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MODELLING GAS HYDRATE EQUILIBRIA USING THE ELECTROLYTE NON-RANDOM TWO-LIQUID (ENRTL) MODEL

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ABSTRACT

The semi-empirical electrolyte NRTL (eNRTL) model [1,2,3,4], also referred to as the model of Chen, is a versatile model for the excess molar Gibbs energy, capable of describing multicomponent electrolyte systems over wide ranges of state conditions. The model represents the excess Gibbs molar energy as the sum of two contributions, the first one of which accounts for long range electrostatic forces between ions, and the second one for the short range forces between all species. In single solvent systems, the long range interaction contribution consists of a term originating from the Pitzer-Debye-Hückel (PDH) equation [5]. A modified version of the Non-Random-Two-Liquid (NRTL) local composition model of Renon and Prausnitz [6] accounts for the short range interaction between all the species in their immediate neighbourhood. The most general form of the eNRTL activity coefficient expressions for both, individual species as well as mean ionic quantities have been implemented in the JAVA language. Model parameters for different strong electrolytes are provided by means of a data bank in the xml file format. The program code of the model implementation has been incorporated into the program package "gashydyn" developed in our group and allowing for performing equilibrium calculations involving gas hydrate phases. The correctness of the program implementation of the eNRTL expressions has been verified by comparing the results of numerous examples with corresponding literature results, including the composition dependence of the mean ionic activity coefficient of binary salt + solvent mixtures as well as of ternary salt 1 + salt 2 + mixtures. For the ternary systems, the influence of different values for the salt-salt binary interaction parameter is illustrated. Calculations on HLV phase equilibria of ternary H_2O + salt + gas and quaternary H_2O + salt + gas 1 + gas 2 systems have been performed. The calculations are based upon an equation of state approach for the gas phase, the van-der-Waals and Platteeuw model for the clathrate hydrate phase and the eNRTL model to account for the liquid phase non-idealities. The results reveal that a satisfying correlation of the experimental p-T-phase equilibrium data can be achieved with results ranging from around 1 to 15 %.

Keywords: modeling, gas hydrate, eNRTL model, electrolytes, phase equilibrium, CO_2, CH_4

NOMENCLATURE

A_ϕ – Pitzer-Debye-Hückel constant []

α – nonrandomness factor []

ϕ – Osmotic coefficient []

G – Boltzmann kind factor []

G_m^E – Excess molar Gibbs energy [J·mol^{-1}]

γ – Activity coefficient []

I – Ionic strength []

m – Molality [mol kg^{-1}]

N_{Av} – Avogadro's constant [mol^{-1}]

$N_{exp\,data}$ – Number of experimental data points []

ν – stoichiometric coefficient []

p – Pressure [bar, MPa]

ϑ – Celsius temperature [°C]

R – Perfect gas constant [J·K^{-1}·mol^{-1}]

σ_{rel} – Root mean square deviation (relative) []

T – Temperature [K]

τ – Energetic interaction coefficient []

x – Mole fraction []

X – Effective mole fraction []

Y – Ionic charge fraction []

z – Charge number of ionic species i []

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subscripts

A – Anion with charge number $z_A < 0$

calc – Calculated

C – Cation with charge number $z_C > 0$

CA – Binary salt composed of ν_C cations and ν_A anions

exp – Experimental

i,j,k – Any kind of species

LR – Long range interaction contribution

l – Index numbering experimental data point

m – molar

m – Molecular species and referring to molal concentration scale, respectively, depending on the context

SR – Short range interaction contribution

s – solvent species

x – referring to mole fraction concentration scale

w – water

superscripts

$*$ – unsymmetric convention for normalization of activity coefficients

∞ – infinite dilution

$\circ$ – pure component state

$\ominus$ – Standard value (here: molality $= 1\,\text{mol}\,\text{kg}^{-1}$)

$^{-}$ – concentration quantity based on stoichiometric mole numbers

INTRODUCTION

In electrolyte systems both, electrically neutral molecular species as well as charged particles are present [1]. Due to the additional presence of long-ranging electrostatic interactions between the ions being inversely proportional to square of their mutual distance, the thermodynamics of electrolyte solutions is significantly more difficult than the treatment of nonelectrolyte systems [7]. Contrary, the forces acting between ions and molecules and molecules and molecules, respectively, are dominant on shorter distances. Hence, in electrolyte solutions, three types of interactions have to be distinguished [1]: a) Ion-ion interactions (electrostatic, long-ranging); b) Ion-molecule interactions (dominant interactions: electrostatic forces between ions and permanent dipoles, large compared to thermal energies [8], short-range in nature); c) Molecule-molecule interactions (electrostatic forces between permanent dipoles, induction forces between induced dipoles, dispersive forces between non-polar molecules, short-range in nature). These microscopic characteristics of electrolyte solutions are to be taken into account by semi-empirical models capable of describing appropriately the thermodynamics of electrolyte systems.

Numerous semi-empirical excess Gibbs energy expressions have been proposed for electrolyte systems (e.g. by Bromly (1973) [9], Pitzer 1973 [10], by Cruz and Renon (1978) [11], by Chen et al., 1982, 1986, 2001 [1,2,12], by Iliuta et al., 2002 [13]; Papaiconomou et al., 2002 [14]) [3]. Models for the excess Gibbs energy of electrolyte solutions taking into account the nature of the different forces by individual terms often represent the excess molar Gibbs G_m^E energy explicitly as a sum of a long-range and a short range contribution. From these G_m^E model equations expressions for the activity coefficients of electrolyte solutions can explicitly be derived. Variations or equivalents of the Debye-Hückel theory typically comprise the term accounting for the long-range interactions attributed to electrostatic forces between ions [3]. The short-range term is represented by modified versions of well-proven expressions for nonelectrolyte systems that account for the contributions arising from the short-range local interactions of various kinds [3]. The approach used for the short-range contribution can be empirical or based on molecular theory [7]. The model of Pitzer (1973) [10] and the eNRTL model of Chen et al. (1982, 1986, 2004, 2008, 2001) [1-4,12] have gained the widest recognition among the excess Gibbs energy models for electrolyte solutions. Both models have received wide acceptance in industrial practice of thermodynamic modeling of electrolyte systems [3]. In comparison with the model of Pitzer [10], the model of Chen et al. has no limitations with regard to the concentration range and can also treat mixed solvent-systems. Since it principally can describe electrolyte solutions over the whole concentration range, saturated solutions, fused salt and non-electrolyte mixtures are covered as special cases by the model equations [3].

THE ENRTL MODEL

The eNRTL model describes the excess Gibbs molar energy of – in the most general case – a multicomponent electrolyte system by referring to the basic microscopic characteristics of electrolyte solutions. Therefore, the model accounts explicitly for the long ranging inter-ionic forces and the short range forces acting between the various species present in the solution by splitting up the excess Gibbs molar energy G_m^{E*} into the sum of $G_{m,LR}^{E*}$ and $G_{m,SR}^{E*}$, respectively, according to:

$$G_m^{E*} = G_{m,LR}^{E*} + G_{m,SR}^{E*} \qquad (1)$$

where $G_{m,LR}^{E*}$ stands for the long-range and $G_{m,SR}^{E*}$ for the short range contribution to G_m^{E*}. The asterix denotes the unsymmetric reference state (see explanations below).

