IMPACT 6 …ON TECHNOLOGY: Supercritical fluids

Supercritical carbon dioxide, $scCO_2$, is at the centre of attention for an increasing number of solvent-based processes. The critical temperature of CO_2, 304.2 K (31.0 °C) and its critical pressure, 72.9 atm, are readily accessible, CO_2 is cheap, and it can readily be recycled. The density of $scCO_2$ at its critical point is $0.45\,g\,cm^{-3}$. However, the transport properties of any supercritical fluid (its diffusion behaviour, viscosity, and thermal conductivity) depend strongly on its density, which in turn is sensitive to the pressure and temperature. For instance, mass 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 mass density of the supercritical fluid, so small increases in pressure, particularly close to the critical point, can have very large effects on solubility. Because the relative permittivity (dielectric constant) of a supercritical fluid is highly sensitive to the pressure and temperature, it is possible to run a reaction in polar and nonpolar conditions without changing the solvent, so solvent effects can be studied.

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 or fats from milk. The supercritical fluid is also increasingly being used for dry cleaning, which avoids the use of carcinogenic and environmentally damaging 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. As a result, there is less resistance to the transfer of solutes through the column and separations may be effected rapidly or with high resolution.

The principal problem with $scCO_2$ is that it is not a very good solvent and surfactants (detergent-like molecules) 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 d-metal complexes. There appear to be two principal approaches to solving this problem with solubility. One option 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 °C and its critical pressure is 218 atm. 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 those involving ions to those involving radicals.