High pressure phase behavior of binary water - light organic and ternary water - light organic - salt systems

a literature review, and a theoretical treatment of the salt effect

by R.J.A. Smits

December 1995

Supervisors: prof. dr ir J. de Swaan Arons dr ir C.J. Peters ir P.J. Smits

Laboratory of Applied Thermodynamics and Phase Equilibria Faculty of Chemical Engineering and Materials Science Delft University of Technology

SUMMARY

In order to develop SuperCritical Water Oxidation (SCWO) processes for the destruction of ChloroFluoroCarbohydrates (CFC's), more experimental data on the phase behavior of water-CFC and water-CFC-salt systems is needed.

First a general review is given of high pressure phase equilibria, according to the classification of van Konynenburg and Scott. A general description of waterhydrocarbon mixtures will follow that.

Since no data were found on water-CFC and water-CFC-salt systems at near critical conditions of water, the attention was focused on water-organic and water-organic-salt systems with light organic compounds.

For this purpose the phase behavior of binary water mixtures of methane, ethane and carbon dioxide are investigated at near critical conditions. For these binary systems the location of the critical curve is described, as well as other characteristic aspects of these systems. The location of the three phase curve and the upper critical endpoint are also discussed, for the mixtures containing ethane and carbon dioxide. In the water-methane system no three phase curve, and consequently no upper critical endpoint, are present.

The phase behavior of ternary water mixtures with methane and sodium chloride, methane and calcium chloride, ethane and sodium chloride, and carbon dioxide and sodium chloride are discussed. For these ternary systems the effect of salt on the resulting phase behavior is described.

Finally an extensive treatment of the salt effect is given.

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1. INTRODUCTION

The last 10 to 15 years water at supercritical conditions has become of interest as a medium to destruct all kinds of toxic wastes. For example explosives, propellants, agents for chemical weapons and polychlorinated biphenyls (PCB's). The reason for this interest is that at these exotic conditions water behaves as a non-polar solvent.

Most of the properties of a fluidum depend strongly on the density and as a result on the temperature. One of the most important properties for predicting the solubility in a fluidum is the dielectric constant, ϵ . The dielectric constant of water at ambient conditions (T=273 K, ρ =1000 kg/m³) equals to ϵ =90. In the critical point (T=647 K, ρ =300 kg/m³), however, ϵ =6, so the dielectric constant of water decreases with increasing temperature [1]. This decrease in ϵ and the fact that in dense supercritical water the intermolecular association is considerably reduced [2], transforms water gradually



Fig 1.1: Approximate presentation of the dielectric constant of water [1]

from a polar into a non-polar solvent at higher temperatures. Because of these effects, non-polar organics are miscible with supercritical water to form a homogeneous phase.

In this homogeneous phase the organics can be oxidized both by flameless oxidation or by flaming combustion [3]. Oxidation in supercritical water has an efficiency of over 99.9 % with water, carbon dioxide and - for halogenated organics - acids as the main reaction products. This so called SuperCritical Water Oxidation (SCWO) has some advantages over the traditionally used incineration.

- no emission to the atmosphere due to processing in a closed system
- lower temperatures, namely 500-600 °C as compared to 2000-3000 °C in an incinerator
- no formation of NO_x and SO₂
- energy-sufficient at 10 % wastes, as compared to 30 % in an incinerator

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Introduction

A disadvantage of SCWO is that it is highly corrosive, so special alloys are to be used.

It is just this corrosiveness of supercritical water that makes it a good environment for the destruction of compounds that are usually very hard to treat. These compounds include chlorinated and/or fluorinated organics (CFC's) that can be treated with destruction efficiencies of 99.99 % This clearly illustrates the potential of SCWO in the destruction of CFC's.

In order to develop processes for CFC destruction, there is a need for more experimental data on the phase behavior of these systems, so we have to improve our understanding of thermodynamic and molecular properties of mixtures in the supercritical region of water.

In this literature review two aspects that play an important role in developing SCWO processes are investigated.

The main objective is to give an overview of the available thermodynamic data on water-organics and water-organics-salt systems, with light organic compounds, at near-critical conditions. Some attention has also been payed to three phase equilibria that may occur in these systems.

The second aspect that has been considered in this review is the, so called, salt effect.

Since there is little information published on the main subject, more attention is payed to high pressure phase equilibria in general.

For the same reason a more extensive treatment of the salt effect is given.

2. CLASSIFICATION OF FLUID PHASE EQUILIBRIA

2.1. Introduction

In 1980 *van Konijnenburg and Scott* [4] published their renowned article on the general classification of fluid phase equilibria. They were the first to develop a general classification, which is based on the van der Waals equation of state. This method has been accepted all over the world for the classification of fluid phase equilibria.

van Konijnenburg and Scott extensively treated a number of binary phase diagrams and evaluated the various types of phase equilibria that could be calculated with the Van der Waals equation of state. The possible phase diagrams are classified according to the nature of their p,T-projections. The classification is based on the presence or absence of three phase lines and, when present, on the way critical curves are connected to them. In their study, solid phase equilibria were not taken into account.

Type I mixtures only have a lg-critical curve, whereas type II and VI also have a II-critical curve. Distinct Ig- and II-critical curves are found in types II and VI. Types III, IV and V have a critical curve that is separated into two or more parts, that can no longer be identified as liquid-gas or liquid-liquid.

Beside the described classification, *van Konijnenburg and Scott* also made another distinction, this time into classes instead of types. A mixture belongs to class 1, if the critical points of both pure components are connected by a continuous critical curve. Types I and II belong to class 1. If there is no continuous critical curve connecting both pure component critical points, the mixture belongs to class 2. Types III, IV and V belong to class 2. Type VI is assigned to a third class, because it is characterized by a closed liquid-liquid immiscibility loop.

Another remarkable aspect of type VI, is the fact that this type of phase behavior can not be calculated with the Van der Waals equation of state. Type VI can only be observed experimentally.

A more extensive description of the several types of phase behavior is given in Section 2.2. Since type III phase behavior is of main interest in this review, this is followed in Section 2.3 by a discussion on the water - n-alkane systems, which show a type III-HA phase behavior.



Fig 2.1: The six main types of phase behavior, according to van Konynenburg and Scott [5]

2.2. Treatment of the different types of phase behavior

2.2.1. Type I phase behavior

Mixtures with a continuous lg-critical curve without liquid-liquid immiscibility is characterized as type I phase behaviour. This type of phase behaviour occurs when the two components, in the mixture, are chemically similar and/or have comparable critical properties. The crystallization of one of the components can prevent a liquid-liquid phase separation at low temperatures.

Figure 2.2 shows that the lg-critical curve can have a number of different shapes. The shape of curve (*a*) is extremely rare, here partial immiscibility occurs at temperatures higher than the critical temperatures of both components. This kind of phase behavior is also called gas-gas immiscibility of the third kind. Mixtures with curve (*b*) as a critical curve are very common, they occur when there are moderately large differences between the critical temperatures or volumes of both pure components. Components that have very similar critical properties, usually exhibit an almost linear critical curve (curve c). Mixtures whose critical loci concave upwards, frequently show a pressure minimum (curve d). If the critical curve goes through a temperature minimum, as in curve (*e*), the mixture usually has a maximum pressure azeotrope. Curve (*f*) also has a temperature minimum and is concave upwards. n-Alkanol - n-alkane systems are known to exhibit this shape of the critical curve.



