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Green Solvents and Green Technology for Green Chemistry: A Review

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Abstract: Many industrial processes involve the use of significant quantities of toxic and hazardous chemical solvents in reaction systems and other stages, impacting both the environment and businesses. Researching green technology involves developing environmentally safe chemicals suitable for commercial and technological applications. Promising alternatives for solvent production include supercritical and subcritical fluids, natural and recycled solvents, and ionic liquids that remain liquid at room temperature. This overview explores the types of solvents, their applications, and their potential as eco-friendly industrial solvents.

Keywords: Solvents, Solvency, Waste Minimization, Green Chemistry, Green Technology, Sustainable Development,

INTRODUCTION

Green solvents are eco-friendly chemical solvents utilized in the field of green chemistry. They gained significant attention in 2015, following the UN's establishment of a new development plan focused on sustainability, which highlighted the importance of green chemistry and green solvents in achieving a more sustainable future. These solvents are engineered to be more environmentally friendly, coming from sustainable agricultural crops or other eco-friendly processes and serving as substitutes for petrochemical solvents. Key features of green solvents include their ability to be recycled easily, biodegrade quickly, and have low toxicity. The preference for green solvents is on the rise due to their reduced environmental impact. However, these solvents still pose risks to human health and the environment. While some green solvents are understood to be safe, others remain uncertain or have not yet been categorized. Here, we present selected information from the safety data sheets of common green solvents. According to a recent study [1], solvents contribute to 60% of industry emissions and 30% of all volatile organic compound emissions globally. In line with the EU's environmental policy for 2010–2050, there is a significant focus on reducing the use of hazardous solvents in industries, reflecting the expansion of P.T. Anastas's concept of "green chemistry" beyond academic circles [2]. Although solvents are necessary for various processes such as breaking up materials, transferring mass and heat, altering structures, separating components, and cleaning, the development of green solvents aims to replace petroleum-based solvents with those derived from natural resources and substitute hazardous solvents with safer alternatives. Water, considered the ideal solvent, is utilized in processes such as emulsion polymerization and hydro distillation. While many organic and organometallic drugs are insoluble in water, researchers are exploring ionic liquids that remain liquid at room temperature, supercritical or subcritical fluids, and natural or recycled solvents as promising alternatives [3].

Liquidity, Solvency, and Solvents

Liquidity, solvents, and mixtures are part of our daily routines, from brewing a cup of coffee (which involves adding sugar and cleaning the mug) to shampooing hair in the bath, from applying and removing nail polish to cleaning an apple under running water before consuming it, from painting to consuming liquid pain relievers for headaches. Are these mixtures or solutions? What distinguishes a gel, a mixture, a suspension, and a solution? Therefore, mixtures and solvents play a crucial role in various branches of chemistry [4], including the behavior of phases, the characteristics of solids, liquids, and gases, and the attributes of mixtures predominantly composed of liquids and solids. The process of dissolving involves Van der Waals forces, ionic and dipolar interactions, hydrogen bonding, and the transfer of charges. The nature of the liquid significantly influences the speed and temperature of a reaction [5].

Ionic Solvents

Recent studies have shown that ionic liquids (ILs) have piqued the interest of both researchers and businesses over the past 15 years [6]. These organic salts have the unique ability to dissolve at temperatures below 100 °C, making them incredibly versatile. One of their main advantages is their low volatility, as well as their non-flammability and overall chemical, thermal, and electrical safety. Furthermore, their composition of ionic species, often a bulky organic cation and an organic or metal anion, allows for solvent modifications to meet specific requirements [7, 8]. With over 50,000 academic articles and 5,000 patents already published in the field of ILs, it's clear that their potential for technological and environmental impact is significant.

Consumption, Disposal, and Contamination of Solvents

The environment and other elements are impacted by pollution, chemical usage, and excessive water consumption. Historically, this activity involved the use of less-than-ideal solvents such as benzene, 4-carbon disulphide, and carbon tetrachloride before being upgraded [9, 10]. Industrial users are now decreasing their reliance on toxic, flammable solvents that can generate peroxides, including diethyl ether, di-isopropyl ether, hexane, and ethylene glycol dimethyl ether, due to their detrimental properties. Industrial usage of solvents is widespread (see Table 1).

Table 1. List of many common applications for solvents

Analytical processes	Industrial applications
Solvent extraction	Hydrometallurgy Waste water treatment
Cleaning	Metal degreasing Dry cleaning
Formulations	Dispersant Lubricants
Coating	Paints Varnishes
Chemicals production	Reaction medium Production purification

Organic and Sustainable Sources of Solvents

Glycerol serves as a viable alternative to petroleum-based solvents due to the safety, environmental friendliness, and biodegradability of natural component solvents like deep eutectic solvents, cholinium-based ILs, and renewable source solvents such as methanol, ethanol, esters, 2-methyl-tetrahydrofuran, and hydrocarbon solvents. Glycerol is non-toxic, biodegradable, and can be reused [11, 12, 13].

