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## Equations of State for the NaCl-H<sub>2</sub>O-CH<sub>4</sub> System and the NaCl-H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub> System: Phase Equilibria and Volumetric Properties above 573 K

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**Abstract**—An equation of state (EOS) based on thermodynamic perturbation theory is presented for the NaCl-H<sub>2</sub>O-CH<sub>4</sub> system. This equation consistently reproduces *PvTX* properties and phase equilibria with an accuracy close to that of data in the temperature, pressure and concentration ranges from 648 K to 873 K, 0 to 2500 bar and up to 2.37 mol % NaCl. Good agreement with recent ternary immiscibility data from 673 K to 873 K suggests that the EOS may provide accurate predictions for NaCl concentrations as high as 40 mol %. We could not find any experimental data above 873 K that can be used to validate the predictions of the EOS inside the ternary. However, parameters for the mixed ternary system were established from parameters evaluated for pure and binary systems and accurate combination rules. Therefore, predictions in the ternary should be reliable to the high temperatures and pressures where the EOS for the lower order systems are valid (about 1300 K and 5000 bar). Using the same combining approach, an EOS for the quaternary NaCl-H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub> is constructed on the basis of parameters from our earlier model for the NaCl-H<sub>2</sub>O-CO<sub>2</sub> system and the present NaCl-H<sub>2</sub>O-CH<sub>4</sub> model. This suggests that predictions of the quaternary EOS are reliable also to about 1300 K and 5000 bar. Copyright © 2003 Elsevier Science Ltd

### 1. INTRODUCTION

Methane bearing fluids have been reported in many geologic settings, such as geothermal systems (White et al., 1963), geopressured-geothermal reservoirs (Kharaka et al., 1985; Riney, 1992), tectonic melanges (Vrolijk et al., 1988), midocean ridge hydrothermal systems (Kelly, 1996), and high-grade diagenetic and low-grade metamorphic zones (Mullis et al., 1994). Knowledge of the thermodynamic properties, particularly phase equilibria, of these fluids is essential to the interpretation of these Earth processes. For example, it has been shown that fluid immiscibility contributes to the evolution of systems such as oil deposits (Alston et al., 1985; Dubessy et al., 2001), Mississippi Valley ore deposits (Hanor, 1979), porphyry ore deposits (Ramboz, 1979), circulating sea-floor hydrothermal fluids (Welhan and Craig, 1979; Bischoff, 1980; Fournier, 1987), geothermal fluids (Truesdell and White, 1973) and metamorphic fluids (Crawford, 1981). In addition, *PvTX* properties are used extensively in fluid flow simulators (Lichtner, 1985; Pruess, 1987) and in interpretations of fluid inclusion data (Ramboz et al., 1985; Diamond, 1990; Bodnar, 1995).

The compositions of natural aqueous solutions are complex. However, NaCl is the major salt component and CO<sub>2</sub> as well as CH<sub>4</sub> are the most frequently encountered gases. Therefore, an adequate model for the interpretation of many geological processes is provided by the behavior of the quaternary system: NaCl-H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub>. Because our understanding of aqueous solutions is imperfect, it is not yet possible to construct models based wholly on first principles, and model development must rely heavily on experimental data. However, the range of temperature and pressure where geological processes can occur

is extremely large, and experimental data are available for only a relatively low *T-P* region and a limited composition range (see Table 1). Therefore, to reliably extrapolate experimental data, it is very important to develop modeling technology that is as soundly based on the theory of dense fluids as possible. Following the work of Anderko and Pitzer (1993) and their predecessors (Boublik, 1970; Stell et al., 1972, 1974; Gubbins and Twu, 1978; Cotterman et al., 1986; Dimitrelis and Prausnitz, 1986), we (Duan et al., 1995) developed an EOS for the important NaCl-H<sub>2</sub>O-CO<sub>2</sub> system based on thermodynamic perturbation theory. Combining rules and pure or binary system parameters were used to establish parameters for mixed systems within the ternary with poor data availability. When data in the mixed systems were available, adjustable mixing parameters were used to improve the fit to the mixed system data. This model predicts properties including *PvTX* relations, immiscibility, solubilities and activities with an accuracy close to that of experimental data from 573 to ~1300 K, 0 to over 5000 bar, and up to 12 mol % NaCl mole fraction.

As in the CO<sub>2</sub> containing system, the immiscibility region of the NaCl-H<sub>2</sub>O system is greatly increased by the addition of CH<sub>4</sub>. Here, we present an EOS for the NaCl-H<sub>2</sub>O-CH<sub>4</sub> system that is based on the same formalism as was used for the NaCl-H<sub>2</sub>O-CO<sub>2</sub> EOS and that is applicable to a similar *TPX* range. Both models are then used to form a model of the quaternary NaCl-H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub> system. The same approach to treat mixtures in the ternary models was used to parameterize this model. We could not find any data for the quaternary system that can be used to validate the final model. However, the agreement of our ternary EOS predictions with available data and the testing of the accuracy of the combination rules (see below) suggest that this EOS will provide at least a good approximation of the thermodynamic properties of the quaternary system to high temperature and pressure.

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Table 1. Available thermodynamic data\* in the NaCl-H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub> system.

| Systems                                           | T(K)     | P(bar)  | Data type                                      |
|---------------------------------------------------|----------|---------|------------------------------------------------|
| H <sub>2</sub> O                                  | 273-2073 | 1-24000 | PVT, VLE                                       |
| CO <sub>2</sub>                                   | 220-1273 | 0-5000  | PVT, VLE                                       |
| CH <sub>4</sub>                                   | 100-773  | 0-3000  | PVT, VLE                                       |
| H <sub>2</sub> O-CO <sub>2</sub>                  | 273-1073 | 1-5000  | VLE, PVT, solubility                           |
| H <sub>2</sub> O-CH <sub>4</sub>                  | 273-698  | 1-2500  | VLE, PVT, solubility                           |
| CO <sub>2</sub> -CH <sub>4</sub>                  | 220-520  | 1-1000  | VLE, PVT                                       |
| H <sub>2</sub> O-CO <sub>2</sub> -CH <sub>4</sub> | 423      | 345     | solubility                                     |
| NaCl-H <sub>2</sub> O                             | 260-1073 | 1-8000  | VLE, mineral solubility, PVT, osmotic pressure |
| NaCl-H <sub>2</sub> O-CO <sub>2</sub>             | 273-1073 | 1-3000  | PVT, VLE, gas solubility                       |
| NaCl-H <sub>2</sub> O-CH <sub>4</sub>             | 273-873  | 1-2500  | PVT, VLE, gas solubility                       |

\* There are very few data points (<10 in general) outside of the T-P ranges listed here.