On the origin of the two contributions

In the eNRTL model, the long range contribution is modeled by a Debye-Hückel term as modified by Pitzer [5], i.e., $G_{m,LR}^{E*} = G_{m,PDH}^{E*}$. In the derivation of the Pitzer-Debye-Hückel (PDH) as well as the Debye-Hückel equation, the solvent is treated as a dielectric continuum. The thermodynamic set of independent variables underlying these equations is the one of the so-called McMillan-Meyer-framework [15], that is to say temperature, molar volume, the chemical potential of the solvent and the mole numbers of all solute species. Therefore the Pitzer-Debye-Hückel (PDH) equation is based on an unsymmetric reference state whereby $G_{m,PDH}^{E*}$ vanishes when the solvent mole fraction reaches unity:

$$\lim_{x_s \to 1} G_{m,PDH}^{E*} = 0 \qquad (2)$$

where x_s denotes the mole fraction of the solvent species (for the definition of different concentration quantities used to describe the composition of electrolyte solutions see further below.). $x_s \to 1$ is equivalent to the condition $\sum_{i \neq s} x_i \to 0$, explaining the term "unsymmetric". $G_{m,PDH}^{E*}$ vanishes if the pure component state is approached for the solvent, but the state of infinite dilution for the solute species.

A modified version of the Non-Random-Two-Liquid (NRTL) model of Renon and Prausnitz [6]

is used to describe the short range contribution $G_{m,SR}^{E*}$. The NRTL model is based on the local composition concept, i.e., $G_{m,SR}^{E*} = G_{m,mod\text{-}NRTL}^{E*} = G_{m,LC}^{E*}$ In contrast to the Pitzer-Debye-Hückel model, the modified NRTL model is based on a symmetric reference state, i.e., it provides an expression for $G_{m,SR}^{E}$, the symmetric molar excess Gibbs energy rather than for $G_{m,SR}^{E*}$. As reference states the model uses the pure liquid solvent, and the hypothetically homogeneously mixed pure molecular and electrolyte solutes, respectively:

$$\lim_{\overline{x}_s \to 1} G_{m,SR}^{E} = 0 \qquad (3)$$

$$\lim_{\overline{x}_m \to 1} G_{m,SR}^{E} = 0, \qquad (4)$$

$$\lim_{\overline{x}_{CA} \to 1} G_{m,SR}^{E} = 0, \qquad (5)$$

Where $\overline{x}_s$, $\overline{x}_m$ and $\overline{x}_{CA}$ denote the stoichiometric mole fractions (see explanations below) of the solvent, the molecular solute components, and the electrolyte solute components, respectively.
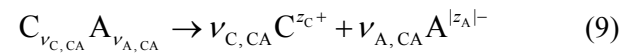
The composition of the system

In the most general case considered here the system is a multicomponent electrolyte solution consisting of $N_m + 1$ molecular components $m_0, m_1, \dots, m_{N_m}$, where $m_0 = s = w$ stands for the molecular solvent component (here water), and $m_1, \dots, m_{N_m}$ for the additional molecular solute species, respectively, in addition to N_C cationic species $C_1, \dots, C_{N_C}$ and N_A anionic species $A_1, \dots, A_{N_A}$, respectively. The corresponding sets of species are denoted by S_m, S_C and S_A, i.e.

$$S_m = \left\{ m_0, m_1, \dots, m_{N_m} \right\} \qquad (6)$$

$$S_C = \left\{ C_1, \dots, C_{N_C} \right\} \qquad (7)$$

$$S_A = \left\{ A_1, \dots, A_{N_A} \right\} \qquad (8)$$

The systems treated here are comprised of strong electrolytes $C_{\nu_{C,CA}} A_{\nu_{A,CA}}$ (abbreviated as CA) which dissociate completely into $\nu_{C,CA}$ cations C^{z_C+} and $\nu_{A,CA}$ anions $A^{|z_A|-}$ according to:

$$C_{\nu_{C,CA}} A_{\nu_{A,CA}} \to \nu_{C,CA} C^{z_C+} + \nu_{A,CA} A^{|z_A|-} \qquad (9)$$

The system composition can either be characterized by means of the mole fraction x_i of any species i, calculated from the corresponding mole numbers of n_j according to:

$$x_i = \frac{n_i}{\sum\limits_{j \in S_m \cup S_C \cup S_A} n_j} \quad \text{(for all } i \in S_m \cup S_C \cup S_A) \quad (10)$$

The composition can also be described terms of the amount of the chemical components regardless of what happens to their particles when being dissolved. These quantities are called here "overall", "apparent" or "stoichiometric quantities". For example, the overall molality $\bar{m}_k$ of component k is defined as:

$$\bar{m}_k = \frac{\bar{n}_k}{\bar{n}_s M_s} \quad \text{(for all } k \in \{S_m \cup S_{CA}\} \backslash \{s\}) \quad (11)$$

Activity coefficients

The activity coefficient $\gamma_{x,i}$ describing the non-ideality of a phase (mostly applied to quantify the liquid phase non-ideallities) can be derived from an expression for the excess molar Gibbs energy G_m^E according to:

$$\ln \gamma_{x,i} = \frac{1}{RT} \left(\frac{\partial \left(n G_m^E \right)}{\partial n_i} \right)_{T,p,n_{j \neq i}} \quad (12)$$

With the symmetrically referenced activity coefficient $\gamma_{x,i}$, the unsymmetrically referenced activity coefficient can be gained by

$$\gamma_{x,i}^* = \frac{\gamma_{x,i}}{\gamma_{x,i}^\infty} \quad \text{(for all } i \in \{S_m \cup S_C \cup S_A\} \backslash \{s\}) \quad (13)$$

Where $\gamma_{x,i}^\infty$ refers to the activity coefficient at infinite dilution. The activity coefficient refers to the mole fraction as composition scale. Conversion to the value referring to the molality is done by:

$$\gamma_{m,i}^* = \gamma_{x,i}^* x_s \quad \text{(for all } i \in \{S_m \cup S_C \cup S_A\} \backslash \{s\}) \quad (14)$$

The long range interaction contribution

As outlined above, in the framework of the eNRTL model the long-range contribution to G_m^{E*}, $G_{m,LR}^{E*}$, is accounted for by a version of the Debye-Hückel expression as modified by Pitzer [4]:

$$\frac{G_{m,LR}^{E*}}{RT} = \frac{G_{m,PDH}^{E*}}{RT} = -4 A_\phi \left(M_s m^\ominus \right)^{-1/2} \frac{I_x}{\rho} \ln \left(1 + \rho I_x^{1/2} \right) \quad (15)$$

In eq. (15) R denotes the universal gas constant, T the absolute temperature, M_S the molecular weight of solvent, A_ϕ the Pitzer-Debye-Hückel constant, $m^\ominus$ the standard value of the molality, ρ the closest approach parameter, and I_x the ionic strength, defined with respect to the mole fraction concentration scale, respectively. A_ϕ in turn can be expressed by:

$$A_\phi = \frac{1}{3} \left(\frac{2 \pi N_{Av} \rho_s^\circ}{1000} \right)^{1/2} \left(\frac{e^2}{\varepsilon_s^\circ k_B T} \right)^{3/2}, \quad (16)$$

where N_{Av} and k_B stands for the Avogadro and the Boltzmann constant, respectively, e for the elementary charge and ρ_s° and ε_s° for the density and the dielectric constant, of the solvent, respectively. The symbols for ρ_s and ε_s are endowed with the superscript "$\circ$" to indicate that a pure solvent is assumed here. I_x is defined through the relation:

$$I_x = \frac{1}{2} \sum_{i \in S_C \cup S_A} z_i^2 x_i \quad (17)$$

The summation in eq. (17) runs over all ions in the solution.

In case of water being the solvent, i.e., $s \equiv w$, the Debye-Hückel parameter $A_\phi = f(T)$ is provided as an empirical function in the temperature by Chen et al. (1982) [1]. The function was obtained from a data correlation of the A_ϕ-values reported by Silvester and Pitzer [16] and was also used here. The closest approach parameter is in accordance with the work of Chen and co-workers set to a value of 14.9 [1,2].

