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Electrolyte CPA equation of state for very high temperature and pressure reservoir and basins applications

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Abstract

In this work, an electrolyte version of the Cubic Plus Association (eCPA) equation of state has been adapted to systems containing CH₄, CO₂, H₂O and NaCl (up to 5 molal) at temperatures and pressures up to 773 K and 200 MPa. Its purpose is to represent the phase behavior (including salting-out effect and critical point) and the phase densities in a range of temperature and pressure encountered in deep reservoir and basins. The goal of the parameterization proposed is not to reach a very high accuracy for phase equilibrium and volumetric properties, but rather to develop a semi-predictive approach to model the different phase and volumetric behaviors of this system while allowing an easy extension to other compounds.

Without salt, predictions for pure component vapor pressures and liquid molar volumes present an average absolute deviation (AAD) lower than 3 % compared to experimental reference values. The pure component molar volumes out of saturation show an AAD lower than 4 %. The highest deviations in densities are observed as expected in the vicinity of the critical coordinates of pure water and this effect increases when gases or salts are added to the system. For each binary system, CH₄ + CO₂, CH₄ + H₂O and CO₂ + H₂O, binary interaction parameters have been fitted to correctly predict the shape of the fluid phase envelopes (including all critical points) in the entire temperature and pressure range considered (219 K to 633 K and up to 250 MPa). The methane concentration in both phases of the CH₄ + CO₂ binary system is represented with an AAD lower than 9 %. The methane solubility in water is represented within 16 % and 8 % for the methane content of the vapor. The CO₂ solubility in water is within 26 %, while the CO₂ in the vapor phase shows an average deviation of 12 %. All molar volumes are represented with an AAD lower than 3 %. The few VLE experimental data which were found for the CH₄ + CO₂ + H₂O ternary system are fairly well predicted with the model without extra parameter and confirm the ability of the eCPA equation of state to be extended to multi-component systems. In the presence of salts, gas + ion binary interaction parameters have been fitted, and all phase equilibrium are qualitatively correctly described, and more specifically the salting out effect. The solubility of methane or CO₂ in brines, up to 5 molal, is represented with an AAD of 33 % in a large temperature and pressure range (up to 673 K and 150 MPa). It should be noticed that for high temperatures, experimental data are relatively scarce and not always consistent. No data exist for water content of the vapor phase in these conditions.

The new eCPA model can be easily extended to other components (including ions) to better represent real fluid behavior in very deep reservoir conditions.

Keywords: Vapor liquid equilibrium, volumetric behavior, electrolyte CPA equation of state (eCPA), NaCl electrolyte, water, CO₂, CH₄, critical point.

1. Introduction

Nowadays, oil and gas operators are exploring ever deeper reservoirs and basins where temperature and pressure can be very important. Typical fluids encountered are composed of salt water with hydrocarbons and light gases such as methane or carbon dioxide. To understand and model fluid behavior in extreme conditions of temperature and pressure, it is necessary to rely on a thermodynamic model able to predict densities and phase equilibrium of real fluids, including mutual solubilities, critical points and salinity effects.

A common approach to calculate phase equilibrium in geophysical applications consists in associating an electrolyte activity model (e.g. Pitzer model (Pitzer, 1973)) to calculate the activity of the various species in the aqueous phase, and an equation of state to calculate the fugacity of the compounds in the vapor phase (e.g. Duan et al., 1992b; Duan et al., 2006; Duan and Mao, 2006; Duan and Sun, 2003; He and Morse, 1993). Although quite accurate, such an approach is restricted to the subcritical domain: at the critical point, properties of the liquid and the vapor phases converge, which is not ensured if a different model is used for each phase. Moreover, using a model based on activity coefficients for the liquid phase does not allow to calculate its density. A homogeneous thermodynamic approach is thus needed to predict densities and phase equilibrium in both subcritical and supercritical conditions: this means that the same equation of state should be used to model both liquid and vapor phases. The availability of equations of state able to treat electrolytic systems in very high temperature and pressure ranges is very limited in the literature. Soreide and Whitson (Soreide and Whitson, 1992) have proposed a model based on the Peng-Robinson equation of state. The attractive term of water in the liquid phase is corrected to take into account the salinity of the solution, while the attractive term of water in the vapor phase remains unchanged. Thus, this model behaves similarly as with a heterogeneous approach (different binary parameters for each phase), making critical point calculations impossible. Sorensen et al. (Sorensen et al., 2002) have proposed to model gas solubility in brines using the Soave-Redlich-Kwong equation of state coupled with the Huron-Vidal mixing rules. However, this approach has been tested only in subcritical domain, and is not suitable to calculate accurately liquid phase densities. More recently, Ji et al. (Ji et al., 2005) have modeled the $\text{CO}_2+\text{H}_2\text{O}+\text{NaCl}$ system using an electrolyte version of the SAFT equation of state. This model appears accurate to predict both phase densities and phase equilibrium, but it is restricted in temperature (473 K) and pressure (60 MPa) and does not cover the supercritical domain. For many years, Duan's group has developed specific equations of states which are today widely used for geochemical applications. These models are often parameterized to reproduce either phase equilibrium (e.g. Duan et al., 1992a; Duan et al., 2003) or volumetric properties (e.g. Duan et al., 1996; Hu et al., 2007; Mao et al., 2010) with very good accuracy. Many empirical interaction parameters (binary, ternary and quaternary parameters) have to be adjusted, requiring thus a large number of experimental data. Although very accurate, such models are not fairly predictive.

In this work, we propose another model to represent simultaneously phase equilibrium and volumetric properties of geological fluids (including electrolytes) for high temperature and high pressure applications: the electrolyte Cubic Plus Association equation of state (eCPA). Initially developed for water + salts systems (Inchekel et al., 2008), this equation of state has been extended to electrolytic systems involving methane but in a restricted temperature range (de Hemptinne et al., 2006). In this work we propose an extension of this model to the system $\text{CH}_4 + \text{CO}_2 + \text{H}_2\text{O} + \text{NaCl}$ for a wide range of temperatures (up to 773 K) and pressures (up to 200 MPa). Our goal is not to reach a very high accuracy for phase equilibrium and volumetric properties, but rather to develop a semi-

predictive approach to model this system while allowing an easy extension to other compounds. This is achieved using an equation that is now widely accepted, has semi-theoretical foundations (Kontogeorgis, 2006), and has a small number of empirical parameters. Doing so, phase densities, gas solubility, critical points and salting out effect are correctly estimated.

This paper is organized as follows: the eCPA model is detailed in section 2 with a description of the various contributions to the total Helmholtz free energy. In section 3 we present the parameters that are used to model pure component properties (excluding salt). Section 4 is devoted to the H₂O + NaCl system: the parameters used to represent properties (up to 7 molal NaCl) are presented together with the deviations between experimental data and representation from the model. The selected physical properties are vapor pressure, molar volumes at and out of saturation, NaCl mean activity coefficient and osmotic coefficient. Section 5 treats the modeling of the binary salt-free systems CH₄+CO₂, CH₄+H₂O and CO₂+H₂O, with a focus on the description of the critical point. Finally, the modeling of the full system with CH₄ + CO₂ + H₂O + NaCl is presented in section 6.

2. Model

Modeling phase equilibrium of the CH₄ + CO₂ + H₂O + NaCl system is quite complex due to the combination of different types of components such as water, gas as well as ionic species. The CH₄ + CO₂ binary system does not exhibit strong non ideality and is satisfactorily represented using a conventional cubic equation of state such as Soave-Redlich Kwong (SRK) (Soave, 1972). Yet, the hydrogen bonds result in a strong organization of water molecules. This supplementary degree of complexity can be obtained with the Cubic Plus Association model (CPA) proposed by Kontogeorgis et al. (Kontogeorgis et al., 1996). Finally, NaCl dissociates when dissolved in water to form ions and electrostatic interactions are added to this complex system. The electrolyte Cubic Plus Association, as proposed by Inchekel et al. (eCPA) (Inchekel et al., 2008) uses two electrolyte terms and its residual Helmholtz free energy can be written as a combination of different contributions:

$$A^{res} = A^{SRK} + A^{assoc} + (A^{MSA} + A^{Born}) \quad (1)$$

A^{SRK} is relative to Van de Waals interactions (attraction, repulsion) and is based on the work of Soave (Soave, 1972). It is expressed as:

$$\frac{A^{SRK}}{RT} = \frac{\sum_i \sum_j n_i n_j a_{ij}}{RT \sum_i n_i b_i} \ln \frac{V}{V + \sum_i n_i b_i} + \sum_i n_i \ln \frac{V}{V - \sum_i n_i b_i} \quad (2)$$

Where n stands for the number of mole, R is the ideal gas constant, T is the absolute temperature, V the volume, a the attractive parameter and b the covolume.

The attractive parameter (a_{ij}) between species i and j is obtained from a classical mixing rule:

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (3)$$

Where a_i stands for the attractive parameter for the pure compound i , and k_{ij} (by default set to zero) allows to empirically tune interactions between species.

The Soave alpha function (Soave, 1972) is used to represent the temperature dependency of the attractive parameter for non-ionic species:

$$a_i(T) = a_{c,i} \left[1 + m_i \cdot \left(1 - \sqrt{T/T_{c,i}} \right) \right]^2 \quad (4)$$

T is in K and the specific parameters to each species used in this term ($a_{c,i}$, m_i and $T_{c,i}$) are presented in the Table 1, together with b_i of the equation (2).

For ions a similar formalism is used, but as their critical temperature is not clearly defined, it is substituted by the reference temperature of 298.15 K, because most data are available at that temperature. The attractive parameter for ionic species is therefore written as:

$$a_i(T) = a_{0,i} \left[1 + m_i \cdot \left(1 - \sqrt{T/298.15} \right) \right]^2 \quad (5)$$

In order to limit the number of parameters of the model, the repulsive term for the ions is obtained from the ionic diameter (σ_b^{hs}), which will be used for electrolyte terms of the equation of state, as:

$$b_i = \frac{N_{av} \pi (\sigma_{b,i}^{hs})^3}{6} \quad (6)$$

Where N_{av} is Avogadro's constant.

