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# Role of Green Solvents in Sustainable and Eco-viable Chemistry: A Review

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***Abstract***

*The environmental impact from solvent waste of chemical industries underscores the current need to find "greener" and more sustainable alternatives. "Green Chemistry" or "Sustainable Technology", as it is known today, can be shortly defined as a chemical working process, utilizing raw materials, eliminating waste and avoiding the use of toxic and hazardous reagents and solvents. Solvents define the major part of environmental performance of processes in chemical industry and also impact on cost, safety and health issues. Thus, the present review article focuses on the various aspects and applications of 'green' solvents.*

***Keywords:*** *Green Solvents, Supercritical Fluids, Ionic Liquids, Ethyl Lactate, Green Chemistry*

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## Introduction

Green chemistry focuses on the design of solvents that are eco-friendly, less harmful, have similar or preferably more efficiency than conventional solvents. Major environmental and economic damage is caused by conventional solvents due to release of volatile organic compounds (VOCs), hazardous air pollutants (HAPs), flammable, toxic chemicals and energy intensive separation processes. Moreover many solvents such as diethyl ether, tetrahydrofuran (THF) can form highly explosive organic peroxides upon exposure to oxygen and light and Chloroform and benzene are carcinogenic. In pharmaceutical industries, 80 % of the raw materials used in chemical processes are solvents. Solvents are required in chemical syntheses in pharmaceutical industries, chemical processing industries:

- To dissolve the reactants
- To stabilize a transition state formed during a chemical reaction
- To promote a reaction path
- To control the thermal exchange during the reactive event
- To purify the product
- To analyze the reaction mixture and run purity tests

Regulations under U.S. Pollution prevention act 1990 forces the industries to minimize the release of hazardous chemicals into the environment. Solvent use in chemical processes is main culprit in 80 % resource utilization, 70 % photochemical ozone depletion potential, 75 % energy requirement and about 50 % green house gases emission. Technologically viable and economically suitable solutions are required for replacement of traditional solvents by "greener" solvents that can promote sustainable chemistry. Greenness of solvents can be analyzed on the basis of its source & sustainability of its source, atom efficiency, energy processes, reusability and product separation processes and toxicity of by-products. Some principles of green chemistry focus on judicious use of solvents along with high product yield and selectivity without harming the economic and environmental viability of chemical processes [1] Greenness of a green solvent is determined by different factors as shown in Fig.1

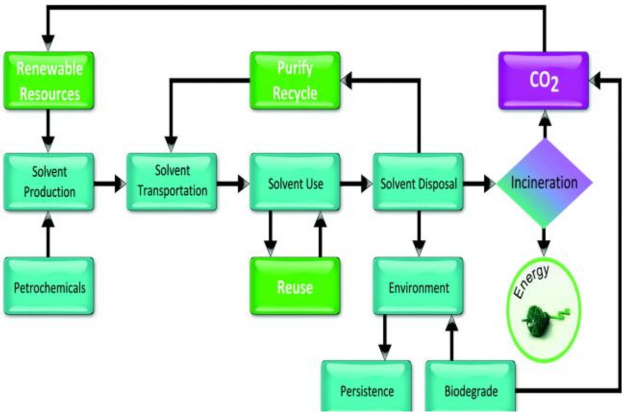


**Fig.1.** Factor that decide "greenness" of a solvent

Greener solvents such as supercritical fluids, ionic liquids, water and bio-solvents are discussed in this review and form basis of many cleaner chemical technologies that have reached commercial development.

## Supercritical fluids

Supercritical fluids represent the state of a substance above its critical temperature and pressure. In supercritical state the fluid exhibits intermediate behavior between that of a liquid and gas. In particular, SCFs have liquid like densities, gas like viscosities and diffusivities intermediate to that of a liquid and gas [2]. In general, SCFs differ from ordinary solvents in having both liquid-like solubilizing capacities whereas retaining high diffusivities and low viscosities of the gas phase. SCFs (Supercritical fluids) possess unusual physical properties which make them excellent media for carrying out various kinds of chemical reactions. These unusual properties are:

- Dissolving power of SCFs is comparable to that of liquids near their critical point.
- More compressibility as compared to dilute gases.
- "tunable" physical properties such as dielectric constant, density, refractive index etc. These adjustable properties of SCFs make them solvents for wide range of solutes [3].