The general expression for the long range interaction contribution to the activity coefficient is derived from eq. (15) and eq. (12):

$$\ln \gamma_{x,i,LR}^* =$$
$$-A_\phi \left(M_s m^\ominus \right)^{-1/2} \left(\left(\frac{2 z_i^2}{\rho} \right) \ln \left(1 + \rho I_x^{1/2} \right) + \frac{z_i^2 I_x^{1/2} - 2 I_x^{3/2}}{1 + \rho I_x^{1/2}} \right) \quad (18)$$

The expression above is valid for all types of species, ionic as well as molecular solute and solvent species, i.e., $i \in S_m \cup S_C \cup S_A$.

The modified NRTL model describing the short range contribution to multicomponent systems

Based on the theoretical framework of the binary version of the model [1], the modified NRTL model is generalised to systems containing $N_m + 1$ molecular species $m_0, m_1, \ldots, m_{N_m}$, N_C cationic species $C_1, \ldots, C_{N_C}$ and N_A anionic species $A_1, \ldots, A_{N_A}$. The molecular component m_0 ($m_0 \equiv s$. $s = w$ assumed here) is regarded as the solvent component, treated differently with regard to the normalisation of its activity coefficient.

The reference value for defining the short range contribution of the excess molar Gibbs energy is the residual molar Gibbs energy of the pure molecular component/species for molecular species $m \in S_m$ and the hypothetically homogeneously mixed completely dissociated liquid electrolyte mixture [2] is used as reference state for the residual molar Gibbs energy of ionic species $C \in S_C$ and $A \in S_A$ respectively

$$G_{m,m\text{-cell}}^{R\circ} = g_{mm} \quad \text{(for all } m \in S_m) \tag{19}$$

$$G_{m,C\text{-cell}}^{R\circ} = z_C \sum_{A' \in S_A} Y_{A'} g_{A'C} \quad \text{(for all } C \in S_C) \tag{20}$$

$$G_{m,A\text{-cell}}^{R\circ} = |z_A| \sum_{C' \in S_C} Y_{C'} g_{C'A} \quad \text{(for all } A \in S_A) \tag{21}$$

With regard to the activity coefficients for the individual ionic species the symmetrical reference frame implies that the activity coefficients approach unity only, if for a given $C \in S_C$ (or $A \in S_A$) all other ions vanish except for another single counter ion $A \in S_A$ (or $C \in S_C$). This corresponds to the state of the pure, hypothetically homogeneously mixed liquid pure electrolyte component CA. In eqs. (20) and (21), Y_A and Y_C stand for the so-called ionic charge fractions defined according to:

$$Y_C = \frac{X_C}{\sum_{C' \in S_C} X_{C'}} \tag{22}$$

$$Y_A = \frac{X_A}{\sum_{A' \in S_A} X_{A'}} \tag{23}$$

Ín eqs. (22) and (23), X_i are the effective mole fractions X_i of species i which are given by.

$$X_i = x_i C_i \quad C_i = \begin{cases} 1 & \text{for } i \in S_m \\ |z_i| & \text{for } i \in S_C \cup S_A \end{cases} \tag{24}$$

In a manner analogue to the procedure for deriving the $G_{m,SR}^E$-expression for binary mixtures, the corresponding equation for multicomponent systems is derived:

$$
\begin{aligned}
\frac{G_{m,SR}^E}{RT} &= \sum_{m \in S_m} X_m \frac{\sum_{j \in S_m \cup S_C \cup S_A} X_j G_{jm} \tau_{jm}}{\sum_{k \in S_m \cup S_C \cup S_A} X_k G_{km}} \\
&+ \sum_{C \in S_C} X_C \sum_{A' \in S_A} Y_{A'} \frac{\sum_{j \in S_m \cup S_A} X_j G_{jC,A'C} \tau_{jC,A'C}}{\sum_{k \in S_m \cup S_A} X_j G_{jC,A'C}} \\
&+ \sum_{A \in S_A} X_A \sum_{c'} Y_{C'} \frac{\sum_{j \in S_m \cup S_C} X_j G_{jA,C'A} \tau_{jA,C'A}}{\sum_{k \in S_m \cup S_C} X_k G_{kA,C'A}}
\end{aligned} \tag{25}
$$

where the Boltzmann kind factors G_{jm} for $j = m'$ ($m' \in S_m$), $j = C$ ($C \in S_C$) and $j = A$ ($A \in S_A$) are for any $m \in S_m$ are calculated according to:

$$G_{m'm} = \exp\left(-\alpha_{m'm} \tau_{m'm}\right) \tag{26}$$

$$G_{Cm} = \sum_{A \in S_A} Y_A G_{CA,m} \tag{27}$$

$$G_{Am} = \sum_{C \in S_C} Y_C G_{CA,m} \tag{28}$$

and $G_{CA,m}$ in turn is given by:

$$G_{CA,m} = \exp\left(-\alpha_{CA,m} \tau_{CA,m}\right) \tag{29}$$

The same mixing rule is applied to calculate the nonrandomness factors α_{Cm} and α_{Am} from the independent nonrandomness factors $\alpha_{CA,m} \equiv \alpha_{m,CA}$:

$$\alpha_{Cm} = \sum_{A \in S_A} Y_A \alpha_{CA,m} \quad \text{(for all } C \in S_C) \tag{30}$$

$$\alpha_{Am} = \sum_{C \in S_C} Y_C \alpha_{CA,m} \quad \text{(for all } A \in S_A) \tag{31}$$

Having defined G_{jm} and α_{jm} for $j = C$ ($C \in S_C$) and $j = A$ ($A \in S_A$), the dimensionless interaction energy parameters τ_{jm} can now be derived for any $m \in S_m$:

$$\tau_{Cm} = -\frac{\ln G_{Cm}}{\alpha_{Cm}} \tag{32}$$

$$\tau_{\mathrm{A}m} = -\frac{\ln G_{\mathrm{A}m}}{\alpha_{\mathrm{A}m}} \qquad (33)$$

While the dimensionless interaction energy parameters $\tau_{\mathrm{AC,A'C}}$ and $\tau_{\mathrm{CA,C'A}}$ are further basic parameters of the model, $\tau_{m\mathrm{C,AC}}$ and $\tau_{m\mathrm{A,CA}}$ are composition dependent quantities to be calculated by:

$$\tau_{m\mathrm{C,AC}} = \tau_{\mathrm{C}m} - \frac{\alpha_{\mathrm{CA},m}}{\alpha_{m\mathrm{C,AC}}}\left(\tau_{\mathrm{CA},m} - \tau_{m,\mathrm{CA}}\right)$$

(for all $m \in S_m$, $\mathrm{C} \in S_\mathrm{C}$, $\mathrm{A} \in S_\mathrm{A}$) $\qquad (34)$

$$\tau_{m\mathrm{A,CA}} = \tau_{\mathrm{A}m} - \frac{\alpha_{\mathrm{CA},m}}{\alpha_{m\mathrm{A,CA}}}\left(\tau_{\mathrm{CA},m} - \tau_{m,\mathrm{CA}}\right)$$

(for all $m \in S_m$, $\mathrm{C} \in S_\mathrm{C}$, $\mathrm{A} \in S_\mathrm{A}$) $\qquad (35)$

