Advances with supercritical fluids [review]

Werner H. Hauthal

Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Johannisallee 29, D-04103 Leipzig, Germany

Abstract

In the last decade, supercritical fluids more and more have been proved as environmentally benign media for chemical and related processes. Many new processes and products have been developed, using the inherent physical and chemical properties of supercritical fluids. Moreover, these processes also promise economic effects. The prerequisites for this success however, are a sound knowledge of physico-chemical properties of – and phenomena in – supercritical mixtures and the availability of other chemical engineering data. This requires an effective exchange of knowledge between a large number of branches of science. In the following, a lot of recent papers will be cited, which should give an overview of actual results on fundamentals and their applications. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Sustainable chemistry; Supercritical fluids; Fluid phase equilibria; Phenomenology; Solvatochromism; Models; Equations of state; Chemical engineering data; Supercritical fluid extraction; Chemical syntheses and reactions; Materials processing; Dyeing; Review

1. Introduction

In the following, an overview of more recent publications on applications of supercritical fluids in chemistry and chemical engineering technologies is given in a tabular form (titles of the publications with some explaining key words; the keywords also outline the relations to related topics). Using supercritical fluids is one possibility to carry out chemistry and chemical technologies in a sustainable manner (“green chemistry”). Supercritical CO₂ (or other supercritical fluids) are an environmentally benign alternative to conventional industrial solvents. Among others, they offer possibilities to reduce the size of reactor volumes to a great extent, and to accelerate chemical processes. The rapid expansion of supercritical solutions (RESS) process, e.g., allows the production of powders with a narrow distribution curve of the (therefore well defined) particle sizes, what is very important for the applications of those powders in several industrial branches.

In Section 2 some papers are cited, which underline the significance of supercritical fluids for a sustainable chemistry. Furthermore, some references referring to research activities in the US, Japan and Germany. In the Sections 3.1 to 3.5 attention will be paid to the scientific fundamentals for using supercritical fluids (phenomenology, theories, and chemical engineering data). It should be underlined, that chemical mixtures under supercritical conditions may have some more components (supercritical fluid, modifier), much more extended ranges of temperature, pressure (density), and much more complicated phase diagrams, as well as novel phenomenological effects. In this context, the further development of global phase diagrams deserves attention as basis of any reliable development of chemical engineering applications (syntheses, separation operations and others).

The recent development of solvent databases, other chemical engineering data and computational methods as aids in the selection and/or design of feasible or optimal environmentally benign solvent alternatives for specific applications is another prerequisite. Papers dealing with experimental results and calculation methods are cited in Sections 4.1 to 4.3.

The Sections 5.1 and 5.2 should give some impressions of the applications of supercritical fluids in the chemical engineering practice in different branches of industry (e.g., chemistry, environmental, textile finishing...
and dyeing). Concerning syntheses in supercritical fluids and analytical methods, however, the monograph of Jessop and Leitner (Jessop and Leitner, 1999) is recommended for more extensive information.

2. Green chemistry/sustainable chemistry with supercritical fluids. Research activities

2.1. Reviews and some recent conference reports

- Supercritical fluids: Clean solvents for green chemistry (in German: “Nachhaltige Chemie”) (Poliako et al., 1999);
- Supercritical carbon dioxide: The ”greener” solvent (Black, 1996);
- Solvents – Molecular trees for green chemistry (Brennecke, 1997);
- Solvent replacement for green processing (Sherman et al., 1998);
- New applications of supercritical fluids (Brennecke, 1996);
- Use of supercritical fluids for different processes including new development (Marr and Gamse, 1990);
- Fourth Italian Conference on Supercritical Fluids and their Applications (1999) (Reverchon, 1999);
- High Pressure Engineering, Proceedings in International Meeting of the GVC-Fachausschüβ Hochdruckverfahrens technik, Karlsruhe, 3–5 March, 1999 (Polymers, materials, hydrothermal treatment, reactions, phase equilibria and thermodynamics, natural food processing, particle formation, separation techniques) (GVC, 1999);
- Fifteenth Montreux Symposium on Liquid Chromatography–Mass Spectrometry, Supercritical Fluid; Chromatography–Mass Spectrometry, Capillary Electrophoresis–MS and Tandem-MS – Montreux (Switzerland), 1–13 November, 1998 (van der Greef, 1999);
- Fourth International Symposium on Supercritical Fluids, 11–14 May, 1997, Sendai, Japan; ¹

2.2. Research activities

- Green chemistry and green engineering in the US (Longanecker, 1999);
- Supercritical Fluid Research Group at Pacific Northwest National Laboratory (PNNL), Richland, WA, USA, http://www.pnl.gov/scrfluid/inex.html ² (Yonker et al., 1997);
- Research activities on supercritical fluid science and technology in Japan – A review (coal-tar pitch, thermodynamic properties, intermolecular potential functions, saturated-liquid densities, phase equilibria, infrared spectroscopy);
- Research activities on supercritical fluid (SCF) science and technology (primarily) under the Japanese government funded; priority research area on supercritical fluids.

²Presidential (Clinton/Gore) Green Chemistry Challenge Award for “Design and Application of Surfactants for Carbon Dioxide” (1997).
I Solution Structures. Simulations and spectroscopic experiments to study the interactions in sc-fluids and clustering dynamics.


III Separations and Processing. Exploration of applications of SCF for separating and processing natural products, biomass, coal and coal liquids, polymers, and ceramics.

