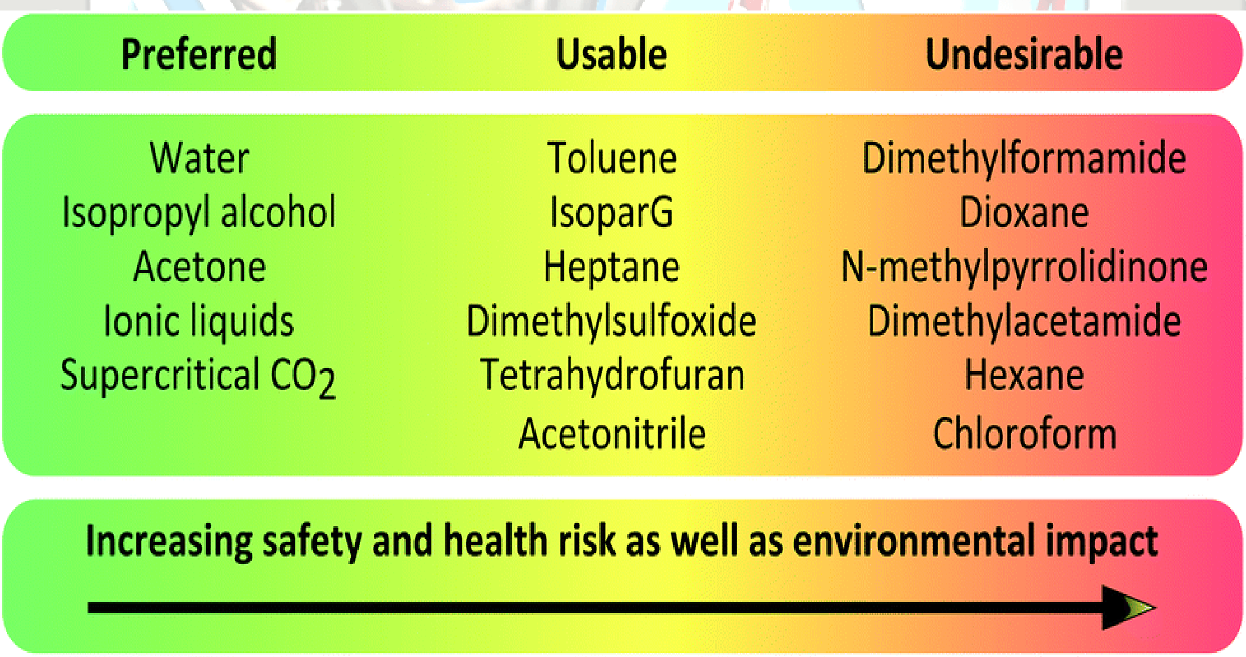
Green solvent has a lower environmental impact compared to other conventional petroleum based solvents.

- **Completely biodegradable**
- **Can be recycled**
- **Non-corrosive**
- **Non-carcinogenic**
- **Non-ozone depleting**
- **Attractive solvent properties**
- **Produced from renewable re-sources**

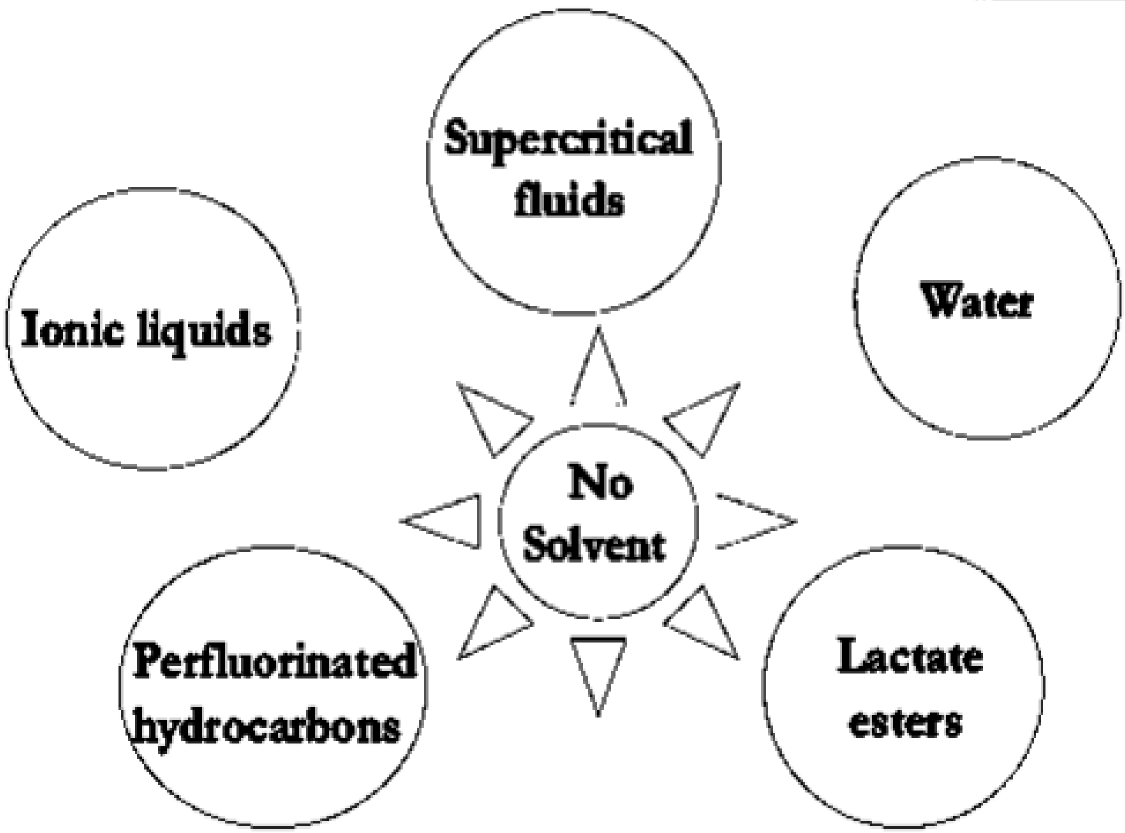
What are the types of green solvents?