Whereas $\tau_{\mathrm{CA},m}$ and $\tau_{m,\mathrm{CA}}$ are regarded as independent model parameters, $\alpha_{m\mathrm{C,AC}}$ and $\alpha_{m\mathrm{A,CA}}$ are set to:

$$\alpha_{m\mathrm{C,AC}} = \alpha_{\mathrm{C}m} \qquad (36)$$

$$\alpha_{m\mathrm{A,CA}} = \alpha_{\mathrm{A}m} \qquad (37)$$

Applying eq. (12) to $G_{m,\mathrm{SR}}^\mathrm{E}$ as defined by eq. (25) and differentiating the expression with respect to the molecular species for $i = m$ ($m \in S_m$) leads to the desired expression for calculating the natural logarithm of the symmetrically referenced activity coefficient of molecular species m, $\ln\gamma_{x,m,\mathrm{SR}}$:

$$\ln\gamma_{x,m,\mathrm{SR}} = \frac{\displaystyle\sum_{j \in S_m \cup S_\mathrm{C} \cup S_\mathrm{A}} X_j G_{jm}\tau_{jm}}{\displaystyle\sum_{k \in S_m \cup S_\mathrm{C} \cup S_\mathrm{A}} X_k G_{km}}$$

$$+ \sum_{m' \in S_m} \frac{X_{m'} G_{mm'}}{\displaystyle\sum_{k \in S_m \cup S_\mathrm{C} \cup S_\mathrm{A}} X_k G_{km'}}\left(\tau_{mm'} - \frac{\displaystyle\sum_{j \in S_m \cup S_\mathrm{C} \cup S_\mathrm{A}} X_j G_{jm'}\tau_{jm'}}{\displaystyle\sum_{k \in S_m \cup S_\mathrm{C} \cup S_\mathrm{A}} X_k G_{km'}}\right)$$

$$+ \sum_{\mathrm{C} \in S_\mathrm{C}} \sum_{\mathrm{A'} \in S_\mathrm{A}} \frac{Y_{\mathrm{A'}} X_\mathrm{C} G_{m\mathrm{C,A'C}}}{\displaystyle\sum_{k \in S_m \cup S_\mathrm{A}} X_k G_{k\mathrm{C,A'C}}}\left(\tau_{m\mathrm{C,A'C}} - \frac{\displaystyle\sum_{j \in S_m \cup S_\mathrm{A}} X_j G_{j\mathrm{C,A'C}}\tau_{j\mathrm{C,A'C}}}{\displaystyle\sum_{k \in S_m \cup S_\mathrm{A}} X_k G_{k\mathrm{C,A'C}}}\right)$$

$$+ \sum_{\mathrm{A} \in S_\mathrm{A}} \sum_{\mathrm{C'} \in S_\mathrm{C}} \frac{Y_{\mathrm{C'}} X_\mathrm{A} G_{m\mathrm{A,C'A}}}{\displaystyle\sum_{k \in S_m \cup S_\mathrm{C}} X_k G_{k\mathrm{A,C'A}}}\left(\tau_{m\mathrm{A,C'A}} - \frac{\displaystyle\sum_{j \in S_m \cup S_\mathrm{C}} X_j G_{j\mathrm{A,C'A}}\tau_{j\mathrm{A,C'A}}}{\displaystyle\sum_{k \in S_m \cup S_\mathrm{C}} X_k G_{k\mathrm{A,C'A}}}\right)$$

(38)

Since the activity coefficient for the solvent species $m = m_0 \equiv \mathrm{s} = \mathrm{w}$ is normalised according to the pure component reference frame which is in accordance with the asymmetric convention, no further adjustment of the value derived from eq. (38) is needed for the case of $\ln\gamma_{x,m,\mathrm{SR}}$ with $m = m_0 \equiv \mathrm{s} = \mathrm{w}$. Contrary, in order to calculate the

activity coefficients for the molecular solute species ($m \in S_m \setminus \{\mathrm{s}\}$), normalization of the activity coefficient to the reference frame of infinite dilution would be required. However, since the presence of molecular solutes the liquid phase was neglected in our calculations, the corresponding formula is not mentioned here.

Deriving the activity coefficients requires the calculation of the first partial derivative of the $G_{\mathrm{SR}}^\mathrm{E}$-function with respect to n_i, the mole number of species i. Since the ionic charge fractions Y_C and Y_A appear in the expression for $G_{\mathrm{SR}}^\mathrm{E}$ (explicitly and implicitly via the mixing rules for the concentration dependent model parameters), this step involves the calculation of $(\partial Y_\mathrm{C}/\partial n_i)_{T,p,n_{j \neq i}}$ and $(\partial Y_\mathrm{A}/\partial n_i)_{T,p,n_{j \neq i}}$. Performing the differentiations leads to the result that $(\partial Y_\mathrm{C}/\partial n_i)_{T,p,n_{j \neq i}}$ vanishes only for $i = m, \mathrm{A}$, but not for $i = \mathrm{C}$ (the inverse holds for the derivative $(\partial Y_\mathrm{A}/\partial n_i)_{T,p,n_{j \neq i}}$). While the derivative vanishes in any case if it the differentiation is executed with respect to the mole number of a molecular species, n_m ($m \in S_m$), it remains finite if the differentiation of the ionic charge fraction for a given ion is performed with respect to the mole number of an ion of the same charge number. Hence, when deriving $\gamma_{x,\mathrm{C,SR}}$ and $\gamma_{x,\mathrm{A,SR}}$ the derivatives $(\partial Y_\mathrm{C}/\partial n_i)_{T,p,n_{j \neq i}}$ and $(\partial Y_\mathrm{A}/\partial n_i)_{T,p,n_{j \neq i}}$ lead to considerably more complicated expressions compared to the expression for $\ln\gamma_{x,m,\mathrm{SR}}$. To simplify the calculations and resulting expressions, Chen and Evans [2] have therefore set $(\partial Y_\mathrm{C}/\partial n_i)_{T,p,n_{j \neq i}} = (\partial Y_\mathrm{A}/\partial n_i)_{T,p,n_{j \neq i}} = 0$. Only in 2008, Bollas et al. [4] presented a version of the model, in which the simplifying assumption for deriving $\gamma_{x,\mathrm{C,SR}}$ and $\gamma_{x,\mathrm{A,SR}}$ had been removed. In the early model version based on the simplification [2], the functions for $\ln\gamma_{x,\mathrm{C,SR}}$ and $\ln\gamma_{x,\mathrm{A,SR}}$ read:

$$\frac{\ln\gamma_{x,\mathrm{C,SR}}}{z_\mathrm{C}} = \sum_{\mathrm{A} \in S_\mathrm{A}} Y_\mathrm{A} \frac{\displaystyle\sum_{j \in S_m \cup S_\mathrm{A}} X_j G_{j\mathrm{C,AC}}\tau_{j\mathrm{C,AC}}}{\displaystyle\sum_{k \in S_m \cup S_\mathrm{A}} X_k G_{k\mathrm{C,AC}}} \qquad (39)$$

$$+ \sum_{m \in S_m} \frac{X_m}{\displaystyle\sum_{k \in S_m \cup S_\mathrm{C} \cup S_\mathrm{A}} X_k G_{km}} G_{\mathrm{C}m}\left(\tau_{\mathrm{C}m} - \frac{\displaystyle\sum_{j \in S_m \cup S_\mathrm{C} \cup S_\mathrm{A}} X_j G_{jm}\tau_{jm}}{\displaystyle\sum_{k \in S_m \cup S_\mathrm{C} \cup S_\mathrm{A}} X_k G_{km}}\right)$$

