

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.

ABD 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-

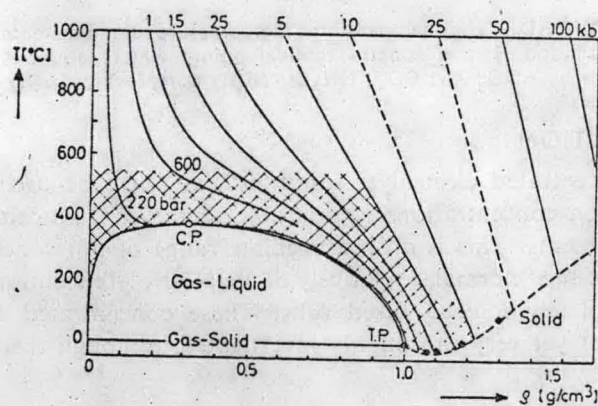


Fig. 1. Temperature-density diagram of water. — Isobars measured; ----- isobars interpolated.

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

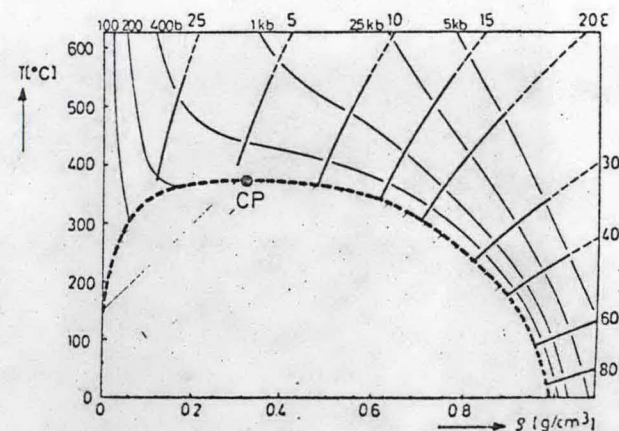


Fig. 2. Static dielectric constant ϵ of water as a function of temperature and density ρ . ----- Measured values; ----- calculated values; ----- isobars.

ϵ of liquid water at moderate temperatures, Kirkwood⁽⁹⁾ used the equation

$$(\epsilon - 1)(2\epsilon + 1)/9\epsilon = (4\pi\rho/3)\alpha + (4\pi\rho\mu^2/9kT)g_K \quad (1)$$

Here ρ is the number of particles per unit volume, α the isotropic polarizability, and μ the strength of the molecular dipoles within the dielectric environment. The quantity g_K is the *Kirkwood correlation factor*, introduced to take into account short-range ordering between dipoles. Extensive discussions of Eq. (1) and of methods of estimating the dipole strength within the dielectric and of calculating g_K in liquid water are given elsewhere.^(9,10)

If neighboring dipoles are uncorrelated, one should find $g_K = 1$. At 0°C in liquid water g_K is about 2.9. The evaluation of g_K from the experimental ϵ data of Fig. 2 shows that g_K decreases with increasing temperature and decreasing water density, as would be expected.^(8,11) It appears, however, that even at the critical density and at supercritical temperatures of 400° and 500°C, g_K is still about 1.6, indicating a considerable degree of dipole correlation.

Very recent experimental results obtained for the dielectric constant of supercritical dense hydrogen chloride with a similar technique⁽¹²⁾ showed that, at corresponding supercritical conditions, g_K is only about 1.05 for this

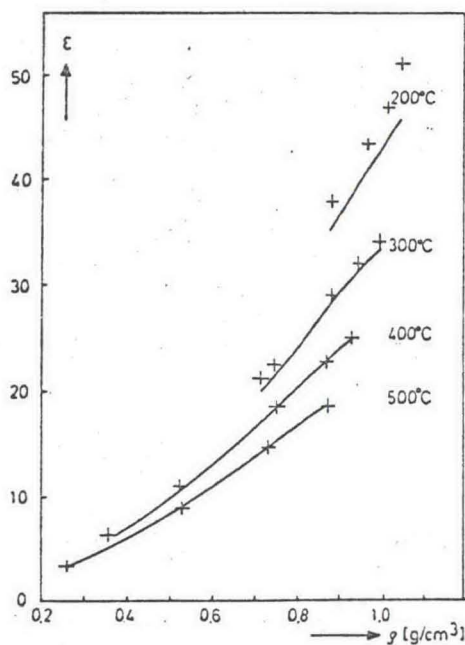


Fig. 3. Static dielectric constant of water ϵ as a function of density and temperature. + Experimental values; — calculated.

