

SPECIAL ASPECTS OF FLUID SOLUTIONS AT HIGH PRESSURES AND SUB- AND SUPERCRITICAL TEMPERATURES

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Abstract - At high temperatures water substance loses its typical aqueous characteristics to a considerable extent and, at sufficiently high density, it becomes an almost "non-aqueous", although highly polar and "water-like" solvent. Selected recent experimental examples are given. PVT-data and transport coefficients are shown and discussed. The dielectric constant of supercritical dense water is compared with analogous data for freons, methanol and other compounds. High pressure miscibility and critical curves of binary aqueous systems with nonpolar partners are discussed. Spectroscopic, particularly Raman measurements were made. Ion formation in pure water and in supercritical dilute and concentrated salt solutions is demonstrated by conductivity. The transition to fused salts is discussed.

INTRODUCTION

In recent years, a considerable number of new and extended experimental methods of investigation have made it possible to include properties of dense fluids at high temperatures into the discussions of the fluid state in general. Quite often, phenomena at supercritical temperatures offer themselves more easily to theoretical interpretation and can improve the understanding of the more complicated behaviour of ordinary liquids. - In the field of solutions, obviously the solvents with polar molecules assume a particularly important role because of their pronounced intermolecular interactions. Within this group water will always command special attention. This is also appropriate in a discussion on nonaqueous solvents, since at high temperatures water substance loses its typical aqueous characteristics to a considerable extent and becomes indeed almost a "nonaqueous", although highly polar and "water-like" solvent. This behaviour shall be demonstrated with several, more recent experimental examples, and comparisons shall be made with other nonpolar and polar fluids, as well as with highly ionized media as fused salts.

PROPERTIES OF PURE FLUIDS

The critical point in the PVT-surface is always important, since it is beyond the critical temperature, where the intermolecular distance of solvent molecules can be varied continuously over a wide range. Fig. 1 gives critical temperatures and pressures for a selection of substances. For most substances, which are of interest here, critical temperatures do not exceed several hundred K, and critical pressures remain below 200 bar. This does not apply to fused salts and metals, for which our knowledge is still very limited. Certainly, water is among the best investigated fluids over wide ranges of temperatures and pressures. A temperature - density - diagram is shown in Fig. 2. The existing steam tables reach to about 1000 °C and 1000 bar. The results of static density measurements extend to about 1000 °C and nearly 10 kbar. Above 25 kbar shockwave data are available. In order to obtain the normal density of 1 gcm⁻³ at 500 °C, a pressure of about 9 kbar is needed. Pressures of more than 20 kbar are necessary to reach this density at 1000 °C (Ref. 1).

In order to derive approximate high pressure properties of other polar fluids from those of water, the use of corresponding state methods appear advisable.

	T_c (K)	P_c (bar)
Ar	151	49
CH ₄	191	46
C ₂ H ₄	282	50
CO ₂	304	74
NH ₃	406	113
CH ₃ OH	513	81
C ₆ H ₆	562	49
H ₂ O	647	220
BiCl ₃	1178	119
Hg	1765	1510
K	2200	155
NaCl	3500?	250?
Cu	6000?	4000?
W	23000?	10000?

Fig. 1. Critical temperatures and critical pressures for a selection of substances. Data with a ? are based on estimates.

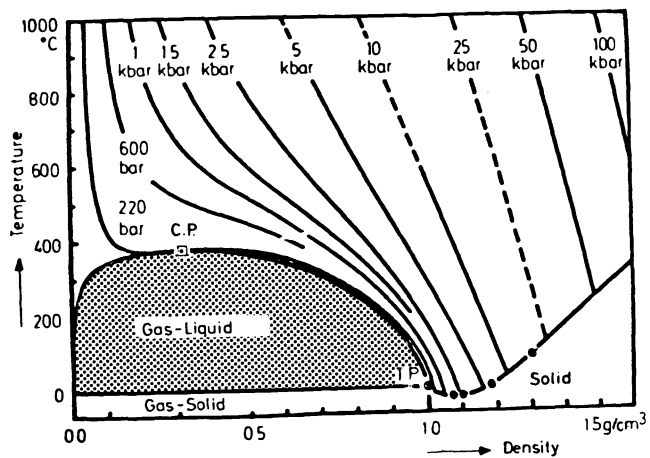


Fig. 2. A temperature-density diagram of water with isobars.

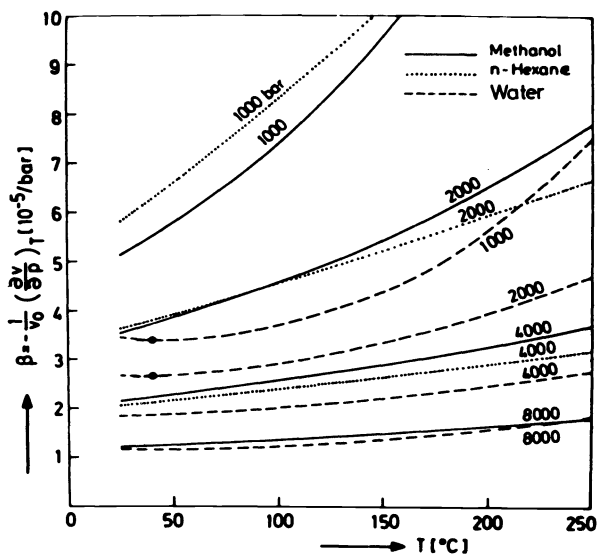


Fig. 3. Compressibility β of methanol, n-hexane and water at high pressures and elevated temperatures (Ref. 2).

