SUPERCRITICAL EXTRACTION

Jonin T.M.
Nestle, Switzerland

Adjadj L.P.
Laboratorium für Technische Chemie/LTC, Switzerland

Rizvi S.S.
Food Science Department, Cornell University, USA

Keywords: Supercritical, carbon dioxide, extraction, solubility, process examples, food applications

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Summary

Under atmospheric conditions, materials can be found in three different forms: *solid*, *liquid*, and *gaseous*. A fourth state, called *supercritical*, can be reached by tuning temperature and pressure above the critical point. The physical properties of supercritical fluids are intermediates between those of gases and liquids: high density, high diffusivity, low viscosity, and high solubilizing power. Such fluids can be referred to as *compressible liquids* or *dense gases*.

The tunable properties of supercritical fluids are used in the extraction of hops and

various spices, for decaffeination of coffee, tea, and cocoa bean, as well as for milk fat fractionation or the analysis of wine aroma. Some other types of processes such as extrusion or water treatment are also based on supercritical fluids.

Carbon dioxide is the substance most commonly used for supercritical processes because of its easy-to-reach critical temperature and pressure, its chemical stability, non-flammability, non-toxicity, low cost, stability under radioactive conditions, and the easy recovery of extracts.

1. Introduction

The unique solvent properties of supercritical fluids were first reported well over 100 years ago in 1879 by Hannay and Hogarth, who measured the solubility of several inorganic salts in supercritical ethanol. However, in the 1980s and 1990s supercritical fluids have been used in several industrial processes, including decaffeination of coffee and tea, extraction of hop flavor for the beer industry, and extraction of lipids and aromas from plant material. Other applications of supercritical fluids include their use as solvents for synthesis in supercritical environments or as solvents for supercritical chromatography.

2. Concepts of Supercritical Fluids

A fluid is considered supercritical if it exists at conditions above its critical pressure and temperature. These critical values correspond to conditions in which condensation into a liquid or evaporation into a gas is no longer possible. These values can be easily visualized in the pressure and temperature projection of a phase diagram (Figure 1).
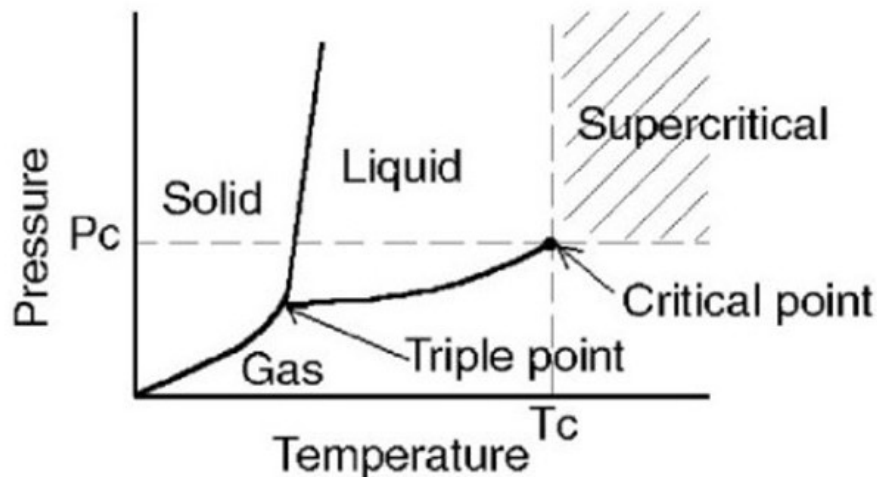

Figure 1. Typical pressure–temperature projection of a phase diagram for a pure material

The transition from a gas-liquid state to a supercritical form can be visualized by the disappearance of the meniscus between the two phases, as it becomes one phase.

Supercritical fluids are used because of the unique properties of such substances.

Supercritical fluids diffuse faster and have a lower viscosity compared to liquids. Table 1 shows the different physical properties of fluids in different states.

The dissolution power of a fluid is directly related to its overall solvation energy, which is determined by the sum of the solute–solvent interactions. As shown in Table 1, the density of supercritical fluids is about three orders of magnitude greater than that of gas; therefore, the dissolving power is increased for supercritical fluids, because as density increases more solute–solvent interactions will occur. Since supercritical fluids have great dissolving power, they are used in a number of ways for purification, extraction, fractionation, and recrystallization of a wide host of materials. In the future, new applications will probably be developed for supercritical fluids, in which case their use will likely become more common in new and existing industrial processes.

State of fluid	Density [g/cm^3]	Diffusivity [cm^2/sec]	Viscosity [g/cm*sec]
Gas P = 1 atm, T = 15-30°C	$(0.6\text{-}2)*10^{-3}$	0.1-0.4	$(1\text{-}3)*10^{-4}$
Liquid P = 1 atm. T = 15-30°C	0.6-1.6	$(0.2\text{-}2)*10^{-5}$	$(0.2\text{-}3)*10^{-2}$
Supercritical P = P$_c$, T = T$_c$ P = 4P$_c$, T = T$_c$	0.2-0.5 0.4-0.9	$0.7*10^{-3}$ $0.2*10^{-3}$	$(1\text{-}3)*10^{-4}$ $(3\text{-}9)*10^{-4}$

Table 1. Order-of-magnitude comparison of the properties of fluids as a function of their state

A list of selected supercritical fluids is given in Table 2. The supercritical fluids most commonly used are carbon dioxide, ethane, ethene, propane, ammonia, and water. However, carbon dioxide is preferred because of its convenient critical temperature, cost, chemical stability, non-flammability, stability in radioactive applications, and non-toxicity. Disposal of carbon dioxide is more environmentally friendly than for most other organic solvents typically used in extraction processes. It can be obtained in large quantities as a byproduct of several reactions, such as fermentation, combustion, and ammonia synthesis.

