



# Thermodynamic modelling of gas semi-clathrate hydrates using the electrolyte NRTL model

Matthias Kwaterski, Jean-Michel Herri

## ► To cite this version:

Matthias Kwaterski, Jean-Michel Herri. Thermodynamic modelling of gas semi-clathrate hydrates using the electrolyte NRTL model. G. Westbrook ; B. Tohidi ; D. Long ; T. Minshull ; R. Anderson. 7th International Conference on Gas Hydrates (ICGH 2011), Jul 2011, Edimbourg, United Kingdom. pp.437, 2011. <hal-00617434>

**HAL Id: hal-00617434**

**<https://hal.archives-ouvertes.fr/hal-00617434>**

Submitted on 29 Aug 2011

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# THERMODYNAMIC MODELLING OF GAS SEMI-CLATHRATE HYDRATES USING THE ELECTROLYTE NRTL MODEL

Matthias Kwaterski<sup>1</sup>, Jean Michel Herri<sup>1,\*</sup>

<sup>1</sup>Centre SPIN, département GENERIC, École Nationale Supérieure des Mines de SAINT-ETIENNE, FRANCE

## ABSTRACT

In this work a modified version of the modelling procedure of Paricaud [1] is presented for describing the solid-liquid equilibria encountered in aqueous solutions of tri-*n*-butylammonium bromide (TBAB) involving a semiclathrate hydrate phase. The theoretical framework is further applied to the description of the solid-liquid-vapour three phase *p*-*T*-lines of the ternary system water + TBAB + methane at different overall TBAB concentrations. For the calculations performed on the ternary system exhibiting a gas semiclathrate hydrate phase, model parameters gained previously for the water + TBAB mixture were used. The thermodynamics of the semiclathrate hydrate phase was modelled by means of the salt hydrate model of Paricaud. For the description of the gas semiclathrate hydrate phase a combination of the salt hydrate model of Paricaud with the Waals-Platteeuw (vdW-P) theory has been applied. An unsymmetric reference frame has been employed to treat the liquid phase, i.e., Henry's constant was adopted for the ideal solubility of methane in the aqueous phase, whereas the fugacity of pure liquid water was adopted as reference state for water. The Soave Redlich Kwong equation of state was used to calculate the fugacities in the gas phase. Whereas the model of Paricaud employs the SAFT equation of state in a  $\phi$ - $\phi$ -approach to account for both, liquid and gas phase non-idealities, the electrolyte NRTL (eNRTL)- $G^E$ -model has been incorporated in our modified model to describe deviations from ideality in the liquid phase. In the calculations, the temperature dependence of the eNRTL-interaction energy parameters has been neglected and instead, ENRTL-coefficients at 298.15 K have been used. The solid-liquid *T*-*x* phase diagram of TBAB was calculated at ambient pressure up to 60% stoichiometric mass fraction of TBAB. By assuming the existence of only type B hydrate a good overall correlation of experimental data found in the literature was achieved by adjusting the values for the standard molar enthalpy of the dissociation and the temperature at the congruent melting point of the semiclathrate hydrate compound. Using these values, phase boundary HLV-lines of the ternary system H<sub>2</sub>O + TBAB + methane, calculated at different stoichiometric concentrations of TBAB in the liquid phase, are displayed and compared with measured results. Average relative deviations  $\langle |\Delta p|/p \rangle$  between experimental data and modeling results between 4 and 44 % show the applicability of the approach presented.

*Keywords:* modeling, semiclathrate hydrate, gas semiclathrate hydrate, eNRTL model, electrolytes, phase equilibrium, tri-*n*-butylammonium bromide, methane

## NOMENCLATURE

$A_\phi$  – Pitzer-Debye-Hückel constant []  
 $\alpha$  – Nonrandomness factor []  
 $C$  – Langmuir constant [ $C$ ] = Pa<sup>-1</sup>  
 $\Delta$  – Indicating a finite difference []  
 $f$  – Fugacity [ $f$ ] = Pa  
 $\phi$  – Osmotic coefficient []  
 $G$  – Boltzmann kind factor []

$G_m^E$  – Excess molar Gibbs energy [ $J \cdot mol^{-1}$ ]  
 $\gamma$  – Activity coefficient []  
 $I$  – Ionic strength []  
 $k_B$  – Boltzmann's constant [ $k_B$ ] = 1 J K<sup>-1</sup>  
 $m$  – Molality [ $mol \cdot kg^{-1}$ ]  
 $\mu$  – chemical potential [ $\mu$ ] = J·mol<sup>-1</sup>  
 $N_{Av}$  – Avogadro's constant [ $mol^{-1}$ ]  
 $N_{exp \ data}$  – Number of experimental data points []

$\nu$  – Stoichiometric coefficient []  
 $p$  – Pressure [bar, MPa]  
 $\theta$  – fraction of sites occupied []  
 $R$  – Perfect gas constant [ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ]  
 $\sigma_{\text{rel}}$  – Root mean square deviation (relative) []  
 $T$  – Temperature [K]  
 $\tau$  – Energetic interaction coefficient []  
 $w$  – Weight fraction []  
 $x$  – Mole fraction []  
 $X$  – Effective mole fraction []  
 $z$  – Charge number of ionic species  $i$  []

subscripts

$A$  – Anion with charge number  $z_A < 0$   
 calc – Calculated  
 $C$  – Cation with charge number  $z_C > 0$   
 $CA$  – Binary salt composed of  $\nu_C$  cations and  $\nu_A$  anions  
 exp – Experimental  
 $i, j, k$  – Any kind of species  
 $l$  – Index numbering experimental data point  
 $m$  – Molar  
 $m$  – Referring to molal concentration scale, respectively, depending on the context  
 $x$  – Referring to mole fraction concentration scale  
 $w$  – Water

superscripts

ref – Reference state  
 \* – Unsymmetric normalization convention  
 $\infty$  – Infinite dilution  
 $\circ$  – Pure component state  
 $\ominus$  – Standard value (here: molality =  $1 \text{ mol kg}^{-1}$ )  
 $\bar{\phantom{x}}$  – concentration quantity based on stoichiometric mole numbers

## INTRODUCTION

In phase equilibria of aqueous electrolyte solutions, solid phases, the so-called salt hydrates, can be encountered, which consist of a lattice structure in which ions are surrounded by a specific number of water molecules. A special type of hydrates, specified as semiclathrate hydrates, can be formed in aqueous solutions of tetraalkylammonium salts. These semiclathrate hydrate phases are built up by a water-anion-framework containing empty dodecahedral cavities and large cavities engaging the alkyl chains of the cations

[2]. In the semi-clathrate hydrates formed by TBAB, the water molecules form cage structures together with the  $\text{Br}^-$  ions, in which the tetra-*n*-butylammonium cation partly occupies four of the larger cages [3]. Such a hydrate is called a semi-clathrate hydrate crystal because a part of the cage structure is broken in order to engage the large tetra-*n*-butylammonium molecule [8].

In the presence of appropriate gases, like  $\text{CH}_4$  or  $\text{CO}_2$ , aqueous tetra-alkyl-ammonium halide systems are capable of forming gas semi-clathrate hydrates. In these solid compounds small gas molecules are engaged in the dodecahedral cavities of the semiclathrate hydrate structure [9]. In contrast to strong electrolytes like  $\text{NaCl}$  who act as gas hydrate inhibitors [4-,5,6], tetra-alkylammonium halides promote the formation of hydrates at around room temperature and at low pressures [1]. For that reason, activities in research and development in the field of (gas) semiclathrate hydrates have been initiated and stimulated, since these systems can be used as refrigerants [7], gas separation [8,9] and gas storage materials [1,10]. The binary  $\text{H}_2\text{O} + \text{TBAB}$  system is characterized by a complex solid liquid (SL) phase behaviour [11,12], reflected in a isobaric SL phase diagram which exhibits regions of different hydrates, the structure and stoichiometric compositions of which have been the subject of some controversy [1]. Nakayama [13] for example states that a hydrate with a hydration number  $\nu_{\text{H}_2\text{O}} = \nu_w = 24$  is formed, whereas Shimada and co-workers [8,16,14,15] found two kinds of hydrates, referred to as type A and B, respectively, of  $\nu_w = 26$  and 38 [1].

