

Aqueous mixtures to supercritical temperatures and at high pressures

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Abstract - Thermophysical properties of dense supercritical water with special emphasis on dielectric permittivity are discussed. Phase diagrams and some critical curves of the binary systems H_2O-H_2 , H_2O-N_2 , H_2O-O_2 , H_2O-CH_4 and H_2O-He to 450 °C and 200 MPa are shown. H_2O-He has a type I critical curve. A rational equation of state to calculate phase diagrams and critical curves for polar-non polar systems is described. Measurements with the ternary system H_2O-CH_4-NaCl are presented. 2 mol per cent of added NaCl shifts the phase separation H_2O-CH_4 by 100 degrees to higher temperatures. The excess Gibbs energy for homogeneous supercritical H_2O-N_2 -mixtures to 200 MPa is shown. The static permittivity of supercritical H_2O -benzene mixtures is presented as an example of dielectric behaviour of polar-non polar mixtures in general.

INTRODUCTION

Supercritical fluids can be good solvents if applied at relatively high density, that is at conditions where the particles are within the range of their mutual interaction potentials (1). This means that densities around and above the critical density are of particular interest. Such supercritical fluids have special properties. The high compressibility permits substantial and continuous changes of thermophysical properties by variation of temperature and pressure only. Often a combination is observed of "liquid-like" and "gas-like" properties, for example high density and high transport coefficients. Extensive or even complete miscibility of unlike partners - for example polar and non-polar - is possible. Continuous variation between non-ionic and ionic behaviour in fluid phases can be obtained and used.

It is obvious that supercritical water must be a particularly interesting solvent. Its critical temperature, pressure and density are 374 °C, 221 bar and 0.32 g cm^{-3} . At temperatures of 400 °C and higher, association by hydrogen bonds is much reduced, but intermolecular interaction with the high dipole moments ($1.83 \text{ debye} = 6.1 \times 10^{-30} \text{ C}\cdot\text{m}$) remains possible. One significant property of water is the static dielectric permittivity, ϵ , the knowledge of which permits a first estimate of solvent properties with ionic, polar or non-polar partners.

The static permittivity of water has been measured to about 500 °C and 5000 bar. The data have been discussed and described by an empirical equation of state as a function of temperature and density (2) (3). The data and equation permit tentative extrapolation to 1000 °C. The results are shown in Fig. 1 with the highest temperature in the foreground.

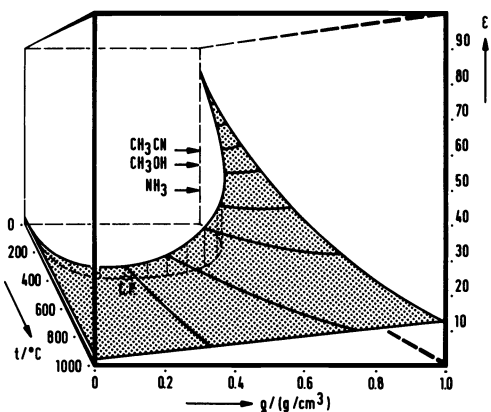


Fig. 1. The static dielectric permittivity, ϵ , of water as a function of temperature, t , and density, ρ , in an approximate presentation.

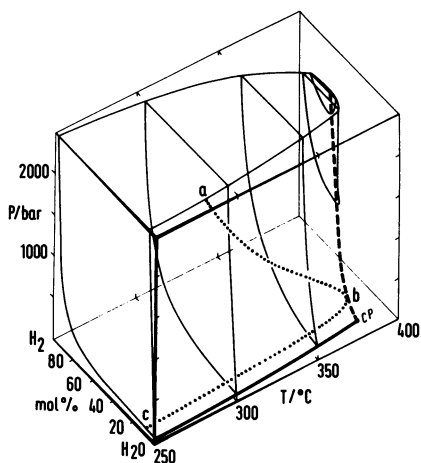


Fig. 2. The temperature-pressure-composition diagram of the system water-hydrogen (8). The isotherms show the shape of the two-phase boundary surface. The vapour pressure curve of pure water ends at the critical point CP. From CP the critical curve of the binary system (dashed) ascends.

