

Application of Green Solvent in Green Chemistry: An overview

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Abstract

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Purpose: Generally, conventional or volatile organic solvents are extracted from petroleum resources and other such resources harmful to living species' environment and wellbeing. Because of this severe threat, researchers developed some eco-friendly alternations to circumvent the difficulties associated with traditional solvents. This review paper provides an overview of different alternatives or substitutes to overcome the toxicity of conventional solvents.

Methodology: The properties of a green solvent, tools, and techniques used to measure the greenness of solvent, its parameters, classification, and applications in various fields are the factors reviewed in this study.

Principal Findings: Chemical and pharmaceutical industries use around 80% of chemical-based solvents out of the total volume for various chemical procedures. The evolution of green chemistry has led to the development of green solvents.

Implications: The use of non-conventional solvents also offers prospects for facilitating the recycling and recovery of the solvents.

Novelty: The novelty of this work includes its eco-friendliness and sustainability over traditional organic solvents. Along with these, green solvents can be recycled for further use. On a green note, we have discussed various types of solvents, parameters, their properties and applications in different fields in this chapter. And all of them possess some unique characteristics and advantages over conventional organic solvents. Some of them are completely eco-friendly and others in a way require some research and enhancement in techniques to behave like one.

INTRODUCTION

Solvents have gained much consideration due to the apprehension of green chemistry (Pollet *et al.* 2014, Breeden *et al.* 2012, Earle *et al.* 2000, Pena-Pereira *et al.* 2015, Clark *et al.* 2015). It can be associated with its vivid applications, resulting in higher amounts in chemical reactions, particularly during the purification of substances or formulations (Abou-Shehada *et al.* 2016, Constable *et al.* 2007). Solvents play a significant role in the environmental presentation of developments in biochemical and chemical industries since they directly influence cost, safety, and wellbeing. "Green" solvent refers to limiting solvents in the chemical industry to decrease their negative impact on the environment. The increasing cognizance of the ongoing requirement for green, eco-friendly and sustainable technologies has focused on using less harmful techniques and atomically effective catalytic procedures to produce pharmaceuticals and chemicals. Another characteristic that has received scientists' consideration in this field is using an alternative reaction medium that avoids the difficulties of numerous traditional volatile organic solvents. The usage of a non-conventional reaction medium offers chances for simplifying the recovery and recycling of the solvent. As reaction mediums, diluters, and separation methods, solvents have broad applications in chemical industries. Solvents combine the reactants/catalysts in an organized way to distribute heat and momentum as reaction mediums (Reichardt 1979). It is also responsible for the selectivity and activity of different compounds. The nature of the solvent, physical, chemical, or biological, decides its selection criteria.

Liquid-liquid bi-phase solvent proved to be a practical criterion for recovering and recycling solvents and replacing traditional solid heterogeneous solvents. Numerous methods like aqueous bi-phase catalysis, liquid-liquid bi-phase catalysis, fluorosol bi-phase catalysis, supercritical CO₂, ionic liquids, and other such combinations are studied and compared. And it was concluded that "the best solvent is no solvent" (Sheldon 2005). In case there is a requirement for any solvent, then water could be considered the best solvent, and the processing of reaction in an aqueous bi-phasic medium has attracted industries due to its wide applications

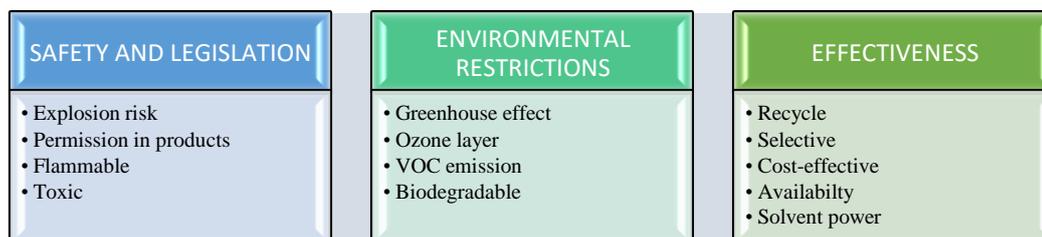


Figure 1: Parameters of an ideal solvent

Although water is considered one of the best alternatives to traditional solvents, its application is limited due to the insignificant solubility of many organic and organometallic compounds in it. The use of conventional organic, petroleum-based solvents usually permits the dissolution of varied forms of solids, liquids, and gases together with contamination of air, water, and land. Similarly, ionic liquids (Wasserscheid *et al.* 2003) and per fluorinated solvents (Horvath *et al.* 1994) have been used as recyclable, eco-friendly reaction mediums, but they proved to be non-biodegradable and poisonous; along with that, their manufacturing is also correlated to the use of large volumes of hazardous and volatile organic solvents. The practical application of supercritical fluids and supercritical CO₂ has been limited because of their high critical characteristics, although they are testified as green solvents (Jessop *et al.* 1999). In an experiment performed by Yaocai and co-workers, 2021 (Bai *et al.* 2021) cathode materials were recovered via advanced separation procedures on basis of recyclization of cathode scraps. This was a green solvent-based separation technique for the recovery of cathode. Other such example of use of green solvent in recent studies include formation of amide bond which has wide scope in chemical and pharmaceutical industries via use of green solvents like deep eutectic solvents and ionic liquids over organic solvents like dichloromethane, N,N-dimethylformamide etc. performed by Debora and co-workers, 2022 (Procopio *et al.* 2022).

How to measure how “green” a solvent is?

Christian Capello and co-workers, 2007 (Capello *et al.* 2007) proposed an inclusive context for the eco-friendly assessment of solvents that emphasizes the eco-friendly nature of the solvent during the production of chemicals and convenience and wellbeing. The outline of the project is associated with assessing some definite substance-associated threats with the quantification of discharges and the use of resources for the complete lifetime of a solvent. The anticipated framework has experimented on 26 organic-based solvents. It was concluded from the results that simple alcohols (ethanol, propanol) or alkanes (pentane, hexane) were found to be environmentally benign solvents. In contrast, the other organic solvents like acids, dioxane, formaldehyde, acetonitrile, and tetrahydrofuran need to be forbidden since they were not found to be eco-friendly. In addition to this, a case study was performed where the anticipated framework was applied to evaluate several alcohol-water or pure-alcohol combinations used for the solvolysis of p-methoxybenzoyl chloride. The results showed that methanol-water or ethanol-water mixtures were environmentally benign solvents compared to pure-alcohol or propanol–water combinations.

PROPERTIES

Solvents play a vital role in the reaction process, and still, they do not participate in the reaction mechanism themselves. From the choice of solvent to its quantity, everything matters in a reaction compared to any other secondary material. It makes the solvents the most significant supplementary waste material in the responses associated with its use (Sheldon 2005). To reduce the content of destructiveness caused by solvents on the well-being of humans and ecology have been studied from numerous perspectives. For attaining this, sustainable, eco-friendly steps should be adopted at the beginning of the chemical reaction mechanism. Few guidelines were set for the eco-friendly selection of the solvent. A few of them are listed below (Curzons *et al.* 1999):

- Exposure potential
- Inherent safety
- Emissions on incineration
- Environmental impact on water
- Environmental impact on air
- Ease of recovery and recycling
- Mineralization through wastewater treatment
- Volatile organic carbon
- Health hazard: Acute or chronic toxic effects on humans

Tools and techniques for the selection of solvent: green solvent selection guides

Techniques discussed in the last few decades and the advancement in these techniques were reviewed to examine their advantages and disadvantages. Efforts have been made to select solvent via colour-coded selection criteria, which determines the progress in using the solvent system over the years. These eco-friendly tools are used to discuss the problems directly to users, promoting the use of green alternatives and suppressing the use of traditional hazardous solvents. This awareness resulted in the decrease of undesirable solvents (Kim *et al.* 2008). The solvent selection guide has created a positive environment, and now they have not been scrutinized closely enough in the reviews on this topic (Eastman *et al.* 2015, Welton 2015). The need to intuitively select classes and their application on different weightings, and the need for clarification, indicate that these tools need to be assessed with a similar level of scientific interrogation so that it would be feasible for the application of chemists. In a survey led by Prat and co-workers (Prat *et al.* 2014) on solvent selection guides, chemists' increased awareness of the use of green alternatives of solvent over conventional ones has been supportively congregated. The agreement between major pharmaceutical companies on solvent selection guides recommends a rational level of maturity in this sensible domain.

New selection guides for traditional solvents are fundamentally reiterating prevailing tools, emphasizing consensus. A final and definite report of the idea of the greenness of solvent has not been indicted by the contract between solvent selection guides, but the format of the solvent selection guide has reached its potential. The absence of sustainability norms applied in solvent selection guides specifies that mostly all solvent tools are specific to a narrower set of necessities explaining the wellbeing and safety of workers in combination with ecological release issues. In most of the solvent selection guides, the renewability of the feedstock has not been considered. One of its censures involves that mostly the calculation behind the assessment is not transparent. Based on the regulation threshold, the easily accessible procedures have proven supportive in manufacturing transparent assessments which applies to newer solvents (Capello *et al.* 2007, Prat *et al.* 2016). These approaches are very sensitive in case of which method has been applied to them since it alters with deviation in data (Tobiszewski *et al.* 2015). If the procedure is not interpreted, it is useless to expect potential users to trust its outcomes.