Fig 2.2: Six possible types of critical curves in type I mixtures [5]



Fig 2.3: Three possible types of critical curves in type II mixtures [5]

2.2.2. Type II phase behavior

Type II mixtures also have a continuous lg-critical curve, but in contrast with type I, this is only part of the critical curve. A llg-three phase line is present in between the vapor pressure curves of the pure components. The second part of the critical curve, the II-critical curve, starts on the llg-three phase line in an upper critical endpoint (II-UCEP) and then runs to high pressures. This type of phase behavior occurs with moderate interactions between the molecules.

Figure 2.3 shows the three variations in which the II-critical curve may occur. The II-critical curve has a negative slope and goes to high pressures and low temperatures (curve a). It may also have a positive slope, and thus runs to high pressures and temperatures (curve b). Finally the II-critical curve can have a negative slope in the II-UCEP, and goes to high pressures and low temperatures. After going through a temperature minimum, the II-critical curve gets a positive slope and runs to high pressures and temperatures (curve c).

Most of the type two mixtures have their llg-three phase line positioned above the vapor pressure curve of the most volatile component. This type of phase behaviour implies a heterogeneous azeotrope, and is thus called type II-HA. Type II-HA is found if two liquids of similar vapor pressure are only partially miscible.

2.2.3. Type III phase behavior

Type III phase behavior is characterized by two distinct parts of the critical curve. The upper part starts in the critical point of the least volatile component and runs to high pressures. The lower part of the critical curve starts in the critical point of the most volatile component and ends on the llg-three phase line in an lg-UCEP. This type of phase behavior is observed with very large size differences between the molecules, and very large interactions between them.

Figure 2.4 shows four different ways in which the upper part of the critical curve may occur. It may have a pressure maximum as well as a pressure minimum (curve a). This type of phase behavior is called type III_m , where m refers to pressure minimum. The upper part of the critical curve can also just run to high pressures and low temperatures (curve b). When examining curves (*c*) and (*d*), a new concept is introduced, namely gas-gas immiscibility. If the upper part of the critical curve goes to high pressures and temperatures, it is called gas-gas immiscibility of the first kind (curve d). If, however, the upper part of the critical curve

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Classification of fluid phase equilibria

goes through a temperature minimum while running to high pressures, gas-gas immiscibility of the second kind applies (curve c).

As with type II phase behavior, the llg-three phase line may be positioned in between both vapor pressure curves of the pure components or above the vapor pressure curve of the most volatile component. In the latter situation, heterogeneous azeotropy occurs, and is consequently called type III-HA. Examples of type III-HA are found in water - n-alkane systems, which will be treated extensively in section 2.3.



Fig 2.4: Four possible types of critical curves in type III mixtures [5]



Fig 2.5: Type IV phase behavior [5]

2.2.4. Type IV phase behavior

Type IV phase behaviour is characterized by three distinct parts of the critical curve. One part is a II-critical curve that starts on the IIg-three phase line in an II-UCEP and runs to high pressures. Another part, starts in the critical point of the most volatile component and ends at a second IIg-three phase line in an Ig-UCEP. The third part of the critical curve, of which the nature changes gradually in the p,T-plane, starts in the critical point of the least volatile component and ends on the second IIg-three phase line in a lower critical endpoint (LCEP). Near the critical point of the least volatile character. However, near the LCEP it has a liquid-liquid character. With moderate interactions and size differences between the molecules, this type of phase behavior is observed.

2.2.5. Type V phase behavior

Type IV mixtures that do not have a steep II-critical curve, are characterized as type V. This type of phase behavior occurs with moderate size differences between the molecules.

Examples of type V phase behaviour are the systems containing n-alkanes, with large size differences.

It is possible that the II-critical curve is absent, because it is obscured by the appearance of a solid phase.



Fig 2.6: Type V phase behavior [5]

2.2.6. Type VI phase behavior

Type VI phase behavior is characterized by a continuous lg-critical curve connecting both vapor pressure curves of the pure components and a closed II-critical curve. This II-critical curve starts on the IIg-three phase line in a LCEP and ends on the same IIg-three phase line in an II-UCEP (diagram a).

Figure 2.7 shows three other possibilities of type VI phase behavior. A II-critical curve can also appear at high pressures. This can occur in addition to (diagram b) or without (diagram c) the low pressure II-critical curve. Diagram *(c)* can be regarded as a special case of type I phase behavior. If the low pressure IIcritical curve is interfered by the high pressure II-critical curve, a so called 'immiscibility tube' appears (diagram d).

Type VI phase behavior is found in mixtures with strong molecular interactions, such as hydrogen bonding.



Fig 2.7: Four possibilities of type VI phase behavior [5]

2.3. Discussion on the term gas-gas immiscibility

The term gas-gas immiscibility has been used for a long time. It was introduced by Kamerling Onnes and Keesom, in 1907. Since, above the critical point, gas and liquid can not be distinguished as such, it is better to use the term fluid-fluid immiscibility. However, it is still appropriate to use the term gas-gas immiscibility. This term is also used in this review.

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2.4. Classification of water - hydrocarbon systems

As water-hydrocarbon mixtures usually exhibit type III phase behavior, more attention on this type will be given.

A study by *Brunner* [7] shows the p,T-projections of critical and three phase curves for 23 water - n-alkane systems (Figure 2.8).

As can be observed in Figure 2.8, the shape of the llg-three phase lines and of the critical curves of the mixtures change systematically with the number of carbon atoms, i. All critical curves are interrupted and show gas-gas equilibria of the second kind.

Because there is no temperature region in which methane and water are both liquid, it is obvious that the llg-three phase line and the lg-UCEP do not exist for this mixture. Beside methane, all other water - n-alkane mixtures have a llg-three phase line that is positioned above the vapor pressure curve of the most volatile component, and terminates at an lg-UCEP. The position of the llg-three phase line characterizes these systems as type III-HA according to van Konynenburg and Scott.

For i=2 to 26 the llg three phase line runs to an Ig-UCEP. Because the waterrich phase has a higher density than the alkane-rich phase, the gas becomes identical to the alkane-rich phase in the Ig-UCEP. As a result, the critical curve that starts from this Ig-UCEP ends in the critical point of the alkane. The second branch of the interrupted critical curve for these systems, including i=1, starts in the critical point of water and in passing through a temperature minimum rises steeply to high pressures and temperatures. In systems from i=7 to 26 this second branch of the critical curve also has a pressure minimum between the critical point of water and the temperature minimum, thus making it of the III-HA_m type.

With the number of carbon atoms increasing further, the temperature of the Ig-UCEP rises further. When this temperature is in the range of the critical point of water, the density of the water-rich phase decreases faster than that of the alkane-rich phase. Until finally the water-rich phase has a lower density than the alkane-rich phase before the Ig-UCEP is reached. Now the two liquid phases reverse in the gravitational field (barotropic effect) and the gas phase becomes identical with the water-rich phase in the Ig-UCEP. This means that the critical curve that starts from the Ig-UCEP now ends in the critical point of water. This barotropic effect on the IIg three phase line occurs with all mixtures with $i \ge 28$.



Fig 2.8: Survey of the p(T) projections of the llg three-phase lines and of the two branches of the interrupted lg-critical curves of (*n*-alkane + water). Indicated numbers are carbon numbers of the *n*-alkane; _____O, vapour pressure and critical point of water; _____O, vapour pressure and critical point of the *n*-alkane; _____O, llg three-phase line and lg-UCEP. To allow easier review, only the high-pressure branches of the lg-critical curve for the eight mixtures with i = 1, 3, 6, 12, 18, 24, 30, and 36, are plotted. So as not to complicate the curves, measured p(T) points have not been indicated besides the lg-UCEPs. [7]

3. BINARY MIXTURES OF WATER WITH CH₄, C₂H₆ OR CO₂

3.1. The H₂O - CF₄ system

3.1.1. Introduction

Beside the importance of high pressure phase behavior of methane - water mixtures for supercritical water oxidation, it also finds some practical applications in natural gas reservoirs [10]. The phase behavior determines the maximum methane recovery. Natural gas aquifers is another field in which this system is very important. These natural gas aquifers may become significant sources of energy [11].

