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Alternative Solvents: Shades of Green

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Abstract:

The use of alternative reaction solvents is reviewed in terms of life cycle. Supercritical CO_2, ionic liquids, fluorous solvents, water, and renewable organics are compared on the basis of their solvency, ease of use, reusability, health and safety, environmental impact, and economic cost.

1. Introduction

Since the beginning of the Green Chemistry movement 10 years ago, the need for alternative solvents for reactions has been one of the major issues we have faced. Recognition of the need for new technology led to a substantial research effort worldwide with new or at least enhanced subject areas, notably ionic liquids, supercritical (and near-critical) fluids, and fluorous solvents. Books,[1,2] special issues of journals,[3] and entire conferences[4] were dedicated to these emerging topics. The use of water as a solvent for organic chemistry, we would argue, was already well established, and while there have been more research, new applications, and new concepts based on organic reactions in water, it has not attracted the same attention the others have—possibly because it is simply less glamorous than new solvents, and the intellectual property is more difficult to control. Similarly, solvent-free chemistry has been known as long as organic chemistry has been practiced, and it is experiencing a resurgence thanks to better understanding of "dry state" reactions and the use of microwave heating techniques. All of these have in their own way sought to address the now widely recognised problems of working with volatile organic solvents (environmental damage, toxicity, hazards in handling), by providing an "alternative". It is striking how different the approaches are—inorganic systems (water, $scCO_2$), involatile systems (ionic liquids), easily recyclable systems (fluorous solvents and $scCO_2$), and avoiding the problems altogether (no solvent). The diversity of approach in a way reflects both the enormity and complexity of the challenge (with so many different solvent applications in modern industry, commerce, and everyday life) and the shortage of success with large-scale applications which effectively leaves the field wide open with countless opportunities for the use of alternative reaction media.

In this article we will critically review the use of alternative solvents in chemistry. Rather than follow the well-trodden path of discussing in turn the reactions that have been performed in each major type of alternative solvent, we will instead structure our article in terms of what we consider to be the fundamental issues: life cycle analysis (so as to establish the "green" and sustainability aspects from the outset), solvency (so as to consider what is needed in the application and how the alternatives manage to meet these needs), and application (to consider practical issues in both process and product).

2. Solvent Life Cycle Assessment

The use of solvents is habitual in chemistry, to the point where solventless reactions are the exception and reactions in solution are the norm. The organic chemistry taught in schools and, to a large extent, in universities, is the chemistry of the liquid phase. The common question is "which solvent" rather than "do I need a solvent"? Can generations of chemists be wrong? In many cases, the use of the solvent is justified in terms of heat and mass transfer or in terms of directing a reaction along a particular pathway. However, solvent-free organic reactions, even between two solids, are more common than is perhaps recognised and should certainly be considered at the design stage of a process.[5] In 1998, Anastas and Warner proposed 12 principles of "green chemistry"[6] that included recognition that the use of auxiliary compounds, including organic solvents, was problematic and needed to be addressed. Over the previous decades, organic solvents had been associated with a series of environmental and health issues which led to this scrutiny: benzene, carbon tetrachloride, and chloroform, three solvents which had been favourites amongst synthetic chemists, were removed from general use due to their toxic and carcinogenic effects; chlorofluorocarbons (CFCs) were outlawed because of their ozone-depleting effects, and volatile organic compounds (VOCs) were implicated in the production of photochemical smog. Since then, a huge research effort has been directed towards alternatives to chlorinated solvents and VOCs in general. In particular, biphasic technologies, using fluorous and ionic liquids along with aqueous systems and supercritical carbon dioxide, have formed the main thrust of a movement that has been termed "alternative reaction media". These alternatives have frequently been described as green