The expected analogies, however, are not always found in the high pressure region. This is demonstrated in Fig. 3, where the compressibility of methanol and n-hexane, derived from recent measurements, is shown in comparison with water between 25 and 250 °C and from 1000 to 8000 bar (Ref. 2). At 1000 bar the compressibility of methanol is surprisingly similar to that of the non-polar hexane, while water deviates considerably. At 8000 bar, however, the compressibility of the alcohol is nearly equal to that of water. The peculiar structural properties of the water appear to be largely destroyed. It is evident, that the usual corresponding state estimates have to be applied with discretion at very high density.

For a first assessment of the potential chemical applications of a polar non-aqueous solvent, the knowledge of the static dielectric constant or permittivity and of a transport property, preferably diffusion coefficients or viscosity coefficients is important.

A comprehensive compilation and critical review of the experimental data of the dielectric constant of water to 550 °C and 5 kbar has been made recently (Ref. 3), and it has also been possible to derive an empirical "equation of state" for this quantity which will permit extrapolation to even higher supercritical conditions (Ref. 4). Fig. 4 gives an impression of the general behaviour of the dielectric constant of a typical polar fluid within a wide range of conditions. New experimental results for CHF_3 are plotted as isobars up to 2 kbar (Ref. 5). Increasing temperature and decreasing pressure always lowers the dielectric constant. A plot with isochors instead of isobars would look qualitatively similar. For the purpose of comparison, curves of constant values of the dielectric constants of HCl , H_2O , CH_3CN and CH_3OH are shown on a diagram of reduced temperature against reduced density in Fig. 5 (Ref. 6). The first three compounds have dipole moments close to 1, 2 and 4 Debye units. While at room temperature the dielectric constant of methyl cyanide (Ref. 7) is only half as high as that of water, both compounds show about the same values of five to six at critical conditions. Dense supercritical water can well have values of ten or twenty or more, thus resembling in this respect some of the more polar organic solvents at ordinary conditions. Diagrams as this may serve to approximately predict unknown dielectric constants of other polar fluids at unusual conditions.

For the discussion of kinetic phenomena, diffusion coefficients and ion mobilities are obviously of special interest. Unfortunately experimental data for

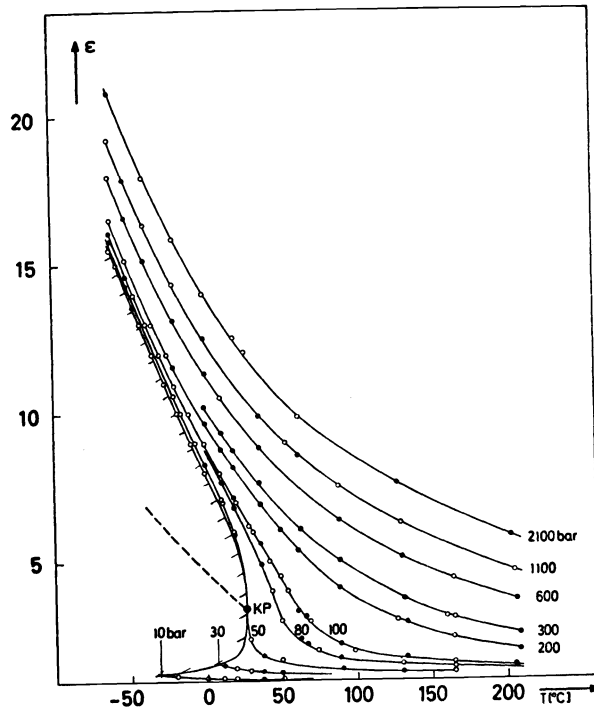


Fig. 4. Isobars of the static dielectric constant of CHF_3 as functions of temperature (Ref. 5).

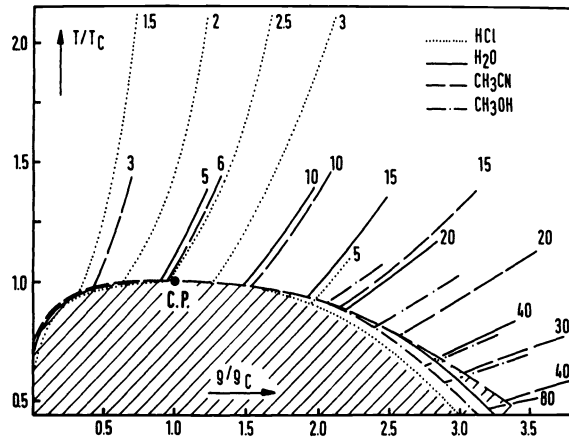


Fig. 5. Curves for constant values of the static dielectric constant of HCl , H_2O , CH_3CN and CH_3OH within a diagram of reduced temperature and density. CP: Critical point.

these quantities at high temperatures and pressures are still limited for technical reasons. The same is true for thermal conductivity. Viscosity data, however, are somewhat easier to determine and a wider selection is available. Viscosity data can be of use in this context, if only by application of the familiar Walden-rule, according to which the product of viscosity with ion mobility or diffusion coefficient respectively, of a certain dissolved species may remain almost constant over a wide range of conditions. The viscosity of water up to 250 °C as a function of density is shown on the right hand side of Fig. 6 from experiments which were extended to 5 kbars of pressure. It may be interesting to compare the behaviour of viscosity to that of the thermal conductivity of water in the same region. On the left hand side of Fig. 6 such data are shown which have been obtained very recently with the so-called pulse-heated-wire method (Ref. 8). The near-linearity of the isotherms is striking and the - in comparison with viscosity - reversed temperature dependence at constant densities should be noticed. This is to a large extent caused by the influence of the specific heat.