The term A^{asso} in equation (1) accounts for association phenomena between species and especially for hydrogen bonds formation. It originates from Wertheim's theory (Wertheim, 1984). It can be expressed as:

$$\frac{A^{assoc}}{RT} = \sum_i n_i \sum_{A_i} \left(\ln(X^{A_i}) - \frac{1}{2} X^{A_i} + \frac{1}{2} \right) \quad (7)$$

X^{A_i} describes the non-bonded fraction of associating sites of type A of the compound i and is obtained by solving :

$$X^{A_i} = \frac{1}{\left[1 + \rho \sum_j x_j \sum_{B_j} (X^{B_j} \Delta^{A_i B_j}) \right]} \quad (8)$$

Where ρ is the molar density and x_j the molar fraction of the compound j . The association strength ($\Delta^{A_i B_j}$) between two sites is calculated as follows:

$$\Delta^{A_i B_j} = g(\rho) [\exp(\varepsilon^{A_i B_j} / RT) - 1] b_{ij}^3 \beta^{A_i B_j} \quad (9)$$

In this equation, $g(\rho)$ is the simplified radial distribution function and is obtained from :

$$g(\rho) = \frac{1}{1 - 1.9 \frac{n b}{4V}} \quad (10)$$

Where :

$$b = \sum_i \sum_j x_i x_j b_{ij} \quad (11)$$

With:

$$b_{ij} = \frac{b_i + b_j}{2} \quad (12)$$

ε^{A,B_j} and β^{A,B_j} are interaction parameters between associating sites. They are determined from pure compound parameters using the so-called 'CR1' combining rule (Derawi, 2002):

$$\varepsilon^{A,B_j} = \frac{\varepsilon^{A_i} + \varepsilon^{B_j}}{2} \quad (13)$$

$$\beta^{A,B_j} = \sqrt{\beta^{A_i} \beta^{B_j}} \quad (14)$$

An important parameter for the calculation of this energy is the number and the type of associating sites for each compound. In this work, a 4C association scheme is adopted for water, according to the nomenclature of Huang and Radosz (Huang and Radosz, 1990). It means that a molecule of water has two electronegative sites and two electropositive sites. The CO₂ molecule is modeled with a single electronegative site. It means that a CO₂ molecule cannot be associated with another CO₂ molecule, but only with an electropositive site of water, thus mimicking the formation of carbonates.

Electrostatic interactions (ionic species) are considered with the A^{MSA} term from the Mean Spherical Approximation (MSA) approach detailed by Blum (Blum, 1975; Blum, 1977) from the expression of Ball et al. (Ball et al., 1985):

$$\frac{A^{MSA}}{RT} = -\frac{N_{Av} e^2}{4\pi D_0 DRT} \sum_i \frac{n_i Z_i^2 \Gamma}{1 + \Gamma \sigma_{b,i}^{MSA}} + \frac{V\Gamma^3}{3\pi N_{Av}} \quad (15)$$

The screening length (Γ) is obtained by solving iteratively:

$$4\Gamma^2 = \frac{N_{Av} e^2}{D_0 DRT} \sum_i \frac{n_i}{V} \left(\frac{Z_i^2}{1 + \Gamma \sigma_{b,i}^{MSA}} \right) \quad (16)$$

D is the solution relative dielectric constant, D_0 is the vacuum permittivity ($8.855 \cdot 10^{-12}$ F.m⁻¹); e is the elementary charge ($1.602 \cdot 10^{-19}$ C); Z_i is the valence of ion i and $\sigma_{b,i}^{MSA}$ is the diameter of ion i .

The relative dielectric constant of the solution (D) is obtained from the value of pure water (D_s) using the Schmidt correlation (Schmidt and Grigull, 1982), coupled to Simonin's model (Simonin, 1997) to account for salinity. The Schmidt correlation is the following:

$$D_s = 1 + \left(\frac{7.62571}{T^*} \right) \rho^* + \left(\frac{244.003}{T^*} - 140.569 + 27.7841T^* \right) \rho^{*2} + \left(\frac{-96.2805}{T^*} + 41.7909T^* - 10.2099T^{*2} \right) \rho^{*3} + \left(\frac{-45.2059}{T^{*2}} + \frac{84.6395}{T^*} - 35.8644 \right) \rho^{*4} \quad (17)$$

Where $T^* = \frac{T}{298.15}$ (T in K) and $\rho^* = \frac{v_0}{v}$ with v_0 : molar volume of pure water at atmospheric pressure and 278.15 K ($v_0 = 18 \cdot 10^{-6}$ m³/mol) and v : molar volume of the solution.

The Simonin model is expressed as:

$$D = \frac{D_s}{1 + \sum_i \alpha_i x_i} \quad (18)$$

As suggested by Inchekel et al. (Inchekel et al., 2008), the tunable parameter α_i , is set to 5.08 for the H₂O + NaCl system. This value represents fairly well the decrease of the dielectric constant of the system while salinity increases.

The difference of permittivity between the ideal gas reference state, assimilated to vacuum permittivity, and the permittivity of the ionic solution is taken into account in the residual Helmholtz energy calculation by the A^{Born} term (Born, 1920) expressed as:

$$\frac{A^{Born}}{RT} = -\frac{N_{av}e^2}{4\pi D_0 RT} \left(1 - \frac{1}{D}\right) \sum_i \frac{n_i Z_i^2}{\sigma_{b,i}^{Born}} \quad (19)$$

$\sigma_{b,i}^{Born}$ is the diameter of the ion i and in order to reduce the number of parameters, we chose to use:

$$\sigma_{b,i}^{hs} = \sigma_{b,i}^{MSA} = \sigma_{b,i}^{Born} = \sigma_{b,i} \quad (20)$$

In this work, NaCl is assumed to be excluded from the vapor phase if two fluid phases coexist. Similarly, we consider totally dissociated Na⁺ and Cl⁻ ions in the dense phase. So 1 mole of NaCl in the system accounts for 2 moles of ions. Both of these assumptions are not entirely correct, especially when the fluid approaches the critical point of water, but the resulting system description was sufficient for our purpose.

3. Pure compounds properties

Parameters for pure components excluding ions (Na⁺ and Cl⁻) are the ones proposed by Kontogeorgis's group (Kontogeorgis et al., 2008; Tsivintzelis et al., 2010; Tsivintzelis et al., 2011) and can be found in Table 1. Only cross-associating volume of CO₂ (which has no effect on pure component properties) has been adjusted in this work to obtain a better accuracy for phase equilibrium of CO₂+H₂O binary system specifically at high temperature.

Table 1. Pure component parameters used for eCPA equation of state. T_c is the critical temperature, a_c the attractive term at the critical point, b the covolume, m the parameter used in equation (4), ε the association energy parameter, β the association volume parameter. In the association scheme, ed stands for electron donor, ea for electron acceptor.

	T_c (K)	a_c (Pa.m ⁶ .mol ⁻¹)	b (m ³ .mol ⁻¹)	m (-)	number of associating site	Association scheme	ε/R (K)	β (m ³ .mol ⁻¹)
H ₂ O (Kontogeorgis et al., 2008)	647.35	0.122735	0.0000145	0.67359	4	2ed-2ea (4C)	2003.12	0.06920
CO ₂ (Tsivintzelis et al., 2011)	304.19	0.350790	0.0000272	0.76020	1	0ed-1ea	1412.59	0.01313*
CH ₄ (Tsivintzelis et al., 2010)	190.55	0.232040	0.0000291	0.44718	0	-	-	-

*: the association volume of CO₂ was adapted compared to the original (Tsivintzelis et al., 2011).

Properties of pure components at saturation (vapor pressure and liquid molar volume) have been compared to the DIPPR correlations (Rowley et al., 2011), while densities out of saturation are confronted to representation from the REFPROP software (Lemmon, 2006).

Deviations are presented as Average Absolute Deviation (AAD), defined as:

$$AAD(\%) = \frac{100}{N_{data}} * \sum_{N_{data}} \left| \frac{F_{cal} - F_{exp}}{F_{exp}} \right| \quad (21)$$

Where N_{data} is the number of data, F a physical property such as pressure, molar volume, phase composition, osmotic coefficient or mean activity coefficient, which is either calculated from the model (*cal*), or originating from experimental data (*exp*).

The Table 2 shows AAD for vapor pressures, saturated liquid molar volumes and molar volumes out of saturation for pure H₂O, CO₂ and CH₄.

Table 2. AAD (%) for pure compound properties

	Vapor pressure	Saturated liquid molar volumes	Out of saturation molar volumes
H ₂ O	0,9	1,8	2,0
CO ₂	0,6	1,5	3,7
CH ₄	1,2	2,8	2,5

For each compound, vapor pressures are very well represented from triple point to critical point with an AAD lower than 1.2% and the highest deviations are lower than 3 %. Liquid molar volumes at saturation are fairly well represented with an AAD lower than 3 %. The highest deviations are focused in the vicinity of critical points, with deviations as high as 15 % for water. Representation of densities out of saturation with eCPA model agrees well with the representations from REFPROP software for each component from 373 K to 773 K and from 10 to 250 MPa. AAD are lower than 4 % for the three components. Deviations for methane are homogeneous in the investigated conditions, even if it increases with pressure. A similar behavior is observed with carbon dioxide, with higher degradation of the representation at very high pressures. Water densities out of saturation are generally well represented for the entire range of temperature and pressure studied and the highest deviations are found from its critical point to 773 K and 50 MPa with deviations about 10 %.