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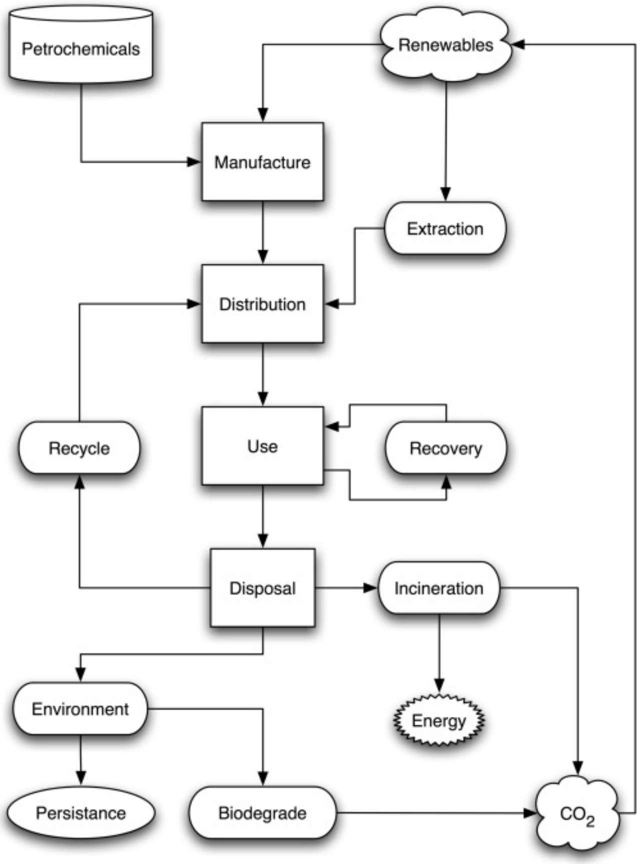

Figure 1. **Life cycle flow chart for solvent usage. Primary life cycle stages are represented by rectangles.**

solvents. However, solvent replacement in itself cannot make an inefficient reaction into a green one. The whole process must be considered, and the solvent (or lack thereof) is only one part of this jigsaw. The atom efficiency, energy use, demands on nonrenewable resources, and transport costs must all be taken into account. Let us consider the life cycle of a solvent (which will also serve as an illustration of a typical life cycle for other chemical products), Figure 1.

2.1. Manufacture. First, the solvent must be manufactured, usually from petrochemical feedstocks. This may involve cracking and distillation of a crude oil fraction in the case of simple and aromatic hydrocarbons, or more complex synthetic routes where oxygen and halogen atoms are introduced. Some solvents, such as acetone, may be byproducts from other chemical transformations. Both fluorous and ionic liquids typically require multistage syntheses, and the increased impact of the extra manufacturing and purification steps need to be weighed carefully against the advantages of separation and reuse that these alternative media may bring to a process. CO_2 and water do not require manufacture as such, although there are energy requirements for their respective condensation and purification. Solvents do not necessarily come from petrochemical resources, and historically, the earliest organic liquids were extracted from biomass (the word "organic" was originally coined for molecules that were derived from living organisms). For example, 19th century syntheses of benzene and toluene involved extraction from tree resin. Several renewable liquids that may function as solvents are available. Liquid fatty acids, esters (biodiesel), bioethanol, glycerol, limonene, and of course ethanol and acetic acid may all be produced from renewable resources and should be considered as possible replacement solvents. Extraction and purification may still be necessary.

2.2. Distribution. Second, the solvent must be distributed to the place of use. This is an aspect of the life cycle that may be forgotten, but with rising oil prices and concern about CO_2 emissions, the impact of transporting chemicals is becoming increasingly important, from both economic and environmental viewpoints. When renewables are to be considered, it makes sense to choose a product which may be supplied locally, otherwise the environmental benefits over nonrenewable alternatives may be negated by the impact of transporting the solvent. For example, it would make no sense to import bioethanol from Brazil, a major producer, to Europe (although this is happening at present in the energy sector, hopefully to encourage local production). We would hope that, in the near future, some kind of labeling system may be introduced that would let process chemists know exactly where a solvent (or other chemical feedstock) has been manufactured and how far it has travelled, so that they can make informed decisions on use. This is analogous to the concept of food miles, where discerning customers in supermarket wish to know not only what they are buying but also where it came from. Water and CO_2 are available worldwide and thus may usually be sourced close to the site of use.