Reactions carried out in SCFs possess benefits of high reaction rates, improved selectivity and elimination of mass transfer problems. Increased reaction rates and selectivity of reactions in SCFs are due to high solubility of reactant gases in SCFs, rapid diffusion of solutes into, out of, and within the supercritical phase, weakening of the solvation around reacting species, local clustering of reactants or solvent and reduction of cage effect in radical reactions. SCFs which are of utter importance in green chemistry are- $scCO_2$ and $scH_2O$.

## Supercritical carbon dioxide ($scCO_2$)

$scCO_2$ is fluid state of $CO_2$ at or above its critical temperature (304.1 K) & critical pressure (73.8 bar) as shown in Fig.2. As a reaction medium the attractive physical and toxicological inertness properties of supercritical carbon dioxide ($scCO_2$) have made it superior to conventional organic solvents. These properties are:

- $scCO_2$ has liquid-like density and gas-like viscosity and consequently leads to high solubility and rapid mass transfer velocity.
- Slight change of pressure near the critical point of $CO_2$ modify the solvent properties such as density, viscosity, diffusivity and polarity to change constantly from approximate gaseous to similar liquid state.
- Separation of $CO_2$ from the reaction mixture is energy-efficient and a product can be obtained by simple treatment.
- More importantly, $CO_2$ is inexpensive, nonflammable, nontoxic, environmentally friendly and one of the reaction media, which is favored for Green chemistry research.
- In addition it has an efficient mass-transfer, is completely miscible with gaseous reactants, and is very easy to separate from the product.

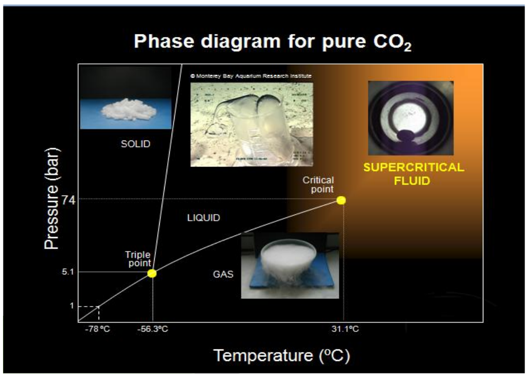


**Fig.2.** Phase diagram for pure $CO_2$

## Applications of $scCO_2$

- It is very efficient and "greener' solvent for extraction of essential oils [4], for decaffeination of coffee beans (Fig.3) [5], recovery of alkaloids such as theophylline, theobromine and pilocarpine among others [6].

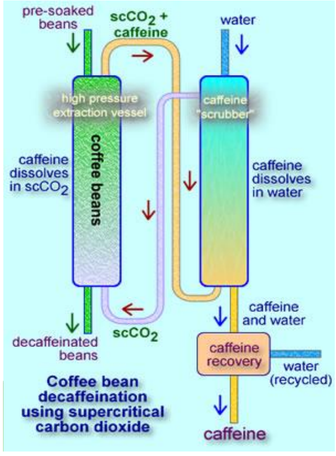


**Fig.3.**Coffee bean decaffeination using supercritical carbon dioxide

- $scCO_2$ is used in many chemical reactions as a reactant or reaction media. Styrene carbonate has been synthesized with 100% selectivity and 100% yield from styrene oxide and $scCO_2$ using $ZnBr_2$ and the quarternary salt n-$Bu_4NI$ as the catalyst [7].