Since green solvents can be produced via a variety of processes as illustrated earlier, there are a variety of green solvents currently available in the industry.

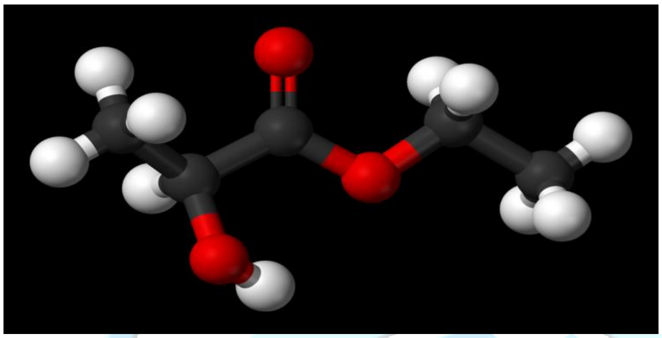


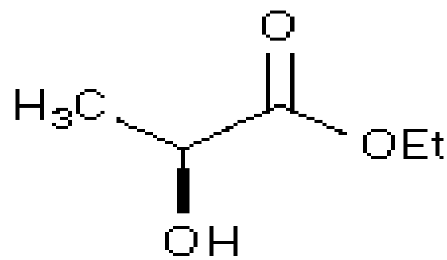


Greener Solvent Alternatives



Ethyl lactate





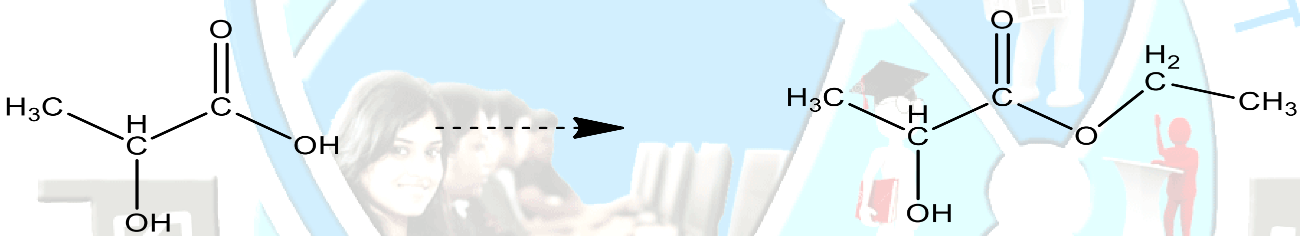
- Chemical formula — $C_5H_{10}O_3$
- Molar mass — 118.132 g·mol^{-1}
- Appearance — Clear to slightly yellow liquid
- Density — 1.03 g/cm^3
- Melting point — −26 °C (−15 °F; 247 K)
- Boiling point — 151 to 155 °C (304 to 311 °F; 424 to 428 K)
- Solubility in water — Miscible
- Solubility in ethanol and most alcohols — Miscible

➢ Ethyl lactate is a green solvent derived from processing corn.

➢ Ethyl lactate is the ester of lactic acid.

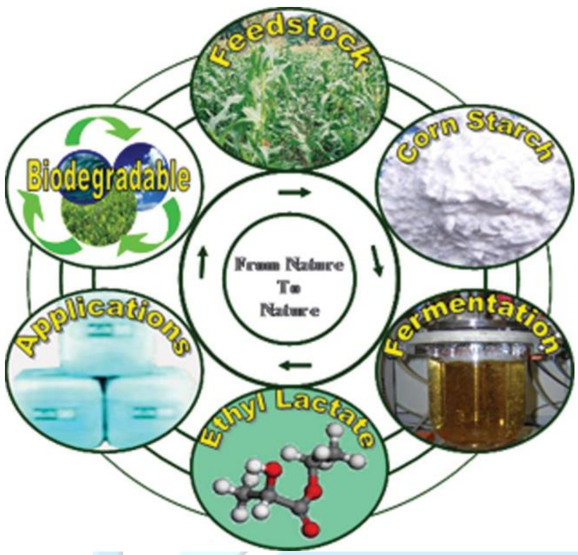
➢ Ethyl lactate is an environmentally benign solvent with effectiveness comparable to petroleum-based solvents.