2.3. Use. The third stage in the solvent life cycle is its use. This is where careful choice of solvent may allow design of a process that is more efficient in terms of energy and chemical consumption. Due to solvation effects a chemical equilibrium or mechanistic pathway may be altered or an activation energy reduced, which may allow the process to proceed with greater selectivity, at a lower temperature, or with a reduced exotherm and concomitant cooling requirements, than in a less appropriate choice of solvent. Solvent selection itself is not a simple matter. In fact the properties of solvents have been studied and classified in more detail than perhaps any other class of organic compounds, and there are myriad scales of solvency which measure dielectric constant, dipole moment, ability to accept or donate electron pairs or protons, along with cohesive pressure and numerous solubility and spectroscopic parameters.[1,7] Cohesion is generally associated with "polarity"—a polar solvent is often a cohesive one—and Hildebrand used this to create one of the first scales of solvent polarity, noting that liquids were miscible if the difference in the square root of the cohesive pressure is less that 3.4. For processing, the viscosity, density, melting and boiling points, and volatility must be considered, along with safety issues such as flash point, reactivity, and corrosiveness. However, making sense of all of this data is not necessarily simple, and the chemist may be faced with a daunting amount of information. This has led to the development of algorithms for solvent selection to aid the decision-making process, and from a green chemistry point of view it is encouraging to see that these systems take into

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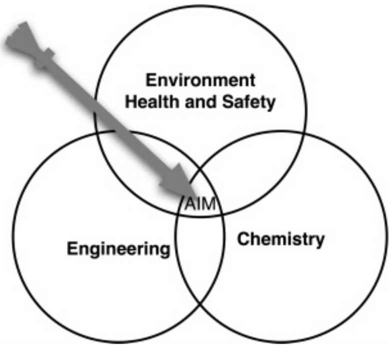

Figure 2. **Aims of solvent selection algorithms are to find an ideal media that meets environmental, chemical, and engineering criteria (ref 8).**

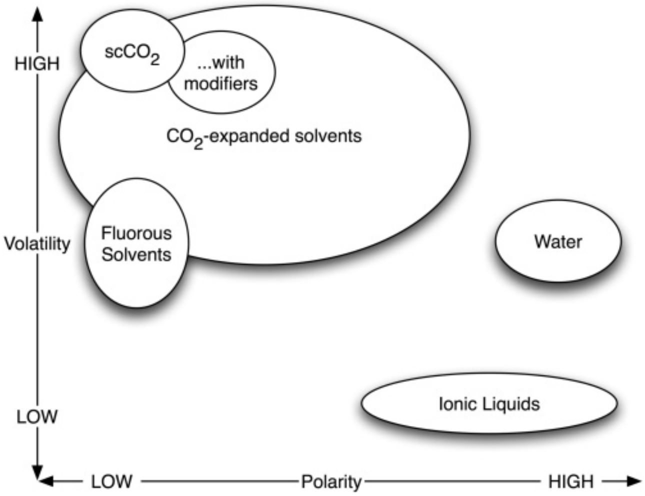

Figure 3. **Typical polarity and volatility characteristics of alternative reaction media.**

account environmental, health, and safety issues as well as chemical and engineering considerations (Figure 2).[8] Processes involving solvents are frequently designed with recovery, reuse, and recycling in mind, although the energy required to recover and purify the solvent must be accounted for, and it has been estimated that about 50% of the energy used in chemical processes is consumed in purification of products and recycled streams.[9] This is one of the reasons why biphasic systems are so attractive, as they can make separation and recovery much more efficient and less energy intensive.

Fluorous solvents have very low polarity and are generally quite volatile, although this depends upon chain length (Figure 3). As there are (at least in theory) billions of possible ionic liquid structures, it is impossible to categorise these simply. Broadly, however, they have medium-to-high polarity and low-to-zero volatility (although some may be distilled at greatly reduced pressure. Supercritical CO_2 is a weak solvent with low polarity, although this may be modified by addition of a small amount of another solvent or surfactant.[10] Pressurised CO_2 is also beginning to be used as a cosolvent in so-called expanded media, in which the quantities of organic solvent may be reduced and the solvation properties adjusted by tuning the operating pressure.[11] The extreme volatility of CO_2 makes solvent removal facile—simply releasing the pressure completely removes the solvent. Also, because supercritical fluids completely fill the entire reaction vessel, it may be used for polymerization reactions inside moulds to form low-density monolithic polymer parts.[12]