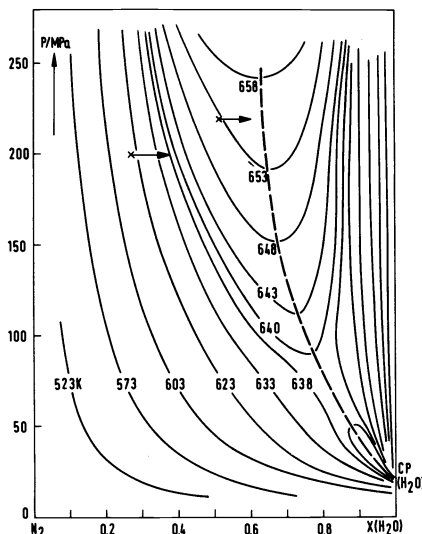


Fig. 3. Isotherms on the two-phase equilibrium boundary surface for the water-nitrogen system on a pressure-mole fraction, x , plane (13). (Crosses show points from an earlier determination by Tsiklis et al.(26)).

The familiar high values of ϵ occur only in the region of low temperatures and high densities. At supercritical temperature and higher density one finds ϵ -values in the range from ten to thirty, that is values similar to those observed with polar organic liquids. For comparison, data for methyl cyanide, methanol and liquid ammonia at 0 °C are shown. Thus one should expect that water around 400 °C and at densities above 0.3 g cm⁻³ is still a tolerable electrolytic solvent and also miscible with non-polar partners. A number of such supercritical binary aqueous systems have been investigated. Some properties together with new, recent examples will be discussed below. The experimental investigation of aqueous mixtures at such conditions poses technical problems - for example concerning corrosion - which have to be solved but can not be discussed in detail here.

BINARY MIXTURES, CRITICAL PHENOMENA

An important characteristic of the miscibility of high temperature water with other partners is the critical curve of the respective systems. Binary systems have a critical curve which extends uninterrupted between the critical points of the pure components, if these are relatively similar like, for example, two alkanes. If the two components differ considerably in polarity or molecular size, the critical curve is interrupted into two branches. A higher branch begins at the critical point of the higher boiling component and proceeds to high pressures, either by passing through a temperature minimum (Type II) or by advancing immediately to higher temperatures (Type I). The critical curve is an envelope of the two phase region. At temperatures above the temperatures of the critical curve the two components are completely miscible (4)(5).

The critical curves of systems of water and nonpolar partners are usually of the interrupted type. Several of such systems have been investigated experimentally. Among these are H₂O-Ar (6), H₂O-Xe(7), H₂O-H₂(8), H₂O-CO₂(9), H₂O-CH₄(10)(11) and H₂O-C₂H₆(12). More recently H₂O-N₂(13), H₂O-O₂(14) and H₂O-He(15) were investigated. As an example Fig. 2 illustrates the three-dimensional shape of the two-phase equilibrium surface and the critical curve in the water-hydrogen system. The dashed critical curve begins at the critical point of pure water, CP, and ascends almost vertically in the pressure-temperature projection. It is obvious that at 400 °C water and hydrogen are completely miscible, at least to 2500 bar. An isobar at 2500 bar and several isotherms are shown in the diagram, as well as an isopleth a-b-c (curve for constant composition) at 90 % water. The following diagrams will show isotherms, isobars and isopleths for three recently experimentally investigated aqueous systems.

In Fig. 3 a set of isotherms in the projection on the pressure-mole fraction plane is shown for the water-nitrogen system (13). The critical curve has a flat minimum around 639 K, thus the system, like most other known aqueous systems, belongs to the type II group. Detailed tables for phase equilibrium data are shown elsewhere (13). The Fig. 4 gives a number of isobars at 1000 bar. The water-nitrogen isobar corresponds to the data of Fig. 3. The water-oxygen system was investigated in the same region of conditions (14). Its isobar at 1000 bar comes very close to the water-nitrogen curve. This is also true for the critical curve, at least above 500 bar. Although this behaviour could be expected, it is not entirely obvious,

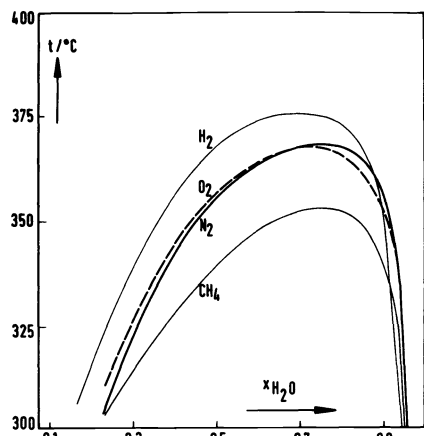


Fig. 4. Isobars at a pressure of 1000 bar on the two-phase equilibrium boundary surface of four water-gas systems. The two-phase regions are below these isobars.