$$+ \sum_{\mathrm{A} \in S_\mathrm{A}} \sum_{\mathrm{C'} \in S_\mathrm{C}} \frac{X_\mathrm{A} Y_{\mathrm{C'}} G_{\mathrm{CA,C'A}}}{\displaystyle\sum_{k \in S_m \cup S_\mathrm{C}} X_k G_{k\mathrm{A,C'A}}}\left(\tau_{\mathrm{CA,C'A}} - \frac{\displaystyle\sum_{j \in S_m \cup S_\mathrm{C}} X_j G_{j\mathrm{A,C'A}}\tau_{j\mathrm{A,C'A}}}{\displaystyle\sum_{k \in S_m \cup S_\mathrm{C}} X_k G_{k\mathrm{A,C'A}}}\right)$$

$$\frac{\ln \gamma_{x,\mathrm{A,SR}}}{|z_\mathrm{A}|} = \sum_{C \in S_C} Y_C \frac{\sum_{j \in S_m \cup S_C} X_j G_{j\mathrm{A,CA}} \tau_{j\mathrm{A,CA}}}{\sum_{k \in S_m \cup S_C} X_k G_{k\mathrm{A,CA}}} \qquad (40)$$

$$+ \sum_{m \in S_m} \frac{X_m}{\sum_{k \in S_m \cup S_C \cup S_A} X_k G_{km}} G_{\mathrm{A}m} \left(\tau_{\mathrm{A}m} - \frac{\sum_{j \in S_m \cup S_C \cup S_A} X_j G_{jm} \tau_{jm}}{\sum_{k \in S_m \cup S_C \cup S_A} X_k G_{km}} \right)$$

$$+ \sum_{C \in S_C} \sum_{\mathrm{A}' \in S_A} \frac{X_C Y_{\mathrm{A}'} G_{\mathrm{AC,A'C}}}{\sum_{k \in S_m \cup S_A} X_k G_{k\mathrm{C,A'C}}} \left(\tau_{\mathrm{AC,A'C}} - \frac{\sum_{j \in S_m \cup S_A} X_j G_{j\mathrm{C,A'C}} \tau_{j\mathrm{C,A'C}}}{\sum_{k \in S_m \cup S_A} X_k G_{k\mathrm{C,A'C}}} \right)$$

The corresponding activity coefficients at infinite dilution derived from eqs. (39) and (40), are:

$$\frac{\ln \gamma_{x,\mathrm{C,SR}}^\infty}{z_\mathrm{C}} = \lim_{X_s \to 1} \frac{\ln \gamma_{x,\mathrm{C,SR}}}{z_\mathrm{C}} = \sum_{\mathrm{A} \in S_A} Y_\mathrm{A} \tau_{s\mathrm{C,AC}} + G_{\mathrm{C}s} \tau_{\mathrm{C}s} \qquad (41)$$

$$\frac{\ln \gamma_{x,\mathrm{A,SR}}^\infty}{|z_\mathrm{A}|} = \lim_{X_s \to 1} \frac{\ln \gamma_{x,\mathrm{A,SR}}}{|z_\mathrm{A}|} = \sum_{\mathrm{C} \in S_C} Y_\mathrm{C} \tau_{s\mathrm{A,CA}} + G_{\mathrm{A}s} \tau_{\mathrm{A}s} \qquad (42)$$

The basic model parameters

The basic parameters of the model that are to be adjusted to binary solvent + electrolyte systems are the nonrandomness factor $\alpha_{\mathrm{CA,s}}$ and the dimensionless energetic interaction parameters $\tau_{\mathrm{CA,s}}$ and $\tau_{s,\mathrm{CA}}$ being weak but well behaved functions of temperature. In practice, the nonrandomness factor is often set a priori to a fixed value (0.2 for electrolyte-solvent-pairs). Hence, only two parameters are needed to describe a solution of a single electrolyte [1,2].

In multicomponent systems, containing - besides the solvent additional molecular solutes as well as ionic species, the independent model parameters are: $\alpha_{mm'}$, $\alpha_{\mathrm{CA},m}$, $\alpha_{\mathrm{CA,CA'}}$, $\alpha_{\mathrm{AC,AC'}}$, $\tau_{mm'}$, $\tau_{m'm}$, $\tau_{\mathrm{CA},m}$, $\tau_{m,\mathrm{CA}}$, $\tau_{\mathrm{AC,AC'}}$, $\tau_{\mathrm{AC',AC}}$, $\tau_{\mathrm{CA,CA'}}$, $\tau_{\mathrm{CA',CA}}$. Again, the nonrandomness factors are often fixed to a constant value. $\tau_{mm'}$, $\tau_{m'm}$ (and possibly $\alpha_{mm'}$) are adjusted to molecule-molecule binary systems (these are the values that can be taken from data sources for the original NRTL-model). $\tau_{\mathrm{AC,AC'}}$, $\tau_{\mathrm{AC',AC}}$, $\tau_{\mathrm{CA,CA'}}$, and $\tau_{\mathrm{CA',CA}}$ (and possibly also $\alpha_{\mathrm{CA,CA'}}$ and $\alpha_{\mathrm{AC,AC'}}$) can be adjusted to ternary solvent + salt$_1$ + salt$_2$ systems involving electrolytes having one ion in common. Actually it can be set $\tau_{\mathrm{AC,AC'}} = -\tau_{\mathrm{AC',AC}}$ and $\tau_{\mathrm{CA,CA'}}$, $= -\tau_{\mathrm{CA',CA}}$. Good results are even obtained by setting these parameters to zero [2]. This is an example showing the predictive capabilities of the model.

MODELLING AND DISCUSSIONS

Verification of the correctness of the model implementation

The correctness of the eNRTL-model implementation was verified by numerous selected examples including osmotic coefficient data on binary and activity, osmotic coefficient as well as solubility data on ternary electrolyte systems, respectively.

Binary solvent + salt systems: osmotic coefficients of alkali and earth alkali halide solutions

The selected examples of this subsection cover the modeling of experimental data on binary solvent + salt systems. The calculations performed were inspired by the examples presented in the publications of Chen et al. (1982) [1] and Chen and Evans (1986) [2] and intended to check the correctness of the code. The osmotic coefficient of single salt solutions of alkali halide and magnesium and calcium halides have been modeled using data for the solvent-salt interaction coefficients reported in [2].
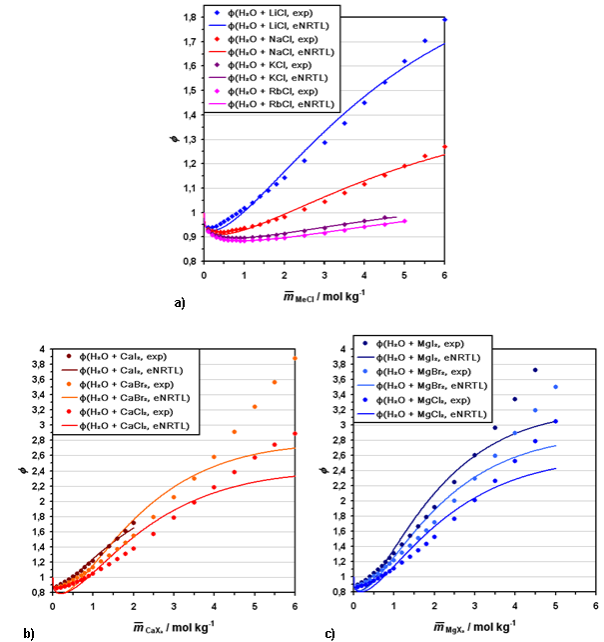

Figure 1: Osmotic coefficients of a) alkali metal, b) magnesium and c) calcium halide solutions at 25 °C.

