2nd Edition

RSC Green Chemistry Series

Francesca M Kerton and Ray Marriott

Alternative Solvents for Green Chemistry

RSC Publishing

Alternative Solvents for Green Chemistry 2nd Edition

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RSC Publishing

RSC Green Chemistry No. 20

ISBN: 978-1-84973-595-7
ISSN: 1757-7039

A catalogue record for this book is available from the British Library

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Published by The Royal Society of Chemistry,
Thomas Graham House, Science Park, Milton Road,
Cambridge CB4 0WF, UK

Registered Charity Number 207890

For further information see our web site at www.rsc.org

Printed in the United Kingdom by CPI Group (UK) Ltd, Croydon, CR0 4YY, UK

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2^{nd} Edition

RSC Green Chemistry

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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 3 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 4 describes the solvent properties of water. It is already used quite widely on an industrial

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scale, particularly in emulsion polymerisation processes and hydrodistillations. However, some of the most exciting results have come in the field of synthetic 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 5, which describes supercritical fluids. The focus here is on the nonflammable options, that is, carbon dioxide and water. Modifications that are performed on substrates in order to make them soluble in supercritical carbon dioxide are outlined. 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 6. 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, nonvolatile 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) are discussed in Chapter 7. 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 nonvolatile 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 8, 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 9) and switchable and tunable solvents (Chapter 10). Unreactive low molecular weight polymers or those with low glass transition temperatures can be used as nonvolatile 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 nonvolatile to volatile or between polar and nonpolar environments by the application of an external stimulus. Gas-expanded liquids will also be discussed in Chapter 10, as carbon dioxide can be used as a solubility switch and to reduce the environmental burden of conventional solvents.

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 minimise 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.

I would like to thank the editors of the RSC Green Chemistry Series, James Clark and George Kraus, for the opportunity to contribute to this important group of books. Also, I would like to acknowledge Merlin Fox (the commissioning editor) and the staff at RSC Publishing involved with this series, particularly, Annie Jacob, who has been advising and helping me all along the way. Finally, I would like to thank my husband, Chris Kozak, for his patience, support and motivational input during the writing of this book.

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1st Edition, June 2008

Since publication of the first edition, research in the field of greener solvents has continued at a pace, with special issues dedicated to field being published in several journals (for example, issue 6 of *Green Chemistry* in 2012). I am happy to welcome a co-author to this edition. Ray has applied his experience in an industrial setting to overhaul the chapter on industrial applications (Chapter 11) and provides a new chapter on legislation in this area (Chapter 2). All chapters have received some updating – some more than others. Switchable solvents were relatively new phenomena when the first edition was published and discoveries in this field have grown significantly. I thank Prof. Philip Jessop for tips in this area. Also, RTIL based research has continued to grow exponentially, and significant research in the use of alternative solvents in biomass transformations and biocatalysis has been published. More detailed toxicological studies have been performed on RTILs and applications of bioderived solvents have become more wide spread. A new chapter on the use of green solvents in education and solvent awareness for the general public has been added (Chapter 12).

Finally, I would like to thank the editors and publishers of this book, especially, Merlin Fox and Rosalind Searle for their patience. My husband, family and research group are also thanked for their support while I revised the book.

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CHAPTER 1

Introduction

1.1 Introduction

One of the twelve principles of green chemistry asks us to 'use safer solvents and auxiliaries'.[1–3] Solvent use also impacts some of the other principles and therefore, it is not surprising that chemistry research into the use of greener, alternative solvents has grown enormously.[4–11] If possible, we should try to avoid using them and, if needed, we should try to use inocuous substances. In some cases, particularly in the manufacture of bulk chemicals, it is possible to use no added solvent, or so-called 'solvent free' conditions. Yet in most cases, including speciality and pharmaceutical products, a solvent is required to assist in processing and transporting of materials. Alternative solvents suitable for green chemistry are those that have low toxicity, are easy to recycle, are inert and do not contaminate the product. So-called 'green' solvents have been used in diverse areas, for example, polymer chemistry,[12] biocatalysis,[13] nanochemistry,[14] and analytical chemistry.[15] There is no perfect green solvent that can be applied to all situations and therefore, decisions have to be made. The choices available to an environmentally-concerned chemist are outlined in the following chapters. However, we must first consider the uses, hazards and properties of solvents in general.

