Edited by Paul T. Anastas

# Green Solvents





Volume 4: Supercritical Solvents

Volume Editors: Walter Leitner Philip G. Jessop



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# Handbook of Green Chemistry

Volume 4 Supercritical Solvents

Volume Edited by Walter Leitner and Philip G. Jessop



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#### Foreword

For several centuries, **Chemistry** has strongly contributed to a fast and almost unlimited trend of progress and innovation that have deeply modified and improved human life in all its aspects. But, presently, chemistry is also raising fears about its immediate and long-term impact on the environment, leading to a growing demand for development of "green chemistry" preserving the environment and natural nonrenewable resources. Changing raw materials to renewable sources, using low energy-consumption processes, reprocessing all effluents and inventing new environment-friendly routes for the manufacture of more efficacious products are immense challenges that will condition the future of mankind.

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In this context of sustainable development, Supercritical Fluids (SCF) and Gas-Expanded Liquids (GXL) are of rapidly-growing interest because either they are nontoxic and non-polluting solvents (like carbon dioxide or water) or they help one to avoid harmful intermediates through new processing routes. After two decades of development of new extraction/fractionation/purification processes using SCFs mainly  $CO_2$  - with about 250 industrial-scale plants now in operation around the world, other applications have been and will be at the centre of new developments for the present decade and the coming one:

- Manufacture of high-performance materials including pharmaceutical formulations, bio-medical devices and many specific polymeric, inorganic or composite materials, either by physical processes or chemical synthesis;
- New routes of chemical or biochemical synthesis, coupled with product purification;
- Innovative waste management and recycle.

It has to be understood that moving to SCF or GXL media for chemical synthesis shall not be considered as a "simple" substitution of "classical" organic solvents, but imposes a complete "reset" of knowledge of synthesis routes, reaction schemes and parameters. One main difference is related to the physico-chemical properties of these fluids that are both "tunable" solvents and separation agents. Some are also reactants at the same time. Because of these properties, reaction rate and selectivity are very different from those observed in liquid media, as well exemplified by

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hydrogenation reactions over heterogeneous catalysts. Moreover, many new environmentally-friendly processes using  $CO_2$  and water lead to innovative high-tech materials (especially nano-structured materials), biomass conversion and waste treatment such as, for example, PET-residues recycling by hydrothermal depolymerisation.

This is why this new edition based upon the 1999 book "Synthesis using Supercritical Fluids" but deeply revised and dealing with new areas, arrives at an optimal moment when scientists and engineers are facing the new challenges of sustainable development and demand for higher-performance products. In the fast-changing world of science, this update is a necessary tool offered to help the scientific community appreciate the opportunities presented by these fluids and to prepare chemists and engineers to incorporate these techniques in their process "tool-box".

March 2009

Michel Perrut

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#### Preface

Reactions under supercritical conditions have been used for industrial production on various scales for most of the 20th century, but the current intense academic interest in the science and applications of supercritical fluids (SCFs) dates from the mid 1980's (Figure 1) and the application of SCFs in the chemical synthesis of organic molecules or materials became a "hot topic" starting in the early 1990's. Processes involving SCFs can be conducted in a fully homogeneous monophasic fluid or in biphasic systems. Biphasic conditions can involve a supercritical or subcritical gas as the upper phase and a gas-expanded liquid (GXL) below. The optimum situation is often a delicate balance of thermodynamic and kinetic boundaries for a given transformation. This book is intended to introduce the reader to the wide range of opportunities provided by the various synthetic methodologies developed so far for synthesis in SCFs and GXLs.



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Applications of SCFs include their use as solvents for extractions, as eluents for chromatography, and as media for chemical reactions. All of these are worthy topics for extensive scientific and technical discussion, and in fact have been topics of books in the past. We decided that a satisfactory coverage of all three topics would not be possible in a single monograph of a reasonable size, and therefore we chose to cover only one. While extractions such as decaffeination of coffee and chromatography such as the supercritical CO<sub>2</sub>-based preparative chromatography used in the pharmaceutical industry are great examples of the environmental and economic benefits of SCFs, we focus here on chemical synthesis where the fluid is not only used as a mass separation agent, but also directly affects the molecular transformation.

Supercritical fluids and gas-expanded liquids may be alternatives to liquid solvents, but they are neither simple nor simply replacements of solvents. The experimental chemist could not modify a written synthetic method by simply crossing out the word "benzene" and replacing it with the words "supercritical carbon dioxide". Many other modifications to the procedure would be necessary, not only because of the need for pressurized equipment but also because of the inferior solvent strength of many SCFs. On the other hand, additional degrees of freedom in the reaction parameters emerge from the high compressibility of SCFs, allowing density to be introduced as an important variable. At the same time, mass transfer can be greatly enhanced in the presence of SCFs. Selective separation and compartmentalization of elementary processes in multiphase systems offer another parameter that can be exploited especially in catalytic processes. These are only some of the reasons why the result of a chemical synthesis can sometimes be dramatically changed, often for the better, by this solvent switch. If such beneficial effects can be combined with the benign nature of many SCFs such as CO2 or H2O, they can contribute to the development of more sustainable chemical processes, explaining why SCFs and GXLs are often referred to as "Green Solvents".