IV Reactions. Research on homogeneous and heterogeneous reactions which include carboxylations, photo-induced, Fischer–Tropsch synthesis, enzyme reactions, and material conversions, new processes for converting waste cellulose and polymers into chemical intermediates and processes for producing thin films and metal oxides are shown to have great promise. (Saito, 1995)

- Objectives of the new working group “Umwelt – und ressourcenschonende Synthesen und Prozesse” of the German Chemical Society’s (GDCh) FG “Environmental Chemistry and Ecotoxicology” as well as the First Symposium “Nachhaltigkeit (sustainability) in der Chemie und ihren Produkten”, 23–25 August 1999, Tübingen, Germany (Bayer and Lenoir, 1998).
- The contributions of synthesis research on the way to sustainability (Winterfeldt, 1999).
- The search for environmentally friendly processes (Bolm et al., 1999).
- Deutsche Forschungsgemeinschaft (DFG): Priority program “Supercritical fluids as solvents and reaction media” (Increases of reaction rates, amnonlylation, amination, degradation of pollutants, homogeneous catalysis, enzymatic catalysis, and others).

3. Fundamentals

3.1. Supercritical fluids—general

- The physical state of supercritical fluids (structure, hydrothermal reactions, liquid water, 1000 bar, spectroscopy) (Gorbaty and Bondarenko, 1998);
- Supercritical water. The properties and applications to chemical reactions as a medium (Ikushima, 1998);
- Supercritical Water (Franck and Weingärtner, 1999);
- Hydrogen-bonding in light and heavy water under normal and extreme conditions (water model, MD, MC simulations, central-force model, vapor coexistence curve, polarizable water) (Guillot and Guissani, 1998);

(1) Fluid–fluid and solid–fluid phase equilibria including the critical behavior of binary mixtures,
(2) Liquid–liquid phase separations at very high pressures up to about 3 GPa in a diamond anvil cell,
(3) The high-pressure phase behavior of ternary systems exhibiting cosolvency andmiscibility windows,
(4) The solubilities of dyestuffs in supercritical solvents by static or flow methods,
(5) The determination of binary diffusion coefficients of low-volatile substances in supercritical solvents such as CO2 by a dynamic method,
(6) Solvatochromism under pressure as a measure of solute–solvent interactions.

3.2. Fluid phase equilibria – phenomenology

General:
- Phase equilibrium investigations of fluid systems at high pressures (Schneider, 1993),
- High pressure investigations on fluid system – A challenge to experiment, theory and application (Schneider, 1991).

Phenomena:
- Barotropy (Pohler et al., 1996),
- The building-up of phase diagrams (Calado and Congia Lopes, 1999),
- Closed-loop liquid–liquid immiscibility (binary-fluid mixtures, phase-behavior, 2-component solutions, microscopic effects, directional attractive forces, weak interacting isotropic fluids) (Yelash and Kraska, 1999a),
- Closed-loop critical curves (2-component solutions, phase-diagrams, mixtures) (Yelash and Kraska, 1999a; Yelash et al., 1999),
- Cosolvency effect and miscibility windows (binary and ternary mixtures of supercritical CO2 with tetradecanoic acid and docosane up to 43 MPa and 393 K (Pohler and Schneider, 1995). . .of sc-CO2 with a 1-alkanol and an n-alkane up to 100 MPa and 393 K (Pitla et al., 1998),
- Co-volume effects on the closed-loop liquid-liquid immiscibility in binary fluid (cross co-volume, double critical end point (DCEP) line, critical pressure step point (CPSP) line, critical pressure flat point (CPFP) (Yelash and Kraska, 1999b),
- Enhancement factors of solids in supercritical gases (empirical evaluation method) (Vetere, 1998),
- Fluid opacity (application for determining the phase behavior of binary mixtures near the critical loci – CO2 plus ethane and CO2 plus propane (Martin et al., 1999),
- Global phase behavior/diagram (Yelash and Kraska, 1999a; Yelash et al., 1999),
- Influence of a generalized attraction term of an equation of state on the phase behaviour (Yelash et al., 1999);
• Liquid–liquid immiscibility (vapour–liquid-, liquid–liquid-equilibria, 2-component solutions, alkanes) (Yelash et al., 1999);
• Modifier effects in supercritical CO₂ extraction from various solid matrices (analyte/matrix interaction, analyte/modifier/matrix complex, solvatochromic parameters, solvent modification, environmental samples) (Jeong and Chesney, 1999);
• Patterns of solid–fluid phase equilibria: New possibilities? (Garcia and Lukx, 1999);
• Unusual chemical thermodynamics (Sandler, 1999b).

