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The use of environmentally sustainable bio-derived solvents in solvent extraction applications—A review

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ABSTRACT

Replacement of volatile organic compounds (VOCs) by greener or more environmentally sustainable solvents is becoming increasingly important due to the increasing health and environmental concerns as well as economic pressures associated with VOCs. Solvents that are derived from biomass, namely bio-derived solvents, are a type of green solvent that have attracted intensive investigations in recent years because of their advantages over conventional VOCs, such as low toxicity, biodegradability and renewability. This review aims to summarize the use of bio-derived solvents in solvent extraction applications, with special emphasis given to utilization of biodiesels and terpenes. Compared with the conventional VOCs, the overall performance of these bio-derived solvents is comparable in terms of extraction yields and selectivity for natural product extraction and no difference was found for metal extraction. To date most researchers have focused on laboratory scale thermodynamics studies. Future work is required to develop and test new bio-derived solvents and understand the kinetic performance as well as solvent extraction pilot plant studies.

1. Introduction

Solvent extraction is an effective separation technique widely used in a variety of applications, ranging from separations in analytical chemistry [1,2] to industrial processes in hydrometallurgy [1,3–6], pharmaceutical [7–9], food engineering [9–11] and waste treatment [8,12,13]. Solvent extraction takes advantage of the solubility difference of a solute in two immiscible liquid phases (usually one organic and one aqueous phase) in contact with each other to attain separation. Solute A, which initially is dissolved in only one of the two phases, gradually distributes between the two liquids with the process of reaction or diffusion at the interface and eventually reaches equilibrium. Concentrations of solute A in organic and aqueous phases are $[A]_{org}$ and $[A]_{aq}$ respectively and the distribution ratio, D_A (also called the distribution coefficient), of the solute is defined as the ratio of "the total concentration of the substance in the organic phase to its total concentration in the aqueous phase, usually measured at equilibrium" [1].

$$D_A = \frac{[A]_{org}}{[A]_{aq}} \qquad (1)$$

If a second solute B is present, the corresponding distribution ratio is indicated by D_B and so forth. The solutes A and B can be separated if D_A and D_B are different.

The organic phase solvents used in solvent extraction applications have been predominantly Volatile Organic Compounds (VOCs). The World Health Organization (WHO) defines VOCs as organic compounds with boiling points between 50 °C and 260 °C [14], including aliphatic and aromatic hydrocarbons, halogenated hydrocarbons, some esters, ethers, alcohols, aldehydes and ketones. Many of these VOCs are highly flammable (*e.g.* hydrocarbons), toxic (*e.g.* exposure to hexane causes central nervous system effects and neurotoxic effects), and detrimental to the environment (*e.g.* halogenated hydrocarbons deplete ozone). Due to these health and environmental problems, the legislation upon utilization of VOCs is becoming increasingly stricter, for example REACH [15]—the Registration, Evaluation and Authorisation of Chemicals—a regulation of the European Union, is implementing stricter rules for the use of a large number of solvents resulting in their applications becoming very expensive or even prohibited as well as increasing the cost for storage and disposal of hazardous solvents. The unsteady supply and rising price of VOCs pose further problems to their utilization. The price of crude oil, which is the main raw material for VOCs, has experienced an overall increase with some fluctuations in the past two decades [16–18]. Considering these environmental regulations, health concerns as well as the increasing price and unsteady supply of crude oils, the search for green solvents is imperative for sustainable development of chemical processes [19].

Numerous alternative solvents to VOCs have been developed and they are categorized into seven classes by Kerton *et al.* [20] including water, supercritical fluids, renewable solvents, ionic liquids and eutectic mixtures, fluorous solvents, liquid polymers and switchable solvent systems. So far there is no systematic method to determine how "green" a

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solvent is and the greenness of a solvent also depends on how it is used. “Recognising whether a solvent is actually green” is regarded as one of the four grand challenges in the field of green solvent research by Jessop [21]. For example, ionic liquids (IL) are widely regarded as green solvents as they are stable and non-volatile. However, the IL [Bmim][BF4] was found to have larger life cycle environmental impact than several conventional solvents for their use in manufacture of cyclohexane and in a Diels-Alder reaction by life cycle assessment (LCA) [22]. Nevertheless, LCA is only one method for assessing the greenness of a solvent, and other factors such as recycling, health hazards and boiling point should also be taken into consideration. The global pharmaceutical company, GlaxoSmithKline, compiled a “Solvent Selection Guide” [23] which scores solvents using impacts such as environmental waste, environmental impact, health, process safety and LCA [24]. Additionally, the “Twelve Principles of Green Chemistry” proposed by Anastas and Warner, lists the principles required to make a greener chemical, process or product [25].