Water is an extremely cohesive solvent, which in some cases works against its ability to dissolve compounds of low polarity. For a solvent to dissolve a compound successfully, the free energy change required to separate solvent−solvent and solute−solute interactions must be outweighed by the solvation energy of the system (Figure 4). The heat of solvation (hydration) for many nonpolar organic compounds (e.g., hexane) in water is *exothermic*, Despite this, they are not usually miscible, which indicates that the entropy change is unfavorable. The water must reorganise itself around the organic molecule and this is working against the cohesive pressure of the water: although the payback on bonding to a nonpolar solute is enthalpically satisfying for the water, the entropy change outweighs this. The utility of water as a solvent for nonpolar compounds may be improved by superheating (water at 308 °C and 22 MPa is completely miscible with toluene[13]) or by addition of surfactants. The latter may often make separation more complex. Water is frequently used in biphasic and emulsion reactions and is commonly used in purification procedures. Water does have a high-energy cost for evaporation, associated with its high heat capacity and latent heat of vaporisation, and also contaminated water is difficult to purify.

2.4. Disposal. Whilst solvents may be reused or recycled via distillation, biphasic separation, or other recovery method, eventually the end-of-life scenario must be considered. A common disposal route for volatile organic solvents is via incineration, and it may be possible to recover the heat energy from this process, effectively using the waste stream as a fuel to drive local heating or electricity generation. However, if the solvent is impure or contains halogens or other heteroatom functions, a residue will be left which must be treated and disposed of. The exhaust gases from the incineration must also be treated (Figure 5).[14]

In certain cases, due to leakages, spills, or product design (e.g., aerosols and paints), there is accidental or intentional release of solvent to the environment. In these cases it is vital that the solvent breaks down over an acceptable time scale, either through photochemical or biodegradation processes. Supercritical CO_2 has little environmental impact, and it may safely be released to the environment simply by venting the reaction. Contaminated water from aqueous phase reactions may be difficult to deal with, as it may need to be thermally or biologically treated before it is released to the environment. Fluorocarbons are not flammable by them-

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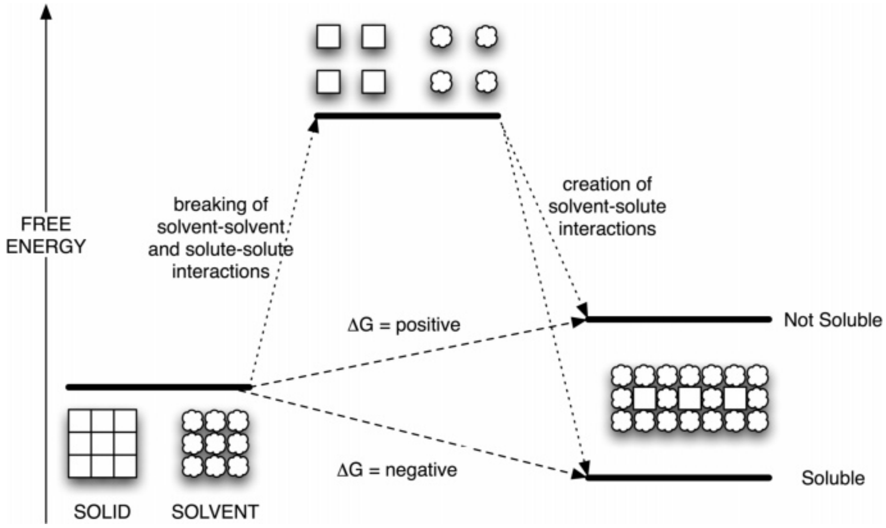