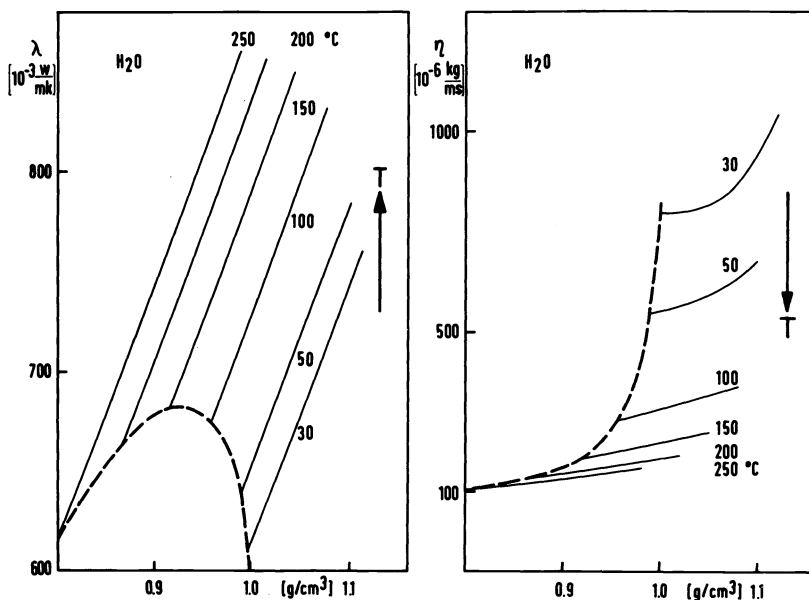


Fig. 6. Thermal conductivity λ and viscosity η of water as functions of density at constant temperatures (Ref. 8).

In this connection it is valuable to see the variation of the thermal conductivity of a normal fluid over a comparably wide range of conditions. For this purpose Fig. 7 gives new values of the thermal conductivity of toluene as isotherms in dependence of density (Ref. 9). The isotherms are not exactly linear but only slightly curved. It is clear, that extrapolations on the basis of a limited number of experimental thermal conductivities are possible, if enough PVT-data at high pressures are available to use the density dependence. The positive temperature dependence at isochoric conditions is quite general.

SUPERCRITICAL SOLUTIONS

At temperatures in the vicinity of the critical temperature or above, the miscibility of polar with nonpolar fluids at high densities may be considerable or even complete, and this miscibility can easily be changed by pressure variation. A number of possible technical applications are at present under investigation, particularly in the fields of gas chromatography, purification, extraction, oil recovery and mineral synthesis. Knowledge of supercritical aqueous solutions is of importance for the increasing investigation of fluid inclusions in natural mineral crystals. The extent of the region of incomplete

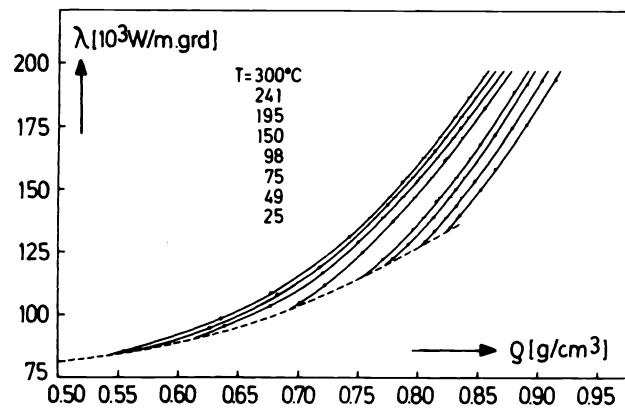


Fig. 7. Isotherms of the thermal conductivity λ of toluene as functions of temperature.

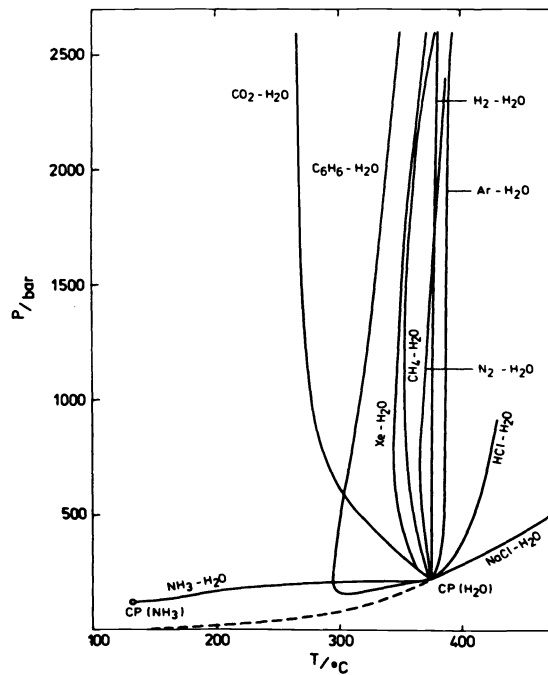


Fig. 8. Critical curves of several binary aqueous systems.