The modeling results are displayed in Figure 1, along with corresponding experimental data given

by Robinson and Stokes [8]. The root mean square relative deviations between the experimental and the calculated data, defined according to:

$$\sigma_{\phi,\,\text{rel}} = \sqrt{\frac{1}{N_{\text{exp data}}} \sum_{l=1}^{N_{\text{exp data}}} \left(\frac{\phi_{\text{exp},\,l} - \phi_{\text{calc},\,l}}{\phi_{\text{exp},\,l}} \right)^2} \qquad (37)$$

are displayed in Table 1. As can be verified in Table 1, the values of $\sigma_{\phi,\,\text{rel}}$ generated in this work reproduce the corresponding $\sigma_{\phi,\,\text{rel}}$-values of Chen and Evans [1].

Salt	$\sigma_{\phi,\,\text{rel}}$ [a]	$\sigma_{\phi,\,\text{rel}}$ [b]	$\overline{m}_{\text{CA, max}}$
LiCl	0,0227	0,024	6
NaCl	0,0118	0,012	6
KCl	0,0023	0,002	4,8
RbCl	0,0015	0,002	5
CaCl$_2$	0,0238	0,025	2,5
CaBr$_2$	0,1235	0,13	6
CaI2	0,0220	0,024	2
MgCl$_2$	0,0838	0,09	5
MgBr$_2$	0,0896	0,09	5
MgI$_2$	0,1036	0,11	5

Table 1: Root mean square deviation between calculated and experimental data for a) results of [a]this work and of [b]Chen et al. (1986) [2]

Ternary solvent + salt$_1$ + salt$_2$ systems

Calculations on ternary solvent + salt$_1$ + salt$_2$ systems have been performed in order to provide evidence for the correctness of the program implementation for the general case of multinary electrolyte solutions. The two different salts in these systems have one of their ions in common, i.e., they are of either the type $H_2O + C_1A + C_2A$ or $H_2O + CA_1 + CA_2$. Osmotic coefficients ϕ mean molar activity coefficients $\gamma^*_{m,\pm,\text{CA}}$ and salt solubilities have been calculated and compared to their corresponding results found in the literature.

Osmotic coefficient of the H$_2$O+NaCl+LiCl system

In a first example the osmotic coefficient ϕ (Figure 2) has been calculated for the system $H_2O + NaCl + LiCl$ at $T = 298.15\ \text{K}$ and constant total stoichiometric molality $\overline{m}_{\text{NaCl+LiCl}} = 2\ \text{mol}\,\text{kg}^{-1}$

as function of the relative amount of LiCl in the salt mixture. The latter is expressed in terms of the stoichiometric mole fraction of LiCl $\overline{x}_{\text{LiCl, NaCl+LiCl}} = \overline{m}_{\text{LiCl}} / (\overline{m}_{\text{NaCl}} + \overline{m}_{\text{LiCl}})$ in the binary $NaCl + LiCl$ subsystem. The example was chosen in an attempt to reproduce Figure 2 given in [2] (Figure 2 b)).
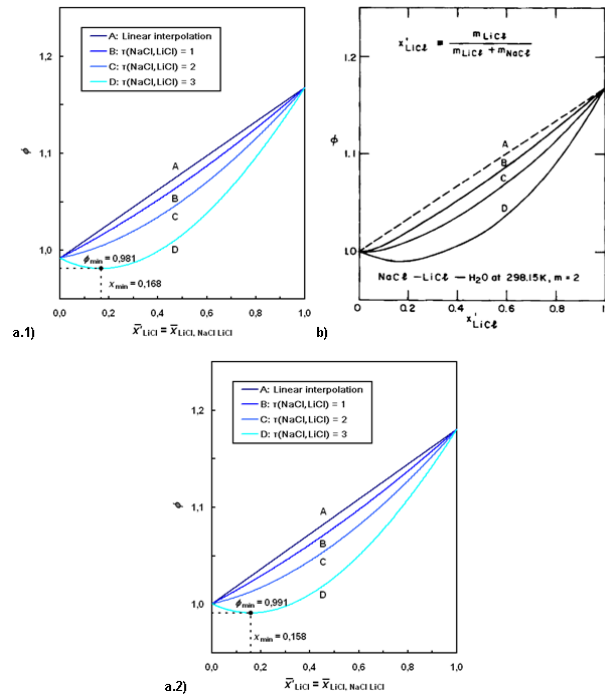

Figure 2: Osmotic coefficient of the system $H_2O + NaCl + LiCl$ at constant total stochimetric molality $\overline{m}_{\text{NaCl+LiCl}} = 2\ \text{mol}\,\text{kg}^{-1}$ and $T = 298.15\ \text{K}$ as function of the molar salt fraction $\overline{x}_{\text{LiCl, NaCl+LiCl}} = \overline{m}_{\text{LiCl}} / (\overline{m}_{\text{NaCl}} + \overline{m}_{\text{LiCl}})$. Figures a.1) and a.2) this work with solvent-salt parameters given in [2] and [1], respectively, and salt-salt-parameters 1,2,3 for B-D). b) from [2] with salt-salt-parameters 0, 1, 2.

Besides the linear interpolating line of curve A, ϕ was calculated with different values for the salt$_1$ + salt$_2$-interaction parameters. Chen et al. claimed that curves B, C, and D, correspond to parameter values of $\tau_{\text{Na}^+\text{Cl}^-,\text{Li}^+\text{Cl}^-} = -\tau_{\text{Li}^+\text{Cl}^-,\text{Na}^+\text{Cl}^-}$, $= 0$, 1, and 2 and a value for the non-randomness factor 0.2 [2]. Although they do not explicitly mention the source for their energetic interaction parameters, it can be assumed that they are taken from the values published in the same article which are reproduced in a.1) of Table 1. By using the same values for $\tau_{\text{CA,w}}$ and $\tau_{\text{w,CA}}$ and 0, 1, 2 the curves of [2] could not be reproduced. However,

when incrementing the values by one setting $\tau_{Na^+Cl^-,Li^+Cl^-} = -\tau_{Li^+Cl^-,Na^+Cl^-} = 1, 2, 3$, the curves B-D, could nearly be generated. However, since the correctness of the Java implementation has been checked independently through calculations performed by using the computer algebra software Mathcad (version 14), it is believed that the results calculated in this work are correct.

The influence of a change in the parameters $\tau_{CA,w}$ and $\tau_{w,CA}$ on ϕ of the binary sub-mixtures is demonstrated by means of Figure a.2) where the parameters previously published by Chen et al. [2] (see Table 2) have been used in the calculations.

Parameter source	salt	$\tau_{CA,w}$	$\tau_{w,CA}$
a.1) [2]	NaCl	–4.5916	9.0234
	LiCl	–5.1737	10.1242
a.2) [1]	NaCl	–4.549	8.885
	LiCl	–5.154	10.031

Table 2: Values of binary water-salt interaction coeffcients used to model the ternary system H_2O + NaCl + LiCl for curves a.1) and a.2).

