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Description of vapour-liquid phase equilibria of the H_2O-NaCl system between 100 and 900°C with a thermodynamic model based on the Mean Spherical Approximation

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Abstract: The Mean Spherical Approximation (MSA) of the ion-dipole mixture is used to describe the vapour-liquid equilibria of the H_2O-NaCl system. Comparison with experimental data reveals that the H_2O-NaCl mixture cannot be solely modelled by the MSA ion-dipole model. Discrepancies have been significantly reduced by taking into account NaCl ion pair formation in vapours at all temperatures and in high-temperature liquids (T >387°C). A van der Waals interaction term must be included at lower temperatures (T <387°C) and is believed to describe effects of the solvation of ions by water molecules or short-range interactions between anions and cations. The model has been fitted in the 100-850°C temperature range, and represents experimental data with a good accuracy from dilute aqueous solutions to fused salts. This model provides insights on the effects of electrostatic interactions (ion-ion, ion-dipole, dipole-dipole) and stresses the importance of NaCl ion pair formation and other effects on the vapour-liquid equilibria of the H_2O-NaCl system.

Key-words: H_2O-NaCl system, equation of state, liquid-vapour equilibria, Mean Spherical Approximation.

Introduction

The H_2O-NaCl system plays an important role in geological processes. Of major importance is the liquid-vapour immiscibility of saline fluids at high pressures and temperatures, that occurs in the crust (geothermal systems, ...). In particular, formation of ore deposits is largely controlled by the large solubility difference of metals between a coexisting saline liquid and steam (formation of porphyry copper deposits, Ahmad & Rose, 1980). A good knowledge of the thermodynamic properties of such fluids is therefore necessary in order to understand such phenomena. However, the H_2O-NaCl system represents one of the most difficult systems to tackle from a thermodynamic point of view, as it is characterized by complex interactions between molecules and ions. A solution to such a complex problem can only be approached by using simplifications.

The first simplification is to treat electrolyte solutions as a system of electric charges (the ions) embedded in a dielectric continuum (the solvent). This approximation is commonly referred to as the "primitive model", and provides a simple framework for the derivation of theoretical models. Primitive models are frequently based on the pioneering work of Debye & Hückel (1923a and b), who derived a theory describing the effects of electrostatic long-range interactions between ions immersed in a solvent. However, the Debye-Hückel model is valid only at very low electrolyte concentrations (below 0.01 molal). Nevertheless, it forms a limiting law that any model must check at infinite dilution. To extend the application range of primitive models, more or less semi-empirical terms, that attempt to describe ion-ion and ion-solvent interactions at higher electrolyte concentrations, must be added to the Debye-Hückel term. Two primitive models are commonly used in geochemistry.

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The first one is the Pitzer model (Pitzer *et al.*, 1984), which is based on a virial-type expansion and is successful up to 300°C and for NaCl molalities below 6 molal. The second one is the Helgeson-Kirkham-Flowers model (1981), which includes a Debye-Hückel term (describing Coulombic ion-ion interactions), a Born term (describing ion-solvent interactions), and a Brønsted term (describing specific short-range interactions between anions and cations, Brønsted, 1922). Attempts have been done to extend the Pitzer model to higher temperatures (between 300 and 450°C) and more saline compositions (Pitzer & Simonson, 1986; Pabalan & Pitzer, 1990). However, extensive multiparametric fitting is required to achieve a good agreement with experimental data and to make up for the insufficiencies of the theoretical basis of primitive models at these high temperatures and electrolyte concentrations. Thus, there is a need for more elaborate theories of electrolyte solutions.

One possibility is to treat the solvent as a mixture of interacting spheres, and not as a dielectric continuum. Such an approach, more realistic, is called the "nonprimitive model". Some of these attempts are based on the van der Waals and other cubic equations of state (Bowers & Helgeson, 1983; Søreide & Whitson, 1992), that are known to be efficient in describing mixtures of nonpolar molecules. For electrolyte solutions, these models are not adequate and their use leads also to rather complex empirical relations containing a high number of fitting parameters. The most difficult step is clearly the description of long-range Coulombic interactions. As a result, equations of state, that are available at the present time for water-salt systems, are most successful when ions are absent. Such a case occurs in low-density vapours and in liquid phase at high temperatures (above 300°C), for which the drastic decrease of dielectric constant causes the extensive formation of NaCl ion pairs. One can, for example, mention the Pitzer & Pabalan (1986) equation describing the thermodynamics of NaCl in steam, or the Anderko & Pitzer (1993) equation of state, that reproduces accurately the liquid-vapour phase equilibria above 300°C. The Anderko & Pitzer model is based on a theory of statistical mechanics, describing the thermodynamic properties of a mixture of dipolar hard spheres. However, this equation of state uses also a large number of fitting parameters. As this equation ignores the presence of ions, one may then wonder whether the fitted part of the Anderko & Pitzer equation of state does not actually take into account the effects of ions (which are nevertheless present in small amounts). Moreover, these fitting parameters do not have a clear physical meaning, and this means that the equation of state cannot be used for predictive purposes and can exhibit strange behaviour when other properties are investigated (see the projection of the calculated critical curve of the H_2O-NaCl system on a T-x_{NaCl} plot, Thiéry, 1996a and b). This example illustrates well the need to develop an equation of state with a strong theoretical background, that is able to describe explicitely ion-ion, ion-solvent and solvent-solvent interactions.

New advances in statistical mechanics and computer simulations have been performed in the last thirty years, and several theories are now available for describing explicitely all types of interactions occurring in electrolytic fluids. Promising theoretical developments use the so-called "integral equations". These are equations that exactly describe the influence of all surrounding particules on two interacting particules (Fernandez-Prini, 1992). However, approximations must be used to solve these integral equations. The Mean Spherical Approximation (MSA) is one of these approximations, and allows the derivation of the analytical equations for the thermodynamic properties of any type of fluid. Different types of interactions (ion-ion, ion-dipole, dipole-dipole, ion-quadrupole, ..., induction forces, dispersion forces, and repulsion forces (Prausnitz *et al.*, 1986) exist in an electrolyte fluid, and phenomema such as formation of ion pair and polyatomic clusters (Oelkers & Helgeson, 1990) occur also. A MSA model describing all these types of interactions would be untractable. Thus, it is better to start from a simpler physical picture, and then to analyse eventual discrepancies between experimental data and the model in light of the assumptions that have been done. In this study, the H_2O-NaCl is first assimilated as a mixture of ions and dipoles. The MSA solution for a mixture of ionic and polar hard spheres has been developed in a series of papers (Adelman & Deutch, 1974; Blum, 1978; Blum & Wei, 1987; Holovko & Protsykevich, 1987; Høye & Lomba, 1988; Høye *et al.*, 1988; Pizio *et al.*, 1988; Vericat & Blum, 1980; Wei & Blum, 1987). Equations are complex and up to now, there is only one quantitative application of the ion-dipole MSA theory for the H_2O-NaCl system. This is the equation of