By whatever means a general-purpose solvent selection guide is formed, these tools are still not able to precisely describe the selection of solvent guide for specific applications. Solvent selection guides which are specific to certain reactions are now accessible (Skowerski *et al.* 2014, McGonagle *et al.* 2013, MacMillan *et al.* 2013), in which the solvents are ranked based on their presentation (not greenness). The need for the solvent in chromatography as a mobile phase is apparent and so important that the solvent selection guide for this application precedes all other tools (Thoma 1965, Abbot *et al.* 1991), and has rejuvenated as a topic of research (Tayerly *et al.* 2012, MacMillan *et al.* 2012). The greenness of the solvent can be balanced with technological needs via solvent guide, and alternate procedures of computational solvent optimisation (Tobiszewski *et al.* 2015, Murray *et al.* 2016). The criteria of separation of EHS and technological considerations determine an issue mentioned in the CHEM 21 solvent selection guide, where gentle solvents with high boiling points like glycerol, are supposed to impose undesirable ecological impacts (Prat *et al.* 2016). The energy demand for recycling solvents which are immiscible in water and have low boiling points is less than that of other solvents (Capello *et al.* 2007). Although a solvent which is miscible in water and has a high boiling point is considered to be green in terms of its characteristic solvent properties since ecological impact, toxicity and perseverance in aqueous solvents and exposure risks of workers are minimum. Distillation alternatives like the separation of membrane require further advancement (Vankelecom *et al.* 2005). In the case of chemical systems where tunable solvents are used, distillation is entirely avoidable (Abou-Shehada *et al.* 2016, Jessop 2011), but, currently, this is outside the possibility of selection guides.

The balance between conflicting contemplations is hard to make flawless, but to effectively discuss this issue with the user of the solvent selection guide is much harder. The ecological impact of any solvent is entirely dependent on its use by the chemical industry and further the control over solvent emissions and waste generated by it. This consideration should be kept in mind by solvent users. The future of solvent selection will certainly need a better sophistication in the choice of solvents based on a sustainable supply chain, and more research needs to be conducted in the field of application-specific tools and life-cycle assessments (Diorazio *et al.* 2016). To achieve this more data, need to be collected, particularly for newer solvents in consideration of their impact on the environment and their physical properties. The current purpose of the general-purpose solvent selection guide is to enlarge its exposure to neoteric solvents to compare them with conventional solvents, and subsequently initiate research in designing new solvents (Vanderveen *et al.* 2014).

Some significant problems were found during the selection of solvents using solvent-based extraction procedures. A few of them are discussed below (Kokosa 2019):

1. Limit or eradicate the use of toxic solvents like benzene, chloroform, carbon tetrachloride, dichloromethane, tetrachloroethene and in preparation of solvent extraction-based sample.
2. Avoid usage of highly volatile solvents like pentane in extraction procedures.
3. Limitation on the usage of solvents' limited solubility with an aqueous medium, adulteration of water samples like xylenes, decanes, cyclohexanes etc.
4. Use of solvents with a modest boiling point, viscosity and surface tension such as m-xylene, decane, 1-octanol etc.
5. Use of solvents such as hydrophobic deep eutectic solvents, 1-dodecanol and 1-undecanol which easily melt at near room temperature.
6. Use minimal volumes of ionic liquids as extraction solvents and avoid usage of ionic liquids which contain imidazole and hexafluorophosphate (PF₆) groups because of their toxic side effects.
7. Consideration of pure water as a green solvent.

Parameters

(Gu and Jerome, 2013) projected 12 measures for a solvent to be considered a green solvent on basis of whether it is accessible, renewable, cost-effective, toxic, biodegradable, efficient, can be recycled, evaluation, fabrication, flammability, stable, and storage. Some of the parameters of a solvent to be considered green: (Hackl *et al.* 2018)

1. A solvent would be considered green in case it is more efficient than the prevalent solvents for a specific application. More efficient in a way that it follows the principles of green chemistry. It should be sustainable and cost-effective.

There is no absolute greenness of a solvent depending on the context of its application and although this term is relatively used. The greenness of a solvent should be measured through the life cycle assessment method done for other chemical solvents and procedures.

2. The development of green substitutes over conventional organic solvents is recommendable. But new techniques need to be developed too. It includes the growth of ephemeral (Fischer *et al.* 2016) and switchable (Jessop *et al.* 2010) solvents which are used during a specific procedure only. As reaction mediums, these are favourable for effective separation of the reaction products.
3. Ternary eco-friendly combinations of solvents like water-ethanol-ethyl acetate are widely used for extraction and purification purposes. It is advantageous because a minor alteration in temperature could persuade the separation of the reversible phase.
4. Along with green solvents, green co-solvents or solubilisers need to be developed for forming water-soluble hydrophobic molecules. Research must be done in this area since many known hydrotropes are unable to fulfil the norms of chemically green material.
5. Ionic liquids are extensively overvalued as green solvents. Natural deep eutectic solvents and natural hydrotropic mixtures proved to be a better substitute. Although, their application area needs some more progress. The higher viscosity and hydrophilicity of these solvents are noteworthy drawbacks; however, studies have been done where these issues have been discussed and overcome (Zhang *et al.* 2014, Bajkacz *et al.* 2017). Natural hydrotropic mixtures can be directly extracted from plants, but these are not yet used. This could be an interesting topic for research shortly.

CLASSIFICATION OF SOLVENTS



Figure 2: Classification of green solvents

Bio-based solvents: from waste to solvent

According to the agricultural sector, these solvents can be divided into three types:

1. Cereal/sugar
2. Oleoproteagineous
3. Wood.

Bio-based solvents which are derivatives of the cereal/sugar sector are chiefly obtained from the natural fermentation of sweet juices confined to plants like wheat, sugarcane, sugar beet, corn, etc. Bioethanol (ethanol which is a derivative of vegetables) is formed by 60% of sugarcane and 40% of other crops (Gupta *et al.* 2015). In addition to this, fermenting glucose could produce numerous varieties of molecules, which have found their application as bio-based solvents like sorbitol, esters of lactic acid, derivatives of succinic acid and other such solvents (Fine *et al.* 2013). Lignocellulose residues which are derivatives of manufacturing of cereals, particularly from straw and wood waste can be oppressed leading to the formation of furfural, accentuated as one of the top value-added chemicals, which is a derivative of biomass. Hydrogenation of furfural could produce solvents like 2-methyl tetrahydrofuran which can be used to replace hexane during the extraction of vegetable oils (Sicaire *et al.* 2015) and aromas (Filly *et al.* 2015).

The oleo-proteinous solvents are chiefly derived from seeds rich in vegetable oils, like soya, sunflower and colza. The chief bio-based molecules which have been derived from oleo-proteinous solvents are esters of fatty acids and are derived from glycerol.

The chief bio-based solvents are obtained from conifers like pines or fruit peels. The chief bio-based solvents which are native to the wood sector are terpenes, hydrocarbons, $C_{10}H_{16}$ kinds of solvents, D-limonene and alpha-pinene and beta-pinene. The main sources of limonene are via steam distillation of by-products of peels obtained from the orange juice industry. Alpha-pinene and beta-pinene are obtained via steam-distillation of oleoresins confined to pines or can be extracted from gum turpentine which is a kind of essential oil obtained by distillation of pine gum or black liquor from paper mills.

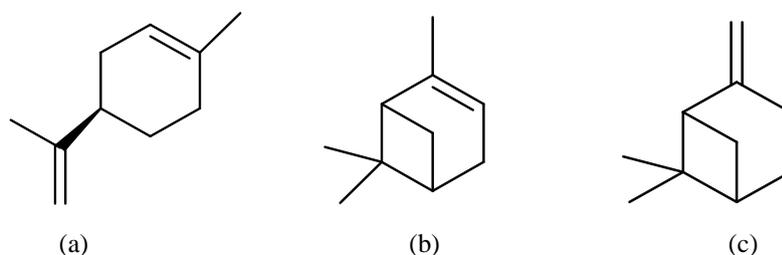


Figure 3: Chemical structure of wood sector bio-based solvents (a) D-limonene (b) α -pinene (c) β -pinene

Ionic liquids

Ionic liquids are a group of non-molecular solvents or organic salts which consists of an organic positive part known as cation and an organic/inorganic negative part known as an anion in the liquid state and at ambient conditions. The solubility of ionic liquids ranges from polar to non-polar compounds. They have low combustibility and vapour pressure at room temperature while their thermal and chemical stability is quite higher, most of the ionic liquids are biodegradable (Bera *et al.* 2016). They can be easily synthesized and are versatile and tunable, which favours the formation of application-specific ionic liquids and some of their derivatives are ionic liquid based-surfactants, polymeric ionic liquids, and magnetic ionic liquids (Trujillo-Rodriguez *et al.* 2019). Because of its unique and reliable properties, this area has been under research for the last few years in comparison to other solvents like amphiphilic and deep eutectic solvents (PŁotka-Wasyłka *et al.* 2017). One of the most widely used liquid-phase microextraction procedures is dispersive liquid-liquid microextraction (DLLME) because of its outstanding characteristics such as high extraction efficiency, and fast and simple operation. Even in the case of dispersive liquid-liquid microextraction, halogenated solvents are substituted by ionic liquids (Trujillo-Rodriguez *et al.* 2013). Most of the ionic liquids are stable over a wide range of temperatures and have numerous combinations of cations-anions.