Structural investigations and reactions:
• Are there hydrogen bonds in supercritical water? (proton NMR chemical shift for water (25–600°C, 1–400 bar), large changes in chemical shift (4.1 ppm) through changes in the hydrogen bond network; there are still 29% as many hydrogen bonds at 400°C and 400 bar as for room temperature water, thermodynamic properties, computer-simulation) (Hoffmann and Conradi, 1997a).
• Hydrogen bonds in supercritical methanol and ethanol? (chemical shift measurements of the hydroxyl protons in methanol and ethanol up to 450°C and over a wide range of pressures, MD simulation, NMR, density, diffraction, mixtures, alcohols) (Hoffmann and Conradi, 1998b).
• Hydrogen exchange reactions in supercritical media monitored by in situ NMR (hydrogen exchange rate can be adjusted by changing pressure (density) at a constant sc-temperature, deuteration reactions, high-temperature high-pressure NMR, supercritical methanol, ethanol and water) (Hoffmann and Conradi, 1998a).
• Acceleration of synthetic organic reactions using supercritical water: noncatalytic Beckmann and pinacol rearrangements (great increase in the local proton concentration around the organic reactants, homogeneous catalysis, oxidation, high-pressure and high-temperature FTIR, Raman-spectroscopy, cyclohexanone-oxime, liquid and superheated water, CO₂) (Ikushima et al., 2000).
• Raman spectroscopy study on the dynamic behavior of nitrate anion in zinc nitrate solution at high temperatures and pressure (supercritical water oxidation, hydration, MD, light-scattering, aqueous-solutions, hydrothermal solutions, electrolyte-solutions, carbonate anions) (Ikushima and Arai, 1998).
• Raman spectral studies of aqueous zinc nitrate solution at high temperatures and at a high pressure of 30 MPa (direct measurement of dynamic behavior of ions in an aqueous solution at high temperatures and pressure using Raman spectroscopy, ion-solvent interactions, relaxation, perpendicular diffusion constant, slightly damped free-rotor (SDFR) model, oxidation, hydration, MD, simulation, supercritical water, hydrothermal solutions, electrolyte-solutions) (Ikushima et al., 1998).
• Micropolarity of sodium bis(2-ethylhexyl) sulfosuccinate reverse micelles prepared in supercritical ethane and near-critical propane (E-t(30) values, microemulsion phases, AOT reverse micelles, spectroscopy, supercritical ethane, near-critical propane, 2,6-diphenyl-4-(2,4,6-triphenylpyridinio)-phenolate, water) (Shervani and Ikushima, 1999).
• In situ spectroscopy of polymers subjected to supercritical CO₂ – plasticization and dye impregnation (PMMA segmental mobility, poly(methyl methacrylate) films, impregnate disperse Red 1 dye polymer film, enhanced diffusion process, hydrogen bonding, Ft-ir, UV/Vis) (Kazarian et al., 1997).

3.3. High-pressure phase equilibria – solubilities

General:
• Phase equilibrium data needs for the design of supercritical fluid extraction columns (Nunes da Ponte et al., 1999);
• Critical temperatures, pressures, and densities for the mixtures CO₂–C₃H₈, CO₂–nC₆H₁₄, C₂H₆–C₃H₈, and C₃H₈–nC₂H₁₀ method of calculation) (Vanpoolen and Holcomb, 1999);
• Ternary phase equilibria for the NaCl–Na₂SO₄–H₂O system at 200 and 250 bar up to 400°C (solubility data, hydrothermal, ternary, vapor–liquid and solid–fluid equilibria, liquid–vapor relations, NaCl–H₂O, 300–500°C) (Dipippo et al., 1999);
• Predicting the approximate solubilities of (hydrocarbon) solids in dense CO₂ (Trabelsi et al., 1999);
• Environmental Pollution (Sandler, 1999a).

Solubility of:
• behenic acid in supercritical carbon dioxide with n-pentane or n-octane cosolvents (Guan et al., 1999);
• behenic acid and ethylbehenate in sc-CO₂ (fatty acids, immobilized lipase, stearic-acid, triolein) (Nakaya et al., 1999);
• chelating agents and metal-containing compounds in supercritical fluid CO₂ (Review) (Smart et al., 1997);
• anthraquinone dyes in sc-CO₂ investigations by a flow method (Wagner et al., 1999a);
• disperse and Mordant dyes in supercritical CO₂ (Guzel and Ackerman, 1999);
• disperse dyes in supercritical CO₂ (Ozcan et al., 1997; Tusek and Golob, 1999);
• dyestuffs in near- and supercritical fluids up to 180 MPa (1,4-bis-(n-alkyl-amino)-9,10-anthraquinone dyestuffs, solid–fluid phase equilibria, UV/Vis-spectroscopy, beta-carotene, CO₂, nitrous oxide, critical region, all-trans) (Tuma and Schneider, 1999);
• PAH in supercritical CO₂ (Yamini and Bahramifar, 2000);
• PAH in subcritical water from 298 K to 498 K (PCBs, extraction, chromatography) (Miller et al., 1998);
• PAH (cholesterol, pyrene, chrysene, perylene, benzo[g]perylene) in sc-CO₂ from 313 to 523 K and pressures from 100 to 450 bar (Miller et al., 1996);
• chlorinated hydrocarbons in sc-CO₂ from 313 to 413 K and at pressures from 150 to 450 bar (PAHs, CO₂ extraction efficiencies, environmental samples, fluids, solids, cholesterol) (Miller et al., 1997);
• PCB (individual polychlorinated biphenyl congeners in supercritical fluids: CO₂, CO₂/MeOH and CO₂/n-C₄H₁₀) (Anitescu and Tavlarides, 1999);
• TNT and wax and their fractionation from an explosive material using a supercritical fluid (Ashrafkhorsani and Taylor, 1999);
• veterinary sulfonamides in sc-CO₂ by a recirculating equilibrium method (fluid extraction, recovery) (Hampson et al., 1999).