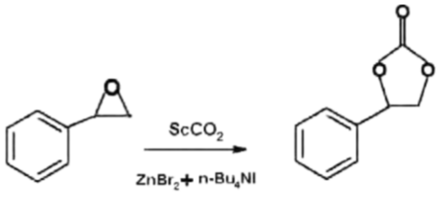


**Fig.4.** Reaction of styrene oxide with $CO_2$ to styrene carbonate in the presence of $scCO_2$

Due to high solubility of catalytic complexes of Rh in $scCO_2$, these catalytic systems can be used for hydroformylation of alkenes to aldehydes [8].

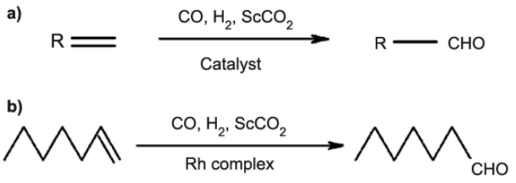


**Fig. 5**.(a). Hydroformylation reaction; (b). Hydroformylation of 1-hexene in $scCO_2$

- $ScCO_2$ has been successfully employed as a green solvent in material synthesis for the synthesis of material nanoparticles, high performance polymers, porous organic materials etc.
- Biodiesel production by esterification/transesterification of fatty acids or triglycerides in $scCO_2$ has been gaining increasing research interest.

### Supercritical water

$scH_2O$ is state of water at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist.

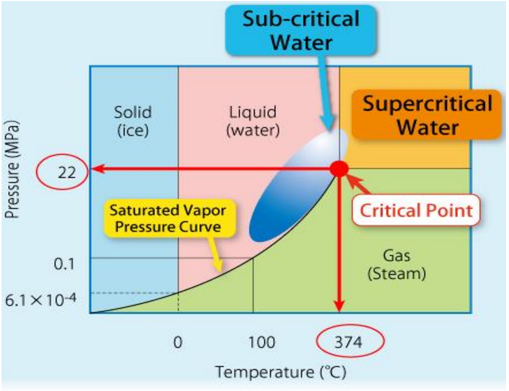


**Fig.6.** Phase diagram of pure water

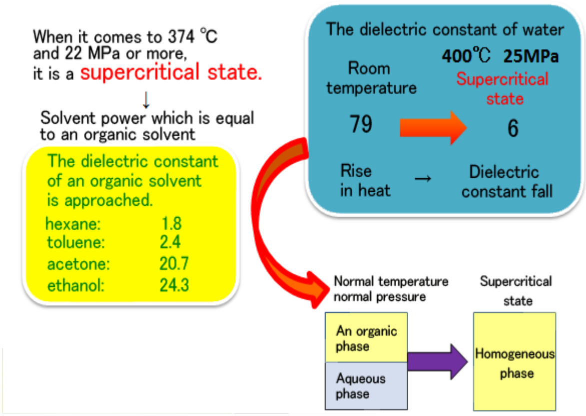


**Fig. 7.** Switchable properties of supercritical water

### Applications

- SCWO takes advantage of the thermodynamic behaviour of water above its critical point
- ($T_c$ =675 K, $P_c$ =22.2 MPa), when its hydrogen bonds are significantly weakened, and its density, thermal conductivity and dielectric constant all dramatically drop, rendering SCW to be nonpolar and completely miscible with all organic compounds and gases as shown in figure 8.[9].