Figure 4. **Free energy diagram for solvent−solute interactions.**

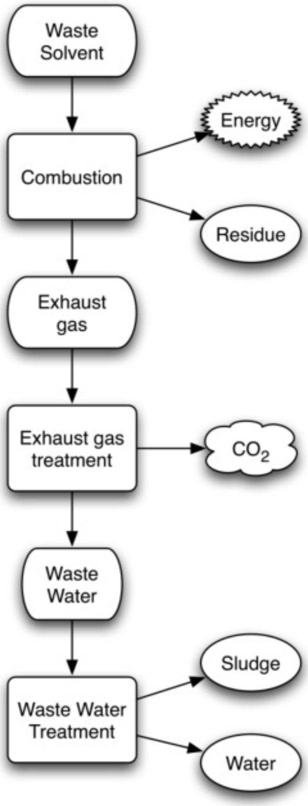

Figure 5. **Solvent incineration flow chart.**

selves, and their incineration requires the input of energy and may also lead to dangerous acidic by-products that must be further treated. The release of perfluorocarbon formulations to the environment is of concern because of their high global warming potential and long atmospheric lifetimes, and as they do not biodegrade, perfluorocarbons bioaccumulate.[15] Perfluoroalkyl ethers, (with structures $[(CF_2)_nO]_m$), have much shorter environmental lifetimes and may prove to be more viable alternatives for biphasic reactions, although fluorous degradation products may persist in the environment. Solvent disposal strategies for ionic liquids are uncertain at this point in time, but are undoubtedly structure-dependent, and their environmental fate requires further study. However, it is sensible to design future generations of ILs with biodegradation in mind.

3. Alternative Solvents in Chemical Processes

3.1. Applications of Alternative Solvents. In process chemistry alternative solvents have been put forward as replacements for a diverse range of organic solvents from volatile halocarbons to less volatile dipolar aprotic solvents. The primary reason for substitution has been to avoid the environmental impact resulting from the accidental loss of VOCs on handling, use in process, and subsequent reaction workup and separation. Health and safety factors such as toxicity and flammability are also a major concern. Chemical manufacturing industries including pharmaceuticals are under enormous pressure to minimise the use of VOCs with some of these (notably dichloromethane) being most targeted. In seeking replacements for these various solvent types it is important to remember that the enormous range of organic solvents of very diverse properties has enabled process-specific solvents to be used in many cases. The ideal reaction solvent will have the right blend of solvation properties (hydrogen bonding, polarisability, ion binding, etc.) to maximise reaction routes but be unreactive in the system while enabling facile postreaction separation and recycling, plus acceptable health and safety issues and cost. Safe disposal routes can also be an important factor.

Solvents are established in numerous processes ranging from chemical synthesis to cleaning and formulation. Most of the application areas offer opportunities for substitution of existing VOC solvents, and successful case studies are scattered around the various and diverse application areas. These include the now well-established use of $scCO_2$ as an extraction solvent for natural products, as a synthesis solvent in fine chemical synthesis, as a processing medium for materials manufacture and control of crystallisation,[16] and

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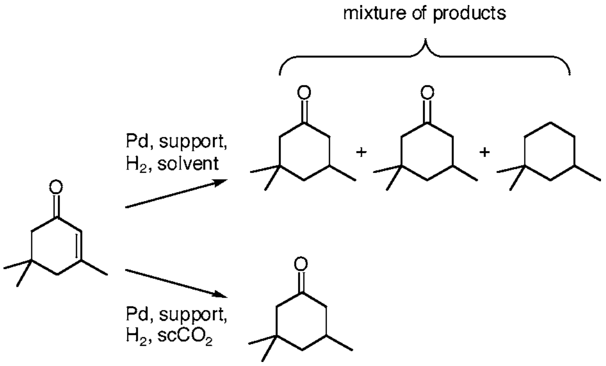

Figure 6. **Hydrogenation of isophorone to form trimethylcyclohexanone using a Pd catalyst. The reaction is much more selective under supercritical conditions than in conventional solvents.**

as a "dry" cleaning solvent in the semiconductor industry.[17] For example, it is used by Thomas Swann & Co. as a solvent for a Pd-catalysed hydrogenation reaction that proceeds with high efficiency (Figure 6).[18] Ionic liquids are used commercially in electroplating, as wetting agents and as carriers for reactive gases, as well as being generated in situ as a synthesis solvent in chemical manufacturing.[19] Water is much more established in chemical processes including chemical synthesis, notably biocatalytic reactions (where water is the normal solvent) as well as numerous inorganic synthetic reactions and countless cleaning applications (often in the presence of a surfactant) and formulations. We are not aware of any substantial commercial use of fluorous solvents in chemical processing, and they have only small-volume speciality uses as products (e.g., for high throughput synthesis).