fluid. One might conclude that the relatively high Kirkwood factors indicate a considerable degree of association by hydrogen bonding in dense supercritical water. Caution is necessary, however, since it has been demonstrated that the experimental ϵ data of water between 200° and 500°C and 0.1 and 1.0 g-cm⁻³ can be calculated rather well without using the concept of hydrogen bonding.^(13,14) No adjustable parameters had to be used besides the dipole moment, polarizability, and diameter of water molecules. For such calculations, the general expressions for the dielectric constant of a fluid of hard cores with embedded point dipoles presented by Wertheim⁽¹⁵⁾ have been used. This is shown in Fig. 3.

3. INFRARED SPECTRA

More detailed information about the association of water by hydrogen bonding can be obtained from infrared and Raman spectra. Particularly well suited for this purpose is the study of the absorption of the OD stretching vibration around 2500 cm⁻¹ of HDO diluted in H₂O because of the absence of interference of other vibrations in this frequency range. Figure 4 gives several absorption curves for this vibration of HDO in ordinary water at a constant density of about 1 g-cm⁻³ from 30° to 400°C and at 400°C down to 0.01 g-cm⁻³.⁽¹⁶⁾ The frequency of the maximum shifts from 2507 to 2720 cm⁻¹, the value for the Q Branch of the OD vibration in dilute HDO gas. This shift of the maximum frequency, as well as the decrease of intensity, has been considered as an indication of decreasing association by hydrogen bonds.

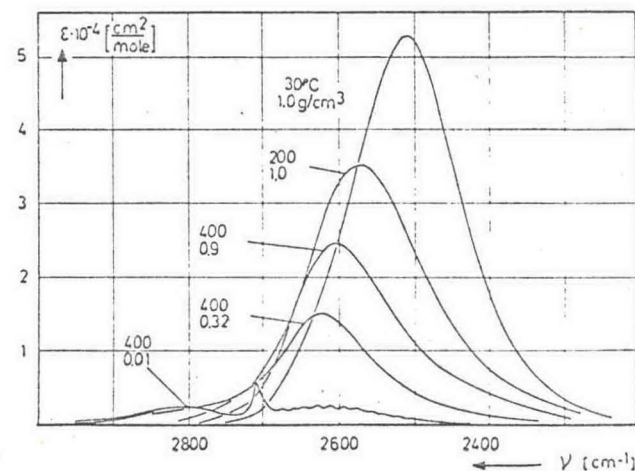


Fig. 4. Infrared OD vibration bands of 9.5 mole % HDO in H₂O at different temperatures and densities.

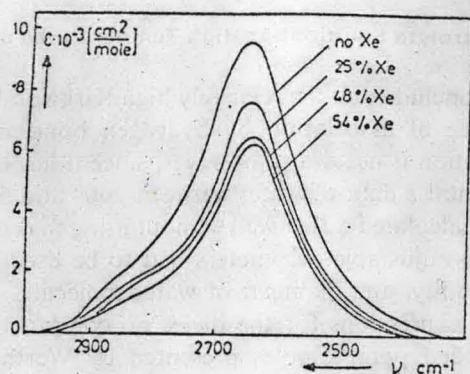


Fig. 5. Infrared OD vibration bands of HDO diluted in H_2O as a function of increasing amounts of added xenon. The temperature is $400^\circ C$, and the total water density for all curves is 0.17 g-cm^{-3} .

It is interesting to investigate the question as to what extent this OD bond at dense supercritical conditions will be affected by the addition of very high concentrations on nonionic but highly polarizable second components to the fluid phase. Experiments of this kind have been made recently with Xe-HDO- H_2O and CO_2 -HDO- H_2O mixtures.⁽¹⁷⁾ Xe and CO_2 have been chosen because both particles have similar size, although for CO_2 , in contrast to Xe, a specific interaction with water molecules even at $400^\circ C$ could be expected. Both Xe and CO_2 are completely miscible with water at $400^\circ C$. Figures 5 and 6 give selected absorption curves at $400^\circ C$, which should be compared with the relevant curves of Fig. 4.

In Fig. 5 the absorption of HDO in H_2O at a total water density of 0.17 g-cm^{-3} is shown. Three other curves demonstrate the influence of added increasing amounts of xenon while the water density remains constant. Two of these curves belong to mixtures with almost equal numbers of Xe and H_2O .

