CHEMICAL REVIEWS

Volume 99, Number 2 February 1999

Supercritical Fluids: Introduction

Chemistry deals largely with the structures and behavior of molecules in gas, liquid, and solid phases. Supercritical fluids (SCFs) present a grand opportunity to discover a range of novel chemical phenomena unseen in these conventional phases. Although SCF has been a matter of continuing scientific interest since the past century, its potential benefits to chemistry have not been fully realized. Every stable compound has a triple and critical point. Any gaseous compound becomes supercritical when compressed to a pressure higher than the critical pressure (P_c) above the critical temperature (T_c). Properties of SCFs are different from those of ordinary liquids and gases and are tunable simply by changing the pressure and temperature. In particular, density and viscosity change drastically at conditions close to the critical point. The solvating power is much smaller than that of conventional fluid solvents, but this can be utilized to generate unique molecular clusters or assemblies in homogeneous phase. Such phenomena have already been recognized in spectroscopic studies, and the same effects are expected to change chemical reactivity and selectivity.

SCFs also offer a series of technical advantages. Their characteristics have been exploited in chromatography and chemical engineering, particularly in a variety of extraction and separation processes, but SCFs can also be used as reaction media. They form a single-phase mixture with gaseous reactants, sometimes avoiding a rate-limiting mass-transfer step and thus enhancing reaction rates. Currently, large-scale chemical manufacture is facing a serious solvent problem in connection with environmental concerns. Regulation of the use of hazardous organic solvents such as chlorinated hydrocarbons is becoming increasingly stringent and spurs the development of environmentally conscious, economical reaction media. This is a matter of urgency. Supercritical carbon dioxide ($scCO_2$), readily accessible with a T_c of 31 °C and a P_c of 73 atm, has excellent potential for achieving this goal. It is abundant, inexpensive, nonflammable, nontoxic, and environmentally benign. It has a high solubility for nonpolar organic compounds. Although its ability to dissolve polar, ionic, or polymeric compounds is exceedingly limited, small amounts of a polar entrainer or an appropriate surfactant dramatically change the micorenvironment to greatly increase the solubility of such substances. Perfluorinated compounds are particularly effective for this purpose, expanding greatly the applicability of CO_2. The permutability is unlimited. Since the use of $scCO_2$ allows facile separation of reactants, catalysts, and products, it may eventually be used as a substitute for environmentally less acceptable solvents. However, despite a variety of attractive features, the use of SCFs for organic synthesis and polymerization remains largely unexplored. SCFs other than CO_2 also exhibit interesting properties. In view of the high scientific and technological potentials of this subject, the state of the art is illustrated in this special issue of *Chemical Reviews*.

The issue treats both fundamentals and applications of SCFs. Three of the 11 articles focus on basic physical aspects of SCFs that affect molecular chemistry. Kajimoto describes solvation in SCFs and its effect on energy transfer and chemical reactivity of organic compounds. A perspective on solvent density inhomogeneities in SCFs is provided by Tucker, while fluid multiphase behavior in systems of near-critical CO_2 is analyzed by Peters and Gauter. Brennecke and Chateauneuf summarize various homogeneous organic reactions as mechanistic probes in SCFs. The next subject to be examined is catalysis. Baiker comprehensively reviews heterogeneous catalysis in SCFs, while Jessop, Ikariya, and Noyori survey the progress of homogeneous catalysis using organometallic complexes. The latter type of catalysis is based on inorganic and metalloorganic coordination chemistry in SCFs, which is detailed by Darr and Poliakoff. But intriguing science in SCFs is not limited to well-defined small molecules, and their use extends to polymer chemistry. Kendall, Canelas, Young, and DeSimone present an extensive review on polymerization in SCFs that includes chain-growth and step-growth polymerizations, and Kirby and McHugh deal with phase diagrams of polymer/SCF mixtures and with the behavior of homopolymers, copolymers, and fluoropolymers in these unorthodox fluids. In connection with "green" technology, water is another ideal SCF medium. Surprisingly, unlike ambient liquid water, scH_2O is relatively nonpolar but highly acidic, although it requires harsh conditions (T_c = 374

10.1021/cr980085a CCC: $35.00
Published on Web 01/22/1999

°C and P_c = 218 atm). This phase can be used to decompose chemical wastes as well. A treatise on chemical synthesis and conversion in scH_2O is provided by Savage. Finally, Mesiano, Beckman, and Russell cover biocatalysis under SCF conditions, including parameters affecting enzymatic reactions and applications.

Compared to conventional liquid solvents, SCFs are not a panacea; they have both merits and disadvantages. Many chemical reactions are better performed in ordinary fluid solutions. However, SCF exploitation still is a young and unexplored subject. The local inhomogeneity of SCFs is among the most noteworthy, although scientific knowledge of this aspect remains scarce. A systematic study of molecular behavior in SCFs affecting ground- and transition-state properties in chemical reactions will greatly increase the utility in both science and technology. I hope that the present compilation provides a preview of future directions.

As Guest Editor, I thank all the authors for their contributions to produce this timely issue. I also gratefully acknowledge the immense editorial effort of Josef Michl and capable assistance of Susan Robeck.

Ryoji Noyori
Nagoya University

CR980085A