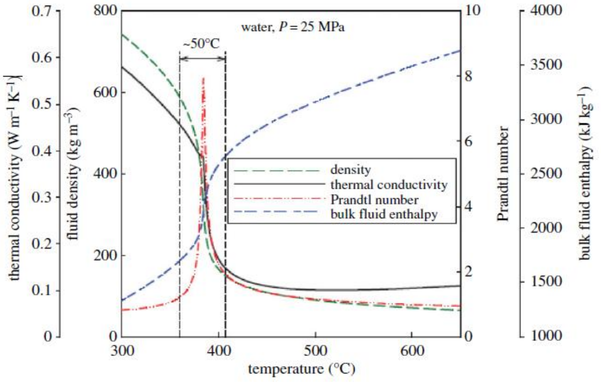


**Fig.8.** Variations of selected thermo-physical properties of water near critical point

- $ScH_2O$ has the ability of dissolving large amount of oxygen or other oxidants and organic compounds so it is used to decompose organic compounds by SCWO (supercritical water oxidation) [10],[11],[12]. SCWO can be used for treatment of waste sludges [13], Chemical warfare agents and rocket propellents [14] and industrial waste water streams [15]. Use of SCWO at industrial level is limited by the fact that it causes corrosion and scaling to the machinery. As a result of higher heat capacity in comparison to steam, supercritical water is used as heat carrier in power plants since the 1930's to increase the efficiency in comparison to subcritical steam cycles [16]. Also, the usage of supercritical water in the next generation of nuclear power plants is considered to be a feasible option [17]. For a large number of chemical reactions, which are currently operated with organic solvents, supercritical water is borne in mind as an alternative. Due to the benign and non-toxic nature, the occurrence of water in a multitude of systems as reactant or by-product and the comparably easy separation step of water from organic compounds are the main supportive arguments for supercritical water as medium of choice [18].
- $scH_2O$ added with ZnO or HCl is effective in promoting devulcanisation and oil development.
- In $scH_2O$, rate of cellulose decomposition is increased 100 to 10,000 times as compared to conventional methods which employs conventional acid catalysed decomposition [19].

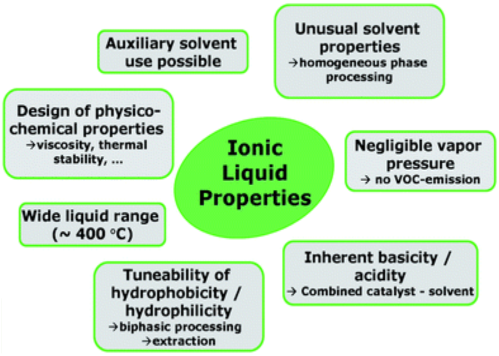
### Ionic liquids

Ionic liquids (ILs) are pure organic salts that have a melting point below 100°C. Some are liquid at room temperature (RTIL).The cation usually contains nitrogen with four covalent bonds. These are liquid at room temperature, yet their vapor pressure is very low or negligible in comparison to conventional organic solvents [20]. It can be explained on the basis of electrostatic force of attraction between ions in ionic liquids that hold the ions strongly and reduces their escaping tendency.

### Properties of ILs

ILs are also known as 'designer solvents' since they give the opportunity to tune their specific properties for a particular need.The researchers can design a specific IL by choosing negatively charged small anions and positively charged large cations, and these specific ILs may be utilized to dissolve a certain chemical or to extract a certain material from a solution. The fine-tuning of the structure provides tailor-designed properties to satisfy the specific application requirements. The physical and chemical properties of ILs are varied by changing the alkyl chain length on the cation and the anion. Ionic liquids have several tremendous characteristic features that render it preferable over the traditional type of solvents.
As solvents, ILs possess several advantages over conventional organic solvents, which make them environmentally compatible [21],[22],[23],[24]:

- ILs have the ability to dissolve many different organic, inorganic and organometallic materials.
- ILs are highly polar.
- ILs consist of loosely coordinating bulky ions.
- ILs do not evaporate since they have very low vapor pressures.
- ILs are thermally stable, approximately up to 300 ◦C
- Most of ILs have a liquid window of up to 200 ◦C which enables wide kinetic control.
- ILs have high thermal conductivity and a large electrochemical window.
- ILs are immiscible with many organic solvents.
- ILs are nonaqueous polar alternatives for phase transfer processes.
- The solvent properties of ILs can be tuned for a specific application by varying the anion cation combinations [25].



Researchers explained that ILs remain liquid at room temperature due to the reason that their ions do not pack well [26].

