

Concentrated Electrolyte Solutions at High Temperatures and Pressures¹

E. U. Franck²

Received February 7, 1973

A survey is given of recent experimental results obtained from high-temperature, high-pressure investigations with water, aqueous solutions, and ionic fluids. Data on the static dielectric constant of water to 550°C and 5 kbar are given and discussed with respect to their relation to water structure. Infrared and Raman spectra of HDO in pure water have been obtained to 400°C and 4 kbar, which give information on hydrogen bonding. Xe-H₂O and CO₂-H₂O mixtures were investigated in the infrared. Ni(II) and Cu(II) complexes were investigated by absorption spectroscopy in aqueous solutions of high chloride content to 350°C and 2-6 kbar. The gas-liquid critical point of ammonium chloride was found at 880°C and 1635 bars. This fluid appears to be predominantly ionic even in the critical region. The possibility of converting pure polar fluids such as ammonia and water into concentrated ionic solutions by self-ionization at very high pressures is mentioned.

KEY WORDS: High temperature; high pressure; static dielectric constant; infrared and Raman spectra; critical point; water; aqueous solutions; ammonia; HDO; Xe; CO₂; NH₄Cl; Ni(II) complexes; Cu(II) complexes.

1. INTRODUCTION

The term "concentrated electrolyte solutions" will here be used for fluid mixtures with ion concentrations comparable to the concentrations of the nonionic components. This is an intermediate range of ion concentrations between those of the "normal," relatively dilute electrolyte solutions and the highly or completely ionized fused salts. These concentrated electrolyte solutions are not yet very thoroughly investigated, although their peculiar

¹ This paper was presented at the symposium, "The Physical Chemistry of Aqueous Systems," held at the University of Pittsburgh, Pittsburgh, Pennsylvania, June 12-14, 1972, in honor of the 70th birthday of Professor H. S. Frank.

² Institute of Physical Chemistry and Electrochemistry, University of Karlsruhe, Germany.

APD 11 1974

properties are of considerable fundamental and practical interest. Investigations in this range often require, however, application of elevated temperatures and pressures in order to obtain the necessary solubilities or sufficient ranges of stability of certain complex ionic species. Thus knowledge of relevant properties of dense polar solvents at high temperatures is desirable for the discussion of the concentrated electrolytic solutions.

Recent investigations have provided new information of this kind which will be presented below. The dielectric constant has been measured and examined in dense supercritical water and hydrogen chloride. The OH stretching vibration was investigated as an indicator for water association in pressurized pure water and concentrated solutions by infrared and Raman techniques. The stability of heavy metal complexes, particularly of copper complexes, was investigated spectroscopically in solutions to 350°C. The ionization of pure liquid ammonium chloride to the critical point and of very highly pressurized fluid water and ammonia was studied by conductivity measurements.

Figure 1 gives a temperature-density diagram of water which extends to 1000°C and 1.6 g·cm⁻³. The critical point CP (374°C, 221 bars) and the triple point TP are indicated on the gas-liquid coexistence curve in the lower left part. The points of the broken line extending to the right from TP denote the transitions between the different high-pressure modifications of ice. To about 10 kbar the isobars are based on static experiments.^(1, 2) At pressures above 25 kbar, water densities have been derived from shock-wave experiments.⁽³⁾

In order to evaluate the properties of water at high pressures and temperatures as an electrolytic solvent, knowledge of the dielectric constant, infrared and Raman spectra, and the viscosity are particularly useful. The cross-

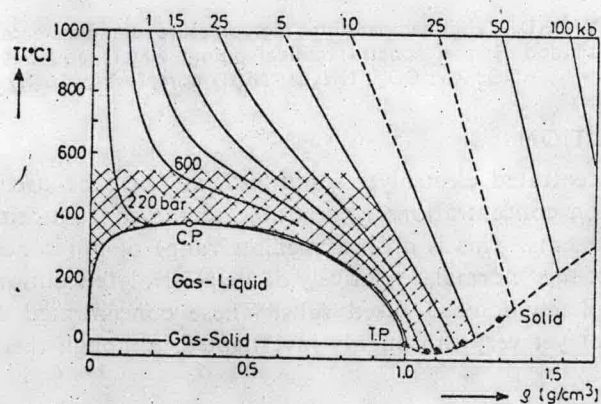


Fig. 1. Temperature-density diagram of water. — Isobars measured; ----- isobars interpolated.

hatched area in Fig. 1 approximately indicates the region where these phenomena have been investigated experimentally in recent years. Dielectric constant and spectra will be discussed below. The viscosity has been measured to 500°C and 3.5 kbar.⁽⁴⁾ At 500°C and 0.2 and 0.8 g·cm⁻³, respectively, the viscosity has been found to be 3.8×10^{-4} and 10.5×10^{-4} P. This means that the viscosity at these conditions is lower than that of liquid water at room temperature by a factor of 10 or 20. Diffusion coefficients and ion mobilities are correspondingly high. Viscosity and other physical properties of water at high pressures and high temperatures are reviewed elsewhere.⁽⁵⁾

2. DIELECTRIC CONSTANT

The static dielectric constant of water is to a large extent determined by the peculiar structural properties caused by hydrogen bonds. Thus this quantity is not only interesting as such but also as a means of obtaining structural information. Earlier measurements of the dielectric constant to 400°C and 2 kbar^(5, 6, 7) were made and discussed. Recent experiments were performed to 550°C and 5 kbar.⁽⁸⁾ The capacity of a condenser of gold-palladium mounted inside an autoclave was determined at frequencies between 0.1 and 1 MHz. The geometry of the condenser could be changed at high temperatures and pressures. Figure 2 gives a compilation of results as curves of dielectric constants superimposed on isobars of a temperature-density diagram. Within a wide range of supercritical temperatures and densities, the constant has values between 5 and 25. This corresponds to dielectric properties of certain polar organic liquids at normal conditions. To calculate the dielectric constant

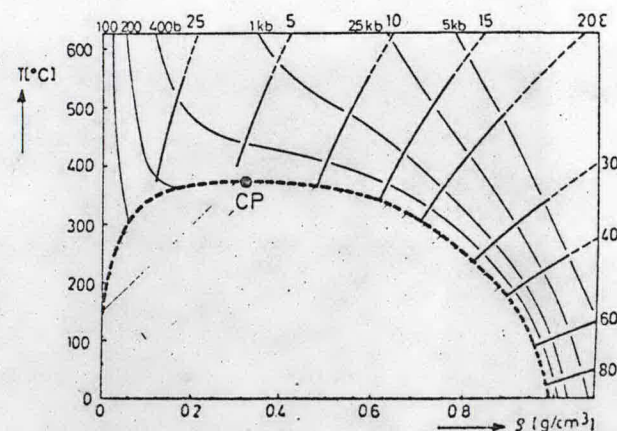


Fig. 2. Static dielectric constant ϵ of water as a function of temperature and density ρ . ----- Measured values, ----- calculated values; ----- isobars.