Supercritical Solvents (CO$_2$, H$_2$O).

Prof. Attilio Citterio
Dipartimento CMIC “Giulio Natta”
https://iscamapweb.chem.polimi.it/citterio/it/education/course-topics/
Supercritical Fluids.

- Above 31.1 °C and 73 atm ($T_{cr}$ and $P_{cr}$) carbon dioxide behaves as a supercritical fluid and shows properties of both a liquid and a gas.
- It fills the container, like a gas, and dissolves substances like a liquid.
- Once the critical temperature and pressure have been reached the two distinct phases of liquid and gas are no longer visible. The meniscus can no longer be seen. One homogenous phase called the "supercritical fluid" phase occurs.

With an increase in temperature the meniscus begins to diminish.

The liquid density falls due to expansion and the gas density rises as more of the substance evaporates.
Comparison of Physical and Transport Properties of Gases, Liquids and SCFs.

<table>
<thead>
<tr>
<th>Property</th>
<th>Gas</th>
<th>SCF</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density ( (g \cdot cm^{-3}) )</td>
<td>(10^{-3})</td>
<td>(0.1-1)</td>
<td>(1)</td>
</tr>
<tr>
<td>Viscosity ( (g \cdot cm^{-1} \cdot s^{-1}) )</td>
<td>(10^{-4})</td>
<td>(10^{-3}-10^{-4})</td>
<td>(10^{-2})</td>
</tr>
<tr>
<td>Diff. Coeff. ( (cm^{2} \cdot s^{-1}) )</td>
<td>(10^{-2}-10^{-1})</td>
<td>(10^{-4}-10^{-3})</td>
<td>(10^{-5})</td>
</tr>
</tbody>
</table>
A supercritical fluid (SCF) is any substance at a temperature and pressure above its critical values. Critical temperature is the temperature above which a pure gas cannot be liquefied regardless pressure values. They have properties intermediate between gases and liquids, which can be controlled by both temperature and pressure. Typical critical data are:

<table>
<thead>
<tr>
<th>Substance</th>
<th>$T_c$ (°C)</th>
<th>$P_c$ (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>31.1</td>
<td>73.8</td>
</tr>
<tr>
<td>Fluoroform</td>
<td>25.9</td>
<td>48.2</td>
</tr>
<tr>
<td>Water</td>
<td>374.0</td>
<td>220.6</td>
</tr>
<tr>
<td>Ammonia</td>
<td>132.4</td>
<td>113.2</td>
</tr>
<tr>
<td>Ethane</td>
<td>32.2</td>
<td>48.7</td>
</tr>
<tr>
<td>Methanol</td>
<td>239.5</td>
<td>8.08 MPa</td>
</tr>
</tbody>
</table>

$\text{CO}_2$ is unpolar $\therefore$ high volumes and pressure are necessary to liquefy (high energetic costs). Co-solvents are added to increase the polarity.

Water becomes SC at higher temperatures and pressures than $\text{CO}_2$. 

**Common Supercritical Fluids.**
Why Use sc-Fluids?

- Increased mass transport
- Gases are totally miscible
- No surface tension
- Excellent for infusion and extraction
- Inert and non-toxic
- Inexpensive fluids
- Environmentally compatible
- Solvent is tuneable with pressure

P.G. Jessop, T. Ikaraya and R. Noyori. Science, 1995, 269, 1065: see also:
Carbon Dioxide (CO$_2$).

- Similar advantages to water:
  - Natural, cheap,
  - Plentiful (0.04% of atmosphere and now rising!)
  - Available in >99.9% pure form, €90/$110 per 25 kg.
  - By-product of brewing, ammonia synthesis, combustion
  - Non-flammable
  - TLV = 5000 ppm

- Supply chain and related technology already established;
- Non-toxic and properties well understood
  - Asphyxiant at high concentrations (excludes oxygen from lungs)
- Easily removed and recycled, and can be disposed of with no net increase in global CO$_2$;
  - Simple product isolation by evaporation, to 100% dryness.
- No solvent effluent, renewable;
- Potential for product processing (extraction, particle formation, chromatography, etc.).
Pressure-Temperature Phase Diagram for CO₂.

- **Melting line**
- **Liquid**
- **Boiling line**
- **Solid**
- **Supercritical fluid**

Pressure (bar) vs. Temperature (°C)

- **Melting line**
- **Boiling line**
- **Solid**
- **Gas**

**CP**

- **P_c = 73.8 bar**
- **T_c = 31.06°C**
Pure CO$_2$ PTV Diagram and Projections.
Other Advantages of scCO$_2$.