The use of volatile organic compounds significantly contributes to environmental degradation and fire hazards. Previous assumptions regarding the environmental friendliness of natural solvents, like cholinium-based ILs and deep eutectic solvents, have been confirmed by studies [14–16], which attested to the low toxicity of their constituent components or ions. Recent research efforts have been dedicated to exploring deep eutectic fluids and glycerol replacements, which have demonstrated potential as environmentally friendly solvents.

Alternatives for Solvents

The use of different solvents can either lower or completely remove fumes. A significant shift in the fields of reaction engineering and process technology is needed to get rid of toxic substances and other pollutants. One approach is to replace chemicals with solvents. While (i) is the more frequent approach in the industry, there are ongoing efforts from both the private sector and academic institutions to enhance the effectiveness and quality of finding suitable replacements for conventional industrial liquids. Researchers often opt for (ii) when they secure funding from private entities. It's crucial to minimize the release of toxic chemicals for the sustainability of operations. Consequently, there is a focus on developing fluids and process systems from renewable biomass sources in both the private and academic sectors. The areas of research include "solvents from alternative renewable sources" and "biosolubilities or bio-derived solvents."

Instructions for Solvents in the Drug Industry

Creating medicines involves a complex series of chemical steps and the use of liquid or solvent solutions. The process of separating materials across state lines and cleaning them up is done using solvents. This is the reason why the pharmaceutical sector has a very high E-factor (kg/kg) of waste to useful products [17]. Due to the expenses and negative impacts, people are searching for ways to minimize waste and pollution.

Choosing Solvents and Their Production

Choosing solvents systematically could possibly improve understanding and insight into chemistry. The processes of forming molecules with specific physical or chemical characteristics and/or delineating the "chemical space" through numerical data for categorizing molecules are two main approaches [18]. Numerous research efforts [19] have focused on what are referred to as "green" compounds. The nature of the solute and solvent influences the behavior of the solvent. Research and thorough investigation into this relationship have been carried out in both commercial and academic settings by individuals such as Snyder, Hildebrand, Hansen, Gutmann, Winstein, Reichardt, Kamlet, Taft, Abrahams, Katritzky, and Marcus. Solvents from carbohydrates For ethanol, the American Conference of Governmental Industrial Hygienists (ACGIH) has set a short-term exposure limit of 1000 ppm to avoid irritating the respiratory system. The French National Agency for Food, Environmental, and Occupational Health Safety (ANSES) has recommended a short-term exposure limit of 100 mg/m3 for butan-1-ol, a solvent used in paints, cleaners, and degreasers, to prevent irritation of the eyes and upper respiratory tract. Since 1998, the ACGIH has proposed an 8-hour exposure limit (ELV) of 20 ppm for butan-1-ol to prevent irritation of the upper respiratory tract and eyes. Male rats exposed to THFA show signs of reproductive toxicity, and it also affects the development of fetuses and embryos in rats. The American Industrial Hygiene Association suggested an ELV of 2 ppm for THFA in 1993, based on the no-observed-effect level from two subchronic studies in rats and dogs.

Chemical Solvents, Their Impact on Nature and Environmentally Friendly Solvents

Solvents come in many different shapes and sizes and are notoriously hard to copy. The progress and pace of research and development (R&D) in both the private sector and the academic world have been slow and inconsistent. This is a detailed overview of the situation. Historically, the focus of green chemistry was on "green" reaction liquids; however, the current focus has shifted to the origin, application method, control measures, and final disposal of the liquid. Initiatives to enhance worker safety by minimizing solvent use led to a decrease in exposure to the most dangerous substances. Environmental concerns prompted the push to reduce solvent use in the 1970s and 1980s. Initially, alternatives were introduced due to their greater accessibility.

The information gathered by John Andraos (2013) suggests that it's not possible to achieve high technology efficiency, ensure worker safety, and minimize environmental impact at the same time. This means we need to look beyond just the chemical properties of a liquid to understand its waste production. Surprisingly, studies might show that creating a product or intermediate with a "green" solvent can actually be less efficient and more wasteful than using a "non-green" solvent. "Green" or solvent-free options are often preferred in research on green chemistry [20, 21]. Similar studies can also be found in [22, 23, 24]. Yet, a lot of the literature focuses on claimed benefits that are "greener," "cleaner," "harmless," "environmentally friendly," "environmentally benign," "environmentally green," "environmentally acceptable," "eco-friendly," and "sustainable," without any proof from toxicology or eco toxicology. The impact of these processes on an industrial scale is rarely talked about in these publications.

The use of green solvents is increasingly preferred because of their lower environmental impact. These solvents still present dangers for human health as well as for the environment. However, for a number of green solvents, their impact is still unclear, or at least, not categorized yet. Listed here is selected information from the safety data sheets of common green solvents

Table 2. Selected details of widely used green solvents.