3.4. Solvatochromism/partition coefficients

• Solvatochromism in supercritical fluids (IR- and UV-spectroscopy, solvent polarity parameters, phase-behavior, indicators, basicity, shifts) (Maiwald and Schneider, 1998);
• Solvatochromism in supercritical fluids (solvatochromic solubility parameters pi and beta of the pure fluids CO₂, N₂O, CCIF₃, SF₆, and NH₃) (Schneider, 1998b);
• Solvatochromic study of basic cosolvents in supercritical ethane (Hafner et al., 1997);
• Study of interactions in supercritical fluids and SFC by solvatochromic LSER (statistical thermodynamic treatment, molecular interactions, solvent strength, correlation of SFC retention data with solute solvatochromic parameters) (Weckwerth and Carr, 1998);
• Interpretation of solubility and solvation of phenol blue in sc-CO₂ based on solute-solvent interaction evaluated by solvatochromism) (Sasaki et al., 1999);
• Partition coefficients of organic substances in two-phase mixtures of water and CO₂ at pressures of 8 to 30 MPa and temperatures of 313–333 K (phase equilibria, SFE, ternary mixtures, new apparatus, phenol, benzoic acid, benzyl alcohol, 2-hexanone, vanillin, caffeine) (Brudi et al., 1996);
• Partition coefficients of aromatic organic substances in two-phase mixtures of water and CO₂ at pressures from 8 to 30 MPa and at temperatures of 313–333 K. Part II (enhancement factor, enthalpy of hydration, phase equilibria, solubility, solids, CO₂) (Wagner et al., 1999b);
• Partitioning of solutes and cosolvents between supercritical CO₂ and polymer phases (impregnation, dyeing, partition coefficient, diffusion, Ft-ir, UV/Vis, poly(methyl methacrylate), cross-linked poly(dimethysiloxane), cosolvents (methanol, acetone)) (Kazarian et al., 1998);
• Supercritical CO₂ soil partition coefficients (PAHs, chlorobenzenes, equilibrium, SFE) (Gray et al., 1995).

3.5. Systematics, models, equations of state and other correlations

• Global phase diagrams and their applications to fluid mixtures at high pressures (Deiters);
• Global phase diagram (Kraska, 1999);
• High pressure investigations of fluid mixtures – Experimental basis of GPD (Schneider, 1999);
• Van der Waals-like GPD (Quasi-binary mixtures, liquid–liquid immiscibility, tricritical phenomena) (Scott, 1999);
• A classification of phase diagrams of ternary fluid systems (Bluma and Deiters, 1999);
• From global phase diagrams to new optimized equations of state (Yelash and Kraska, 1999a);
• A three-phase ternary model for CO₂-solid–liquid equilibria at moderate pressures (CO₂-naphthalene–(toluene, n-pentane), cosolvents, SFE, volatile matter of mineral coals, PR/Stryjek-Vera e.o.s.) (Darocha et al., 1996);
• General phase behavior in nonionic microemulsion systems (Burauer et al., 1999);
• E.o.s. for aqueous ethanol mixtures (270–420 K; pressures up to 200 MPa) (Takiguchi and Uematsu, 1999);
• Prediction of VLE using Peng–Robinson and Soave–Redlich–Kwong equation of state (Ghosh, 1999);
• Prediction and correlation of triglyceride-solvent solid–liquid equilibria with activity coefficient models (theory, excess functions, sc-CO₂, polymer-solutions, solubility, UNIFAC, acid, fat) (Smith et al., 1998);
• Prediction of the critical locus in binary mixtures using e.o.s. – I. Cubic e.o.s., classical mixing rules, mixtures of methane–alkanes (supercritical equilibria, phase-behavior, GPD, critical lines, unlike pair parameter (k₁₂), calculation method, RK e.o.s., PR e.o.s., fluid mixtures, high pressures, low temperatures) (Polishuk et al., 1999);
• Prediction of solid–fluid equilibria in sc-CO₂ using LSER (activity coefficient, enthalpy of fusion, partial molar volumes, infinite dilution, calorimetric measurement, solubility parameters, phase-equilibria, chromatography, phenanthrene, enthalpies, solvents, solute–solvent interaction model, liquid- and gas-like densities) (Bush and Eckert, 1998);
• An e.o.s. describing the critical region: extension to high pressure (liquid vapor equilibria, thermodynamic properties, temperature relation, binary mixtures, CO₂, fluids, cross-over, density) (Leonhard and Kraska, 1999).
4. Chemical engineering data