Ionic Liquids are comparatively a new class of chemicals, which have found their application as an alternative to toxic solvents which are a threat to our environment. The most widely prevalent application part of ionic liquids includes the synthesis of organic molecules, catalysation, and extraction. They are salts since they are completely formed by ions. The cationic part of the ionic liquid can be quaternary ammonium or phosphonium, imidazole, pyridine, while the anionic part can be a hexafluorophosphate, triflate, halogen, trifluoroborate.

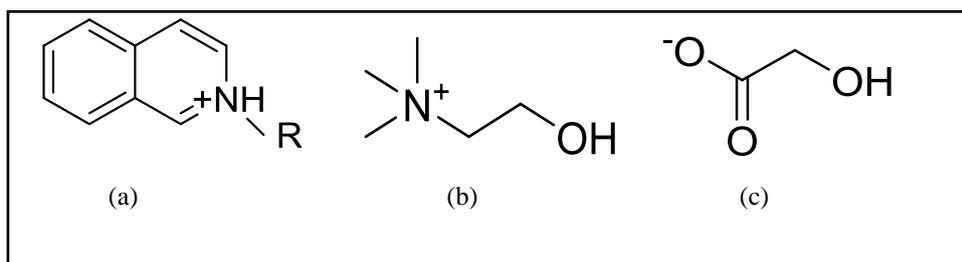


Figure 4: Some commonly used cations and anions in ionic liquids (a) Isoquinolinium (b) Cholinium (c) Glycolate.

Since the coordination of ions is poor so their liquid state is thermodynamically favourable. And because of this, ionic liquids remain in a liquid state at room temperature and below 100 °C. If salt has melting point below the melting point of water only in that case a compound can be considered an ionic liquid. All ionic liquids are not environmentally friendly, some of them are carcinogenic and harmful which even leads to difficulty in their manufacture. Besides that, they are preferred over conventional solvents because of their unique characteristics such as they are versatile and considered “green”. These characteristics like melting point, density, and viscosity can be altered by adjusting ionic structure according to the requirements.

Deep eutectic solvents

These solvents can be prepared by mixing a hydrogen bond acceptor compound and a hydrogen bond donor compound in a variable ratio (Cunha *et al.* 2018). The melting point of the resultant solvent should be lower than the melting points of the individual components. A few examples of hydrogen bond acceptors include quaternary ammonium or phosphonium

salts, while those of hydrogen bond donors include amines, alcohols, carboxylic acids etc. In other words, these are a combination of solids having low melting points generally below 100°C which further combine to form a solvent with a melting point lower than the latter. For example, when choline chloride (having a melting point of 302°C) was mixed with urea (having a melting point of 133°C) in a 1:2 molar ratio, it resulted in the formation of a deep eutectic solvent with a melting point of 12°C. General and most widely used deep eutectic solvents include choline chloride and carboxylic acids mixed with hydrogen-bond donors like glycerol, succinic acid, urea, and citric acid (Fischer *et al.* 2016). These solvents resemble properties to those of ionic liquids like simple fabrication processes, variable viscosity, polarity, and density. Although, their fabrication is quite cost-effective in comparison to ionic liquids and is even less toxic than conventional ionic liquids (Kudlak *et al.* 2015, Clarke *et al.* 2018).

Natural deep eutectic solvents are those solvents which are formed by natural substances, predominantly by primary metabolites like amino acids, sugars and organic acids. Their extraction characteristics are quite good in comparison to deep eutectic solvents: their viscosity can easily be altered, are highly sustainable, have high solubility in case of both polar and non-polar compounds and most importantly they attain their liquid state below 0°C. These are prevalently preferred for the extraction of natural components from plants, food and other natural mediums (Owczarek *et al.* 2016). These solvents are safe and less toxic and are highly biodegradable, hence making them the greenest option as an alternative to conventional organic solvents. Deep eutectic solvents were mainly developed as extraction solvents in dispersive liquid-liquid microextraction for the extraction of organic compounds or metal ions from oil or aqueous samples.

In addition, these can be formed via a variety of easily accessible compounds by simple fabrication processes and that's too cost-effective. They exist as liquids over wide temperature ranges and exhibit low vapour pressure. These can be used as solvents when the following conditions would be fulfilled:

- a) The eutectic point should be less than the melting point of the individual components and much lower than that of the resultant solvent mixture.
- b) The eutectic point is dependent on the molar composition of the mixture.
- c) They remain liquid at room temperature (Smith *et al.* 2014, Liu *et al.* 2018, Martins *et al.* 2019).

The eutectic solvents can be fabricated via the following processes: evaporation, heating and stirring process and freeze-drying process (Espino *et al.* 2016). Although out of these three, heating and stirring are widely used since it is simple and easy to operate and most importantly in processes where heating is not required. Research has been done to develop some green, eco-friendly processes for the fabrication of deep eutectic solvents. Gomez and co-workers, 2018 (Gomez *et al.* 2018), proposed a microwave-assisted process for the fabrication of deep eutectic solvents that includes a fabrication time of 20 seconds with a loss in energy consumption up to 650 times in comparison to that of the heating and stirring process.

Magnetic solvents

Magnetic deep eutectic solvents and magnetic ionic liquids form by the integration of salts of nickel, iron, and manganese into the fabricated deep eutectic solvents or ionic liquids. They are used as extraction solvents in processes like dispersive liquid-liquid microextraction and other such processes. These solvents are specifically used for collecting solvent which will be useful in the extraction of dispersive liquid-liquid microextraction, either in the presence or absence of solvent-assisted dispersion (An *et al.* 2017, Khezeli *et al.* 2017).

Supramolecular solvents

These are nano-structured liquids which are formed by amphiphiles via sequential or self-assembly methods occurring on nano and molecular scales. These solvents do not combine with a water molecule and get dispersed in a continuous phase which consists of a colloidal solution of surfactant clusters by effects like electrolytic, pH, temperature etc. (Ballesteros-Gomez *et al.* 2010, Ballesteros-Gomez *et al.* 2009, Garcia-Fonseca *et al.* 2016). These solvents consist of polar and polar regions in nanosized or molecular-sized micelles when formed in an aqueous medium (Rezaei *et al.* 2013, Lopez-Jimenez *et al.* 2010, Moral *et al.* 2009). These solvents possess different types of polarities to interact with analytes and these interactions can be accustomed via alteration of hydrophobicity and polarity of the amphiphilic groups (Rezaei *et al.* 2013, Lopez-Jimenez *et al.* 2010, Moral *et al.* 2009). In addition to supramolecular solvents, the extraction efficiency increases when containing high-concentration amphiphilic groups in lesser amounts (50-1000 µL).

Switchable hydrophobicity solvents

These are newer solvents having polar and apolar regions with distinct physical characteristics. The conversion of solvents from polar to non-polar and vice-versa can be achieved in a fast, simple, promptly reversible, and précised manner. This characteristic is as simple as using and controlling tools of day-to-day life such as switching on- and off-light appliances or controlling or altering the speed of the fan (Yilmaz *et al.* 2015, Soyak *et al.* 2016, Yilmaz *et al.* 2015). These solvents are formed by secondary amines and tertiary amines which are polar in behaviour. For example, protonation of amine bicarbonate or alkyl carbonate salts with water when CO₂ is present and at 1 atmospheric pressure. This reaction proceeds via the protonation of amines and is exothermic.



Supercritical fluids

This is a new-generation technology which has gained pace as an alternative to organic conventional procedures of reaction, fractionation, extraction, separation, processing of materials, formation of particles, and their study (Jessop *et al.* 1999, Williams *et al.* 2000, Hyde *et al.* 2001, Senorans *et al.* 2002, Sarrade *et al.* 2003, Goodship *et al.* 2004, Prajapati *et al.* 2004, Yeo *et al.* 2005, Aymonier *et al.* 2006, Martinez 2008, Mishima 2008, Sunarso *et al.* 2009, Ramsey *et al.* 2009, Herrero *et al.* 2010). Supercritical fluids can be well-defined as the state of an element, mixture or compound above its critical temperature and pressure, but lower than the pressure needed to condense it into a solid. Here the fluids exist in a transition phase between the liquid phase and gas phase. The macroscopic presence of the fluids is a homogeneous and opalescent system without any distribution in phase due to the indistinguishable values of the densities of the liquid phase and the gas phase. Nonetheless, this fluid does not have a specific agglomeration state. They possess liquid-like density with gas-like transportable characteristics and reasonable solvent power, which can further be altered with any variation in temperature and pressure. Some of the important components which are used in supercritical fluids are listed here, such as water, ethane, ethene, propane, carbon oxide, xenon, ammonia, and nitrous oxide. Because of its properties as less toxic, flammable, cost-effective, easily accessible, stable and eco-friendly, carbon dioxide is widely used in supercritical fluids. Additionally, the critical point requirements are 31°C and 74 bar which can be easily attained. Supercritical carbon dioxide is applicable in different fields like fabrication of polymers, drug delivery, manufacturing of protein and ceramic powders, and coating with powder.

