

Walrafen in his paper. If the Raman spectra of the OD stretching vibration of HDO in H₂O are shown again in Fig. 7, it is mainly to draw attention to the I⁺ curves in the lower part, which appear to exhibit an isosbestic point at 2575 cm⁻¹. This may support the assumption of two distinguishable hydrogen-bonded and non-hydrogen-bonded states of the OD groups.

Figure 8 demonstrates the influence of the addition of increasing amounts of an electrolyte on the maximum frequency of the OD vibration. KI was used mainly because of the large ion sizes and good solubility. Curve a, derived from Fig. 7, gives the values for pure HDO-H₂O mixtures. At low temperatures, a pronounced increase of the maximum frequency with KI concentration is observed, while at 400°C the salt acts in the opposite direction and reduces the maximum frequency, although to a lesser extent. Around 180°C there is a crossover region. The effect at lower temperatures has been observed and discussed earlier. The present results at 25°C are in agreement with those of previous authors.⁽²⁰⁾ A quantitative discussion of the results of Fig. 8 may not be justified without a decomposition of the asymmetric bands into components and a proper estimate of the specific interaction between iodide ions and water molecules. The "structure-breaking" effect of the electrolyte up to about 200°C is very obvious, however. At 400°C, where pure water does not have much structure any more, a certain "structure-making" influence of the ions seems to predominate, perhaps by ion hydration.

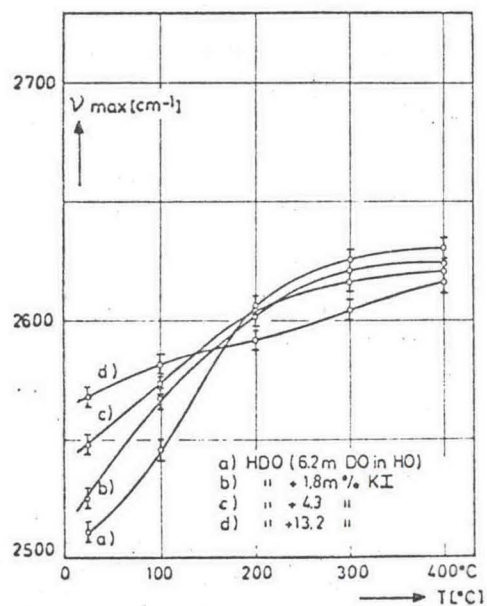


Fig. 8. Maximum frequency of Raman OD vibration band of HDO diluted in H₂O with increasing concentrations of added KI. Total solution density constant at 1.0 g-cm³.

Raman spectroscopy can also be used to examine existence ranges of dissolved metal complexes, which cannot be very well investigated in the visible or ultraviolet regions.⁽²¹⁾ This applies particularly to corrosive high-temperature, high-pressure solutions. Many of these are of interest for power-plant corrosion problems and as hydrothermal fluids in geochemistry. Lead chloride and zinc chloride solutions, for example, have considerable geochemical interest, and ZnCl₂ has been extensively investigated as fused salt and in low-temperature, concentrated aqueous solutions. It is possible to extend laser Raman investigations of concentrated aqueous ZnCl₂ solutions to 400°C.

Figure 9 gives several first results obtained at a constant pressure of 2.5 kbar with a high-pressure Raman cell equipped with sapphire windows and irradiated with an argon-ion laser beam. Observation was vertical to the beam direction. The two vertical bars indicate major bands found with molten ZnCl₂.⁽²²⁾ For the melt, the band at 305 cm⁻¹ is ascribed to the monomer ZnCl₂, and the band at 266 cm⁻¹ to a complex ZnCl₄²⁻. From Fig. 9 it appears as if in the concentrated aqueous solutions with increasing temperature a shift occurs from mainly fourfold-coordinated ionic complexes towards a predominance of lower-coordinated molecular monomers.

5. SOLUTION SPECTRA IN THE VISIBLE AND NEAR ULTRAVIOLET

In the zinc chloride solutions, an increase of temperature seems to favor the less highly coordinated complexes. Similar behavior has been observed with several other complex-forming metals at high temperatures by means of absorption spectra in the visible and ultraviolet regions. Complexes of

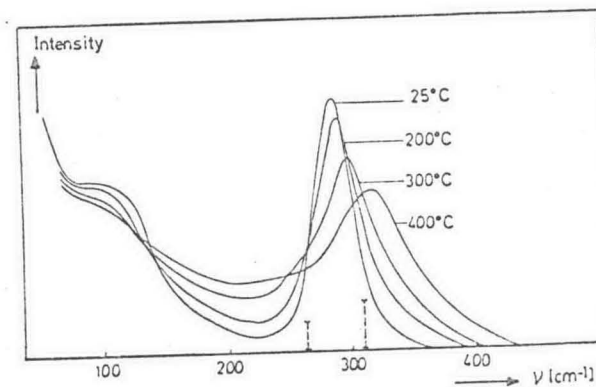


Fig. 9. Raman bands of aqueous ZnCl₂ solutions (7 m) at 2.5 kbar between 25° and 400°C. ----- Fused ZnCl₂.

bivalent cobalt, nickel, and copper are examples which to some extent can be used as a kind of probe to obtain additional information on water properties in solutions at unusual conditions.