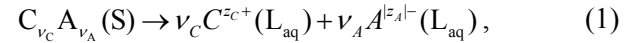
Concerning the modeling of the phase behaviour of gas semiclathrate hydrates, successful efforts have been made Mohammadi et al. [16] in describing the phase behaviour of the ternary system  $\text{H}_2\text{O} + \text{TBAB} + \text{H}_2$ . However, the modeling approach of Mohammadi and co-workers [21] is based on a neural network algorithm. In contrast, the model of Pericaud [1] has been, to the best of our knowledge, the first thermodynamic modeling approach to describe the phase behavior of systems capable of forming gas semiclathrate hydrates. To set up the framework for modelling the gas semi-

clathrate hydrates, Pericaud combines the approach established for salt hydrates [1] and semi-clathrate hydrates with the model of van der Waals and Platteeuw [17] for gas hydrates. As Pericaud points out, “an accurate prediction of SLE in electrolyte systems first requires a reliable thermodynamic model to compute the properties of electrolyte aqueous solutions” [1]. For that purpose, he has used the square-well version of the SAFT-VRE (Statistical Associating Fluid Theory with Variable Range for Electrolytes) electrolyte equation of state proposed by Galindo et al. [18]. In this work a modification of the model approach of Paricaud is presented in which in contrast to the use of the SAFT-VRE equation of state the electrolyte NRTL model of Chen et al. [19-,20,21] (eNRTL-model) is incorporated into the model to describe the liquid phase non-idealities. The model has been successfully applied to the binary  $\text{H}_2\text{O} + \text{TBAB}$  system and the HLV-equilibrium obtained for the  $\text{H}_2\text{O} + \text{TBAB} + \text{CH}_4$  system.

## THERMODYNAMIC MODEL FOR SEMI-CLATHRATE HYDRATES PHASES

In this section, the theoretical framework of the model of Pericaud [1] for describing the salt, semiclathrate as well as gas semiclathrate hydrates is presented. The corresponding equations enable the modeling of solid-liquid phase, solid-liquid-vapour phase and combined chemical and phase equilibria encountered in binary systems of the type  $\text{H}_2\text{O} + \text{CA}$  (abbreviation for a binary electrolyte  $\text{C}_{\nu_C, \text{CA}} \text{A}_{\nu_A, \text{CA}}$  composed of  $\nu_{\text{C,CA}}$  cations  $\text{C}^{z_C+}$  and  $\nu_{\text{A,CA}}$  anions  $\text{A}^{|z_A| -}$ ) and  $\text{H}_2\text{O} + \text{TBAB}$ , as well as the ternary system of the type  $\text{H}_2\text{O} + \text{TBAB} + \text{gas}$ . Depending on the overall concentration of the electrolyte component, different solid phases are formed over defined intervals of the electrolyte concentration. Using  $T$ ,  $p$  and  $x$  as the set of independent (intensive) variables, that is, the temperature, the pressure and the set of mole fractions of the independent chemical species (or components), the phases being present in a stable equilibrium state over defined regions of concentrations are characterized through a minimum in the total Gibbs energy function. For all the different types of phase

equilibria dealt with in detail below, it is assumed that the solid electrolyte is dissolved in the liquid aqueous phase by completely dissociating into its ions according to:



and that no ion pairing is encountered in the liquid phase.

The presentation of the model is slightly different from the original publication for the solid-liquid equilibria in salt hydrate and semi-clathrate systems. The equations are derived directly by starting from the conditions of the equality of the intensive system variables temperature, pressure and chemical potential in all phases. In this respect, the presentation given here resembles more the way as published by Tumakaka et al. [22]. Thereby, consequent use has been made of standard thermodynamic quantities [23].

## Isobaric equilibria between an ice phase and an electrolyte solution

The solid-liquid equilibrium between an ice phase I ( $\text{H}_2\text{O} (\text{I})$ ) and the liquid aqueous solution of a (binary) electrolyte  $\text{C}_{\nu_C} \text{A}_{\nu_A} (\text{aq}) (= \text{CA} (\text{L}_w))$  at constant temperature  $T$  and pressure  $p$  is experimentally detected in the region of low overall electrolyte concentration in this type of binary mixture. The thermodynamic conditions for describing the I- $\text{L}_w$  equilibrium can be stated as:

$$T^{\text{I}} = T^{\text{L}_w} (= T) \quad (2)$$

$$p^{\text{I}} = p^{\text{L}_w} (= p) \quad (3)$$

$$\mu_w^{\text{I}} (T^{\text{I}}, p^{\text{I}}, x_w^{\text{I}} = 1) = \mu_w^{\text{L}_w} (T^{\text{L}_w}, p^{\text{L}_w}, x_w^{\text{L}_w}) \quad (4)$$

According to the set of independent variables  $T$ ,  $p$  and  $x$ , the underlying thermodynamic potential describing the equilibrium is the Gibbs free energy. Since the solid ice phase is a pure phase by its nature, the corresponding chemical potential is fully described by its dependency on  $T$  and  $p$ :

$$\mu_w^{\text{I}} (T^{\text{I}}, p^{\text{I}}, x_w^{\text{I}} = 1) = \mu_w^{\circ, \text{I}} (T^{\text{I}}, p^{\text{I}}), \quad (5)$$

where the superscript indicates the pure component property. In contrast to  $\mu_w^{\text{I}}$ , the chemical potential of liquid water,  $\mu_w^{\text{L}_w} (T, p, x_w^{\text{L}_w})$ , depends on the composition of the phase and is given by:

$$\begin{aligned} & \mu_w^{L_w}(T, p, x_w^{L_w}) \\ &= \mu_w^{\circ, L_w}(T, p) + RT \ln x_w^{L_w} \gamma_w^{L_w}(T, p, x_w^{L_w}), \end{aligned} \quad (6)$$

where  $\mu_w^{\circ, L_w}(T, p)$  is the chemical potential of pure liquid water at temperature  $T$  and pressure  $p$ ,  $R$  denotes the universal gas constant,  $x_w^{L_w}$ , the mole fraction, and  $\gamma_w^{L_w}$  activity coefficient of water in the liquid aqueous phase.  $\gamma_w^{L_w}$  is defined with respect to the Raoult's law reference frame implying the following converging behavior:

$$\lim_{x_w \rightarrow 1} \gamma_w^{L_w} = 1 \quad (7)$$

Upon inserting eq. (5) and eq. (6) into eq. (4), the equilibrium condition turns into:

$$\mu_w^{\circ, I}(T, p) = \mu_w^{\circ, L_w}(T, p) + RT \ln x_w^{L_w} \gamma_w^{L_w}, \quad (8)$$

Introducing the standard chemical potential of water  $\mu_w^{\ominus, \Pi}(T)$  in the respective phase  $\Pi = I$  and  $\Pi = L_w$ , respectively, according to:

$$\mu_j^{\ominus, \Pi}(T) = \mu_j^{\circ, \Pi}(T, p) + \int_p^{p^{\ominus}} V_{m,j}^{\circ, \Pi}(T, p) dp, \quad (9)$$

where  $V_{m,j}^{\circ, \Pi}$  is the molar volume of pure  $j$  in the condensed phase  $\Pi$  and  $p^{\ominus} = 0.1 \text{ MPa}$  is the standard pressure, and applying eq. (9) to  $j = w$  for  $\Pi = I$  and  $\Pi = L_w$ , respectively, the  $\mu_w^{\circ, \Pi}(T, p)$ 's in eq. (8) can be eliminated.

$$\begin{aligned} \ln x_w^{L_w} \gamma_w^{L_w} &= -\frac{\mu_w^{\ominus, L_w}(T) - \mu_w^{\ominus, I}(T)}{RT} \\ &+ \frac{1}{RT} \int_p^{p^{\ominus}} (V_{m,w}^{\circ, L_w} - V_{m,w}^{\circ, I}) dp, \end{aligned} \quad (10)$$

