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Some aspects of green solvents

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ABSTRACT

Chemical solvents constitute around 80% of the total volume of chemicals used in many important chemical processes, especially fine chemical manufacturing. Unfortunately, these solvents are often volatile organic compounds from petroleum resource bearing several health and environmental risks. Numerous researchers take these two aspects as a reason to search for novel green solvents to replace the conventional ones. As a consequence, there are an increasing number of publications dealing with green solvents. In this review, we discuss the definition and accuracy of the term “green solvent”. We explain our urgent request for application-oriented research in this field. Finally, we point out some promising and interesting kinds of solvents, solvent systems and solubilization concepts for a successful research towards “greener solvents”.

1. Introduction

In their 12 Principles of Green Chemistry, Anastas and Warner [1] explicitly claim the use of “safer solvents and auxiliaries”. And who would contradict this claim? Consequently, there are an uncountable number of scientific articles dealing with “green solvents”. The question is, how much will remain from all these academic efforts? Will there be a chance for all these new solvents to come into the market, if only for some speciality applications? In this context, we would like to make some comments on the ongoing research and future directions of green solvents.

2. No-solvent systems

The best solvent is sometimes no solvent. In full agreement with the fifth Principle of Green Chemistry [1], it has been shown that there are relevant chemical and industrial processes, in which solvents can be completely avoided. Of course, this is not always possible. If the lack of the solvent causes dangerous overheating or leads to a higher energy demand, these disadvantages would foil the advantage of a solvent-free process.

For many years, reasonable effort has been made on the preparation of polymers in the absence of conventional reaction solvents. Indeed, there are industrial polymerization processes avoiding the use of solvents, like melt polymerization or solid state polymerization. For example, PET is commercially produced by melt polymerization followed by a solid state polymerization process [2–4]. It is even possible to prepare polymers (e.g., poly(phenylene vinylene)) by ensuring close contact of the reacting molecules in a ball milling process within minutes [5]. The ball milling method is not only known in polymer science but also in organic synthesis. Besides avoiding the use of organic solvents, it exhibits further advantages like high energy efficiency and reduced reaction times [6]. Solvent-free microwave extraction is another elegant technique worth to mention. Developed in 2004 by Lucchesi et al. [7,8], it is used for the extraction of essential oils from fresh plant materials in a microwave-assisted dry distillation process. It is a rapid method that delivers a powerful alternative to the conventional water-consuming and long-lasting hydrodistillation.

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3. Water as a solvent

Some scientists try to replace organic solvents by water, as it bears several advantages, like a low hazard potential, high availability and low cost. It also exhibits interesting aspects concerning reactivity: uncommon selectivities, influences of hydrogen-bond network on reaction behaviour, adjustable pH values, use of salts for the salting-in or salting-out effect and the application of biphasic reaction systems. Hence, it is certainly a valuable approach, but it should be kept in mind that water has also some disadvantages: its temperature-restricted range of liquid state and especially its significant heat capacity, which makes distillation processes extremely energy consuming. The same is true for pervaporation and reverse osmosis. All these techniques may be necessary when water must be separated from a non-volatile reaction product or impurities. In these cases, the high energy consumption may lead to the choice of another solvent.

Nevertheless, many promising results have been published over the years following this approach [9–11]. For example, the Diels–Alder reaction in water has been widely studied since 1980, when Rideout and Breslow [12] reported a certain rate acceleration using water as reaction medium. In all those studies on organic reactions in water, water is used both under atmospheric pressure and under higher pressures. In the latter case, reaction conditions with elevated temperatures are often adopted to reach the so-called subcritical water region, which is in general the liquid water phase above the boiling point at ambient pressure (100 °C) and below the critical point (374 °C, 22.1 MPa). Physical and chemical properties of subcritical water show a significant dependence on temperature and pressure, so that solvent properties are strongly influenced and adjustable. By keeping the pressure rather low, glass containers with decently thick walls could even still be used. Subcritical water can be considered as a promising solvent for biomass processing, for example, the conversion of lignin-derived compounds into value-added fuel products with and without addition of industrial gases [13–15]. In addition, various organic reactions could be successfully performed under "hydrothermal" conditions, that is, in water at temperatures between 150 and 250 °C [16,17].

4. Classical green solvents

Replacing conventionally used solvents by green solvents is a very wide field of research and development. A first general requirement is to define what a green solvent is. Gu and Jérôme [18] proposed 12 criteria that green solvents should fulfil related to availability, price, recyclability, grade, synthesis, toxicity, biodegradability, performance, stability, flammability, storage and renewability. Doubtlessly, this is a reasonable collection of conditions. However, it also demonstrates the dilemma of classifying a solvent as green, as in most of the cases not all requested parameters can be fulfilled by one solvent. What if the solvent in hand only complies with 11, 10 or 9 out of the required 12 characteristics of green solvents? Can it still be considered as green?

As a result, we should be precise about the meaning of a green solvent. It is clear that it is a relative term. Even Anastas and Warner [1] defined green chemistry as a reduction of harm and not as processes that do not cause any harm. Consequently, a new and apparently benign solvent can be termed green when it is "greener" as compared to the conventionally used solvent that should be replaced and when clear evidence can be given for this assumption.

In nearly all cases, the ultimate choice will be a compromise between several requirements, as it is schematically resumed in Fig. 1:

As recently proposed by Jessop [20], the best way to estimate the environmental impact of a solvent is a life cycle assessment (LCA), as it is done for many other chemical substances. It considers the whole fate of a solvent from the manufacturing until its disposal or recycling. Such an LCA must be done for each specific application of the solvent. It may turn out that a solvent is green (meaning less harmful than another one) for one process, but not for another process. For example, and as it was discussed in Section 3, water may be a green solvent, but whenever its distillation or other ways of purification are required, this can be very energy-consuming and changes the greenness of water for a given process.

During the last years, an almost uncountable number of articles and several excellent reviews and monographs have been published. They provide a very useful overview of a large variety of solvents and their classification as more or less green solvents [18,20–30]. It would be beyond the scope of the present article to go into details; the interested reader is referred to the literature. Still, we would like to emphasize on some particular points. Although we will not present LCAs, some interesting aspects will be mentioned. As a consequence, the picture will necessarily not be complete.

Talking about *classical green solvents*, we are thinking of already existing solvents that are Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) registered and may already find some applications in chemical industry and formulation. There are several issues we would like to mention regarding this kind of solvents:

(1) The biogenic origin of a solvent is neither a sufficient nor even a good criterion of the greenness of a solvent. For example, the bio-based furfural is considered as a renewable and sustainable platform chemical for the production of numerous value-added chemical compounds [31,32]. However, it is classified as toxic and carcinogenic. On the other hand, there is a class of petrol-based solvents that are eco-friendly showing a good human safety environment profile, for example, 3-methoxy-3-methyl-butane-1-ol [28,33].

(2) It is worth defining the sectors of application, in which green solvents are most urgently needed. According to Jessop [24], these are "solvents of high basicity/low polarity, high basicity/high polarity and low basicity/medium-to-high polarity. In other words, we lack replacements for amines, HMPA, halogenated solvents and aromatic solvents". Especially for these classes of solvents, it is difficult to find greener substitutes (please

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