4. H₂O + NaCl system

As NaCl is the only salt studied in this work, it has been chosen to use the same values of attractive parameters (equation 5) for both ions Na⁺ and Cl⁻ to represent the physical properties of salt water. The pure ion parameters have been adjusted on salt water vapor pressures, saturated and out of saturation molar volumes, NaCl average activity coefficients and water osmotic coefficients, for molalities up to 7. The optimized parameters are given in Table 3.

The segment diameter parameter accounts for electrolytic contributions as well as repulsion forces, and differs for Na⁺ and Cl⁻.

Table 3. Parameters for ions used for eCPA equation of state. σ_b is the solvated diameter of the ion (equation (20)), and a_0 and m_1 the parameters of equation (5).

	σ_b (Å)	a_0 ($T_0 = 298$ K) ($\text{Pa}\cdot\text{m}^6\cdot\text{mol}^{-2}$)	m_1
Na^+	1.6	1.162	-0.987
Cl^-	4.3		

Table 4 shows the AAD obtained using this parameterization for various properties of the $\text{H}_2\text{O} + \text{NaCl}$ system, as well as the number of experimental data, the temperature range and the maximal salinity of the experimental data used for the regression.

Table 4. AAD (%) for $\text{H}_2\text{O} + \text{NaCl}$ properties.

	AAD %	<i>n</i> data	Temperature range	Salinity max. (molality)	Ref.
Saturated vapor pressure	2.7	1094	[298 ; 673 K]	7.8	(Apelblat and Korin, 1998;berling et al., 1999;Bischoff and Rosenbauer, 1988;Crovetto and Wood, 1991;Filiz and Gülen, 2008;Galobardes et al., 1981;Gardner et al., 1963;Hakuta et al., 1975;Hubert et al., 1995;Jablczynski, 1922;Jablczynski and Kon, 1923;Johnston, 1907;Kahlenberg, 1900;Khaibullin and Borisov, 1966;Kiepe, 2002;Kovyrzina et al., 1966;Kuramochi et al., 1997;Lannung, 1934;Legrand, 1836;Leopold and Johnston, 1927;Markowitz and Boryta, 1961;Mashovets et al., 1973;Mokbel et al., 1997;Parisod and Plattner, 1981;Smith et al., 1954;Sourirajan and Kennedy, 1962;Tammann, 1888;Urusova and Ravich, 1971)
Molar volume at saturation	4.6	1238	[273 ; 713 K]	5.7	(Apelblat and Manzurola, 1999;Elis and Golding, 1963;Fabuss et al., 1966;Khaibullin and Borisov, 1966;Kiepe et al., 2003a;Korosi and Fabuss, 1968;Patel and Kishore, 1995;Potter and Brown, 1977;Rodnyanskii and Galinker, 1955;Rogers and Pitzer, 1982;Shreiber and Tikhii, 1973)
Molar volume out of saturation	4.0	5947	[273 ; 773 K]	5.7	(Ellis, 1966;Gehrig et al., 1983;Gorbachev et al., 1974;Grant-Taylor, 1981;Hilbert, 1979;Potter and Brown, 1977;Rogers and Pitzer, 1982;Zarembo and Fedorov, 1975)
NaCl mean ionic activity coefficient	3.0	1021	[298 ; 573 K]	6.7	(Akerloef, 1930;Brown and MacInnes, 1935;Downes, 1970;Esteso et al., 1989;Gibbard et al., 1974;Glazkova et al., 1997;Hamer and Wu, 1972;Harned and Cook, 1939;Hernandez-Hernandez et al., 2007;Hernandez-Luis et al., 1995;Hernandez-Luis et al., 2004;Hernandez-Luis et al., 2009;Hernandez-Luis et al., 2010;Janz and Gordon, 1943;Ji et al., 2001;Khoshkbarchi and Vera, 1996;Lanier, 1965;Lebed and Aleksandrov, 1964;Morales et al., 2009;Pearce and Nelson, 1932;Platford, 1968;Rabie et al., 1999;Robinson and Stokes, 1949;Robinson and Sinclair, 1934;Safona et al., 1986;Schindler and Waelti, 1968;Schneider et al., 2003;Stokes and Levien, 1946;Vlasov, 1963;Wang et al., 1994;Wilczek-Vera et al., 2006;Yan et al., 1994;Yao et al., 1999;Zhao et al., 2008)
H ₂ O osmotic coefficient	2.5	752	[298 ; 573 K]	10.2	(Amado and Blanco, 2004;Apelblat and Korin, 1998;Baabor et al., 1994;Blanco et al., 2008;Boyd, 1977;Burge, 1963;Downes, 1973;Downes and Pitzer, 1976;Filippov et al., 1986;Gibbard et al., 1974;Guendouzi et al., 2001;Hamer and Wu, 1972;Janz and Gordon, 1943;Koennecke et al., 1997;Liu and Lindsay, Jr., 1972;Miljevic et al., 1981;Nasirzadeh et al., 2004;Partanen and Minkkinen, 1993;Rard and Archer, 1995;Robinson and Stokes, 1949;Salabat et al., 2005;Scatchard et al., 1938;Smith, 1939;Stokes and Levien, 1946;Vlasov, 1963;Wigent and Leifer, 1984;Wu et al., 1969;Yin et al., 2007)

Experimental vapor pressures are reproduced with an AAD of 2.7 % for temperatures up to 673 K and NaCl salinity up to 7.8 molal. Evolutions with temperature of the ratios of brine saturation vapor pressure over pure water vapor pressure are illustrated in Figure 1 for different salinities. The top first dotted line shows the deviation between pure water vapor pressure predicted by eCPA model and the representation from the DIPPR correlation (Rowley et al., 2011) up to the water critical point. Thereafter the decrease of vapor pressure while increasing salinity shown by the experimental data is well represented by the model particularly at moderate temperatures.

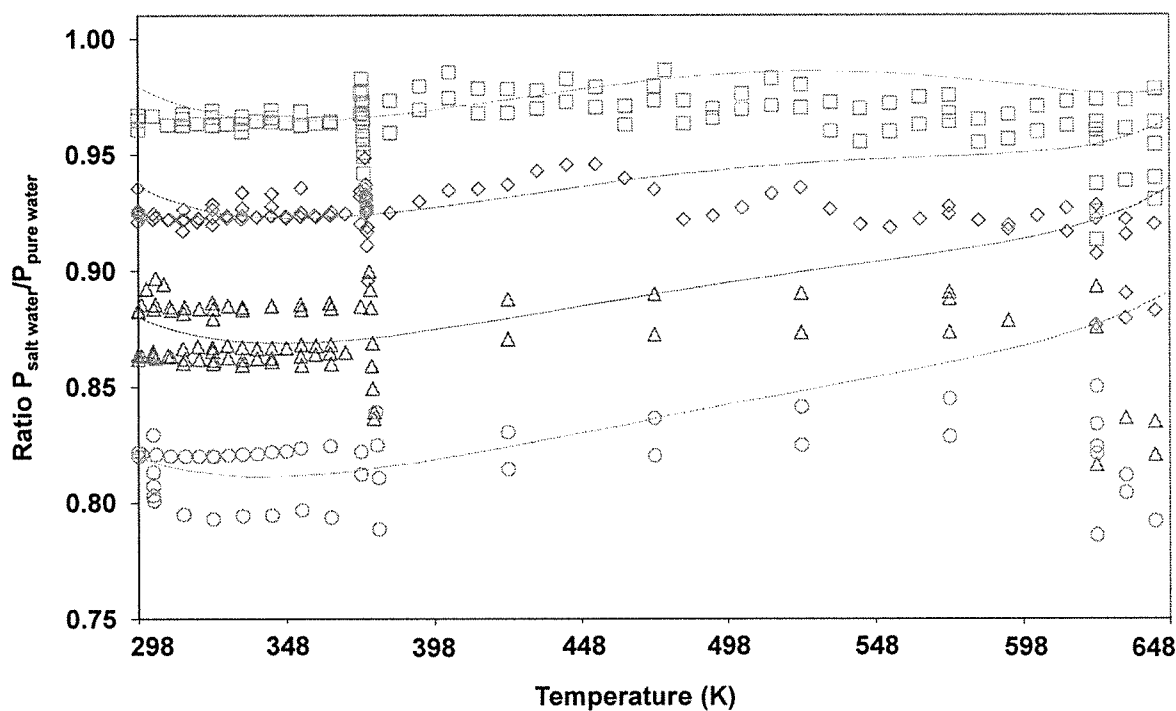


Figure 1. Influence with temperature of salinity on the brine vapor pressures compared to pure water vapor pressure estimated by the DIPPR reference correlation (Rowley et al., 2011). NaCl molalities: 0.7 (\square); 1.9 (\diamond); 3.4 (\triangle) and 4.9 (\circ). Symbols are experimental data. Lines are the model representations.

Experimental molar volumes at and out of saturation up to 5.7 molal of NaCl are represented respectively with an AAD of 4.6 % for temperatures up to 713 K and of 4.0 % for temperatures and pressures up to 773 K and 400 MPa. Generally, molar volumes are worst represented at temperatures higher than water critical temperature together with pressures below 100 MPa.

Experimental water osmotic coefficients are represented with an AAD of 2.5 % for NaCl salinity up to 10 molal and temperatures as high as 573 K. Experimental determination of NaCl mean ionic activity coefficients are also available up to 573 K for NaCl salinity up to 6.7 molal. These last data are represented with an AAD of 3 % and are illustrated in Figure 2. Both salinity and temperature effects are quite well represented by the eCPA model.