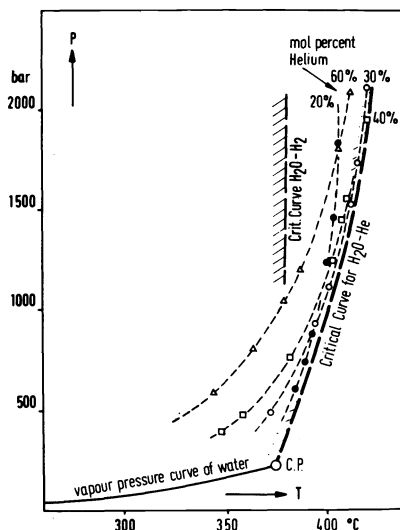


Fig. 5. Isopleths (curves for constant composition) experimentally determined for the water-helium system (15). The (dashed) critical curve is of type I. Part of the water-hydrogen curve for comparison.

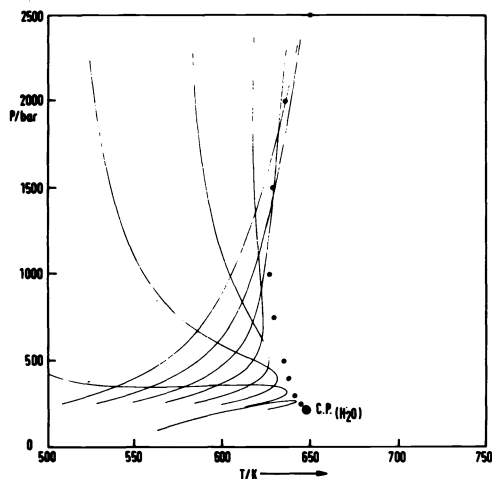


Fig. 6. Calculated spinodal isopleths for the water-methane system (11). The full circles are experimentally determined points on the critical curve. The critical curve should also be an envelope of the spinodals. The agreement is satisfactory.

since at room temperature and normal pressure the solubility of oxygen gas in water is about twice as high as that of nitrogen gas. This difference in behaviour, which seems to be mainly caused by the difference in size of O_2 and N_2 molecules, disappears at high temperature. One very recently investigated combination is the water-helium system. Fig. 5 shows a set of experimental isopleths (15). The critical curve as an envelope characterizes this system clearly as of type I. It is interesting to observe that the maximum critical solution temperatures mostly occur around seventy mole per cent of water, and that the critical curves for very different non-polar partners in the aqueous systems at high pressures are found within a relatively narrow range of temperatures not far from the critical temperature of pure water.

These observations are confirmed by calculation. Several approaches have been used by different groups to calculate phase equilibrium surfaces and critical curves (16). The inclusion of small polar molecules in such calculations is naturally difficult. A successful attempt with a "rational" equation of state has been made to describe aqueous systems (11). Care was taken to ensure that coefficients and functional relations in this equation are closely related to molecular models. The equation contains a repulsion and an attraction term. The repulsion term is constructed using hard sphere molecular dynamics computer simulation results with a modified Carnahan-Starling function. The attraction term uses a square-well potential. Potential parameters are derived from critical data of the components. Molecular diameters and potential-well parameters are combined for interaction of unequal particles by linear and quadratic mixing rules. An asymmetry factor for the combination of square-well depth values was derived from experimental water-nitrogen data and applied unchanged for other systems. Fig. 6 shows a set of calculated spinodal curves for the water-methane system together with experimental points for the critical curve. Since the envelope of spinodal curves is the same as the envelope of the binodal curves on the phase equilibrium surface, Fig. 6 shows that the calculation can produce the critical curve well, without any adjustments to experimental water-methane data. Calculation of binodal points on the fluid-fluid equilibrium surface and of mixture functions in the supercritical homogeneous range for this and other systems are possible and are shown elsewhere (11).