The characteristics of supercritical fluids differ from those of ordinary gases and liquids such as they are highly soluble, diffusive, viscous and heat efficient etc. and by altering the temperature and pressure conditions, their tunability can be increased. The densities and viscosities of the fluids severely alter near the critical point. The reaction rates show an increase and are selected because of the higher solubility of reactant gases, fast diffusing efficiency of solvents, solvation efficiency weakens and formation of reactant and solvent clusters. The fluids are recyclable and permit the separation of dissolved compounds via the release of pressure.

Per-fluorinated Solvents

The fluoruous mediums like per-fluorocarbons or perfluorinated solvents are evolving solvents and are under research due to their outstanding characteristics (Cornils 1997, Curran 1998, Barthel-Rosa *et al.* 1999, Cavazzini *et al.* 1999, Kitazume 2000, Curran 2001, Gladysz *et al.* 2004, Hobbs *et al.* 2007, Zhang *et al.* 2008, Zhang 2009). They are less toxic and chemically less reactive but miscible in organic solvents. Additionally, they exhibit flammability, and high densities and are less soluble in water and organic solvents and are less volatile too. Because of the low polarizing efficiency of carbon and fluorine bond electrons and the absence of many lone pairs of fluorine, they possess weak Vander-Waals forces of interaction. It signifies that, in addition to organic solvents, the substitution of molecules of per-fluoroalkane via other molecules, requires interaction energy. Hence, gases are highly soluble in per-fluorinated compounds.

Amphiphilic solvents

These solvents are divided into three main classes which are further divided into seven groups. The three main classes include ionic surfactants, non-ionic surfactants, carboxylic acids and alcohols. The methods are useful in terms of cost, simple processing, high separation capability, non-toxic extractant, and pre-concentration of a variety of analytes. Cloud point extraction technique was the first coacervate-based extraction technique and micelle-assisted extraction which were first presented in the 1970s and is still being widely used. Liquid-liquid extraction procedures are being substituted by coacervate-based extraction (Ferrera *et al.* 2004). Its application area is quite wide. Such extraction techniques prove to be useful in the separation and pre-concentration of pesticides, heavy metals, tenacious organic pollutants, pharmaceutical constituents, azo dyes, and other such mediums. The most widely practiced surfactants in this area include PONPE 7.5, Triton X-100, Triton X-114 etc. (Plotka-Wasyłka *et al.* 2017, Ferrera *et al.* 2004, Fang *et al.* 2000).

In analytical chemistry, amongst these solvents, surfactants have been extensively operated since due to low toxicity they prove to be one of the best alternatives over harmful organic solvents (Melnik *et al.* 2015). When surface-active solvents are mixed with water having a higher concentration than critical micelle concentration, they self-assemble themselves leading to the formation of micelles that agglomerates with strong solvation characteristics, which further permits their interaction with different polarity compounds. That is why, diverse micelle-assisted extraction approaches have been enhanced over years, where conventional extraction solvents are being substituted by solvents. The micelle-assisted extraction technique can be supported via ultrasounds or microwaves to enhance the micelle-analyte interaction. Surfactants allow the growth of preconcentration systems, where a small volume of the surfactant is added to the sample, and its separation is encouraged by alteration in the environment of the solution, promoting dissimilar ratios of surfactant- and aqueous-rich phase. The alteration includes variations in temperature during extraction via cloud-point extraction which involves the presence of non-ionic or zwitterionic surfactants and variations in pH or the addition of salt/solvent during coacervation extraction.

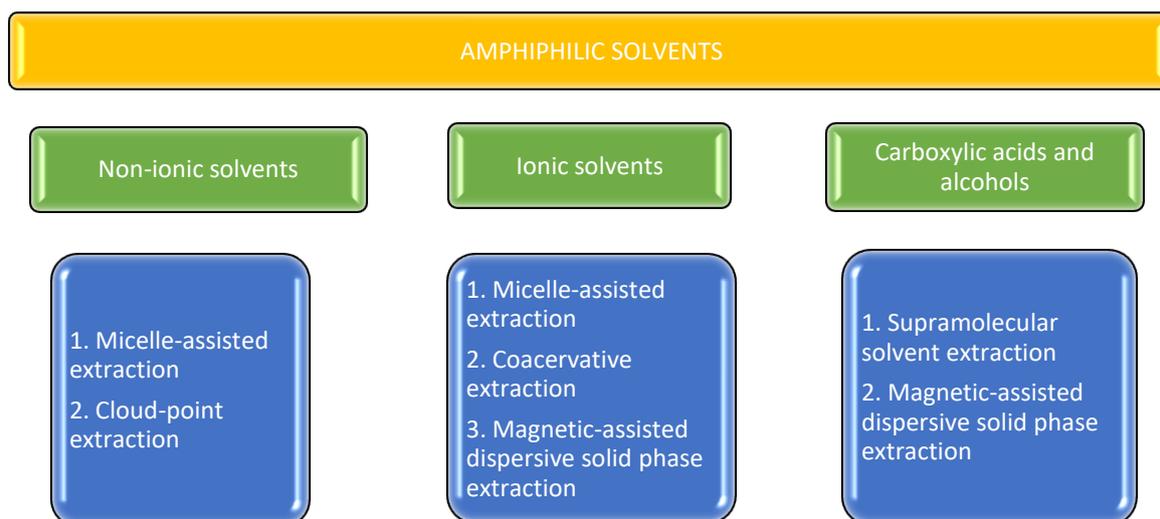


Figure 5: Classification of amphiphilic solvents

APPLICATIONS

1. A switchable hydrophilicity solvent system is based on a lipophilic tertiary amine, like N, N-dimethylcyclohexylamine which applies to the manufacture of multilayer packaging materials and recovering of materials like low-density polyethene and aluminium. Its use is extremely efficient, without cooperation with the quality of the recovered materials (Samori *et al.* 2017).
2. Natural deep eutectic solvents can be used for extracting bioactive compounds from plant species. Based on research it was concluded that areas, where natural deep eutectic solvents have been used for extraction of biologically active compounds, have better solubility efficiency than that in water and lipids.
3. The growth of solvent-free green procedures has received substantial consideration in the synthesis of organic compounds due to their outstanding properties. They are highly effective and selective, have simple separation and purification techniques, insignificant reaction conditions, are eco-friendly and are beneficial for industries as well as the environment (Tanaka 2003). Solvent-free organic reactions generally involve the fabrication of a liquid phase ahead of a reaction, i.e., the formation of a eutectic melt of unvarying distribution in which the reactants being in proximity can react in a controlled way (Rothenberg *et al.* 2001). For example, protonation and de-protonation reactions like Tishchenko reactions, Condensation reactions, Metathesis reactions etc.
4. The solvent-free sublimation process has been found applicable for the fabrication of fibrillar nanostructures from low molecular weight organo-gelators having 1-D structures (Tsekova *et al.* 2009). This procedure was found to be extremely suitable to evade uncontrollable solvent effects.
5. With the help of a precision milling scheme possessing physio-chemical characteristics the solvent-free fabrication of nanoscale zero-valent iron had been stated, which was remarked as a substituent to fabrication by chemical methods (Li *et al.* 2009).
6. Green solvent's usage enhances the selectivity pattern and activity during catalysis, which involves all types of catalysis whether bio-catalysis, heterogeneous or homogeneous catalysis.
7. Terpenes, a kind of isoprene have been extensively used for the extraction of natural products from waste Biomass as a substitute for the prevalent practice of hexane in biomass extractions because of low polarity and hydrogen bonding (Gu *et al.* 2013).
8. Extraction of fatty acid alkyl esters and glycerol derivatives from lipids. Transesterification of triglycerides with alcohol to yield biodiesel in the form of alkyl esters of fatty acids along with glycerol, which can be further used as solvents (Ciriminna *et al.* 2015, Knothe *et al.* 2011). In addition, glycerol can act as a substitute for other hazardous chemicals and solvents, valorising this gradually predominant waste product (Ciriminna *et al.* 2015).

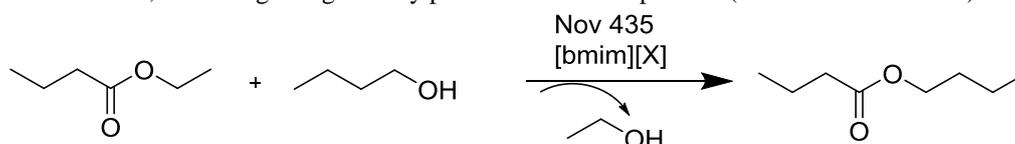


Figure 6: Transesterification reaction where X= BF₄ or PF₆

9. Extraction of furfural from biomass of lignocellulose. Furfural proves to be an effective chemical in industries for the manufacture of varied products (Cai *et al.* 2014). Recently, furfural has been indirectly extracted from sugars rather than the biomass of cellulose, although its direct extraction would lower the cost of manufacture/extraction and its harmful effects (Cai *et al.* 2014). Furfural applications include the formation of plastic products and stripping of

paints, dissolution of cellulosic products like cellulose acetate, nitrocellulose (Trickey 1927) and elimination of aromatic compounds and other pollutants from rosin (Trimble 1941).