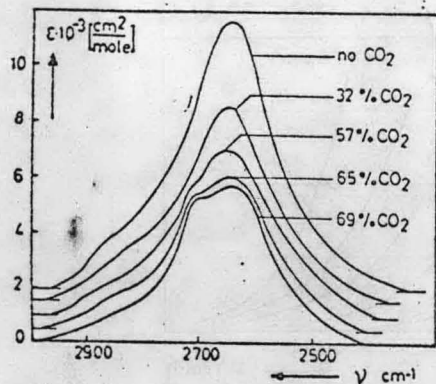


Fig. 6. Infrared OD absorption bands of HDO diluted in H_2O as a function of increasing amounts of added CO_2 . The temperature is $400^\circ C$, and the total water density for all curves is 0.17 g-cm^{-3} .

particles. Apart from a certain reduction of intensity, the effect of the xenon on the character of the band is insignificant. The bands of Fig. 6, obtained in analogous experiments with CO_2 , are different. A shoulder at 2700 cm^{-1} appears at 57 mole % CO_2 and develops into a separate band at 69 mole %. This band may be produced by deuterated carbonic acid molecules. PVT data of CO_2 - H_2O mixtures at high pressures and supercritical temperature do not exclude formation of such carbonic acid molecules.⁽¹⁸⁾ This assignment is not yet conclusive, however. Investigation of the absorption in the region of C-O vibrations (1400 cm^{-1}) would be desirable, but the sapphire windows of the high-pressure infrared cell are opaque at such wavelengths. Perhaps Raman measurements would be possible.

It would be interesting to observe the hydrogen-oxygen stretching vibration in a binary system of water and a simple salt from pure water through the region of concentrated solutions to the pure fused salt. Most simple salts have melting points that are too high. Sodium hydroxide, however, melts at $318^\circ C$. Measurements of the absorption of the stretching vibration of normal water in liquid NaOH- H_2O mixtures have been made at present at Karlsruhe to 2 kbar and $350^\circ C$, where the two compounds are completely miscible. It appears as if even at this temperature the whole range of compositions from pure H_2O to pure NaOH can be investigated with sapphire windows, although with some difficulty.

4. RAMAN SPECTROSCOPY

The Raman spectra of pure water at high pressure,⁽¹⁹⁾ and the conclusions to be drawn from these, have been thoroughly discussed already by G. E.

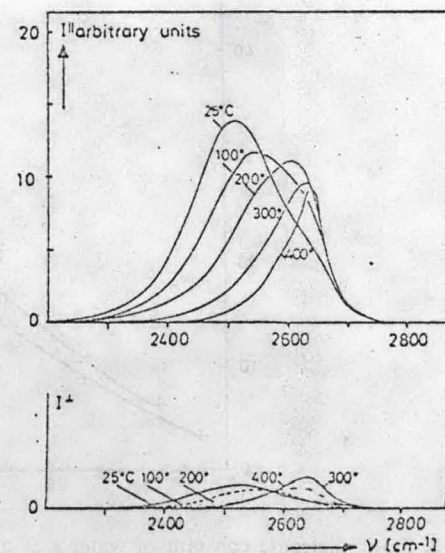


Fig. 7. Raman band of the OD vibration of HDO diluted in H_2O at a constant water density of 1.0 g-cm^{-3} from 25° to $400^\circ C$. Upper part: I^i , parallel polarization relative to laser beam. Lower part: I^4 , vertical polarization.

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.

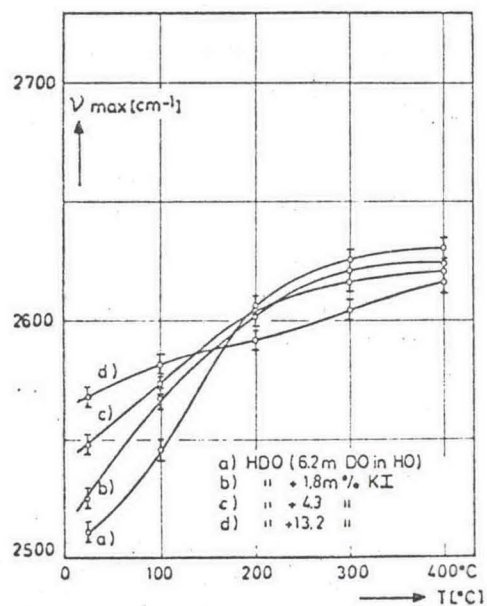


Fig. 8. Maximum frequency of Raman OD vibration band of HDO diluted in H₂O with increasing concentrations of added KI. Total solution density constant at 1.0 g-cm³.

