

IMPACT 4 ON TECHNOLOGY

Supercritical fluids

Supercritical carbon dioxide, scCO_2 , is the centre of attention for an increasing number of solvent-based processes. The critical temperature, $31.0\text{ }^\circ\text{C}$ (304.2 K), and pressure, 72.9 atm (7.39 MPa), are readily accessible and carbon dioxide is cheap. The mass density of scCO_2 at its critical point is 0.45 g cm^{-3} . However, the transport properties of any supercritical fluid depend strongly on its density, which in turn is sensitive to the pressure and temperature. For instance, densities may be adjusted from a gas-like 0.1 g cm^{-3} to a liquid-like 1.2 g cm^{-3} . A useful rule of thumb is that the solubility of a solute is an exponential function of the density of the supercritical fluid, so small increases in pressure, particularly close to the critical point, can have very large effects on solubility.

A great advantage of scCO_2 is that there are no noxious residues once the solvent has been allowed to evaporate; so, coupled with its low critical temperature, scCO_2 is ideally suited to food processing and the production of pharmaceuticals. It is used, for instance, to remove caffeine from coffee. The supercritical fluid is also increasingly being used for dry cleaning, which avoids the use of carcinogenic and environmentally deleterious chlorinated hydrocarbons.

Supercritical CO_2 has been used since the 1960s as a mobile phase in *supercritical fluid chromatography* (SFC), but it fell out of favour when the more convenient technique of high-performance liquid chromatography (HPLC) was introduced. However, interest in SFC has returned, and there are separations possible in SFC that cannot easily be achieved by HPLC, such as the separation of lipids and of phospholipids. Samples as small as

1 pg can be analysed. The essential advantage of SFC is that diffusion coefficients in supercritical fluids are an order of magnitude greater than in liquids, so there is less resistance to the transfer of solutes through the column, with the result that separations may be effected rapidly or with high resolution.

The principal problem with scCO_2 is that the fluid is not a very good solvent and surfactants are needed to induce many potentially interesting solutes to dissolve. Indeed, scCO_2 -based dry cleaning depends on the availability of cheap surfactants, so too does the use of scCO_2 as a solvent for homogeneous catalysts, such as metal complexes. There appear to be two principal approaches to solving the solubilizing problem. One solution is to use fluorinated and siloxane-based polymeric stabilizers, which allow polymerization reactions to proceed in scCO_2 . The disadvantage of these stabilizers for commercial use is their great expense. An alternative and much cheaper approach is poly(ether-carbonate) copolymers. The copolymers can be made more soluble in scCO_2 by adjusting the ratio of ether and carbonate groups.

The critical temperature of water is $374\text{ }^\circ\text{C}$ (647 K) and its pressure is 218 atm (221 MPa). The conditions for using scH_2O are therefore much more demanding than for scCO_2 and the properties of the fluid are highly sensitive to pressure. Thus, as the density of scH_2O decreases, the characteristics of a solution change from those of an aqueous solution through those of a non-aqueous solution and eventually to those of a gaseous solution. One consequence is that reaction mechanisms may change from ionic to radical.