Preface

Everyone is becoming more environmentally conscious and therefore, chemical processes are being developed with their environmental burden in mind. Of course, this also means that more traditional chemical methods are being replaced with new innovations. This includes new solvents.

Solvents are everywhere, but should they be? They are used in most areas including synthetic chemistry, analytical chemistry, pharmaceutical production and processing, the food and flavour industry and the materials and coatings sectors. But, the principles of green chemistry guide us to use less of them, or to use safer, more environmentally friendly solvents if they are essential. Therefore, we should always ask ourselves, do we really need a solvent? Chapter 2 explains some of the challenges and successes in the field of solvent-free chemistry, and the answer becomes apparent: not always!

In the introductory chapter, some of the hazards of conventional solvents (e.g. toxicity and flammability) and their significant contribution to waste streams are highlighted. The general properties of solvents and why and where they are used are outlined. Additionally, EHS (Environmental, Health and Safety) assessments and life cycle analyses for traditional and alternative solvents are described. It becomes clear that often a less hazardous VOC is available and that although only "light green" (or at least "less black") in colour, they can be used as an interim measure until a more satisfying option becomes available. In each of the subsequent chapters, where possible, the use of an alternative solvent is described for a range of chemical applications including extractions, synthetic and materials chemistry. At the beginning of each of these chapters, some of the advantages and disadvantages of that medium are laid out.

Water is often described as Nature's solvent; therefore Chapter 3 describes the solvent properties of water. It is already used quite widely on an industrial scale, particularly in emulsion polymerization processes and hydrodistillations. However, some of the most exciting results have come in the field of synthetic

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chemistry. Recently, 'on-water' reactions have shown that hydrophobic (water insoluble) compounds can achieve higher rates dispersed in water compared to reactions in conventional solvents or under solvent-free conditions. Water can also be used at very high temperatures and under pressure in a near-critical or supercritical state. Under these conditions, its properties are significantly altered and unusual chemistry can result. This is further discussed in Chapter 4, which describes supercritical fluids. The focus here is on the non-flammable options, that is, carbon dioxide and water. Modifications that are performed on substrates in order to make them soluble in supercritical carbon dioxide are described. Additionally, the benefits of the poor solvating power of carbon dioxide, e.g. selective extractions, are highlighted and its use in tuning reactivity through its variable density is described.

In addition to water and carbon dioxide, there is an increasing availability of solvents sourced from renewable feedstocks including ethanol, ethyl lactate and 2-methyl-tetrahydrofuran. The properties of these solvents and their potential as replacements to petroleum-sourced solvents are discussed in Chapter 5. Renewable feedstocks and their transformations are a growing area of green chemistry and they have significantly impacted the solvent choice arena. In addition to renewable VOC solvents, non-volatile ionic liquid and eutectic mixture solvents have been prepared from renewable feedstocks and are looking to be very promising alternatives in terms of toxicity and degradation. These and other room temperature ionic liquids (RTILs) will be discussed in Chapter 6. The field of RTILs has grown dramatically in the last ten years and the range of anions/cations that can be used to make these non-volatile solvents is continually expanding. Although some of these media may be more expensive than other alternatives, the chance to make task-specific solvents for particular processes is very exciting. RTILs, alongside fluorous solvents, have also made a large impact in the area of recyclable homogeneous catalysts. Fluorous solvents, as described in Chapter 7, show interesting phase behaviour and allow the benefits of a heterogeneous and homogeneous system to be employed by adjusting an external variable such as temperature. Recent advances in this area will be discussed, for example, supported fluorous chemistry, which avoids the use of large amounts of fluorous solvents and might be more amenable to industrial scale processes.

Possibly the least explored and newest options available to the green chemist are liquid polymer solvents (Chapter 8) and switchable and tunable solvents (Chapter 9). Unreactive low molecular weight polymers or those with low glass transition temperatures can be used as non-volatile solvents. In particular, poly(ethyleneglycols) and poly(propyleneglycols) have been used recently in a range of applications. Probably the most important recent additions to our toolbox are switchable solvents. New molecular solvents have been discovered that can be switched from non-volatile to volatile or between polar and non-polar environments by the application of an external stimulus. Gas-expanded liquids will also be discussed in Chapter 9, as carbon dioxide can be used as a solubility switch and to reduce the environmental burden of conventional solvents.

Although many advances in the area of alternative solvents have originated in academia, many alternatives are already in use on an industrial scale. For example, supercritical carbon dioxide is used in coffee decaffeination and natural product extractions, as an alternative solvent in dry-cleaning and as a solvent in continuous flow hydrogenation reactions. An overview of these and some other industrial processes that use alternative solvents will be described in Chapter 10.

Unfortunately, as will become clear to readers, there is no universal green solvent and users must ascertain their best options based on prior chemistry, cost, environmental benefits and other factors. It is important to try and minimize the number of solvent changes in a chemical process and therefore, the importance of solvents in product purification, extraction and separation technologies has been highlighted.

There have been many in-depth books and reviews published in the area of green solvents. Hopefully, readers will find this book a readable introduction to the field. However, some cutting-edge results from the recent literature have been included in an attempt to give a clearer picture of where green solvents are today. For more comprehensive information on a particular solvent system, readers should look to the primary literature and the many excellent reviews of relevance to this field in journals such as Green Chemistry and Chemical Reviews.

Certain solvent media can be fascinating in their own right, not just as 'green' solvent alternatives! Therefore, we must not be blind to our overall goal in reducing the environmental burden of a particular process. Hopefully, readers of this book will be able to make up their own minds about the vast array of solvents available for a greener process, or even come up with a new addition for the green chemistry toolbox. Although many advances have been made during the past decade, the most exciting results are surely yet to come.

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