Another advantage of using supercritical CO_2 is that once the extract returns to standard conditions of pressure and temperature, the CO_2 returns to a gas phase and the extracted product precipitates since it is no longer soluble in the gas. Therefore, there is no need for an additional separation step, as in the case of other solvents used in the food industry.

Substance	T$_c$ [K]	P$_c$ [MPa]	Critical density [g/cm^3]
Methane	190.6	4.60	0.162
Ethylene	282.4	5.03	0.218
Chlorotrifluoromethane	302.0	3.92	0.579
Carbon dioxide	304.2	7.38	0.468
Ethane	305.4	4.88	0.203
Propylene	365.0	4.62	0.233
Propane	369.8	4.24	0.217

Ammonia	405.6	11.30	0.235
Diethyl ether	467.7	3.64	0.265
n-Pentane	469.6	3.37	0.237
Acetone	508.1	4.70	0.278
Methanol	512.6	8.09	0.272
Benzene	562.1	4.89	0.302
Toluene	591.7	4.11	0.292
Pyridine	620.0	5.63	0.312
Water	647.3	22.00	0.322
Xenon	289.7	5.84	1.113

Table 2. Selected supercritical fluids and their supercritical properties

Applications using these fluids include: extraction of carbonaceous material using supercritical ammonia; removal of polychlorinated dibenzodioxins, polychlorinated dibenzofurans, and stickies from fibers using supercritical propane; and reacting aromatic polyester with supercritical methanol to provide dimethyl aromatic dihydric carboxylic acid and dihydric alcohol.

In order to increase the solubility of polar compounds in a non-polar supercritical fluid a co-solvent, or entrainer, can be used. This increases the polarity of the supercritical fluid and therefore increases the interaction between the solute and the solvent. Typical co-solvents are generally used in proportions from 1 to 10 percent. Selected co-solvents include acetone, hexane, octane, methanol, ethanol, 1-propanol, and 2-propanol.

The effects of non-polar co-solvents for solubility enhancement in supercritical CO_2 have been studied. Since carbon dioxide has low polarizability, the solubility of hydrocarbons is limited, but by adding small amounts of alkane co-solvent it was possible to enhance their solubility significantly. Among the co-solvents tested were pentane, octane, and undecane. Using octane, investigators were able to increase the phenanthrene solubility up to five times.

Solubility values can also be predicted using equations of state. For a system containing more than two components, mixing rules are introduced that take into account the interactions between the different components. A good review of the fundamental principles of supercritical fluids was written in 1986.

Modeling of lipid solubility has been studied in numerous publications. One research team described a model to compute the solubility values of fatty acids and triglycerides, either pure or in mixture. Three fatty acids and their corresponding triglycerides were used: lauric acid, myristic acid, palmitic acid, trilaurin, trimyristin, and tripalmitin.

3. Solubility Measurement Techniques

In order to set up a process for supercritical extraction of a raw material the first step is to measure its solubility in supercritical fluid. There are two commonly used approaches: using a dynamic or flow-through system or using a static or recirculation system.

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Biographical Sketches

L.P. Adjadj is currently a Ph.D. student at the Swiss Federal Institute of Technology Zurich (ETHZ). He is studying the applications of ultrasonic spectroscopy as a general method for particle sizing in

suspensions. He completed his D.E.S. (Superior Study Diploma) while in an exchange program between the University of Lausanne and the Food Science Department of Cornell University, Ithaca, NY. His work was focused on flavor carriage by supercritical CO_2 during extrusion. He holds a Chemical Engineering degree from the Swiss Federal Institute of Technology, Lausanne (EPFL). In his graduate thesis, he screened different ordered catalysts for steam reforming of methanol.

Thierry Jonin is currently working as a Project Manager at the Informatic Department in Nestlé, Switzerland. In 2000, he obtained a D.E.S. (Superior Study Diploma) from the University of Lausanne, Switzerland, for work completed in the field of supercritical CO_2, entitled "Solubility of methyl anthranilate in supercritical CO_2 as a function of pressure, temperature, and co-solvent," under the supervision of Dr. S.H. Rizvi in the Food Science Department, Cornell University, Ithaca, NY, USA. Previously, he graduated in 1998 from the Chemistry Department at the University of Lausanne, Switzerland. His graduate thesis entitled "Study of moisture sorption isotherms of milk powders" was completed at the Nestlé Research Center, Vers-chez-les-Blancs, Switzerland.

Syed Rizvi is professor of Food Process Engineering in the Department of Food Science, Cornell University, Ithaca, NY. His laboratory is engaged in research on experimental and theoretical aspects of bioseparation processes, high pressure extrusion with supercritical fluids, physical and engineering properties of biomaterials, and novel food processing technologies. A major long-term goal is to develop new and improved unit operations for value-added processing of food and biomaterials. Derivative goals include new techniques for measurement and control of processes and properties for industrial applications. He has published over 100 technical papers, co-authored/edited six books, and holds eight patents.