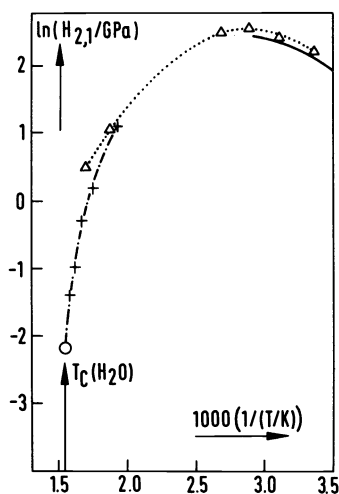


Fig. 7

Fig. 7. Values of the Henry constant, H_{21} , for the water-nitrogen system as a function of the reciprocal temperature. Crosses from a new determination (13). Other parts from existing tables. High Henry constants correspond to lower solubility of nitrogen in water (17).

Fig. 8. High temperature shift of isopleths on the two-phase equilibrium boundary surface of water-methane caused by the addition of sodium chloride (20). (Indicated NaCl-percentages are mol per cent relative to the amount of water in the system). Dashed curves: Isopleths for the water-methane binary system. Dotted curve: Critical curve for the binary system (no NaCl). Dashed-dotted curve: Critical curve for the water-NaCl-system

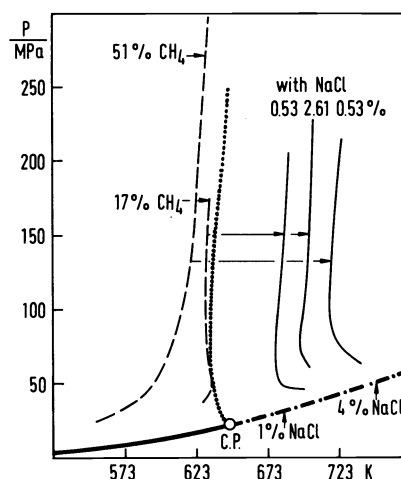


Fig. 8

Although the title of this presentation refers to supercritical temperatures, a short digression to lower temperatures will be made. The high pressure measurements with the water-nitrogen system, which led to the diagram of Fig. 3, also permitted the construction of a curve of the Henry constant for nitrogen in water at equilibrium water pressure to the critical point. This curve is shown in Fig. 7. The maximum of the Henry constant at moderate temperatures is found for many other gases (17). The end value at the critical point is calculated using assumptions concerning the mixed second virial coefficient (13).

TERNARY SYSTEMS

The addition of a salt like sodium chloride to systems like water-methane certainly causes vapour pressure lowering and salting-out effects. It can also be expected that the fluid-fluid phase separation and the critical curve are affected by the addition of an electrolyte. A shift of the critical curve towards high temperatures seems likely. Experiments with the ternary system water-carbon dioxide-sodium chloride have been made which show that small amounts of salt can indeed increase the critical mixture temperatures by one hundred degrees (18)(19). With an improved apparatus, using the so-called synthetic method, an investigation of the influence of small and moderate salt additions to the water-methane system was made (20). A small part of the results is presented in Fig. 8. Two isopleths of the binary system for 17 and 51 mol per cent methane are shown together with the analogous isotherms shifted with the addition of 0.53 and 2.61 mol per cent sodium chloride by 50 to 100 degrees to higher temperatures. To the left of these five isopleths is, as always, the range of two-phase behaviour. A similar diagram (Fig. 9) gives the shift for one isopleth of the water-carbon dioxide-sodium chloride system. The shift is of the same magnitude. A set of isobars with results from several isopleths is shown in Fig. 10 for a pressure of 1500 bar. The extension of the two-phase region is substantial. Much higher salt concentration could not be investigated because of insufficient solubility. The isobars are not continued to lower and higher concentrations in Fig. 10 because additional phase equilibria are to be expected there. An attempt to calculate or at least qualitatively predict these large phase separation shifts can be made with application of the same equation of state mentioned above. Only instead of the critical point of pure water, one respective point on the critical curve of the binary system water-salt is used. The critical curve was determined by Kennedy et al. (21). Temperature and pressure along this curve increase with increasing salt content. Two different salt contents are marked in the diagram. Thus, for tentative calculation, the ternary system is considered as quasi binary with the aqueous salt solution as one component. The results are satisfactory with low salt contents and the quasi-binary approach seems to be promising.