4.1. Diffusion coefficients/mass transfer

- Diffusion coefficients in supercritical fluids: available data and graphical correlations (acid methyl esters, SFC, molecular-diffusion (MDif), tracer diffusion (TD), aromatic-hydrocarbons, n-hexane, naphthalene, binary systems) (Suarez et al., 1998).
- Theoretical studies of energetics and diffusion of aromatic compounds in sc-CO₂ (MD, Lennard-Jones, ab-initio, benzene dimer, force-field, hard-sphere, CO₂ dimer, model) (Coelho et al., 2000).
- Infinite-dilution diffusion coefficients in supercritical and high-temperature liquid solvents (calculation method, SFC, TDM, TD, MDif, organic-compounds, binary systems, benzene, naphthalene) (He, 1998a).
- Prediction of binary diffusion coefficients of solutes in supercritical solvents (SFC, TD, MDif, transport, organic compounds, benzene, naphthalene, CO₂, acid) (He, 1997).
- Estimation of infinite-dilution diffusion coefficients in supercritical fluids (SFC, TD, MDif, organic compounds, binary systems, benzene, naphthalene, CO₂, acid) (He and Yu, 1997).
- Physical properties and structure of supercritical water (self-diffusion) (Nakahara and Matubayasi, 1999).
- Steady-state parallel plate apparatus for measurement of diffusion coefficient in sc-CO₂ (SFC, binary mixtures, equilibria, acid methyl-esters, naphthalene, benzene, caffeine) (Tuan et al., 1999b).
- TD coefficients of solutes in supercritical solvents (method of calculation, SFC, MD, organic compounds, binary systems, benzene, naphthalene, transport, acid) (He et al., 1998).
- TD coefficients of benzene in dense CO₂, at 313.2 K and 8.5–30 MPa (experiment, transport properties, binary diffusivity, benzene, TDM, SFC, esters) (Funazukuri and Nishimoto, 1996).
- A kinetic approach for predicting diffusivities in dense fluid mixtures (statistical mechanics, mixture, binary diffusion coefficients, hard-sphere theory, TD, self-diffusion, transport-properties, aromatic hydrocarbons, liquid cyclohexane, repulsive forces) (Dariva et al., 1999a).
- Dense fluid self-diffusion coefficient calculations using perturbation theory and molecular dynamics (smooth-sphere theory, hard-sphere theory, repulsive forces, pressure, temperature) (Coelho et al., 1999).
- Binary diffusion coefficients of low-volatile substances in supercritical solvents (Schneider, 1998a).
- Importance of thermal diffusion in high subcritical and supercritical aqueous solutions (electrochemical cells, high temperature, coefficients, electrolytes, NaNO₃ aqueous solutions, forced convection, Lewis number, Soret coefficient) (Lvov et al., 1998).
- Prediction of diffusion coefficients of liquid and solid solutes in supercritical solvents (SFC, CO₂, TD, MDif, organic compounds, binary systems, benzene, naphthalene, transport, acid) (He, 1998b,c).
- Mass transfer in polymers in a sc-CO₂-atmosphere (diffusion of CO₂ in poly-(ethylene-terephthalate), diffusion of disperse dyes in PET (strongly depends on the dye), mass transfer mechanism in the amorphous regions of polymers, membrane separations of gas–fluid mixtures, generation of foams, extraction of impurities, new experimental method to determine diffusion coefficients, gravimetric measurements of mass transport, swelling of polymers in CO₂, glassy polymers, sorption) (von Schnitzler and Eggers, 1999).
- Numerical modeling of mass transfer in the supercritical antisolvent process (counterdiffusion model, droplet swelling, particle formation, two-way mass transfer, compressed fluid antisolvent, droplet vaporization, fine particles, precipitation, powders, crystallization, microspheres, solubilities (Werling and Debenedetti, 1999).

4.2. Other properties

- Measurement and modeling of viscosity of sc – CO₂/biomaterial(S) mixtures (corresponding states, prediction, fatty-acids, oils) (Tuan et al., 1999a);
- high-pressure viscosity of polystyrene solutions in toluene plus CO₂ binary mixtures (polymer-solutions, density, miscibility, poly(dimethylsiloxane), antisolvent, temperature) (Yeo et al., 2000);
- liquid densities at high pressures (alkanes, alkenes) (Aalto and Keskinen, 1999);
- the density of hydrogen fluoride at high pressures to 973 K and 200 MPa (e.o.s., high temperature, sc-fluid) (Franck et al., 1999);
- partial molar properties from solute retention in SFC: thermodynamic framework, advantages, and limitations (dilute near-critical mixtures, partial molar properties, fugacity coefficient, solute retention, temporal column parameters, pressure phase-equilibria, infinite dilution, statistical thermodynamics, generalized treatment, critical point) (Roth, 1998);
- on the unique behavior of molar excess enthalpies for the supercritical fluid mixtures (MC simulation, Lennard-Jones mixtures) (Fujihara et al., 1997);
- calorimetry in the near-critical and supercritical regions. Nitrous oxide + hydrocarbon mixtures (Renuncio et al., 1999);
• the Lewis number under supercritical conditions (pre-mixed flames, curvature) (Harstad and Bellan, 1999);
• on transport properties of hot liquid and sc-water and their relationship to the hydrogen bonding; (correlation analysis, diffusion coefficient, self-diffusion, MD, hydrogen bonding, viscosity, mechanism, 1000°C, mechanism) (Marcus, 1999);
• heat transfer from sc-carbon dioxide in tube flow: A critical review (Pitla et al., 1998).

4.3. Corrosion behaviour of construction materials

• Corrosion in supercritical water oxidation systems: A phenomenological analysis (Kriksunov and Macdonald, 1995).

Corrosion behaviour of:

• inorganic materials in subcritical and supercritical aqueous solutions (Kaul et al., 1999);
• nickel-base alloy 625 (NiCr22Mo9Nb, 2.4856) and ceria stabilized tetragonal zirconia polycrystal (Ce-TZP) against oxidizing aqueous solutions of hydrofluoric acid (HF), hydrobromic acid (HBr), and hydriodic acid (HI) at sub- and supercritical temperatures (Kritzer et al., 1999d);
• nickel-base alloy 625 in sub- and supercritical aqueous solutions of HNO3 in the presence of oxygen (high-temperature, chloride, waste) (Kritzer et al., 1999b);
• nickel-base alloy 625 in sub- and supercritical aqueous solutions of HC1 and H2SO4 (Kritzer et al., 1999c);
• tantalum in oxidizing sub- and supercritical aqueous solutions of HCl, H2SO4 and H3PO4 (Friedrich et al., 1999).