- Carbon dioxide is a non polar molecule since the dipoles of the two bonds cancel one another.
- High compressibility
  - Large change in solvent properties for relatively small change in pressure – infinite range of solvent properties available (low viscosity and zero surface tension)
  - Ability to tune solvent to favour a particular reaction pathway simply by optimising temperature or pressure (tuneable density)
- Cosolvents can further modify solvent properties (“Tunable” properties)
- High diffusivity offers potential for increase reaction rates.
- Potential for homogeneous catalytic processes.
  - High solubility of light gases, some catalysts and substrates; bring all together in single homogeneous phase (hydrocarbons and derivatives with less than 20 carbon atoms, but not big molecules, i.e. oils, waxes, fats, polymers, proteins, sugars)
- Inert to oxidation; resistant to reduction
  - Excellent medium for oxidation and reduction reactions.
Change of Solvent Power of CO₂ from Pressure.

$Hildebrand \ Parameter (\text{cal cm}^{-3/2})$

$310 \ K = 37 \ °C$

$320 \ K = 47 \ °C$

$330 \ K = 57 \ °C$
Problems using scCO$_2$.

- **Moderate pressures required**
  - Standard HPLC apparatus used in lab, reactors made of stainless steel, many commercially available.
  - Can be expensive for large scale work.

- **Weak solvent**
  - Relatively non-polar, but high quadrupole moment. Use of co-solvents (MeOH, MeCN, THF, toluene)
  - CO$_2$ exhibits a low dielectric constant, low polarizability/volume
  - Simple modification of reagents to improve solubility.

- **Energy considerations**
  - Compression of CO$_2$ requires energy
  - Energy consumption reduced minimal decompression and recycling.

- **CO$_2$ is a Lewis acid** - reacts in the presence of good nucleophiles
  - Often reversible (acid behaviour in H$_2$O), can be exploited synthetically
Current Consumer Related Applications of CO₂ Technology.

- Carbonated drinks
- Leavening agents in baking
- Solvent extraction
  - Decaffeinating coffee and tea
  - Extracting bitterness from hops to make beer
  - Defatting cocoa powder
  - Extracting spices and aromatic plants
- Surface coating
- Fumigation (1% in air will eliminate pests in greenhouses)
- Degreasing and dry cleaning applications
- Welding
- pH control (e.g. effluent streams, pulp and paper mills)
- Refrigeration (dry ice, mechanical systems)
- Fire extinguishers
- Life jackets
Can sc-Fluids be Scaled up?

One of the biggest chemical reactions (polyethylene production) is carried out under SC conditions.

Natural products such as Caffeine and hops extract are obtained using scCO$_2$.

Spray painting process use scCO$_2$ to reduce VOC emissions (>’80%).

Known are also some continuous synthesis which use sc-fluids with capacity of up to 1000 tonnes per year.

But Also:

- Textile dyeing
- 157 nm photoresist processing
- Self assembly
- Nanoparticles

http://www.thomas-swan.co.uk/
SOAKING green coffee beans in water doubles their size, allowing the caffeine to dissolve into water inside the bean.

CAFFEINE REMOVAL occurs in an extraction vessel. Caffeine diffuses into this supercritical carbon dioxide, along with some water.

DECAFFEINATED BEANS at the bottom of the vessel are removed, dried and roasted.

RECOVERY of dissolved caffeine occurs in an absorption chamber. A shower of water droplets leaches the caffeine out of the supercritical carbon dioxide.
Particle Formation.

- Two main complementary techniques:
  - RESS – Rapid expansion of supercritical solution
  - SAS – Solvent/AntiSolvent Precipitation
- Allow for the processing of a wide range of materials into solid phases with useful properties and morphologies, e.g. pharmaceuticals, protein macroparticles, explosives.

Dry Cleaning with scCO$_2$.

- Current methods use perchloroethylene
  - 1.5 Million tons used per year (North America)
  - Hazardous air pollutant and suspected carcinogen
  - Contaminates drinking water supplies
  - Contributes to photochemical smog
  - <5% recycled
  - Requires heating to remove solvent residues
  - Characteristic odour

- New process use liquid CO$_2$
  - Requires surfactant (to be recycled)
Dry Cleaning with scCO$_2$.

- No unpleasant odors
- No heat required for drying – energy efficient and kinder on clothes
- Possible tax credits and reduced regulatory monitoring
- Utilizes same CO$_2$ used by food and drink distributors
- Related technology also used for degreasing (e.g. metal parts), semiconductor photoresist removal and spin coating.
- Is a relevant byproduct of biorefinery industry.
Surfactants.