It is only fair to say that we are still far away from a detailed understanding of all the effects of using SCFs and GXLs. More basic research will be needed before we learn how to exploit the benefits in the most efficient way. In the meantime, it is our hope that the chemist or engineer considering using one of these fluids as a medium for a reaction will turn to this volume to find out both what has been done, how to do it, and, more importantly, what new and innovative directions are yet to be taken.

At this point, we must offer a safety warning and disclaimer. Supercritical fluids are used at high pressures and in some cases at elevated temperatures. The chemist contemplating their use must become acquainted with the safety precautions appropriate for experiments with high pressures and temperatures. Some SCFs also have reactive hazards. The safety considerations mentioned in Chapters 1 and 2 are meant neither to be comprehensive nor to substitute for a proper investigation by every researcher of the risks and appropriate precautions for a contemplated experiment.

We have selected the chapter topics to guide the reader through the process of planning and carrying out chemical syntheses in SCFs and GXLs. The subjects include a brief overview of the historical development and current use, as well as a description of equipment, methods, and phase behaviour considerations. The properties of biphasic conditions and gas-expanded liquids are spelled out in chapter 4, and all these themes are elaborated upon in the largest part of the book which is devoted to various types of chemical reactions involving SCFs and GXLs as solvents and/or reactants. The emphasis is on synthetic reactions, rather than reactions tested for the purpose of investigating near-critical phenomena.

This book represents a partial update of our 1999 book on "Chemical Synthesis Using Supercritical Fluids", but most of the chapters are entirely new and the selection of topics is not the same. We therefore encourage readers, if they want more information, to look up the 1999 book.

The contributors to the present volume, all leading experts in the field, have given us a wide view of the types and methods of chemistry being performed in supercritical fluids and expanded liquids. Many of the techniques that the reader will find described in these pages have been laboriously developed by these contributors and their colleagues. We gratefully thank all of the contributors for agreeing to take time out from their research schedules to write chapters for this volume.

We also thank the following people and institutions for providing us with information or photographic material on the historical aspects and the industrial use of SCFs: Dr. J. Abeln (Forschungszentrum Karlsruhe), Dr. U. Budde (Schering AG), Dr. H.-E. Gasche (Bayer AG), Dr. P. Møller (Poul Møller Consultancy), Dr. T. Muto (Idemitsu Petrochemical), Prof. G. Ourisson and the Académie des Sciences, Dr. A. Rehren (Degussa AG), M.-C. Thooris (Ecole Polytechnique Palasieau) and representatives of Eco Waste Technology and General Atomics.

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Finally, and most importantly, we dedicate our own contribution to this book to our wives and families, for all their love and understanding throughout the years and especially during the preparation of this volume.

February 2009

Philip Jessop and Walter Leitner

#### About the editors

#### Series Editor



**Paul T. Anastas** joined Yale University as Professor and serves as the Director of the Center for Green Chemistry and Green Engineering there. From 2004–2006, Paul was the Director of the Green Chemistry Institute in Washington, D.C. Until June 2004 he served as Assistant Director for Environment at the White House Office of Science and Technology Policy where his responsibilities included a wide range of environmental science issues including furthering international public-private cooperation in areas of Science for Sustainabil-

ity such as Green Chemistry. In 1991, he established the industry-governmentuniversity partnership Green Chemistry Program, which was expanded to include basic research, and the Presidential Green Chemistry Challenge Awards. He has published and edited several books in the field of Green Chemistry and developed the 12 Principles of Green Chemistry.

#### **Volume Editors**



**Philip Jessop** is the Canada Research Chair of Green Chemistry at Queen's University in Kingston, Ontario, Canada. After his Ph.D. (Inorganic Chemistry, UBC, 1991) and a postdoctoral appointment at the University of Toronto, he took a contract research position in the Research Development Corp. of Japan under the supervision of Ryoji Noyori, investigating reactions in supercritical CO<sub>2</sub>. As a professor at the University of California-Davis (1996–2003) and then at Queen's University, he has studied green solvents, the con-

version of waste  $CO_2$  to useful products, and aspects of  $H_2$  chemistry. He has presented popular chemistry shows to thousands of members of the public.