5. Chemistry and chemical engineering

5.1. Supercritical fluid extraction

General:
• SFE (Clifford, 1999);
• Selectivity in SFE. Recovery of pesticides from model matrices (CO2-methanol, soil, residues) (Berglof et al., 1999);
• Supercritical Fluid Chromatography and Extraction. [Review] (PAHs, off-line SFE, ASE, light-scattering detection, chiral stationary-phase, polymethylsiloxane encapsulated particles, enzyme-immunoassay analysis, benchtop MS, linked immunosorbent assay) (Chester et al., 1998);
• design and analysis of supercritical extraction processes (process optimization, rational use of energy, solubility) (Gani et al., 1997);

Industrial process development:
• Countercurrent multistage gas extraction (SFE) processes (supercritical fluid (gas) extraction, phase equilibria, height of theoretical stages or transfer units, hydrodynamics of countercurrent flow, simulation, packing materials, pressure drop, flooding points, cost analysis) (Brunner, 1998);
• advances in sc-CO2 technologies (fluid chromatography, antisolvent, extraction, separation) (Sihvonen et al., 1999);
• design of a SFE process for separating mixtures incurred in enzyme-catalyzed reactions (model system: transesterification of ethyl acetate and isoamyl alcohol yielding ethanol and isoamyl acetate in sc-CO2, countercurrent extraction, RK e.o.s, integrated process scheme) (Chrisochoou and Schaber, 1996);
• energy analysis of sc-CO2 extraction processes (energy analysis, supercritical extraction cycles) (Smith et al., 1999).

Environmental:
• enhanced catalyst reactivity and separations using water/CO2 emulsions (hydrogenation, microemulsions, environment) (Jacobson et al., 1999b);
• SFE of bioaccumulated mercury from aquatic plants (solid materials, metal-ions, recovery, pH) (Wang and Wai, 1996);
• supercritical CO2 extraction as a clean degreasing process in the leather industry (fat, recovery, sheepskins, disperse dyes, fibers) (Marsal et al., 2000);
• supercritical CO2 extraction of soil-water slurries (PAH, phenolics, soil extraction, gas extraction, organics, model prediction for a three-phase system using two-phase partitioning data, octanol-water partitioning correlation for soil-water partition coefficients) (Green and Akgerman, 1996);
• influence of water on the SFE of naphthalene from soil (innovative soil remediation technology, partition coefficient, mass transfer coefficient, pollutants, matrices, sorption, water content below 10%) (Smyth et al., 1999).

• soil component interactions with 2,4-dichlorophenoxyacetic acid under supercritical fluid conditions (sc-CO2 modified with benzoic acid/methanol, selected model soil components, adsorption to mineral surfaces, diffusionlimited release from porous materials, pH-dependent partitioning between solid and sc-fluid phases, derivatization, pesticides, herbicides, gibbsite, goethite, illite, silica gels, humic acid, sodium humate) (Roquette et al., 1996);
• removal of polychlorodibenzodioxin and dibenzofuran from fly ash (Gabarra et al., 1999);
• chlorofluoroalkanes from rigid polyurethane foams (polymer recycling) (Filardo et al., 1996);
• petroleum hydrocarbons from soil by mechanical shaking (PAH) (Schwab et al., 1999);
• oil contaminant removal from drill cuttings by supercritical extraction (HFC-134a and propane as the extractive solvents, reduction of oil-based mud contamination of drill cuttings to a level allowing offshore disposal, possible use of oil-based mud in environmentally sensitive areas as a major benefit for drilling operations, commercial process design and cost estimate) (Eldridge, 1996);
• recovery of s-triazine herbicides and associated breakdown products from granulated activated carbon using SFE (CO2/acetone, activated carbon, flow rate, recovery, degradation, pesticides, adsorption, efficiency, pollutants, atrazine, simazine, deethylatrazine, diethylsimazine) (Robertson and Lester, 1995);
• chemical recycling of phenol resin by supercritical methanol (terephthalic acid, poly(ethylene-terephthalate), polyethylene, decomposition, degradation) (Ozaki et al., 2000).

5.2. Chemical syntheses and reactions

General:
• Chemical synthesis using supercritical fluids (supercritical fluids as media for chemical reactions (motivation for use of SCFs in modern chemical synthesis), Phase Behavior and Solubility, physical properties as related to chemical reactions, experimental techniques (high pressure reaction equipment design, extraction and related separation techniques, precipitation and crystallization techniques, microemulsions, emulsions and latexes), spectroscopy of solutions (vibrational spectroscopy, NMR spectroscopy, UV, EPRS, X-ray and related spectroscopic techniques), reactions in SCF (synthesis of inorganic solids, synthesis of coordination compounds, Stochiometric organic reactions, photochemical and photoinduced reactions, polymerizations in dense CO2, free-radical polymerization in reactive SCFs, metal-complex catalyzed reactions, heterogeneous catalysis, enzymatic catalysis, phase transfer and ammonium salt catalyzed reactions) [Monograph] (Jessop and Leitner, 1999b);
• Chemical reactions in supercritical fluids [review] (sc-CO2 and water as reaction media, homogeneous catalysis, increased rates and selectivities because of high solubility of reactant gases, rapid diffusion between phases, weaker solvation of the catalyst, transition metal complex, Diels–Alder reaction, Trotsch synthesis reaction, organometallic photochemistry) (Ikariya et al., 1995).
• Chemistry in supercritical water (Bröll et al., 1999).
• Organic chemical reactions in supercritical water [review] (pressure aqueous environments, high-temperature chemistry, near-critical water, Raman-spectroscopic measurement, continuum electrostatics model, acid–base behavior, hydrothermal reactions, phenol oxidation, S(n)2 reaction) (Savage, 1999).
• Investigating the synthesis potential in supercritical water (Krammer et al., 1999).
• Chemical synthesis in supercritical carbon dioxide. “The Better Solution?” “Supercritical CO2 is an environmentally benign solvent for chemical synthesis with homogeneous transition metal catalysts. The unique properties of this medium allow efficient catalyst recycling and can lead to increased activities and selectivities. The design of CO2-soluble catalysts is of particular importance for the application of this novel solvent” (Leitner, 2000).
• Solvation in supercritical fluids: its effects on energy transfer and chemical reactions [review] (charge-transfer-state, liquid transition region, X-ray-scattering, rotational friction coefficients, diffusion-controlled reactions, electron-transfer reactions, pyrene excimer formation, highly excited azulene, free-space model) (Kajimoto, 1999).
• Solvent density inhomogeneities in supercritical fluids [review] (Lennard–Jones fluid, continuum electrostatics model, MD simulation, compressible dielectric fluid, solute-solute correlations, transfer-state formation, reaction-rate constants, MC simulation, highly excited azulene, charged hardsphere) (Tucker, 1999).
• Thermodynamic studies of chemical equilibrium in sc-CO2/cosolvent solutions using UV-Vis spectroscopy preferential clustering, tautomeric equilibrium, benzophenone, ethane) (Lu et al., 1999).