10. The use of switchable solvents would decrease energy consumption during separation and recyclable solvents and catalysts (Jessop 2015). These have found application in various biomass-assisted extractions such as extraction of phenols from biomass of lignocellulose with N, N-dimethylcyclohexylamine (Fu *et al.* 2014), fractionation of lignocellulose from spruce wood via the use of switchable ionic liquids (Anugwom *et al.* 2012), pre-treatment of lignocellulose by using “switchable” butadiene sulfone through temperature (Atilio de Frias *et al.* 2014). Other applications like recovery of solvents and purity of the product need further optimization (Boyd *et al.* 2012).
11. Use of pressurized carbon dioxide in biorefineries because of selective solubility of compounds with low polarizing power (Jessop 2011, Payne *et al.* 2010) and to contemplate conversion of reactions like manufacturing of biodiesel (Soh *et al.* 2014). Supercritical and dense carbon dioxide is highly diffusive and less viscous in comparison to other liquid solvents allowing diffusion of solid-biomass matrices (Mantell *et al.* 2013, Marriott *et al.* 2012). This characteristic was found useful in the effective and selective extraction of oils from a variety of feedstocks including microalgae (Soh *et al.* 2011, Mendes *et al.* 1994, Mendes *et al.* 1995, Herrero *et al.* 2006), fish (Dunford *et al.* 1997, Sprague *et al.* 2010) and oilseeds.

CONCLUSION

Green solvents have been widely used in the synthesis of organic compounds and analytical chemistry. On a green note, we have discussed various types of solvents, parameters, their properties and applications in different fields in this chapter. And all of them possess some unique characteristics and advantages over conventional organic solvents. Some of them are completely eco-friendly and others in a way require some research and enhancement in techniques to behave like one. Additionally, their extent of greenness and efficiency of safety for wellbeing need some depth studies in this field to confirm their agreement with the principles of green chemistry. Eventually, the use of such solvents will enhance a more sustainable industrial environment. Processes like recovery, recycling, and regeneration of solvents need some further research so that the extraction process of the solvents would be cost-effective and economical.

REFERENCES

1. Abbott, T.P., Kleiman, R. (1991). Solvent selection guide for counter-current chromatography. *J Chromatogr A.*, 538, 109-118. [https://doi.org/10.1016/S0021-9673\(01\)91627-9](https://doi.org/10.1016/S0021-9673(01)91627-9)
2. Abou-Shehada, S., Clark, J.H., Paggiola, G., Sherwood, J. (2016). Tunable solvents: shades of green. *Chem Eng Process.*, 99, 88-96. <https://doi.org/10.1016/j.cep.2015.07.005>
3. Abou-Shehada, S., Clark, J.H., Paggiola, G., Sherwood, J. (2016). Tunable solvents: shades of green. *Chem Eng Process.*, 99, 88-96. <https://doi.org/10.1016/j.cep.2015.07.005>
4. An, J., Rahn, K.L., Anderson, J.L. (2017). Headspace single-drop microextraction versus dispersive liquid-liquid microextraction using magnetic ionic liquid extraction solvents. *Talanta.*, 167, 268-278. <https://doi.org/10.1016/j.talanta.2017.01.079>, PMID:28340720
5. Anugwom, I., Maki-Arvela, P., Virtanen, P., Willfor, S., Sjöholm, R., Mikkola, J.P. (2012). Selective extraction of hemicelluloses from spruce using switchable ionic liquids. *Carbo. Poly.*, 87(3), 2005–2011. <https://doi.org/10.1016/j.carbpol.2011.10.006>
6. Atilio de Frias, J. A., Feng, H. (2014). Pretreatment of furfural residues with switchable butadiene sulfone in the sugarcane bagasse biorefinery. *Green Chem.*, 16(5), 2779–2787. <https://doi.org/10.1039/c3gc42632g>
7. Aymonier, C., Loppinet-Serani, A., Reveron, H., Garrabos, Y., Cansell, F. (2006). Review of supercritical fluids in inorganic materials science. *J Super Fluid.*, 38, 242-251. <https://doi.org/10.1016/j.supflu.2006.03.019>
8. Bai, Y., Essehli, R., Jafta, C.J., Livingston, K.M., Belharouak, I. (2021). Recovery of Cathode Materials and Aluminum Foil Using a Green Solvent. *ACS Sustainable Chemistry & Engineering*, 9(17), 6048–6055. <https://doi.org/10.1021/acssuschemeng.1c01293>
9. Bajkacz, S., Adamek, J. (2017). Evaluation of new natural deep eutectic solvents for the extraction of isoflavones from soy products. *Talanta.*, 168, 329-335. <https://doi.org/10.1016/j.talanta.2017.02.065>, PMID:28391863
10. Ballesteros-Go'mez, A., Rubio, S., Pe'rez-Bendito, D. (2009). Potential of supramolecular solvents for the extraction of contaminants in liquid foods. *J. Chromatogr. A.*, 1216(3), 530-539. <https://doi.org/10.1016/j.chroma.2008.06.029>, PMID:18603255
11. Ballesteros-Gomez, A., Sicilia, M.D., Rubio, S. (2010). Supramolecular solvents in the extraction of organic compounds. A review. *Anal. Chem. Acta.*, 677(2), 108-130. <https://doi.org/10.1016/j.aca.2010.07.027>, PMID:20837178
12. Barthel-Rosa, L.P., Gladysz, J.A. (1999). Chemistry in fluororous media: a user's guide to practical considerations in the application of fluororous catalysts and reagents. *Coord Chem Rev.*, 192, 587-605. [https://doi.org/10.1016/S0010-8545\(99\)00102-2](https://doi.org/10.1016/S0010-8545(99)00102-2)
13. Bera, A., Belhaj, H. (2016). Ionic liquids as alternatives of surfactants in enhanced oil recovery-a state-of-the-art review. *J. Mol. Liq.*, 224, 177-188. <https://doi.org/10.1016/j.molliq.2016.09.105>
14. Boyd, A.R., Champagne, P., McGinn, P.J., MacDougall, K.M., Melanson, J.E., Jessop, P.G. (2012). Switchable hydrophilicity solvents for lipid extraction from microalgae for biofuel production. *Bio. Technol.*, 118, 628–632. <https://doi.org/10.1016/j.biortech.2012.05.084>, PMID:22721685