state of Lvov & Wood (1990) for the calculation of the density of aqueous NaCl solutions. It can be applied at temperatures from 0 to 700°C and at pressures between 1 bar and 10 kbar, *i.e.* at common conditions in the crust. The interest of such an equation of state is its firm theoretical background and its ability to reproduce accurately experimental data with few fitted parameters. The purpose of this paper is to extend the work of Lvov & Wood (1990) to the modelling of liquid-vapour phase equilibria of the H_2O-NaCl system over the wide range of conditions relevant to geological systems (100°C < T < 900°C, and for NaCl composition up to the halite saturation). A brief presentation of the theoretical core of this equation of state is done in the first part. In the second part, values of the physical parameters of the model (dipole moment, dipole size and ion size) are determined. In the third part, first application of the equation of state reveals large deviations between the model and experimental data. Discrepancies are interpreted and modifications of the model are proposed. These modifications are applied in the fourth part. Results are discussed.

Theory

The Mean Spherical Approximation

As stated above, the Mean Spherical Approximation is a technique, which allows one to derive the thermodynamic properties of a fluid from the energy potentials $u_{ij}(r)$ of all particule (i-j) pairs existing in a mixture. It uses the notion of radial distribution function, denoted as $g_{ij}(r)$, which gives the probability of finding a particule (j) at a distance r from the particule (i) of interest. The use of radial distribution functions is particularly interesting, as their knowledge for all types of particule pairs is sufficient for calculating exactly the thermodynamic properties of a fluid (Goodstein, 1975; Fernandez-Prini, 1992). However, the derivation of $g_{ij}(r)$ from $u_{ij}(r)$ is a much more difficult step, and this is this problem that the Mean Spherical Approximation attempts to address.

In a dilute fluid, a remarkable simple relation between $g_{ij}(r)$ and $u_{ij}(r)$ exists:

$$g_{ij}(r) = \exp(-\beta u_{ij}(r)). \quad (1)$$

Eq. (1) is no more valid in dense fluids, for which the influence of all neighbouring particles must be taken into account. This can be formally described by the Ornstein-Zernike equation (Goodstein, 1975):

$$g_{ij}(r) = 1 + c_{ij}(r) + \sum \rho_k \int [g_{ik}(r) - 1] c_{kj}(r,r') dr dr', \quad (2)$$

where the second term on the right-hand side, $c_{ij}(r)$, is called the direct correlation function and describes the direct influence of $u_{ij}(r)$ on $g_{ij}(r)$. The third term represents the indirect influence of all surrounding particles and is a summation over all kinds of k particules around the (i-j) pair with the density ρ_k. It is worth to note that the Ornstein-Zernike equation is a theoretical one, which is exact, and which decomposes clearly the effects of the pair (i-j) and all surrounding pairs (i-k) and (k-j) on $g_{ij}(r)$. This is an integral equation, which introduces $c_{ij}(r)$ as a new unknown. As a consequence, other relations are needed to solve the Ornstein-Zernike equation. The most evident relation expresses the impenetrability of hard spheres representing the particles:

$$g_{ij}(r) = 0, \text{ for } r < \sigma_{ij}, \quad (3)$$

For the case $r > \sigma_{ij}$, there is no firm guideline, and one possibility is to state that:

$$c_{ij}(r) = u_{ij}(r) / kT, \quad (4)$$

where k is the Boltzmann constant, and T is the temperature. This relation strictly holds for $r \rightarrow \infty$ and is the approximation, that is commonly referred to as the Mean Spherical Approximation.

The equation of state

In this study, the MSA solution for a mixture of ionic and polar hard spheres (Adelman & Deutch, 1974; Blum, 1978; Blum & Wei, 1987; Høye & Lomba, 1988; Høye *et al.*, 1988; Wei & Blum, 1987) is applied to describe the thermodynamic properties of the H_2O-NaCl system. The diameter (σ_d) of the dipoles is different from that of the ions, but anions and cations are assumed to have the same size. The more realistic MSA solution for different sizes of cations and anions has been recently developed using more complex equations (Blum & Wei, 1987; Wei & Blum, 1987; Holovko & Protsykevich, 1987). Thus, the present model is a compromise between simplicity and reality.

The equation of state for the ion-dipole mixture is formulated by means of an analytical expression of the Helmholtz free energy and is split into two contributions:

$$A = A^{hs} + A^{MSA}. \quad (5)$$

The first term, A^{hs}, takes into account the repulsive forces between hard spheres, whereas the second one, A^{MSA}, describes the influence of ion-ion, ion-dipole and dipole-dipole interactions, as calculated by the MSA. The Helmholtz free energy, A^{hs}, for a mixture of hard spheres is given by the Boublik (1970) equation of state. The complete equations for the calculation of A^{MSA} are given in Lvov & Wood (1990), and in Thiéry (1996b). All thermodynamic properties have been obtained by analytical differentiations of the Helmholtz free energy with respect to the temperature, molar volume and composition. Derivatives up to the fourth order are analytically calculated by using a software package (Thiéry, 1996a and b) for differentiation and thermodynamic calculations. This was necessary because of the length and complexity of the mathematical expressions.

Determination of dipole moment, dipole size and ion size

The MSA for the ion-dipole mixture is characterized by three physical parameters (the dipole moment, the diameter of the dipole and of the ion), that must be fitted in order to get a good agreement with experimental data.

Dipole moment and dipole size

The first step is the estimation of the parameters for the water, which are the dipole moment and the dipole size. The procedure usually used for the determination of parameters of the van der Waals equation of state can be similarly applied. Values of the dipole moment (μ^c) and size, σ^c_d, at the critical point have been obtained by solving the following equations at T = 374.1°C and P = 221 bar.

$$(\partial^2 A/\partial V^2)_{T,V,n_i} = 0, \quad (6a)$$

$$(\partial^3 A/\partial V^3)_{T,V,n_i} = 0. \quad (6b)$$

Solving this nonlinear set of equations yields the following values: μ^c = 2.243 Debye and σ^c_d = 2.331 Å. The dipole moment for the isolated H_2O molecule (in low-density vapour phase) is 1.85 Debye, but the formation of hydrogen bonds modifies the electric properties of water (Hasted, 1972). The effective dipole moment of water in the liquid phase is higher because of the reorientation and the polarizability of water molecules, and a value of 2.45 Debye is cited at 0°C (Hasted, 1972). It is even remarkable to note that Monte-Carlo simulations reproduce accurately the properties of liquid water when a dipole moment of 2.24 Debye is used (de Pablo *et al.*, 1991; Strauch & Cummings, 1993). Last, the distance between two oxygen atoms in the ice is 2.76 Å, which is quite close to the value of 2.331 Å estimated for σ^c_d. Thus, the MSA applied to water yields values for the dipole moment and size, that are far from unrealistic.