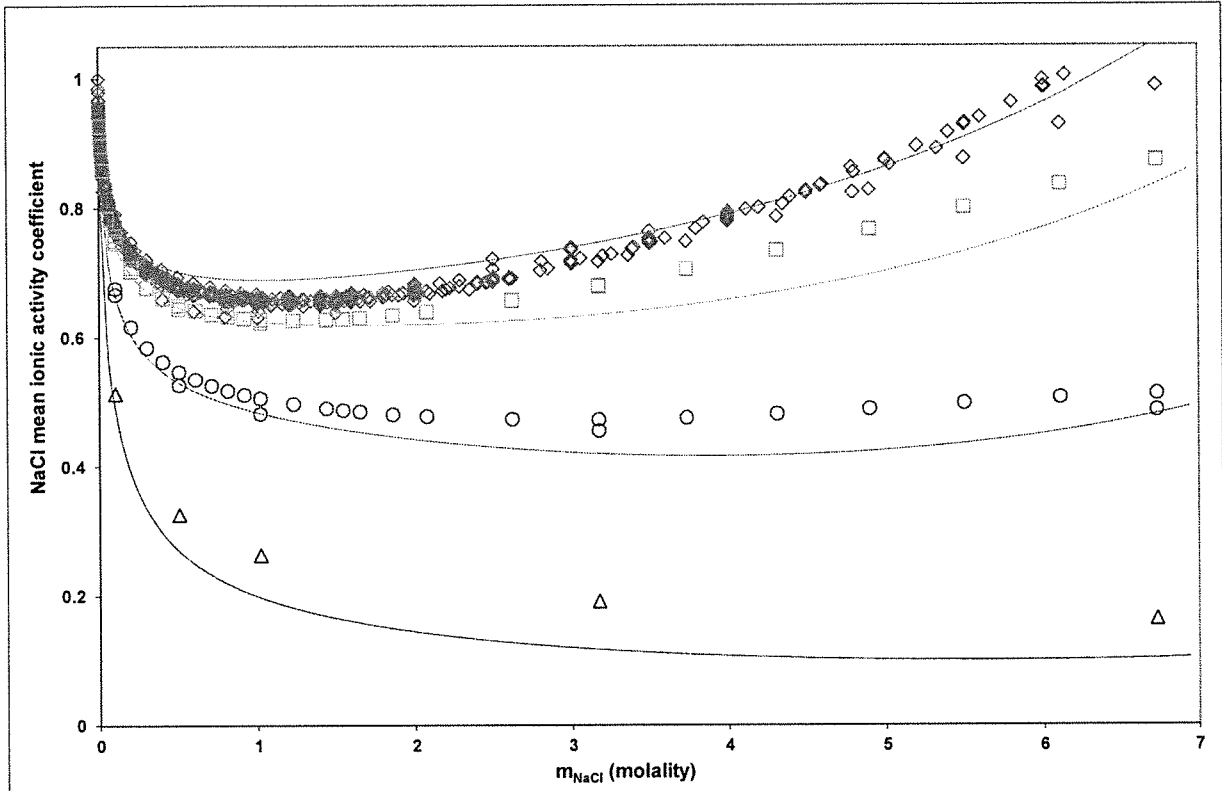


Figure 2. Evolution with NaCl molality of the NaCl mean ionic activity coefficient at 298 K (\diamond); 373 K (\square); 473 K (\circ) and 573 K (\triangle). Symbols are the experimental data. Lines are the model.

5. $\text{CH}_4 + \text{CO}_2$, $\text{CH}_4 + \text{H}_2\text{O}$ and $\text{CO}_2 + \text{H}_2\text{O}$ systems

The system $\text{CH}_4 + \text{CO}_2$ is modeled using a binary interaction parameter (k_{ij} in equation (3)) equal to 0.0882. This value is directly taken from literature (Tsivintzelis et al., 2011) and, as shown by these authors, this parameter allows a good reproduction of phase equilibrium and densities of this system.

The systems $\text{CH}_4 + \text{H}_2\text{O}$ and $\text{CO}_2 + \text{H}_2\text{O}$ are particularly difficult to model at high temperature and pressure due to the presence of one (liquid-vapor) or even two (liquid-vapor and liquid-liquid) critical points, as illustrated on Figure 3 and Figure 4.

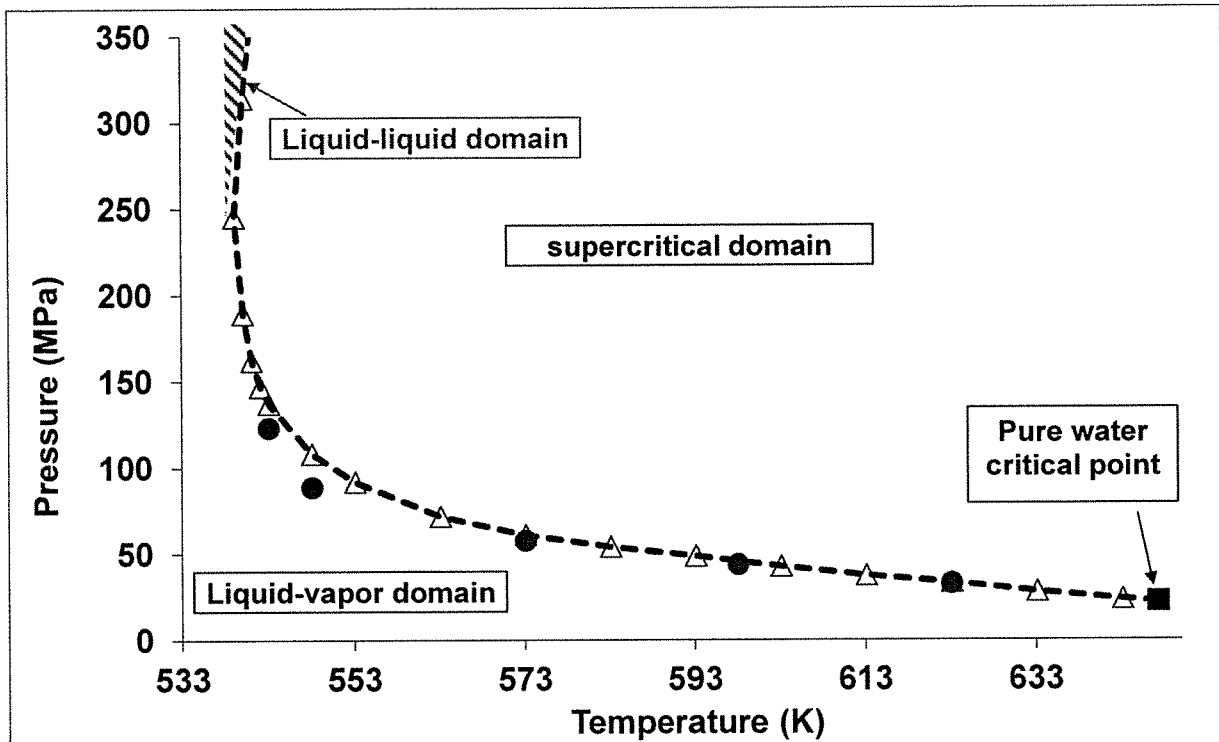


Figure 3. Locations of critical points in the CO₂ + H₂O system. Symbols are the experimental critical points (filled circles: Takenouchi et al. (Takenouchi and Kennedy, 1964); open triangles: Todheide et al. (Todheide and Franck, 1963)). The dotted line is a guide for the eyes. The hachured area stands for the liquid-liquid domain.

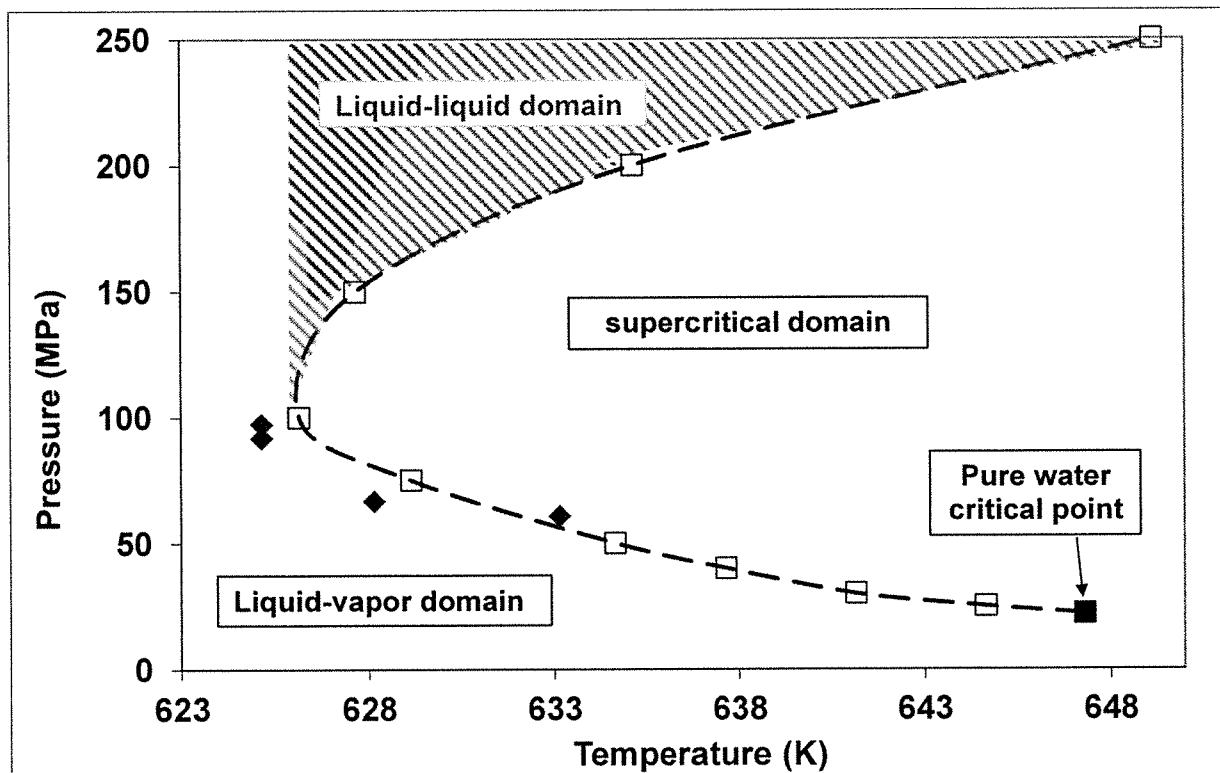


Figure 4. Locations of critical points in the CH₄ + H₂O system. Symbols are the experimental critical points (filled diamonds: Sultanov et al. (Sultanov et al., 1971; Sultanov, 1972); open squares: Welsch (Welsch, 1973)). The dotted line is a guide for the eyes. The hatched area stands for the liquid-liquid domain.