Combination of bulky and asymmetrical cations and evenly anions form a regular structure namely a liquid phase. The low melting points of ILs are a result of the chemical composition. The combination of larger asymmetric organic cation and smaller inorganic counterparts lower the lattice energy and hence the melting point of the resulting ionic medium. In some cases, even the anions are relatively large and play a role in lowering the melting point [27]. Most widely used ILs and their structures are given in Fig.9

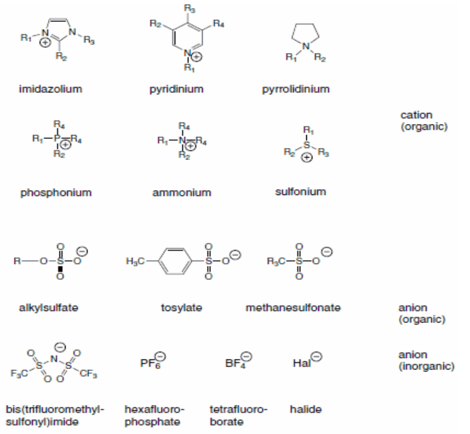
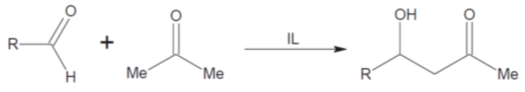


**Fig. 9.** Commonly used ILs (www.sigmaaldrich.com)

### Applications of ILs

Recently, researchers have discovered that ILs are more than just green solvents and they have found several applications such as replacing them with volatile organic solvents, making newmaterials, conducting heat effectively, supporting enzyme-catalyzed reactions, hosting a variety of catalysts, purification of gases, homogenous and heterogeneous catalysis, biological reactions media and removal of metal ions [28].

Examples for the use of ionic liquids are the synthesis of thiazoles [29], which are important in organic and medicinal chemistry for the condensation of aldehydes and ketones with hydroxylamine hydrochloride using 1-butyl-3-methylimidazolium hydroxide ([bmim]OH) or the condensation of indoles with benzaldehydes under microwave conditions with 1-benzyl-3-methylimidazolium hydrogensulfate ([bnmim][HSO4]) as a catalyst [30]. The reaction products are used in tumor chemotherapy [31].
Also Friedl-Crafts acylations can be carried out with inorganic Lewis acidic ionic liquid catalysts like [bmim]Cl-AlCl3 [32]. Aldol condensation and Doebner condensation (as shown in fig 10 and 11) can be carried out in ILs [33].



R = Ph, 4-$O_2NC_6H_4$, 2-$O_2NC_6H_4$, 4-$BrC_6H_4$, 4-$MeC_6H_4$, i-Pr, 3-$O_2NC_6H_4$.

**Fig. 10.** Simple Aldol reaction using ILs

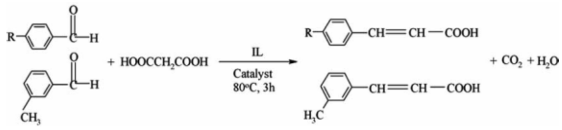


**Fig. 11.** IL catalyzed Doebner condensation

- The great advantage of using ILs for nanoparticle synthesis is that they can be tuned to serve as both the reducing and protecting agent. ILs are ionic compounds, therefore solvation and protection of metal ions is superior in ILs compared to conventional organic solvents [34]. ILs form a protective layer which provides both steric and electronic protection against agglomeration [35]. Alcohol ionic liquids (AILs) have been used due to their great reducing capabilities in the formation of AuNPs [34].