Considering the previous, one would expect to find a considerable amount of available data. This is however not the case, there are not too many publications dealing with this system. Another problem is the fact that most of the literature found was either written in russian or is a doctoral dissertation, and therefore hard to obtain. As a result these reports have not been examined.

p,V,T,x-data of the methane - water system were investigated up to 723 K and 200 Mpa [10,12]. The solubility of methane in water is examined up to 600 K [13]. A review of solubility data of this system was given up to 633 K [14]. Also a correlation of solubility and phase equilibrium data was presented using a multiparameter equation of state [11].

3.1.2. Description

The phase diagram of a methane - water mixture shows two vapor pressure curves, one for each component. The vapor pressure curve of methane terminates at the critical point of pure methane, T_c =190.6 K and p_c =4.6 MPa [7]. The vapor pressure curve of water ends at the critical point of pure water, T_c =647.1 K and p_c =22.1 MPa [7]. Most n-alkane - water systems have a llg-three phase line below (type III) or above (type III-HA) the vapor pressure curve of the alkane. Since there is no common range of temperature in which both pure components in the mixture are liquid, the llg-three phase line as well as the lg-UCEP do not exist for this system [7]. As a result, the critical line is uninterrupted and begins in the critical point of pure water. It then proceeds to lower temperatures and higher pressures, and after going through a temperature minimum runs to high pressures.

The critical curve has a very steep slope in the critical point of water, -1.39 MPa/K [7]. As a result, the temperature minimum occurs at very high pressures.The exact location seems to be questionable. *Shmonov et al* [10] observed

Binary mixtures of water with CH₄, C₂H₆ or CO₂

the temperature minimum at approximately 628 K and 70 MPa. After examining Figure 3.1 as given by *Shmonov et al* [10], *Danneil et al* [15] and *Brunner* [7] it seems that this value may not be accurate. As will be mentioned in the next paragraph, the temperature minimum of ethane is located at 623.1 K and 73.0 MPa [15]. The temperature minimum of propane is located at 621.7 K and 46.3 MPa [7]. As the number of carbon atoms increase the pressure of the temperature minimum of the methane - water system should be higher than 73.0 MPa. Looking at the data shown in Figure 3.1 [10], the temperature minimum seems to be located at approximately 625 K and 95 MPa. These values are in reasonable agreement with *Welsch* [16] who published 626 K and 99 MPa. The temperature minimum occurs at a composition of 25 mole percent methane. As a result this system exhibits gas-gas immiscibility of the second kind.

Figure 3.2 shows the pressure-composition diagram of the water - methane system at different temperatures [11].



Figure 1. Comparison between experiment (Δ , this work, derived from ref 7; O, ref 8; \Box , ref 5) and theory (—) for the critical locus of methane + water using the Guggenheim ($\xi = 0.80, \zeta = 0.935$) and Heilig-Franck ($\xi = 0.83, \zeta = 0.92$) equations of state.



Fig 3.2: High pressure vapor-liquid equilibria for the water - methane system [11]

3.1.3. Other aspects

Figure 3.3 shows the molar excess volume-pressure plots at different temperatures [12]. The molar excess volumes are determined by using the experimental p,V,T and x data of the binary mixture and those of the pure components.

$$V_m^E(p,T,x) = V_m(p,T,x) - (1-x) V_m(p,T,0) - x V_m(p,T,1)$$
 (3.1)

All these isotherms exhibit clear maxima at pressures between 25 and 30 MPa. Increasing the water content in the mixtures causes the molar excess volume to drop.



Fig 3.3: Excess molar volume of a H_2O - CH_4 binary mixture vs. pressure at 653.15 K. Weight fractions of water: 0.2(1), 0.4(2), 0.6(3), 0.8(4) and 1.0(5) [12]



Fig 3.4: Virial coefficients of a H_2O - CH_4 binary mixture vs. weight fractions of water x; T=523.15(1), 573.15(2), 623.15(3) and 653.15 K(4) [12]

Since it can be convenient to represent the volumetric and thermodynamic properties of gases and gas mixtures by the virial equation of state, Figure 3.4 shows the second and third virial coefficient as a function of the composition at different temperatures [12]. This is done because virial coefficients are of interest in providing a link between experimental work and intermolecular forces [17].

3.2. The H₂O - C₂H₆ System

3.2.1. Introduction

Ethane - water mixtures are of interest in both geochemistry and in the chemical and petrochemical industries [18].

p,T,x,y-data of this system is determined up to 673 K and 370 MPa [15]. These experimental data were compared with calculations using a corresponding states theory [19]. A review of the solubility of this system is given up to 473 K [14, 20]. An extensive study of this system near the critical point of ethane is presented, in order to determine the location of the Ig-UCEP [18].

3.2.2. Description

The phase diagram of the ethane - water system consists of two vapor pressure curves of both pure components. These vapor pressure curves end respectively at the critical point of ethane, T_c =305.3 K and p_c =4.9 MPa, and at the critical point water [7].

As most alkane - water systems, the ethane - water system has an llg-three phase line, positioned above the vapor pressure curve of ethane.

Morrison [18] determined the location of the lg-UCEP to be just 0.022 K under the critical temperature of pure ethane. The lg-UCEP is reached at a composition of $5.5 \cdot 10^{-4}$ mole percent of water. This means that this system is of type III-HA, with a very small lower part of the critical curve. The llg-three phase line lies at a temperature lower than the critical temperature of pure ethane (Figure 3.5). Water at these very small concentrations affects the ethane not as a highly polar hydrogen-bonding material, but as a small relatively unpolarizable molecule.

The critical curve for this system is





interrupted and consists of a lower and an upper part. The lower part of the critical curve connects the critical point of pure ethane with the llg-three phase line in the

Binary mixtures of water with CH_4 , C_2H_6 or CO_2

Ig-UCEP. The upper part of the critical line starts in the critical point of pure water, then proceeds to lower temperatures and higher pressures. After going through a temperature minimum at 623 K and 73.0 MPa [15] it runs to high pressures. Figure 3.6 gives a qualitative representation of the p,T,x-space [15]. The composition at which the temperature minimum occurs is approximately 22.0 mole percent ethane [15].

The slope, of the upper part of the critical curve in the critical point of water, is less steep than that of methane but is still negative: -0.43 MPa/K. This means that gas-gas immiscibility of the second kind occurs.

Figure 3.7 shows the pressure-composition diagram of the water - ethane system at various temperatures [15].



Fig 3.6: A qualitative representation of the p,T,x-space of the ethane - water system [15]



Fig 3.7: Pressure-composition projections of the ethane - water system [15]

3.3. The H₂O - CO₂ system

3.3.1. Introduction

The binary mixture of carbon dioxide and water is of importance in many branches of physical science. The high pressure high temperature region is especially important in geochemistry. Results can be applied to hydrothermal activity, problems of hot springs and ore deposits [22,23]. It is also relevant for tertiary oil recovery and power plant technology [24]. Considering this, it is not surprising that a comparatively large amount of studies are published dealing with the carbon dioxide - water system.

p,V,T,x-data of homogeneous mixtures of carbon dioxide and water were determined up to 873.2 K and around 350 MPa [22,23,25-30]. An evaluation on the solubility of this system was given up to the critical point of water [31]. The solubility of carbon dioxide in water was examined up to 642.5 K [24,32]. Since the llg-three phase line is so close to the vapor pressure curve of carbon dioxide, the carbon dioxide - water system has been studied in detail near the critical point of carbon dioxide [18].