## 2. THE EQUATION OF STATE

An equation of state will produce accurate predictions for the largest region of intensive variable space when its functional form captures the qualitative behavior of a system as a function of  $TvX$ . Here, we use the compressibility equation,  $Z = Pv/RT$ , where  $P$  is pressure in bars,  $v$  is molar volume, and  $T$  is temperature in K. Since we use the compressibility equation as our equation of state, the Helmholtz free energy,  $a$ , may be obtained from this equation via integration using:

$$Z = -v[\partial(a/RT)/\partial v]_T. \quad (1)$$

In EOS construction using perturbation theory, the equation of state for the system is written as a sum of contributions from a reference system and a perturbation term (Stell et al., 1972, 1974; Twu and Gubbins, 1975; Gubbins and Twu, 1978; Cotterman et al., 1986; Dimitrelis and Prausnitz, 1986; Anderko and Pitzer, 1993; Duan et al., 1995). Criteria for reference system selection are that the potential interactions incorporated in the system qualitatively represent the interactions between the particles in the real system. In addition, its thermodynamic behavior should be represented by relatively simple analytic forms based on approximate theories of dense fluids. We chose  $TvX$  as independent variables. Perturbation corrections account for differences between the real system and the idealized reference system. The better the reference system, the lower the magnitude and complexity of the perturbation terms needed to represent the measured behavior and the better the extrapolation properties of the EOS.

In calculating the contribution of the reference system (see Anderko and Pitzer, 1993; Duan et al., 1995) to the compressibility, we assume that NaCl is associated for temperatures above 573 K, that H<sub>2</sub>O and NaCl are hard sphere molecules with dipole moments, and that CO<sub>2</sub> and CH<sub>4</sub> are hard spheres without dipoles. The reference system is divided into a hard

sphere contribution and a contribution that accounts for the dipole interactions. The perturbation term is based on the virial equation. This leads to the following equation for  $Z$ :

$$Z = Z^{hd} + Z^{dip} + Z^{per}. \quad (2)$$

The hard-sphere contribution (including mixing),  $Z^{hd}$ , is calculated using the equations of Boublik (1970). The dipole contribution,  $Z^{dip}$ , is modeled using the equations given by Stell et al. (1972, 1974). The perturbation contribution,  $Z^{per}$ , which accounts for the residual effects, is represented by the virial term proposed by Anderko and Pitzer (1993). Mixed systems are treated by developing parameters from those of lower systems (e.g., pure systems and binaries) using combination rules. When data are available for mixtures, mixing parameters are adjusted to optimize the fit to the data. The mixing rules for these equations have been summarized in Anderko and Pitzer (1993) and Duan et al. (1995). For convenience, we have included a compilation of all the equations and definitions required to calculate  $Z$  in Appendix 1. The equations for the fugacity coefficient (free energy) are given in Eqns (A1-A23) in the appendix of Duan et al. (1995). In that paper,  $\Delta\mu_{i,per}$  should be divided by  $RT$ . Several typographical errors found in the presentation of equations in Anderko and Pitzer (1993), and have been corrected here in Appendix 1.

## 3. PARAMETERIZATION

The parameters for pure NaCl and H<sub>2</sub>O and the binary interaction parameters for NaCl-H<sub>2</sub>O mixtures are adopted from Anderko and Pitzer (1993) except that the temperature ( $\theta$ ) functions, where  $\theta = T(K)/100$ , for the parameters,  $a_{NaCl}$  and  $\gamma_{H_2O-NaCl-NaCl}^0$  should read:  $a_{NaCl} = \{14.412 + 5.644 \exp[-0.4817(\theta-8.959)^2] - 10 \exp[-0.6154(\theta-5.403)^{3.26}]\} \cdot 10^6$  and  $\gamma_{H_2O-NaCl-NaCl}^0 = 2.057 + 0.06552(\theta-9.73157) +$

Table 2. Temperature functions for parameters for the pure CH<sub>4</sub> system.

|                                                            |                                                                              |
|------------------------------------------------------------|------------------------------------------------------------------------------|
| $\mu_{CH_4}$ (D)                                           | 0                                                                            |
| $b_{CH_4}$ (cm <sup>3</sup> · mol <sup>-1</sup> )          | 44.0                                                                         |
| $a_{CH_4}$ (bar · cm <sup>6</sup> · mol <sup>-1</sup> )    | $(2.3309527 - 1.547078/T_r + 3.4764764/T_r^2 - 2.26654635/T_r^4) \cdot 10^6$ |
| $(ac)_{CH_4}$ (bar · cm <sup>6</sup> · mol <sup>-1</sup> ) | $-2.79922367e + 06 - 1.55522557e + 06/T_r$                                   |
| $(ad)_{CH_4}$ (bar · cm <sup>6</sup> · mol <sup>-1</sup> ) | $1.04079403e + 07 + 1.0029429e + 07/T_r$                                     |
| $(ae)_{CH_4}$ (bar · cm <sup>6</sup> · mol <sup>-1</sup> ) | $-4.31589522e + 07$                                                          |

$$T_r = T(K)/190.555.$$

Table 3. Temperature functions for mixing parameters for the binary system H<sub>2</sub>O-CH<sub>4</sub>.

|                                                        |                                                                                                                                                                                                  |
|--------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\alpha_{ij}$                                          | $-9.66938 + 0.017232T - 8.0121744e-06T^2 + 1856.526/T$ ; if $T < 623.15$ K<br>$1.8132932 - 4.084253e-04T + 1.11761627e-07T^2 - 416.07276/T$ ; if $623$ K $< T \leq 712$ K<br>1.0; if $T > 712$ K |
| $\gamma_{ij}, \gamma_{ijj}$                            | 1.0                                                                                                                                                                                              |
| $\delta_{ijij}, \delta_{ijijj}, \delta_{ijijj}$        | 1.0                                                                                                                                                                                              |
| $\epsilon_{ijijj}, \epsilon_{ijijj}, \epsilon_{ijijj}$ | $-1.24172253 + 2.55545498e-03T - 8.0087098e-07T^2 + 477.226866/T$                                                                                                                                |
| $\epsilon_{ijijj}$                                     |                                                                                                                                                                                                  |

i and j represent CH<sub>4</sub> and H<sub>2</sub>O, respectively.

$0.2058 \exp[-1.604(\theta-5.667)^2]$ . To complete the parameterization for the ternary NaCl-H<sub>2</sub>O-CH<sub>4</sub> system, the parameters for pure CH<sub>4</sub>, the binary mixture interaction parameters for H<sub>2</sub>O-CH<sub>4</sub> and NaCl-CH<sub>4</sub> and the ternary interaction parameters for NaCl-H<sub>2</sub>O-CH<sub>4</sub> must be evaluated.

The principal problem with developing EOS models for the NaCl-H<sub>2</sub>O-CH<sub>4</sub> and NaCl-H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub> systems is the lack of sufficient data in the mixed systems. For convenient reference and to stimulate more data collection research, we summarize the available data for the quaternary system in Table 1. Note that the data for the binary H<sub>2</sub>O-CH<sub>4</sub> are scarce and that there is only a single data point for the H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub> ternary. Even the data in the pure CH<sub>4</sub> system are limited.