The temperature dependence of the standard chemical potential  $\mu_w^{\ominus, \Pi}$  can be expressed by means of the caloric quantities  $H_{m,w}^{\ominus, \Pi}$  and  $C_{p,m,w}^{\ominus, \Pi}$ , the standard value of the molar isobaric heat capacity and the enthalpy in phase  $\Pi$  according to:

$$\begin{aligned} \frac{\mu_w^{\ominus, \Pi}(T)}{T} &= \frac{\mu_w^{\ominus, \Pi}(T_0)}{T_0} + H_{m,w}^{\ominus, \Pi}(T_0) \left( \frac{1}{T} - \frac{1}{T_0} \right) \\ &- \int_{T_0}^T \left( \int_{T_0}^{T'} C_{p,m,w}^{\ominus, \Pi}(T'') dT'' \right) \frac{dT'}{T'^2} \end{aligned} \quad (11)$$

where  $T_0$  is an appropriate reference temperature. Upon evaluating  $\mu_w^{\ominus, \Pi}(T)/T$  according to eq. (11) for the phase  $\Pi = I$  and  $\Pi = L_w$ , respectively, using as the reference temperature  $T_0$  the

temperature of the solid-liquid phase transition of pure water at  $p = p^{\ominus}$ ,  $T^{IL_w} = T^{IL_w}(p^{\ominus})$ , and inserting the resulting expressions into eq. (10), the phase equilibrium condition appears in the form

$$\begin{aligned} \ln x_w^{L_w} \gamma_w^{L_w} &= -\frac{H_{m,w}^{\ominus, L_w}(T^{IL_w}) - H_{m,w}^{\ominus, I}(T^{IL_w})}{R} \left( \frac{1}{T} - \frac{1}{T^{IL_w}} \right) \\ &+ \frac{1}{R} \int_{T^{IL_w}}^T \left( \int_{T^{IL_w}}^{T'} (C_{p,m,w}^{\ominus, L_w}(T'') - C_{p,m,w}^{\ominus, I}(T'')) dT'' \right) \frac{dT'}{T'^2} \\ &+ \frac{1}{RT} \int_p^{p^{\ominus}} (V_{m,w}^{\circ, L_w} - V_{m,w}^{\circ, I}) dp \end{aligned} \quad (12)$$

Since  $T^{IL_w}$  and  $p^{\ominus}$  represent the state conditions at which pure liquid water is in equilibrium with an ice phase, the difference of the standard chemical potentials  $\mu_w^{\ominus, L_w}(T^{IL_w}) - \mu_w^{\ominus, I}(T^{IL_w})$  vanishes due to the thermodynamic requirement that the chemical potentials in both phases have to be equal. Abbreviating the differences accompanying the I- $L_w$ -phase transition of pure water, i.e., molar quantities upon fusion of ice at  $T^{IL_w}$  as  $\Delta_1^{L_w} H_{m,w}^{\ominus}(T^{IL_w})$ ,  $\Delta_1^{L_w} C_{p,m,w}^{\ominus}(T)$  and  $\Delta_1^{L_w} V_{m,w}^{\circ}(T, p)$ , respectively, leads to:

$$\begin{aligned} \ln x_w^{L_w} \gamma_w^{L_w} &= \frac{\Delta_1^{L_w} H_{m,w}^{\ominus}(T^{IL_w})}{RT} \left( \frac{T}{T^{IL_w}} - 1 \right) \\ &+ \frac{1}{R} \int_{T^{IL_w}}^T \left( \int_{T^{IL_w}}^{T'} \Delta_1^{L_w} C_{p,m,w}^{\ominus}(T'') dT'' \right) \frac{dT'}{T'^2} \\ &+ \frac{1}{RT} \int_p^{p^{\ominus}} \Delta_1^{L_w} V_{m,w}^{\circ}(T, p) dp \end{aligned} \quad (13)$$

Simplifying eq. (13) by assuming that the temperature dependence of  $\Delta_1^{L_w} C_{p,m,w}^{\ominus}(T)$ , and the pressure dependence of  $\Delta_1^{L_w} V_{m,w}^{\circ}(T, p)$  are negligible and taking them as their values at  $T^{IL_w}$  and  $p^{\ominus}$  allows for an evaluation of the integrals:

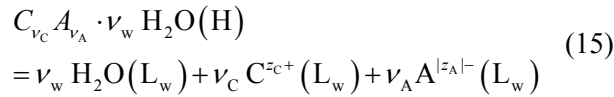
$$\begin{aligned} \ln x_w^{L_w} \gamma_w^{L_w} &= \frac{\Delta_1^{L_w} H_{m,w}^{\ominus}(T^{IL_w})}{RT} \left( \frac{T}{T^{IL_w}} - 1 \right) \\ &+ \frac{\Delta_1^{L_w} C_{p,m,w}^{\ominus}(T^{IL_w})}{R} \left( \frac{T^{IL_w}}{T} + \ln \left( \frac{T}{T^{IL_w}} \right) - 1 \right) \\ &+ \frac{\Delta_1^{L_w} V_{m,w}^{\circ}(T^{IL_w}, p^{\ominus})}{RT} (p^{\ominus} - p) \end{aligned} \quad (14)$$

In this form the equilibrium condition contains measurable quantities and, provided that a suitable model for the activity coefficient

$\gamma_w^{L_w}(T, p, x_w^{L_w})$  is given, it represents an implicit equation in the three independent variables  $T$ ,  $p$  and  $x_{H_2O}^L$  that can be solved numerically if two properties are set. Whereas Pericaud [1] uses the SAFT equation of state [18] as a model for describing the activity coefficient while in our work, the eNRTL model of Chen et al. [19-21] is intended to be used for that purpose.

### Equilibrium between a (salt or semicathrate) hydrate phase and a liquid electrolyte solution

The dissociation of a salt or semicathrate hydrate  $C_{V_C} A_{V_A} \cdot \nu_w H_2O$  composed of  $\nu_w$  water molecules  $H_2O$ ,  $\nu_C$  cations  $C^{z_C+}$  and  $\nu_A$  anions  $A^{z_A-}$  is to be regarded as a combined chemical reaction and phase equilibrium and can be written as:



It is described by the standard equilibrium constant expressed in terms of the composition as:

$$K^\ominus(T) = \frac{(a_w^{L_w})^{\nu_w} (a_{x,C}^{*,L_w})^{\nu_C} (a_{x,A}^{*,L_w})^{\nu_A}}{a_h^H} \quad (16)$$

$$\times \exp\left(-\frac{1}{RT} \int_p^{p^\ominus} (\nu_w V_{m,w}^{o,L} + \nu_C V_{m,C}^{o,L_w} + \nu_A V_{m,A}^{o,L_w} - V_{m,h}^{o,H}) dp\right)$$

where the subscript symbol ‘‘h’’ here and in the subsequent parts of this report denotes the hydrate compound  $C_{V_C} A_{V_A} \cdot \nu_w H_2O$ .  $a_h^H$  stands for the activity of the hydrate in the solid hydrate phase.  $a_w^{L_w}$ ,  $a_{x,C}^{*,L_w}$  and  $a_{x,A}^{*,L_w}$ , respectively, denote the activity of the water, the cation and anion in the liquid phase.

Whereas the activities of the solute species are normalised to the reference state of infinite dilution, indicated by symbols endowed with an asterisk, the activity of water, regarded as the solvent, is normalised according to the pure component reference state (see further explanations below). Since it is very common to use different concentration scales for solute species in a solution, the subscript  $x$  is additionally attached to the symbols of the activities of the ions (or the neutral salt) in order to emphasize that they are defined here by using the mole fraction scale to quantify the composition.  $V_{m,w}^{o,L}$  and  $V_{m,h}^{o,H}$  denote the molar volume of pure and liquid water and the

hydrate, whereas  $V_{m,C}^{\infty,L_w}$  and  $V_{m,A}^{\infty,L_w}$  stand for the partial molar volume of the cation and the anion at infinite dilution of the salt, respectively.

Taking into account that the solid hydrate phase is a pure phase implies that its activity  $a_h^H$  is unity:

$$a_h^H = 1 \quad (17)$$

In contrast, the activities of the species in the liquid phase depend on the composition of that phase and can, e.g., be expressed as the product of the mole fraction of that species and the corresponding activity coefficient. The activity of water is defined as:

$$a_w^{L_w} = x_w^{L_w} \gamma_w^{L_w} \quad (18)$$

where the activity coefficient of water  $\gamma_w^{L_w}$  is normalized according to eq. (7). The activities  $a_{x,j}^{*,L_w}$  of the ionic species are defined similarly according to:

$$a_{x,j}^{*,L_w} = x_j^{L_w} \gamma_{x,j}^{*,L_w} \quad (j = C, A), \quad (19)$$

However, in contrast to  $a_w^{L_w}$ , the  $a_{x,j}^{*,L_w}$  of the solute species are defined with reference to the hypothetical state of the pure ionic species being in the state of infinite dilution, implying the following converging behavior for the activity coefficient  $\gamma_{x,j}^{*,L_w}$  the solute species:

$$\lim_{x_w \rightarrow 1} \gamma_{x,j}^{*,L_w} = 1 \quad (j = C, A) \quad (20)$$

Normalizing  $\gamma_w^{L_w}$  and  $\gamma_{x,j}^{*,L_w}$  by means of eq. (7), and eq. (20), respectively, corresponds to the so-called ‘‘unsymmetric convention’’.