3.3.2. Description

The carbondioxide - water system has, qualitatively, the same phase diagram as the previously described systems. The critical point of carbon dioxide is located at 304.2 K and 7.3 MPa. The critical curve of this system is discontinuous.

Morrison [18] determined the location of the Ig-UCEP, to be at 304.6 K. This is just 0.372 K above the critical temperature of pure carbon dioxide. The Ig-UCEP is reached at a composition of 1.1 ·10⁻² mole percent water. This means that this system is of type III, with a small lower part of the critical curve. Because the Ilgthree phase line of this system is situated below the vapor pressure curve of carbon



Fig 3.8: The critical temperature of CO_2+H_2O vs. x_{H2O} . The cross (+) marks the end of the critical locus [18]

Binary mixtures of water with CH₄, C₂H₆ or CO₂

dioxide and the dp/dT for the llg-three phase line is positive, the topology of the phase diagram demands a rise of T_c upon the addition of water (Figure 3.8). Beside this, also a carbon dioxide liquid phase is present, that has a higher water concentration than the carbon dioxide vapor phase. This phenomenon can be explained by examining the chemical interaction between carbon dioxide and water. Both the solubility of water is enhanced in liquid carbon dioxide and the increased average attraction in the vapor phase due to the presence of water causes the critical point to rise. The upper part of the critical curve has a temperature



Fig 3.9: Pressure-temperature projection of the critical curve of the water - carbon dioxide system [25]

minimum at 539.2 K at a composition of 41.5 mole percent carbondioxide and at a pressure 250 MPa (Figure 3.9). This is in good agreement with *Takenouchi et al* [23]. As a result gas-gas immiscibility of the second kind occurs. As can be seen in the qualitative representation of the p,T,x-space (Figure 3.10), the p,x-sections split into two parts above this temperature minimum.

Figure 3.11 shows the pressure-composition diagram of the water - carbon dioxide system at different temperatures [25].



Fig 3.10: A qualitative representation of the p,T,x-space of the carbon dioxide water system [25]



Fig 3.11: Pressure-compositions projections of the carbon dioxide - water system [25]

3.3.3. Other aspects

It is interesting to note that barotropy occurs in this system. At high pressures the water rich phase floats on top of the carbon dioxide rich phase, whereas at low pressures the carbon dioxide rich phase floats on top of the water rich phase [23].

This can be explained by examining the densities of water and carbon dioxide as a function of temperature and pressure (Figure 3.12). From this, it can be noted that the relative densities of water and carbon dioxide become equal and then cross at 373 K and approximately 110 MPa. The Figure also shows that at 473 K and 573 K, the relative densities of water and carbon dioxide should become the same at approximately 200 MPa. These data are, however, based on the pure components and not on the mixtures. If the water concentration in the carbon dioxide rich phase and the carbon dioxide concentration in the water rich phase are low, there should not be too much deviation in the density of the mixtures and that of the pure components. It seems that the pressure of density inversion as shown is remarkably close to that estimated in Figure 3.12 [23].



Fig 3.12: The density of water and carbon dioxide at various temperatures and pressures [23]

4. TERNARY MIXTURES OF WATER WITH A SALT AND WITH CH_4 , C_2H_6 or CO_2

4.1. Introduction

Binary fluid systems consisting of water and an organic (non-polar) compound have a two-phase region in the three-dimensional pressure-temperature-composition space. This p,T,x-space is at high temperatures limited by a critical curve which begins at the critical point of water (T_c =647 K, p_c =22.1 MPa).

If moderate amounts of a salt are added, the two-phase region is extended to higher temperatures. This phenomenon is known as the salt effect. The theoretical treatment of the salt effect will be given in the chapter 5.

Quantitive studies of ternary water-organic-salt systems are of interest for several reasons. First of all, it contributes to the general knowledge of the influence of third components on the different types of critical phenomena in binary systems. Secondly, the influence of added salts on high pressure phase equilibria of aqueous mixtures with non-polar compounds provides insight into various aspects of molecular interaction. Finally, it also makes it possible to theoretically discuss and calculate the effect of salts on critical curves of these mixtures.

In addition such phase equilibrium data are relevant for certain fields of gas chemistry. For example, for gas hydrates and research with miniature fluid inclusions in natural crystals. These miniature fluid inclusions may contain methane besides water and salts, thus explaining the importance of knowledge on the ternary methane - water - salt behavior. There is also interest for applications in the exploration and exploitation of oil and natural gas resources.

For the binary water - organic systems, a limited number of publications were found. Taking this into account combined with the fact that ternary systems are very specific, it is not surprising that there are not many publications dealing with these systems.

For the water - methane - salt and the water - ethane - salt systems, only one reference was found per system. For the water - carbon dioxide - salt system three references were found, including two on the solubility of carbon dioxide in aqueous sodium chloride solutions.

4.2. The H_2O - CH_4 - NaCl and H_2O - CH_4 - $CaCl_2$ systems

4.2.1. Introduction

As mentioned in section 4.1, the ternary water - methane - salt systems are important in such fields as geochemistry and natural gas exploitation.

The water - methane - sodium chloride and water - methane - calcium chloride systems have been studied up to 800 K and 250 MPa.

The water - methane - sodium chloride system has been investigated in detail [33]. There are 21 isopleths (pressure-temperature curves on the three dimensional pressure-temperature-composition surfaces at constant composition, x) presented with sodium chloride concentrations of 0.6, 1.7 and 8 weight percent relative to water. The methane concentration ranged from 6 to 71 mole percent. Above 71 mole percent methane, the solubility of the salt in the methane-rich phase is insufficient, and the salt precipitates.

The water - methane - calcium chloride system has been investigated to a lesser degree, only three isopleths are presented.

4.2.2. Description of the H_2O - CH_4 - NaCl system

The binary water - methane system has a region with two coexisting fluid phases, which extends to high pressures and temperatures. This region is limited in the three dimensional pressure-temperature-composition space by a critical curve, which begins at the critical point of pure water (647 K, 22.1 MPa). At temperatures higher than the critical curve, the two components are completely miscible.

The addition of sodium chloride shifts the miscibility region to higher temperatures.



The ternary system $H_2O - CH_4 - NaCl$ with 0.6 weight percent of NaCl (relative to water). Curves at constant composition (isopleths) on the two-phase boundary surface (-----) (see Table 1). Two phase region to the left (shaded) side of the curves. Two isopleths (dashed curves) for the binary $H_2O - CH_4$ system with 16.8 and 62.9 mol percent CH_4 . Two critical curves for the binary sub-systems $H_2O - CH_4$ and $H_2O - NaCl$ (····· and -·-) [33]

Ternary mixtures of water with a salt and with CH₄, C₂H₆ or CO₂





The ternary system $H_2O - CH_4 - NaCl$ with 1.7 weight percent of NaCl (relative to water). Curves at constant composition (isopleths) on the two-phase boundary surface (------) (see Table 2). Two phase region to the left (shaded) side of the curves. Two isopleths (dashed curves) for the binary $H_2O - CH_4$ -system with 16.8 and 62.9 mol percent CH₄. Two critical curves for the binary sub-systems $H_2O - CH_4$ and $H_2O - NaCl$ (-----) [33]

The ternary system H_2O-CH_4 -NaCl with 8 weight percent of NaCl (relative to water). Curves at constant composition (isopleths) on the two-phase boundary surface (----------) (see Table 3). Two phase region on the left (shaded) side of the curves. Two isopleths (dashed curves) for the binary H_2O-CH_4 -system with 16.8 and 62.9 mol percent methane. Two critical curves for the binary sub-systems H_2O-CH_4 and $H_2O-NaCl$ (----- **[33]**

Figure 4.1 to 4.3 show the pressure-temperature projections at different methane concentrations for three different salt concentrations. It is clear that at pressures above 100 MPa, all isopleths proceed very steeply with small increases in temperature. Below 100 MPA, shallow temperature minima are observed.