miscibility in a binary system is in part described by a critical curve. Such critical curves in three-dimensional pressure-temperature-composition diagrams begin at the critical point of one pure substance and proceed to the critical point of the other pure substance. If the two partners differ considerably in polarity or size of molecules, the critical curves are interrupted into two branches. The upper branch begins at the critical point of the higher boiling substance and may proceed to very high pressures and to a so-called upper critical end point (Ref. 10). A collection of such critical curves for binary aqueous systems is shown in Fig. 8. It is based on experimental investigations of several groups (Ref. 11). Up to 3 kbar an upper critical end point was not reached in any of these systems. In some cases the critical curves pass through a temperature minimum, in other cases they proceed immediately from the critical point of pure water towards higher temperatures. Although very different partners are combined with water, the critical curves at pressures of 1000 bar and higher are not very far apart. Only the critical curves of the systems water-carbon dioxide and water-benzene deviate considerably to lower temperatures.

One additional system, which was investigated only recently is shown in Fig. 9.

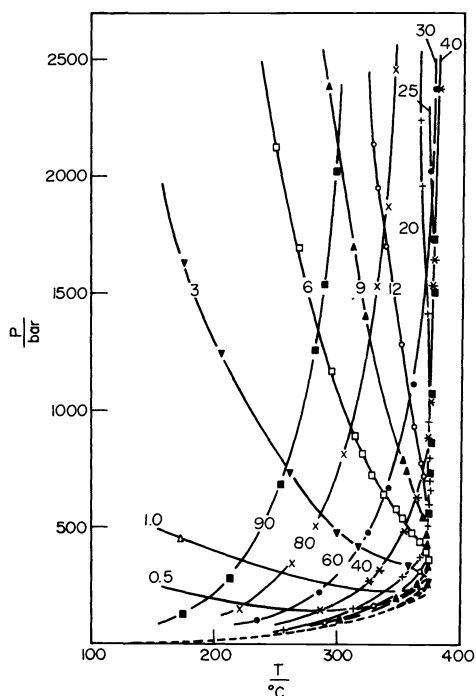


Fig. 9. Experimental isopleths and the critical curve in a pressure-temperature diagram of the water-hydrogen system (Ref. 12).

It is the water-hydrogen-system (Ref. 12) and it is presented as a diagram of isopleths, or curves which show the high temperature boundary of the two-phase region for particular, constant compositions. The critical curve, which is a kind of envelope to these isopleths, has in this case an almost vertically ascending projection on the pressure-temperature surface. This may in part be caused by the small size of the hydrogen molecules. One observes, that above about 375 °C water and hydrogen are completely miscible even at high, liquid-like densities. This behaviour might be used for chemical reactions or electrochemical processes.

Miscibility behaviour of this kind is certainly not restricted to aqueous systems. As another example for a binary system with one polar component Fig. 10 shows the recently investigated critical curve of the methanol-methane system (Ref. 13). The critical curve is also interrupted, but it bends down to quite low temperatures. At high enough pressures, the miscibility of these two partners is complete at 100 °C. The whole surface of the two phase region has been investigated and also the relevant PVT-data of the homogeneous

mixtures. When changing to ethane instead of methane, the increase in size of the nonpolar partner suffices already to produce a quite different, seemingly uninterrupted critical curve.

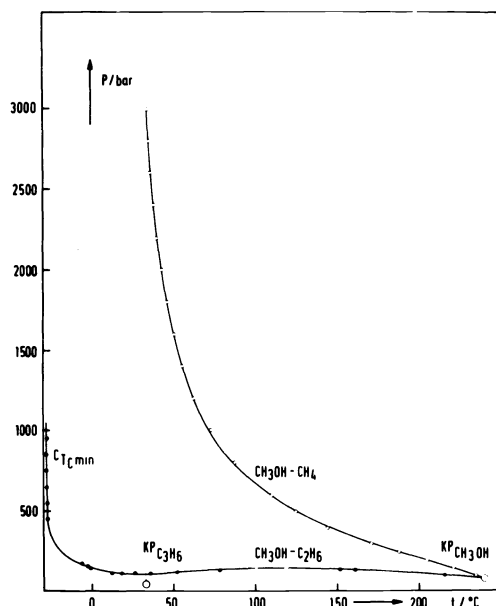


Fig.10. The critical curves for the binary methanol-methane and methanol-ethane systems. Methanol-methane according to (Ref. 13).

It is desirable, to know more of the non-ideal character of such dense supercritical mixtures, that is to investigate the excess Gibbs energy. Unfortunately calorimetric measurements are almost not existent as yet in this range. Fugacities could be derived from a careful analysis of a very large number of excess volume data at least for the binary water-carbon dioxide system. For other systems such experimental excess volume data are not yet sufficient enough. They do give, however, an interesting indication of the deviations from ideality in the supercritical mixture within certain ranges. Fig. 11 presents a recent example of values of excess volumes at 400 °C for the water-hydrogen system mentioned before (Ref. 12). It shall be pointed out only, that