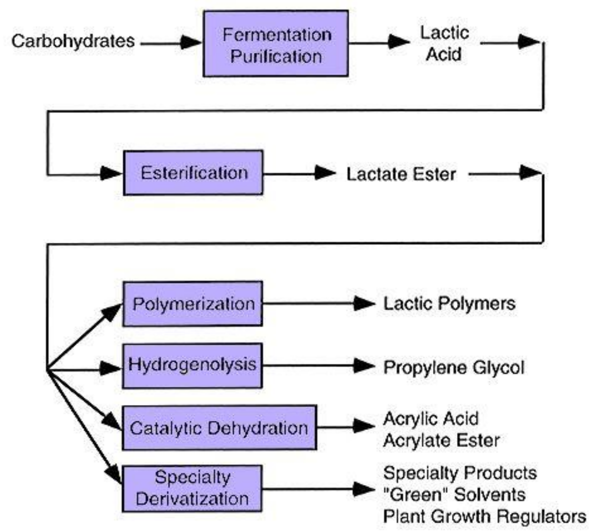
- Lactate esters solvents are commonly used solvents in the paints and coatings industry and have numerous attractive advantages including being **100% biodegradable, easy to recycle, non-corrosive, non-carcinogenic and non-ozone depleting**.
- Ethyl lactate is a particularly attractive solvent for the coatings industry as a result of its high solvency power, high boiling point, low vapour pressure and low surface tension.
- It is a desirable coating for wood, polystyrene and metals and also acts as a very effective paint stripper and graffiti remover.
- Ethyl lactate has replaced solvents including toluene, acetone and xylene, which has resulted in the workplace being made a great deal safer.



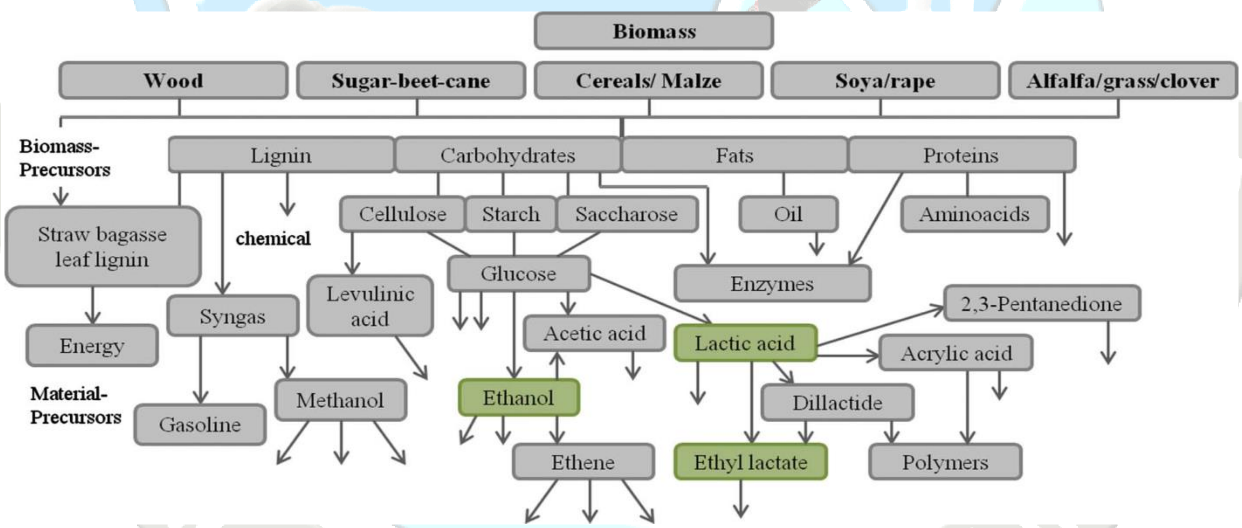
Why it is so important?

- Ethyl lactate can be produced from renewable raw materials that can be a more environmentally friendly alternative to petrochemical solvent
- Ethyl lactate is 100% biodegradable
- Easy to recycle,
- Non-corrosive, non-carcinogenic
- Non-ozone depleting.
- Ethyl lactate can be produced through heterogeneous catalysis without using an excess of any of the reactants