Pressure-composition projections are given for the water - methane - sodium chloride system (Figure 4.4) as well as the water - methane system (Figure 4.5).

Comparing Figure 4.4 with 4.5, it is clear that the general form of the plots are similar, but the position of the saddle point is about 130 K higher in the ternary system. In Figure 4.5 some isotherms below 100 MPa form loops which converge in a point on the pure water axis. This is not possible in the ternary system, these isotherms end on the dashed three phase boundary line where solid salt starts to precipitate.

Figure 4.6 illustrates the salt effect for two methane concentrations. The 51 mole percent methane curve is shifted more than 100 K to higher temperatures by the added 0.53 mole percent sodium chloride. The 17 mole percent methane is shifted about 50 K to higher temperatures by the addition of the same amount of sodium chloride.

The temperature-composition projection at 150 MPa (Figure 4.7) shows a very pronounced shift of the maxima with different salt concentrations.









Fig 4.5:

The binary system $H_2O - CH_4$. Isotherms on the two-phase bound-ary surface projected on the pressure-composition (mole fraction x) plane. The two-phase region is between the two branches of each isotherm = = i Critical many [22] isotherm. ---: Critical curve [33]









Binary systems are represented in the three dimensional pressure-temperaturecomposition space, so if a ternary system has to be described, a four dimensional space is needed. To give a clear graphic representation of this ternary system,

Figure 4.8 and 4.9 give T_{x_1,x_2} plots at 200 and 50 MPa. The left hand side of the prism shows the water - methane phase diagram, whereas at the right hand side the water - sodium chloride phase diagram is shown. After the addition of sodium chloride the two phase region widens, as indicated by the dashed curve (Figure 4.8).

Region I is the region of coexistence of a methane-rich fluid and solid salt. In region II a methane-rich phase coexists with a water-rich phase. Region III indicates the three phase region, in which two fluids and one solid salt phase coexist.

Figure 4.9 is more complex, because the water - sodium chloride plane intersects with the two fluid coexistence region of the binary system.



Isobaric presentation (at 200 MPa) of the PTx_1x_2 phase space of the ternary H_2O-CH_4 -NaCl systems. Dotted planes: Two phase regions of the binary sub-system I, II: two-phase regions, III: Three phase region in the isothermal sections at T_1 and T_2 (see text). Dashed lines in the triangles: approximate range of the measurements with three salt concentrations [33]



Isobaric presentation (at 50 MPa) of the PTx_1x_2 phase space of the ternary H_2O-CH_4 -NaCl system. Dotted planes: Two-phase regions of the binary sub-systems. I, II: two-phase regions, III: three phase region in the isothermal sections at T_1 and T_2 (see text). Dashed lines in the triangles: approximate range of the measurements with three salt concentrations [33]

4.2.3. Description of the H_2O - CH_4 - $CaCl_2$ system

This system was also investigated to compare the influence of a comparable bivalent cation with the sodium chloride system. This specific salt was chosen because it is also highly soluble and it occurs in natural fluid inclusions, which makes it suitable for practical applications.

Figure 4.10 shows the pressure-temperature projections for three different salt concentrations at a methane concentration of 23.5 mole percent. The qualitative features of this system are the same as those for the water - methane - sodium chloride system, mentioned in the previous section.



The ternary system $H_2O - CH_4 - CaCl_2$ with 0.5; 1.6 and 6 weight percent of CaCl₃ (relative to water). Curves at constant composition (isopleths) of 23.5 mol percent of methane (see Table 5). Dashed curve to the left for $H_2O - CH_4$ without CaCl₂. Two phase region to the left (shaded) side of the curves.: Critical curve of the binary $H_2O - CH_4$ -system [33]

4.2.4. Comparison between NaCl and CaCl₂

The temperature is plotted against the ionic strength, I, for a pressure of 100 MPa and methane concentration of 23.5 mole percent (Figure 4.11), in order to compare the effect of increasing amounts of sodium chloride and calcium chloride.

$$I = \frac{1}{2} (m_{+} z_{+}^{2} + m_{-} z_{-}^{2})$$
(4.1)

In this equation m represents the molalities of ions relative to water and the z is the charge of the ion. It can be concluded that the effect of sodium chloride has little influence above I=0.5

If complete ionization is assumed for the ionic strength of calcium chloride, the effect is much smaller than with sodium chloride. It is, however, unlikely that complete dissociation occurs at these conditions, because of the low dielectric constant of the water. Therefore, also a plot is made assuming only mono-valued ions are formed (CaCl⁺). This curve is in reasonable agreement with that of sodium chloride.





Temperature at the phase boundary at a pressure of 100 MPa with 23.5 mole percent of CH₄ in dependence of the ion strength I of the salt. $(---: \text{ calculated for CaCl}_2 \text{ as a mono-valued electrolyte})$ [33]

4.3. The $H_2O - C_2H_6$ - NaCl system

4.3.1. Introduction

This system is important in geochemistry, for example fluid inclusions in natural crystals.

The water - ethane - sodium chloride system has been investigated, using 'Quasi-binary' measurements, up to pressures of 250 MPa and temperatures of 800 K [34]. The ethane concentrations were below 50 mole percent, and salt contents between 0.02 and 2.5 mole percent relative to water were used. This means that the range of very small to moderate amounts of salt were covered.

4.3.2. Description of the $H_2O - C_2H_6$ - NaCl system

In contrast with the ternary water - methane - salt system, for water - ethane - sodium chloride the high temperature part of the curves are measured. The pressure-temperatures projections at different ethane concentrations for four different amounts of salt are shown in Figure 4.12 to 4.15. Again it is very clear that the isopleths are shifted to higher temperatures with increasing salt content.









Ternary mixtures of water with a salt and with CH₄, C₂H₆ or CO₂



This system is more sensitive to the salt concentration than the previously discussed water - methane - salt system. Even at a salt concentration of 0.02 mole percent (0.1 weight percent), the 30 mole percent ethane isopleth is shifted 10 to 15 K to higher temperatures.

From Figure 4.16, it is clear that the ternary isopleths can be assumed to consist of two branches. The steep part is nearly parallel to the water - ethane binary isopleth, whereas the flat part is almost parallel to the water - sodium chloride binary isopleth. From this it can be concluded that depending on certain regions, the interaction of the relevant subsystems are retained.

The phase behavior of this ternary system is described by an isobaric T,x_1,x_2 diagram, at 200 MPa (Figure 4.17). The composition triangles are expanded for this description, because of the small salt fractions used. Again the left hand side of the prism shows the water - ethane, and the right hand side the water - sodium chloride phase diagram. The isothermal triangle contain regions of homogeneous one-phase behavior (near the water-edge), of two-phase and of three-phase equilibria. Figures 4.18 and 4.19 show two isobaric triangles for 100 and 200 MPa, for temperatures between 600 and 800 K. The two-phase region is on the right hand side of these curves. Clearly the region of homogeneous behavior widens with increasing temperature.