Modelling of the H_2O+NaCl+KCl system

As another example of a thermodynamic property of a ternary solvent + salt$_1$ + salt$_2$-system for verifying the correctness of our program code, mean molal activity coefficients of NaCl and KCl in H_2O + NaCl + KCl-solutions have been modeled at 25 °C (Figure 3). The calculations were inspired by Figure 1 presented in the article of Bollas et al. [4]. In that work the authors have performed calculations of $\gamma^*_{m,\pm,NaCl}$ and $\gamma^*_{m,\pm,KCl}$ for different values for the salt-salt-interaction parameters of $\tau_{Na^+Cl^-,K^+Cl^-} = -\tau_{K^+Cl^-,Na^+Cl^-} = 0, 0.25, 0.50$ to compare the performance of the simplified eNRTL equations for $\gamma^*_{x,i}$ ($i \in S_C \cup S_A$) (version published previously by Chen and Evans [2], see Figure 3, b.1)) and the refined version [4] (see b.2) in Figure 3. Since we were able to reproduce the curves of both model versions (see Figures a.1) and a.2)), this also serves as an evidence that the more complicated new model equations had been correctly implemented in our program.
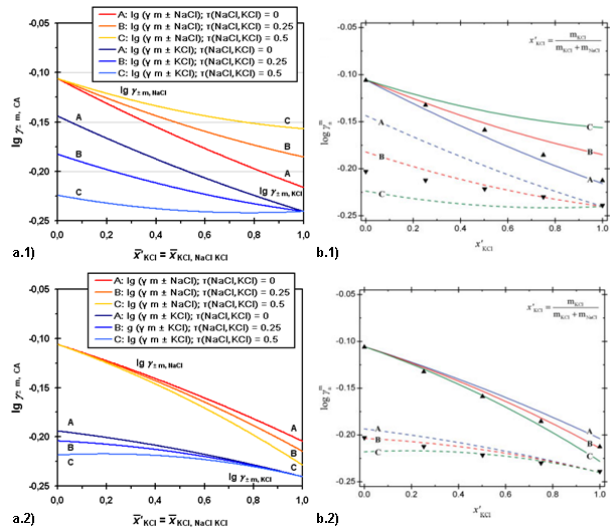
Figure 3: Prediction of mean ionic activity coefficient of a constant total molal H_2O + NaCl + KCl system with various salt-salt energy parameters using the equations for $\gamma^*_{x,C}$ and $\gamma^*_{x,A}$ of Chen and Evans [2] a.1), b.1) and Bollas et al. (2008) [4] a.2), b.2): a) this work, b).

From Figure 3 it can be seen that the refined model possess a greater degree of physical significance since the experimental data are better described by the refined model of Bollas et al. [4] than by the simplified version of Chen and Evans [2].

SL and SSL equilibrium encountered in the H_2O + KI + KCl electrolyte system

As an example for equilibrium calculations performed by using the eNRTL model, the solubility curve at T = 298.15 K and p = 0.1 MPa of the system H_2O + KI + KCl is shown in Figure 4.
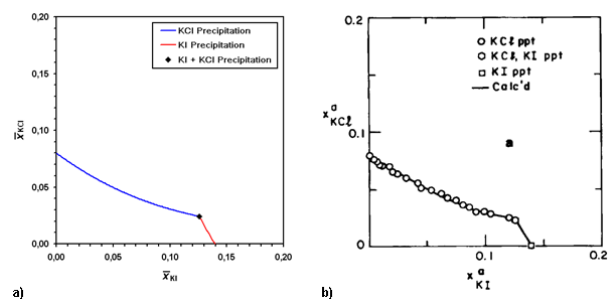
Figure 4: Salt Precipitation in the H_2O + KI + KCl system at T = 298.15 K and p = 0.1 MPa. A) This work, b) [2].

In order to model the solubilties in this ternary electrolyte system, values for the solubility products $K_{sp,KI}$ and $K_{sp,KCl}$ characterizing the solubility of the salts are needed in addition to the model parameters. With $K_{sp,KI} = -4.2346$ and $K_{sp,KCl} = -5.9695$, gained from a data regression [2] of the solubility data of Linke [17], the salt-solvent interaction parameters $\tau_{K^+I^-,w} = -4.1217$, $\tau_{w,K^+I^-} = 7.9408$, $\tau_{K^+Cl^-,w} = -4.1341$, and $\tau_{w,K^+Cl^-} = 8.1354$ and the salt-salt-interaction parameters $\tau_{K^+Cl^-,K^+I^-} = 0.109$, $\tau_{K^+I^-,K^+Cl^-} = 0.124$ [2], the solubility curves were reproduced (Figure 4) well.

Application of the model to the modeling of gas hydrate equilibria

With the eNRTL model equations for the activity coefficients of the different species and the osmotic coefficient for the solvent species implemented in the in-house program package "gashydyn", modeling calculations have been carried out on phase equilibria of ternary and quaternary mixtures involving gas hydrate phases. Different types of aqueous ternary or quaternary electrolyte systems of the type $H_2O + CA + gas$ or $H_2O + C_1A + C_2A + gas$ containing one or two different salts have been modeled. The influence of three different types of strong electrolytes, NaCl, KCl and $CaCl_2$, on the HLV-phase equilibrium for two hydrate forming gases, methane (CH_4) and carbon dioxide (CO_2), has been investigated.

In these calculations an equation of state (EOS) approach (Soave-Redlich-Kwong EOS (SRK) [18]) has been used to describe the gas-phase non-idealities, whereas the hydrate phase was modeled by a modified version of the van der Waals-and-Platteeuw theory [19] (for details of the procedure see Herri et al. (2011) [20]). In the modeling of the deviations from ideality in the liquid phase, it has to be stressed that all solvent salt parameters were taken from the Aspen databank provided by the Aspen Engineering suite version 2006.5 and that salt-salt interaction parameters were (with the exception of the NaCl + KCl salt pair) set to zero. The presence of the gas was in a good approximation (due to the concentration range and the chemical nature of the gases involved) neglected.

HLV Equilibrium data of the systems H_2O + CH_4 + NaCl and 2) H_2O + CH_4 + NaCl + KCl

The first modeling calculations on the three HLV-phase p-T-curves at constant salt concentrations in the liquid phase were carried out for the ternary system 1) $H_2O + CH_4 + NaCl$ and the quaternary system 2) $H_2O + CH_4 + NaCl + KCl$ (Figure 5). Despite the relatively high pressure range ($2 < p/MPa < 10$) covered, the model shows a good overall performance with average relative deviations (marked as numbers in the figure) ranging from 2.8 % for the mixture $H_2O + CH_4$ + NaCl containing 0.94 % NaCl to 7.0 % for the two salt-system with 3.67 % NaCl and 3.54 % KCl.

The deviation quantity was based on the absolute value of the differences between experimental and calculated data and calculated according to:

$$\left\langle \frac{|\Delta p|}{p} \right\rangle = \frac{1}{N_{exp\,data}} \sum_{l=1}^{N_{exp\,data}} \frac{|p_{exp,l} - p_{calc,l}|}{p_{exp,l}} \tag{38}$$

The curves display the potential of the salts as hydrate inhibitors through a rise in pressure with increasing salt concentration.
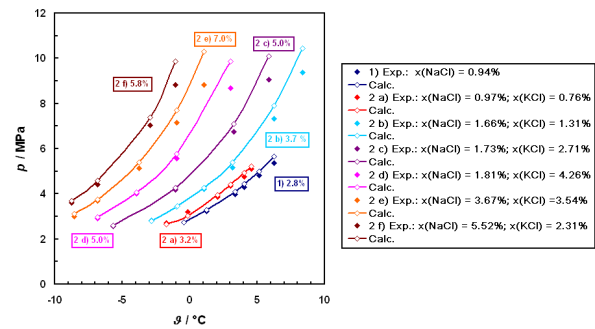

Figure 5. HLV-Equil. data of 1) $H_2O + CH_4$ + NaCl and 2) $H_2O + CH_4 + NaCl$ + KCl. Lines and hollow diamonds: modeling, solid diamonds: exp. data of Dholabhai et al. (1991) [21].

