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Green solvents

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Abstract

Prolonged exposure to solvents has a harmful impact on all living organisms, damaging most organs. Reducing the use of solvents or replacing them with less toxic ones, are two of the most important ambitions of green chemistry. Water, supercritical fluids, ionic liquids, non-toxic liquid polymers and their varied combinations are part of the class of green solvents. They are characterized by low toxicity, convenient accessibility and possibility of reuse as well as great efficiency.

Key words: green solvents, green chemistry, catalysts, environment

Introduction

Concerns have arisen in the field of chemical processing since enormous amounts of poisonous and inflammable solvents are used every day. Each year, more than twenty million tons of waste residues from organic solvents are emitted to the atmosphere, causing unnecessary waste of solvents and polluting the environment [1]. Despite the fact that organic solvents, such as DMSO, DMF, acetone as well as aromatic ones e.g. benzene, toluene and chlorinated solvents (CHCl) contribute to environmental pollution, they are still used in large amounts [6]. Prolonged exposure to solvents has a harmful impact on all systems present in living organisms, damaging mainly respiratory and nervous systems [6,3]. Moreover, the use of hazardous solvents is deleterious to organs, e.g. carbon tetrachloride and chloroform are hepatotoxic [2,4]. The kidney failure occurs while glycol ethers and chlorinated solvents are used [2].

Furthermore, working with some solvents like halogenated hydrocarbons, petroleum distillates and diethylene glycol may lead to renal tubular necrosis, even after a short period of time [5]. According to the data published by WHO, about 1/4 of the current diseases occur as a result of long term exposure to environmental pollutants. Due to synthetic chemicals discharge or an accumulation of natural chemicals, pollutants reach toxic levels. High levels of pollutants lower the number of wildlife, impair the ecosystem and possess a threat to a human health [2]. Reducing the use of solvents or replacing them with less toxic ones is one of the most relevant aims of green chemistry (Fig.1) [7].

All facts mentioned above attract great interest among academia and industries for use of green solvents.

Fig. 1. Major aims of green chemistry [24].

Green solvents

It is commonly acknowledged that the process efficiency is highly dependent on the solvent type. Owing to their special properties, green solvents improve chemical processes, lower the use of solvents and decrease the processing steps [2,7].

Water [8,9], supercritical fluids [10-12], ionic liquids [13-15], non-toxic liquid polymers [16-19] and their diverse combinations are part of the class of green solvents. They are characterized by low toxicity, convenient accessibility and the possibility of reuse as well as great efficiency. An ideal green solvent would also mediate reactions, separations or catalyst recycling [23].

An idea of green chemistry is aiming for replacement of commonly used solvent with 'green' ones, resulting in a reduced environmental impact. However, it leads to discussions about supremacy of one green solvent over another [13, 20]. Ionic liquids have been especially negated for their complicated synthesis and toxicity [20], although so has water [13,21]. A choice of an optimal solvent for a reaction is crucial and it significantly affects the outcome (Fig.2) [7,22].

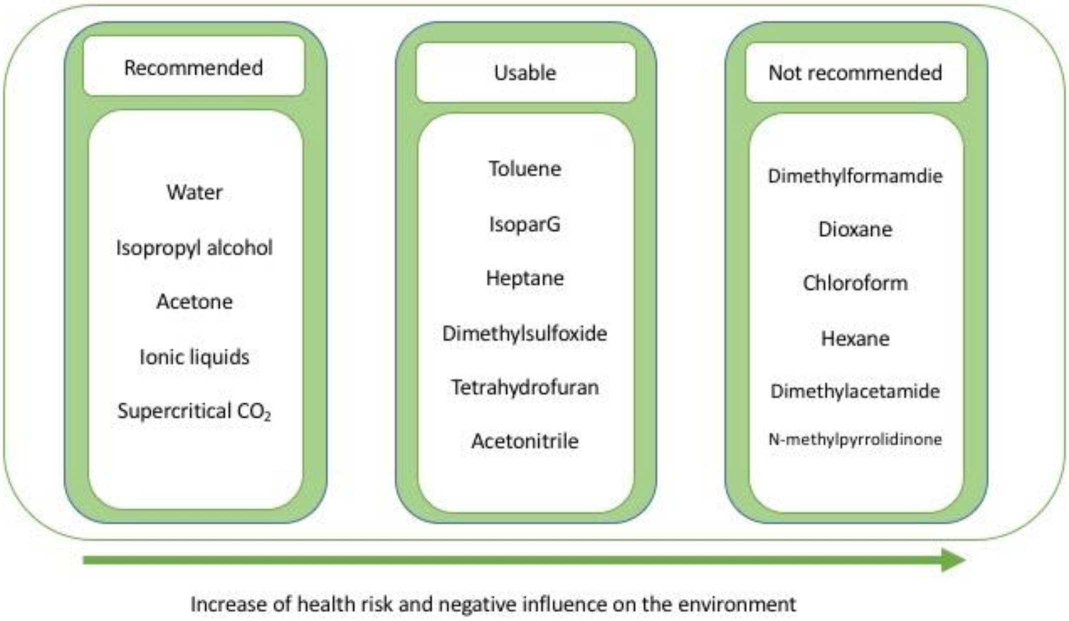

Fig. 3. Solvent selection guide for membrane fabrication [25].