Comparison of an experimental pressure-temperature isopleth of the ternary H_2O -ethane-NaCl system with two isopleths of the binary subsystems H_2O -ethane and H_2O -NaCl. Shaded area: Twophase region [34]



Qualitative isobaric diagram for the ternary system H₂O-ethane-NaCl at 200 MPa and between 600 and 800 K. a) Binary region ethane-rich and water-rich fluids; b) Binary region ethane-rich fluid and solid salt; c) Binary region water-rich fluid and solid salt; d) Ternary region with two fluids and solid salt [34]



Fig 4.18:





Fig 4.19:

Projection of isothermal experimental fluid-fluid coexistence curves within an isobaric 200 MPa prism. NaCl-scale expanded. Shaded area: Two phase region. [34]

4.4. The $H_2O - CO_2 - NaCl$ system

4.4.1. Introduction

The effect of added sodium chloride on the phase behavior of the water - carbon dioxide system is important in geochemistry, for example with respect to fluid inclusions in minerals.

Accordingly, the phase behavior of water -carbon dioxide - sodium chloride system has been investigated up to 773 K and 300 MPa [35]. Data for 20 isopleths are presented with carbon dioxide concentrations between 0.2 and 85 mole percent, and with a sodium chloride concentration of 6 weight percent relative to water. Also two isopleths with 10 weight percent and two with 20 weight percent salt concentrations are given. The molar volumes were measured at the phase boundary surface, and within the one-phase region. Finally, the excess molar volumes are presented.

The solubility of carbon dioxide in 6 and 20 weight percent sodium chloride solutions are investigated up to 140 MPa and 723 K [36]. The solubility has also been reported up to a molality of 2 and for temperatures up to 600 K [37].

4.4.2. Description of the $H_2O - CO_2$ - NaCl system

Figure 4.20 shows some of the isopleths measured, together with the water sodium chloride binary critical curve of 6 weight percent sodium chloride (0 mole percent carbon dioxide). It shows that a pressure minimum occurs up to 21 mole percent carbon dioxide. At higher carbon dioxide contents, the pressure changes very strongly with small changes in temperature. The dotted curve near 6.7 mole percent is obtained by *Takenouchi et al* [36], and is in reasonable agreement.

To illustrate the extent of the salt effect for this system, Figure 4.21 shows two isopleths. The salt effect for the isopleth in the water-rich region is not very large. The isopleth for a mixture that contains 48 mole percent carbon dioxide is shifted over 100 K to higher temperatures by the addition of 6 weight percent sodium chloride.

Ternary mixtures of water with a salt and with CH₄, C₂H₆ or CO₂



An isobaric presentation at 100 MPa is shown in Figure 4.22. The shaded area above the upper critical point is a range of two coexisting fluid phases, one water-rich and one salt-rich.

The curve on the right hand side of the prism describes the temperature dependence of the solubility, and terminates in the melting point of pure sodium chloride. Below this curve an aqueous solution and a solid salt coexist. The shaded area below the critical point on the left hand side of the prism indicates the region of coexistence of a carbon dioxide-rich and a water-rich fluid phase. Again region I is that of coexistence of a carbon dioxide-rich fluid and solid salt. In region II a carbon dioxide-rich phase coexists with a water-rich phase. Region III indicates the three phase region, in which two fluids and one solid salt phase coexist. The dotted line in Figure 4.22 is not determined, but is assumed.

From the molar volume data of the homogeneous phases, the excess molar volumes were determined in the usual way (see equation 3.1).

Figure 4.23 shows these values for the excess molar volumes, at 100 MPa and for three different temperatures, as a function of the carbon dioxide concentration. Aqueous sodium chloride solutions have negative values for the excess molar volume, so the curves begin with negative values at low carbon dioxide concentrations.

Ternary mixtures of water with a salt and with CH_4 , C_2H_6 or CO_2



Fig 4.22: Isobaric phase diagram at 100 MPa (semiquantitative) for the ternary system H_2O-CO_2-NaCl . CP-points are upper and lower critical points for the binary systems H_2O-CO_2 and $H_2O-NaCl$ [35]



Fig 4.23: Excess molar volume, volume, V^{E} , for three temperatures in the homogeneous supercritical region at 100 MPa, calculated from the volume data of Table 2 for the ternary system (6 weight % of NaCl relative to water). The two broken lines show the excess volume for the binary HQ. Consume investment deating for the ternary system of the ternary system of the ternary system of the ternary system.

for the binary H2O-CO2-system investigated earlier [35]

5. THE SALT EFFECT

5.1. Introduction

The vapor-liquid equilibrium properties of solvent mixtures are influenced by the presence of non-volatile salts. Introduction of a salt into a binary mixture results in a change in the relative volatility of the solvents. This phenomenon is known as the 'Salt Effect'.

Most of the literature cited in this chapter are from two books summarizing the 170th and 175th meeting of the American Chemical Society, entitled: Thermodynamic Behavior of Electrolytes in Mixed Solvents, part I & II. These books give extensive reviews on all kinds of aspects on the salt effect, such as theoretical approaches and data on specific ternary systems.

In explaining the salt effect, the same approach is used as done by *Ohe* [38]. The theories on salt effect treated in this chapter are applicable at normal conditions. At more exotic conditions, such as in the near-critical region, the application of these theories is no longer valid [33].

5.2. Definition of the salt effect

The salt effect is defined as the ratio of relative volatility: α_s/α . Table 4.1 and Figure 4.1 show the salt effect of a number of salts in a 2-propanol - water system [39]. As can be seen in Figure 4.1, regardless of the kind of salt, the salt effect increases linearly with the solubility (X₃: weight fraction of salt).

Table 4.1: Salt effect and solubility in a2-propanol and water system [39]

Salt	a _s /a	X ₃	
CH ₂ COOK	4.52	0.396	
CaBr ₂	4.23	0.359	
MgBr ₂ ·2H ₂ O	4.82	0.314	
CaCl ₂	2.09	0.080	
KI	1.33	0.074	
(CH₃COO)₂Cd	1.20	0.064	
CH₃COONa	1.23	0.021	
MgCl ₂	1.30	0.020	
NaCl	1.18	0.020	
Na ₂ CO ₃	1.11	0.020	



Fig 5.1: Effects of various salts on VLE in a 2-propanol - water system [39]

5.3. Causes and explanation of the salt effect

The salt effect is caused by two phenomena, namely: vapor pressure depression and preferential solvation. Both these phenomena will be briefly discussed.

5.3.1. Vapor pressure depression

The solubility of salt has a certain value for each solvent, so the change in relative volatility depends on the vapor pressure depression of each solvent component.

This means that as the solubility in the higher boiling component becomes greater than that in the lower boiling component, the relative volatility of the lower boiling component to the higher boiling component increases, and vice versa.

5.3.2. Preferential solvation

Preferential solvation will be illustrated by looking at the methanol - ethyl acetate - calcium chloride system as done by *Ohe, Yokoyama, and Nakamura* [39]. Calcium chloride dissolves well in methanol and less easily in ethyl acetate. In this system it is assumed that methanol-calcium chloride interaction is dominant.

Figure 5.2 shows that from methanol mole fractions of 0 up to 0.333 the solubility is zero, which means that, if calcium chloride is dissolved only in methanol, both solvents exist as clustered molecules of one methanol and two ethyl acetate (Figure 5.3). Above 0.333 mole fraction methanol free, non-clustered molecules are present, so that the salt can dissolve. From the extrapolated solubility (mole ratio of calcium chloride to methanol, approximately 1:6) it is thought that calcium chloride and methanol form a solvate of $CaCl_2 \cdot 6CH_3OH$. In forming this solvate, methanol is trapped by calcium chloride and can not easily evaporate, so explaining the decrease in the vapor pressure of methanol.