A good reproduction of saturation properties of water is also required at all temperatures. There is the choice to fit either the dipole moment (μ), or the diameter of the dipole (σ_d), or both as a function of the temperature. The dipole moment and the dipole diameter have an antagonist influence on the volatility of a polar component. The polar component becomes more volatile if the dipole moment is decreased or if the dipole diameter is increased. In this study, we have chosen to keep constant the dipole diameter at a value of 2.331 Å, and to express the dipole moment as a function of the temperature. This choice is partly justified by the fact that the dipole moment does decrease with the temperature, as more and more hydrogen bonds are broken when heating the system (Hasted, 1972).

Another refinement of the model would have been to consider the variation of the dipole moment (varying from 1.8 Debye in low-density vapour phase to above 2.2 Debye in a high-density aqueous liquid) as a function of the density of the aqueous solution. In this study, the density dependence has not been taken into account. This choice is validated by Monte-Carlo simulations, which have shown that saturation properties of water can be represented correctly by using a constant dipole moment, that does not depend on the density (de Pablo *et al.*, 1991).

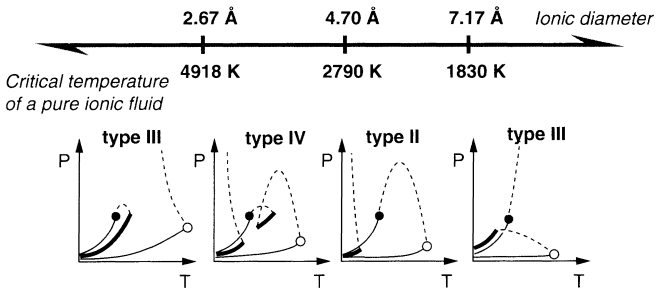

Fig. 1. Influence of the ion diameter (σ_i) on the phase-diagram topology of ion-dipole mixtures (μ = 2.243 Debye, σ_d = 2.331Å). The thin solid lines are the vapour saturation curves of pure fluids. The filled circle is the critical point of H_2O, whereas the empty circle is the critical point of the salt. Dotted curves are the critical curves of the binary system. The thick solid curves represent the pressure-temperature conditions of liquid-liquid-gas equilibria.

Ion size

The third adjustable parameter is the diameter of the ion. But contrary to the water, there is no firm criterion for estimating a value for the ionic diameter. The first possibility would be to adopt a mean value for the crystallographic Pauling radii of the Na^+ and Cl^- ions. Diameters of Na^+ and Cl^- are respectively 0.95 and 1.81 Å, giving a mean value of 1.35 Å (Robinson & Stokes, 1970). Another way would be to consider the thermodynamic properties of pure NaCl, as done by Lvov & Wood (1990). They used a ionic diameter varying between 2.6 and 3.0 Å as a function of temperature, density and composition. Their MSA equation of state for pure salt is found to reproduce properly the volumetric data for molten NaCl when a value of 2.6 Å is used (Lvov & Wood, 1990). Another possibility is to find the best ionic diameter that agrees with the characteristics of the H_2O-NaCl system, that are: (i) the temperature of the NaCl critical point is between 3600 and 4000 K (Knight & Bodnar, 1989; Harvey, 1991); (ii) a continuous critical curve connects the critical points of H_2O and NaCl; (iii) the critical pressures increase with the temperature, at least up to 1123 K (Knight & Bodnar, 1989). A systematic study of the influence of the ionic diameter on the topology of phase diagrams has been carried out in another study (Thiéry, 1996b; Thiéry *et al.*, in press). For a given dipole moment and size (μ = 2.243 Debye and σ_d = 2.331 Å), different types of phase diagrams are obtained when the ionic diameter is modified (Fig. 1) and are classified following the nomenclature of van Konynenburg & Scott (1980). For low ionic diameter (below 2.67 Å), the calculated phase diagram is of type III. The critical curve starting from the ionic component runs to high pressures and does not join the critical point of H_2O. Liquid-liquid-gas equilibria occur at pressures slightly below the saturation pressure of water. For ionic diameters between 2.67 and 4.70 Å, the calculated phase diagrams are of type IV. The critical curve between the critical points of H_2O and NaCl is interrupted by a liquid-liquid-gas curve. For ionic diameters between 4.70 and 7.17 Å, the calculated phase diagrams are of type II. A continuous critical curve connects the critical points of H_2O and NaCl. For ionic diameters above 7.17 Å, the calculated phase diagram is again of type III.

If we choose to constrain the equation of state to reproduce the critical point of NaCl, an ionic diameter between 3.2 and 3.7 Å is found. Such values lead to phase diagrams of type IV. This is in contradiction with the H_2O-NaCl, which is of type II. Conversely, if we constrain the calculated phase diagram to be of type II, the ionic diameters must lie between 4.70 and 7.17 Å. However, such values would yield NaCl critical temperatures between 1830 and 2790 K, far below the expected critical temperature of NaCl (between 3600 and 4000 K). Moreover, a decrease of the critical pressure would be predicted with increasing temperature below 1123 K, and this is in contradiction with the data of Knight & Bodnar (1989).

Thus, it is not possible to find an ionic diameter which agrees with all features of the H_2O-NaCl system, and a compromise must be made. We have chosen to use a constant value of 4.5 Å for the ionic diameter. This yields a NaCl critical temperature of 2911 K. The phase diagram is of type IV. However, the liquid-liquid-gas curve is limited to only a few tenths of degrees near the critical point of water. Therefore, it is barely distinctable in the calculated phase diagrams. Moreover, the calculated critical curve agrees qualitatively with the data of Knight & Bodnar (1989).

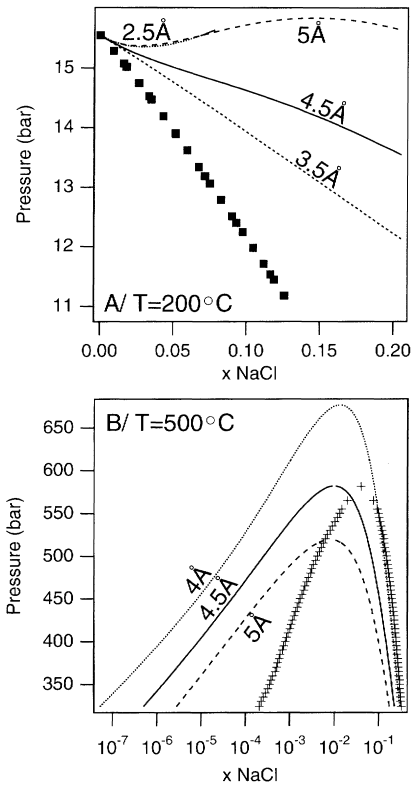

Fig. 2. A) (Pressure - NaCl mole fraction) diagram of the saturation pressures of aqueous NaCl solutions at 200°C. Isotherms are calculated for different ionic diameters (2.5 Å, 3.5 Å, 4.5 Å and 5 Å). Solid squares are smoothed experimental data reported by Haas (1976). B) (Pressure - NaCl mole fraction) diagram for immiscible liquids and gas in equilibria at 500°C. Crosses are smoothed experimental data given by Bischoff (1991). The isotherms are calculated at 4.0 Å, 4.5 Å and 5.0 Å for the ionic diameter and with μ = 2.22 Å and σ_d = 2.331Å.