One example, the absorption of NiCl_2 in a concentrated aqueous NaCl solution, is shown in Fig. 10.⁽²³⁾ The curve for 25°C corresponds to the normal solutions of light green color with two absorption bands caused by two electron transitions of octahedral hexaquo complexes. The pressure of 500 bars at room temperature has little influence on the spectrum. Temperature increase to 300°C at the same pressure produces blue solutions with a strong, broad band at 680 nm. It is caused by a combination of bands from octahedral and tetrahedral complexes. The tetrahedral complexes appear to predominate. Additional spectra indicate that this kind of complex becomes the only stable form in 10 *m* lithium chloride solutions at this temperature and at pressures between 150 and 300 bars. A detailed analysis of the magnitude of the extinction coefficients suggests that trichloromonoquo and dichlorodiaquo tetrahedral complexes are the most abundant types. It can be shown from Fig. 10 that pressures of several kbar increase the range of stability of higher-coordinated aquo complexes to temperatures which may even be above the critical temperature of pure water.

Recently, absorption spectra of copper solutions were also obtained to 400°C and 2 kbar.⁽²⁴⁾ A special high-pressure optical cell had to be designed in which the solution samples were only in contact with sapphire and Teflon at high temperatures. Increasing amounts of LiCl (up to 14 *m*) have been added.

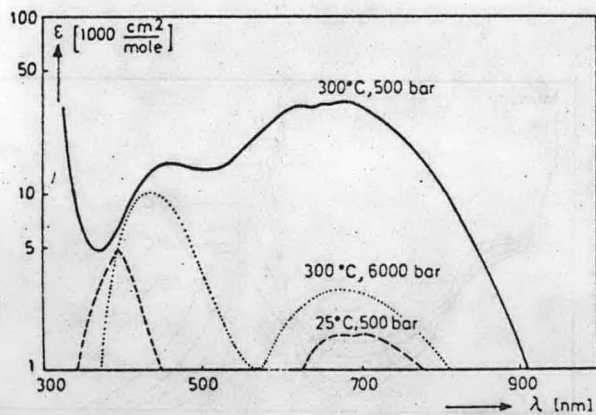


Fig. 10. Absorption spectrum of NiCl_2 (0.025 *m*) in aqueous NaCl solution (4.0 *m*) at high temperature and pressure.

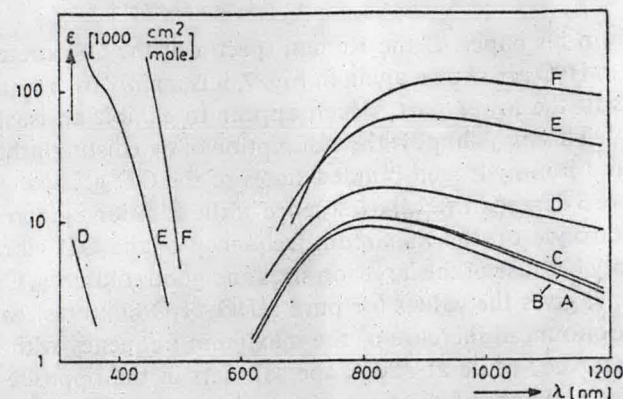


Fig. 11. Absorption spectra of CuCl_2 and $\text{Cu}(\text{ClO}_4)_2$ in water and aqueous LiCl solutions of various concentrations at 25°C and 2 kbar. (A) $\text{Cu}(\text{ClO}_4)_2$, 0.050 *m*; (B) CuCl_2 , 0.0499 *m*; (C) CuCl_2 , 0.0124 *m* + LiCl , 0.10 *m*; (D) CuCl_2 , 0.0100 *m* + LiCl , 1.0 *m*; (E) CuCl_2 , 0.0095 *m* + LiCl , 5 *m*; (F) CuCl_2 , 0.0097 *m* + LiCl , 10 *m*.

In Figs. 11 and 12 a series of absorption curves at 2 kbar is given for 25° and 350°C. Absorption changes caused by pressure variations between 500 and 2000 bars did not exceed the range of experimental uncertainty of the data. Higher pressures could not be applied for technical reasons. Curves A give the absorption of dilute copper perchlorate solutions for comparison.

Curves B to F belong to copper(II) chloride solutions with increasing amounts of lithium chloride. Below 600 nm, portions of the "charge-transfer bands" are visible. At higher wavelengths, one has the "d-d bands," caused by transitions between d-levels, which are mainly considered here.

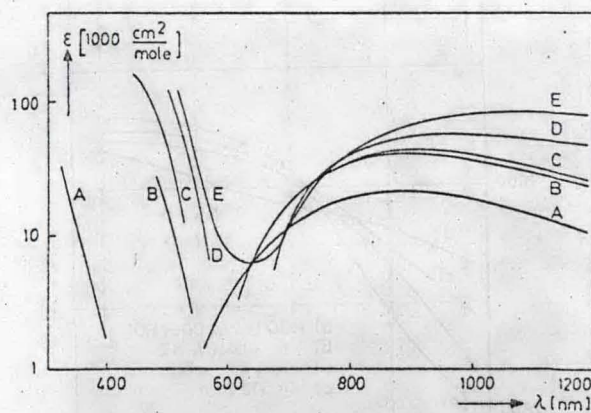


Fig. 12. Absorption spectra of CuCl_2 and $\text{Cu}(\text{ClO}_4)_2$ in water and aqueous LiCl solutions of various concentrations at 350°C and 2 kbar. (A) $\text{Cu}(\text{ClO}_4)_2$, 0.050 *m*; (B) CuCl_2 , 0.0499 *m*; (C) CuCl_2 , 0.0124 *m* + LiCl , 0.10 *m*; (D) CuCl_2 , 0.0100 *m* + LiCl , 1.0 *m*; (E) CuCl_2 , 0.0095 *m* + LiCl , 5.0 *m*.