Syntheses/reactions:
• Supercritical water oxidation: state of the art (Schmieder and Abeln, 1999);
• Oxidation of hydrogen and carbon monoxide in sub- and supercritical water – reaction kinetics, pathways, and water-density effects, (1) Experimental results (sensitivity analysis, oxygen mixtures) (Holgate and Tester, 1994b), (2) Elementary reaction modeling (OH + CO, rate-constant, temperature dependence, pressure-dependence, self-reaction, gas-phase, HO2, mechanism, combustion) (Holgate and Tester, 1994a);
• Kinetics and mechanism of methane oxidation in supercritical water (modelling, combustion chemistry, hydrogen) (Savage et al., 1998);
• Separation and destruction of environmental pollutants by oxidation in CO2 (Dahmen and Dinjus, 1999);
• Hydrolysis and oxidation in subcritical and supercritical water: connecting process engineering science to molecular interactions (waste treatment, methanol oxidation, fundamental kinetics, ion solvation, ab-initio, transport-properties, neutron-diffraction, spectroscopic measurement, hydrogen) (Tester and Cline, 1999);
• Hydrolysis of esters in subcritical and supercritical water (kinetics, mechanism, ion-product, oxidation, conversion, methanol, acid) (Krammer and Vogel, 2000);
• Kinetic study of hydrolysis of methylene chloride from 100°C to 500°C (sc-water, rate constants, oxidation, ground water) (Salvatieria et al., 1999);
• Incorporation of parametric uncertainty into complex kinetic mechanisms: Application to hydrogen oxidation in supercritical water (fundamental kinetics, diffusion, CO, methanol) (Phenix et al., 1998);
• Hydrotherm oxidation of model molecules and industrial wastes (SCWO, methanol) (Cansell et al., 1998);
• Rate of dibenzyl ether decomposition in supercritical water (decomposition kinetics, hydrogen transfer-reactions, coal, pyrolysis, kinetics) (Funazukuri et al., 1997);
• Catalytic hydrodesulfurization of dibenzoithiophene through partial oxidation and a water-gas shift reaction in sc-water (Tropsch synthesis reaction, coal-tar pitch, fluid, extraction) (Adschiri et al., 1998);
• Homogeneous organic reactions as mechanistic probes in supercritical fluids [review] (solvation ultrafast dynamics, laser flash-photolysis, Diels-Alder reaction, solvent-density dependence, transfer-state formation, highly excited azulene, continuum electrostatics model, diffusion-controlled reactions, free-radical polymerization, time-resolved fluorescence) (Brennecke and Chateauneuf, 1999);
• Highly regio- and enanto-selective rhodium-catalysed asymmetric hydroformylation without organic solvents (sc-CO₂, phosphine-phosphite ligands, enantioselective hydroformylation, homogeneous catalysis, hydrogenation, complexes, olefins, propylene, perfluoroalkyl-substituted ligand (R,S)-3-(HF6)-F-2-BINAPHOS, substitution pattern of the ligand) (Francio and Leitner, 1999);
• Supercritical fluids in heterogeneous catalysis [review] (Fischer–Tropsch synthesis, near-critical conditions, Pt/γ-Al₂O₃ catalyst, homogeneous catalysis, selective synthesis, reaction volumes, recycle reactor) (Baiker, 1999);
• The continuous acid-catalyzed dehydration of alcohols in supercritical fluids: a new approach to the cleaner synthesis of acetals, ketals, and ethers with high selectivity (Compressed liquid water, tert-butyl alcohol, Nafion-h catalyst, heterogeneous catalysis, 1-propanol dehydration, organic-reactions, solid superacids, CO₂, cyclic ethers) (Gray et al., 1999);
• Ammonolysis with supercritical NH₃ (amine, kinetics, sc-reaction) (Wang et al., 1999);
• Synthesis of 1,4-diaminocyclohexane in supercritical ammonia (amination, cobalt-iron, catalytic amines, alcohols, transformation, diols) (Fischer et al., 1999a);
• Cobalt-catalyzed amination of 1,3-propanediol: effects of catalyst promotion and use of supercritical ammonia as solvent and reactant (1,3-diaminopropane, 1,3-propanediol, effect of iron and lanthanum promotion, aliphatic amines, copper, alcohols, methyamines, adsorption, nickel, XPS) (Fischer et al., 1999b);
• Supercritical fluids as media for chemical and biochemical reactions (Ikushima and Arai, 1998);
• Supercritical fluids – an interesting medium for chemical and biochemical processes (FT–IR study on the structures of reverse microemulsions in supercritical ethane, ester synthesis catalyzed by a lipase in CO₂, inverted micelles, reversed micelles, aerosol, angle neutron-scattering, interfacial activation, near-critical region, candida-rugosa lipase, OT) (Ikushima, 1997);
• Effect of Pressure on an enzymatic reaction in a supercritical fluid (Erickson et al., 1990);
• Enzyme catalyzed reactions in dense gases (enzymes, esterification, high pressure, mass transfer, mucor-mieliepi lipase, oleic-acid esters, n-butyl oleate, immobilized lipase, organic-solvents, esterification, transesterification, pressure, fluids) (Knez et al., 1998);
• Polymerizations in supercritical CO₂ [review] (compressed fluid diluents, consistent-field-theory, dispersion polymerization, methyl-methacrylate, microcellular materials, emulsion stabilization, metathesis catalysts, elevated pressures, glass transitions, olefin metathesis) (Kendall et al., 1999);
• Electrochemistry in near-critical and supercritical fluids. 9. Improved apparatus for water systems (23–385°C) – the oxidation of hydroquinone and iodide (Liu et al., 1997);
• Electroorganic synthesis using supercritical CO₂ (Reactive-metal anode, electrochemical carboxylation, sacrificial anodes, acids, bromides, voltammetry) (Tokuda, 1999);
• Novel synthesis methods for new materials in solid state chemistry (borohydrides, electrochemical oxidation reduction, intercalation deintercalation, mechanical alloying, nanoparticles, nitrogen dioxide, soft chemistry, electrochemical oxidation, structural relationships, oxides, La₃CuO₄, lithium, temperature, reduction) (Etourneau, 1999);
• Remarkable pressure-dependent changes in diastereoselectivity in supercritical carbon dioxide (Anon., 1999);
• Carbon dioxide and metal centres: from reactions inspired by nature to reactions in compressed CO₂ as solvent [review] (CO₂ activation, carbamato metal complexes, enzyme models, semiconductor photo-catalysis, homogeneous catalysis, copper-catalyzed oxidation, CO₂-soluble chelating-agents, light induced photofixation, CO₂ reduction, transition-metals, active-sites) (Walther et al., 1999);
• Laser-induced oxidation reactions of ethane in sc-CO₂ (KrF excimer laser, photo-induced oxidation, Herzberg photoabsorption, oxygen, recombination, resonance, fluids, gases, O₂) (Otomo et al., 1999);