### Ethyl lactate

Ethyl lactate (ethyl-2-hydroxypropanone) is very important green solvent that possesses the ability of replacement of conventional organic solvents. It is synthesized by esterification between lactic acid and ethanol. Greenness of ethyl lactate is due to:

- It can be synthesized from bio-based sources instead of petroleum.
- It is recyclable and biodegradable solvent.
- It is less volatile so do not emit out VOCs into the atmosphere and do not cause ozone depletion.
- It can be used as reaction medium because of its easily “tunable” polarity. Polarity of ethyl lactate can be altered by addition of polar solvent water in different extents. So it can be made to dissolve wide variety of organic solvents.
- Ethyl lactate is non-corrosive, non-carcinogenic, non-ozone depleting, good solvent for variety of purposes, commonly used in paint and coating industry, and have high solvency power, high boiling point, low surface tension.

### Applications

Ethyl lactate is an agrochemical solvent being used in food, pharmaceutical and cosmetic industries. Recently, it is being widely investigated to replace the solvents employed in various synthetic processes, with the intention of making the whole process more environmentally benign. Ethyl lactate is also an important solvent in coating industry due to its high solvency power, high boiling point and low surface tension. Other than being used as a solvent, it is a monomer for the manufacturing of biodegradable polymer [36].

Ethyl lactate is a novel, sustainable and environmental-friendly solvent as compared to other solvents produced from petroleum industry which are toxic for human consumption. Comparably, ethyl lactate has high flash point, non-toxic, nonflammable, non-corrosive, non-carcinogenic, nonozone depleting, low volatility, low viscosity and it is completely biodegradable into CO2 and water. Studies show that ethyl lactate has a very low human and animal toxicity at wide range of concentration exposures [37]. The US Food and Drug Administration has approved the use of ethyl lactate in food and pharmaceutical products.

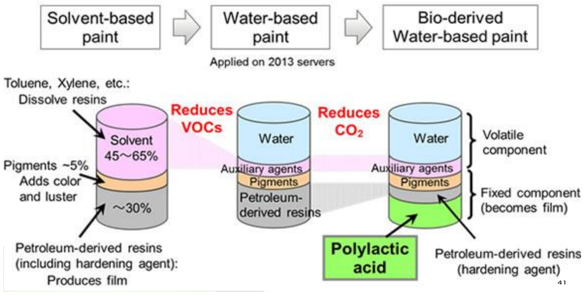


**Fig.** Movement of paint industry towards bio-derived solvents

Ethyl lactate exerts polarity in the range of acetronitrile. It is capable to form intra- and intermolecular hydrogen bonding, either as a proton donor or acceptor [38]. On top of that, it has the ability to form Van der Waals interactions in oils [39]. As a result, ethyl lactate can dissolve in both aqueous and hydrocarbon solvents and it is capable to extract compounds of a wide range of polarity [40]. In pharmaceutical industry, ethyl lactate is applied to disperse biologically active compounds without destroying their pharmacological activity. Therefore, the stability of heat- and light sensitive compounds, such as carotenoids and vitamin E in ethyl lactate should be better than in other relatively strong organic solvents. The price of ethyl lactate is becoming lower because the production itself is sustainable instead of depending on the fluctuating and increasing price of crude oil, which is non-renewable. Advancement in ethanol and lactic acid production are continuously developed to further reduce the production cost of ethyl lactate. These include the production of ethanol from cellulosic biomass and the production of lactic acid from grass juice [41].

Strati and Oreopoulou (2011) found that ethyl lactate, other than being an environmental-friendly solvent, is the most efficient solvent to extract carotenoids (lycopene) from tomato waste at 70$^0$C, as compared to acetone, ethyl acetate, hexane and ethanol. Even at ambient temperature, ethyl lactate was able to extract more lycopene than other solvents at higher temperature. 30 min was found to be adequate to extract lycopene from tomato waste. Prolonged extraction was undesirable due to isomerisation and oxidation of carotenoids at high operating temperature [40].

### Conclusion

To achieve near-total “Greenness” in chemical processes, we need to focus on every aspect of the chemical reaction. The aim of all research must be to study the totality of reality. Solvents that also serve as catalysts must be employed. Biodegradable solvents must be preferred. EHS aspects of all novel and conventional must be studies before their widespread use.

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