Synthesis in water

Despite the fact that water causes many problems as a solvent in organic synthesis, purification methods, and separating final products, in recent years it has become more popular in organic reactions. In some cases, water stimulates reactions through a dissolution of reagents and ensures selectivity. Moreover, oxygen is not soluble in water which can be an advantage for metal catalysts. In last decade water has become a really popular solvent thanks to its properties such as being harmless for the environment and it has been documented in a large amount of papers [26-28].

It is known that water is the most used solvent in all biochemical reactions taking place in nature [27]. Notwithstanding, water is a suitable solvent only for organic chemicals, containing polar groups e.g. alcohols or carboxylic acids. However, two decades ago special selectivity present in aqueous solutions was also observed in water suspensions, where one soluble element interacted with a poorly soluble one [1,27,31]. Lately, many researchers have observed an excellent acceleration of a reaction in such a suspension, named by them: reactions on water [27,29,30]. It would be an understatement to say that water is just an environmentally friendly solvent, it possesses exceptional properties that are substantially unique, associated to the hydrophobic effect [27].

Supercritical carbon dioxide and supercritical water

A supercritical liquid is a substance at a temperature and pressure above their respective critical levels, where is so distinct phase between gas and liquid [26, 32]. A supercritical liquid can act like a gas, pass trough solid materials or like liquids, dissolving other materials. Moreover, when both temperature and pressure are near the critical point, changing them even slightly can result in serious density alterations.

Supercritical liquids are an apt replacement of organic solvents for industrial and lab processes. In general, carbon dioxide (sCO_2- supercritical carbon dioxide) and water are most commonly used supercritical fluids. They are considered to be green solvents [26]. Due to the great solubility in many polymers, sCO_2 is an irreplaceable component of polymer processing. What more, the choice of less harmful fluids (sCO_2) instead of conventional organic solvents is an advantage to the environment [26,33].

Ionic Liquids in Organic Synthesis

Lately, ionic liquids received a lot of attention from scientists due to their unique properties and abilities [34]. Ionic liquids consist of a mixture of cations and anions, molten salts. Their melting points reach 100ºC which makes them a great alternative to convenient solvents in organic syntheses. Most often they possess quaternary ammonium cations and inorganic anions. Despite this fact, ionic liquids do not precisely meet all “green” conditions, they are still quite promising alternative solvents [26].

There is a wide range of applications that ionic liquids are used for. They have been used for battery production, lubricants, plasticizers, solvents, mass spectrometry matrices, solvents for nanomaterials production, extraction reactions, gas absorption agents and among other things [35].

They are non-volatile and non-flammable hence they could work in high-vacuum systems and exclude possible contaminants. Ionic liquids do not form a homogeneous mixture with many organic solvents and produce an anhydrous polar alternate option for two-phase systems. Additionally, they may provide immiscible polar phases with water, when they are hydrophobic [36].

Non-toxic liquid polymers

Liquid polymers comprise a group of non-volatile solvents that gained the attention, because of a possibility of using them in conjunction with $scCO_2$ as media, for homogeneous catalysis with catalyst recovery. Their task as a solvent in reactions and a catalyst is alike to that provided by ionic liquids in biphasic catalysis. Nevertheless, liquid polymers are not as polar as ionic liquids, they should be rather considered as a supplement to ionic liquids, not a substitution.

PEG (polyethylene glycol) is rightfully called a green chemical, because it is inflammable, non-volatile, non-toxic to humans, animals and aqueous environment. Additionally, the polymer is biodegradable by bacteria found in sewage and soil [16-19, 37-39]. PPG (polypropylene glycol) is the next non-toxic liquid having similar properties as PEG, however it is slightly less biodegradable [18,37,40]. PDMS (polydimethylsiloxane) and dialkylether-capped PEG showed to be significantly less biodegradable and PTHF (polytetrahydrofuran) in hydrous emulsion a variant is toxic to *Daphnia magna.*

To sum up, all polymers presented above have successfully proved to have the potential to be extensively employed as media, for various reactions and catalysis [37].

Conclusion

An idea of green chemistry is aiming for replacement of commonly used solvent with “green” ones, resulting in a reduced environmental impact. However, it leads to discussions about supremacy of one green solvent over another. In the future scientists will have to focus more on the solvent selection, basing on sustainable development and environmental protection. To select properly, more data about new solvents chemo-physical properties and their environmental impact is needed. Citing Elon Musk “We have no desire to do the best green chemistry. We will do the best chemistry, and it will happen to be green”.

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