5.3. Supercritical fluid (materials) processing

• Processing with supercritical solvents (Mcclain, 2000);
• Cleaning of metal parts and components by compressed CO₂ (Dahmen et al.);
• Dyeing to be clean: use supercritical carbon dioxide (high-pressure investigations, solubility, impregnation, extraction, fibers, films, spectroscopy, polymers, azo-dyes) (Kazarian et al., 1999a);
• Supercritical fluid dyeing of PMMA films with azo-dyes (transition, diffusion of azo-dyes in a CO₂-swollen matrix of PMMA, tuning by changing the system pressure, dye partitioning, dye solubility, 180 Mpa, in situ UV-visible spectroscopy, polymers, methacrylate) (West et al., 1998);
• Dyeing of poly-olefin fibers in supercritical carbon dioxide part 2. Influence of the dye structure on the dyeing result and fastness properties (Bach et al., 1998a);
• Dyeing of synthetic fibers in supercritical carbon dioxide (Bach et al., 1999b);
• Experience with the UHDE CO₂-dyeing plant on a technical scale. Part II: concepts for the development of the pilot plant in respect of a scaling up of the machine (Bach et al., 1999a);
• Correlation of solubility data of azo disperse dyes with the dye uptake of poly(ethylene terephthalate) fibers (PETP) in supercritical carbon dioxide (Bach et al., 1999b);
• Applications of vibrational spectroscopy to characterize poly(ethylene terephthalate) processed with supercritical CO₂ ('solvent-free' processes for advanced processing of packaging materials and supercritical fluid dyeing of textiles, increased degree of crystallinity, supercritical dyeing of PET samples with azo dyes, crystallization, morphology and structure, surface orientation, plasticization, impregnation, fibers, films, FT–IR, Fₜ-raman) (Kazarian et al., 1999b);
• Recycling of oil-contaminated grinding sludge (Dahmen and Djinus, 1999);
• Supercritical CO₂ processing for submicron imaging of fluouropolymers (hexafluoropropylene, inorganic substrate; silicone polymers; phase-behavior; solubility; copolymers; photoresist; architecture; adhesion) (Sundararajan et al., 2000).

6. Conclusions

Although not complete, the tables include a large amount of actual aspects, terms and references (including many reviews about both general and more special topics), which possibly may be helpful in getting further informations about certain topics from the cited original literature. The sources are from different disciplines of science, e.g., organic, analytical chemistry, physical chemistry/chemical physics, chemical and other fields of engineering, environmental, material sciences, and many others.

Synergies of using supercritical fluids and micro-emulsions as well as additional aspects of supercritical fluids (materials) processing, however, may be subject of another paper.

Acknowledgements

Financial support from the Fonds der Chemischen Industrie e.V., Frankfurt am Main, is gratefully acknowledged.

References