It is interesting to compare the most high-profile types of alternative solvents against each of these key criteria for determining effectiveness as a widely useful process solvent (Table 1). We have included solvents based on or derived from bioplatform molecules as another class of alternative solvents. While still being VOCs, they are truly renewable and less harmful than many VOCs. These advantages, coupled with the anticipated substantial growth in the availability of such chemicals, make it prudent to see how they compare. Our (arbitrary) scoring system gives equal weighting to all of these criteria. In this way we placed $scCO_2$ and water as the "best" alternatives to traditional VOCs; their relatively poor solvent power for many chemicals is more than counterbalanced by their more desirable handling, ease of separation, and low environmental impact. Our assessment of ionic liquids is that, currently, their disadvantages outweigh their excellent solvent properties and "designer solvent" features although their score could be improved in the light of new generations of ILs with more favorable data on health and safety (the recent report of the flammability of many ILs is not encouraging).[20] It may also be possible in the future with sufficient data to subclassify ILs since some clearly have much more desirable properties than others. Fluorous solvents score particularly badly; again, any useful process features (ease of separation and reuse) seem overwhelmed by cost and life-cycle-wide concerns over their sustainability. Given the fundamental drive to avoid VOCs it is perhaps surprising to see the new bioplatform molecules come out well in our scoring system. While a reduction in the use of VOCs and, as important, better control in their use (to minimise escape into the atmosphere) are very important, we do see a continued role for VOCs especially if they satisfy other "acceptability criteria" such as being derived from renewable resources and having low toxicity. Water and $scCO_2$ are fundamentally limited as solvents, and there are numerous, especially organic, chemicals which have unsatisfactorily low solubilities in them. Thus, we see a portfolio of solvents for future process chemistry—$scCO_2$ and water where possible and, where necessary, VOCs, which should preferably be renewable; for the foreseeable future other alternatives are likely to be used only in speciality applications. Table 2 compares key features of some representative solvents. It should be noted that it is difficult to give reliable costs as markets change rapidly and the true cost of water and CO_2 depend on location and efficiency of condensation or purification. Building a $scCO_2$ reactor close to a power station or air distillation plant would make commercial sense. Renewable organic solvents will, of course, have similar physical properties to those from petrochemical feedstocks, and ethyl lactate seems particularly promising in terms of its environmental, health, and safety characteristics as it is nontoxic (even edible!). It is currently approximately twice the cost of nonrenewable solvents, although market forces may improve this in the future.

3.2. Alternative Solvents in Products. In products such as home and personal care formulations, cleaning agents, aerosols, coatings, etc., there are greater health and safety concerns due to the direct exposure of the consumer or other layman (cleaner, painter, gardener, etc.); however, the limited experience of the user (compared to that for operating a chemical manufacturing plant, for example) is also likely to lead to greater accidental and uncontrolled loss of the solvent in use or storage. Halogenated solvents have been largely replaced in some products (e.g., aerosols) but not in others (e.g., dry cleaning) while other VOCs continue to be used in numerous other products. As with chemical processes we can see clear environmental and other advantages to replacing VOCs with some of the more popular alternative solvents. Supercritical CO_2 is now being used in dry cleaning, albeit to a very limited extent, and ionic liquids are being studied for some specialist cleaning applications. Solvent-free products are also now common and should be used wherever possible—no solvent comes without some environmental burden—although if the efficiency of use of the substance carried (e.g., an insecticide) is significantly reduced, then complex environmental load calculations would need to be carried out to determine the best option. Water has also been

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Table 1. **Advantages and disadvantages for alternative solvents; score in parentheses is arbitrary grading on a scale of 1 (poor) to 5 (very good) in each category**