Model insufficiencies and remedies

A first comparison of the MSA equation of state with pressure-temperature-composition experimental data of liquid-vapour equilibria is shown in Fig. 2. These first attempts clearly reveal that the sole use of the MSA is not appropriate for reproducing the experimental data. Modifications of the model must be brought.

"Pathology" of the model

At low temperatures (for example, at 200°C, Fig. 2A), the MSA model significantly overestimates the NaCl mole fraction of the liquid, whatever the diameter of the ion. Moreover, liquid-liquid-gas immiscibility occurs if the ionic diameter is too low (σ_i = 2.5 Å, for example) or too large (σ_i = 5 Å). The situation is more problematic at high temperatures (at 500°C, for example, Fig. 2B). Significant discrepancies appear between the calculated NaCl mole fractions and experimental data, both in the liquid and the vapour. The MSA model predicts a very low amount of ions in the vapour (y_{NaCl} below 10^{-5}) and in the liquid. A better agreement with liquid composition can be obtained (σ_i = 4.0 Å), but in this case, the pressure is strongly overestimated in the critical region. Moreover, Fig. 2B also shows that the use of a variable ionic diameter as a function of temperature, density and composition, as done by Lvov & Wood (1990), would not be sufficient to obtain a good agreement with the experimental data. All these observations suggest that some essential features of the H_2O-NaCl system are lacking in the present model.

There is a temperature (387°C), at which the MSA model predicts NaCl compositions in the saturated liquids, which is in close agreement with experimental data. Above this temperature, the model underestimates x_{NaCl}, whereas below 387°C, x_{NaCl} values are overestimated. This temperature is chosen as a limit for analysing the cause of the deficiencies of the model and for proposing remedies. This choice will clear up afterwards.

Remedy at high temperatures (T > 387°C)

At the present stage of development of the model, the most questionable point is the absence of ion pairs and larger clusters (Oelkers & Helgeson, 1990). At supercritical temperatures of water, NaCl behaves as a weak electrolyte, as has been demonstrated by conductometric measurements (Quist & Marshall, 1968; Marshall, 1990). The dielectric constant of the fluid decreases dramatically when molar volume or temperature are increased. This decrease of the dielectric constant favours formation of ion pairs (Helgeson *et al.*, 1981). Thus, for liquids above 300°C and for vapours at all temperatures, the NaCl ion pair becomes the dominant species over Na^+ and Cl^- ionic species. Observed discrepancies at high temperatures are not surprising and can only be reduced by taking into account formation of ion pairs. This could explain why the liquid and va-

pour phases are more enriched in NaCl than predicted by the MSA theory. The NaCl ion pair is a strong dipole, and therefore, this species should be considered in our modelling. In other words, the adequate theoretical model to be considered is not the binary ion-dipole system of H_2O dipoles and equivalent Na^+ and Cl^- ions, but the ternary system including the NaCl dipole. Moreover, a chemical equilibrium should be taken into account at each step of the iterative liquid-vapour phase equilibria calculations. This complicates the calculations a lot. Furthermore, the MSA solution for a mixture of two types of dipoles and ions has not yet been established, and would probably lead to more complex equations. All these reasons pushed us to simplify the model by assuming that the dipole moment of NaCl ion pairs is similar in strength with the applied dipole moment of H_2O (2.243 Debye).

Obviously, this is wrong as a value of 9 Debye has been estimated for the dipole moment of the NaCl ion pair (McClellan, 1963–1989). However, water molecules solvate the ion pair (Pitzer & Pabalan, 1986), and this hydration probably decreases the strength of the electrostatic field around the NaCl ion pair.

But, the greater advantage of this assumption is that calculation of chemical equilibria can be avoided. The complex ternary (H_2O, NaCl° ion pair, dissociated NaCl) system is replaced by the binary system of ions and dipoles.

The association of Na^+ and Cl^- ions is treated *a posteriori* by considering a law of mass action:

$$Na^+ + Cl^- = NaCl, \tag{7a}$$

with

$$K = \frac{z(NaCl°)}{z(Na^+)\, z(Cl^-)}, \tag{7b}$$

where K is the association constant, and $z(NaCl°)$, $z(Na^+)$ and $z(Cl^-)$ are the mole fractions of NaCl°, Na^+, and Cl^-. Note here that K is not a true reaction constant, as activities are replaced by the mole fractions. Thus, our association constant K incorporates the effects of activity coefficients.

Once a liquid-vapour equilibrium has been solved for the ion-dipole mixture, $z(H_2O)$, $z(Na^+)$, $z(Cl^-)$ and $z(NaCl°)$ mole fractions are calculated from the z_i mole fraction of ions in the ion-dipole system by:

$$z\,(Na^+) = z\,(Cl^-) = z_i / 2\,, \tag{8a}$$

$$z(NaCl°) = 4Kz_i^2, \tag{8b}$$

$$z\,(NaCl, \text{dissociated}\,) = z_i\,, \tag{8c}$$

$$z\,(NaCl, \text{total}\,) = z_i\,(1+4Kz_i)\,, \tag{8d}$$

$$z\,(H_2O) = z_i\,(1+4Kz_i)\,. \tag{8e}$$

Remedy at low temperatures (T < 387°C)