- A molecule that contains a polar portion and a non polar portion.
- A surfactant can interact with both polar and non polar molecules.
- A surfactant increases the solubility of the otherwise insoluble substances.
- In water, surfactant molecules tend to cluster into a spherical geometry
  - non polar ends on the inside of the sphere
  - polar ends on the outside
- These clusters are called **micelles**.
Micelle Structure of a Surfactant.
Natural and Synthetic Surfactants.

Natural
• Biodegradable
• Commonly soft
• Expensive

e.g.:
• esters of fatty acids
• ethoxylate alcohols
• alcohol ether sulfates
• esters of sucrose

Synthetic
• Frequently not very biodegradable
• Economic
• Wide variety/activity

e.g.:
• alkyl benzene sulfonates
• ethoxylate alcohols
• alkyl phenol ethoxylates
• quaternary ammonium salt
Surfactants for LCO$_2$ or scCO$_2$.

- Must have both CO$_2$-philic (CO$_2$ loving) and CO$_2$-phobic functionality.
- In 1994, Joseph M. DeSimone of the University of North Carolina State University published his discovery that polyacrylate polymers having perfluorinated residues are soluble in liquid or supercritical CO$_2$ present surfactant properties if they contain aromatic groups (copolymers).

\[
\text{CO}_2\text{ phobic Fragment}
\]

\[
\text{CO}_2\text{ phyllic Fragment}
\]

Micelle Structure for a CO$_2$ Surfactant.

Solvent Carbon dioxide

Chain segment “CO$_2$-phylic”

Chain segment “CO$_2$-phobic”
### Supercritical CO$_2$ Surfactants.

<table>
<thead>
<tr>
<th>Surfactant Type</th>
<th>Solubility (wt.%)</th>
<th>Emulsion Morphology</th>
<th>γ Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO$_2$ H$_2$O</td>
<td>(Stability in h)</td>
<td>Max. W$_o$ (mN/m)</td>
</tr>
<tr>
<td>CF$_3$O(CF$_2$CF$<em>2$O)$</em>{7,15}$OCF$_2$COOH</td>
<td>&gt;3 &lt;0.1</td>
<td>(5 sec – 54 min)</td>
<td>W/C 13.9 1.6-3.4</td>
</tr>
<tr>
<td>HOOCF$_2$(CF$_2$CF$<em>2$O)$</em>{2,7}$OCF$_2$COOH</td>
<td>~2 -</td>
<td>W/C</td>
<td>8.5 -</td>
</tr>
</tbody>
</table>

Other Industrial Uses of scCO$_2$.

Union Carbide Technology

- Solution for surface coating
- Replaces 40-90% of VOCs with CO$_2$.
  - Coatings on aerospace parts
  - Adhesion promoters on plastics

- Food Industry
  - Chocolate biscuits
  - Extraction of natural materials (Essential oils and fragrances)
  - Additives

- CO$_2$ Refrigeration
- scCO$_2$ SCF chromatography.

Technologies for Coating by scCO$_2$.

Rapid Expansion of Supercritical Solutions (RESS)

- **Gas Anti-Solvent (GAS)**
- **Precipitation with a Compressed Anti-solvent (PCA)**
Chemical Synthesis in scCO$_2$.

- Fluoropolymer (e.g. Teflon) synthesis:

  ![Fluoropolymer Synthesis Diagram]

  - Extremely important polymers
  - Dupont $40M$ development facility
  - Previous methods used CFCs
  - Easy polymer isolation and drying, and minimal waste

Reactions in scCO$_2$.

Homogeneous Catalytic Reactions in Supercritical CO$_2$:

- Catalytic copolymerization of CO$_2$ with Epoxides

\[
\begin{align*}
\text{Epoxide} + \text{CO}_2 & \xrightarrow{\text{Catalyst}} \text{Polyester} + \text{CO}_2 \\
\end{align*}
\]

- Asymmetric Catalytic Hydrogenation of Enamides

\[
\begin{align*}
\text{Enamide} + \text{H}_2 & \xrightarrow{\text{Catalyst}} \text{Enamide} \\
\end{align*}
\]

Tumas, Los Alamos National Laboratory
Lab scCO$_2$ Reactors.
Lab Equipment Design with \( \text{scCO}_2 \).
### Factors influencing extraction efficiency

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Pressure</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Structure and particle size of raw material
- Mass of CO$_2$ per mass of raw material

### Solubility

<table>
<thead>
<tr>
<th>Very soluble</th>
<th>Sparingly soluble</th>
<th>Insoluble</th>
</tr>
</thead>
<tbody>
<tr>
<td>non-polar and moderately polar molecules</td>
<td>Chlorophyll, waxes and carotenoids</td>
<td>Sugars, proteins</td>
</tr>
<tr>
<td>&lt;500 MW</td>
<td></td>
<td>Tannins, amino acids, pesticides</td>
</tr>
</tbody>
</table>

**Examples:** Triterpenoids, Oleic acid, dodecanol, Waxes

alkaloids, lipids <C22
Liquid CO$_2$ Extraction with Entrainers.