15. Breeden, S.W., Clark, J.H., Macquarrie, D.J., Sherwood, J. (2012). Green techniques for organic synthesis and medicinal chemistry. *Green Solvents*. Wiley, Chichester. 241-261. <https://doi.org/10.1002/9780470711828.ch9>
16. Cai, C.M., Zhang, T., Kumar, R., Wyman, C.E. (2014). Integrated furfural production as a renewable fuel and chemical platform from lignocellulosic biomass. *J. Chem. Technol. Biotech.*, 89(1), 2–10. <https://doi.org/10.1002/jctb.4168>
17. Capello, C., Fischer, U., Hungerbühler, K. (2007). What is a green solvent? A comprehensive framework for the environmental assessment of solvents. *Green Chem.*, 9(9), 927. <https://doi.org/10.1039/b617536h>
18. Capello, C., Fischer, U., Hungerbühler, K. (2007). What is a green solvent? A comprehensive framework for the environmental assessment of solvents. *Green Chem.*, 9, 927-934. <https://doi.org/10.1039/b617536h>
19. Cavazzini, M., Montanari, F., Pozzi, G., Quici, S. (1999). Perfluorocarbon-soluble catalysts and reagents and the application of FBS (fluorous biphasic system) to organic synthesis. *J Fluorine Chem.*, 94, 183-193. [https://doi.org/10.1016/S0022-1139\(98\)00358-3](https://doi.org/10.1016/S0022-1139(98)00358-3)
20. Ciriminna, R., Katryniok, B., Paul, S.B., Dumeignil, F., Pagliaro, M. (2015). Glycerol-Derived Renewable Polyglycerols: A Class of Versatile Chemicals of Wide Potential Application. *Org. Process Res. Dev.*, 19(7), 748–754. <https://doi.org/10.1021/op500313x>
21. Clark, J.H., Farmer, T.J., Hunt, A.J., Sherwood, J. (2015). Opportunities for biobased solvents created as petrochemical and fuel products transition towards renewable resources. *Int J Mol Sci.*, 16, 17101-17159. <https://doi.org/10.3390/ijms160817101>, PMID:26225963 PMCID:PMC4581186
22. Clarke, C.J., Tu, W.-C., Levers, O., Bröhl, A., Hallett, J.P. (2018). Homogenous catalysis in supercritical fluids. *Chem Rev.*, 118, 747-800. <https://doi.org/10.1021/acs.chemrev.7b00571>, PMID:29300087
23. Constable, D.J.C., Jimenez-Gonzalez, C., Henderson, R.K. (2007). Perspective on solvent use in the pharmaceutical industry. *Org Process Res Dev.*, 11, 133-137. <https://doi.org/10.1021/op060170h>
24. Cornils, B. (1997). Fluorous biphasic systems-the new phase-separation and immobilization technique. *Angew Chem Int Ed.*, 36, 2057-2059. <https://doi.org/10.1002/anie.199720571>
25. Cunha, S.C., Fernandes, J.O. (2018). Extraction techniques with deep eutectic solvents. *Trac Trends Anal Chem.*, 105, 225-239. <https://doi.org/10.1016/j.trac.2018.05.001>
26. Curran, D. (2001). Fluorous techniques for the synthesis and separation of organic molecules. *Green Chem.*, 3(1), G3-G7. <https://doi.org/10.1039/b100266j>
27. Curran, D.P. (1998). Strategy-level separations in organic synthesis: from planning to practice. *Angew Chem Int Ed.*, 37, 1174-1196. [https://doi.org/10.1002/\(SICI\)1521-3773\(19980518\)37:9<1174::AID-ANIE1174>3.0.CO;2-P](https://doi.org/10.1002/(SICI)1521-3773(19980518)37:9<1174::AID-ANIE1174>3.0.CO;2-P)
28. Curzons, A.D., Constable, D.C., Cunningham, V.L. (1999). Solvent selection guide: a guide to the integration of environmental, health and safety criteria into the selection of solvents. *Clean Prod Process.*, 1, 82-90. <https://doi.org/10.1007/s100980050014>
29. Diorazio, L.J., Hose, D.R.J., Adlington, N.K. (2016). Toward a more holistic framework for solvent selection. *Org Process Res Dev.*, 20, 760-773. <https://doi.org/10.1021/acs.oprd.6b00015>
30. Dunford, N.T., Temelli, F., LeBlanc, E. (1997). Supercritical CO₂ extraction of oil and residual proteins from Atlantic mackerel (*Scomber scombrus*) as affected by moisture content. *J. Food Sci.*, 62(2), 289–294. <https://doi.org/10.1111/j.1365-2621.1997.tb03987.x>
31. Earle, M.J., Seddon, K.R. (2000). Ionic liquids green solvents for the future. *Pure App Chem.*, 72, 1391-1398. <https://doi.org/10.1351/pac200072071391>
32. Eastman, H.E., Jamieson, C., Watson, A.J.B. (2015). Development of solvent selection guides. *Aldrichimica Acta.*, 48, 51-55.
33. Espino, M., de los Ángeles Fernández M., Gomez, F.J.V., Silva, M.F. (2016). Natural designer solvents for greening analytical chemistry. *TrAC - Trends Anal. Chem.*, 76, 126-136. <https://doi.org/10.1016/j.trac.2015.11.006>
34. Fang, V, Yeung, H.W., Leung, H.W., Huie, C.W. (2000). Micelle-mediated extraction and preconcentration of ginsenosides from Chinese herbal medicine, *J. Chromatogr. A.*, 904(1), 47-55. [https://doi.org/10.1016/S0021-9673\(00\)00911-0](https://doi.org/10.1016/S0021-9673(00)00911-0)
35. Ferrera, Z.S., Sanz, C.P., Santana, C.M., Rodriguez, J.J.S. (2004). The use of micellar systems in the extraction and pre-concentration of organic pollutants in environmental samples. *Trends Anal. Chem.*, 23(7), 469-479. [https://doi.org/10.1016/S0165-9936\(04\)00732-0](https://doi.org/10.1016/S0165-9936(04)00732-0)
36. Filly, A., Fabiano-Tixier, A.S., Fernandez, X., Chemat, F. (2015). Alternative solvents for extraction of food aromas. Experimental and COSMO-RS study. *LWT - Food Sci. Technol.*, 61, 33-40. <https://doi.org/10.1016/j.lwt.2014.11.021>
37. Fine, F., Vian, M.A., Tixier, A.-S.F., Carre, P., Pages, X., Chemat, F. (2013). Les agro-solvants pour l'extraction des huiles végétales issues de graines oléagineuses. *OCL*, 20, A502. <https://doi.org/10.1051/ocl/2013020>
38. Fischer, V., Touraud, D., Kunz, W. (2016). Eco-friendly one pot synthesis of caffeic acid phenethyl ester (CAPE) via an in-situ formed deep eutectic solvent. *Sustain. Chem. Pharm.*, 4, 40-45. <https://doi.org/10.1016/j.scp.2016.08.002>
39. Fischer, V., Touraud, D., Kunz, W. (2016). Eco-friendly one-pot synthesis of caffeic acid phenethyl ester (CAPE) via an in-situ formed deep eutectic solvent. *Sustain. Chem. Pharm.*, 4, 40-45. <https://doi.org/10.1016/j.scp.2016.08.002>

40. Fu, D., Farag, S., Chaouki, J., Jessop, P.G. (2014). Extraction of phenols from lignin microwave-pyrolysis oil using a switchable hydrophilicity solvent. *Bioresour. Technol.*, 154, 101–108. <https://doi.org/10.1016/j.biortech.2013.11.091>, PMID:24384316
41. Garci'a-Fonseca, S., Ballesteros-Go'mez, A., Rubio, S. (2016). Restricted access to supramolecular solvents for sample treatment in the enzyme-linked immunosorbent assay of mycotoxins in food, *Anal. Chem. Acta.*, 935, 129-135. <https://doi.org/10.1016/j.aca.2016.06.042>, PMID:27543022
42. Gladysz, J.A., Curran, D.P., Horvath, I.T. (2004). Handbook of fluoros chemistry. Wiley-VCH, Weinheim. <https://doi.org/10.1002/3527603905>
43. Gomez, F.J.V., Espino, M., Fernández, M.A., Silva, M.F. (2018). A Greener Approach to Prepare Natural Deep Eutectic Solvents. *Chem Select.*, 3, 6122-6125. <https://doi.org/10.1002/slct.201800713>
44. Goodship, V., Ogur, E.O. (2004). Polymer processing with supercritical fluids. Rapra review reports. Rapra Technology Ltd, Shawbury.
45. Gu, Y., Jerome, F. (2013). Bio-based solvents: an emerging generation of fluids for the design of eco-efficient processes in catalysis and organic chemistry. *Chem. Soc. Rev.* 42, 9550-9570. <https://doi.org/10.1039/c3cs60241a>, PMID:24056753
46. Gupta, A., Verma, J.P. (2015). Sustainable bio-ethanol production from agro-residues: a review. *Renew. Sustain. Energy Rev.*, 41, 550-567. <https://doi.org/10.1016/j.rser.2014.08.032>
47. Häckl, K., Kunz, W. (2018). Some aspects of green solvents. *Comptes Rendus Chimie.*, 21(6), 572-580. <https://doi.org/10.1016/j.crci.2018.03.010>
48. Herrero, M., Cifuentes, A., Ibanez, E. (2006). Sub-and supercritical fluid extraction of functional ingredients from different natural sources: Plants, food-by-products, algae and microalgae: A review. *Food Chem.*, 98(1), 136–148. <https://doi.org/10.1016/j.foodchem.2005.05.058>
49. Herrero, M., Mendiola, J.A., Cifuentes, A., Ibanez, E. (2010). Supercritical fluid extraction: recent advances and applications. *J Chroma A.*, 1217, 2495-2511. <https://doi.org/10.1016/j.chroma.2009.12.019>, PMID:20022016
50. Hobbs, H.R., Thomas, N.R. (2007). Biocatalysis in supercritical fluids, in fluoros solvents, and under solvent-free conditions. *Chem Rev.*, 107, 2786-2820. <https://doi.org/10.1021/cr0683820>, PMID:17564485
51. Horvath, I.T., R' abai, J. (1994). Facile catalyst separation without water: ' fluoros biphasic hydroformylation of olefins. *Science.*, 266, 72-75. <https://doi.org/10.1126/science.266.5182.72>, PMID:17814001
52. Hyde, J.R., Licence, P., Carter, D., Poliakoff, M. (2001). Continuous catalytic reactions in supercritical fluids. *App Cat A Gen.*, 222, 119-131. [https://doi.org/10.1016/S0926-860X\(01\)00835-3](https://doi.org/10.1016/S0926-860X(01)00835-3)
53. Jessop, P.G. (2011). Searching for green solvents. *Green Chem.*, 13, 1391-1398. <https://doi.org/10.1039/c0gc00797h>
54. Jessop, P.G. (2011). Searching for green solvents. *Green Chem.*, 13(6), 1391–1398. <https://doi.org/10.1039/c0gc00797h>
55. Jessop, P.G. (2015). Switchable solvents as media for synthesis and separations. *Aldrichimica Acta.*, 48, 18–21.
56. Jessop, P.G., Leitner, W. (1999). Chemical synthesis using supercritical fluids. Wiley, Weinheim. <https://doi.org/10.1002/9783527613687>, PMCid:PMC1756857
57. Jessop, P.G., Leitner, W. (1999). Chemical synthesis using supercritical fluids. Wiley-VCH, Weinheim. <https://doi.org/10.1002/9783527613687>, PMCid:PMC1756857
58. Jessop, P.G., Phan, L., Carrier, A., Robinson, S., Dürr, C.J., Harjani, J.R. (2010). A solvent having switchable hydrophilicity. *Green Chem.*, 12, 809. <https://doi.org/10.1039/b926885e>
59. Khezeli, T., Daneshfar, A. (2017). Synthesis and application of magnetic deep eutectic solvents: novel solvents for ultrasound-assisted liquid-liquid microextraction of thiophene. *Ultrason. Sonochem.*, 38, 590-597. <https://doi.org/10.1016/j.ultsonch.2016.08.023>, PMID:27562909
60. Kim Alfonsi, K., Colberg, J., Dunn, P.J., Fevig, T., Jennings, S., Johnson, T.A., Kleine, H.P., Knight, C., Nagy, M.A., Perry, D.A., Stefaniak, M. (2008). Green chemistry tools to influence a medicinal chemistry and research chemistry-based organisation. *Green Chem.*, 10, 31-36. <https://doi.org/10.1039/B711717E>
61. Kitazume, T. (2000). Green chemistry development in fluorine science. *J Fluorine Chem.*, 105, 265-278. [https://doi.org/10.1016/S0022-1139\(99\)00269-9](https://doi.org/10.1016/S0022-1139(99)00269-9)
62. Knothe, G., Steidley, K.R. (2011). Fatty acid alkyl esters as solvents: evaluation of the kauri-butanol value. Comparison to hydrocarbons, dimethyl diesters, and other oxygenates. *Ind. Eng. Chem. Res.*, 50(7), 4177–4182. <https://doi.org/10.1021/ie1023172>
63. Kokosa, J.M. (2019). Selecting an extraction solvent for a greener liquid-phase microextraction (LPME) mode based analytical method. *Trends Anal. Chem.* 118, 238-247. <https://doi.org/10.1016/j.trac.2019.05.012>
64. Kudłak, B., Owczarek, K., Namiesnik, J. (2015). Selected issues related to the toxicity of ionic liquids and deep eutectic solvents- a review. *Environ Sci Poll Res.*, 22, 11975-11992. <https://doi.org/10.1007/s11356-015-4794-y>, PMID:26040266
65. Li, S., Yan, W., Zhang, W. (2009). Solvent-free production of nanoscale zero-valent iron (nZVI) with precision milling. *Green Chem.*, 11, 1618-1626. <https://doi.org/10.1039/b913056j>
66. Liu, Y., Friesen, J.B., McAlpine, J.B., Lankin, D.C., Chen, S.-N., Pauli, G.F. (2018). Natural Deep Eutectic Solvents: Properties, Applications, and Perspectives. *J. Nat. Prod.*, 81, 679-690. <https://doi.org/10.1021/acs.jnatprod.7b00945>, PMID:29513526 PMCid:PMC5913660