### 3.1. The Pure CH<sub>4</sub> System

The EOS in the Appendix includes hard sphere, dipole and perturbation contributions to the compressibility,  $Z$ . Since the dipole moment of CH<sub>4</sub> is zero,  $Z^{dip}$  is zero. The van der Waals

co-volume,  $b_{CH_4}$ , appears in the hard sphere (Eqns A2-A6) and perturbation contributions (Eqns A21 to A28). This parameter and the parameters,  $a$ , ( $ac$ ), ( $ad$ ) and ( $ae$ ), in the perturbation term, Eqn. (A21 to A32) are evaluated by fitting Eqn. (A1) to  $PvT$  data for the pure CH<sub>4</sub> system. These data were reviewed by Duan et al. (1992a). 1001 data points, covering a range of 273 to 773 K and 0 to 3000 bar, were used in the parameterization. All the data sets agree within  $\sim 0.45\%$  in density. Table 2 gives the resulting temperature dependence for the pure CH<sub>4</sub> system parameters. The calculated PVT values have a standard error of 0.49% in density. The maximum deviation is 2.1% at 1000 bar and 273 K. We could not find any data for the pure CH<sub>4</sub> system above 773 K. However, calculations of this CH<sub>4</sub> EOS deviate less than 1.5% in volume up to  $\sim 1300$  K and 5000 bar from those of our corresponding states EOS that has been shown to be accurate well beyond the T-P range of the experimental data (Duan et al., 2000). The present CH<sub>4</sub> EOS is also in good agreement (within 1.7% in density) with the high pressure point of Triklis and Linshits (1967) at 673 K and 8106 bar.

### 3.2. The Binary H<sub>2</sub>O-CH<sub>4</sub> System

Mixed system parameters in the hard sphere and dipole contributions,  $Z^{hd}$  and  $Z^{dip}$ , to the compressibility equation are determined from pure system parameters by combination rules originally given by Boublik (1970), Stell et al. (1972, 1974) and slightly modified by Anderko and Pitzer (1993) and Duan et al. (1995) (see Eqns. A2 to A20).

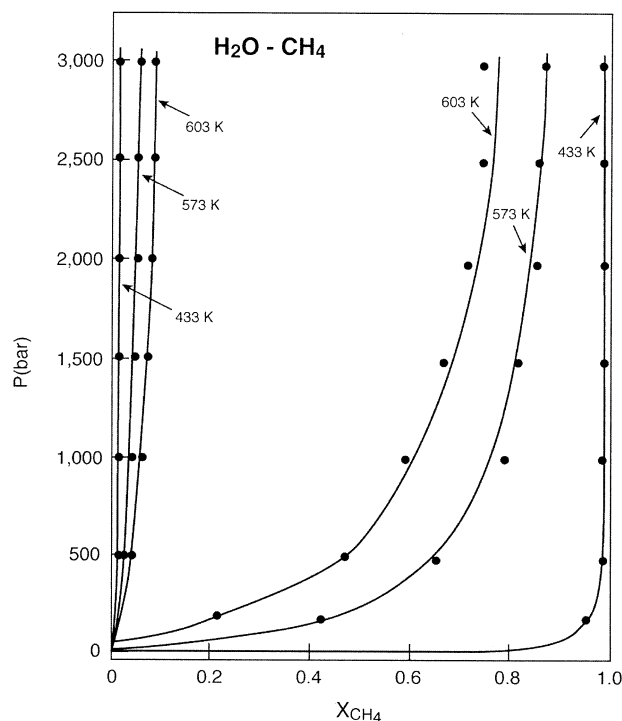


Fig. 1. Liquid-vapor phase equilibria in the system H<sub>2</sub>O-CH<sub>4</sub>. The solid line is the prediction of the EOS of this study, and the symbols are the data of Sultanov et al. (1971, 1972).

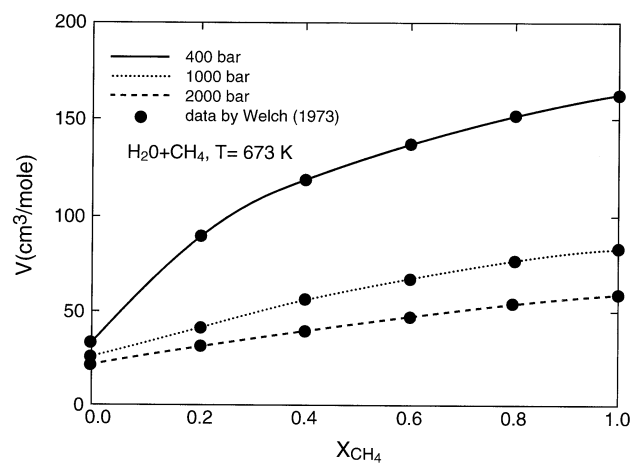


Fig. 2. Comparison of the experimental volumetric properties of the mixtures in the system H<sub>2</sub>O-CH<sub>4</sub> with the prediction of this EOS. The symbols are data of Welsch (1973).

Table 4. Comparison of experimental molar volumes of H<sub>2</sub>O-CH<sub>4</sub> mixtures with the EOS of this study (When the mixing parameters are not adjusted).

| T(K)   | P(bar) | x(H <sub>2</sub> O) | x(CH <sub>4</sub> ) | v exp* (cm <sup>3</sup> /mol) | v cal (cm <sup>3</sup> /mol) |
|--------|--------|---------------------|---------------------|-------------------------------|------------------------------|
| 673.15 | 400    | 0.8                 | 0.2                 | 88.6                          | 88.72                        |
| 673.15 | 1000   | 0.8                 | 0.2                 | 40.31                         | 41.89                        |
| 673.15 | 2000   | 0.8                 | 0.2                 | 30.94                         | 31.87                        |
| 673.15 | 400    | 0.5                 | 0.5                 | 127.76                        | 126.24                       |
| 673.15 | 1000   | 0.5                 | 0.5                 | 60.44                         | 60.81                        |
| 673.15 | 2000   | 0.5                 | 0.5                 | 42.47                         | 430.1                        |
| 673.15 | 400    | 0.2                 | 0.8                 | 149.3                         | 147.8                        |
| 673.15 | 1000   | 0.2                 | 0.8                 | 74.27                         | 74.14                        |
| 673.15 | 2000   | 0.2                 | 0.8                 | 51.45                         | 51.61                        |

The mixed system parameters in the perturbation term are determined using the combining rules given in Eqns. (A22 to A32). These rules combine parameters from pure system EOS (Walas, 1985; Anderko and Pitzer 1991). When data in the mixed system are available, the mixing parameters,  $\alpha_{ij}$ ,  $\gamma_{ijk}$ ,  $\delta_{ijkl}$ , and  $\varepsilon_{ijkl}$ , in the perturbation term (see Eqns. A29 to A32) are adjusted to improve the fit to these data. In this binary system, the indices:  $i, j, k, l$  and  $m$  stand for H<sub>2</sub>O or CH<sub>4</sub>. The  $PvTX$  ranges of the available data for evaluating the mixing parameters are summarized in Table 1.

Table 3 gives the temperature functions for the mixing parameters in the H<sub>2</sub>O-CH<sub>4</sub> EOS. Phase coexistence can be calculated from the EOS using the fugacity equations given in Duan et al. (1995) (see the correction cited in section 2, above). Parameters were evaluated from the solvus (phase equilibria) data of Sultanov and Skripka (1971), Sultanov et al. (1972) and Welsch (1973) in the temperature range 423 to 633 K. Most of Welsch's solvus data agree with those of Sultanov and Skripka (1971) and Sultanov et al. (1972) within 4 mol %. However, at 573 K the deviation is as large as 10 mol %. We give more weight to the data of Sultanov and Skripka (1971) and Sultanov et al. (1972) in the parameterization because these data are more consistent with the solubility data that we have reviewed in an earlier publication (Duan et al., 1992c). The solubility curves above 573 K from synthetic fluid inclusions measurements (Zhang and Frantz, 1992) are consistent with the solvus data of Welsch (1973) and were not used in the parameterization. The  $PvTX$  data of Welsch (1973) from 673 to 698 K and up to 2000 bar and the excess volume data at 653 K of Bazayev et al. (1974) were also used in evaluating the mixing parameters. Figures 1 and 2 illustrate the agreement of the EOS predictions for the H<sub>2</sub>O-CH<sub>4</sub> system with data.