Upon introducing eqs. (17), (18), (19) into eq. (16) and taking the logarithm, the equilibrium condition reads:

$$\ln K^\ominus(T) \quad (21)$$

$$= \nu_w \ln x_w^{L_w} \gamma_w^{L_w} + \nu_C \ln x_C^{L_w} \gamma_{x,C}^{*,L_w} + \nu_A \ln x_A^{L_w} \gamma_{x,A}^{*,L_w}$$

$$- \frac{1}{RT} \int_p^{p^\ominus} (\nu_w V_{m,w}^{o,L} + \nu_C V_{m,C}^{o,L_w} + \nu_A V_{m,A}^{o,L_w} - V_{m,h}^{o,H}) dp$$

Replacing  $\ln K^\ominus(T)$  in the relation above by considering that

$$RT \ln K^\ominus(T) = -\Delta_{\text{dis}} G_m^\ominus(T) = \quad (22)$$

$$-\mu_h^{\ominus,H}(T) - \nu_w \mu_w^{\ominus,L_w}(T) - \nu_C \mu_{x,C}^{\ominus,L_w}(T) - \nu_A \mu_{x,A}^{\ominus,L_w}(T)$$

leads to

$$\frac{\mu_h^{\ominus, H}(T) - \nu_w \mu_w^{\ominus, L_w}(T) - \nu_C \mu_{x,C}^{\ominus, L_w}(T) - \nu_A \mu_{x,A}^{\ominus, L_w}(T)}{RT} \quad (23)$$

$$= \nu_w \ln x_w^{L_w} \gamma_w^{L_w} + \nu_C \ln x_C^{L_w} \gamma_{x,C}^{*, L_w} + \nu_A \ln x_A^{L_w} \gamma_{x,A}^{*, L_w}$$

$$- \frac{1}{RT} \int_p^{p^\ominus} (\nu_w V_{m,w}^{\circ, L} + \nu_C V_{m,C}^{\circ, L_w} + \nu_A V_{m,A}^{\circ, L_w} - V_{m,h}^{\circ, H}) dp$$

In eq. (22) the subscript “dis” in  $\Delta_{\text{dis}} G_m^\ominus(T) = \Delta_{\text{I}} G_m^\ominus(T)$  indicates that the change in standard molar Gibbs energy is accompanying a particular type of chemical reaction, the reaction equilibrium of the hydrate dissociation. For the hydrate in the solid hydrate phase and the liquid water in the liquid aqueous phase, the standard chemical potential, respectively, is defined as:

$$\mu_j^{\ominus, \Pi}(T) = \mu_j^{\circ, \Pi}(T, p) + \int_p^{p^\ominus} V_{m,j}^{\circ, \Pi} dp, \quad (24)$$

for  $j = w$  and  $\Pi = L_w$  and  $j = h$  and  $\Pi = H$ , respectively. For the solute species  $j = C, A$  in the liquid phase, the standard chemical potential is defined as:

$$\mu_j^{\ominus, L_w}(T) = \lim_{x_w^{L_w} \rightarrow 1} (\mu_j^{L_w}(T, p, x_w^{L_w}) - RT \ln x_j^{L_w})$$

$$+ \int_p^{p^\ominus} V_{m,j}^{\circ, L_w} dp \quad (25)$$

While both terms in the limes expression of eq. (25) diverge individually their sum remains finite [25].

If the temperature dependence of the standard chemical potentials in eq. (23) is considered for all the species by means of eq. (11), like it was previously done for  $\mu_w^{\ominus, \Pi}(T)/T$ , eq. (23) reads:

$$\frac{\mu_h^{\ominus, H}(T) - \nu_w \mu_w^{\ominus, L_w}(T) - \nu_C \mu_{x,C}^{\ominus, L_w}(T) - \nu_A \mu_{x,A}^{\ominus, L_w}(T)}{RT} =$$

$$\frac{\mu_h^{\ominus, H}(T_{\text{cgr}}^{\text{HL}_w}) - \nu_w \mu_w^{\ominus, L_w}(T_{\text{cgr}}^{\text{HL}_w}) - \nu_C \mu_{x,C}^{\ominus, L_w}(T_{\text{cgr}}^{\text{HL}_w}) - \nu_A \mu_{x,A}^{\ominus, L_w}(T_{\text{cgr}}^{\text{HL}_w})}{RT_{\text{cgr}}^{\text{HL}_w}} \quad (26)$$

$$\frac{1}{R} \left( \frac{H_{m,h}^{\ominus, H}(T_{\text{cgr}}^{\text{HL}_w}) - \nu_w H_{m,w}^{\ominus, L_w}(T_{\text{cgr}}^{\text{HL}_w})}{- \nu_C H_{m,C}^{\ominus, L_w}(T_{\text{cgr}}^{\text{HL}_w}) - \nu_A H_{m,A}^{\ominus, L_w}(T_{\text{cgr}}^{\text{HL}_w})} \right) \left( \frac{1}{T} - \frac{1}{T_{\text{cgr}}^{\text{HL}_w}} \right) +$$

$$\frac{1}{R} \int_{T_{\text{cgr}}^{\text{HL}_w}}^T \left( \int_{T_{\text{cgr}}^{\text{HL}_w}}^{T'} (\nu_w C_{p,m,w}^{\ominus, L_w}(T'') + \nu_C C_{p,m,C}^{\ominus, L_w}(T'') + \nu_A C_{p,m,A}^{\ominus, L_w}(T'') - C_{p,m,h}^{\ominus, H}(T'')) dT'' \right) \frac{dT'}{T'^2}$$

$$= \nu_w \ln x_w^{L_w} \gamma_w^{L_w} + \nu_C \ln x_C^{L_w} \gamma_{x,C}^{*, L_w} + \nu_A \ln x_A^{L_w} \gamma_{x,A}^{*, L_w}$$

$$- \frac{1}{RT} \int_p^{p^\ominus} (\nu_w V_{m,w}^{\circ, L_w} + \nu_C V_{m,C}^{\circ, L_w} + \nu_A V_{m,A}^{\circ, L_w} - V_{m,h}^{\circ, H}) dp$$

Thereby,  $T_{\text{cgr}}^{\text{HL}_w} = T_{\text{cgr}}^{\text{HL}_w}(p^\ominus)$ , the congruent melting temperature of the hydrate at  $p = p^\ominus$  is taken as the reference temperature  $T_0$ .

The linear combinations of the standard molar quantities  $Z_{m,i}^{\ominus, \Pi}$  ( $Z = H, C_p; i = h, w, C, A$ ) as well as of  $V_{m,w}^{\circ, L_w}$ ,  $V_{m,C}^{\circ, L_w}$ ,  $V_{m,A}^{\circ, L_w}$  and  $V_{m,h}^{\circ, H}$  appearing in eq. (26) have a physical significance similar to  $\Delta_{\text{dis}} G_m^\ominus(T)$ , since they represent the changes accompanying the dissociation reaction of the hydrate:

$$\Delta_{\text{dis}} Z_m^\ominus(T) = \nu_w Z_{m,w}^{\ominus, L_w}(T) + \nu_C Z_{m,C}^{\ominus, L_w}(T) + \nu_A Z_{m,A}^{\ominus, L_w}(T) - H_{m,h}^{\ominus, H}(T) \quad (27)$$

$$\Delta_{\text{dis}} V_m^{\text{ref}}(T, p) =$$

$$\nu_w V_{m,w}^{\circ, L_w}(T, p) + \nu_C V_{m,C}^{\circ, L_w}(T, p) + \nu_A V_{m,A}^{\circ, L_w}(T, p) - V_{m,h}^{\circ, H}(T, p) \quad (28)$$