HLV equilibrium data of the system $H_2O + CH_4$ + NaCl + $CaCl_2$

In second example involving methane, HLV-phase equilibrium calculations were performed on the quaternary mixture $H_2O + CH_4 + NaCl + CaCl_2$ (Figure 6). While the range of temperature and pressure ($-8 < \vartheta/°C < 8$, $2 < p/MPa < 10$) as well of the absolute deviations between experimental

data (Dholabhai et al. (1991) [21]) and modeling results (between 2 % and 6 %) are of the same order of magnitude as for the previous mixtures, the overall electrolyte concentration is significantly smaller. However, since the 2-1-electrolyte $CaCl_2$ with the bivalent cation Ca^{2+} is involved, the range of ionic strength is not smaller. Not only does $CaCl_2$ release three ions due to dissociation in solution, but the Ca^{2+} also possess a higher charge and charge density which increases its potential of being involved in hydration processes. Nevertheless, the performance of the eNRTL model for this mixture containing CH_4 as a hydrate forming gas is still very good.
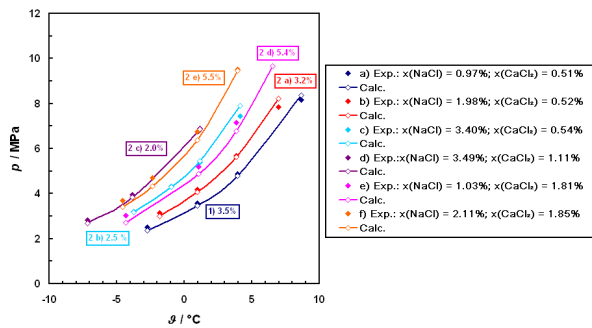
Figure 6: HLV Equilibrium Data of the System $H_2O + CH4 + NaCl + CaCl2$. Lines and hollow diamonds: modeling, solid diamonds: exp. data of Dholabhai et al. (1991) [21].

HLV-equilibrium in the Systems 1) $H_2O + CO_2$ + NaCl and 2) $H_2O + CO_2$ + NaCl + KCl

The second gas, the hydrate equilibria of which are investigated, is carbon dioxide. The mixtures based on CO_2 as gaseous constituent further contain either 1) NaCl or 2) NaCl and KCl (Figure 7). For the single salt system, the maximum stoichiometric mole fraction of NaCl amounts to $\overline{x}_{NaCl} = 0.04$, whereas for the NaCl + KCl-system the maximum overall mole fraction $\overline{x}_{NaCl} + \overline{x}_{KCl}$ is almost 7 %. At a smaller pressure range of $0 < p/MPa < 4$ a very good performance of the eNRTL model is found for this system with relative deviations mostly between 1 and 2 %.

Like in the previous cases (Figure 5 and Figure 6), Figure 7 shows that the strong electrolytes NaCl and KCl act as hydrate inhibitors, causing the

temperature (at a given pressure) to fall, or the pressure to rise (at a given temperature) for hydrate formation with increasing salt mole fraction.
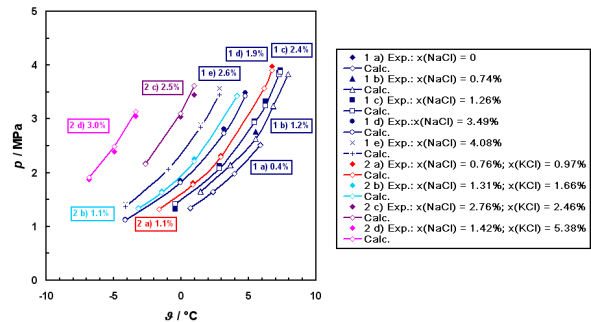

Figure 7. HLV Equil. data of 1) $H_2O + CO_2 + NaCl$ and 2) $H_2O + CO_2 + NaCl + KCl$. Lines and hollow diamonds: modeling, solid diamonds: exp. data of Dholabhai et al. (1993) [22].

HLV Equilibrium Data of the System $H_2O + CO_2 + NaCl + CaCl_2$

The HLV-phase equilibrium calculations on the quaternary mixture $H_2O + CO_2 + NaCl + CaCl_2$ (Figure 8) reveal that on a similar pressure interval as in the previous example, higher deviations between calculated and experimental p values are observed than for the other systems.
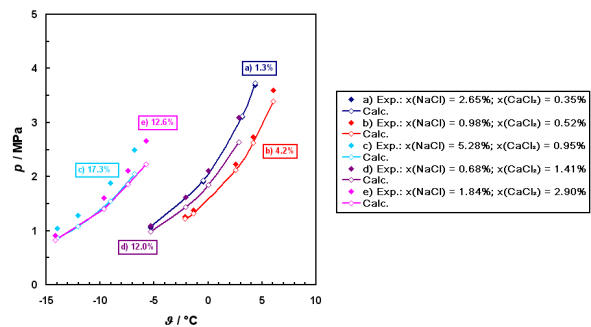

Figure 8. HLV Equil. data of the System $H_2O + CO_2 + NaCl + CaCl_2$. Lines and hollow diamonds: modeling, solid diamonds: exp. data of Dholabhai et al. (1993) [22].

Whereas the result for the two lowest concentrated mixtures is fairly good (with average deviations of 1.3 % and 4.2 % at 2.65 % NaCl and 0.35 % $CaCl_2$ and 0.98% NaCl and 0.52 % $CaCl_2$,), the deviations increase up to between 12 % and 18 %

for the solutions that are higher concentrated. This is most probably due to the influence of the significantly higher degree of hydration of the Ca^{2+}-ion rather than to neglecting the solubility of the CO_2 in the liquid phase for calculating the activity coefficient of the solvent species. Moreover, since the salt-salt parameters between NaCl and $CaCl_2$ were not known, the interaction between the ions of the two salts had to be neglected as well.

CONCLUSIONS

In this article, it is demonstrated by numerous examples that the eNRTL-model of Chen and co-workers [1-4] is implemented successfully in a Java program. The Java code in turn has been incorporated in our "gashydyn" program package allowing for performing – among other features – predictive HLV-gas hydrate equilibrium calculations.

The correctness of the code has been verified by calculations on mean ionic activity coefficients and osmotic coefficients of binary solutions of strong electrolytes and ternary mixtures of the type water + $salt_1$ + $salt_2$ where constituting salts share one common ion. The examples selected to verify the correctness of the implementation were taken from the original articles on the ENRTL model by Chen et al. [1,2,4]. In case of the H_2O+NaCl+LiCl mixture, the shape of the osmotic coefficient curves could not reproduced with the parameter values given in [2]. However, when they were incremented by one, it turned out that the curves were reproduced quite well. Since the results of that calculation had also been checked independently by means the computer algebra software "mathcad", it is believed that the values for the coefficients have been reported erroneously. It could be shown that the eNRTL model provides an accurate description of liquid phase non-ideality of the electrolyte systems over the ranges of state conditions investigated. The model not only correlates thermodynamic data, but possesses also predictive capability using model parameters determined exclusively from data of the constituting binaries and ternary salt-salt systems with a common ion.

The model has subsequently been used in the modelling of HLV-hydrate phase equilibrium data of mixtures involving one or two of the salts NaCl, KCl and $CaCl_2$ and the gases methane and carbon dioxide. In these calculations, the presence of CO_2 in the liquid phase had been neglected with regard to the calculation of the activity coefficient of water. Due to a lack of data, another simplification imposed on the calculation was, with the exception of the NaCl-KCl-salt pair – the negligence of salt-salt-interaction parameters. Despite of these simplifications, the *p-T*-data pairs obtained reveal a good overall performance of the model leading in the average to relative deviations within 2 % to 7 %. Only at higher ionic strengths and in particular when the bivalent Ca^{2+}-ion gets involved, the deviations increase remarkably to reach around 20 %. In a future work this deficiency may be overcome by implementing a version of the model that takes hydration into account [23]. Nevertheless, in view of the simplifications involved in the modeling calculations executed in this work, it can be stated that the results are quite satisfying from an engineering point of view.

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