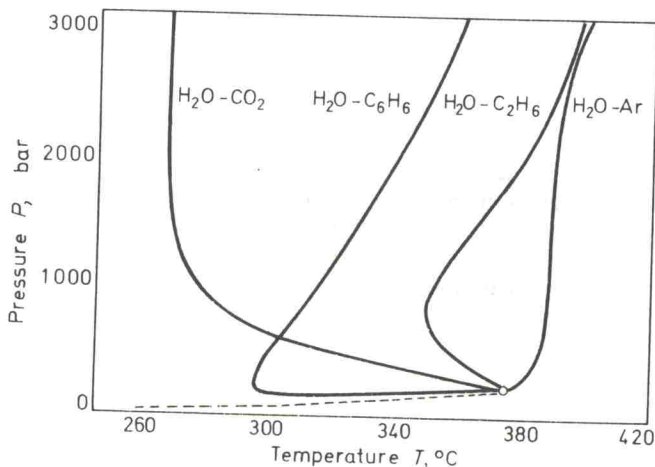Figure 12. Critical curves of several binary aqueous systems.
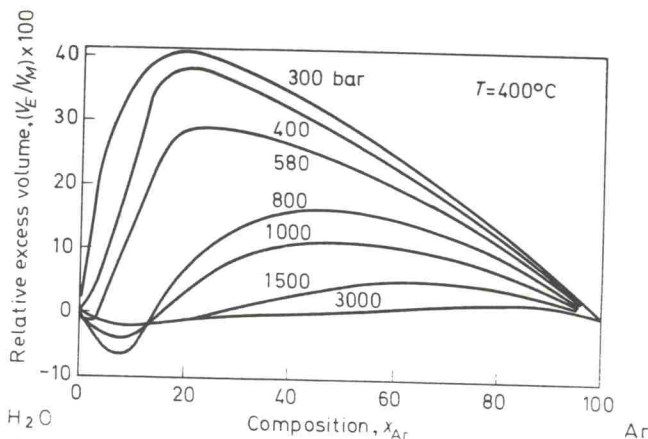

Figure 13. Relative excess volume V_E/V_M of supercritical water–argon mixtures at pressures between 300 and 3000 bar.

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 composition[31]. 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

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example spheres with 'square well' interaction potentials combined with small 'hard sphere' particles[32].

V. CONDUCTANCE OF ELECTROLYTE SOLUTIONS

From the knowledge of the dielectric constant it can be expected that dense water at high temperatures will remain a good electrolytic solvent. *Figure 14* demonstrates the effect of increased pressure on the conductance of three types of electrolytes at relatively low temperatures. Detailed discussions of these phenomena have been given elsewhere [33, 34]. In *Figure 14* the
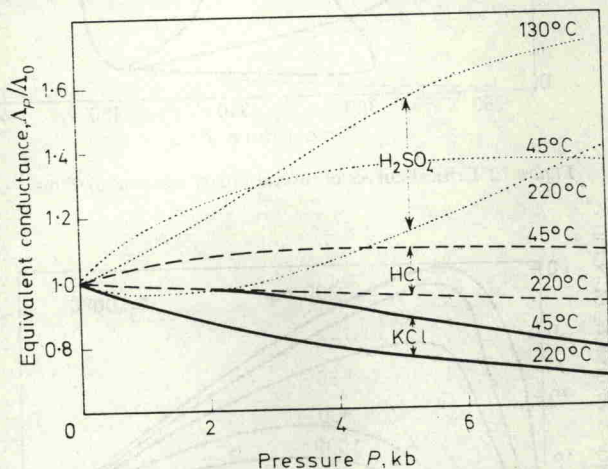

Figure 14. Pressure dependence of the equivalent conductance Λ of 0·001 M KCl, HCl and H_2SO_4 in water.

relative changes of the equivalent conductances with pressure are shown. For a normal strong electrolyte such as potassium chloride, pressure increase causes a decrease in conductance[35]; this is in qualitative accordance with Walden's rule, which predicts that the equivalent conductance should be proportional to the inverse of solvent viscosity. The conductance decrease of potassium chloride with pressure is smaller, however, than estimated by this rule, since the effective ionic radii are not independent of pressure. For hydrogen chloride the conductance decreases only very slightly at 220°C and increases at 45°C. This is due to the enhancement of the abnormal mobility of protons in associated water[36]. A similar effect would be observable for hydroxyl ions. The pressure dependence of the conductance of sulphuric acid, shown in *Figure 14*, can be understood as the result of the combined pressure dependences of water viscosity, abnormal proton mobility and dissociation of HSO_4^+-ions into protons and sulphate ions. The equilibrium constant for this dissociation has a negative temperature dependence and a positive pressure dependence[36]. At 100°C for example, the constant rises from 0.8×10^{-3} to 48×10^{-3} mole/l. if the pressure is increased to 8 kb. The increase of electrolytic dissociation with pressure is mainly due to the