We have not found any data for this system above 698 K. However, the EOS for the end members, H<sub>2</sub>O and CH<sub>4</sub>, are valid to  $\sim 1300$  K and 5000 bar. Therefore, above the  $T$ - $P$  range

of the experimental data, the mixing parameters,  $\alpha_{ij}$ ,  $\gamma_{ijk}$ ,  $\delta_{ijkl}$ , and  $\varepsilon_{ijkl}$ , are set equal to 1 and the mixed system parameters are calculated from pure system parameters alone using the combining rules. This approximation allows the pure system behavior at high temperature and pressure to be extrapolated to the binary.

We tested this extrapolation method by comparing predictions made with the mixing parameters set equal to 1 (mixed system behavior based solely on pure system behavior) with experimental data in H<sub>2</sub>O-CH<sub>4</sub> mixtures. Table 4 gives the results of molar volume comparisons and shows that the combining rules work well for this mixed system. Molar volume predictions of the EOS for the CH<sub>4</sub>-H<sub>2</sub>O system established using the combination rules alone (mixing parameters,  $\alpha_{ij}$ ,  $\gamma_{ijk}$ ,  $\delta_{ijkl}$ , and  $\varepsilon_{ijkl}$ , in Eqns (A29-A32) set equal to 1) agree with measured molar volumes on the average within 1.24% in volume. When the mixing parameters are adjusted fit to the  $PvTX$  data alone, the average discrepancy narrows to  $\sim 1\%$  in volume.

We note that equating the mixing parameters to 1 does not mean ideal mixing. For example, at 673.15 K and 400 bar, a mixture of 50 mol % CH<sub>4</sub> + 50 mol % CO<sub>2</sub> has a volume of 92.2 cm<sup>3</sup>/mol using ideal mixing. The measured volume is 126.76 cm<sup>3</sup>/mol, which is well predicted when the mixing parameters are held to 1.0 (the calculated volume is 126.24 cm<sup>3</sup>/mol).

### 3.3. The NaCl-CH<sub>4</sub> and the NaCl-H<sub>2</sub>O-CH<sub>4</sub> Systems

To include the NaCl-CH<sub>4</sub> interactions in the EOS, we assume that CH<sub>4</sub> has very low solubility in solid and liquid NaCl (melting point 1073 K). Data for the methane system are not available but Gjothiem et al. (1962) reported that the solubility of CO<sub>2</sub> in NaCl ranges from  $4.6 \times 10^{-6}$  to  $6.0 \times 10^{-6}$  moles of CO<sub>2</sub> per cm<sup>3</sup> of molten NaCl in the temperature range 1123 to 1223 K at a CO<sub>2</sub> pressure of 1 atm. The solubility of CH<sub>4</sub> in NaCl should show similar behavior. The solubilities of both NaCl and CH<sub>4</sub> in aqueous systems are high; therefore interactions between the two species may be significant. To evaluate the binary parameters for the NaCl-CH<sub>4</sub> mixed system we used data in the aqueous ternary system NaCl-H<sub>2</sub>O-CH<sub>4</sub>, as was done in evaluating the parameters for the NaCl-CO<sub>2</sub> mixture for the NaCl-H<sub>2</sub>O-CO<sub>2</sub> EOS (Duan et al., 1995).

We found 260 experimental  $PvTX$  data points for the ternary NaCl-H<sub>2</sub>O-CH<sub>4</sub> (Krader 1985; Krader and Frank, 1987). The phase equilibria (immiscibility) data (Lamb et al., 1996), were

Table 5. Temperature functions for mixing parameters for the binary system NaCl-CH<sub>4</sub>.

|                                                                                    |                                                                    |
|------------------------------------------------------------------------------------|--------------------------------------------------------------------|
| $\alpha_{ij}$                                                                      | $-9.91854 + 0.0154923T - 6.1422041e-06T^2 + 2219.4295/T$           |
| $\gamma_{ij}, \gamma_{ji}$                                                         | 1.0                                                                |
| $\delta_{ijj}, \delta_{jjj}, \delta_{ijij}$                                        | 1.0                                                                |
| $\varepsilon_{ijij}, \varepsilon_{ijjj}, \varepsilon_{ijijj}, \varepsilon_{ijjjj}$ | $-1.24172253 + 2.55545498e-03T - 8.0087098e-07T^2 + 477.2268666/T$ |

$i$  and  $j$  represent NaCl and CH<sub>4</sub>, respectively.

Table 6. Temperature functions for mixing parameters for the ternary system NaCl-H<sub>2</sub>O-CH<sub>4</sub>.

|                                                                                                           |                                                                   |
|-----------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------|
| $\gamma_{ijk}$                                                                                            | $2.1535 - 0.0027075T + 1.25e-06T^2$                               |
| $\delta_{ijij}, \delta_{ijij}, \delta_{ijij}$                                                             | 1.0                                                               |
| $\epsilon_{ijik}, \epsilon_{ijik}, \epsilon_{ijik}, \epsilon_{ijikk}, \epsilon_{ijikk}, \epsilon_{ijikk}$ | $-1.24172253 + 2.55545498e-03T - 8.0087098e-07T^2 + 477.226866/T$ |

i, j and k represent NaCl, H<sub>2</sub>O and CH<sub>4</sub>, respectively.

also used in the parameterization process. Both types of data cover a total  $T$ - $P$  range from 648 to 873 K and 600 to 2500 bar and NaCl concentrations up to 2.37 mol %. They were used to find the mixing parameters,  $\alpha_{ij}$ ,  $\gamma_{ijk}$ ,  $\delta_{ijkl}$ , and  $\epsilon_{ijkl}$ , in Eqns. A29 to A32 for the binary NaCl-CH<sub>4</sub> system (Table 5) and for the ternary NaCl-H<sub>2</sub>O-CH<sub>4</sub> system (Table 6). The standard error for these predictions is 4.5% in volume if data with CH<sub>4</sub> mole fractions larger than 0.7 are not included. Data with CH<sub>4</sub> mole fractions larger than 0.7 are not accurately reproduced by this EOS. Figures 3 and 4, and Table 7 provide comparisons of EOS predictions with volume data. Figures 5 to 7 show that phase equilibria in the NaCl-H<sub>2</sub>O-CH<sub>4</sub> system also are well predicted using the mixing parameters. These figures contain data for concentrations as high as 40 mol % NaCl. Please note that only the slopes of the predicted tie-lines and the positions of the two phase boundaries should be compared to the experimental data. The total composition of the tie-lines were chosen to be slightly different from those of the experimental data for clarity.