For the CH₄ + H₂O system, the liquid-vapor critical points appear for a temperature and pressure of 626 K and 97.3 MPa, and finish at the critical point of pure water (647 K, 22.06 MPa). Below the temperature of 626 K, the system exhibits a two-fluid phase equilibrium without critical point. The experimental data of Welsch (Welsch, 1973) also exhibit the existence of liquid-liquid critical points for temperatures and pressures above 626 K and 100 MPa. A liquid-liquid phase equilibrium domain is thus determined for temperatures and pressures above the liquid-liquid critical point line. The system is single phase for temperatures and pressures between the liquid-liquid critical point line and the liquid-vapor critical point line. The CO₂ + H₂O system behaves similarly. It can however be noticed that the liquid-liquid critical point line appears for higher pressures (above 250 MPa), and the minimal temperature for which a liquid-vapor critical point exists is close to 538 K. For both systems, only a very limited number of experimental data are available for the high pressure liquid-liquid equilibrium and the location of the liquid-liquid critical points. Consequently, we only focus in this work on the modeling of the liquid-vapor phase equilibrium.

Without binary interaction parameters, large deviations are often observed in phase equilibrium predictions for the binary systems with H₂O. More specifically, critical points are not correctly predicted. Thus, binary interaction parameters are required to better represent the experimental liquid-vapor phase equilibrium data of the binary systems CH₄ + H₂O and CO₂ + H₂O. These parameters have been fitted to (1) reproduce the gas solubility in the aqueous phase and (2) to represent the phase envelope closure at the appearance of the mixture critical point. Note that for these systems, no volumetric data have been used in the parameter regression. The phase densities given by the model are thus obtained in pure prediction. We also recall that the liquid-liquid domain is not considered in this work. The number of experimental gas solubility data and the temperature and pressure range used to fit the binary interaction parameters are given in Table 5. The temperature and pressure ranges are taken as large as possible to ensure a good extrapolation of the model. However, experimental data at high temperature / high pressure are pondered with a more important weight, as we focus in this work more specifically on these specific conditions.

Table 5. Experimental gas solubility data used for binary interaction parameter regression.

System	<i>n</i> data	Temperature range	Pressure range	Salinity max. (molality)	Ref.
CH ₄ + H ₂ O	1061	[253 ; 623 K]	[0.1 ; 250 MPa]	-	(Addicks et al., 2002;Carroll, 1998;Chapoy et al., 2003;Chapoy et al., 2004b;Culberson, 1951;Culberson and McKetta, 1950;Davis and McKetta, 1960;Dhima, 1998;Duffy et al., 1961;Folas et al., 2007;Gillespie and Wilson, 1982;Kiepe et al., 2003b;Kim et al., 2003;Lekvam and Bishnoi, 1997;Michels et al., 1936;Olds et al., 1942;Rigby and Prausnitz, 1968;Sanchez and de Meer, 1978;Sharma, 1969;Siqueira Campos et al., 2010;Sultanov et al., 1971;Sultanov,

					1972;Tabasinejad et al., 2011;Ugrozov, 1996;Wang et al., 1995;Yang et al., 2001;Yarim-Agaev et al., 1985;Yarrison et al., 2006;Yokoyama et al., 1988)
CO ₂ + H ₂ O	1723	[253 ; 643 K]	[0.1 ; 350 MPa]	-	(Addicks et al., 2002;Carroll, 1998;Chapoy et al., 2003;Chapoy et al., 2004b;Culberson, 1951;Culberson and McKetta, 1950;Kiepe, 2002;Takenouchi and Kennedy, 1964;Todheide and Franck, 1963)(Ai et al., 2005;Anderson, 2002;Bamberger et al., 2000;Bando et al., 2003;Bermejo et al., 2005;Briones et al., 1987;Chapoy et al., 2004a;Crovetto and Wood, 1992;D'souza et al., 1988;Dalmolin et al., 2006;Davis and McKetta, 1960;Dell'Era et al., 2010;Dhima, 1998;Dhima et al., 1999;Dohm et al., 1993;Duffy et al., 1961;Fenghour et al., 1996;Ferrentino et al., 2010;Folas et al., 2007;Fonseca et al., 2007;Gillespie and Wilson, 1982;Gu, 1998;Gui et al., 2010;Iwai et al., 2004;Jackson et al., 1995;Jarne et al., 2004;King et al., 1992;Koschel et al., 2006;Li et al., 2004;Malegaonkar et al., 1997;Marshall et al., 1958;Martin et al., 2009;Mather and Franck, 1992;Morgan and Maass, 1931;Mueller et al., 1988;Nakayama et al., 1987;Nighswander et al., 1989;Novak et al., 1961;Patel et al., 1987;Pohorecki and Mozenski, 1995;Prutton, 1945;Qin et al., 2008;Ruffine and Trusler, 2010;Rumpf et al., 1994;Sako et al., 1991;Servio

					and Englezos, 2001;Silkenbaumer et al., 1998;Siqueira Campos et al., 2010;Stewart and Munjal, 1970)(Valtz et al., 2004;Verbrugge, 1979;Vilcu and Gainar, 1967;Wiebe, 1939;Wiebe and Gaddy, 1940;Zaalishvili, 1940;Zawisza and Malesinska, 1981;Zel'vinskii, 1937;Zheng et al., 1997)
$\text{CH}_4 + \text{H}_2\text{O} + \text{NaCl}$	599	[273 ; 573 K]	[10 ; 150 MPa]	6	(Blount, 1980;Cramer, 1982;McGee et al., 1981;O'Sullivan, 1970)
$\text{CO}_2 + \text{H}_2\text{O} + \text{NaCl}$	509	[277 ; 723 K]	[1 ; 140 MPa]	6	(Bando et al., 2003;Ferrentino et al., 2010;Gu, 1998;Kiepe, 2002;Koschel et al., 2006;Li and Tsui, 1971;Malinin and Kurovskaya, 1975;Malinin and Savelyeva, 1972;Nighswander et al., 1989;Rumpf et al., 1994;Takenouchi and Kennedy, 1965)

In a first step, the binary interaction parameter is fitted individually for each temperature. That allows to plot its trend with temperature, as shown on Figure 5 and Figure 6 for the systems $\text{CH}_4 + \text{H}_2\text{O}$ and $\text{CO}_2 + \text{H}_2\text{O}$, respectively.

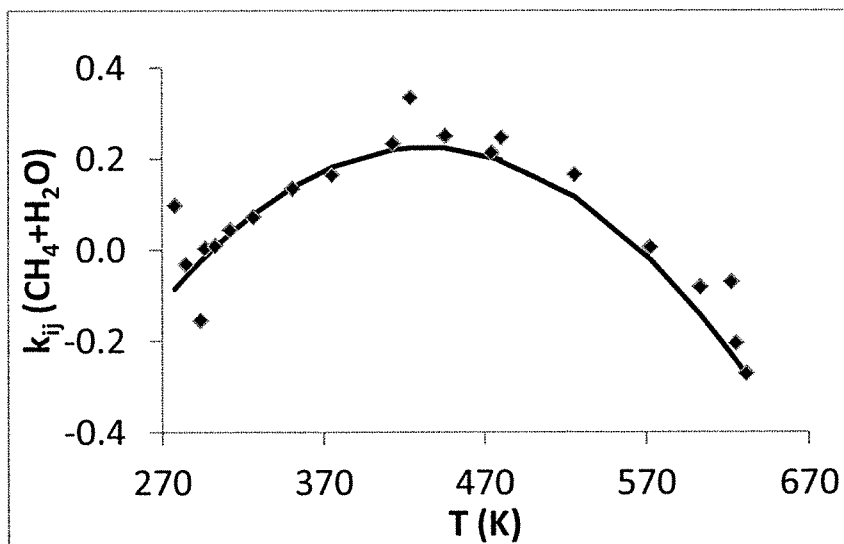


Figure 5. Binary interaction parameters for the $\text{CH}_4 + \text{H}_2\text{O}$ system. Symbols: optimized values for each temperatures. Line: fit of the optimized values (equation (22)).

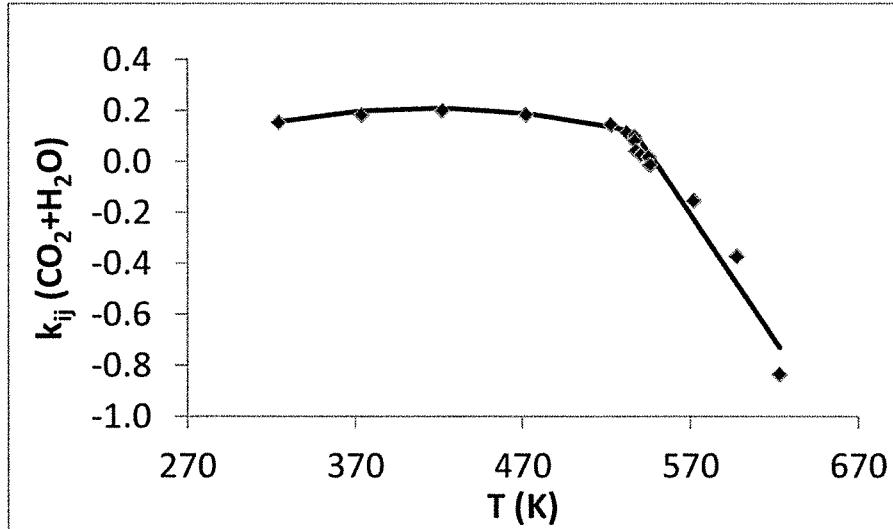


Figure 6. Binary interaction parameters for the $\text{CO}_2 + \text{H}_2\text{O}$ system. Symbols: optimized values for each temperatures. Line: fit of the optimized values (equation (22)).