67. Lo'pez-Jime'nez, F.J., Rubio, S., Pe'rez-Bendito, D. (2010). Supramolecular solvent-based microextraction of Sudan dyes in chilli-containing foodstuffs before their liquid chromatography-photodiode array determination. *Food Chem.*, 121(3), 763-769. <https://doi.org/10.1016/j.foodchem.2009.12.081>
68. MacMillan, D.S., Murray, J., Sneddon, H.F., Jamieson, C., Watson, A.J.B. (2013). Evaluation of alternative solvents in common amide coupling reactions: replacement of dichloromethane and N, N-dimethylformamide. *Green Chem.*, 15, 596-600. <https://doi.org/10.1039/c2gc36900a>
69. MacMillan, D.S., Murray, J., Sneddon, H.F., Jamieson, C., Watson, A.J.B. (2012). Replacement of dichloromethane within chromatographic purification: a guide to alternative solvents. *Green Chem.*, 14, 3016-3019. <https://doi.org/10.1039/c2gc36378j>
70. Mantell, C., Casas, L., Rodríguez, M., de la Ossa, E.M. (2013). Supercritical fluid extraction. *Separat and Puri Tech in Bioref.*, 79-100. <https://doi.org/10.1002/9781118493441.ch4>
71. Marriott, R., Sin, E. (2012). Supercritical CO₂ as an Environmentally Benign Medium for Biorefinery. *Role of Green Chem in Bio Proc and Con.*, 181-204. <https://doi.org/10.1002/9781118449400.ch5>
72. Martínez, J.L. (2008). Supercritical fluid extraction of nutraceuticals and bioactive compounds. CRC Press, Taylor & Francis Group, Boca Raton. <https://doi.org/10.1201/9781420006513.ch2>
73. Martins, M.A.R., Pinho, S.P., Coutinho, J.A.P. (2019). Insights into the Nature of Eutectic and Deep Eutectic Mixtures. *J. Solution Chem.*, 48, 962-982. <https://doi.org/10.1007/s10953-018-0793-1>
74. McGonagle, F.I., MacMillan, D.S., Murray, J., Sneddon, H.F., Jamieson, C., Watson, A.J.B. (2013). Development of a solvent selection guide for aldehyde-based direct reductive amination processes. *Green Chem.*, 15, 1159-1165. <https://doi.org/10.1039/c3gc40359a>
75. Melnyk, A., Namiesnik, J., Wolska, L. (2015). Theory and recent applications of coacervate-based extraction techniques. *Trac Trends Anal Chem.*, 71, 282-292. <https://doi.org/10.1016/j.trac.2015.03.013>
76. Mendes, R. L., Fernandes, H.L., Coelho, J., Reis, E.C., Cabral, J., Novais, J.M., Palavra, A.F. (1995). Supercritical CO₂ extraction of carotenoids and other lipids from *Chlorella vulgaris*. *Food Chem.*, 53(1), 99-103. [https://doi.org/10.1016/0308-8146\(95\)95794-7](https://doi.org/10.1016/0308-8146(95)95794-7)
77. Mendes, R.L., Fernandes, H.L., Coelho, J.A., Cabral, J.M., Palavra, A.M., Novais, J.M. (1994). Supercritical carbon dioxide extraction of hydrocarbons from the microalga *Botryococcus braunii*. *J. Appl. Phycol.*, 6(3), 289-293. <https://doi.org/10.1007/BF02181941>
78. Mishima, K. (2008). Biodegradable particle formation for drug and gene delivery using supercritical fluid and dense gas. *Adv Drug Deli Rev.*, 60, 411-432. <https://doi.org/10.1016/j.addr.2007.02.003>, PMID:18061302
79. Moral, A., Sicilia, M.D., Rubio, S. (2009). Determination of benzimidazolic fungicides in fruits and vegetables by supramolecular solvent-based microextraction/liquid chromatography/fluorescence detection. *Anal. Chem. Acta.*, 650(2), 207-213. <https://doi.org/10.1016/j.aca.2009.07.056>, PMID:19720194
80. Murray, P.M., Bellany, F., Benhamou, L., Bučar, D.K., Tabor, A.B., Sheppard, T.D. (2016). The application of design of experiments (DoE) reaction optimisation and solvent selection in the development of new synthetic chemistry. *Org Biomol Chem.*, 14, 2373-2384. <https://doi.org/10.1039/C5OB01892G>, PMID:26699438
81. Owczarek, K., Szczepanska, N., Plotka-Wasyłka, J., Rutkowska, M., Shyshchak, O., Bratychak, M., Namiesnik, J. (2016). Natural deep eutectic solvents in extraction process. *Chem. Chem. Technol.*, 10(4), 601-606. <https://doi.org/10.23939/chcht10.04si.601>
82. Payne, S.M., Kerton, F.M. (2010). Solubility of bio-sourced feedstocks in 'green solvents'. *Green Chem.*, 12(9), 1648-1653. <https://doi.org/10.1039/c0gc00205d>
83. Pena-Pereira, F., Kloskowski, A., Namieśnik, J. (2015). Perspectives on the replacement of harmful organic solvents in analytical methodologies: a framework toward the implementation of a novel generation of eco-friendly alternatives. *Green Chem.*, 17, 3687-3705. <https://doi.org/10.1039/C5GC00611B>
84. PŁotka-Wasyłka, J., Rutkowska, M., Owczarek, K., Tobiszewski, M., Namiesnik, J. (2017). Extraction of environmentally friendly solvents. *Trac Trends Anal Chem.*, 91, 12-25. <https://doi.org/10.1016/j.trac.2017.03.006>
85. Pollet, P., Davey, E.A., Ureña-Benavides, E.E., Eckert, C.A., Liotta, C.L. (2014). Solvents for sustainable chemical processes. *Green Chem.*, 16, 1034-1055. <https://doi.org/10.1039/C3GC42302F>
86. Prajapati, D., Gohain, M. (2004). Recent advances in the application of supercritical fluids for carbon-carbon bond formation in organic synthesis. *Tetrahedron.*, 60, 815-833. <https://doi.org/10.1016/j.tet.2003.10.075>
87. Prat, D., Hayler, J., Wells, A. (2014). A survey of solvent selection guides. *Green Chem.*, 16, 4546-4551. <https://doi.org/10.1039/C4GC01149J>
88. Prat, D., Wells, A., Hayler, J., Sneddon, H., McElroy, C.R., Abou-Shehada, S., Dunn, P.J. (2016). CHEM21 selection guide of classical- and less classical-solvents. *Green Chem.*, 18, 288-296. <https://doi.org/10.1039/C5GC01008J>
89. Procopio, D., Siciliano, C., Trombino, S., Dumitrescu, D.E., Suci, F., Gioia, M.L.D. (2022). Green solvents for the formation of amide linkages. *Org. Biomol. Chem.*, 20, 1137-1149. <https://doi.org/10.1039/D1OB01814K>
90. Ramsey, E., Sun, Q., Zhang, Z., Zhang, C., Gou, W. (2009). Mini-review: green sustainable processes using supercritical fluid carbon dioxide. *J Environ Sci.*, 21, 720-726. [https://doi.org/10.1016/S1001-0742\(08\)62330-X](https://doi.org/10.1016/S1001-0742(08)62330-X)
91. Reichardt, C. (1979). Solvent effects in organic chemistry. *Verlag Chemie, Weinheim.*
92. Rezaei, F., Yamini, Y., Moradi, M., Daraei, B. (2013). Supramolecular solvent-based hollow fibre liquid-phase microextraction of benzodiazepines. *Anal. Chem. Acta.*, 804, 135-142. <https://doi.org/10.1016/j.aca.2013.10.026>, PMID:24267074