The  $T$ - $P$  range of the NaCl-H<sub>2</sub>O-CH<sub>4</sub> EOS was extended, as in section 3.2, to high temperatures and pressures (1300 K and 5000 bar) using pure and binary system parameters and the

combination rules given in Appendix 1. The accuracy of this extrapolation is supported by the following results in lower systems. The H<sub>2</sub>O EOS provides accurate predictions in the range from 373 to ~1300 K and 5000 bar (Anderko and Pitzer, 1993). The data for the pure CH<sub>4</sub> system extend only to 773 K and 3000 bar but predictions of the CH<sub>4</sub> EOS agree well (within 1.5% in volume) to 1300 K and 6000 bar with our EOS incorporating high  $T$ ,  $P$  molecular simulation results (Duan et al., 2000). Combination rules that establish mixed system parameters from pure system parameters were used to extend the  $T$ - $P$  range of the EOS for the H<sub>2</sub>O-CH<sub>4</sub> binary above that of the available data. The EOS for the NaCl-H<sub>2</sub>O system provides accurate predictions up to ~1300 K and 6000 bar (Anderko and Pitzer, 1993; Duan et al., 1995).

Table 7 compares experimental  $PvTX$  data in the NaCl-H<sub>2</sub>O-CH<sub>4</sub> system with predictions made when the model is fully optimized by adjusting the mixing parameters,  $\alpha_{ij}$ ,  $\gamma_{ijk}$ ,  $\delta_{ijkl}$  and  $\epsilon_{ijkl}$ , and with predictions made when the mixing parameters are set equal to 1.0 (combination rules only). Predictions of the fully optimized EOS (see column 7) have an average error of 1.69% in volume, which is close to that of the experimental data (estimated to be 1.5%). Predictions of the un-optimized (mixing parameters set equal to one) EOS (see column 8) have a smaller average error (1.36% in volume). The error of the fully optimized EOS is higher because the data sets used to evaluate the mixing parameters include phase coexistence as well as  $PvTX$  measurements.

Figure 8 compares experimental immiscibility boundaries and tie-lines in the NaCl-H<sub>2</sub>O-CH<sub>4</sub> system with those predicted when the mixing parameters are adjusted (solid lines) using both  $PvTX$  and immiscibility data, and when the mixing pa-

Table 7. Comparison of experimental PVTX data in the NaCl-H<sub>2</sub>O-CH<sub>4</sub> system with EOS predictions.

| T(K) | P(bar) | x(NaCl) | x(H <sub>2</sub> O) | x(CH <sub>4</sub> ) | v* (exp) | v** (EOS) | v*** (EOS) |
|------|--------|---------|---------------------|---------------------|----------|-----------|------------|
| 800  | 1000   | .0235   | .8765               | .1000               | 43.20    | 41.8      | 42.95      |
| 800  | 1000   | .0209   | .7791               | .2000               | 51.05    | 50.1      | 51.88      |
| 800  | 1000   | .0183   | .6817               | .3000               | 59.20    | 57.6      | 59.67      |
| 800  | 1000   | .0157   | .5843               | .4000               | 66.00    | 64.5      | 66.51      |
| 800  | 1000   | .0131   | .4869               | .5000               | 72.70    | 70.6      | 72.53      |
| 800  | 1000   | .0104   | .3896               | .6000               | 77.70    | 76.4      | 77.80      |
| 800  | 1500   | .0235   | .8765               | .1000               | 34.00    | 33.9      | 34.59      |
| 800  | 1500   | .0209   | .7791               | .2000               | 40.60    | 39.6      | 40.79      |
| 800  | 1500   | .0183   | .6817               | .3000               | 46.00    | 45.0      | 46.35      |
| 800  | 1500   | .0157   | .5843               | .4000               | 50.70    | 49.9      | 51.36      |
| 800  | 1500   | .0131   | .4869               | .5000               | 55.50    | 54.5      | 55.90      |
| 800  | 1500   | .0104   | .3896               | .6000               | 60.00    | 58.8      | 59.98      |
| 800  | 2000   | .0235   | .8765               | .1000               | 30.00    | 30.3      | 30.81      |
| 800  | 2000   | .0209   | .7791               | .2000               | 35.50    | 34.9      | 35.71      |
| 800  | 2000   | .0183   | .6817               | .3000               | 39.30    | 39.2      | 40.17      |
| 800  | 2000   | .0157   | .5843               | .4000               | 43.50    | 43.2      | 44.23      |
| 800  | 2000   | .0131   | .4869               | .5000               | 47.00    | 46.9      | 47.96      |
| 800  | 2000   | .0104   | .3896               | .6000               | 50.70    | 50.5      | 51.36      |
| 800  | 2500   | .0235   | .8765               | .1000               | 27.50    | 28.2      | 28.59      |
| 800  | 2500   | .0209   | .7791               | .2000               | 32.00    | 32.1      | 32.71      |
| 800  | 2500   | .0183   | .6817               | .3000               | 36.80    | 35.7      | 36.51      |
| 800  | 2500   | .0157   | .5843               | .4000               | 40.70    | 39.2      | 40.00      |
| 800  | 2500   | .0131   | .4869               | .5000               | 43.50    | 42.4      | 43.23      |
| 800  | 2500   | .0104   | .3896               | .6000               | 44.80    | 45.5      | 46.21      |

\* Molar volumes (cm<sup>3</sup>/mole); Experimental data (Krader (1985)).

\*\* Molar volumes (cm<sup>3</sup>/mole); EOS calculated (mixing parameters evaluated from PVT and phase equilibrium data).

\*\*\* Molar volumes (cm<sup>3</sup>/mole); EOS calculated (mixing parameters set equal to 1).