- Very small additions of entrainer modify the extraction characteristics of CO$_2$
- Alcohols (including water), ketones and hydrocarbons are most commonly used
- Entrainers modify the polarity and solvating properties of liquid CO$_2$
- Some compounds behave as surfactant agents.
Liquid CO\textsubscript{2} Extraction Circuit.

Bean in

Extractor

Bean Product

dryer

CO\textsubscript{2}/caffeine

LL extractor

Water/caffeine

Flash

Concentrator

CO\textsubscript{2} makeup

Water in

CO\textsubscript{2} recycle

Aqueous Caffeine byproduct

Water in

CO\textsubscript{2}/recycle

Extraction Circuit.
Supercritical CO$_2$ Extraction Circuit.
Industrial Extraction with CO$_2$.

- Decaffeination of Tea and Coffee - SCO$_2$
- Extraction of Hops - LCO$_2$ and SCO$_2$
- **Defatting of cocoa powder** - SCO$_2$
- Extraction of oil seeds - SCO$_2$
- Extraction of spices and aromatic plants - LCO$_2$ and SCO$_2$

**Cocoa defatting (2009)**

Complete removal of fat (<0.5%), no loss of polyphenols, no solvent residues
Extraction of Lipids and Aroma with CO$_2$.

- **Triglycerides** have limited solubility in LCO$_2$
- ScCO$_2$ almost exclusively used for fat and oil extraction
- CO$_2$ extraction reduces post extraction processing
- Oils have lower aroma, colour, free fatty acids and peroxide value
- Resulting residue can be used for animal feed

- Extraction with LCO$_2$ produces *products with an aroma* which closely resembles the starting material
- Extraction at 10°C or less minimises degradation of labile molecules and the formation of undesirable ‘off-notes’
- A greater proportion of higher molecular weight compounds are normally found in CO$_2$ extracts when compared to steam distilled oils
Extracts consist of a variety of fatty acids, including the non-essential ω-6 polyunsaturated fatty acid γ-linolenic acid (GLA), the essential ω-6 polyunsaturated fatty acid linoleic acid (LA), oleic acid, palmitic acid, and stearic acid.
<table>
<thead>
<tr>
<th>Component</th>
<th>CH$_2$Cl$_2$ (%)</th>
<th>Ethanol (%)</th>
<th>Liquid CO$_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alfa acids</td>
<td>35-45</td>
<td>30-40</td>
<td>40-50</td>
</tr>
<tr>
<td>Beta acids</td>
<td>15-20</td>
<td>10-15</td>
<td>18-40</td>
</tr>
<tr>
<td>Other soft resins</td>
<td>3-8</td>
<td>3-8</td>
<td>5-20</td>
</tr>
<tr>
<td>Hard resins</td>
<td>2-5</td>
<td>2-10</td>
<td>None</td>
</tr>
<tr>
<td>Olio volatile</td>
<td>1-3</td>
<td>1-2</td>
<td>2-8</td>
</tr>
<tr>
<td>Fats and Waxes</td>
<td>1-2</td>
<td>Traces</td>
<td>0-5</td>
</tr>
<tr>
<td>Tannins</td>
<td>Traces</td>
<td>1-5</td>
<td>None</td>
</tr>
<tr>
<td>Chlorophyll</td>
<td>&lt;1</td>
<td>Traces</td>
<td>None</td>
</tr>
<tr>
<td>Inorganic salts</td>
<td>&lt;1</td>
<td>0.5-1</td>
<td>Traces</td>
</tr>
<tr>
<td>Residual solvents</td>
<td>&lt;1</td>
<td>0.01-0.1</td>
<td>None</td>
</tr>
<tr>
<td>Water</td>
<td>Traces</td>
<td>1-5</td>
<td>1-5</td>
</tr>
<tr>
<td>Typical yield</td>
<td>28</td>
<td>38</td>
<td>19</td>
</tr>
</tbody>
</table>

(The extraction process maintains integrity of hop components (unchanged from pellet resinous compounds)
The extract represents approximately 25% of the original mass of the pellet.)
Hop Extraction with LCO$_2$.