As seen above (Fig. 2A), at 200°C, our fitted MSA ion-dipole model predicts a larger solubility of NaCl in the aqueous liquid phase than the experimental data. Consideration of ion pair formation, as done by using a law of mass action, would still more increase the discrepancies. This is not surprising, as it is known that Na^+ and Cl^- associate to a smaller extent at lower temperatures. For example, the association constant is 1.41 at 300°C and 0.1 at 200°C (Quist & Marshall, 1968) in saturated liquids at infinite dilution. Therefore, something else is wrong in our model. Reasons of the failure of the MSA ion-dipole model at low temperatures will be discussed in the last paragraph. However, without forwarding some of the conclusions, we propose to use a simple van der Waals attraction (A^{vdW}) term as a correction term, and to modify Eqn. (5) for the Helmholtz free energy as follows:

$$A = A^{hs} + A^{MSA} + A^{vdW}, \tag{9a}$$

$$\text{where } A^{vdW} = -\,a\,/\,V. \tag{9b}$$

The van der Waals parameter, a, is a function of the fluid composition, following a quadratic mixing law (Prausnitz *et al.*, 1986):

$$a = x_d^2\, a_{\text{dipole-dipole}} + 2x_d x_i a_{\text{ion-dipole}} + x_i^2 a_{\text{ion-ion}}, \tag{10}$$

where x_d and x_i are the mole fractions of ions and dipoles, and $a_{\text{dipole-dipole}}$, $a_{\text{ion-dipole}}$ and $a_{\text{ion-ion}}$ are respectively the van der Waals parameters for dipole-dipole, ion-dipole and ion-ion interactions. For the polar component, there is no need to use a van der Waals term with the MSA dipole model. Thus, $a_{\text{ion-dipole}}$ and $a_{\text{ion-ion}}$ can be set to zero, and we propose to use this simple relation:

$$a = x_i^2\, a_{\text{ion-ion}} \tag{11}$$

There remains only one fitting parameter, which is the van der Waals parameter for the ionic component ($a_{\text{ion-ion}}$).

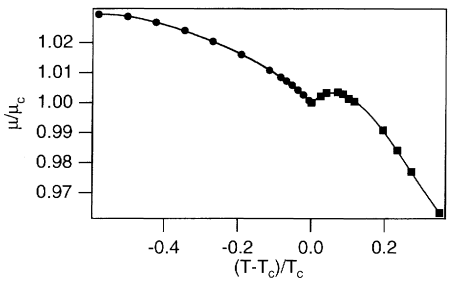

Fig. 3. Variation of the dipole moment as a function of temperature. Solid circles and squares are values of the dipole moment determined respectively by fitting the (pressure-temperature) data for the H_2O saturation curve and the H_2O-NaCl critical curve.

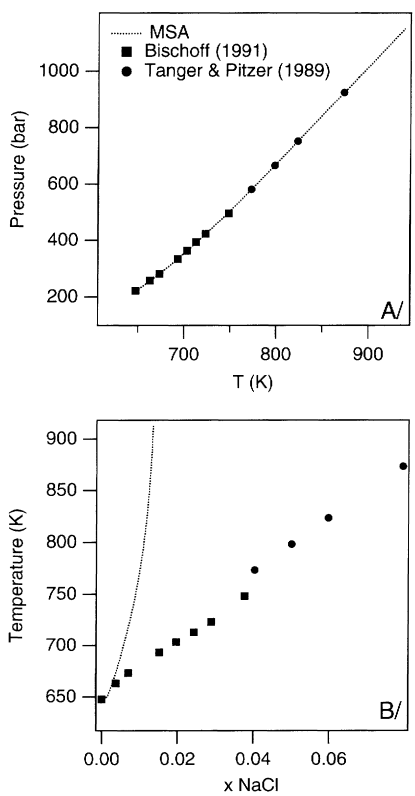

Fig. 4. A) Critical curve calculated by the MSA model (dotted line) in a (pressure-temperature) diagram. Solid squares and filled circles are respectively experimental data reported by Bischoff (1991) and extrapolated values of Tanger & Pitzer (1989). B) idem in a (temperature - NaCl mole fraction) diagram.

Results and discussion

In the last paragraph, it has been shown that additional parameters (association constants, van der Waals attraction term) are necessary with the MSA equation in order to describe the liquid-vapour equilibria of the H_2O-NaCl system. Constant values for the dipole and ion size (σ_d = 2.331 Å and σ_i = 4.5 Å) have been chosen. Now, it remains to evaluate the fitting parameters, which are the dipole moment (μ), the ion association constant (K) and the van der Waals attraction term ($a_{\text{ion-ion}}$), and to compare the prediction of the model with experimental data.

The dipole moment

Two different temperature ranges have been considered for the adjustement of the dipole moment. For temperatures below 374°C, the dipole moment has been obtained by fitting the calculated saturation pressure to experimental data (Haar *et al.*, 1984). The following temperature dependence has been found:

$$\mu/\mu_c = 1 - 0.1240\delta - 0.26051\delta^2 - 0.44201\delta^3 - 0.345\delta^4 \quad (12a)$$

where $\delta = (T - T_c)/T_c$. (12b)

For supercritical temperatures (T>374°C), the dipole moment has been obtained by fitting the calculated critical pressure with experimental data of Bischoff (1991) and extrapolated values from Tanger & Pitzer (1989). The following relation has been obtained:

$$\mu/\mu_c = 1 + 0.11679\delta - 1.1123\delta^2 + 1.3661\delta^3 \quad (13)$$

The dependence of the dipole moment as a function of the temperature is given in Fig. 3. The dipole moment decreases with the temperature, except between 374 and 430°C. This increase of the dipole moment just above the critical point has no physical meaning. It is worth to note that the model is very sensitive to the value of the dipole moment, and use of a smoother function would lead to a significant degradation of the model. Otherwise, the general decrease of the dipole moment is not surprising, as it is caused by the breaking of hydrogen bonds with the temperature. Thus, the increase between 374 and 430°C is believed to be an artefact resulting from the simple assumptions we have adopted (constant size for

the dipoles and the ions). The calculated and experimental H_2O-NaCl critical curves are shown in Fig. 4. As expected, good agreement is obtained on the pressure-temperature plot, but the predicted critical NaCl mole fraction is strongly underestimated if the formation of ion pairs is not taken into account.

The association constants

Association constants have been estimated by considering discrepancies between experimental data of Bischoff & Pitzer (1989) and values calculated by the MSA ion-dipole model:

$$K = (z(\text{NaCl, total})/z_i - 1)/(4z_i). \quad (14)$$

where z (NaCl,total) is the NaCl mole fraction experimentally measured (including Na^+, Cl^- ions and $NaCl^o$ ion pairs), and z_i is the ion mole fraction calculated by the MSA for the ion-dipole mixture. Association constants have been calculated with Eq. (14) by using the liquid-vapour compositions at 500°C plotted in Fig. 5A. Calculated values are given in Fig. 5B and 5C.

Association constants depend on temperature, density and composition of the solutions, and the problem is to find a suitable formulation. Ion pair formation occurs when the dielectric constant decreases (Helgeson *et al.*, 1981). Thus, association is expected to increase dramatically with the temperature and to decrease with the density of the fluid phase. As shown by Marshall & Quist (1967), ion pair formation in aqueous solutions is accompanied by a net release of water molecules, because ion pairs are less hydrated than ions:

$$(Na^+)H_2O_p + (Cl^-)H_2O_q = (NaCl)H_2O_m + n\ H_2O. \quad (15)$$

Thus, an association constant K^o should be used by considering hydrated species:

$$K^o = \frac{a(\text{NACl},H_2O_m)a''(H_2O)}{a(Na^+,H_2O_p)a(Cl^-,H_2O_q)}, \quad (16)$$

where $a(\text{NaCl},H_2O_m)$, $a(Na^+,H_2O_p)$, $a(Cl^-,H_2O_q)$ refer to the activities of the hydrated species.