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

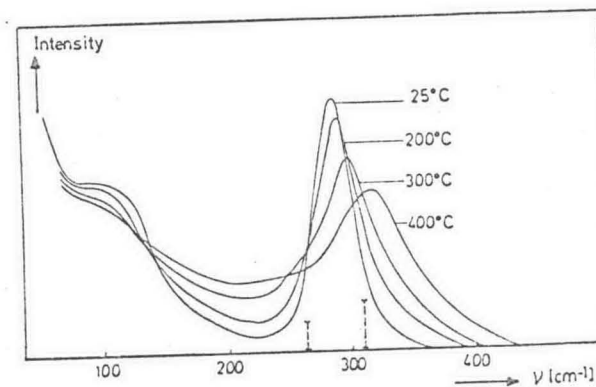


Fig. 9. Raman bands of aqueous ZnCl₂ solutions (7 m) at 2.5 kbar between 25° and 400°C. ----- Fused ZnCl₂.

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.

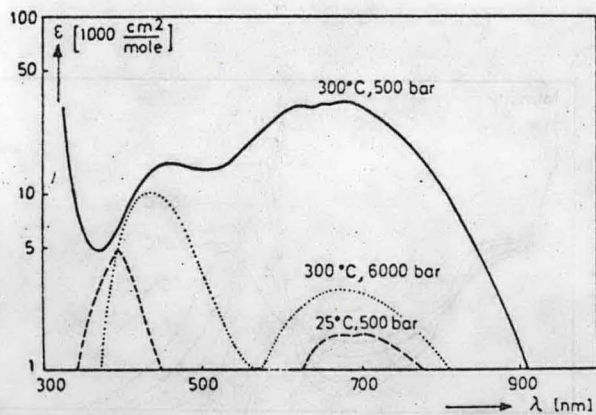


Fig. 10. Absorption spectrum of NiCl_2 (0.025 *m*) in aqueous NaCl solution (4.0 *m*) at high temperature and pressure.

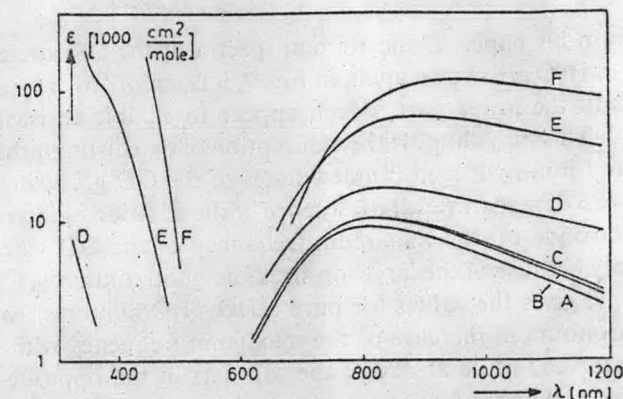


Fig. 11. Absorption spectra of CuCl_2 and $\text{Cu}(\text{ClO}_4)_2$ in water and aqueous LiCl solutions of various concentrations at 25°C and 2 kbar. (A) $\text{Cu}(\text{ClO}_4)_2$, 0.050 *m*; (B) CuCl_2 , 0.0499 *m*; (C) CuCl_2 , 0.0124 *m* + LiCl , 0.10 *m*; (D) CuCl_2 , 0.0100 *m* + LiCl , 1.0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

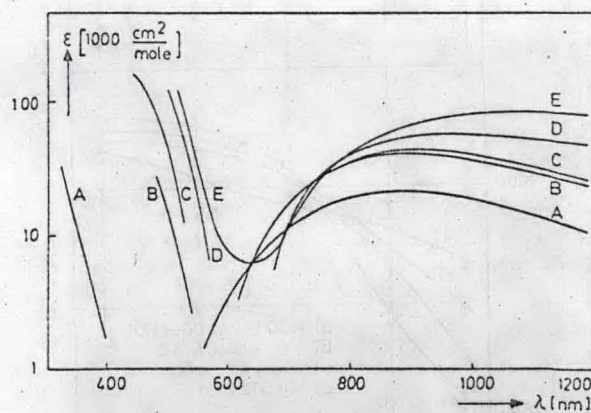
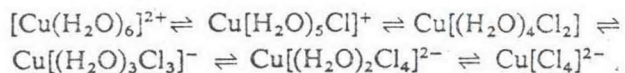


