What is a Supercritical Fluid ?

1. Definition

Supercritical Fluid: Fluid over its **critical** temperature and pressure, exhibiting good solvent power ; in most applications, **carbon dioxide** is used pure or added with a **co-solvent** ; the main interest of supercritical fluids is related to their “ tunable ” properties, that can be changed easily by monitoring pressure and temperature : good solvent power at high densities (temperature near **critical** temperature and pressure much over **critical** pressure) to very low solvent power at low densities (temperature near or higher **critical** temperature and pressure lower **critical** pressure).

2. Carbon dioxide and other fluids

Carbon dioxide : CO2 is a very attractive supercritical fluid for many reasons :

-- very cheap and abundant in pure form (food grade) worldwide ;

-- non flammable and not toxic ;

-- environment-friendly, as non polluting gas and as most of CO2 is manufactured from waste streams (mainly fertilizer plants gaseous effluents) ;

-- critical temperature at 31°C, permitting operations at near-ambient temperature, avoiding product alteration ;

-- critical pressure at 74 bar, leading to “ acceptable ” operation pressure, generally between 100 and 350 bar.

However, carbon dioxide always behaves as a “ non-polar ” solvent that selectively dissolves the **lipids** that are water-insoluble compounds like vegetal oils, butter, fats, hydrocarbons….Carbon dioxide does not dissolve the hydrophilic compounds like sugars and proteins, and mineral species like salts, metals,…

Co-solvent : Organic solvent added to the main fluid (generally carbon dioxide) to modify its solvent power vis-à-vis “ polar ” molecules as the fluid itself is only able to dissolve “ non-polar ” molecules ; generally, the co-solvent is chosen between short-chain alcohols, esters or ketones. For obvious reasons, ethanol is preferred in many cases as it is abundant and cheap in pure forms (food grade, pharmacopoeia grade), not environment hazardous and not very toxic (as it is well known !).

Carbon dioxide is available either in commercial cylinders or spheres of limited volumes, or in bulk from tanks containing between 4 and 30 tonnes of liquefied gas at a pressure of 18 bar and at a temperature around –18°C. These tanks are directly fed from cryogenic trucks as shown on the picture below. The price is very sensitive to the quantity delivered as transportation is the main cost because carbon dioxide is available at very low price in various chemical plants (mainly ammonia plants).

Carbon dioxide supply to SEPAREX tank (4 tonnes) from a cryogenic truck

As most SCF plants require liquid carbon dioxide under a pressure of 45 bar or so, the liquefied gas must be compress form the storage pressure (18 bar) to 50 bar through a pump. For applications in the food and pharmaceutical industries, it is ***mandatory*** to use a "dry" pump to avoid any contamination by pump lubricant.

Moreover, great care must be taken when designing the feed line of liquefied gas to the plant(s) in order to avoid any over-pressure when the flow is stopped and the temperature increases. As detailed below, no section must be without over-pressure protection (relief valve, burst disk,..) as dilatation of the fluid may cause dramatic accidents.
No need to say that drastic precaution must be enforced to avoid the leakage of the whole tank inside a building in case of any problem on one operating plant !

3. Thermodynamic properties

We strongly recommend the reader to use this reference book : "The properties of Gases and Liquids" R.R. Reid, J.M. Prausnitz, E. Poling, McGraw-Hill.

All pure compounds can be found in three states : Solid, Liquid or Vapor (or Gas).
On the (pressure, temperature) diagram, the three regions corresponding to these three states are separated by curves that meet at the **triple point**. Surprisingly, the vaporization/liquefaction curve presents an end point called **critical point (P_c - T_c)** : Beyond

this point, ($P > P_c$ et $T > T_c$), only one phase exists, called **Supercritical Fluid (SCF)** . At the critical point itself, the fluid compressibility becomes infinite :

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \quad et \quad \left(\frac{\partial^2 P}{\partial^2 V}\right)_T = 0$$

meaning that the fluid specific gravity rapidly varies with a slight change in pressure at constant temperature. Moreover, even out of the critical region itself, SCF exhibit large changes in specific gravity – and consequently its solvent power - , as shown on figure 1, and other physico-chemical properties with pressure or temperature.