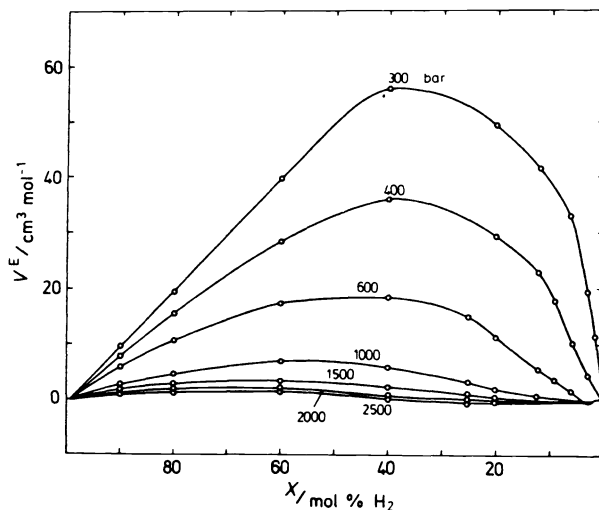


Fig. 11. The variation of the excess volume, V^E , for hydrogen-water mixtures at different pressures. A few points have been omitted for values of V^E near zero and for low concentrations of hydrogen in the interest of clarity (Ref. 12).

above 1000 bar the excess volume almost disappears, and that the slopes of the isobars at the water-rich and the hydrogen-rich ends are different. This is a rather general type of behaviour which has been found in other aqueous systems

as well. Examples are water-argon (Ref. 14), water-methane (Ref. 15) and water-benzene (Ref. 16). There appears to exist a possibility, to describe this phenomenon with relatively simple physical assumptions.

Observing the relatively low temperature values of the high pressure part of the critical curve of the water-carbon dioxide system, one is induced to ascribe this to the known, rather intense interaction between the two kinds of molecules. The attempt, however, to show this by Raman spectra, has not been successful, as demonstrated in Fig. 12. This is a collection of recent experimental results (Ref. 17). On the top of Fig. 12 is a spectrum at 450 °C for pure pressurized carbon dioxide in the 1350 cm^{-1} region. It shows the band pair produced by Fermi resonance between the symmetric C-O stretching and the first overtone of the O-C- bending vibration. If one uses a solution of only 3 mole percent of carbon dioxide in water at similar supercritical conditions, the spectrum changes only slightly (see the second spectrum from above). The spectroscopic detection of a specific interaction between these two partners at high temperatures would probably need other means. It is felt, that infrared techniques would be even less suited. At room temperature a new

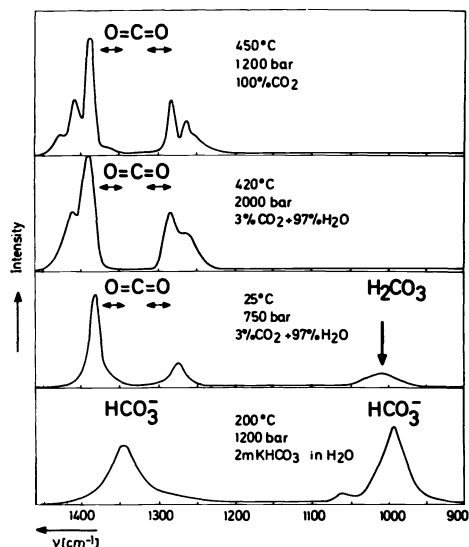


Fig. 12. Raman spectra in the CO-stretching region of CO_2 , CO_2 - H_2O -mixtures and of an aqueous HCO_3^- -solution.

weak Raman band develops at 1000 cm^{-1} , which may indicate the formation of a small amount of carbonic acid. This would be in accordance with existing thermochemical data. One might ask, what occurs to the two-phase boundary surface and the critical curve of the water-carbon dioxide system if one adds small amounts of a third component, for example a salt like sodium chloride. This question was investigated by G.C. Kennedy (Ref. 18) and recently more extensively in Karlsruhe (Ref. 19). The result is, that the addition of only two mole percent of salt can shift the critical curve by one hundred to two hundred degrees K to higher temperatures. An observation, which is important for the geochemistry of hydrothermal systems.

IONIZATION AND ELECTROLYTES

Some fluids of small, highly polar molecules exhibit the phenomenon of self-ionization. Ammonia and acetic acid are among this group and water is certainly the most important. A combination of experiments by various methods has in recent years permitted a comprehensive description of the ionization constant or the ion product of water as a function of water density to temperatures of 1000 °C. Fig. 13 shows the result for a constant density of 1 $\text{g}\cdot\text{cm}^3$. It gives a surprisingly straight line up to 1000 °C for the logarithm of the ion product in dependence of density (Ref. 20). Values for other temperatures and densities can be calculated by the same semiempirical function.

Static as well as shock wave measurements of the electrolytic conductance of water have in the past been carried out to more than 100 kbar of pressure. Using reasonable assumptions about the ion mobilities, approximate values of the ion product could be derived also from these results. Fig. 14 gives the

final outcome of this procedure (Ref. 21). Although at the higher conditions of about 1000 °C and a density of 1.5 or 1.6 g/cm³ the uncertainty of the ion product may be one or two orders of magnitude, it is quite certain, that the ion product at these conditions is around 10⁻² or more, that is twelve orders of magnitude higher than at normal conditions. This means, that about one percent of the water molecules are dissociated into ions. It had been predicted, that at 1600 °C and at a density of 1.8 g/cm³ and higher the dissociation would be nearly complete and water at these conditions would behave like a fused salt "hydronium hydroxide".