Taking into account eqs. (22), (27) and (28), and making the same simplifying assumptions for  $\Delta_{\text{dis}} C_{p,m}^\ominus(T)$  and  $\Delta_{\text{dis}} V_m^{\text{ref}}(T, p)$  like it was done previously for  $\Delta_{\text{I}} C_{p,m,w}^\ominus(T)$  and  $\Delta_{\text{I}} V_{m,w}^{\circ, L_w}(T, p)$  in the treatment of the I-L<sub>w</sub>-phase equilibrium, eq. (26) is converted into:

$$\frac{\Delta_{\text{dis}} G_m^\ominus(T_{\text{cgr}}^{\text{HL}_w})}{RT_{\text{cgr}}^{\text{HL}_w}} + \frac{\Delta_{\text{dis}} H_m^\ominus(T_{\text{cgr}}^{\text{HL}_w})}{RT} \left( 1 - \frac{T}{T_{\text{cgr}}^{\text{HL}_w}} \right)$$

$$+ \frac{\Delta_{\text{dis}} C_{p,m}^\ominus(T_{\text{cgr}}^{\text{HL}_w})}{R} \left( 1 + \ln \left( \frac{T_{\text{cgr}}^{\text{HL}_w}}{T} \right) - \frac{T_{\text{cgr}}^{\text{HL}_w}}{T} \right) \quad (29)$$

$$+ \frac{\Delta_{\text{dis}} V_m^{\text{ref}}(T_{\text{cgr}}^{\text{HL}_w}, p^\ominus)}{RT} (p - p^\ominus)$$

$$+ \nu_w \ln x_w^{L_w} \gamma_w^{L_w} + \nu_C \ln x_C^{L_w} \gamma_{x,C}^{*, L_w} + \nu_A \ln x_A^{L_w} \gamma_{x,A}^{*, L_w} = 0$$

This is the final simplified form of the equilibrium condition describing the coupled reaction and solid-liquid equilibrium between a (semiclathrate-) hydrate phase and the corresponding aqueous electrolyte solution in the binary system  $\text{H}_2\text{O} + C_{\nu_C} A_{\nu_A}$ . At the point with  $p = p^\ominus$  and  $T = T_{\text{cgr}}^{\text{HL}_w}$ , the composition of the liquid phase equals the stoichiometric composition of the hydrate phase,  $\bar{x}^{\text{H}} = (x_w^{\text{H}}, x_C^{\text{H}})^{\text{T}}$ :

$$x_w^{L_w} = x_w^{\text{H}} = \frac{\nu_w}{\nu_w + \nu_C + \nu_A} \quad (30)$$

$$x_C^{L_w} = x_C^{\text{H}} = \frac{\nu_C}{\nu_w + \nu_C + \nu_A} \quad (31)$$

Insertion of these values into eq. (29) and realising that  $x_A^{\text{H}} = 1 - x_w^{\text{H}} - x_C^{\text{H}}$  enables the calculation of  $\Delta_{\text{dis}} G_m^\ominus(T_{\text{cgr}}^{\text{HL}_w})$  [1]:

$$\frac{\Delta_{\text{dis}} G_m^\ominus(T_{\text{cgr}}^{\text{HL}_w})}{RT_{\text{cgr}}^{\text{HL}_w}} = \nu_w \ln x_w^{\text{H}} \gamma_w^{L_w}(T_{\text{cgr}}^{\text{HL}_w}, \bar{x}^{\text{H}}) \quad (32)$$

$$+ \nu_C \ln x_C^{\text{H}} \gamma_{x,C}^{*, L_w}(T_{\text{cgr}}^{\text{HL}_w}, \bar{x}^{\text{H}}) + \nu_A \ln x_A^{\text{H}} \gamma_{x,A}^{*, L_w}(T_{\text{cgr}}^{\text{HL}_w}, \bar{x}^{\text{H}})$$

In eq. (31)  $\gamma_w^{L_w}(T_{\text{cgr}}^{\text{HL}_w}, \bar{x}^{\text{H}})$ ,  $\gamma_{x,C}^{*,L_w}(T_{\text{cgr}}^{\text{HL}_w}, \bar{x}^{\text{H}})$  and  $\gamma_{x,A}^{*,L_w}(T_{\text{cgr}}^{\text{HL}_w}, \bar{x}^{\text{H}})$  stand for the values of the activity coefficients calculated by means of the eNRTL model at  $T_{\text{cgr}}^{\text{HL}_w}$  and  $\bar{x}^{\text{H}}$ .

Numerical values for the standard molar quantities,  $\Delta_{\text{dis}} H_m^{\ominus}(T_{\text{cgr}}^{\text{HL}_w})$  and  $\Delta_{\text{dis}} C_{p,m}^{\ominus}(T_{\text{cgr}}^{\text{HL}_w})$ , are gained through adjustments of the  $\text{HL}_w$ -coexistence curves or to the dissociation enthalpies directly. If values of the standard molar isobaric heat capacity upon hydrate dissociation are measured directly, they can additionally be used to adjust  $\Delta_{\text{dis}} C_{p,m}^{\ominus}(T_{\text{cgr}}^{\text{HL}_w})$ . However,  $\Delta_{\text{dis}} C_{p,m}^{\ominus}(T_{\text{cgr}}^{\text{HL}_w})$  has been set to zero in our calculations.

$\Delta_{\text{dis}} V_m^{\text{ref}}$ , evaluated at  $T_{\text{cgr}}^{\text{HL}_w}$  and  $p^{\ominus}$ , accounts for the effect of pressure on the melting points for the water + salt binary systems [1]. Paricaud points out that “different values for  $\Delta_{\text{dis}} V_m^{\text{ref}}(T_{\text{cgr}}^{\text{HL}_w}, p^{\ominus})$ ,  $\Delta_{\text{dis}} H_m^{\ominus}(T_{\text{cgr}}^{\text{HL}_w})$ ,  $T_{\text{cgr}}^{\text{HL}_w}$  and  $\Delta_{\text{dis}} C_{p,m}^{\ominus}(T_{\text{cgr}}^{\text{HL}_w})$  should be used for different types of hydrates” [1]. He further reports that  $\nu_w$  should be fixed to its experimental value.

### Modelling the HL<sub>w</sub> phase behaviour with a gas semi-clathrate hydrate phase in systems of water, TBAB and a suitable gas

In this section, a multi component system composed of water and a salt  $C_{\nu_C} A_{\nu_A}$  (abbreviated as “CA”), being capable of forming a semiclathrate hydrate phase with water in binary water + CA (e.g. TBAB) mixtures and  $N_{\text{type g}}$  different types of gas molecules is considered. It is further assumed that at a given temperature  $T$  and pressure  $p$  the system exists in a state of equilibrium between a gas semiclathrate hydrate phase (formed by a framework of water and salt molecules in which gas molecules are enclathrated, in the following denoted by  $H_g$ ), a liquid aqueous ( $L_w$ ) and a vapour phase ( $V$ ).

In this theoretical approach, the model presented previously for describing the equilibria encountered in binary water+CA-systems will be combined with the model of van der Waals and Platteeuw [17,24] for gas hydrates. In the latter theory the metastable phase  $\beta$  of the empty lattice made up by the lattice forming compound alone is used as a reference state to define the chemical potential of that compound in the gas hydrate

phase. In the approach for gas-semiclathrate hydrate equilibria, the lattice framework of the host lattice is – in contrast to the one of the “normal” gas hydrates – formed by more than one hydrate former. However, for each particular structure it is built up in a regular, i.e. a stoichiometric way between the hydrate forming components.

In the framework of the final thermodynamic modelling equations, the gas hydrate phase  $H_g$  is treated here as being composed of  $N_{\text{type g}} + 1$  components, one semi-clathrate hydrate component  $C_{\nu_C} A_{\nu_A} \cdot \nu_w \text{H}_2\text{O}$  (i.e., treated as a single chemical compound and, hence, with a fixed stoichiometric composition of  $\nu_C$  cations  $C^{z_C+}$ ,  $\nu_A$  anions  $A^{z_A-}$  and  $\nu_w$  water molecules), abbreviated as h, and  $N_{\text{type g}}$  of gas molecules  $j$  ( $j = 1, \dots, N_{\text{type g}}$ ). Paricaud [1] mentions that it is a “key point” in the development of this model “to consider that the metastable empty  $\beta$  phase can have different structures that correspond to the different semiclathrate hydrate phases observed in the salt +  $\text{H}_2\text{O}$  binary system.” For the TBAB aqueous system, Paricaud assumed two types of hydrates, named type A and B which correspond to hydration numbers of  $\nu_w = 26$  and  $\nu_w = 38$  [1].

### The chemical potential of the semi-clathrate hydrate and the fraction of occupation of the gaseous components

The chemical potential of the gas semiclathrate hydrate including a term that accounts for its dependence on composition, i.e., the degree of occupation by gas molecules, is derived by means of statistical thermodynamics from an expression for the semi-grand partition function  $\Xi$  for the hydrate phase.