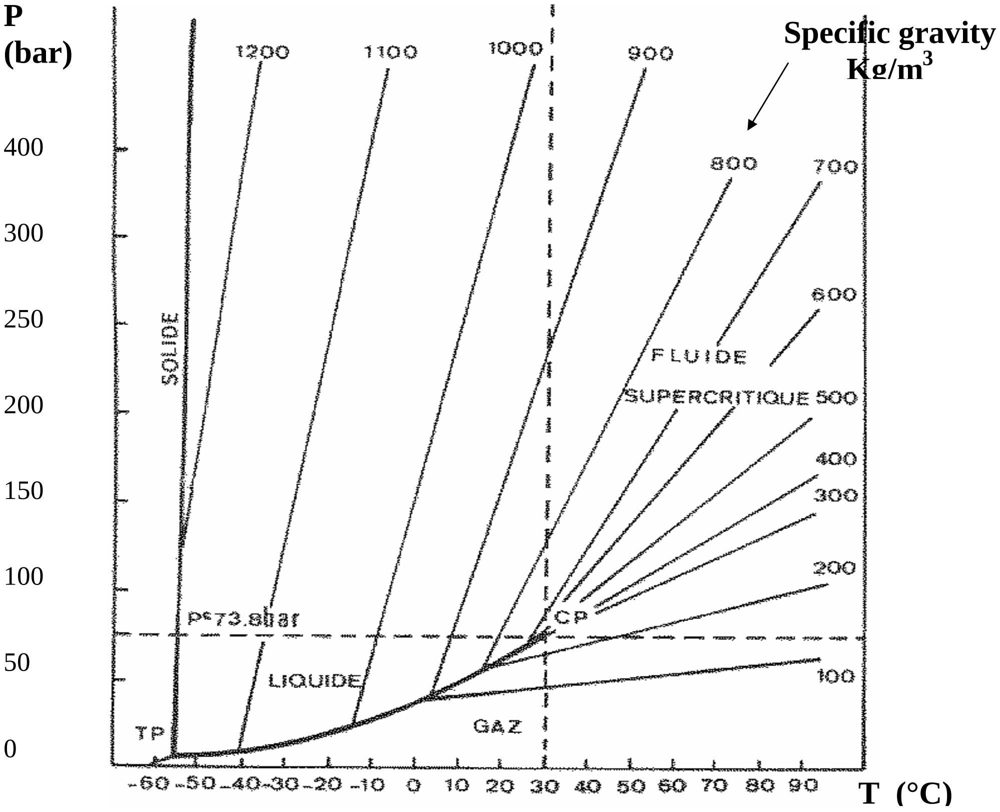

Figure 1 : Diagram (P,T,ρ) of carbon dioxide

Most compounds exhibit a critical pressure in the range of 35 to 60 bar, except water (221 bar) and ammonia (113.5 bar). Critical temperature increases with the complexity of the molecule and very few compounds exhibit a critical temperature between 0 and 50°C (ethane, ethylene, CO2, N2O). Mixtures behave in a more complex way depending on their composition, but “ critical ” phenomena are also observed.

The most interesting characteristics of SCF, on which are based all the SCF processes, is related to their “**tunability**” with pressure and temperature, especially of the tunability of their solvent power.

Polarity :

Solvents are classified according to a scale of polarity depending on their ability to dissolve “ polar ” or “ non-polar ” molecules. Water is the most polar solvent, dissolving all kinds of compounds that can be ionized or that contains hydrophilic moieties like sugars, proteins, amino-acids,….On the contrary, organic solvents like light alkanes (hexane, heptane,…) or chlorinated hydrocarbons do not dissolve these compounds, but only hydrophobic molecules that are not at all soluble in water like fats, oils, hydrocarbons, essential oils,… : they are called non-polar solvents. Other solvents like alcohols, amines, ketones,…exhibit intermediate behavior. Most supercritical fluids behave like **non-polar** solvents exhibiting a strong affinity with lipids and hydrocarbons, but a weak affinity with oxygenated or hydroxylated molecules ; it is possible to tune their polarity by adding a **polar co-solvent** (ethanol or light alcohols, esters or ketones).

Solvent power :

Fluid phase equilibria of mixtures are very complex, and many types of phase diagrams can be found. Recent progresses in thermodynamc modeling permit to predict the phase equilibria of many mixtures ; however, some measurements – that are difficult to perform! - continue to be required to set some interaction parameters that cannot be calculated yet, especially for polar liquids (for example in the case of strong hydrogen-bonding).

Nevertheless, for “simple” systems and relatively low solubility, the empirical correlation proposed by Chrastil can be used to interpret experimental results with a good reliability without any complicated calculations :

$$C = \rho^k \ . \exp [a/T + b]$$

where C is the solute concentration, a, b and k empirical constants ; this correlation shows the extreme dependence of the solubility to the fluid specific gravity ρ. It also shows that :

- Solubility increases with density (or pressure) at constant temperature ;
- Solubility may increase or decrease when temperature is raised at constant pressure.

In all cases, the solubility dramatically decreases when the fluid is depressurized at constant temperature below its critical pressure, with solubility variation of several orders of magnitude. This is the basis of most SCF processes : SCF are used as solvents in the supercritical fluid region to selectively extract some compound(s) before being depressurized to cause the solute(s) precipitation permitting the fluid-solute separation.

It is to be noticed that although water is only slightly soluble in SCF carbon dioxide (1-2 g/kg), it plays a very important role as “co-solvent” for many polar molecules ; in fact, water is present in most applications, especially when natural products are processed.