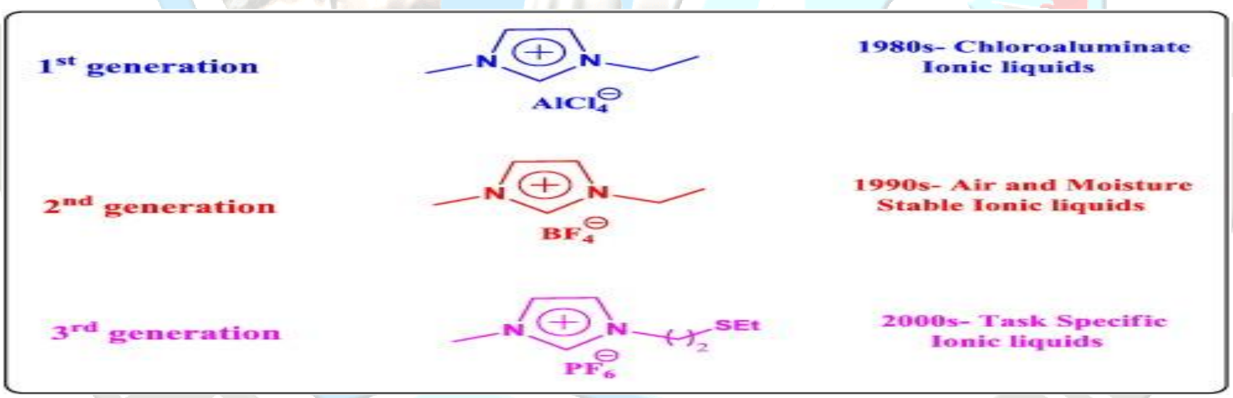


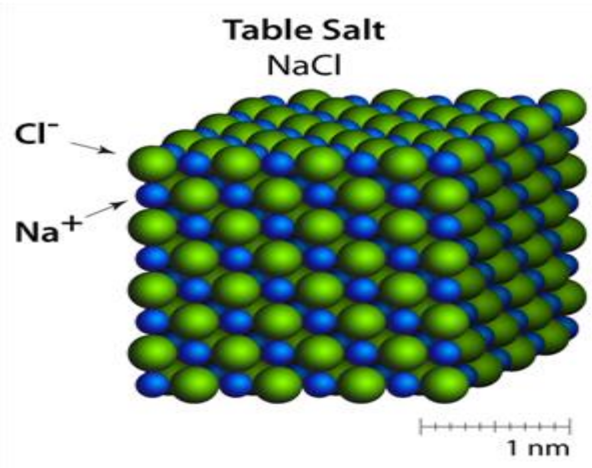
Just for information

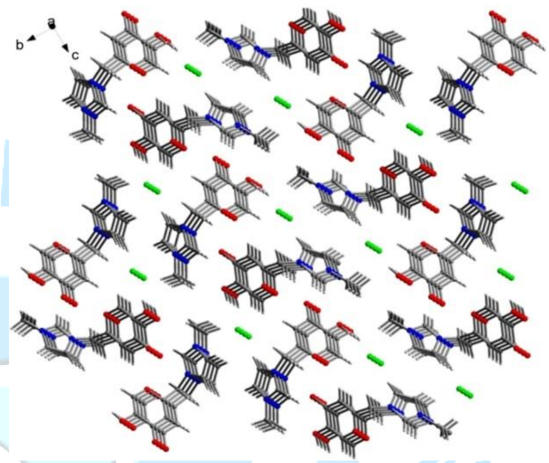


Ionic liquids

- Ionic liquids are mixtures of anions and cations, molten salts, with melting point around 100o C, which can be used as alternative solvents in organic synthesis.
- An ionic liquid (IL) is a salt in the liquid state.
- Any salt that melts without decomposing or vaporizing usually yields an ionic liquid.
- Although the ionic liquids do not completely full with green chemistry principles, they are very promising as alternatives to organic solvent use in synthetic routes and various applications.
- These substances are variously called liquid electrolytes, ionic melts, ionic fluids, fused salts, liquid salts, or ionic glasses.
- Low-temperature ionic liquids can be compared to ionic solutions, liquids that contain both ions and neutral molecules, and in particular to the so-called deep eutectic solvents, mixtures of ionic and non-ionic solid substances which have much lower melting points than the pure compounds.





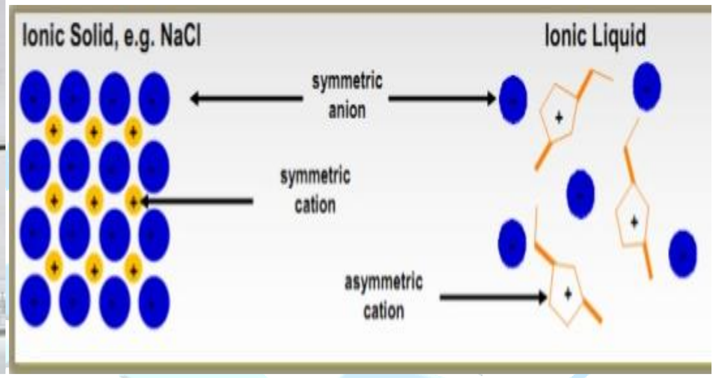


Traditional salts like sodium chloride are able to efficiently pack to form a crystal lattice

With ionic liquids the cation are asymmetrically substituted with different length groups to prevent the packing of the cations/anions into a crystal lattice

Physical properties

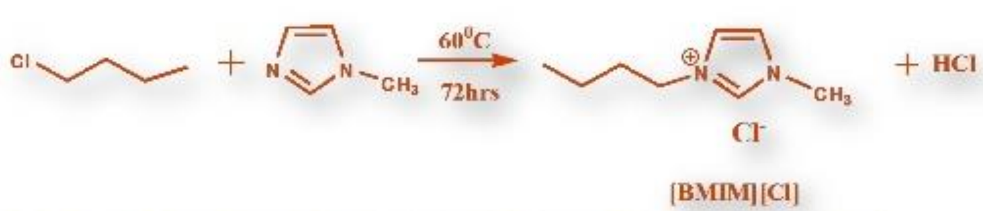
- Ionic liquids are often moderate to poor conductors of electricity,
- non-ionizing (e.g., non-polar),
- highly viscous and
- Frequently exhibit low vapours pressure.
- low combustibility
- thermally stable
- Favourable solvating properties for a range of polar and non-polar compounds
- Electrochemically stable
- Low toxicity
- Non-volatile



Synthesis

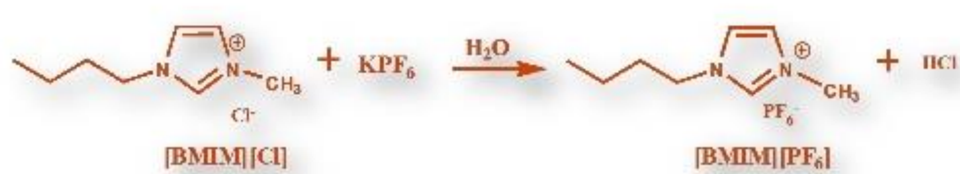
- Two Steps:

(1) Quaternization step



Using HPF_6:

Using KPF_6:



Application

Homogeneous and heterogeneous catalyst

For some applications, ionic liquids offer the advantage of both homogeneous and heterogeneous catalysts. This is because selected ionic liquids can be immiscible with the reactants and products but dissolve the catalysts.