Solvents are used in chemical processes to aid in mass and heat transfer, and to facilitate separations and purifications. They are also an important and often the primary component in cleaning agents, in adhesives and in coatings (paints, varnishes and stains). Solvents are often VOCs (volatile organic compounds) and, therefore, are a major environmental concern as they are able to form low-level ozone and smog through free radical air oxidation processes.[3] Also, they are often highly flammable and can cause a number of

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adverse health effects including eye irritation, headaches and allergic skin reactions to name just three. Additionally, some VOCs are also known or suspected carcinogens. For these and many other reasons, legislation and voluntary control measures have been introduced. For example, benzene is an excellent, unreactive solvent but it is genotoxic and a human carcinogen. In Europe, prior to 2000 gasoline (petrol) contained 5% benzene by volume but now the content is <1%. Dichloromethane or methylene chloride (CH_2Cl_2) is a suspected human carcinogen but is widely used in research laboratories for syntheses and extractions. It was previously used to extract caffeine from coffee but now coffee decaffeination is performed using supercritical carbon dioxide ($scCO_2$). Perchloroethylene (CCl_2CCl_2) is also a suspected human carcinogen and is the main solvent used in dry cleaning processes (85% of all solvents). It is also found in printing inks, white-out correction fluid (*e.g.* Liquid Paper, Tipp-Ex) and shoe polish. $ScCO_2$ and liquid carbon dioxide technologies have been developed to perform dry cleaning, however, such a solvent could not be used in printing inks. Therefore, less toxic, renewable and biodegradable solvents such as ethyl lactate are being considered by ink manufacturers.

Despite a stagnant period for the solvent industry during 1997–2002, currently world demand for solvents, including hydrocarbon and chlorinated types, is growing at approximately 2.3% per year and approaching 20 million metric tons per annum. However, when the less environmentally friendly hydrocarbon and chlorinated types are excluded, market growth is around 4% per annum. Therefore, it is clear that demand for hydrocarbon and chlorinated solvents is on a downward trend as a result of environmental regulations, with oxygenated and green solvents replacing them to a large extent.[16] It should be noted that these statistics exclude in-house recycled materials and, therefore, these figures just represent solvent new to the market and the real amount of solvent in use worldwide is far higher. It also means that annually a vast amount of solvent is released into the environment (atmosphere, water table or soil). Nevertheless the situation is moving in a positive direction, as in the U.S. and Western Europe, environmental concerns have increased sales of water-based paints and coatings to levels almost equal to the solvent-based market. Therefore, it is clear that legislation and public interests are causing real changes in the world of solvents.

The introduction of legislation by the United States Food and Drug Administration (FDA) means that some solvents, *e.g.* benzene, are already banned in the pharmaceutical industry and others should only be used if unavoidable, *e.g.* toluene and hexane. FDA preferred solvents include water, heptane, ethyl acetate, ethanol and tert-butyl methyl ether. Hexane, which is not preferred and is a hazardous air pollutant, is used in the extraction of a wide range of natural products and vegetable oils in the U.S. and according to the EPA Toxic Release Inventory, more than 20 million kg of hexane are released into the atmosphere per year through these processes. For example, a hexane-based extraction process introduced in the 1930s is used to obtain soy oil from crushed soybeans. Hexane losses are of the order of 1 kg per ton of beans processed! Therefore, more environmentally friendly alternatives are in demand and a number of approaches have been studied.[17] It may seem straight forward to substitute hexane with its higher homologue, heptane, when looking at physical and safety data for solvents, Table 1.1. However, heptane is more expensive and has a higher boiling point than hexane, so economically and in terms of energy consumption, a switch is not that simple. Also, heptane does possess many of the same environmental health and safety hazards as hexane e.g. flammability. Therefore, it is clear that much needs to be done to encourage the development and implementation of greener solvents. Futhermore, it should be noted that even if one aspect of a solvent means it can be considered green, other properties of the solvent may detract from its potential benefits. For example, 2Me-THF is bio-derived and is a prefered alternative to THF in many respects. However, we must not be complacent and we need to take care when using it, as recently published toxicological data suggest that it has a similar toxicitiy to THF,[18] and it is a VOC and flammable.

1.2 Safety Considerations, Life Cycle Assessment and Green Metrics

Efforts have been made to quantify or qualify the 'greeness' of a wide range of both green and common organic media.[19,20] In deciding which solvent to use, a number of factors should be considered. Because of the cost and safety of particular alternatives, some options are often ruled out early in the decision-making process. For example, room temperature ionic liquids (RTILs) are much more expensive than water and, therefore, they are more likely to find applications in high value-added areas such as pharmaceuticals or electronics than in the realm of bulk or commodity chemicals. However, a more detailed assessment of additional factors should be performed including a life cycle assessment, energy requirements and waste generation.

A computer-aided method of organic solvent selection for reactions has been developed.[21] In this collaborative study between chemical engineers and process chemists in the pharmaceutical industry, the solvents are selected using a rules-based procedure where the estimated reaction-solvent properties and the solvent-environmental properties are used to guide the decision making process for organic reactions occuring in the liquid phase. These rules (See Table 1.2) could also be more widely used by all chemists, whether computer-aided or not, in deciding whether to use a solvent and which solvents to try first.

The technique was used in four case studies including the replacement of dichloromethane as a solvent in oxidation reactions of alcohols, which is an important area of green chemistry. 2-pentanone, other ketones and some esters were suggested as suitable replacement solvents. At this point, the programme was not able to assess the effects of non-organic solvents due to a lack of available data. However, this approach does hold promise for reactions where a VOC could be replaced with a far less hazardous or less toxic or a

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