From the characteristics outlined above it follows that the overall grand partition function  $\Xi$  will be of the form  $\Xi = \Xi(T, V, N_w, N_C, N_A, \tilde{\mu}_1, \dots, \tilde{\mu}_{N_g})$ . However, it has to be pointed out that the basic variables used to characterise the composition of the empty hydrate, the particle numbers  $N_w$ ,  $N_C$  and  $N_A$ , are not independent of each other. They are rather related through the stoichiometric restriction (in accordance with the chemical reaction defined by eq. (15))



$$d\tilde{\xi} = \frac{dN_w}{\nu_w} = \frac{dN_C}{\nu_C} = \frac{dN_A}{\nu_A} = dN_{CA} \quad (33)$$

where  $\tilde{\xi}$  has the same meaning as like variable to describe the extend of a chemical reaction, the differential of which is equal to the differential of the number of salt “molecules”  $N_{CA}$ . The tilde over  $\xi$ , a variable normally defined on a molar basis, indicates that the quantity is defined with regard to the number of particles rather than the amount of substance of that particular species. Particle related properties are related to molar properties by means of the Avogadro constant  $N_{Av}$ . In deriving the semi-grand partition function for the gas semi-clathrate hydrate,  $\Xi$ , Pericaud [1] follows closely the original work of van der Waals and Platteeuw [17]. In fact, the only difference between the semi-grand partition function to be developed for the gas semi-clathrate hydrate phases and the original grand partition function derived by van der Waals and Platteeuw for gas hydrates phases with hydrates of a single hydrate forming component is that the number of cavities has to be related to a suitable number of one of the lattice forming components. Such a number is e.g. the number of salt “molecular” units  $N_{C_{\nu_C A_{\nu_A}}}$ , which is identical to the number of “molecular” units of the semiclathrate hydrate

$$N_h = N_{C_{\nu_C A_{\nu_A}} \nu_w H_2O} = N_{CA} \quad (34)$$

where the index “h” refers to the molecular unit of the semiclathrate hydrate compound.

In the derivation of the particular expression for  $\Xi$  [17], phase equilibrium between the species in the vapour and the hydrate phase:

$$\forall_{j \in \{1, \dots, N_{type\ g}\}} \left( \mu_j^{H_g} = \mu_j^v \Leftrightarrow f_j^{H_g} = f_j^v \right) \quad (35)$$

is implicitly assumed and incorporated into the equation derived from  $\Xi$  for the fraction of lattice sites  $\theta_{ji}$  occupied by gas molecule  $j$  in the cavity  $i$  via the fugacity  $f_j^v$  of  $j$  in the vapor phase.

The functional relationship for  $\theta_{ji}$  that is derived from  $\Xi$  reads [1,17,24]:

$$\theta_{ji} = \frac{C_{ji} f_j}{1 + \sum_{j=1}^{N_{type\ g}} C_{ji} f_j} \quad (36)$$

Due to the argumentation above, the values of the fugacities  $f_j$  do not only hold for the solid hydrate but evenly for the gaseous phase and can e.g. be calculated by means of a suitable equation of state for the gas phase. In our modeling calculations, the Soave-Redlich-Kwong equation of state [25] was used for that purpose. The  $C_{ji}$  are the so-called the Langmuir constants  $C_{ji}$  which in case of spherical cavities, which can be linked to the cell radial symmetric potential between the particle  $j$  and the host molecules,  $w_{ji}(r)$ , as follows:

$$C_{ji} = \frac{4\pi}{k_B T} \int_0^{R_{cav,i}} \exp\left(-\frac{w_{ji}(r)}{k_B T}\right) r^2 dr \quad (37)$$

where the  $r$  denotes the distance between the centre of mass of the gas molecule and the centre of the cavity,  $R_{cav,i}$  stands for the effective radius of cavity  $i$ , and  $k_B$  for the Boltzmann constant. Whereas a square-well (SW) potential (see e.g. Parrish and Prausnitz [26]) is used by Paricaud [1], we use the Kihara potential in our calculations (see e.g. McKoy and Sinagoglu (1963) [27]. For details on the procedure of adjusting the Kihara potential parameters see Herri et al. (2011) [28]). The following expression is derived from  $\Xi$  for the chemical potential of the gas semiclathrate hydrate  $\tilde{\mu}_{h_g}^{H_g}$  compound:

$$\mu_{h_g}^{H_g} = \mu_h^{\circ, \beta} + RT \sum_{i=1}^{N_{type\ cav}} \nu_i \ln \left( 1 - \sum_{j=1}^{N_{type\ g}} \theta_{ji} \right) \quad (38)$$

### The equilibrium condition for phase equilibria exhibiting a gas semiclathrate hydrate phase

Since the composition dependence of the chemical potential of the gas semiclathrate hydrate is not given in terms of the activity of the semiclathrate hydrate but by the expression derived from the van der Waals and Platteeuw using  $\theta_{ji}$  as composition variable it is not possible to start from eq. (16) to derive the final equilibrium condition. However, eq. (15) is still valid, with the only little difference that the semiclathrate hydrate phase H is now a mixed gas semiclathrate hydrate phase  $H^g$ . The equilibrium condition describing the combined chemical and phase equilibrium given in eq. is:

$$\Delta_r G_m = \Delta_{dis} G_m = \nu_w \mu_w^{L_w} + \nu_C \mu_C^{L_w} + \nu_A \mu_A^{L_w} - \mu_{h_g}^{H_g} = 0 \quad (39)$$

$\Delta_r G_m = \Delta_{\text{dis}} G_m$  is the molar Gibbs free energy change accompanying the dissociation reaction. Eq. (39) in turn is gained from the necessary condition, that the total Gibbs energy in the independent variables  $T$ ,  $p$  and composition is a minimum at equilibrium.

For the ionic species, the state of the pure ions in the hypothetical infinitely dilute state in water is chosen as the reference state for the activity coefficients defined in terms of the mole fraction as composition variable. Hence, the chemical potential for the ionic species  $j = C, A$  is defined by:

$$\mu_j^{L_w}(T, p, x_w^{L_w}) = \mu_j^{\text{ref}, L_w}(T, p) + RT \ln x_j^{L_w} \gamma_{x,j}^{*, L_w} \quad (40)$$

where the reference chemical potential  $\mu_j^{\text{ref}, L_w}(T, p)$  is defined by

$$\mu_j^{\text{ref}, L_w}(T, p) = \lim_{x_w^{L_w} \rightarrow 1} \left( \mu_j^{L_w}(T, p, x_w^{L_w}) - RT \ln x_j^{L_w} \right) \quad (41)$$

Inserting eq. (6) for  $\mu_w^{L_w}$ , eq. (38) defining  $\mu_h^{\text{Hg}}$  and eq. (40) for  $\mu_C^{\text{ref}, L_w}$  and  $\mu_A^{\text{ref}, L_w}$  into eq. (39) leads to:

$$\begin{aligned} \frac{\Delta_{\text{dis}} G_m}{RT} = & \frac{v_C \mu_C^{\text{ref}, L_w}(T, p) + v_A \mu_A^{\text{ref}, L_w}(T, p) + v_w \mu_w^{\text{ref}, L_w}(T, p) - \mu_h^{\text{Hg}}(T, p)}{RT} \\ & v_C \ln x_C^{L_w} \gamma_{x,C}^{*, L_w} + v_A \ln x_A^{L_w} \gamma_{x,A}^{*, L_w} + v_w \ln x_w^{L_w} \gamma_w^{L_w} \\ & - \sum_{i=1}^{N_{\text{type cav}}} v_i \ln \left( 1 - \sum_{j=1}^{N_{\text{type g}}} \theta_{ji} \right) = 0 \end{aligned} \quad (42)$$

If the pressure dependence of the reference chemical potentials is eliminated by introducing standard chemical potentials for all the species, the resulting equation reads

$$\begin{aligned} \frac{\Delta_{\text{dis}} G_m}{RT} = & \frac{1}{RT} \left( v_w \mu_w^{\ominus, L_w}(T) + v_C \mu_C^{\ominus, L_w}(T) + v_A \mu_A^{\ominus, L_w}(T) - \mu_h^{\ominus, \beta}(T) \right) \\ & - \int_p^{p^\ominus} \frac{v_w V_{m,w}^{\ominus, L_w}(T, p) + v_C V_{m,C}^{\ominus, L_w}(T, p) + v_A V_{m,A}^{\ominus, L_w}(T, p) - V_{m,h}^{\ominus, \beta}(T, p)}{RT} dp \\ & v_C \ln x_C^{L_w} \gamma_{x,C}^{*, L_w} + v_A \ln x_A^{L_w} \gamma_{x,A}^{*, L_w} + v_w \ln x_w^{L_w} \gamma_w^{L_w} \\ & - \sum_{i=1}^{N_{\text{type cav}}} v_i \ln \left( 1 - \sum_{j=1}^{N_{\text{type g}}} \theta_{ji} \right) = 0 \end{aligned} \quad (43)$$