After some transformation, Eq. (16) can be written as:

$$\log K = \log K^o - n \log a\ (H_2O), \quad (17)$$

where K is the association constant for the association reaction ($Na^+ + Cl^- = NaCl$) on a water-free basis and n is the hydration number ($n = p + q - m$).

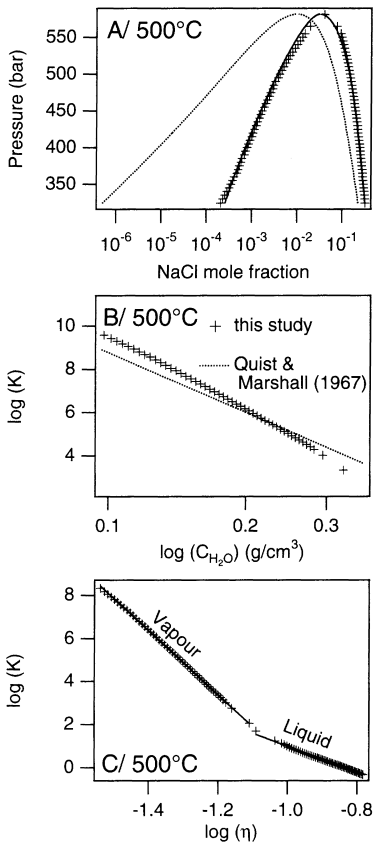

Fig. 5. A) Liquid-vapour equilibria isotherm at 500°C in a (pressure - NaCl mole fraction) diagram. Crosses are smoothed experimental data of Bischoff (1991). The dotted line is the liquid-vapour immiscibility curve calculated by the MSA equation for the ion-dipole mixture. The solid line is the immiscibility curve obtained when the NaCl ion pair formation is considered. B) Logarithmic plot of the association constants (on the molality scale) against the H_2O molarity. Crosses are the association constants determined along the vapour branch using Eq. (14). The points are aligned along a straight line. The dotted line is given by Marshall & Quist (1967) and is plotted for comparison. C) Logarithmic plot of the K constants (on the mole fraction scale) against the reduced density η. Crosses are calculated using Eq. (14) and the smoothed experimental data of Bischoff (1991). Points are aligned along two different lines, one for the vapour and the other for the liquid.

When the association constant is expressed on the molarity unit basis as suggested by Quist & Marshall (1967), the H_2O activity can be replaced by the H_2O molarity (C_{H_2O}):

$$\log K = \log K^{\circ} - n \log C_{H_2O}. \quad (18)$$

On the molality basis, Eq. (18) becomes:

$$\log K = \log K^{\circ} - (n-1) \log C_{H_2O} + \log(M_{H_2O}), \quad (19)$$

where M_{H_2O} is the molar weight of H_2O (M_{H_2O} = 18 g/cm^3).

Conductometric measurements of aqueous solutions of Quist & Marshall (1968) reveal that association constants at infinite dilution for temperatures between 0 and 800°C and for densities below 0.80 g/cm^3 could be fitted by Eq. (19) with a constant K°, that is independent of the density and of the dielectric constant. Thus, the availability of water molecules in the system has a large influence on the value of the association constant. A plot of the logarithm of the fitted association constant (on the molality basis) for the vapour as a function of the logarithm of the H_2O molarity at 500°C is given in Fig. 5B. A straight line is obtained with a slope of -11.7, which corresponds to an hydration number of 12.7. This latter number agrees quite well with the value of 10.2 given by Quist & Marshall (1968). However, deviations are observed (Fig. 5B) between the association constants determined in this study and those measured at infinite dilution by Marshall & Quist (1967) for densities below 0.1 g/cm^3 and above 0.3 g/cm^3 (up to a factor 2 at 1 g/cm^3). Although our model is based on some physical reality, discrepancies are still large. It would be possible to use directly the association constants of Marshall & Quist (1967) with our model, but this would lead to a poor agreement with the experimental data. Moreover, an activity coefficient model should be used for NaCl-bearing fluids in order to calculate the proportion of ion pairs from the mass action law, and the calculation of activity coefficients in electrolyte solutions is not a simple problem either. For all these reasons, it has been preferred to treat the association constants as a fitting parameter. For a given temperature, it was found that the K constant could be well represented by a function like:

$$\log K = A + B \log(\eta), \quad (20a)$$

where η is a reduced density:

$$\eta = (x_d b_d + x_i b_i) / (4V), \quad (20b)$$

V is calculated by the MSA equation of state, and b_d and b_i are the covolumes of the dipolar and ionic components in the system:

$$b_d = 2/3\ \pi N_a \sigma_d^3, \text{ and} \quad (20c)$$

$$b_i = 2/3\ \pi N_a \sigma_i^3. \quad (20d)$$

A plot of the logarithm of the K association constants (on the mole fraction basis) with respect to the logarithm of η is given in Fig. 5C. Two distinct lines are obtained for the liquid and the vapour.

Association constants K (on the mole fraction basis) have been regressed as follows:

for the vapour phase , T<660 K (387°C),

$$\log K_V = 91.536 - 0.1638\ T + (32.051 - 0.07384\ T) \log \eta, \quad (21a)$$

for T>660 K (387°C),

$$\log K_V = -29.548 + 0.019683\ T + (-29.063 + 0.018585\ T) \log \eta, \quad (21b)$$

for the liquid phase, T<660 K (387°C),

$$\log K_L = -\infty, \quad (21c)$$

for 660 K (387°C)< T<773 K (500°C),

$$\log K_L = -14.9541 - 15.261/(T-660) + 0.012944\ T + (-17.3808 - 12.417/(T-660) + 0.014786\ T) \log \eta, \quad (21d)$$

for T>773 K (500°C),

$$\log K_L = -6.74 - 7.77 \log \eta. \quad (21e)$$

An interpolation function has been used in order to ensure a smooth transition in the critical region between vapour and liquid:

$$\log K = (1-\alpha) \log K_L + \alpha \log K_V, \quad (22a)$$

$$\alpha = 1 + \left(\tanh\left(10 \log \frac{\eta}{\eta_c}\right)\right)/2, \quad (22b)$$

where $\log(\eta_c)$ is equal to -1.095.

α takes a value between 0 (for a liquid-like phase) and 1 (for a vapour-like phase).