#### **XX** About the editors

Distinctions include the Canadian Catalysis Lectureship Award (2004), a Canada Research Chair (2003 to present), and the NSERC Polanyi Award (2008). He has chaired the 2007 CHEMRAWN and ICCDU Conference on Greenhouse Gases, will chair the 2010 3<sup>rd</sup> International IUPAC Conference on Green Chemistry, and serves as Technical Director of GreenCentre Canada.



Walter Leitner was born in 1963. He obtained his Ph.D. with Prof. Henri Brunner at Regensburg University in 1989 and was a Postdoctoral Fellow with Prof. John M. Brown at the University of Oxford. After research within the Max-Planck-Society under the mentorship of Profs. Eckhard Dinjus (Jena) and Manfred T. Reetz (Mülheim), he was appointed Chair of Technical Chemistry and Petrochemistry at RWTH Aachen University in 2002 as successor to Prof. Willi Keim. Walter Leitner is External Scientific Member of the Max-Planck-

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His research interests are the molecular and reaction engineering principles of catalysis as a fundamental science and key technology for Green Chemistry. In particular, this includes the development and synthetic application of organometallic catalysts and the use of alternative reaction media, especially supercritical carbon dioxide, in multiphase catalysis. Walter Leitner has published more than 170 publications in this field and co-edited among others the first edition of "Synthesis using Supercritical Fluids" and the handbook on "Multiphase Homogeneous Catalysis". Since 2004, he serves as the Scientific Editor of the Journal "Green Chemistry" published by the Royal Society of Chemistry. The research of his team has been recognized with several awards including the Gerhard-Hess-Award of the German Science Foundation (1997), the Otto-Roelen-Medal of Dechema (2001), and the Wöhler-Award of the German Chemical Society (2009).

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# Introduction

1

Philip Jessop and Walter Leitner

#### 1.1 What is a Supercritical Fluid (SCF)?

A supercritical fluid is a compound, mixture, or element above its critical pressure  $(p_c)$  and critical temperature  $(T_c)$  but below the pressure required to condense it into a solid (Figure 1.1). This definition is modified from that of IUPAC [1], which unfortunately omits the clause concerning condensation into a solid. That the melting curve extends over the supercritical region [2–4] is often forgotten even though the pressure is not always impractically high. For example, the minimum pressure required to solidify supercritical CO<sub>2</sub> is only 570 Mpa [5].

1

The conditions under which SCFs are investigated are often described in terms of "reduced temperature" ( $T_r$ ) and "reduced pressure" ( $p_r$ ), defined as the actual values of T and p divided by  $T_c$  and  $p_c$ , respectively (Equations 1.1 and 1.2). The "law of corresponding states" as introduced by van der Waals [6] implies that compounds behave similarly under the same values of the reduced variables. This allows valuable comparisons of different compounds under various conditions, but deviations can be substantial in close proximity to the critical point.

$$T_{\rm r} = T/T_{\rm c} \tag{1.1}$$

$$p_{\rm r} = p/p_{\rm c} \tag{1.2}$$

The properties of SCFs are frequently described as being intermediate between those of a gas and a liquid. This Janus-faced nature of SCFs arises from the fact that the gaseous and liquid phases merge together and become indistinguishable at the critical point. Figure 1.2 shows how the meniscus between the phases disappears upon reaching the critical point for CO<sub>2</sub>. Not all properties of SCFs are intermediate between those of gases and liquids; compressibility and heat capacity, for example, are significantly higher near the critical point than they are in liquids or gases (or even in the supercritical state further from the critical point). Although the properties of a compound may change drastically with pressure near the critical point, most of them show no discontinuity. The changes start gradually, rather than with a sudden onset, when the conditions approach the critical point.

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SCF

gas

T (°C)

**Figure 1.1** The phase diagram of  $CO_2$  [192, 193]. The critical and triple points are shown as filled circles. The inset (with a linear pressure scale) shows an expanded view of the area around the critical point; the tear-shaped contour indicates the compressible region.

It is common to refer to the somewhat ill-defined region where such changes are noticeable as the "near-critical" region. Technically, the "near-critical region" extends all around the critical point, but the expression is commonly used to refer to the nonsupercritical section only. The very similar expression "compressible region" refers to the area around the critical point in which the compressibility is significantly greater than would be predicted from the ideal gas law. In fact, the compressibility at the critical point itself approaches infinity, and hence the speed of sound in the fluid reaches a minimum; a method for the determination of critical data of mixtures based on this phenomenon has been devised [7]. Although a significant portion of the compressible region lies inside the SCF section of the phase diagram, there is also overlap with the liquid and vapor regions as well (Figure 1.1, inset). Thus, even liquids have significant compressibility near the critical point, although they are virtually incompressible at



Figure 1.2 The meniscus separating liquid and gaseous  $CO_2$  disappears when the critical point is reached by heating liquid  $CO_2$  in a closed vessel. A small amount of a highly  $CO_2$ -soluble and brightly colored metal complex [194] was added for better contrast.