The optimized binary parameters for the $\text{CH}_4 + \text{H}_2\text{O}$ system exhibit a parabolic trend. This is why in a second step, a second order temperature dependency is proposed for this parameter:

$$k_{ij}(T) = k_{ij}^0 + k_{ij}^1 \cdot T + k_{ij}^2 \cdot T^2 \quad (22)$$

Where T is the temperature in K. The parameters k_{ij}^0 , k_{ij}^1 and k_{ij}^2 are given in Table 6.

The optimized parameters for the $\text{CO}_2 + \text{H}_2\text{O}$ system show two distinct trends: below 537 K (temperature for which the critical point appears), moderate values are obtained (between 0 and 0.2), and they are fitted with a second-order temperature dependency. For temperature above 537 K, the values of k_{ij} drastically decrease, and become largely negative (up to -0.8). Such very high negative values for this parameter is a consequence of the strong attraction of water and CO_2 in this temperature range where critical points are present. The optimized k_{ij} are fitted in this domain with a first-order temperature dependency. The same approach is followed for the other binary systems investigated. Table 6 shows the parameters determined for equation (22) for each system. These binary interaction parameters are found to be a good compromise to reproduce simultaneously gas solubility in water, critical point appearance, and phase density.

Table 6. Binary interaction parameters for the eCPA model

System	VLE data range (K)	k_{ij}^0	k_{ij}^1	k_{ij}^2
$\text{CH}_4 + \text{CO}_2$ (Tsvintzelis et al., 2011)	219 - 301	0.08820	0	0
$\text{CH}_4 + \text{H}_2\text{O}$	283 - 663	-2.18100	0.01111	$-1.27902 \cdot 10^{-5}$
$\text{CO}_2 + \text{H}_2\text{O}$	323 - 537	$-9.12960 \cdot 10^{-1}$	$5.40410 \cdot 10^{-3}$	$-6.49667 \cdot 10^{-6}$
	537 - 623	5.39448	$-9.82899 \cdot 10^{-3}$	-
$\text{CH}_4 + [\text{Na}^+ \text{ and } \text{Cl}^-]$	286 - 563	1.47532	$-7.33268 \cdot 10^{-3}$	-
$\text{CO}_2 + [\text{Na}^+ \text{ and } \text{Cl}^-]$	298 - 673	0.40050	$2.24613 \cdot 10^{-3}$	$-1.40671 \cdot 10^{-5}$

Figure 7 presents experimental and calculated pressure-composition diagrams for CH₄ + H₂O binary system from 373 to 633 K. Trends shown by the liquid-vapor equilibrium data are fairly well reproduced by the model in the entire range of temperature, even if the critical pressure of the mixture is slightly over predicted as well as methane solubility. Molar volumes are generally well represented for this system and only conditions in the continuity of pure water critical coordinates are also not well represented, viz. for temperatures close and above pure water critical temperature for high H₂O content.

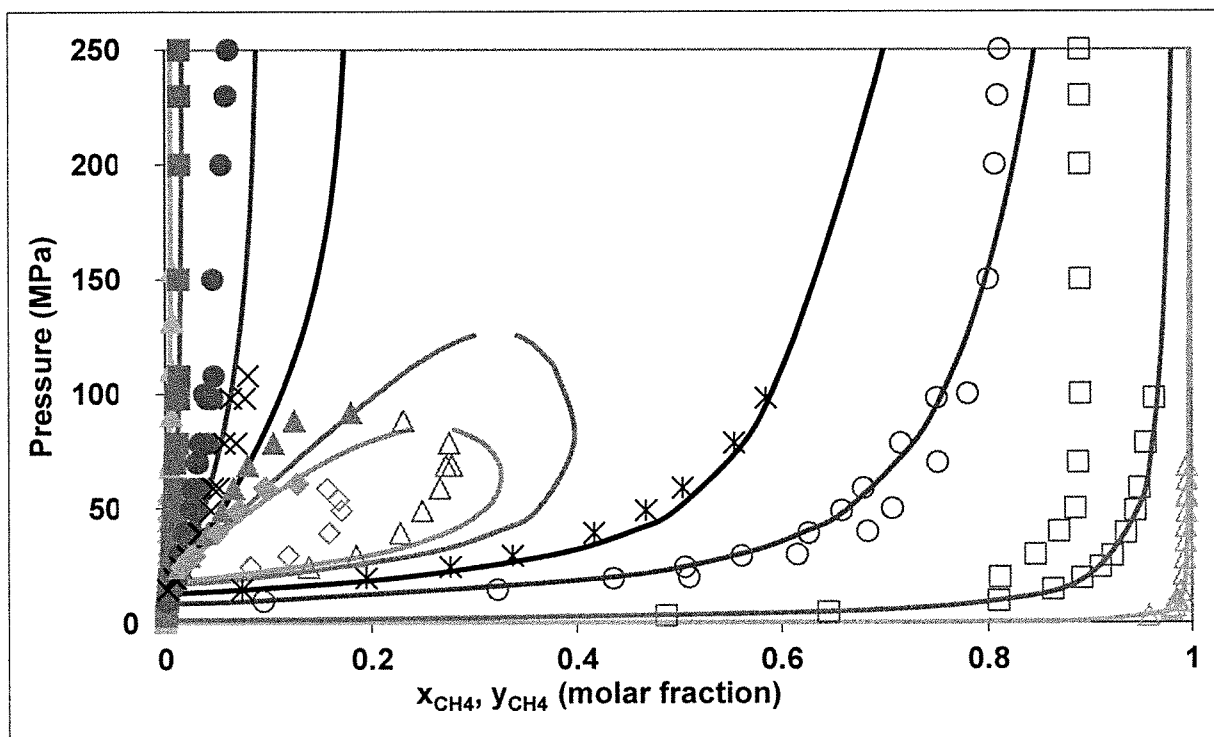


Figure 7. VLE for CH₄ (1) + H₂O (2) binary system at 373 K (Δ), 473 K (\square), 573 K (\circ), 603 K ($*$), 625 K (\diamond) and 633 K (\triangle). Empty symbols refer to experimental vapor phase composition (y_{CH_4}) while full symbols refer to experimental liquid phase composition (x_{CH_4}). Lines are the model representations.

Experimental and calculated liquid-vapor equilibrium for the CO₂ + H₂O binary system are shown in Figure 8 between 373 and 623 K. Even if increasing the cross-association strength between CO₂ and H₂O (using a larger association volume for CO₂) has improved the VLE representation for the binary system, it is still not sufficient to well reproduce both liquid and vapor composition at high temperature. As a consequence, CO₂ liquid phase composition is well reproduced, but CO₂ vapor phase compositions are over predicted by the model at 473 and 533 K. It is worth noticing that experimental data for vapor phase composition are very scarce in literature at high temperature. More specifically at 533 K, two experimental data sets are available (Takenouchi and Kennedy, 1964; Todheide and Franck, 1963) but are not really consistent. The acquisition of new experimental data would be useful for modeling this system in such extreme conditions. Although not included in the regression parameter database, molar volumes are generally well represented for this system but in the same way as observed with CH₄ + H₂O system, the model fails to reproduce accurately molar volumes particularly at temperatures close and above water critical temperature for high H₂O content.

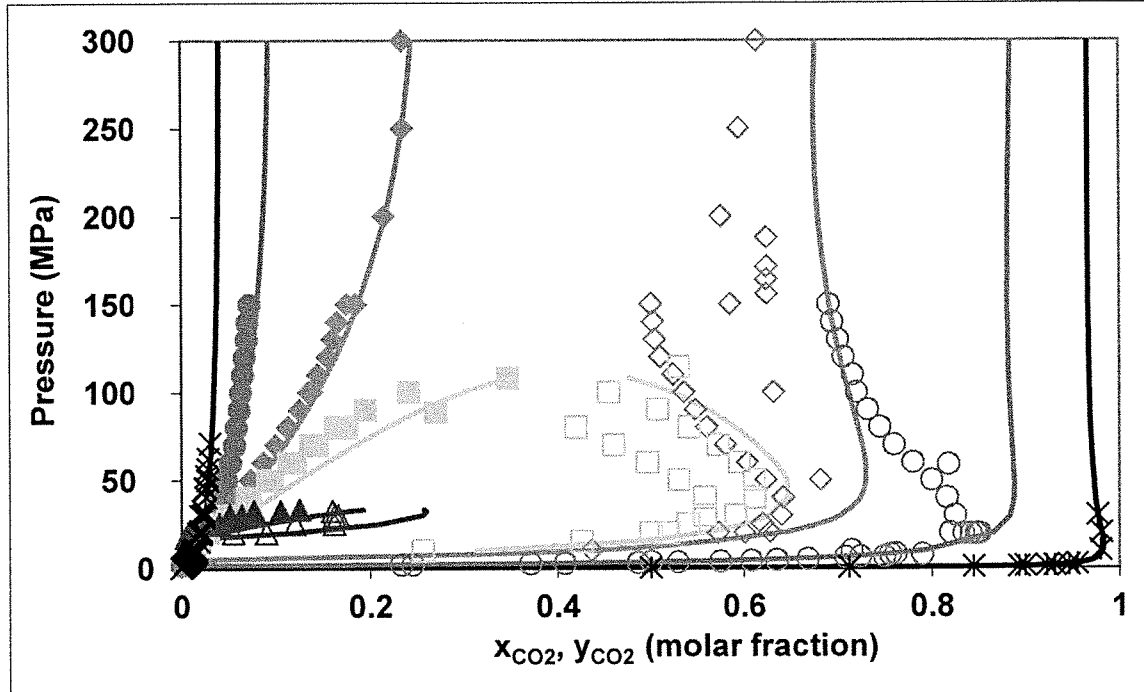


Figure 8. VLE for CO₂ (1) + H₂O (2) binary system at 373 K (*), 473 K (O), 533 K (◇), 548 K (□) and 623 K (△). Empty symbols refer to experimental vapor phase composition (y_{CO_2}) while full symbols refer to experimental liquid phase composition (x_{CO_2}). Lines are the model representations.