% of extract

Extraction time ($h$)

$\alpha$-acids* (humulones)

$\beta$-acids (lupulones)

$R = CH_2CH(CH_3)_2$ humulone lupulone
$CH(CH_3)_2$ cohumulone colupulone
$CH(CH_3)CH_2CH_3$ adhumulone adlupulone

*La frazione di composti dell'estratto precipitati con Pb(OAc)$_2$ è detta acidi alfa.
### Matricaria recutita: Composition and Formation of Chamazulene Oil During Steam Distillation.

<table>
<thead>
<tr>
<th></th>
<th>Steam distilled %</th>
<th>Liquid CO₂ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-farnesene</td>
<td>18.4</td>
<td>14.5</td>
</tr>
<tr>
<td>spathulenol</td>
<td>&lt;0.1</td>
<td>1.5</td>
</tr>
<tr>
<td>α-bisabolol oxide B</td>
<td>19.4</td>
<td>4.6</td>
</tr>
<tr>
<td>α-bisabolone oxide A</td>
<td>12.0</td>
<td>3.1</td>
</tr>
<tr>
<td>α-bisabolol</td>
<td>&lt;0.1</td>
<td>3.7</td>
</tr>
<tr>
<td>chamazulene</td>
<td>15.4</td>
<td>1.3</td>
</tr>
<tr>
<td>α-bisabolol oxide A</td>
<td>9.9</td>
<td>23.5</td>
</tr>
<tr>
<td>Dicycloethers (MW 200)</td>
<td>2.7</td>
<td>37.8</td>
</tr>
<tr>
<td>Colour</td>
<td>Blue</td>
<td>Yellow</td>
</tr>
</tbody>
</table>

Matricine → pro-chamazulene → Chamazulene (artifact)
Supercritical Water.

Critical point
$P \approx 22 \text{ MPa and } T = 374^\circ \text{ C.}$

Below critical Point Temperature
Isotherm shows discontinuity.
Especially on intersection with saturation line.

Above Critical point
Isotherm shows no discontinuity
SCW is in gas like state.

Gives:
Liquid like density
Gas like viscosity.
A process in water at raised temperatures and pressures is called a hydrothermal process. The concept comes originally from the geology. The picture on the left shows a simplified overview about different hydrothermal processes and includes the vapour pressure curve of the water.
Supercritical Water (3).
Thermal Physical Properties at Critical Temperature.

- Properties variation as $C_p$, $k$, $h$ and $\mu$ are indicated in figure.
- Large properties variation noticed in pseudo-critical region.
- The large increase in convective coefficient is indicated near pseudo-critical line.
- The steep decrease in $\mu$ and $k$ is noticed.
Dielectric constant of water dependent from temperature/pressure. SC-Water present a dielectric constant between 2 and 30, similar to nonpolar solvents, i.e. hexane ($\varepsilon = 1.8$), and polar solvents, i.e. methanol ($\varepsilon = 32.6$).

Therefore, with SC-Water is possible dissolve organic compounds insoluble in water at ambient condition. Salts have instead low solubility in these conditions.
Water ionic product behaviour 
\( K_w = [H^+][OH^-] \);

- at 25°C and \( P = 1 \) atm, \( K_w \) is \( 1 \times 10^{-14} (\text{mol/l})^2 \).

- At higher temperature and pressure conditions, this value increase. At \( 34.5 \text{ MPa} \) pressure, a maximum value of \( 1 \times 10^{-11} (\text{mol/l})^2 \) is reached (minimum – log \( K_w \)) near 300°C.

Under these conditions, we have \([H^+] = 3 \times 10^{-6} \text{ mol/l}\), with an increase of about 30 times of concentration at room conditions. SC-water can be a potential acid catalyst.
• Located just south of the Equator, at the southern end of the mid-Atlantic Ridge

• 3 kilometers beneath the surface of the ocean

• Temperatures measured between 407°C – 464°C by remotely operated submersibles

• Immense pressure & temperature combine to create an anomaly that has both liquid and vapor qualities

• Provide essential nutrients to locally adapted organisms, microbes, & phytoplankton.
Waste Treatment by Oxidation in Supercritical Water.

- Technology able to complete decomposition of all types of recalcitrant compounds in short time, producing \( \text{CO}_2 \), \( \text{H}_2\text{O} \) and inorganic salts.

- Main problems arise from corrosion phenomena associated to higher acidity of water in SC conditions.
Oxidations in SC-Water.

Equipment for oxidation in supercritical water