Finally, it is also important to say that, due to their non-polar character, SCF are also used as “**anti-solvent**” in polar organic solvents where they readily dissolve, leading to a significant decrease of their polar character, and causing precipitation of compounds previously dissolved in these solvents.

Thermodynamic cycle :

The basic diagram when designing and operating a SCF plant (whatever its size !) is the Pressure-Enthalpy diagram (so-called Mollier diagram), or possibly the Temperature-Entropy diagram for those who prefer. On these diagrams, it is easy to represent the behavior of the fluid that, in most cases, can be assimilated as a pure fluid, except when a significant content of co-solvent is added to the pure fluid. It becomes easy to read the phase state (liquid, gas, supercritical fluid), the enthalpy to supply at the heat exchangers or to remove at the condenser, …

We do handle the Mollier diagrams of the most common SCF (carbon dioxide, propane, butane, nitrous oxide, HFC,…) ; moreover, SEPAREX currently uses a software (from Professor Jaubert ENSIC – Nancy) permitting to calculate most thermodynamic data for pure compounds, knowing only their chemical formulas.

In literature, thousands of articles can be found on high-pressure fluid phase equilibria covering a very wide range of compounds and operating conditions. But happily, it is not always necessary to handle detailed thermodynamic data on the processed mixtures to design the SCF processes, especially when complex mixtures are treated.

4. Transport properties

Refer to : “The properties of Gases and Liquids” R.R. Reid, J.M. Prausnitz, E. Poling, McGraw-Hill, for viscosity, thermal conductivity, diffusivity and surface tension evaluation.

Moreover, the SCF transport properties are very attractive as they are dense as liquids but “mobile” like gas (very low viscosity, intermediate diffusivity), as shown on table 1. So, mass transfer (and similarly heat transfer) is fast in SCF in comparison with liquid solvents or water. Moreover, SCF rapidly diffuse in porous media, easing either extraction from solid materials or impregnation of solutes into porous media.

Table 1: Comparison of average properties of gases, liquids and SCF

	Liquid	Supercritical $T \sim T_c$ $P \sim 1$ to 4 P_c	Gas (at room T et P)
Specific Gravity $\rho (kg.m^{-3})$	600 - 1600	100 - 900	0.6 - 2
Viscosity η (Pa.s)	10^{-3}	$10^{-5} – 10^{-4}$	10^{-5}
Diffusivity D ($m^2.s^{-1}$)	10^{-9}	10^{-8}	10^{-5}

5. Biological properties

Carbon dioxide - that is by far the most common SCF – exhibits biocide properties and is very active on fungi, bacteria and viruses. It has only a very low toxicity on humans, although asphyxia happens when it accumulates in non-ventilated areas, especially in lower parts of buildings (cellars, …). N_2O has different biological properties and it is commonly used for anesthesia (Note : Its use exposes to other hazards as it must be considered as a comburant that may lead to explosion when contacted with flammable solutes). Light hydrocarbons are not toxic (but present a very important explosion hazards). HFC are neither toxic nor flammable, but can decompose in highly toxic gases when submitted to a flame.

6. General process concepts

The processes using SCF are founded on the specific properties of these fluids, particularly on the possibility to vary their solvent power over a wide range : They are used as “good” solvents (extraction solvents, chromatography eluents, reaction media) when operating conditions leads to a high specific gravity (high pressure, temperature near the critical temperature), and they are later turned into compressed gases with very low solvent power (pressure below the critical pressure, temperature over the liquefaction temperature at this pressure) in order to perform fluid-solute separation.

It has to be emphasized that one of the main interest of SCF is related to the ability to set very precisely their solvent power vis-à-vis different compounds by tuning pressure, temperature and co-solvent content : This permits to perform very selective fractionation of complex mixtures that cannot be resolved with classical organic solvents or by any other process. This is used either for sorting compounds belonging to the same chemical family but differing by their carbon numbers (i.e. fatty acids or oligomers/polymers), or of similar molecular mass but with slightly different polarities.

Moreover, it is possible to combine this “tunable” solvent power with selective means known in chemical engineering for completing difficult separations :

- For fractionation of liquid mixtures, high-performance multi-stage counter-current packed or stirred columns are preferred ; to increase selectivity, a reflux of extract is performed either by operating a temperature gradient along the contactor on pilot-scale equipment (causing solvent power decrease and consequently precipitation of the less-soluble compounds that reflux in liquid phase) or by an external reflux on large-scale equipment ;
- Multi-stage separation of the fluid-solute mixture through separators in series operated at decreasing pressures in order to fractionate the solute according to its affinity with the fluid ;
- Combination of extraction or fractionation with selective adsorption of the solute mixture dissolved in the depressurized fluid onto a selective adsorbent ;
- Adsorption of the most volatile compounds of the solute in order to avoid recycling with the fluid and important losses of such compounds or selectivity decrease.