A comparison of our association constants at infinite dilution with those of Quist & Marshall (1968) is given in Fig. 6. At temperatures above 400°C, our model underestimates the K° association constants in solutions at infinite dilution and

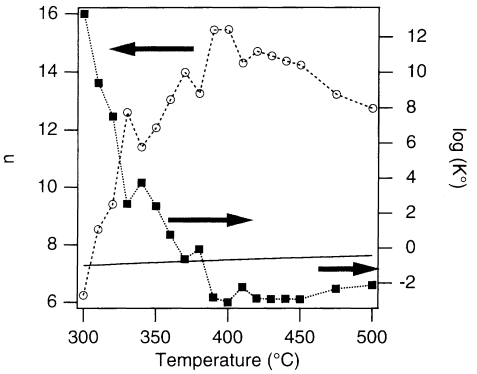

Fig. 6. Evolution of the parameters describing ion association as a function of the temperature. Filled squares are the logarithmic values of the K° association constants (on the molality scale) at infinite dilution and for a density of 1 g/cm^3, that have been estimated from the data reported by Bischoff (1991). Empty circles are the hydration numbers. The straight line represents the smoothed K° values given by Quist & Marshall (1968).

for a density of 1 g/cm^3 by a factor of two when compared to the constants of Quist & Marshall (1968). But both association constants follow the same trend as a function of temperature. The predicted hydration number decreases with the temperature from 15.4 at 400°C to 12.7 at 500°C. These values are larger than the value of 10.2 estimated by Quist & Marshall (1968). Our association constants are in good agreement with values of Quist & Marshall (1968) for densities between 0.2 and 0.3 g/cm^3 (see Fig. 5B). Below 400°C, major discrepancies are observed between our model and association constants of Quist & Marshall (1968). Values of log(K°) strongly increase when the temperature is lowered. Overestimation of dissociation constants at infinite dilution up to a factor of 14 is observed for all densities. This alteration of the model is due to our approximation to neglect association in NaCl-rich saturated liquids below 387°C.

Comparison of vapour-liquid equilibria calculated by our model with the smoothed experimental data reported by Bischoff (1991) are given in Fig. 7A and 7B for temperatures between 400 and 500°C. The agreement with experimental data is good, although the equation of state is slightly less accurate than the equation of Anderko & Pitzer (1991). Relative deviations for the pressure and compositions are mostly below 3%. At higher temperatures (500–800°C), the only available experimental data are those of Bodnar (1985), reviewed by Chou (1987), that have been obtained on synthetic fluid inclusions trapping H_2O-NaCl fluids of known composition. A good agreement of the MSA equation of state, combined with association constants given by Eq. (21e), is found with experimental data (Fig. 8). Considering the low number of fitting parameters and the simplicity of Eq. (21e), it is believed that the model can be extrapolated to higher temperatures. It is interesting to note that the equation of state is applied here to mixtures which are rich in NaCl, and have properties closer to fused salts than aqueous solutions.

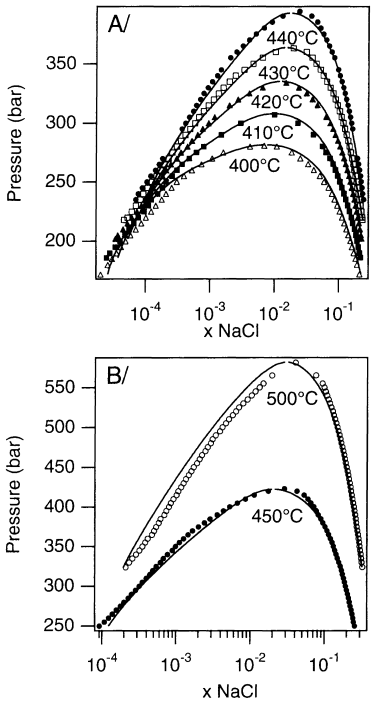

Fig. 7. A) Comparison of the liquid-vapour immiscibility curves calculated from the equation of state with the smoothed data reported by Bischoff (1991) in a pressure-NaCl mole fraction diagram at 400°C, 410°C, 420°C, 430°C and 440°C. B) Comparison of the liquid-vapour immiscibility curve calculated from the equation of state with the smoothed data reported by Bischoff (1991) in a (pressure - NaCl mole fraction) diagram at 450°C and 500°C.

The van der Waals attraction term

Below 387°C, discrepancies between the MSA for the ion-dipole mixture and the H_2O-NaCl system

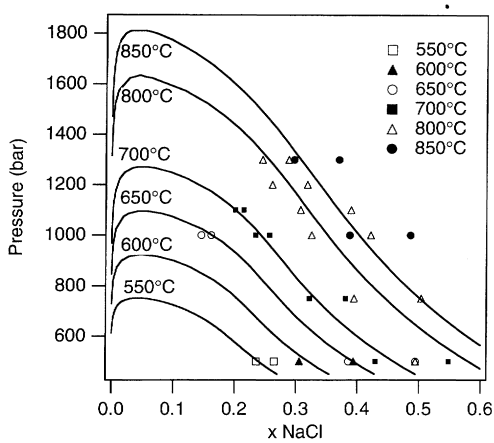

Fig. 8. Comparison of the liquid-vapour immiscibility curves calculated from the equation of state with data of Bodnar (1985) and reviewed by Chou (1987) in a (pressure - NaCl mole fraction) diagram at 550°C, 600°C, 650°C, 700°C and 800°C.

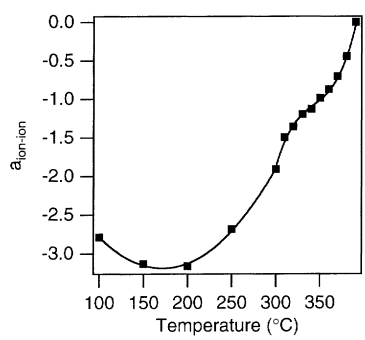

Fig. 9. Dependence of the $a_{ion-ion}$ parameter on the temperature, estimated by fitting the smoothed data reported by Haas (1976) and Bischoff (1991).

have been reduced by considering a van der Waals term ($a_{ion-ion}$). Experimental data of Haas (1976) for saturated liquids have been used to fit the $a_{ion-ion}$ parameter at different temperatures. The dependence of the $a_{ion-ion}$ parameter is given in Fig. 9. As expected, $a_{ion-ion}$ tends to zero when the temperature approaches 387°C. As it can be observed in Fig. 9, the $a_{ion-ion}$ parameter cannot be represented by a simple function of the temperature. The following expressions have been obtained for the $a_{ion-ion}$ parameter:

for T between 373 K (100°C) and 573 K (300°C),

$$a_{ion-ion} = 12.32 - 0.069712\ T + 0.000078335\ T^2, \quad (23a)$$

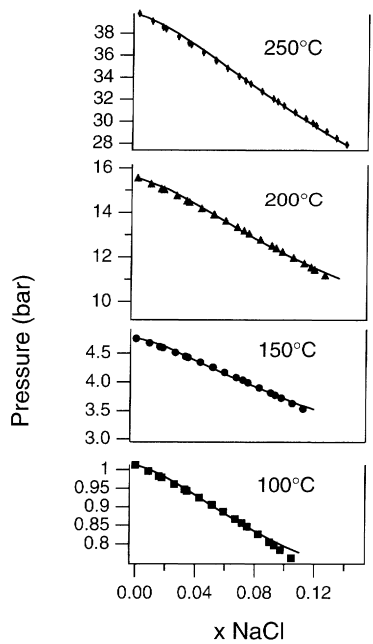

Fig. 10. Comparison of the liquid-vapour immiscibility curves calculated from the equation of state with the smoothed data reported by Haas (1976) in a (pressure - NaCl mole fraction) diagram at 100°C, 150°C, 200°C and 250°C.