If a) the temperature dependence of the chemical potentials is introduced, like it was done previously for the binary system  $\text{H}_2\text{O} + \text{TBAB}$ , b) the linear combinations of the respective partial molar quantities are identified with their changes accompanying the dissociation reaction, and the general relation above by assuming that  $\Delta_{\text{dis}} C_{p,m}^{\ominus}(T)$  and  $\Delta_{\text{dis}} V_m^{\text{ref}}(T, p)$  are independent

of temperature and temperature and pressure, respectively, over the  $T$  and  $p$  range considered, like it was done previously for the cases of the I- $L_w$  phase equilibrium as well as the H- $L_w$  equilibrium obtained in the binary  $\text{H}_2\text{O} + \text{CA}$  systems results in the following form of the equilibrium condition

$$\begin{aligned} \frac{\Delta_{\text{dis}} G_m}{RT} = & \frac{\Delta_{\text{dis}} G_m^{\ominus}(T_{\text{cgr}}^{\text{HL}_w})}{RT_{\text{cgr}}^{\text{HL}_w}} + \frac{\Delta_{\text{dis}} H_m^{\ominus}(T_{\text{cgr}}^{\text{HL}_w})}{RT} \left( 1 - \frac{T}{T_{\text{cgr}}^{\text{HL}_w}} \right) \\ & + \frac{\Delta_{\text{dis}} C_{p,m}^{\ominus}(T_{\text{cgr}}^{\text{HL}_w})}{R} \left( 1 - \frac{T_{\text{cgr}}^{\text{HL}_w}}{T} + \ln \frac{T_{\text{cgr}}^{\text{HL}_w}}{T} \right) \\ & + \frac{\Delta_{\text{dis}} V_m^{\text{ref}}(T_{\text{cgr}}^{\text{HL}_w}, p^\ominus)}{RT} (p - p^\ominus) + v_C \ln x_C^{L_w} \gamma_{x,C}^{*, L_w} + v_A \ln x_A^{L_w} \gamma_{x,A}^{*, L_w} \\ & + v_w \ln x_w^{L_w} \gamma_w^{L_w} - \sum_{i=1}^{N_{\text{type cav}}} v_i \ln \left( 1 - \sum_{j=1}^{N_{\text{type g}}} \theta_{ji} \right) = 0 \end{aligned} \quad (44)$$

In eq. (44),  $T_{\text{cgr}}^{\text{HL}_w} = T_{\text{cgr}}^{\text{HL}_w}(p^\ominus)$  stands for the temperature of the congruent melting point of the semiclathrate hydrate, i.e., the temperature of the phase transition  $\beta \rightarrow L_w \equiv \text{H} \rightarrow L_w$  at  $p = p^\ominus$ .

### The eNRTL model for describing liquid phase non-idealities

The eNRTL model provides an expression for the excess Gibbs molar energy of electrolyte systems and has been presented and discussed in detail in another communication to this conference [29]. It is used in our model to calculate the activity coefficients of the solvent and the ionic species in the liquid phase, respectively. In the attempt to model the phase behavior of the ternary  $\text{H}_2\text{O} + \text{TBAB} + \text{CH}_4$  system presented here, the temperature dependence of the activity coefficients was neglected and the values for the interaction coefficients at 298.15 K,  $\tau_{\text{H}_2\text{O}, \text{TBAB}} = 8.3169$  and  $\tau_{\text{TBAB}, \text{H}_2\text{O}} = -3.6717$  as published by Belvèze et al. [30] had been used in the calculation. The nonrandomness factor was set to  $\alpha_{\text{H}_2\text{O}, \text{TBAB}} = 0.2$ . The values published by Belvèze et al. [30] in turn were obtained from adjusting the model equations to the isothermal mean molal activity coefficient data of Lindenbaum and Boyd [31].

### MODELLING AND DISCUSSIONS

Before the modified model of Paricaud [1] using the eNRTL-model instead of the SAFT-equation of state can be applied to the methane semiclathrate hydrate system, the  $\text{H}_2\text{O} + \text{TBAB}$

semicathrate phase boundary has to be described in order to gain values for  $T_{\text{cgr}}^{\text{HL}_w}$  and  $\Delta_{\text{dis}} H_m^\ominus(T_{\text{cgr}}^{\text{HL}_w})$ .

### Modelling of the binary water+TBAB system exhibiting a semi-clathrate hydrate phase

Applying eq. (29) to the  $\text{H}_2\text{O}+\text{TBAB}$  systems enables the calculation of the isobaric  $T$ - $x$ -phasediagram. The applicability of the equations requires a model capable of accurately representing the liquid phase non-idealities. The parameter  $\Delta_{\text{dis}} G_m^\ominus(T_{\text{cgr}}^{\text{HL}_w})$  is then calculated from eq. (32) by using eqs. (30) and (31) evaluated for the two hydrate structures. We have selected the eNRTL parameters of the system as published by Belvèze et al. [30]. At 25 °C the mean ionic activity coefficient is correlated quantitatively as shown in Figure 1. The description of the osmotic coefficient data is less precise, but still satisfying (Figure 2).  $\Delta_{\text{dis}} V_m^{\text{ref}}(T_{\text{cgr}}^{\text{HL}_w}, p^\ominus)$ . With these data, the  $T$ - $x$ -equilibria for the type A and B structures in the  $\text{H}_2\text{O}+\text{TBAB}$  system could be described successfully by adjusting  $T_{\text{cgr}}^{\text{HL}_w}$  and  $\Delta_{\text{dis}} H_m^\ominus(T_{\text{cgr}}^{\text{HL}_w})$  to the experimental data of Oyama et al. (2005) [12] and Lipkowski et al. (2002) [32].

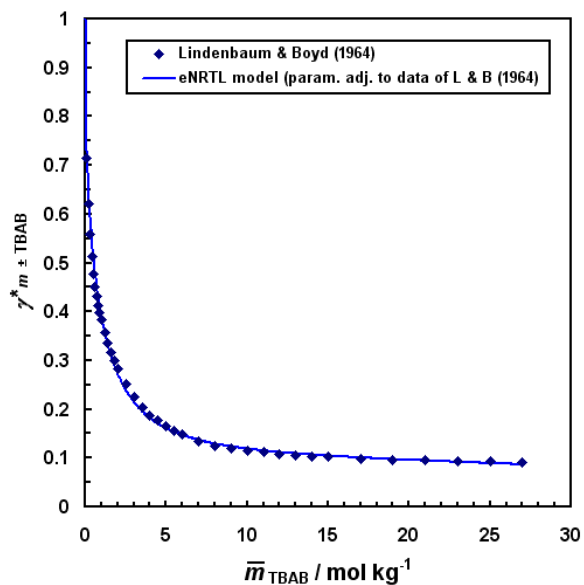


Figure 1: Mean molal activity coefficient of TBAB in aqueous solution at  $T = 298.15$  K and  $p = 0.1$  MPa as function of the overall TBAB molality using eNRTL interaction parameters of Belvèze et al. [30]. (◆) Exp. Data [31].

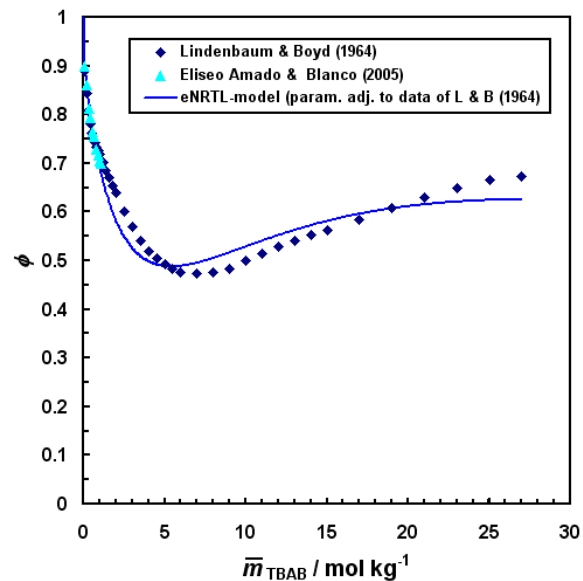


Figure 2: Osmotic coefficient of TBAB aqueous solutions at  $T = 298.15$  K and  $p = 0.1$  MPa as function of the overall TBAB molality using eNRTL interaction parameters of Belvèze et al. [30]. (◆) Exp. Data [31].