Recently, electric conductivity measurements in shock-compressed pure water have been carried out to pressures of about 500 kbar and to temperatures of

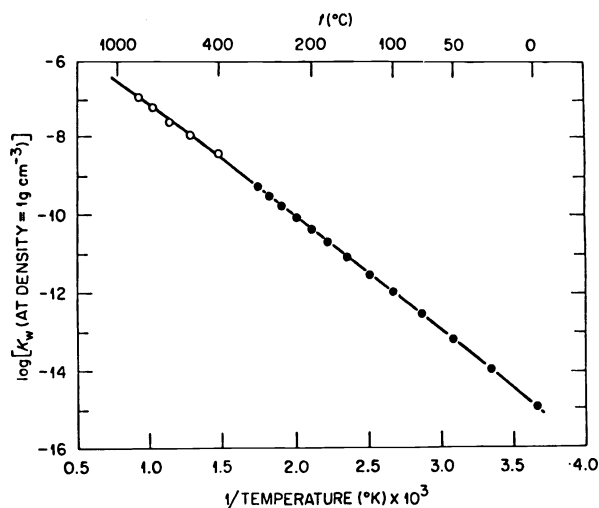


Fig. 13. Ion product of water at a constant density of 1 g cm⁻³ from 0 °C to 1000 °C (Ref. 20).

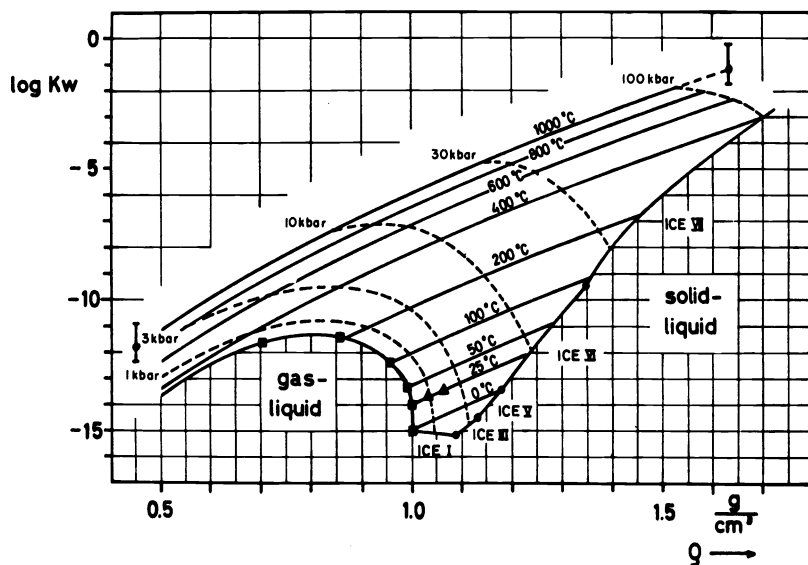


Fig. 14. The logarithm of the ion product of water, $\log K_w$, in dependence of density, pressure and temperature (Ref. 21).

at least several hundred degrees Celsius (Ref. 22). The conductance at first rises steeply with increasing pressure until values near $10 \text{ ohm}^{-1} \text{ cm}^{-1}$ are reached between 200 and 300 kbar. At higher pressures the conductance remains within this region, and that means close to the specific conductance of molten sodium hydroxide. Since a water density of about 2 g cm^{-3} should have been obtained at 200 kbar, these shock wave results are considered as a confirmation for the above hypothesis, that water can be transformed into a ionic, salt-like fluid by sufficiently high pressures and temperatures.

Obviously, high pressure supports ion formation in aqueous solutions because the water in the hydration spheres around the ions is denser than ordinary water. This hydration effect should be particularly evident from the investigation of partial molar volumes of salts in aqueous solutions at high temperatures. Specific volume measurements with $\text{H}_2\text{O}-\text{NaCl}$ solutions have been extended to 400°C , 4000 bar and 25 weight percent of salt (Ref. 23). The new volume data are slightly lower than those of an extensive recent literature compilation (Ref. 24). None of the older data, however, extend beyond 1000 bar. In Fig. 15 isobars of the partial molar volume of sodium chloride of infinite dilution, derived from the above mentioned measurements, are plotted as functions of temperature. The agreement with previous data for 20 bar (Ref. 25) and for saturation vapour pressure (Ref. 26) is good. It is interesting to observe the high negative values at elevated temperatures. They appear to be consistent with an average hydration number of the cations and anions of about 5 to 6. It is reasonable, that at constant water density the partial molar volume of the salt should remain almost independent of temperature.

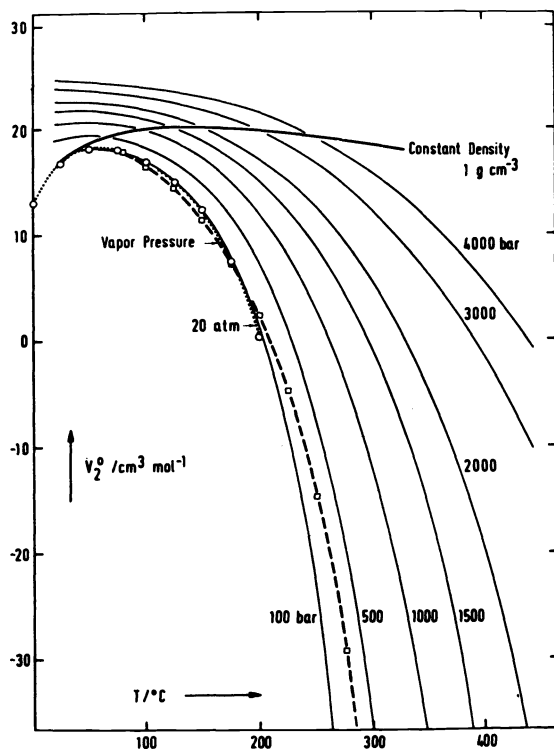


Fig. 15. Partial molar volume V_2^0 at infinite dilution for sodium chloride in water in dependence of temperature for several high pressures (Ref. 23).