for T between 573 K (300°C) and 660 K (387°C),

$$a_{ion-ion} = -1382.3 + 6.7191\ T - 0.010909\ T^2 + 0.005912\ T^3, \quad (23b)$$

and for $T > 660$ K (387°C),

$$a_{ion-ion} = 0. \quad (23c)$$

A comparison of calculated values from the equation with smoothed experimental data between 100 and 390°C reported by Haas (1976) and Bischoff (1991) is visualized in Fig. 10, 11A and 11B. The agreement with experimental data is good (relative deviation for the pressure below 2%, and for the mole fractions below 1%). Before giving interpretations of the meaning of this van der Waals term, some words should be given on the nature of the correction it brings to the MSA ion-dipole model. The activity of H_2O in the saturated liquid can be calculated by:

$$a_{H_2O} = f_{H_2O} / f^{\circ}_{H_2O} \approx P / P_{sat}, \quad (24)$$

where f_{H_2O} is the fugacity of H_2O in the mixture, $f^\circ_{H_2O}$ is its value in the reference state (the pure solvent at the saturation point), and P_{sat} is the saturation pressure of pure water at the temperature of interest. For example, at 200°C and x_{NaCl} = 0.12, a look at Fig. 2A reveals that the MSA ion-dipole model (with an ion diameter of 4.5 Å) yields a H_2O activity of 0.95 instead of the correct value of 0.73. Thus, the ion-dipole model overestimates the H_2O activity below 387°C. This means also that the activity coefficient of ions (including both Na^+ and Cl^- ions) is underestimated (this is a consequence of the Gibbs-Duhem relation). Thus, the function of the van der Waals term is to decrease the water activity and to increase the activity coefficient of ions.

Two interpretations can be given to the underestimation of activity coefficients of ions by the MSA ion-dipole model. The first one is given by some authors (Henderson *et al.*, 1986; Jin & Donohue, 1991), who note that nonprimitive models tend to underestimate strongly the activity coefficients of ions. Such a problem would be inherent to the assumptions, on which nonprimitive models are built (Jin & Donohue, 1991). Nonprimitive models do not take into account the solvation of ions. Water molecules form a sheath around the ions, and this leads to a weakening of the magnitude of long-range Coulombic forces between ions. Thus, a correct treatment of electrolyte solutions should consider this screening effect.

The second interpretation, which can be given, is found when looking at the similarities of our equation of state with the HKF model (Helgeson *et al.*, 1981). Indeed, the HKF model is composed of three terms. Two of them (the Debye-Hückel term and the Born term) describe ion-ion and ion-solvent interactions. Such type of interactions are described in our model by the MSA ion-dipole model. The third term, the so-called "Brønsted" or "Guggenheim" term describes specific short-range interactions between anions and cations (Brønsted, 1922), and its contribution is also to increase the activity coefficient of ions. Thus, the van der Waals term of our model could well play the same role.

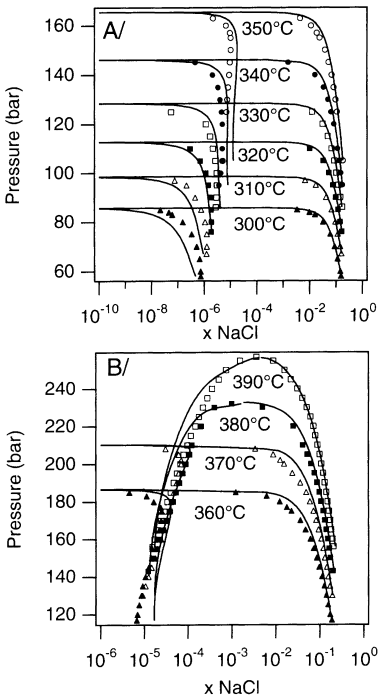

Fig. 11. A) Comparison of the liquid-vapour immiscibility curves calculated from the equation of state with the smoothed data reported by Bischoff (1991) in a (pressure - NaCl mole fraction) diagram at 300°C, 310°C, 320°C, 330°C, 340°C and 350°C. B) Comparison of the liquid-vapour immiscibility curves calculated from the equation of state with the smoothed data reported by Bischoff (1991) in a (pressure - NaCl mole fraction) diagram at 360°C, 370°C, 380°C and 390°C.

Conclusion

This study represents one step further towards the understanding of the thermodynamic properties of H_2O-NaCl fluids and, in particular, of the liquid-vapour immiscibility. A heavy theoretically sound equation of state is applied here for the modelling of the liquid-vapour equilibria of the H_2O-NaCl system. The MSA solution for the theoretical ion-dipole mixture has been chosen here, as it is able to give an analytic and realistic representation of the ion-ion, ion-dipole and dipole-dipole interactions. However, first comparison of this physical model with liquid-vapour experimental data clearly reveals that it cannot be directly used for modelling of the properties of the H_2O-NaCl system. Large discrepancies occur indeed between the calculated and measured NaCl compositions for saturated vapours and liquids at all temperatures. These discrepancies have been strongly reduced by taking into account the speciation of fluids. By fitting association constants for the ion pair formation, it was then possible to reproduce

the experimental data above 387°C with a good accuracy. Below 387°C, the MSA ion-dipole model predicts too high salinities in saturated liquids. The incorporation of a van der Waals term in the Helmholtz free energy allows one to reproduce the experimental data within experimental error. It is believed that this term represents either the effect of the solvation of ions by water molecules, or specific short-range interactions between anions and cations. Despite of the severe assumptions of the model, it is remarkable that the fitted association constants lie in the same range of magnitude as the constants measured by Quist & Marshall (1968). This clearly shows the robustness of such an approach. At the present time, the MSA ion-dipole model is the single equation of state, which is applicable from dilute aqueous solutions to fused salts. Moreover, the model uses a low number of fitting parameters, that have in addition a clear physical meaning (dipole moment, ion and dipole diameters). Thus, the MSA ion-dipole model represents a promising way for the construction of predictive models describing the thermodynamic properties of geological fluids.

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