Table 7 presents deviations between experimental data and model description for liquid-vapor phase equilibrium (liquid and vapor phase composition) and molar volumes (V_m) out of saturation for the binary systems studied.

Table 7. AAD (%) between experimental data and model description using eCPA equation of state for liquid-vapor equilibrium (VLE) and molar volumes for binary systems.

System	x_l (AAD %)	y_l (AAD %)	V_m (AAD %)
CH ₄ (1) + CO ₂ (2) (Tsivintzelis et al., 2011)	6	9	1.7
CH ₄ (1) + H ₂ O (2) (this work)	16	8	2.6
CO ₂ (1) + H ₂ O (2) (this work)	26	12	2.8

The CPA-family equation of state has already proved its ability to be extended to multi-component systems from parameterizations carried out on binary systems only. As an example for this application, co-solubility data of Qin et al. (Qin et al., 2008) for the ternary system CH₄ + CO₂ + H₂O at 375 K are correctly represented using only the binary interaction parameters of Table 6. Deviations on vapor pressures and vapor phase composition between experiments and model predictions are reported in Table 8 and shown in Figure 9. The highest deviations are found to predict water molar fraction in the vapor phase where experimental values are very low (about 0.02). It can be concluded here that the VLE behavior is well predicted by the eCPA model, showing its ability to be extended to multi-component mixtures with only binary interaction parameters.

Table 8. AAD (%) between prediction using eCPA equation of state and experimental data for vapor pressure and vapor phase composition in the CH₄ + CO₂ + H₂O ternary system at 375 K.

Vapor pressure	y_{CH_4}	y_{CO_2}	y_{H_2O}
5.6%	2.9%	3.0%	35.1%

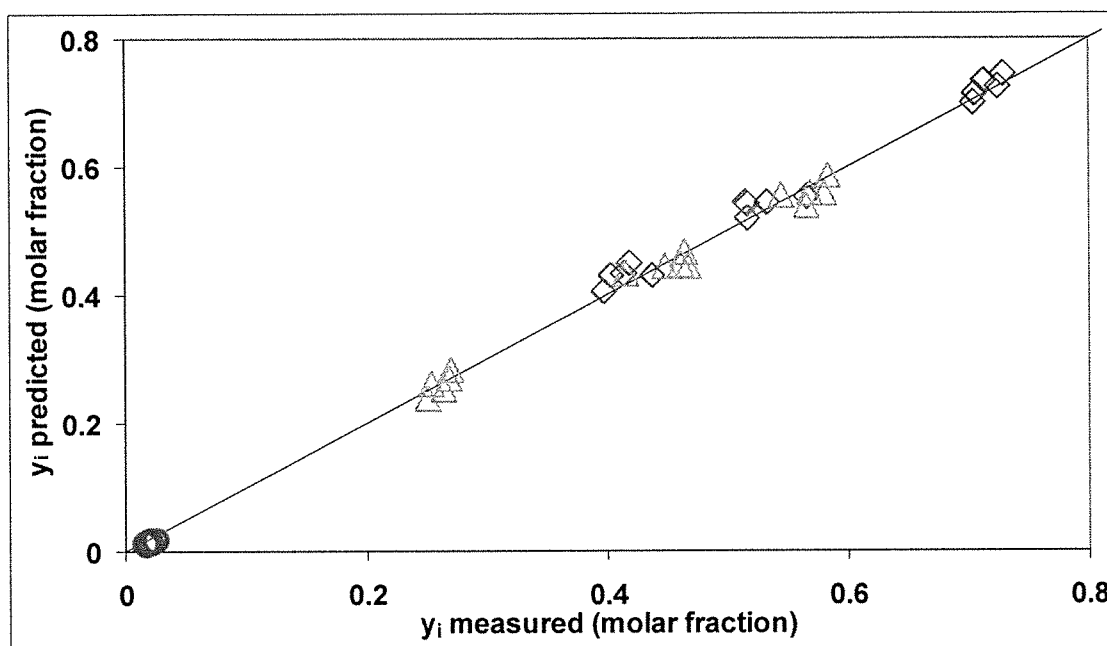


Figure 9. Comparison between experimental and predicted vapor phase composition for the CH₄ + CO₂ + H₂O ternary system at 375 K. y_{CH_4} (Δ); y_{CO_2} (\diamond); and y_{H_2O} (\circ).

6. CH₄ + H₂O + NaCl and CO₂ + H₂O + NaCl systems

The addition of electrolytes in an aqueous solution is known to reduce the gas solubility (“salting-out” effect). A consequence is the disappearance or the displacement of the mixture critical point to higher temperature and pressure than for a salt-free solution. In order to reproduce such a behavior, it is necessary to introduce in the model binary interaction parameter between the light gas molecule (CH₄ or CO₂) and the ions (Na⁺ and Cl⁻). These parameters have been fitted in this work to reproduce the gas solubility for a large range of temperatures, pressures and salinities. No volumetric data have been included in the parameter regression database. The phase densities of these systems are thus obtained in pure prediction. The gas solubility experimental data and conditions used for this optimization are given in Table 5. The optimized parameters are reported in Table 6.

As illustrated on Figure 10, the salting out effect observed for the CH₄ + (H₂O + NaCl) pseudo-binary system is correctly predicted by the eCPA model. This figure compares experimental and calculated CH₄ solubility at 408 K for NaCl salinity ranging from 0 to 5.6 molal. Although at this temperature methane solubility is very low, the model reproduces correctly experiments with and without NaCl for salinities up to about 5 molal. It is worth noticing that no vapor composition data has been found in literature to validate the model predictions. Furthermore, only few density (molar volumes) experimental data have been found for this system. They have all been generated at 800 K

for pressures ranging from 10 to 250 MPa and NaCl salinity between 0.6 and 1.3 molal. At such high temperature, the average deviations are ranging from 10 % at 250 MPa to 50 % at 100 MPa.

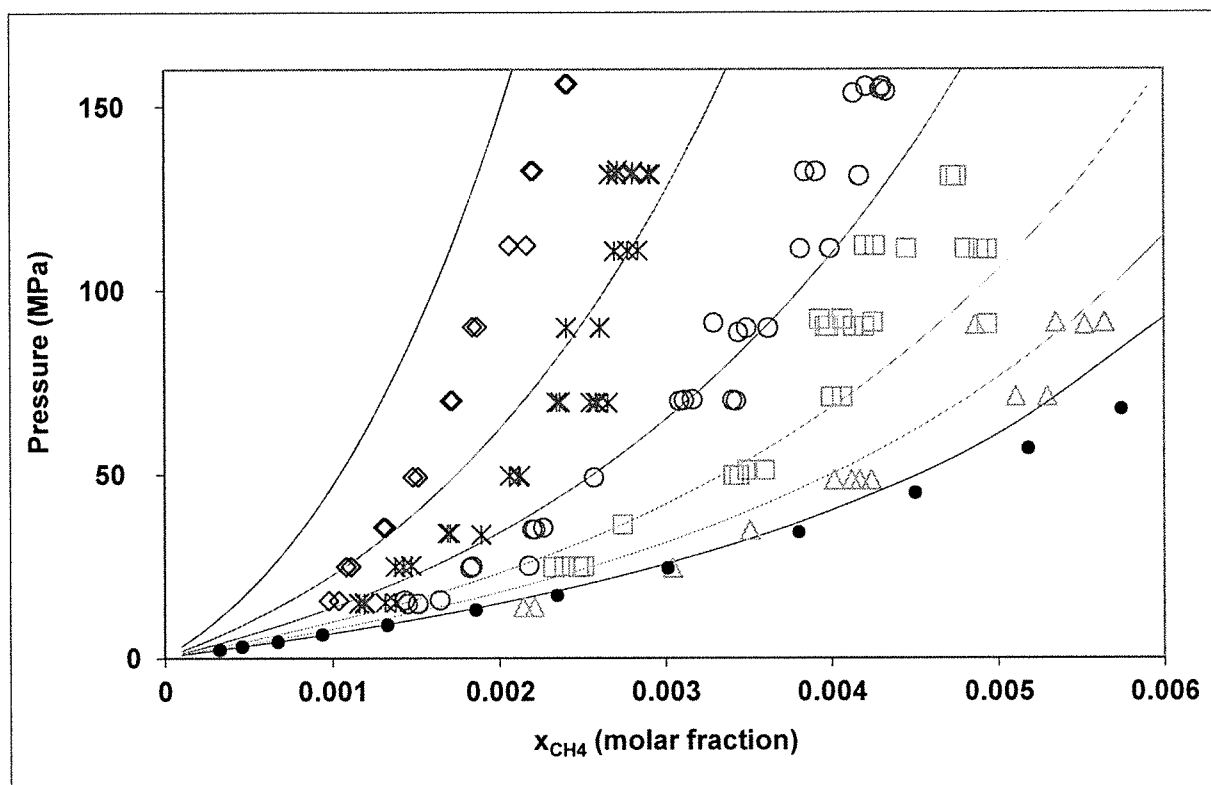


Figure 10. Solubility for CH_4 (1) + $(\text{H}_2\text{O} + \text{Na}^+ + \text{Cl}^-)$ (2) pseudo-binary system at 408 K for NaCl molality 0.00 (●); 0.86 (△); 1.8 (□); 2.9 (○); 4.2 (*) et 5.6 (◇). Symbols are experimental data. Lines are the model representations.