Supercritical water in a wide range of densities has still a high enough dielectric constant to permit the partial or complete ionic dissociation of dissolved electrolytes. The entropy decrease connected with the formation of hydrogen spheres is still not great enough to prevent hydration and ion formation. Such electrolytic solutions at supercritical temperatures must have a very high conductivity, because the ion mobilities are much higher than in ordinary liquid water. Numerous conductance investigations with supercritical aqueous solutions have been made during the last two decades. A typical example is shown in Fig. 16, where isotherms of the equivalent conductivity

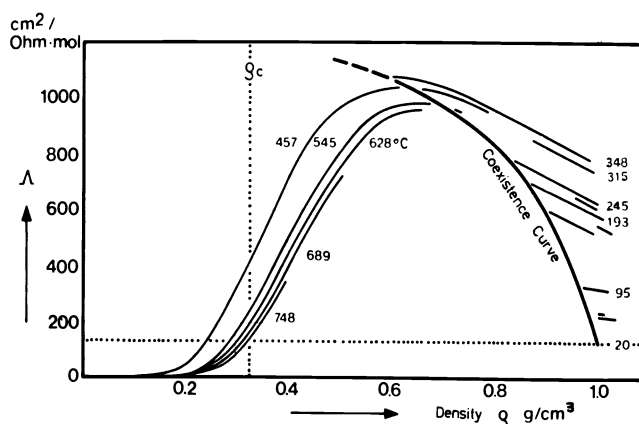


Fig. 16. Equivalent conductance λ of 0.01 molal aqueous KCl solutions at several temperatures in dependence of solution density.

of potassium chloride for a very dilute solution are shown in dependence of water density (Ref. 27). Below $0.2 \text{ g}\cdot\text{cm}^{-3}$ water density, KCl is so weakly ionized, that the conductance is negligible. Around $0.6 \text{ g}\cdot\text{cm}^{-3}$, however, the ion dissociation of the salt is almost complete and the equivalent conductance of the salt is about seven times as high as at normal conditions. With further density increase the conductance is lowered again because of an increase of water viscosity and - accordingly - a decrease of ion mobility. A survey of conductances of 0.01 molal KCl-solutions to 800°C and 12 kbar is available (Ref. 28). The highest values of the specific conductivity for such a solution are reached at 500°C and 6 kbar with $730 \times 10^{-5} \text{ ohm}^{-1}\text{cm}^{-1}$ while the value at 25°C and normal pressure is 140×10^{-5} . Above about 500°C the conductance declines at all pressures to 12 kbar.

One might expect, that much higher electrolytic conductances could be obtained with high temperature solutions of high salt concentrations, since the solubilities can be high. This expectation is confirmed only to some extent. Since the dielectric constant of dense supercritical water is reduced, the effective charge carrier concentration naturally is considerably lower than the values calculated formally from the analytical salt concentration. The molar conductance of several concentrated alkali halide solutions has been measured to 600°C and about 3 kbar. Sodium chloride is among these halides (Ref. 29) (Ref. 30). As a further example, concentrated calcium chloride solutions have been studied very recently (Ref. 31). The results for 6 molal solutions are shown in Fig. 17, where the molar conductance is plotted as a function of the density relative to the density at normal conditions. Comparison with Fig. 16 shows, that the maximum values of the conductance are considerably lower, and that the temperature dependence above 300°C is only moderate. An analysis of the possible associations which occur in these high temperature solutions has to wait for additional, and more detailed information than conductance alone can provide.

It is interesting to see, that the decrease of the molar conductance from very dilute solutions to the concentrations of Fig. 17 leads already into the vicinity of the region of the molar conductances which one expects for fused sodium chloride or calcium chloride.

Another interesting procedure is, to vary the dielectric constant of a solvent continuously, and to observe the behaviour of an electrolyte under such conditions. Water-dioxane mixtures have been used for this purpose in the past. Dioxane, however, is not inert and participates also in the solvation of ions.

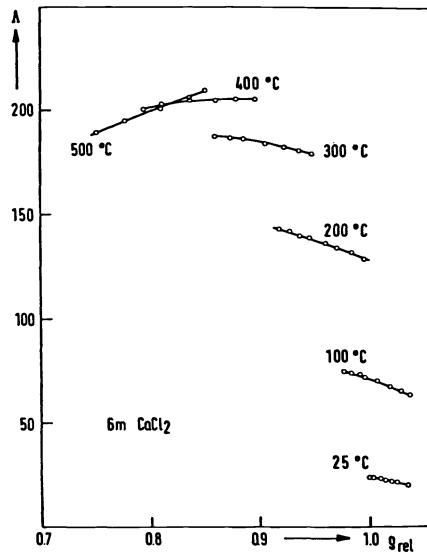


Fig. 17. Molar conductance Λ of 6 molal aqueous CaCl_2 solutions.