Bio-derived solvents are a group of solvents that are produced in a biorefinery from a range of renewable sources such as plants and algae. These solvents are of low toxicity, environmentally benign and biodegradable, and are therefore classified as green solvents. “Use of renewable feedstocks” is among the “Twelve Principles of Green Chemistry”, and Chemat *et al.* [26] also list the “use of bio-solvents” as one of their six principles of green extraction. It is believed that replacement of conventional VOCs by bio-derived solvents may be faster than other alternative solvents (such as ionic liquids and CO_2 switchable solvents) as the technologies required for their use are similar to the present VOCs enabling easier implementation and lower costs. This paper aims to summarize the applications of bio-derived solvents in solvent extraction processes with particular emphasis given to utilization of biodiesels and terpenes.

Fig. 1. Life cycle of bio-derived solvents.

2. Application of Bio-derived Solvents in Solvent Extraction

2.1. Overview of bio-derived solvents

Bio-derived solvents are produced from biomass in a biorefinery which is defined as “a facility that integrates biomass conversion processes and equipment to produce fuels, power and chemicals from biomass” [27]. Biomass includes a wide range of sources including energy crops (*e.g.* corn), forest products (*e.g.* wood), aquatic biomass (*e.g.* microalgae) and waste materials (*e.g.* urban wastes). After being used, these bio-derived solvents can be biodegraded (Fig. 1). Chemists are striving to build a bio-platform for biorefinery to replace the conventional petroleum refinery to overcome those environmental and societal challenges. Twelve bio-sourced platform chemicals that can be produced either biologically or chemically from natural carbohydrates feedstocks have been identified by the U.S. Department of Energy as building bricks for a biorefinery [27]. Searching for new bio-derived solvents attracted intensive study in recent years and numerous new solvents have been discovered. However, not all of them can be used in solvent extraction as there are some specific requirements for solvents to be used for this application.

2.1.1. Potential bio-derived solvents for solvent extraction

To replace VOCs in a solvent extraction process, ideally the new solvent needs to have low toxicity, good solute selectivity, high capacity for desired solute, non-flammability, inertness to equipment materials, sufficiently high interfacial tension, minimal viscosity and reasonable cost. Moreover, the solubility of the solvent in water should be sufficiently low so as to minimize solvent losses during extraction. Admittedly there are some other solvents that are insoluble in many organic solvents can be used in solvent extraction besides water, such as sulfolane and propylene carbonate, whereas they are much less popular than water. Despite some studies investigating the physicochemical properties of newly derived solvents [28–33], information is far from comprehensive. From this point of view, solubility of a solvent in water can be used as a prerequisite to evaluate suitability of solvents for applications in solvent extraction. A collection of bio-derived solvents and their solubilities in water are listed in Table 1, which shows that biodiesels, terpenes and 2,5-dimethylfuran (DMF) are insoluble in water and thus have the potential to be used in solvent extraction processes.

Table 1
Solubilities of bio-derived solvents in water

Solvents	Examples	Solubility in water	Reference
Alcohols	Ethanol	Soluble	[27]
	Glycerol	Soluble	[27,34]
Glycerol derivatives	Over 60 species	Mostly soluble	[31]
Esters	Biodiesels (SBME)	Insoluble	[35]
	Ethyl lactate	Soluble	[17,36]
Acids	Gluconic acid	Soluble	[37]
Terpenes	D-Limonene	Insoluble	[36]
	α-Pinene	Insoluble	[36]
p-Cymene	*p*-Cymene	Insoluble	[36]
Furfural family	Furfural	Soluble	[38]
	Furfuryl alcohol	Soluble	[39]
	Levulinic acid	Soluble	[40]
	Ethyl levulinate	Soluble	[41]
	Butyl levulinate	Soluble	[41]
γ-Valerolactone	γ-Valerolactone	Soluble	[42]
Furan derivatives	2-Methyltetrahydrofuran	Soluble	[36]
	2,5-Dimethylfuran (DMF)	Insoluble	[43]
Dihydrolevoglucosenone	Dihydrolevoglucosenone (Cyrene)	Soluble①	[44]

①Experimental determination is not available, however, it is likely to be miscible with water from its Hansen Solubility Parameters.

The physical properties of the potential bio-derived solvents and hexane are given in Table 2. Viscosities of these bio-derived solvents are quite low, making them easy to handle in solvent extraction applications. The density of solvents used in solvent extraction is recommended to be about 0.8 $g\cdot ml^{-1}$ to aid phase separations [45]. The densities of