"This has the advantages of a solid for immobilizing the catalyst, with the advantages of a liquid for allowing the catalyst to move freely"

Biological reactions media

"Enzymes are also stable in ionic liquids, opening the possibility for ionic liquids to be used in biological reactions, such as the synthesis of pharmaceuticals"

Treatment of high-level nuclear waste

"Ionizing radiation does not affect ionic liquids, so they could even be used to treat high-level nuclear waste"

Removing of metal ions

In another application, Davis and Rogers have designed and synthetized several new ionic liquids to remove cadmium and mercury from contaminated water. When these water-insoluble ionic liquids come in contact with contaminated water, they snatch the metal ions out of water and sequester them in the ionic liquid.

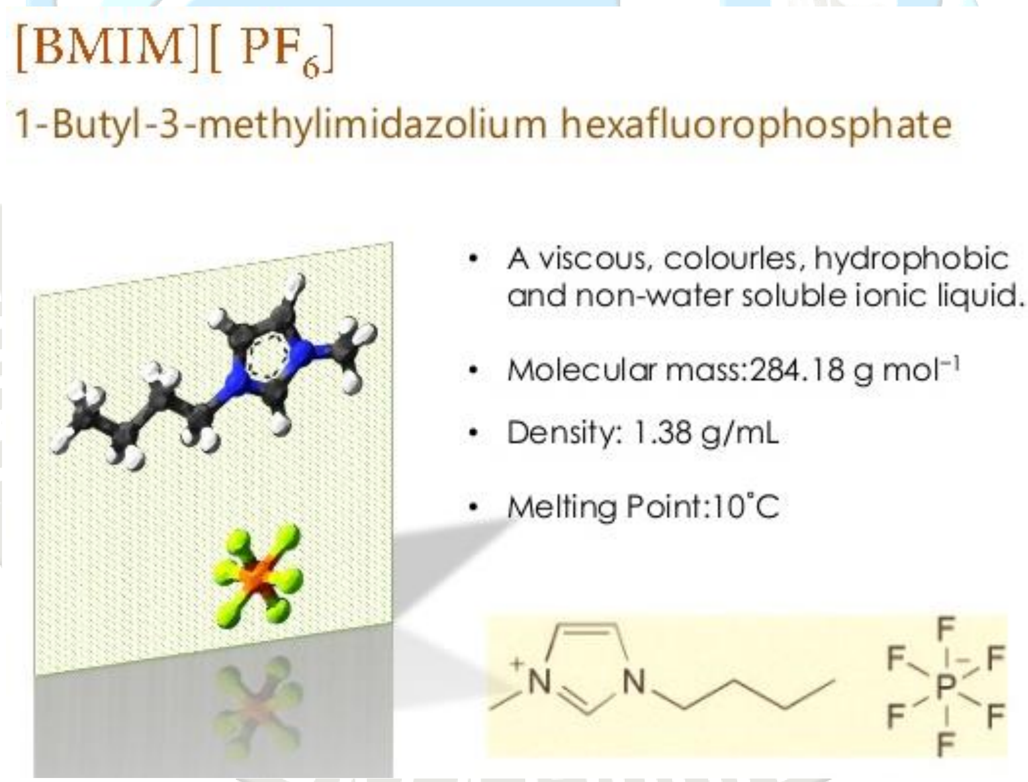
Solar thermal energy

Ionic Liquids are potential heat transfer and storage media in solar thermal energy systems. Concentrating solar thermal facilities such as parabolic troughs and solar power towers focus the sun's energy onto a receiver, which can generate temperatures of around 600 °C (1,112 °F). This heat can then generate electricity in a steam or other cycle. For buffering during cloudy periods or to enable generation overnight, energy can be stored by heating an intermediate fluid.

Batteries

ILs can replace water as the electrolyte in metal-air batteries. Ionic Liquids are attractive because of their low vapor pressure, increasing battery life by drying more slowly.

Nomenclature



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Supercritical fluid (SCF)

What is Supercritical fluid (SCF)?

- A **supercritical fluid** (**SCF**) is any substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist. It can effuse through solids like a gas, and dissolve materials like a liquid.

The fluid is said "supercritical" when it is heated above its critical temperature and compressed above its critical pressure.

- In addition, close to the critical point, small changes in pressure or temperature result in large changes in density, allowing many properties of a supercritical fluid to be "fine-tuned".
- Supercritical fluids are suitable as a substitute for organic solvents in a range of industrial and laboratory processes.