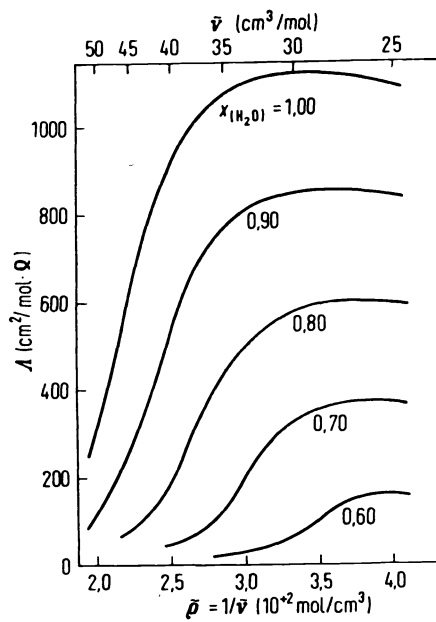


Fig. 18. Equivalent conductance Λ of KCl in supercritical water-argon mixtures (0.0005 mole KCl per kg water). x : mole fraction of water. \bar{v} : molar volume of the mixture.

Argon certainly is a totally inert diluent, and - as can be seen in Fig. 8 - is completely miscible with water even at high, liquid-like density above 400 °C. Such water-argon mixtures with mole fractions $x(\text{water})$ from 1.00 down to 0.60 and with pressures up to 3800 bar and at a temperature of 440 °C have been prepared. Small quantities of potassium chloride (between 0.0001 and 0.01 mole KCl per kg water) were added and the equivalent conductance determined (Ref. 32). Results are shown in Fig. 18. At constant particle number densities up to 40 mole percent of the water is replaced by argon. Accordingly the dielectric constant of the mixed solvent is calculated to vary from 20 to 4. After making appropriate estimates for the solvent viscosities, formal equilibrium constants for the association of potassium and chloride ions to ion pairs could be derived and discussed. Such a description is certainly simplified. Ternary mixtures of this type, namely water - inert gas - salt, are important in nature and do occur, for example, frequently in fluid inclusions (Ref. 19).

A further example of a continuous variation from nearly complete ionic dissociation to sparingly ionized or insulating states can be observed with certain pure salts at supercritical conditions. Not many salts have moderate critical temperatures, are chemically stable and are not too corrosive to be investigated. Ammonium chloride is such a case. Another example is bismuth trichloride, which has a critical temperature of 905 °C. The specific conductivity of this salt could be measured to 1200 °C and 4000 bar (Ref. 33,34). Fig. 19 shows a diagram, where the logarithm of the specific conductance is plotted in dependence of temperature. At 1000 bar and higher the specific conductance remains in the order of $1 \text{ ohm}^{-1}\text{cm}^{-1}$, at all temperatures, which

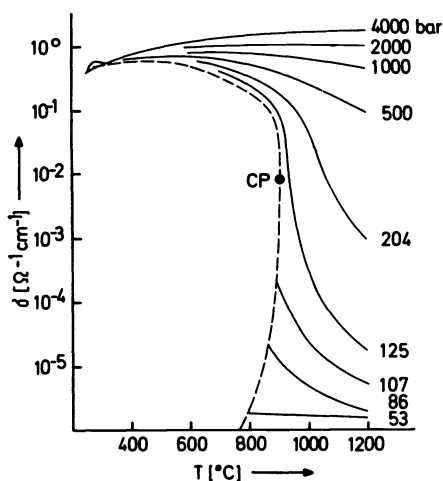


Fig. 19. Specific conductance of bismuth trichloride at supercritical conditions

means, that the salt remains a predominately dissociated, ionic fluid. Below 100 bar, however, the conductance remains very low.

With the reasonable assumption that the dissociation reaction of BiCl_3 leads mainly to BiCl_2^+ and BiCl_4^- ions and with an estimate of the ionic mobilities, a degree of ionization α of the salt can be estimated. Fig. 20 shows the resulting α -values, plotted for constant temperatures in dependence of density. Although the error bars have certainly to be relatively large, it appears, that the salt dissociates to about one percent in the critical region and that $\alpha = 1$ is approached if the density is raised to more than $3 \text{ g}\cdot\text{cm}^{-3}$ which is close to "normal" density.

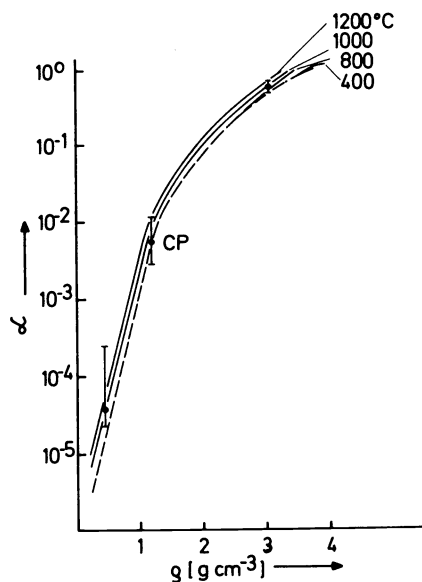


Fig. 20. Degree of dissociation α of bismuth trichloride

The selected examples presented here, may be suited to demonstrate, that indeed supercritical dense water as a solvent has some resemblance to more normal polar nonaqueous liquids, and that investigation of supercritical fluids in general offers possibilities to study several types of continuous transition between insulating and conducting, between ionic and molecular behaviour. It may also have become suggestive, to consider new practical applications for such polar dense supercritical fluids.

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