

extends to high temperatures and intersects the C_1C_2 critical curve at 'critical end points'. The silica-water system is an example for this behaviour²³.

Two fluid components which are not too different, as for example ethane and hexane, have a normal critical curve as in the upper left diagram of

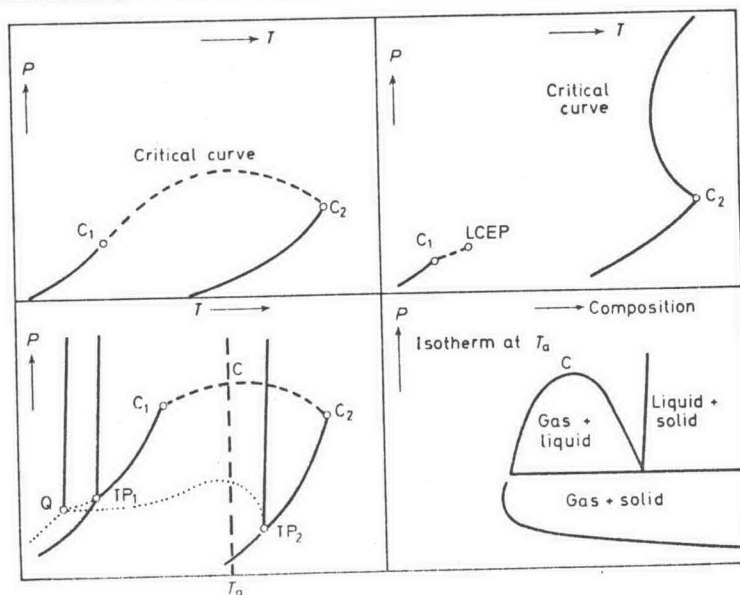


Figure 11. Critical curves of two-component systems.

Figure 11. If there is a greater difference in size, polarity, etc., the critical curve may also be interrupted at a lower critical end point (LCEP) with an upper branch as shown in the upper right diagram of Figure 11. This behaviour can be interpreted as an interference between a liquid-liquid miscibility range with the liquid-gas critical curve²⁴. If this upper branch of the critical curve has a minimum temperature as in the diagram then the behaviour described by the critical curve at pressures higher than the pressure of this minimum temperature is sometimes called 'gas-gas-immiscibility'. It has been predicted by van der Waals and was demonstrated experimentally first by Krichevskii^{25,26} with nitrogen and ammonia in 1940. Since then, other examples have been found^{24,26} and discussed²⁷. Among these are carbon dioxide-water²⁸, benzene-water²⁹, ethane-water³⁰ and argon-water³¹. The upper branches of the critical curves of these systems are shown in Figure 12.

They begin at the critical point of water and have a minimum temperature with the exception of the water-argon system. The range of complete miscibility is always on the right side, that is on the high temperature side, of these curves. One can have homogeneous mixtures of liquid-like densities at all

AQUEOUS SOLUTIONS AT HIGH PRESSURES AND TEMPERATURES

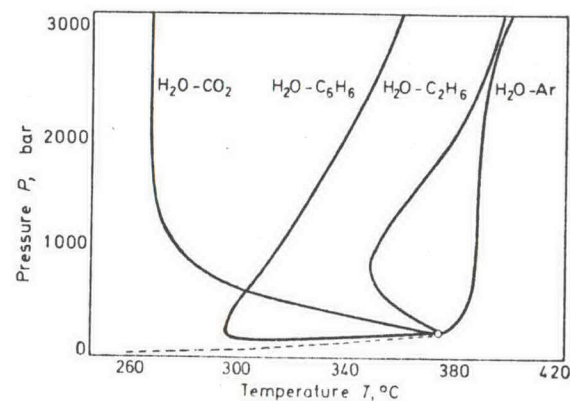


Figure 12. Critical curves of several binary aqueous systems.

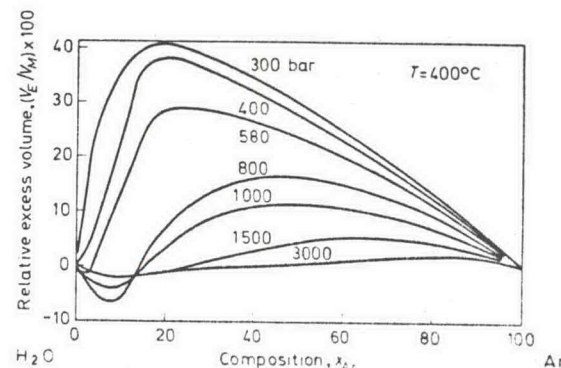


Figure 13. Relative excess volume V_E/V_M of supercritical water-argon mixtures at pressures between 300 and 3000 bar.

concentrations if the pressure can be raised to the order of about 2 kb at temperatures higher than the critical temperatures at these pressures. Such dense gaseous mixtures may find practical applications.

The water-argon system may also be representative for combinations of other small inert molecules with water. Figure 13 gives an indication of the amount and character of deviation from ideal behaviour of the supercritical argon-water mixtures. The molar excess volume V_E divided by the molar volume of the mixture at the respective conditions V_M has been plotted for 400°C as a function of composition³¹. While the excess volume at relatively low pressure is large and positive, it reduces to a few per cent at 3 kb. The S-shaped behaviour with negative excess volumes at high water concentrations can be qualitatively explained with relatively simple models, for