**Figure 1.3** The density and the solvent power (as expressed by the Hildebrand parameter) of  $scCO_2$  as a function of temperature and pressure [8, 9].

 $T_r \ll 1$ . Liquid phases at temperatures below, but not too far below,  $T_c$  are called "subcritical liquids", whereas "subcritical gases" are those at pressures below  $p_c$ .

When working with an SCF, it is valuable to refer to a plot of the dependence of density (*d*) on pressure and temperature, as presented for supercritical CO<sub>2</sub> (scCO<sub>2</sub>) in Figure 1.3. Note that the density changes sharply but continuously with pressure in the compressible region, illustrating the properties outlined above. At higher pressures, the density changes occur more gradually. The critical density  $d_c$  (i.e. *d* at  $T_c$  and  $p_c$ ) is the mean value of the densities of the gas phase and the liquid phase and amounts to 0.466 g ml<sup>-1</sup> for CO<sub>2</sub>. The reduced density is defined in analogy with the other reduced variables (Equation 1.3). The density data shown in Figure 1.3 correspond to the bulk density of the medium, but density fluctuations lead to microscopic areas of decreased and increased local densities in SCFs ("local density augmentation"). Because of the very large compressibility, these density fluctuations are most pronounced very near to the critical point. If the fluctuations are of the same order of magnitude as the wavelength of visible light, scattering of the light leads to critical opalescence, which may be apparent as a clouding or coloration of the SCF and can also be used to determine the critical point.

 $d_{\rm r} = d/d_{\rm c} \tag{1.3}$ 

Many solvent properties are directly related to bulk density and will therefore have a pressure dependence similar to that shown in Figure 1.3. The best known example is the continuous variation in "solvent power" over a fairly wide range, which provides the basis for the technical use of SCFs in highly selective natural product extractions. The solvent power is a rather ill-defined property, but there have been experimental approaches to devise scales for liquid solvents. One of the most successful attempts

#### 4 1 Introduction

was put forward by Hildebrand and Scott [8]; the so-called Hildebrand parameter for solvent power was found to be directly proportional to the density of SCFs [9], as shown in Figure 1.3 for CO<sub>2</sub>. Some typical organic solvents are marked on the Hildebrand scale for comparison to give some indication of the tunability of the solvent power of CO<sub>2</sub>. It should be apparent from the diagram that in order for a SCF to have significant solvating ability, it must usually have a  $d_r$  of >1. Note, however, that the concentration of a solute in a compressed gas or SCF does not depend on solvation only, but also involves volatility as an important parameter. Changing the solvating ability of an SCF will have different effects on the solubility of individual solutes.

The possibility of using SCFs as "tunable solvents" not only for supercritical fluid extraction (SFE) but also for chemical reactions is one of the many interesting features associated with their application in modern synthesis. Before we discuss the many potential benefits in detail (Section 1.3), it seems appropriate to give a brief introduction to some practical aspects of the use of SCFs on a laboratory scale.

#### 1.2 Practical Aspects of Reactions in Supercritical Fluids

Considerations when selecting a SCF to serve as a reaction solvent include critical temperature, solubilizing power, inertness, safety, environmental impact, and cost. An attractive scenario is to use one of the reagents as the supercritical solvent; many reactions in SCFs in industry use a reagent as the solvent. Inorganic and organic compounds which are frequently used as SCFs are listed, together with leading references for their volumetric behavior, in tables in Chapter 2. Because most organic syntheses are performed between room temperature and 120 °C, SCFs with critical temperatures around room temperature are most commonly used; these are CO<sub>2</sub>, ethane, ethylene, fluoroform, nitrous oxide, and the partially fluorinated methanes and ethanes. For many reasons, including inertness, safety, impact, and cost, scCO<sub>2</sub> is the most popular of these.

The purity of the SCF is an important consideration in the planning of a synthesis. Low concentrations of impurities can have noticeable effects on the volumetric and phase behavior of SCFs. For example, helium can be present in commercial  $CO_2$  because it is sometimes added as a "head-gas" to ensure nearly complete delivery of the cylinder contents and this has been found to affect the use of scCO<sub>2</sub> as a solvent for analytical and preparative purposes [10–12]. The He head-gas is unnecessary if a cooled pump is used for  $CO_2$  delivery. Purity can also have an effect on the cost of the SCF. For some materials, especially the  $C_2$  or higher hydrocarbons, the price is highly dependent on the purity and very high purities are prohibitively expensive.

Specialized equipment is required for experiments with supercritical fluids, as described in more detail in Chapter 2, mainly because of the requirements to work at elevated pressures and/or temperatures. The physical and chemical properties of the SCFs can sometimes present hazards to the experimentalist [13]. All researchers in the field should search the literature for information concerning the hazards of the materials with which they are working. The following information is presented as a