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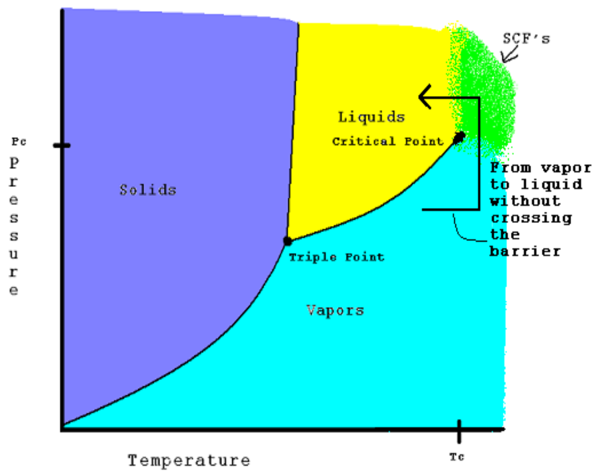
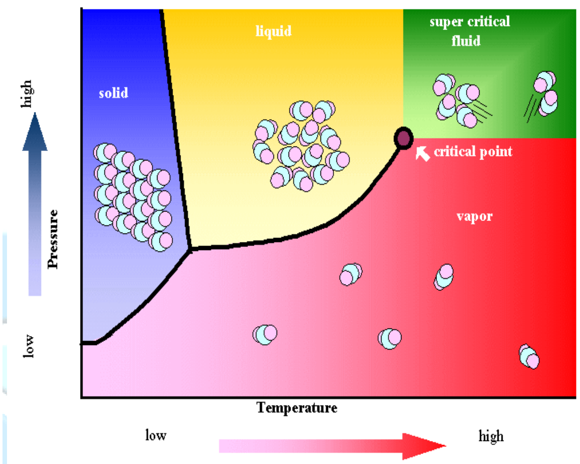




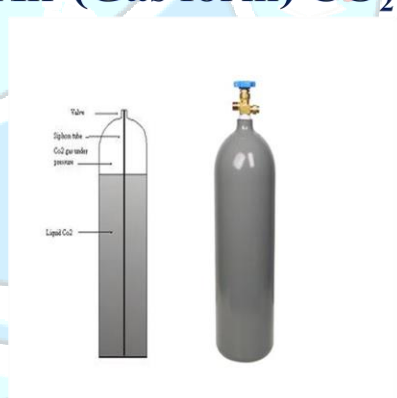
- In general terms, supercritical fluids have properties between those of a gas and a liquid.
- In the supercritical region, the fluid exhibits particular properties and has an intermediate behavior between that of a liquid and a gas.
- In particular, supercritical fluids (SCFs) possess liquid-like densities, gas-like viscosities and diffusities intermediate to that of a liquid and a gas.
- The most widely used supercritical fluids are CO2 and water.

Supercritical CO2 fluid

What is supercritical CO_2?

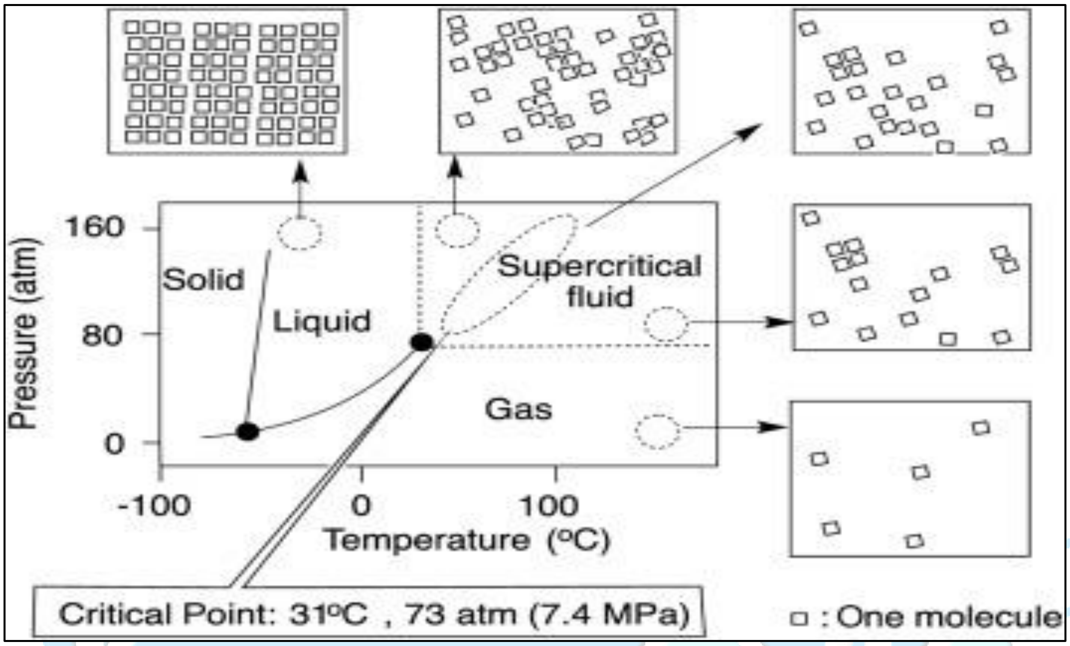
- Carbon dioxide (CO2) is the most widely used supercritical fluid.
- This is because CO2 is **cheap, chemically inert, non-toxic, non-flammable and readily available at high purities and at low costs**.
- Besides, the critical point of CO2 is easily accessible (critical temperature 31°C and critical pressure 74 bar) allowing the fluid to be used at mild conditions of temperatures (40-60°C) without leaving harmful organic residues.
- Due to its interesting properties Supercritical CO2 can be described as a "green" solvent.
- **Supercritical carbon dioxide** (sCO_2) is a fluid state of carbon dioxide where it is held at or above its critical temperature and critical pressure.