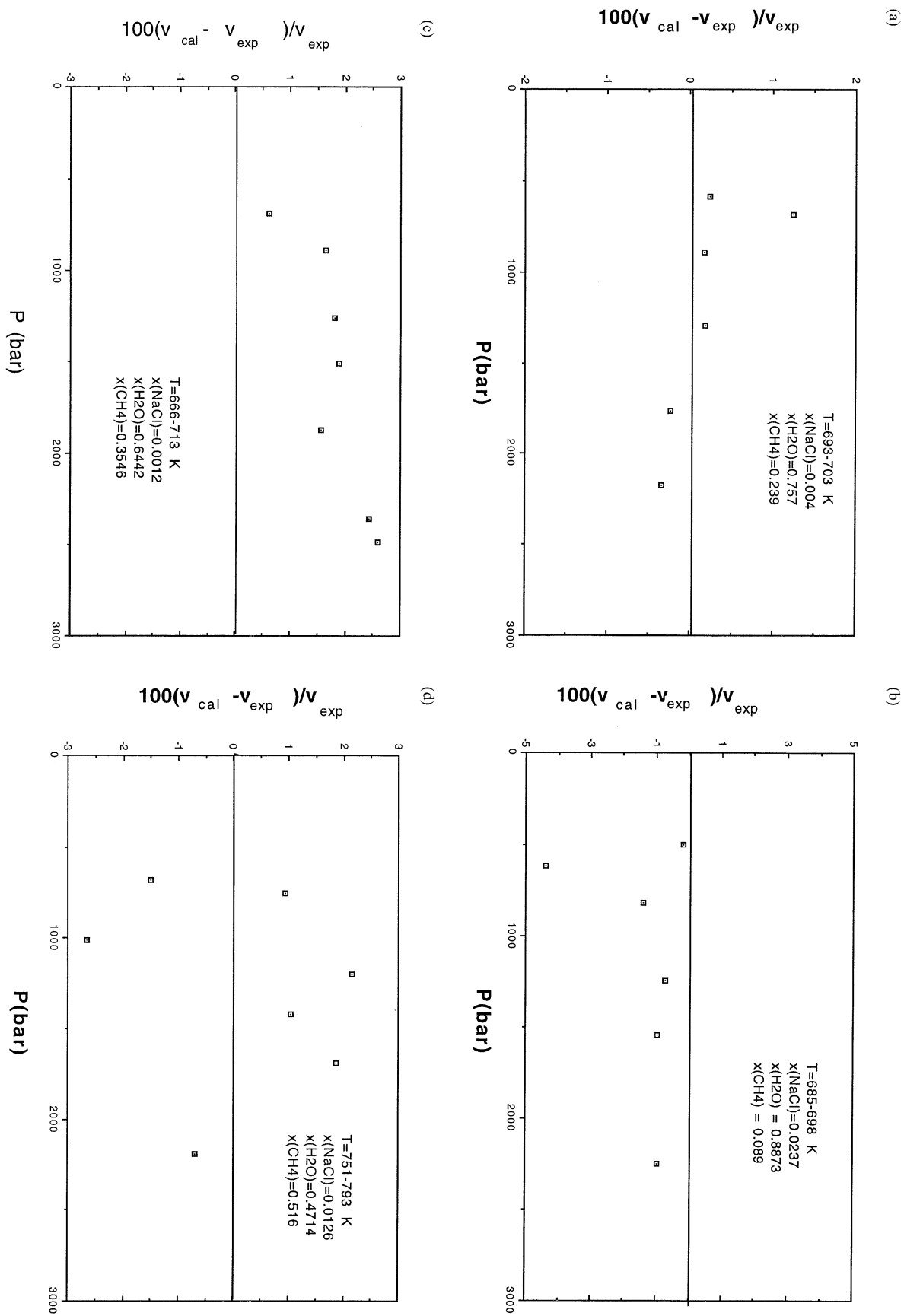


Fig. 3. (a-d). Comparison of the experimental volumetric properties of mixtures in the NaCl-H<sub>2</sub>O-CH<sub>4</sub> system with the predictions. The experimental data are from Krader (1985).

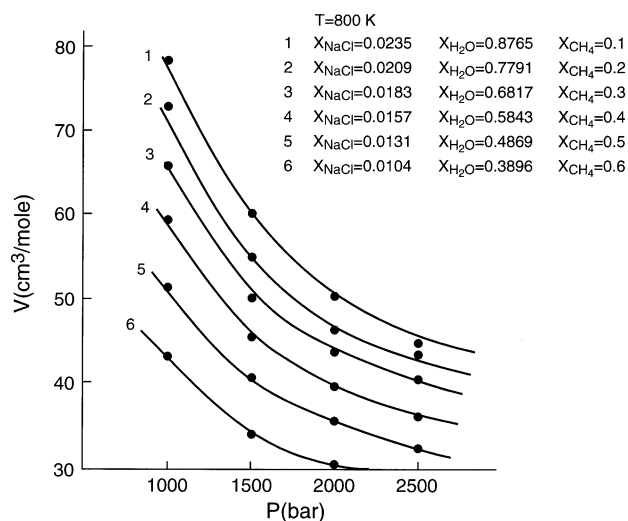


Fig. 4. Comparison of measured molar volumes in the ternary system NaCl-H<sub>2</sub>O-CH<sub>4</sub> with the predictions of the EOS. The symbols represent the data of Krader and Franck (1987).

parameters are set equal to 1.0 (dotted lines). Although there is some loss of accuracy, the phase coexistence lines are still well predicted when extrapolating behavior in lower order systems to the ternary. The good agreement of the unoptimized (mixing parameters set equal to 1) EOS is significant and represents a substantial improvement over the assumption of ideal mixing. This system has considerable excess mixing. For example, for the datum at  $T = 800$  K,  $p = 1000$  bar,  $X(\text{NaCl}) = 0.0131$ ,  $X(\text{H}_2\text{O}) = 0.4869$  and  $X(\text{CH}_4) = 0.50$ , the volume predicted from ideal mixing is  $65.1 \text{ cm}^3/\text{mole}$ . The experimental value is  $72.7 \text{ cm}^3/\text{mole}$ . The unoptimized EOS predicts  $72.53 \text{ cm}^3/\text{mole}$ , which is in excellent agreement with the data.

#### 4. EOS FOR THE NaCl-H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub> SYSTEM

The NaCl-H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub> quaternary system is found in geopressured-geothermal and petroleum reservoirs and in some metamorphic fluids (Thomas et al., 1990; Nwe and Morteani, 1993). Only one data point, which we considered unreliable, was found for this system. However, using the combining rules and pure system, binary and ternary mixed system parameters established for the NaCl-H<sub>2</sub>O-CH<sub>4</sub> EOS (described here) and for the NaCl-H<sub>2</sub>O-CO<sub>2</sub> EOS (Duan et al., 1995), we can build an approximate model for this quaternary system. We have

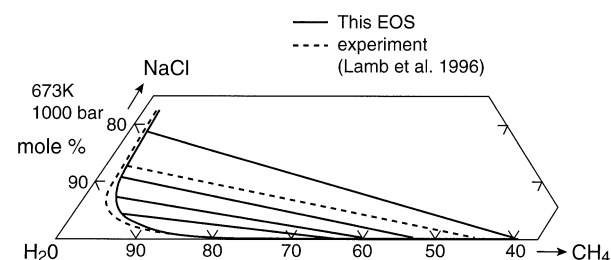


Fig. 5. Comparison of experimental immiscibility boundary and tielines in the ternary NaCl-H<sub>2</sub>O-CH<sub>4</sub> at 673 K and 1000 bar (Lamb et al., 1996) with the prediction of the EOS of this study.

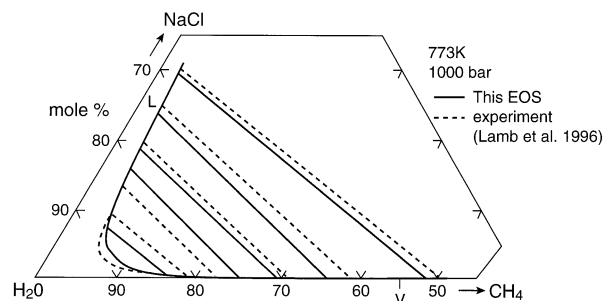


Fig. 6. Comparison of experimental immiscibility boundary and tielines in the ternary NaCl-H<sub>2</sub>O-CH<sub>4</sub> at 773 K and 1000 bar (Lamb et al., 1996) with the prediction of the EOS of this study.

previously published an accurate EOS for the H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub> system (Duan et al., 1992b); however the mixing parameters in this model were not based on the formalism given here in Appendix 1. Therefore new parameters for the CH<sub>4</sub>-CO<sub>2</sub> mixture were evaluated by setting the mixing parameters parameters,  $\alpha_{ij}$ ,  $\gamma_{ijk}$ ,  $\delta_{ijkl}$  and  $\varepsilon_{ijkl}$ , in the perturbation term (Eqns A29 to A32) equal to 1. Comparisons of EOS predictions with the 700  $PvTX$  data points of Reamer et al. (1944) in the CH<sub>4</sub>-CO<sub>2</sub> system showed errors of less than 1%, thereby justifying this approximation. There are not sufficient data to estimate mixing parameters for the H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub> ternary. However, parameters for this mixed system should be well approximated by the combination rules, since these rules work well for the CO<sub>2</sub>-CH<sub>4</sub> binary and H<sub>2</sub>O containing binaries (see above and Duan et al., 1995). We neglect the NaCl-CH<sub>4</sub>-CO<sub>2</sub> ternary interactions in the perturbation contribution. The remaining parameters for the quaternary NaCl-H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub> are established on the basis of the two ternary systems, NaCl-H<sub>2</sub>O-CH<sub>4</sub> and NaCl-H<sub>2</sub>O-CO<sub>2</sub>. We estimate that the resulting NaCl-H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub> EOS should be approximately correct to  $\sim 1300$  K and 5000 bar (see above).