A number of additional measurements were made with calcium chloride instead of sodium chloride (20). The shift caused by the calcium salt is similar, but, compared at equal molar salt concentrations, less pronounced than with sodium chloride. One possible explanation is that around 400 °C and the applied pressures, considering the lowered dielectric permittivity of supercritical water (2), the ionic dissociation of calcium chloride is incomplete and monovalent ions are formed. Evidence for such behaviour was found with electrolytic conductance measurements (22). If the ionic strength of calcium chloride is evaluated with this assumption, the phase separation shift observed at equal ionic strength is very similar to the shift observed with sodium chloride. Analogous behaviour might be assumed for other electrolytes with normally bivalent ions and for certain hydrothermal fluids in geochemistry.

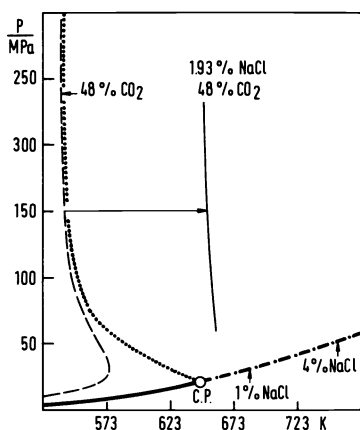


Fig. 9. High temperature shift of one isopleth on the two-phase equilibrium boundary surface of water-carbon dioxide caused by the addition of sodium chloride (mol per cent relative to the amount of water in the system) (19). Dotted curve: Critical curve for the binary system without salt. Dashed-dotted curve: Critical curve for the water-NaCl-system.

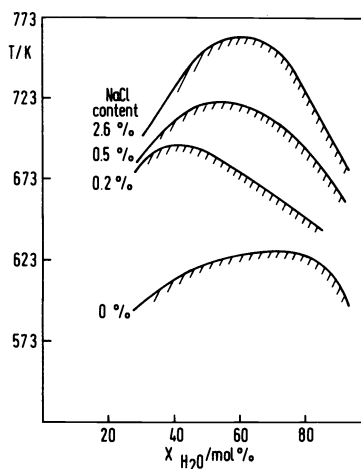


Fig. 10. Isobars at 1500 bar on the two-phase equilibrium boundary surface of water-methane shifted to higher temperatures by increasing amount of added sodium chloride (mol per cent relative to the amount of water in the system).

SUPERCRITICAL HOMOGENEOUS AQUEOUS MIXTURES

The dense supercritical aqueous mixtures provide a unique possibility to study polar-non polar molecular interaction over the whole range of compositions. One relatively easily accessible source of information is the molar volume of mixtures at constant temperatures and pressures. Such molar volumes have been measured for all the above mentioned binary aqueous systems and the excess volumes have been derived, which indicate the degree of deviation from ideal mixing behaviour. At 400 °C the excess volume of the mixtures is positive and generally decreases with increasing pressure. At 2000 bar the excess volume, even for 0.5/0.5 mixtures, amounts to only very few cm^3 per mole. The behaviour is mainly determined by molecular repulsion forces in this region. At very low pressure, excess volumes can be estimated from binary second virial coefficients, B_{12} . Thus, by integration of excess volume isotherms from zero to higher pressures, the excess Gibbs energy at such pressures can be calculated and subsequently transformed into additive terms with the activity coefficients of the partners. Fig. 11 gives a diagram of excess Gibbs energies for the water-nitrogen system as an example (13).