Air (Gas form) CO_2



Liquid CO_2

Dry ice (solid form) CO_2

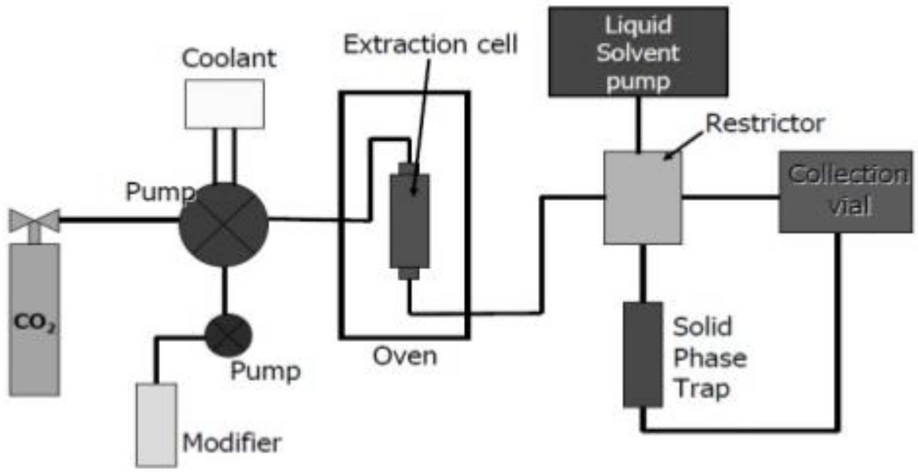


Carbon dioxide (CO_2) is the most widely used supercritical fluid.

- This is because CO_2 is cheap,
- chemically inert,
- non-toxic,
- non-flammable
- Readily available at high purities and at low costs. CO_2 can be described as a "green" solvent.
- Supercritical CO2 is a good solvent for many non-polar, and a few polar, low-molecular-weight compounds
- To increase the solubility of high molecular weight compounds in supercritical CO2, small amounts of polar or non-polar co-solvents may be added

Super critical fluid extraction

It is the process of separating one component from another using supercritical fluid as the extracting solvent



Applications

- In extraction of food and natural products using supercritical or liquid CO_2 can be considered a relatively mature CO_2 technology.
- A wide range of other applications for supercritical CO_2 has been investigated, including chemical reactions, polymer production and processing, semiconductor processing, powder production, environmental and soil remediation and dry cleaning.
- Several of these applications are highlighted here.

Chemical reactions

- Supercritical CO_2 has been tested in a variety of industrially important reactions, such as alkylations, hydroformylations, and hydrogenation, as an alternative reaction medium.
- The incentives to use supercritical CO_2 as reaction medium can include
  (a) Replacement of the conventional organic solvent with a “green” solvent,

(b) Improved chemistry such as reactivity and selectivity,

(c) New chemistry, and

(d) improved separation and recovery of products and catalysts.

- Relatively high rates of molecular diffusion and heat transfer are possible with a homogenous, supercritical-CO_2 reaction-medium.

Polymer production and processing

- Applications of supercritical CO_2 in polymers include polymerization, polymer composite production, polymer blending, particle production, and microcellular foaming.
- At moderate pressure, very few polymers show any significant solubility in CO_2.
- Very high pressure is typically needed to dissolve polymers in supercritical CO_2.
- One example of this application area is a process to produce fluoropolymers using supercritical CO_2 as the reaction medium that was developed by scientists at the University of North Carolina (Chapel Hill).

Semiconductor processing

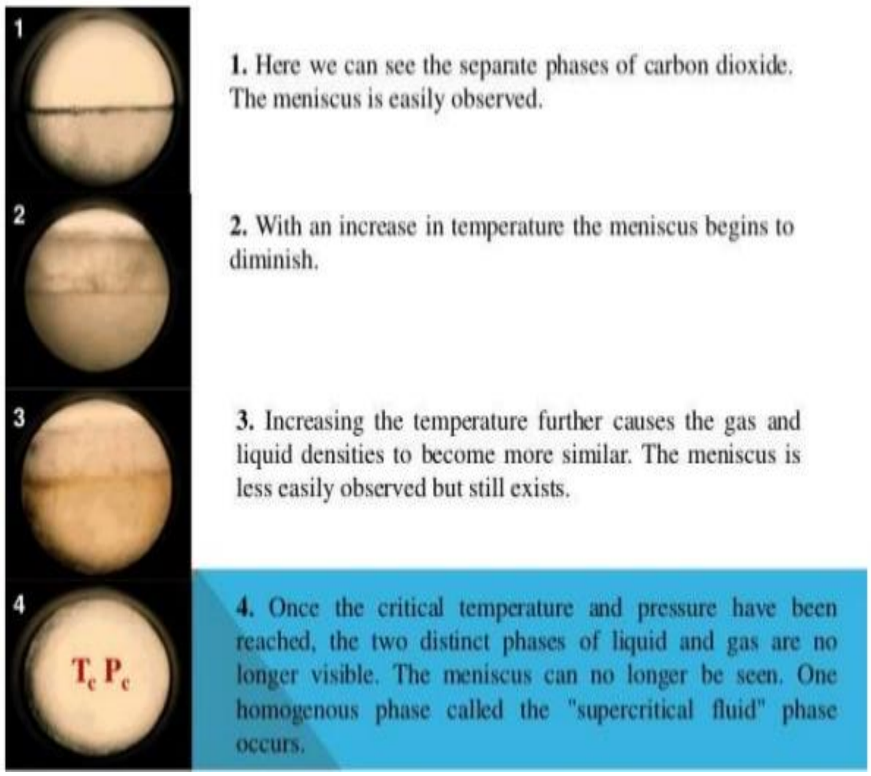
- Currently, chip manufacturing involves many wet-chemical processes that use hydroxyl amines, mineral acids, elemental gases, organic solvents and large amounts of high purity water during chip fabrication.
- One potential application is the use of supercritical CO2 in wafer processing.
- The low viscosity and surface tension of supercritical CO2 allow for efficient cleaning of small feature sizes, which is of great importance with the continued miniaturization of integrated circuits.