As an example of the application of this model, Figure 9

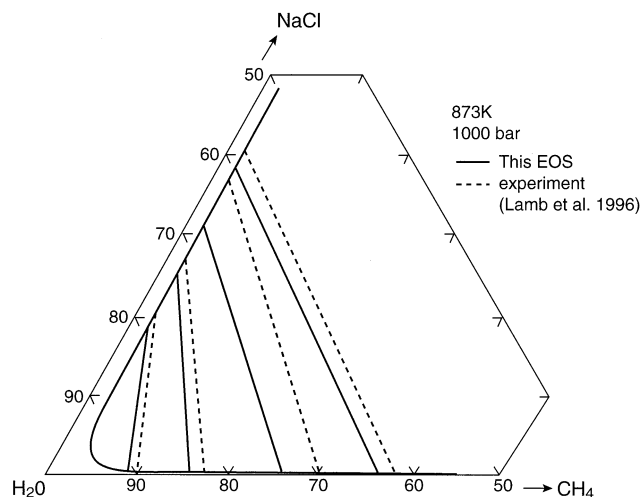


Fig. 7. Comparison of experimental immiscibility boundary and tielines in the ternary NaCl-H<sub>2</sub>O-CH<sub>4</sub> at 873 K and 1000 bar (Lamb et al., 1996) with the prediction of the EOS of this study.

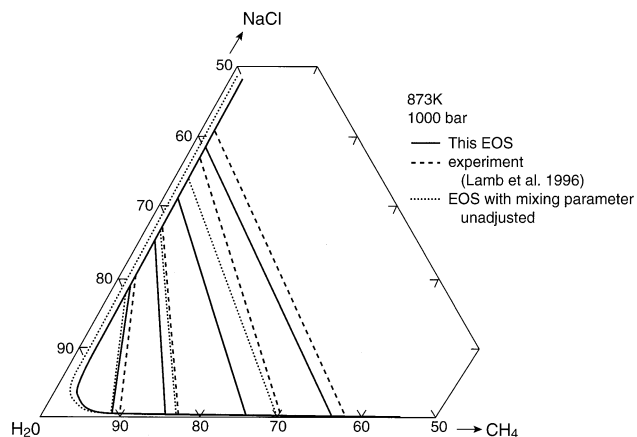


Fig. 8. Comparison of experimental immiscibility boundary and tie-lines in the ternary NaCl-H<sub>2</sub>O-CH<sub>4</sub> system at 873 K and 1000 bar (Lamb et al., 1996): solid lines all parameters adjusted, dotted line mixing parameter set equal to 1.0 (see text), dashed line experiment.

compares the boiling curve of the NaCl-H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub> quaternary system with that of the ternary system NaCl-H<sub>2</sub>O-CO<sub>2</sub>. It can be seen that replacement of 2 mol % of CO<sub>2</sub> by CH<sub>4</sub> will substantially increase the boiling pressure curve.

We recognize that the equations given in Appendix 1 are complicated to program. Therefore, for the convenience of users, we have implemented them in the GEOFLUIDS option on the web site: [geotherm.ucsd.edu](http://geotherm.ucsd.edu). In this implementation, mixing parameters are used when data were available for their evaluation.

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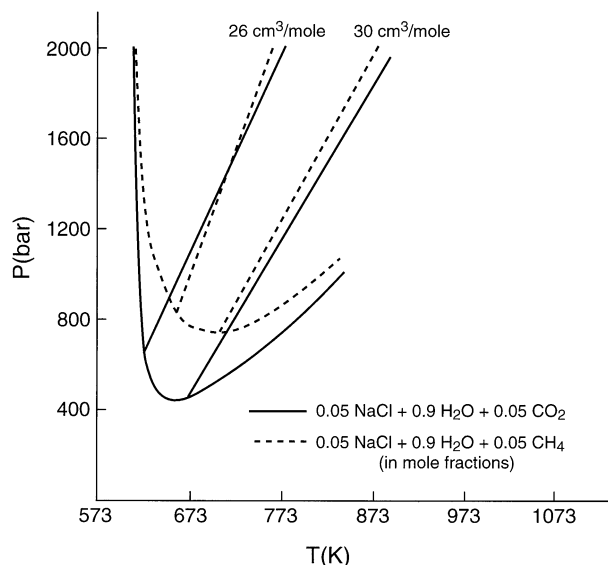


Fig. 9. The boiling curves of the quaternary system 10mol%NaCl-85mol% $\text{H}_2\text{O}$ -3mol% $\text{CO}_2$ -2mol% $\text{CH}_4$  and the ternary system 10mol%NaCl-85mol% $\text{H}_2\text{O}$ -5mol% $\text{CO}_2$ . Above the curves is the single liquid region and below is the two phase liquid-vapor region.

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### Appendix 1

The EOS formalism that we have used follows the development of Anderko and Pitzer (1993) and is based on the compressibility factor,

$$Z = \frac{Pv}{RT} = Z^{hd} + Z^{dip} + Z^{per}, \quad (A1)$$

where  $Z^{hd}$ ,  $Z^{dip}$  and  $Z^{per}$  are hard sphere, dipole moment and perturbation contributions, respectively. The independent variables in this equation are  $v$ ,  $T$  and  $X$ . If  $P$ ,  $T$  and  $X$  are the independent variables desired for an application, the molar volume,  $v$ , can be calculated from Eqn. (A1) by a non-linear solver, such as the bisection method (Press, 1996). The fugacity coefficients are calculated by substituting  $v$  in the equations given in the Appendix of Duan et al. (1995). Liquid-vapor phase equilibria for a given  $T$  and  $P$  are calculated by setting the fugacities of each species equal in the coexisting phases, the resulting equations are solved by the non-linear method of Michelsen (1993). These equations are complicated to program. Therefore, for the convenience of potential users, we have implemented them in the GEOFLUIDS option on the website: geotherm.ucsd.edu.

1. The hard sphere contribution is given by:

$$z_{hd} = \frac{1 + \left(\frac{3DE}{F} - 2\right)\eta_{hd} + \left(\frac{3E^3}{F^2} - \frac{3DE}{F} + 1\right)\eta_{hd}^2 - \frac{E^3}{F^2}\eta_{hd}^3}{(1 - \eta_{hd})^3}, \quad (A2)$$

where

$$D = \sum_{i=1}^n x_i b_i^{1/3}, \quad (A3)$$

$$E = \sum_{i=1}^n x_i b_i^{2/3}, \quad (A4)$$

$$F = \sum_{i=1}^n x_i b_i, \quad (A5)$$

$$\eta_{hd} = \frac{\sum_{i=1}^n x_i b_i}{4v}, \quad (A6)$$

and where  $b_i$  is the van der Waals co-volume of system  $i$  and is evaluated from pure system data.