The supercritical aqueous fluids are also suited to investigate the dielectric permittivity of mixtures of water with a nonpolar partner - combinations which can not normally be produced at room temperature because of insufficient solubility. Measurements of the static dielectric permittivity have been made with water-benzene mixtures at 400 °C and different pressures up to 2000 bar (23). The upper critical consolution point at 2000 bar is at 340 °C. The apparatus - an autoclave with an internal capacitor - permitted simultaneous density determinations of the mixtures. The permittivity of pure water at 400 °C and 2000 bar (density: 0.79 g cm^{-3}) is 20 instead of 78 at normal conditions. Benzene at 400 °C and 2000 bar has a permittivity of 2.1. The addition of ten mol per cent of benzene to water at these temperature and density conditions reduces the permittivity already to one half, that is to ten. On the other hand, the addition of 50 mol per cent of water to the benzene causes

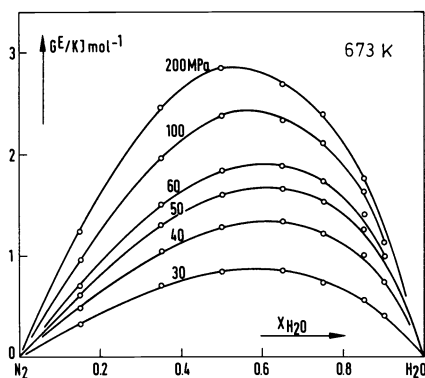


Fig. 11. Excess Gibbs energy, G^E , at 673 K for the water-nitrogen system for different pressures as functions of the water mol fraction (13).

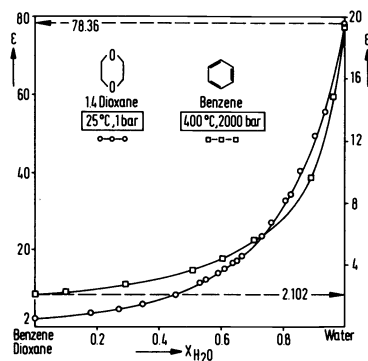


Fig. 12. The static dielectric permittivity for binary water-benzene mixtures (400 °C, 2000 bar) and water-dioxane mixtures (25 °C, 1 bar). Right-hand scale for water-benzene, left-hand scale for water-dioxane (23).

an increase only from two to four. This behaviour is demonstrated in Fig. 12. Superimposed for comparison is a curve for 25 °C water-dioxane mixtures. Pure dioxane at this temperature has a permittivity of about two. Although it has no permanent molecular dipole moment, dioxane is completely miscible with water at room temperature. Obviously, the existence of two opposite local dipole moments within the dioxane molecule can interact sufficiently with the aqueous environment. The presentation in Fig. 12 is such that, with two different vertical scales, the permittivity values for pure water at 25 °C and 400 °C coincide. The scale at the right hand side is for water-benzene, the left hand scale is for water-dioxane. The two curves have similar character, indicating that an analogous description may be possible. For water-benzene a mixing rule using volume fractions of both partners gives reasonable results (23). It is expected that such rules can be developed to calculate dielectric permittivities for other dense supercritical aqueous mixtures, which occur as natural "hydrothermal" fluids, for example, water-carbondioxide, water-nitrogen and water-methane.

MISCELLANEOUS

The supercritical aqueous fluids should also offer new possibilities for chemical reactions which are at present only little explored. The supercritical water is a versatile solvent with high diffusion coefficients and high quenching ability. Technical applications can be envisaged. Oxidation and hydrolysis, for example for waste disposal purposes, have been suggested and used (24). Since methane as well as oxygen are completely miscible with the supercritical water, even the generation of flames in such phases can be considered.

An interesting application of experimentally determined critical curves of water-hydrogen and water-helium is possible in the field of planetary science. The four outer planets Jupiter, Saturn, Uranus and Neptune have mean densities between 0.7 and 1.6 g cm³ only. The greater part of their volume is occupied by dense phases consisting mainly of H₂O and to some extent of NH₃ and CH₄. These phases contain a certain amount of hydrogen and also helium. Stevenson⁷(25) has given a discussion of the assumed structure of Uranus and Saturn. The increase of temperature and pressure with depth can be approximately calculated. Such a curve for Uranus reaches about 1000 K at 4000 bar. It would intersect the experimentally determined critical curve water-hydrogen (Fig. 2) near 650 K and 2000 bar. Under the assumption of sufficiently high hydrogen content in the planet, this means that below this temperature, at smaller depth, phase separation and stratification could occur. At higher temperatures and pressures high degrees of ionic dissociation of the water are to be expected.

In conclusion, it should again be emphasized that dense supercritical fluids, and particularly aqueous fluids, display a very unusual combination of solvent phenomena, which have interest for the basic physics of fluids as well as for chemistry, the geosciences and chemical technology and which certainly deserve continuing investigation.

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