Powder production

- One promising application for supercritical CO2 is the production of micro- and nano-scale particles.
- The pharmaceutical industry currently uses supercritical CO2 mainly to control the powder particle size of products during synthesis.
- The use of supercritical CO2 for micronization of pharmaceutical compounds has several potential advantages over conventional techniques such as spray drying, jet milling and grinding.

- These advantages include minimum product contamination, reduced waste streams, suitability for the processing of thermally, shock or chemically sensitive compounds and the possibility of producing particles with narrow size distribution in a single-step operation.

Just for Knowledge



Supercritical water fluid

- **Water, in the subcritical phase** (pressure: 15 to 100 bar, temperature: 150 to 250°C) can solubilise hydrophobic compounds.
- Therefore, subcritical water (sometimes referred to as hot compressed water) can be used for the extraction of plant materials.
- **In supercritical water** organic compounds and gases become highly miscible and precipitation of inorganic compounds occurs.
- Oxidation reactions in supercritical water can also be performed.
- The critical point of water is much higher than that of CO2.
- However its applications are very promising and some are in the process of industrialization. Processes using subcritical and supercritical water are called hydrothermal processes.
- The properties of supercritical water are very different from ambient liquid water
- For example, supercritical water is a poor solvent for electrolytes, which tend to form ion-pairs. However, it is such an excellent solvent for non-polar molecules, due to its low relative permittivity (dielectric constant) and poor hydrogen-bonding, that many are completely miscible.

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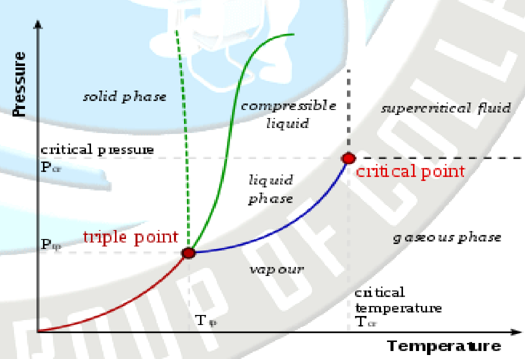

In supercritical water organic compounds and gases become highly miscible and precipitation of inorganic compounds occurs. Oxidation reactions in supercritical water can also be performed.

- Supercritical water has total miscibility with organic fluids and oxygen in supercritical equilibrium and presents a reactive environment capable of oxidizing toxic waste.
- Under extreme conditions (e.g., 2.38 g cm-3, 3000 K), it may be extremely reactive causing explosive reactions.
- The wide range of inorganic material solubility under varying temperature and pressure gives rise to many synthetic processes.
- As with other supercritical fluids, supercritical water has high compressibility and low viscosity.
- Supercritical water can form a homogeneous phase with inorganic and organic substances, and water itself works as an acid or base catalyst.

Extraction

- Supercritical fluids are used in extraction of chemical compounds from natural sources.
- The advantages of supercritical fluid extraction are that it is relatively rapid because of the low viscosities and high diffusivities associated with supercritical fluids.
- The extraction can be selective to some extent by controlling the density of the medium and the extracted material is easily recovered by simply depressurizing, allowing the supercritical fluid to return to gas phase and evaporate leaving little or no solvent residues.

Decaffeination

- Methods for decaffeinating coffee have been available since the early 20th Century.
- The aim is to remove caffeine without removing the compounds that give the coffee its flavor, and without leaving a toxic residue in the beans.
- Caffeine extraction generally takes place on “green" beans, before roasting.
- Extracted caffeine is sold to manufacturers of soft drinks and pharmaceuticals

Supercritical drying

- Drying is a mass transfer process consisting of the removal of water or another solvent by evaporation from a solid, semi-solid or liquid.
- This process is often used as a final production step before selling or packaging products.
- To be considered "dried", the final product must be solid, in the form of a continuous sheet (e.g., paper), long pieces (e.g., wood), particles (e.g., cereal grains or corn flakes) or powder (e.g., sand, salt, washing powder, milk powder).
- A source of heat and an agent to remove the vapor produced by the process are often involved.

Gaseous Anti-solvent

- GAS is a batch process where the precipitator is partially filled with the solution of solute of interest and then the supercritical antisolvent is pumped into the vessel, preferably from the bottom until the fixed pressure is reached.
- The particles precipitate as the gas concentration in the solution increases with pressure. After a holding time, the expanded solution is made to pass through a valve present above the precipitator to wash and clean the precipitated particles.

Supercritical Chromatography

- Supercritical Fluid Chromatography (SFC) is a form of normal chromatography, which is used for the analysis and purification of low to moderate molecular weight, thermally labile molecules. It can also be used for the separation of chiral compounds.
- Principles are similar to those of high performance liquid chromatography (HPLC).