Referring again to Figure 5.2, the solubility of calcium chloride is proportional to the increase in the number of methanol molecules. Since solvated molecules cannot be evaporated, the composition of methanol that participates in vapor-liquid equilibrium, at the liquid phase, decreases. If it is fair to assume that the preferential solvates have no interaction with the volatile components, the vapor-liquid equilibrium relation with salt can be considered the same as the vapor-liquid equilibrium without the salt in which the solvents forming solvates are excluded.









5.4. The salt effect in relation to the salt concentration

The salt effect was successfully correlated to the salt concentration by *Johnson and Further* [40]. For a large number of systems consisting of an alcohol, water and salt.

$$\ln \frac{\alpha_s}{\alpha} = k_s Z \tag{5.1}$$

This correlation holds at constant solvent composition. For inorganic salt systems this correlation is in good agreement, while it becomes poor for with organic salt systems.

Burns and Further [41] tested this equation for ethanol-water systems with ammonium bromide and potassium iodide (Figure 5.4 and 5.5). In both cases the linearity predicted by equation 5.1 is found, although close to saturation some deviation occurs.

Also the values of the salt parameter at various liquid compositions for the ethanolwater - ammonium bromide system were



Fig. 5.4: Salt effect of ammonium bromide on the ethanol-water system, $x_1 = 0.246$ [41]

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determined with their corresponding standard deviation. Figure 5.6 shows the linear relationship between the liquid composition and the salt parameter.



Fig 5.5: Salt effect of potassium iodide on the ethanol - water system, $x_1=0.309$ [41]



5.5. Prediction methods of the salt effect

The most important difference in predicting the salt effect on vapor-liquid equilibria to that of an ordinary solvent system, is that salt is an electrolyte and is non-volatile. As shown previously, the salt effect is caused by vapor pressure depression or by preferential solvation. Because of these two reasons there are two kinds of prediction methods. Most of the methods are based on vapor pressure depression.

First, a generally accepted method based on vapor pressure depression is described, after which a method based on preferential solvation is discussed.

5.5.1. The Boone-Rousseau-Schoenborn method

The Boone-Rousseau-Schoenborn Method is based on estimating the influence of salt concentration on infinite dilution activity coefficients of both components in a pseudo-binary solution [42]. By defining the system in the following way:

- solvent 1, which is salted out, is designated as 1*
- the mixture of solvent 2 and the salt is designated as $2^{\mbox{\scriptsize \star}}$

the system can be treated as binary and the equilibrium relationships is given by

$$\gamma_i^* X_i^* f_i^{*0} = \phi_i^* Y_i^* P$$
 (5.2)

in which

$$x_1^* = \frac{n_1}{n_1 + n_2 + n_3}$$
(5.3)

$$x_2^* = \frac{n_2 + n_3}{n_1 + n_2 + n_3}$$
(5.4)

Since we are dealing with a non-volatile salt $y_i^*=y_i$. Choosing the reference state of each component to be the pure component (1^{*} and 2^{*}) the reference state fugacities are given by

$$f_1^{*0} = P_1^{S} \tag{5.5}$$

$$f_2^{*0} = P_2^{S*} = P_2^{S} - \Delta P_2^{S}$$
(5.6)

Schreiber and Eckert [43] developed a concept to estimate Wilson parameters for binary systems by examination of infinite dilution activity coefficients. This technique was adapted by *Boone et al* [42] for the pseudo binary salt-solvent system and used to determine the effect of salt on activity coefficients.

According to *Long and McDevitt* [44] the salt effect, S_i , was expressed as the ratio of the fugacity of a component in the salt-containing system to the fugacity of that component in the salt-free system at the same ratio of solvent 1 to solvent 2.

$$S_j = \frac{f_j}{f_j} \tag{5.7}$$

in which

$$\frac{x_i}{x_j} = \frac{x_i'}{x_j'} \tag{5.8}$$

Substituting the general fugacity expression gives

$$S_{i} = \frac{X_{i}\gamma_{i}P_{i}^{S}}{X_{i}\gamma_{i}P_{i}^{S}}$$
(5.9)

First component 1 is considered.

Recall that solvent 1 is identical to component 1^{*}, and therefore $f_1=f_1^*$. Substituting this and rearranging gives

$$\frac{\gamma_1^*}{\gamma_1'} = \frac{x_1' P_1'^S S_1}{x_1^* P_1^{*S}}$$
(5.10)

Taking the limit of both sides as x_1^* goes to zero

$$\lim_{x_{1}^{*} \to 0} \frac{\gamma_{1}^{*}}{\gamma_{1}^{'}} \equiv \frac{\gamma_{1}^{*\infty}}{\gamma_{1}^{'\infty}} = \lim_{x_{1}^{*} \to 0} \left[\frac{x_{1}^{*} P_{1}^{*S} S_{1}}{x_{1}^{*} P_{1}^{*S}} \right]$$
(5.11)

According to *King* [45] the salt effect has been successfully correlated by Setschenow's equation

$$S_i = \exp(k_s C_{\theta}) \tag{5.12}$$

With the next two correlations

$$\lim_{x_1^* \to 0} \frac{X_1'}{X_1^*} = \frac{1}{X_2}$$
(5.13)

$$\lim_{x_1^* \to 0} \frac{P_1^{,S}}{P_1^{*S}} = \frac{P_1^{S}(at \text{ boiling point of } 2)}{P_1^{*S}(at \text{ boiling point of } 2^*)} = \frac{P_1^{S}(2)}{P_1^{S}(2^*)}$$
(5.14)

equation (5.11) can be converted into

$$\frac{\gamma_1^{*\infty}}{\gamma_1^{*\infty}} = \frac{1}{x_2} \frac{P_1^{S}(2)}{P_1^{S}(2^*)} \exp(k_s C_{\theta})$$
(5.15)

Now component 2 will be considered.

$$\frac{\gamma_2^*}{\gamma_2'} = \frac{y_2^* x_2' P_2'^s}{y_2' x_2^* P_2^{*s}}$$
(5.16)

In the limit as x_2^* approaches zero, y_2^*/y_2^* is approximately 1. Another approximation that is allowed here is $x_2^*/x_2^* \approx 1$. Therefore, taking the limit of both sides as x_2^* goes to zero gives

$$\lim_{x_2^* \to 0} \frac{\gamma_2^*}{\gamma_2'} = \frac{\gamma_2^{*\infty}}{\gamma_2'^{\infty}} \frac{P_2'(at \text{ boiling point of 1})}{P_2^{*S}(at \text{ boiling point of 1})} = \frac{P_2^S}{P_2^{S} - \Delta P_2^S}$$
(5.17)

From this derivation, it is apparent that, in order to determine the influence of a salt on the vapor-liquid equilibrium behavior of a binary mixture, only estimates of vapor pressure lowering and k_s is needed.

As can be seen after rearranging equation (5.15) to

$$k_{s}C_{\theta} = \ln \left[x_{2} \frac{P_{1}^{s}(2^{*})}{P_{1}^{s}(2)} \frac{\gamma_{1}^{*\infty}}{\gamma_{1}^{*\infty}} \right]$$
(5.18)

The salt parameter, k_s , can be determined by plotting the right hand side against C_e . This plot should be linear with a slope of k_s .

Boone et al [42] constructed these plots (Figure 5.7) and determined the salt parameter for five salts in methanol - water solutions, the values are given in Table 5.2.