Fig. 12. Absorption spectra of CuCl_2 and $\text{Cu}(\text{ClO}_4)_2$ in water and aqueous LiCl solutions of various concentrations at 350°C and 2 kbar. (A) $\text{Cu}(\text{ClO}_4)_2$, 0.050 *m*; (B) CuCl_2 , 0.0499 *m*; (C) CuCl_2 , 0.0124 *m* + LiCl , 0.10 *m*; (D) CuCl_2 , 0.0100 *m* + LiCl , 1.0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

Comparison of the 25°C curves of Fig. 11 with the results and discussions in the literature shows that curves A, B, and C for dilute solutions indicate a predominance of hexaquo complexes. In the yellow solutions F which contain 10 *m* LiCl the tetrahedral complex $(\text{CuCl}_4)^{2-}$ clearly prevails even at 25°C. Temperature increase to 350°C at 2 kbar (Fig. 12) causes enhancement of intensity and red shift, particularly for the solutions with lower chloride content. This is attributable to stronger distortion of the octahedra and increased copper-ligand distances as well as to the exchange of water ligands by chloride. The appearance of the spectra suggests a successive exchange of H_2O by Cl^- with rising temperature and Cl^- concentration, although no band can be detected, which is characteristic for one particular type of aquo-chloro complex. A more detailed discussion is given elsewhere.⁽²⁴⁾ Formally, the sequence of transitions from hexaquo complexes to tetrachloro complexes with increasing temperature and chloride content can be described by



6. AMMONIUM CHLORIDE

Although some of the solutions discussed so far, with electrolyte molalities of 10 or more, have very high ion concentrations, they are still quite different from fused salts where there may be only ions in the fluid. One might ask whether it is possible to study pure ionic fluids at temperatures where the intermolecular distance and possibly the degree of ionization can be changed continuously over wide ranges by variation of pressure. This would be of considerable basic thermodynamic interest because of the possibility of investigating compressible fluids with coulombic interactions. Such dense gaseous ionic fluids may also have some geochemical and technical interest.

It is difficult, though, to find suitable examples. Fused alkali halides have critical temperatures at 2500°C or higher, which at present excludes static high-pressure experiments. At lower temperatures, only small expansions are possible. Salts with lower critical temperatures, BiCl_3 for example, are only ionized to a small extent at critical conditions.^(25, 26) Stable polar fluids such as water and ammonia need very high pressures and temperatures to become higher ionized (see Sec. 7).

From recent experiments, it appears that certain ammonium halides may be examples for fluids which are highly ionized at not-so-high critical temperatures. This is suggested by results obtained with ammonium chloride.⁽²⁷⁾ NH_4Cl has a solid-liquid-gas triple point at 520°C and 48 bar. Using several types of internally heated corrosion-resistant cells, made mainly of sapphire and gold-platinum, it can be shown that NH_4Cl has a single vapor-pressure curve which extends from the triple point to a critical point at

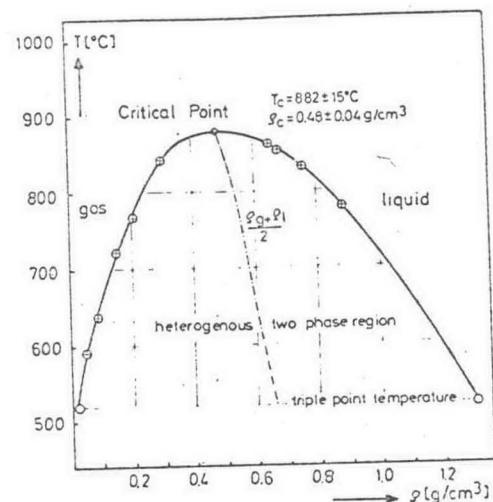


Fig. 13. Gas-liquid coexistence curve of NH_4Cl in a temperature-density diagram.

$882 \pm 15^\circ\text{C}$ and 1635 ± 20 bars. The coexistent gaseous and liquid densities can be measured and are shown in Fig. 13.