93. Rothenberg, G., Downie, A.P., Raston, C.L., Scott, J.L. (2001). Understanding solid/solid organic reactions. *J Am Chem Soc.*, 123, 8701-8708. <https://doi.org/10.1021/ja0034388>, PMID:11535074
94. Samorì, C., Cespi, D., Blair, P., Galletti, P., Malferrari, D., Passarini, F., et al. (2017). Application of switchable hydrophilicity solvents for recycling multilayer packaging materials. *Green Chem.*, 19(7), 1714-1720. <https://doi.org/10.1039/C6GC03535C>
95. Sarrade, S., Guizard, C., Rios, G.M. (2003). New applications of supercritical fluids and supercritical fluids processes in separation. *Sep Purif Technol.*, 32, 57-63. [https://doi.org/10.1016/S1383-5866\(03\)00054-6](https://doi.org/10.1016/S1383-5866(03)00054-6)
96. Señoráns, F.J., Ibañez, E. (2002). Analysis of fatty acids in foods by supercritical fluid chromatography. *Anal Chim Acta.*, 465, 131-144. [https://doi.org/10.1016/S0003-2670\(02\)00208-8](https://doi.org/10.1016/S0003-2670(02)00208-8)
97. Sheldon, R.A. (2005). Green solvents for sustainable organic synthesis: state of the art. *Green Chem.* 7(5), 267-278. <https://doi.org/10.1039/b418069k>
98. Sicaire, A., Abert Vian, M., Fine, F., Carre, P., Tostain, S., Chemat, F. (2015). Solvants alternatifs au n-hexane pour l'extraction d'huiles végétales (Poster).
99. Skowerski, K., Białecki, J., Tracz, A., Olszewski, T.K. (2014). An attempt to provide an environmentally friendly solvent selection guide for olefin metathesis. *Green Chem.*, 16, 1125-1130. <https://doi.org/10.1039/C3GC41943F>
100. Smith, E.L., Abbott, A.P., Ryder, K.S. (2014). Deep Eutectic Solvents (DESs) and Their Applications. *Chem. Rev.*, 114, 11060-11082. <https://doi.org/10.1021/cr300162p>, PMID:25300631
101. Soh, L., Curry, J., Beckman, E.J., Zimmerman, J.B. (2014). Effect of system conditions on biodiesel production via transesterification using carbon dioxide-methanol mixtures in the presence of a heterogeneous catalyst. *ACS Sustainable Chem. Eng.*, 2(3), 387-395. <https://doi.org/10.1021/sc400349g>
102. Soh, L., Zimmerman, J. (2011). Biodiesel production: the potential of algal lipids extracted with supercritical carbon dioxide. *Green Chem.*, 13(6), 1422-1429. <https://doi.org/10.1039/c1gc15068e>
103. Soylak, M., Khan, M., Yilmaz, E. (2016). Switchable solvent-based liquid-phase microextraction of uranium in environmental samples: a green approach. *Anal. Methods.*, 8(5), 979-986. <https://doi.org/10.1039/C5AY02631H>
104. Sprague, M., Bendiksen, E.Å., Dick, J.R., Strachan, F., Pratoomyot, J., Berntssen, M.H., Tocher, D.R., Bell, J.G. (2010). Effects of decontaminated fish oil or a fish and vegetable oil blend on persistent organic pollutant and fatty acid compositions in diet and flesh of Atlantic salmon (*Salmo salar*). *Br. J. Nut.*, 10(10), 1442-1451. <https://doi.org/10.1017/S0007114510000139>, PMID:20193093
105. Sunarso, J., Ismajli, S. (2009). Decontamination of hazardous substances from solid matrices and liquids using supercritical fluids extraction: a review. *J Hazard Mater.*, 161, 1-20. <https://doi.org/10.1016/j.jhazmat.2008.03.069>, PMID:18434005
106. Tanaka, K. (2003). Solvent-free organic synthesis. Wiley-VHC, Weinheim. <https://doi.org/10.1002/3527601821>
107. Taygerly, J.P., Miller, L.M., Yee, A., Peterson, E.A. (2012). A convenient guide to help select replacement solvents for dichloromethane in chromatography. *Green Chem.*, 14, 3020-3025. <https://doi.org/10.1039/c2gc36064k>
108. Thoma, J.A. (1965). Selection of a chromatographic solvent. *Anal Chem.*, 37, 500-508. <https://doi.org/10.1021/ac60223a014>
109. Tobiszewski, M., Tsakovski, S., Simeonov, V., Namieśnik, J., Pena-Pereira, F. (2015). A solvent selection guide based on chemometrics and multicriteria decision analysis. *Green Chem.*, 17, 4773-4785. <https://doi.org/10.1039/C5GC90060C>
110. Trickey, J.P. (1927). Certain Solvent Properties of Furfural and Its Derivatives. *Ind. Eng. Chem.*, 19(5), 643-644. <https://doi.org/10.1021/ie50209a048>
111. Trimble, F. (1941). Furfural as a Solvent. *Ind. Eng. Chem.*, 33(5), 660-662. <https://doi.org/10.1021/ie50377a026>
112. Trujillo-Rodríguez, M.J., Nan, H., Varona, M., Emaus, M.N., Souza, I.D., Anderson, J.L. (2019). Advances of ionic liquids in analytical chemistry. *Anal Chem.*, 91, 505-531. <https://doi.org/10.1021/acs.analchem.8b04710>, PMID:30335970
113. Trujillo-Rodríguez, M.J., Rocío-Bautista, P., Pino, V., Afonso, A.M. (2013). Ionic liquids in dispersive liquid-liquid microextraction. *Trac Trends Anal Chem.*, 51, 87-106. <https://doi.org/10.1016/j.trac.2013.06.008>
114. Tsekova, D.S., Saez, J.A., Escuder, B., Miravet, J.F. (2009). Solvent-free construction of self-assembled 1D nanostructures from low-molecular-weight organogelators: sublimation vs. gelation. *Soft Matt.*, 5, 3727-3735. <https://doi.org/10.1039/b902516b>
115. Vanderveen, J.R., Durelle, J., Jessop, P.G. (2014). Design and evaluation of switchable-hydrophilicity solvents. *Green Chem.*, 16, 1187-1197. <https://doi.org/10.1039/C3GC42164C>
116. Vankelecom, I.F.J., Gevers, L.E.M. (2005). Green separation processes fundamentals and applications. *Membrane Processes.*, Wiley-VCH, Weinheim. 251-270. <https://doi.org/10.1002/3527606602.ch3f>
117. Wasserscheid, P., Welton, T. (2003). Ionic liquids in synthesis. Wiley, Weinheim. <https://doi.org/10.1002/3527600701>
118. Welton, T. (2015). Solvents and sustainable chemistry. *Proc R Soc A.*, 471, 20150502. <https://doi.org/10.1098/rspa.2015.0502>, PMID:26730217 PMCid:PMC4685879
119. Williams, J.R., Clifford, A.A. (2000). Supercritical fluid methods and protocols. Humana Press Totowa, Totowa. <https://doi.org/10.1385/1592590306>
120. Yeo, S.D., Kiran, E. (2005). Formation of polymer particles with supercritical fluids: a review. *J Super Fluid.*, 34, 287-308. <https://doi.org/10.1016/j.supflu.2004.10.006>



121. Yilmaz, E., Soylak, M. (2015). Switchable solvent-based liquid-phase microextraction of copper (II): optimization and application to environmental samples. *J. Anal. At. Spectrometry*, 30(7), 1629-1635. <https://doi.org/10.1039/C5JA00012B>
122. Yilmaz, V., Soylak, M. (2015). Switchable polarity solvent for liquid-phase microextraction of Cd (II) as pyrrolidinedithiocarbamate chelates from environmental samples. *Anal. Chem. Acta.*, 886, 75-82. <https://doi.org/10.1016/j.aca.2015.06.021>, PMID:26320638
123. Zhang, H., Tang, B., Row, K. (2014). Extraction of catechin compounds from green tea with a new green solvent. *Chem. Res. Chin. Univ.*, 30, 37-41. <https://doi.org/10.1007/s40242-014-3339-0>
124. Zhang, W. (2009). Green chemistry aspects of fluororous techniques-opportunities and challenges for small-scale organic synthesis. *Green Chem.*, 11, 911-920. <https://doi.org/10.1039/b820740b>
125. Zhang, W., Cai, C. (2008). New chemical and biological applications of fluororous technologies. *Chem Commun.*, 5686-5694. <https://doi.org/10.1039/b812433g>, PMID:19009050