Representations of experimental and calculated phase equilibrium for $\text{CO}_2 + (\text{H}_2\text{O} + \text{NaCl})$ pseudo-binary system are shown in Figure 11 at 573 K for 0 to 3.4 NaCl molality. The salting out effect illustrated by available experimental data is fairly well reproduced here by the model for NaCl salinities up to 5 molal. Again, no experimental data for vapor phase composition is available in literature. The acquisition of new experimental data would be useful for studying this system in such extreme conditions. Molar volumes are predicted with an average deviation of 28 % for temperatures ranging from 300 to 793 K. The highest deviations (above 40 %) are observed for pressures close to 50 MPa and for temperatures above 573 K.

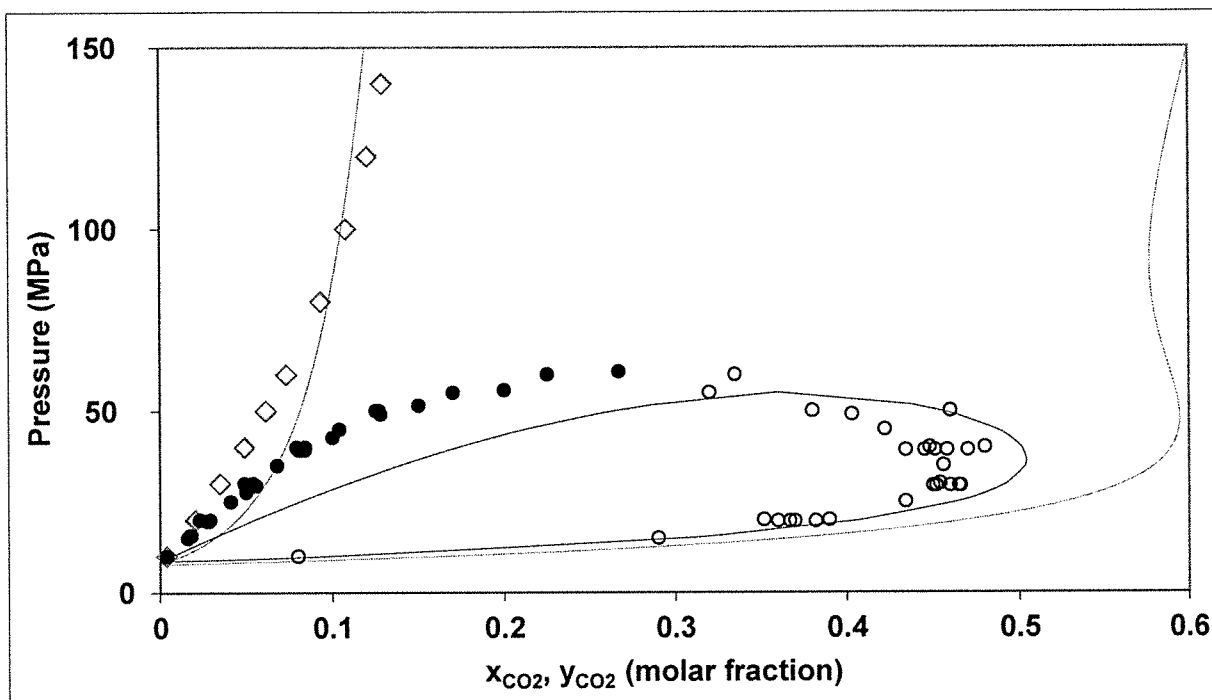


Figure 11. VLE for CO_2 (1) + $(\text{H}_2\text{O} + \text{Na}^+ + \text{Cl}^-)$ (2) pseudo-binary system at 573 K for NaCl molality 0.00 (●) and 3.4 (◇). For the system excluding salt, empty symbols refer to experimental vapor phase composition (y_{CO_2}) while full symbols refer to experimental liquid phase composition (x_{CO_2}). Lines are the model representations.

Finally, Table 9 gives the average deviations obtained for the vapor pressure and molar liquid volumes for these salted systems.

Table 9. AAD (%) between experimental data and model description using eCPA equation of state for liquid-vapor equilibrium (VLE) and molar volumes for $\text{CH}_4 + \text{H}_2\text{O} + \text{Na}^+ + \text{Cl}^-$ and $\text{CO}_2 + \text{H}_2\text{O} + \text{Na}^+ + \text{Cl}^-$ systems.

System	P_{sat} (AAD %)	V_m (AAD %)
$\text{CH}_4 + (\text{H}_2\text{O} + \text{Na}^+ + \text{Cl}^-)$	33	33
$\text{CO}_2 + (\text{H}_2\text{O} + \text{Na}^+ + \text{Cl}^-)$	32	28

7. Conclusions

An electrolyte version of the Cubic Plus Association (eCPA) equation of state has been adapted to systems containing CH_4 , CO_2 , H_2O and NaCl (up to 5 molal) at temperatures and pressures up to 773 K and 200 MPa. Its purpose is to represent the phase behavior (including salting-out effect and critical points) and the densities of phases in a range of temperature and pressure encountered in deep reservoir and basins. The goal of the parameterization proposed is not to reach very high accuracy for phase equilibrium and volumetric properties, but rather to develop a semi-predictive approach to model this system while allowing an easy extension to other compounds.

Among the parameters of the pure molecular species only the cross associating volume of CO₂ has been modified from the literature values, to better represent the high temperatures phase equilibrium of the CO₂ + H₂O binary system. Parameters of the pure ions (Na⁺ and Cl⁻) have been adjusted to represent vapor pressures and mean ionic activity coefficients of brine. Finally, binary interaction parameters between each gas (CO₂ and CH₄) with H₂O and ions have been fitted to represent phase equilibrium with a special focus on critical phase envelope closure and salting out effects.

Without salt, predictions for pure component saturation vapor pressures and liquid molar volumes present an average absolute deviation (AAD) lower than 3 % compared to experimental reference values. The pure component molar volumes out of saturation show an AAD lower than 4 %. The highest deviations in densities are observed in the vicinity of the critical coordinates of pure water and this effect increases when gases or salts are added to the system. For each binary system, CH₄ + CO₂, CH₄ + H₂O and CO₂ + H₂O, binary interaction parameters have been fitted to correctly predict the shape of the fluid phase envelopes (including liquid-vapor critical points) in the entire temperature and pressure range considered (219 K to 633 K and up to 250 MPa). The methane concentration in both phases of the CH₄ + CO₂ binary system is represented with an AAD lower than 9 %. The methane solubility in water is represented within 16 % and 8 % for the methane content of the vapor. The CO₂ solubility in water is within 26 %, while the CO₂ in the vapor phase shows an average deviation of 12 %. All molar volumes are represented with an AAD lower than 3 %. The few VLE data which were found for the CH₄ + CO₂ + H₂O ternary system are fairly well predicted with the model without extra parameter and comfort the ability of the eCPA equation of state to be extended to multi-component systems. In the presence of salts, gas + ion binary interaction parameter have been fitted, and all phase equilibrium are qualitatively correctly described, and more specifically the salting out effect. The solubility of methane or CO₂ in brines, up to 5 molal, is represented with an AAD of 33 % in a large temperature and pressure range (up to 673 K and 150 MPa). It should be noticed that for high temperatures, experimental data are relatively scarce and not always consistent. No data exist for water content of the vapor phase in these conditions.

The new eCPA model can be easily extended to other components including also others ions to better represent real fluid behavior in very deep reservoir conditions.

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List of symbols

a	attractive term in SRK EoS (Pa.m ⁶ .mol ⁻²)
AAD	Average Absolute Deviation (%)

b	co-volume term in SRK EoS ($\text{m}^3 \cdot \text{mol}^{-1}$)
DIPPR	Design Institute of Physical Property Data
D	solution dielectric constant
D_0	vacuum permittivity ($\text{F} \cdot \text{m}^{-1}$)
e	elementary charge (C)
eCPA	electrolyte Cubic Plus Association
F	dummy variable used to present AAD equation
$g(\rho)$	radial distribution function
k_{ij}	binary interaction parameter
m	parameter used in the alpha function
MSA	Mean Spherical Approach
n	number of mole
N	number of data
N_{av}	Avogadro's constant
R	ideal gas constant ($\text{J} \cdot (\text{mol} \cdot \text{K})^{-1}$)
SRK	Soave Redlich Kwong
T	absolute temperature (Kelvin)
v	molar volume ($\text{m}^3 \cdot \text{mol}^{-1}$)
V	volume (m^3)
VLE	Vapor Liquid Equilibrium
x_i	molar fraction of component i in liquid phase
X^A	Unbonded fraction of site A of the molecule i
y_i	molar fraction of component i in vapor phase
Z_i	valence of ion i

Greek letters :

α	tunable parameter used in Simonin's model
β^{A,B_j}	association volume between site A on molecule i and site B on molecule j (\AA^3)
Δ^{A,B_j}	association strength between site A on molecule i and site B on molecule j (\AA^3)
ε^{A,B_j}	association energy of interaction between site A on molecule i and site B on molecule j , per molecule (J)
π	pi number
ρ	molar density of solution ($\text{mol} \cdot \text{m}^{-3}$)

σ_b solvated diameter in eCPA EoS (\AA)

Subscripts:

0 standard property
 A_i site A of the molecule i
c critical
 i applied to component i
 j applied to component j
m molar
s solvent

Superscripts:

* reduced property
0,1,2 iterative values to differ parameters for k_{ij} evolution with temperature
+ positive charge
- negative charge
assoc association
hs hard sphere
res residual

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