At this triple point, the specific conductance of liquid NH_4Cl is $2.07 \text{ ohm}^{-1}\text{-cm}^{-1}$, only 5% lower than that of liquid KCl at the melting point. Liquid NH_4Cl near the triple point is therefore to be considered as an ionic melt. The electrolytic conductance can be measured in the liquid at saturation condition to 850°C —about 32° below the critical temperature.⁽²⁹⁾ Since the liquid at 850°C has expanded already to about twice its molar volume at the triple point, a decrease of ionization and conductance can be expected. Actually, however, the conductance increases, and the ratio of specific conductance over molar volume, the molar conductance Λ at 850°C , is three times higher than Λ_T at the triple point (see Fig. 14). Reasonable

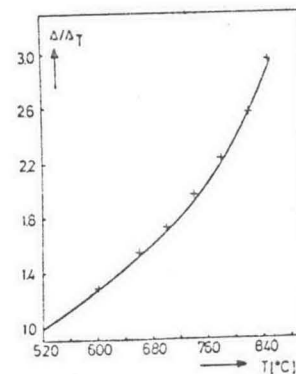


Fig. 14. Relative molar conductivity Λ/Λ_T of liquid NH_4Cl at saturation conditions. Λ_T is the molar conductivity of liquid NH_4Cl at the triple point.

estimates of ion mobilities and utilization of data for fused alkali halides suggest the approximate relation⁽²⁾ for the temperature and density dependence of A for a fully ionized fluid. The quantity E_a is the activation energy for

$$A(T, \rho) = \text{const.} \times e^{-E_a/RT} \rho^{-5.6} \quad (2)$$

ionic conductance at constant density. If $E_a = 3 \text{ kcal-mole}^{-1}$, as for comparable alkali halides, one obtains the curve of Fig. 14. The agreement with the experimental points is good, which would mean that at 850°C liquid NH_4Cl is still an ionic fluid. It is believed that even in the critical region at 882°C the fluid is still predominantly ionized. This may be the first known nonmetallic fluid exhibiting such a behavior. Preliminary investigations with NH_4HF_2 indicate the possibility of similar phenomena.

7. CONCLUSION

It cannot be excluded that pure fluids of small, polar, and stable molecules may become very concentrated electrolyte solutions if self-ionization can be increased by many orders of magnitude. Self-ionization is favored by increasing temperatures and high pressures. From recent static conductance measurements with pure ammonia,⁽²⁹⁾ which were extended to 500°C and 40 kbar, it follows that the ion product at these conditions should be between 10^{-4} and $10^{-3} \text{ mole}^2\text{-liter}^{-2}$. This is still far from a concentrated ionic solution. Similar conductance measurements with water, however, have been made with shock waves and with a static method to 1000°C and more than 100 kbar.^(30, 31) An ion product in the vicinity of $10^{-2} \text{ mole}^2\text{-liter}^{-2}$ for water has been derived from these experiments.

Figure 15, taken from Hamann and Linton,⁽³¹⁾ gives a compilation of ion-product data for pure water as a function of water density obtained from

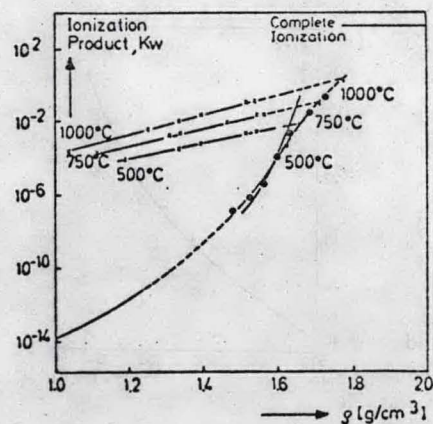


Fig. 15. Ionization product of compressed water as a function of density (after Hamann and Linton⁽³¹⁾). —○—○—○— From shock-wave experiments; ×—×—×—×— from static experiments.

the shock-wave and static measurements. The agreement is good, considering the difficulty of the experiments. The authors have made the well-justified proposition that complete ionization of water at high supercritical temperatures would be achieved if it could be compressed to a density of 1.8 to 2.0 g-cm^{-3} , that is, twice the normal density. This range is indicated in the upper right part of Fig. 15. It is interesting to note that under these conditions the molar volume of $(\text{H}_2\text{O})_2$ would be similar to the molar volume of fused NaOH at normal pressure.

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DISCUSSION

Dr. F. H. Stillinger (*Bell Laboratories, New Jersey*). I am afraid that seeing this $\beta = \frac{1}{2}$ is very disturbing—I am referring to the coexistence curve for