As can be seen in Figure 5.7, the precision of the fit varies among the salts tested. Even though this method does not always give accurate results, the use of these k_s -values to estimate the salt effect on vapor-liquid equilibrium gives a good approximation of vaporliquid equilibrium behavior.





Table 5.2: Values of the salt parameter [42]					
Salt	HgCl ₂	KCI	NaF	LiCI	NaBr
k _s	0.050	0.280	0.195	0.075	0.120

5.5.2. Ohe's method

The description of Ohe's method is based on preferential solvation and is extensively reviewed [46].

5.5.2.1. Preferential solvation number

The formation of preferential solvates is caused by the ionization of salt. The stability of the ion in a solution depends on the magnitude of the dielectric constant of the solvent. In explaining salting out by the formation of preferential solvates, *Debye* [47] derived the following relation between salting out and the dielectric constant of a solvent.

$$v_{1} \ln \frac{x_{2}}{x_{2}^{\infty}} - v_{2} \ln \frac{x_{1}}{x_{1}^{\infty}} = -v_{2} \frac{z_{ion}^{2} \theta_{ion}^{2}}{8 \pi k T} \frac{1}{\epsilon^{2} r^{4}} \frac{\delta \epsilon}{\delta n_{1}}$$
(5.19)

In this equation the first component is a non-electrolyte and the second is an electrolyte, such as water. If $\delta\epsilon/\delta n_1$ is assumed to be constant, it is useful to compare in several solvents the value of $(1/\epsilon^2) \cdot (\Delta\epsilon/\Delta x_1)$. The greater the absolute value of this expression, the greater x_2/x_2^0 and the smaller x_1/x_1^0 . This means that preferential solvation is more likely to occur in the electrolyte component.

If the solvation number of the pure solvent is plotted against the difference of dielectric constant of each solvent (Figure 5.8), it is obvious that the value of S_0 increases with increa-



Fig 5.8: The difference of dielectric constants and solvation number [46]

sing $\Delta \epsilon$. This means that the preferential solvation number can be obtained from observed values of salt effect.

As the concentration of solvent is decreased by the number of solvated molecules the actual solvent composition participating in the vapor-liquid equilibrium is changed. Assuming that the solvate formation occurs with the first component, the actual composition is given by

$$x_{1a} = \frac{x_1 - Sx_3}{(x_1 - Sx_3) + x_2}$$
(5.20)

Since:

$$x_{1} = x_{1}/(x_{1}+x_{2})$$
$$x_{2} = x_{2}/(x_{1}+x_{2})$$
$$x_{1} + x_{2} = 1$$

it follows that

$$x_{1a}' = \frac{x_1'(1-x_3) - Sx_3}{(1-x_3) - Sx_3}$$
(5.21)

This equation can be rewritten into

$$S = \frac{1 - x_3}{x_3} \frac{x_1' - x_{1a'}}{1 - x_{1a'}}$$
(5.22)

This means that by determining x_{1a} from the measured values using the vaporliquid equilibrium relation obtained without adding a salt, the solvation number can be calculated.

When solvation occurs with the second component the next three equations can be derived in exactly the same way.

$$x_{1a} = \frac{x_1}{x_1 + (x_2 - Sx_3)}$$
(5.23)

$$x'_{1a} = \frac{x'_1(1-x_3)}{(1-x_3) - Sx_3}$$
(5.24)

$$S = \frac{1 - x_3}{x_3} \frac{x_{1a}' - x_{1}'}{x_{1a}'}$$
(5.25)

Ohe checked these equations and established the following three relations, that are valid in all cases regardless of the kind of solvents used, the kind of salt, and isothermal or isobaric equilibria.

- (1) The preferential solvation number, S, shows a linear relationship with the liquid phase composition of solvent, x_1 or x_2 .
- (2) When the concentration of salt is not saturated, S increases with increasing mole fraction of the solvent molecule which forms the solvate.
- (3) S increases with a decrease in salt concentration.

An explanation for relation (3) may be that the activity of salt increases and the number of molecules to be solvated increases as the salt concentration decreases.

It seems that these relations are also independent of the salt concentration. To be exact, the above-mentioned linear relation is assumed to exist when x_3 is constant. If the range of salt concentration is narrow, the above-mentioned relations are assumed to be established approximately.

5.5.2.2. Prediction of the salt effect

The procedure for calculating the preferential solvation number, S, has been described above. By reversing this procedure, that means that x_{1a} is determined from S, it is possible to estimate the salt effect using the vapor-liquid equilibrium without the salt.

When the salt concentration is below saturation, S can be expressed as follows

solvation with first component : $S = S_0 \cdot x_1^{'}$ solvation with second component: $S = S_0 \cdot (1 - x_1^{'})$ Accordingly, equations (5.23) and (5.24) are rewritten into

$$x_{1a}' = \frac{x_1'(1-x_3) - S_0 x_1' x_3}{(1-x_3) - S_0 x_1' x_3}$$
(5.26)

$$x_{1a}' = \frac{x_1'(1-x_3)}{(1-x_3) - S_0(1-x_1')x_3}$$
(5.27)

The procedure for predicting the salt effect from the solvation number of pure solvent is as follows

- (1) Decide with what component the salt forms the preferential solvate in the system being predicted.
- (2) Obtain the solvation number, S_0 to be formed by a pure solvent.
- (3) Calculate x_{1a}
- (4) Set the vapor phase composition at x_{1a} in the absence of salt, at x₁ in the presence of salt.

6. CONCLUSIONS AND RECOMMENDATION

The development of SuperCritical Water Oxidation processes for the destruction of CFC's require experimental data on the phase behavior of water-CFC and water-CFC-salt systems.

Since no data were found on these systems, the attention was shifted to water-organic and water-organic-salt systems, with small organic compounds.

The high pressure phase behavior of binary water mixtures containing methane, ethane and carbon dioxide are discussed. For these systems the location of the critical curve and other characteristic aspects are described. For the systems with ethane and carbon dioxide, also the three phase curve and the upper critical endpoint are treated. In the water-methane system no three phase curve occurs, and as a result no upper critical endpoint is present.

Ternary water mixtures of methane with sodium chloride and calcium chloride, ethane and carbon dioxide both with sodium chloride are described. In these systems, both the qualitative and the quantitative effect of added salt is described.

Finally an extensive treatment of the salt effect is given.

Since no experimental data were found on water-CFC systems at near-critical conditions, it is useful to perform some of these experiments. These experiments can help in getting a better understanding of water-CFC systems.

They can also be used in the development of SuperCritical Water Oxidation processes to destruct CFC's.

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8. List of symbols

e _{ion}	electric charge of electron
C _e	salt concentration
f _i	fugacity of component i
k	Boltzmann constant
k _s	salt parameter
n _i	moles of component i
Р	pressure
P ^s (j)	vapor pressure of component i determined at the
	normal boiling point of j
Δ P _i ^s	vapor pressure lowering of component i
r	distance between ions
S .	preferential solvation number
Si	salt effect on component i
S ₀	preferential solvation number of the pure solvent
	with a salt
Т	absolute temperature
Vi	molar volume of component i
X ₃	weight fraction of salt
X _i	mole fraction of component i in liquid
Уi	mole fraction of component i in vapor
Zion	electric charge number
α	relative volatility
ϵ	dielectric constant
Y i	activity coefficient of component i
γ_{i}^{∞}	infinite dilution activity coefficient of component i
$oldsymbol{\phi}_{i}$	fugacity coefficient of component i

<u>subscript</u>

- a free solvent molecule not solvated
- s with salt
- 1 first component
- 2 second component
- 3 third component

List of symbols

superscript

1	salt free
0	reference state
*	pseudo-binary mixture
∞	at r=∞