key solvent properties	ease of separation and reuse	health and safety	cost of use	cradle-to-grave environmental impact	arbitrary score (/25)
Supercritical CO_2					
poor solvent for many compounds; may be improved with cosolvents or surfactants (1)	excellent: facile, efficient, and selective (5)	nontoxic; high-pressure reactors required (4)	energy cost is high; special reactors required; CO_2 is cheap and abundant (3)	sustainable and from multiple source; no significant end-of-life concerns (5)	18
Ionic Liquids (ILs)					
enormously wide range of designer solvents for any reaction; always polar (4)	volatile products easily removed; others less so; reuse may be a problem if high purity is required (2)	very limited data available; some reported to be flammable/toxic (2)	expensive; but some lower-cost ILs will become available in time (2)	normally synthesised from petrochemicals, but sustainable ILs exist; synthesis may be wasteful and energy demanding; environmental fate not well understood (3)	13
Fluorous Solvents					
limited to very nonpolar solutes; best used in biphasic systems (3)	readily forms biphases; may be distilled and reused (4)	bioaccumulative, greenhouse gases; perfluoroethers thought to be less problematic (2)	very expensive (1)	very resource demanding; may persist in environment (2)	12
Water					
dissolves at least small quantities of many compounds; generally poor for nonpolar (3)	may be separated most organics; purification may be energy demanding (3)	non-toxic, non-flammable and safe to handle (5)	very low cost energy costs high (4)	sustainable and safe to the environment; may need purification (4)	19
Solvents Based on/ Derived from Renewables					
wide range: ethers, esters, alcohols and acids are available (4)	may be distilled (4)	generally low toxicity (4)	mixed-cost will decrease with greater market volume (4)	sustainable resources biodegradable VOCs will cause problems (3)	19

Table 2. **Comparison of physical properties and health and safety data for some representative solvents (data from refs 1, 21, and 22 and from commercial materials safety data sheets)**

solvent	relative cost[a]	LD_{50} (rat)/ mg kg^{-1}	TLV[c]/ mg m^{-3}	log P[d]	environmental fate	flash point/ °C	heat capacity[e]/ kJ kg^{-1} K^{-1}	E_T^N [f]
DCM	1	1600	174	1.25	photodegradation ($t_{(1/2)} > 30$ days)	N/A	1.19	0.309
hexane	1	28700	176	4.00	photodegradation ($t_{(1/2)} = 1-10$ days)	−23	2.27	0.009
water	*a*	N/A	*c*	−	no change	N/A	4.18	1.000
CO_2	*a*	N/A (asphyxiant)	5000	−	no change	N/A	0.819	0.09 (variable)
bio-ethanol	1	7060	1880	−0.3	rapid biodegradation	13	2.44	0.654
ethyl lactate	2	>2000[b]	*c*	0.06	rapid biodegradation	61	1.90	polar, acidic [f]

[a] From Aldrich Chemical Co.; water and CO_2 are essentially free resources, but cost of use depends on energy efficiency of purification/condensation processes. [b] Ethyl lactate was found to be a source of food energy for rodents. [c] Threshold limit value, U.S.A. (ACGIH), time-weighted average. Water and ethyl lactate are considered nontoxic. [d] Octanol−water partition coefficient. [e] At 25 °C. [f] Reichardt's solvent polarity scale. Ethyl lactate has a pH of 4 and is sufficiently acidic to protonate the indicator dye.

more widely used in product formulations such as paints and other coatings. In cleaning, superhot water, which is a better solvent for lower polarity compounds than normal water, can also replace VOCs in many applications. Overall we see both no-solvent and water as attractive alternatives for many traditional solvent-based products, with $scCO_2$ and ILs having a smaller range of specialist applications, in part due to the difficulty in handling and/or high costs of these more "exotic" solvents. Where VOCs are very difficult to replace, we should aim to use those compounds derived from bioplatform molecules that are truly sustainable and relatively safe to use; ethyl lactate, ethanol, and methyltetrahydrofuran being examples of these.

4. Conclusions

Despite several years of intense research effort and increasing legislative and other pressure, the field of alternative solvents remains an enormous environmental challenge with traditional VOCs continuing to dominate processes and, to a lesser extent, products. Designer ionic liquid solvents and, in particular supercritical CO_2, are now recognised as useful solvents for a range of applications, but they suffer from several drawbacks that will always constrain their applicability. The problems with more exotic solvent systems, notably fluorous phase, are greater and may severely restrict their use. We believe that water and no-solvent approaches to the problem deserve greater attention; the advantages of these will be even greater as a life cycle approach to solvent assessment, including transportation, becomes more widely adopted. It is not realistic to envisage a complete replacement of VOCs in all applications; rather, we again need to put their well-publicised drawbacks into a life cycle context. In doing this we see a growing case for the use of VOCs derived from renewable resources.

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