Solvents	Hazards
Ethyl lactate	Flammable liquid and vapours causes severe damage. May irritate the respiratory tract.
Ethanol	Highly flammable liquid and vapours. Causes severe eye irritation.
2-Methyltetrahydrofuran.	Highly flammable liquid and vapours. Harmful if swallowed. Causes skin irritation and severe eye damage.
Levulinic acid	Harmful if swallowed. Causes skin irritation and severe eye irritation
Limonene	Flammable liquid and vapours causes skin irritation. May cause skin allergy.

Eutectic Deep Solvents

A fresh category of liquid salts, known as deep eutectic solvents (DESs), are made up of a hydrogen acceptor, like a nontoxic quaternary ammonium salt (such as cholinium chloride), and a naturally occurring uncharged hydrogen-bond donor, such as amines, sugars, alcohols, and carboxylic acids, all mixed in a precise molar ratio. The mixture's freezing point is lowered due to the spreading of charges. It's possible to achieve a liquid at room temperature (freezing point = 12 °C) by mixing urea (133 °C) with choline chloride (302 °C) in a 1:2 molar ratio. Due to their likeness to ILs in terms of being non-reactive, not flammable, having a high viscosity, and their basic ingredients, some people call DESs the fourth generation of ILs. DESs, similar to ILs, are recognized as "designer solvents" because of their flexible molecular structure and chemical makeup. From an environmental and economic standpoint, DESs are an attractive choice due to their minimal ingredients, ease of production, lack of health hazards, and long lifespan. [26] Initially used in biodiesel, metal electrode placement, and electropolishing, choline-based eutectic liquids have expanded into various other fields. These include organic synthesis, biocatalysis, polymer production, electrochemistry, nanomaterials, separation techniques, analysis, medicine, and the extraction of bioactive compounds from plants. Reported applications of DESs span from 104 to 105, with over 300 DES research articles published between 2009 and 2013. While DESs show promise in enhancing technology, health, and the environment, more research is needed to validate these claims. The potential of DESs in biological applications ranges from medication delivery systems to aids for bone repair. DESs break down organic acids, sugars, sugar alcohols, alkanols, amino acids, choline chloride, and betaine at rates 10–100 times faster than water or lipids. This opens up possibilities for DESs in the production of food, medicine, cosmetics, and agrochemicals, eliminating the need for expensive processing steps.

Glycerol and Its Derivatives

Because of its plentiful availability (accounting for 10% of the total output), its low expense, lack of toxicity, non-flammability, ability to decompose naturally, and promising physical (low vapor pressure, stability under normal storage conditions) and chemical characteristics (high affinity, capacity to form robust hydrogen bonds, dissolve a broad spectrum of organic and inorganic substances, enzymes, and transition metal complexes), glycerol is being explored for a range of possible uses. In the field of organic chemistry, glycerol is advantageous as it can be combined with a broad spectrum of substances, including those that are insoluble in water but soluble in glycerol. Substances such as mineral salts, acids, bases, enzymes, and mixtures of transition metals are all vulnerable to glycerol's effects. The reaction byproducts can be separated in the liquid-liquid phase, as ethers and hydrocarbons do not react with glycerol. Glycerol's high melting point (290 °C) and excellent thermal stability enable its use at elevated temperatures, followed by recovery through distillation after contamination by reaction byproducts [32].

Glycerol's high viscosity (1200 cP at 20 °C) and limited solubility of non-polar substances and gases are well-documented challenges. However, both the use of co-solvents and temperatures above 60 °C have been found to decrease viscosity [33–36]. Glycerol's hydroxyl groups undergo chemical transformations in highly acidic or basic conditions, resulting in byproducts. Glycerol is an effective solvent as it preserves the chemical neutrality of hydroxyl groups [37–39].

CONCLUSION

The act of dissolving plays a vital role in the field of chemistry. Liquids are valuable in both industrial and domestic settings, and they can be produced through various chemical disciplines. Replacements for the lost liquid are not as efficient as the primary one. Choosing the right liquid for a specific purpose is challenging because it needs to perform multiple functions. The choice of liquid depends on the specific application. It's important to maintain a balance between achieving physical, scientific, economic, scalability, regulatory, safety, and environmental goals. Over the last decade, there have been significant advancements in different types of solvents, such as ionic liquids, water, supercritical and subcritical fluids (especially supercritical carbon dioxide), and natural and eco-friendly solvents (like deep eutectic solvents, glycerol-based solvents, etc.).

Despite these promising developments, the adoption of supercritical CO2 extraction systems, ionic liquids, and similar solvents is restricted due to their toxicity, biocompatibility, and the challenge of separating products in water-based processes. There are also variations among eco-friendly chemicals. Consumers base their decisions on past research, cost, and environmental impact. Solvents are crucial for the purification, extraction, and separation of materials because they help to slow down the progression of chemical reactions. Therefore, it's necessary to carry out thorough economic and environmental impact evaluations.

Factors such as toxicological, eco-toxicological, environmental, resource depletion, and economic impacts throughout the production chain (from its primary raw material), formulation, application, and disposal or fate should all be taken into account when selecting a solvent that is sustainable.

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