2. The dipolar contribution is given by:

$$Z_{dip} = \eta \frac{\left(1 - \frac{2A_3}{A_2}\right) \frac{\partial A_2}{\partial \eta} + \frac{\partial A_3}{\partial \eta}}{\left(1 - \frac{A_3}{A_2}\right)^2}, \quad (\text{A7})$$

where

$$A_2 = -\frac{4}{3} I_2(\eta) \sum_{i=1}^n \sum_{j=1}^n x_i x_j \frac{b_i b_j}{b_{ij}^2} \eta_{ij} \tilde{\mu}_i^2 \tilde{\mu}_j^2, \quad (\text{A8})$$

$$A_3 = \frac{10}{9} I_3(\eta) \sum_{i=1}^n \sum_{j=1}^n \sum_{k=1}^n x_i x_j x_k \frac{b_i b_j b_k}{b_{ij} b_{jk} b_{ik}} \eta_{ijk} \tilde{\mu}_i^2 \tilde{\mu}_j^2 \tilde{\mu}_k^2, \quad (\text{A9})$$

$$\frac{\partial A_2}{\partial \eta} = -\frac{4}{3} \left[ I_2(\eta) + \eta \frac{\partial I_2(\eta)}{\partial \eta} \right] \sum_{i=1}^n \sum_{j=1}^n x_i x_j \frac{b_i b_j}{b_{ij}^2} \tilde{\mu}_i^2 \tilde{\mu}_j^2, \quad (\text{A10})$$

$$\frac{\partial A_3}{\partial \eta} = \frac{10}{9} \eta \left[ 2I_3(\eta) + \eta \frac{\partial I_3(\eta)}{\partial \eta} \right] \sum_{i=1}^n \sum_{j=1}^n \sum_{k=1}^n x_i x_j x_k \frac{b_i b_j b_k}{b_{ij} b_{jk} b_{ik}} \frac{(b_i b_{jk} b_{ij})^{2/3}}{b^2} \tilde{\mu}_i^2 \tilde{\mu}_j^2 \tilde{\mu}_k^2 \quad (\text{A11})$$

A number of additional parameters in these equations still need to be defined. They are given by:

$$b_{ij} = [(b_i^{1/3} + b_j^{1/3})/2]^3, \quad (\text{A12})$$

$$\eta_{ij} = b_{ij}/4\nu, \quad (\text{A13})$$

$$\eta = \frac{b}{4\nu} = \frac{1}{4\nu} \sum_{i=1}^n \sum_{j=1}^n x_i x_j b_{ij}, \quad (\text{A14})$$

$$\tilde{\mu}_i = \left[ \frac{2908.011 \pi \mu_i^2}{b_i T} \right]^{1/2}, \quad (\text{A15})$$

$$\eta_{ijk} = b_{ijk}/4\nu = (b_i b_{jk} b_{ij})^{1/2}/4\nu, \quad (\text{A16})$$

$$I_2(\eta) = 1 + c_1 \eta + c_2 \eta^2 + c_3 \eta^3, \quad (\text{A17})$$

$$\frac{I_3(\eta)}{I_2(\eta)} = 1 + c_4 \eta + c_5 \eta^2 + c_6 \eta^3, \quad (\text{A18})$$

$$\frac{\partial I_2(\eta)}{\partial \eta} = c_1 + 2c_2 \eta + 3c_3 \eta^2, \quad (\text{A19})$$

$$\frac{\partial I_3(\eta)}{\partial \eta} = (c_1 + 2c_2 \eta + 3c_3 \eta^2)(1 + c_4 \eta + c_5 \eta^2 + c_6 \eta^3) + (1 + c_1 \eta + c_2 \eta^2 + c_3 \eta^3)(c_4 + 2c_5 \eta + 3c_6 \eta^2). \quad (\text{A20})$$

In these equations,  $\mu_i$  is dipole moment. The parameters,  $c_i$ 's, are taken from Anderko and Pitzer (1993):  $c_1 = 1.6054$ ,  $c_2 = -4.4521$ ,  $c_3 = 10.0368$ ,  $c_4 = 0.35147$ ,  $c_5 = -1.83943$  and  $c_6 = 5.95676$ .

3. The perturbation contribution is given by:

$$Z_{per} = -\frac{1}{RT} \left[ \frac{a}{\nu} + \frac{acb}{2\nu^2} + \frac{3adb^2}{16\nu^3} + \frac{aeb^3}{16\nu^4} \right]. \quad (\text{A21})$$

In the above equation,  $a$ ,  $acb$ ,  $adb^2$  and  $aeb^3$  are evaluated from the following mixing rules:

$$a = \sum_{i=1}^n \sum_{j=1}^n x_i x_j a_{ij}. \quad (\text{A22})$$

$$acb = \sum_{i=1}^n \sum_{j=1}^n \sum_{k=1}^n x_i x_j x_k (ac)_{ijk} b_{ijk}, \quad (\text{A23})$$

$$adb^2 = \sum_{i=1}^n \sum_{j=1}^n \sum_{k=1}^n \sum_{l=1}^n x_i x_j x_k x_l (ad)_{ijkl} b_{ijkl}^2, \quad (\text{A24})$$

and

$$aeb^3 = \sum_{i=1}^n \sum_{j=1}^n \sum_{k=1}^n \sum_{l=1}^n \sum_{m=1}^n x_i x_j x_k x_l x_m (ae)_{ijklm} b_{ijklm}^3. \quad (\text{A25})$$

Additional parameters in Eqns. (A22 to A25) are found from pure system parameters using the combining rules:

$$b_{ijk} = [(b_i^{1/3} + b_j^{1/3} + b_k^{1/3})/3]^3, \quad (\text{A26})$$

$$b_{ijkl} = [(b_i^{1/3} + b_j^{1/3} + b_k^{1/3} + b_l^{1/3})/4]^3, \quad (\text{A27})$$

$$b_{ijklm} = [(b_i^{1/3} + b_j^{1/3} + b_k^{1/3} + b_l^{1/3} + b_m^{1/3})/5]^3. \quad (\text{A28})$$

In addition, mixing parameters are defined by the following equations:

$$a_{ij} = (a_i a_j)^{1/2} \alpha_{ij}, \quad (\text{A29})$$

$$(ac)_{ijk} = [(ac)_i (ac)_j (ac)_k]^{1/3} \gamma_{ijk}, \quad (\text{A30})$$

$$(ad)_{ijkl} = [(ac)_i (ac)_j (ac)_k (ac)_l]^{1/4} \delta_{ijkl}, \quad (\text{A31})$$

and

$$(ae)_{ijklm} = [(ac)_i (ac)_j (ac)_k (ac)_l (ac)_m]^{1/5} \varepsilon_{ijklm}. \quad (\text{A32})$$

The parameters,  $\alpha_{ij}$ ,  $\gamma_{ijk}$ ,  $\delta_{ijkl}$ , and  $\varepsilon_{ijklm}$ , are evaluated from experimental data in mixed systems.