### Modelling of the HLV equilibrium occurring in the ternary system water + TBAB + methane

The model has been applied to carry out calculations on the solid-liquid-vapour phase and chemical equilibrium encountered in the ternary system  $\text{H}_2\text{O} + \text{TBAB} + \text{CH}_4$ . Under the state conditions of interest, i.e.  $9 < \vartheta/^\circ\text{C} < 24$  and  $0.05 \leq \bar{w}_{\text{TBAB}}^{\text{L}_w} \leq 0.30$ , the pressure interval ranges from around 0.5 MPa to approximately 40 MPa. By using the parameters obtained from modeling the isobaric  $T$ - $x$ -diagram of the binary sub-system  $\text{H}_2\text{O} + \text{TBAB}$ ,  $\Delta_{\text{dis}} H_m^\ominus(T_{\text{cgr}}^{\text{HL}_w})$  and  $T_{\text{cgr}}^{\text{HL}_w}$ ,  $p$ - $T$ -curves of the three phase HLV equilibrium of the system  $\text{H}_2\text{O} + \text{TBAB} + \text{CH}_4$  could be calculated for different initial concentrations of TBAB in the liquid phase. Hereby, the standard value of the molar isobaric heat capacity change upon hydrate dissociation  $\Delta_{\text{dis}} C_{p,m}^\ominus(T_{\text{cgr}}^{\text{HL}_w})$  was set to zero. For the change in molar volume upon hydrate dissociation,  $\Delta_{\text{dis}} V_m^{\text{ref}}(T_{\text{cgr}}^{\text{HL}_w}, p^\ominus)$ , the value of  $-30 \text{ cm}^3 \text{ mol}^{-1}$  has been used in accordance with Pericaud [1]. In contrast to Pericaud, who has used a square-well potential to calculate the Langmuir constants  $C_{ji}$  [1], the Kihara potential has been used for this purpose in this work [27]. For details

of the calculation procedure, the reader is referred to Herri et al. (2011) [28].

In the modelling calculations, type A semiclathrate hydrate with  $\nu_w = 26$  has been assumed for  $\bar{w}_{\text{TBAB}} = 0.05$ , whereas structure B semiclathrate hydrate with  $\nu_w = 38$  was assumed for the higher concentrated solutions at  $\bar{w}_{\text{TBAB}} = 0.1, 0.2, 0.3$ . The Kihara potential parameters  $\varepsilon$ ,  $\sigma$  and  $a$ , were adjusted to the experimental data, but their values changed only slightly compared to the values obtained for ordinary gas hydrate phases.

The results of the modeling calculations are set out in Figure 3 against experimental data from corresponding literature sources. They are presented as a Clausius-Clapeyron plot, i.e.,  $\ln(p/p^\ominus)$  is plotted against the reciprocal value of the absolute temperature.

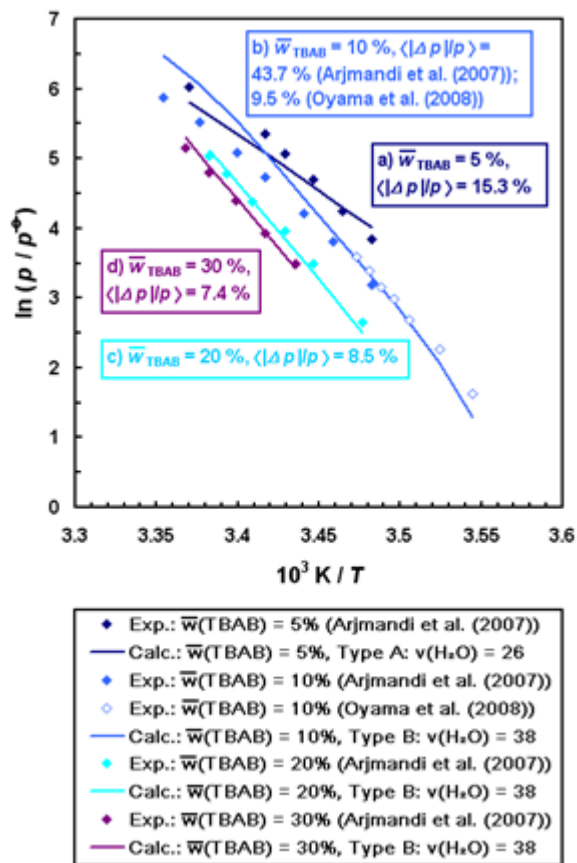


Figure 3: HL V phase boundaries of the ternary system  $\text{H}_2\text{O}+\text{TBAB}+\text{CH}_4$  at  $\bar{w}_{\text{TBAB}} = 0.05, 0.1, 0.2, 0.3$  exhibiting semiclathrate hydrate phases. Experimental data of: (◆) Arjmandi et al. [33], (◇): Oyama et al. [34], (—) modelling results.

Four lines have been generated at overall initial weight fractions of TBAB in the liquid phase of  $\bar{w}_{\text{TBAB}} = 0.05, 0.1, 0.2$  and  $0.3$ . For all of these concentration values experimental data of Arjmandi et al. (2007) [33] were available. In the lower pressure region at  $\bar{w}_{\text{TBAB}} = 0.1$ , the experimental data collection could be supplemented by the results Oyama et al. (2008) [34].

The calculated  $p$ - $T$ -HLV phase boundaries exhibit average relative deviations  $\langle |\Delta p|/p \rangle$  from the corresponding experimental results:

$$\left\langle \frac{|\Delta p|}{p} \right\rangle = \frac{1}{N_{\text{exp data}}} \sum_{l=1}^{N_{\text{exp data}}} \frac{|p_{\text{exp},l} - p_{\text{calc},l}|}{p_{\text{exp},l}} \quad (45)$$

ranging from around 8 % for the phase boundary at  $\bar{w}_{\text{TBAB}} = 0.3$  to 44 % for the line at  $\bar{w}_{\text{TBAB}} = 0.1$  against the data of Arjmandi et al. [33]. In contrast, for the 10 % boundary line, significantly lower deviations from experimental are detected in the region of lower temperature and pressures. The relative average deviations between the pressure values calculated and the corresponding data of Oyama et al. [34] amount to only 9.5 %.

In view of the fact that several simplifying assumptions have been made in the modeling (like e.g. the negligence of the temperature dependence of the eNRTL interaction parameters), the overall performance of the model is quite good and the results are promising.

## CONCLUSIONS

In this article, an attempt has been made to model combined chemical and phase equilibria encountered in the binary  $\text{H}_2\text{O}+\text{TBAB}$  and ternary  $\text{H}_2\text{O}+\text{TBAB}+\text{CH}_4$  system. In both systems semiclathrate hydrate phases are formed in the state conditions of interest.

The approach is based on the thermodynamic model of Paricaud [1] capable of describing mixtures exhibiting salt, semiclathrate as well as (gas) semiclathrate hydrate phases. In the new model of Paricaud [1], fluid phase-nonidealities are accounted for by means of the SAFT-VRE equation of state. For describing the solid-liquid phase-equilibria Paricaud has set up a new model by starting from the thermodynamic principle that the total Gibbs energy of a system in equilibrium at

given  $T$ ,  $p$  and all mole numbers under stoichiometric constraints is at a minimum.

We have presented a modified version of the model of Paricaud [1]. In contrast to the original theoretical framework we have used 1) the eNRTL model of Chen et al. [19-21] to describe liquid phase non-idealities, 2) neglected the gas solubility in the liquid phase in the calculation of the activity coefficients, 3) the SRK-equation of state to describe the gas phase and 4) the Kihara potential for modeling the guest-host interactions in the semi-clathrate hydrate structure.

The binary system  $H_2O+TBAB$  has been described in order to obtain the model parameters  $T_{cgr}^{HL_w}$  and  $\Delta_{dis}H_m^\ominus(T_{cgr}^{HL_w})$ . Using these results our first attempt of modeling the gas semiclathrate hydrates encountered in the  $H_2O+TBAB+CH_4$  system has led to promising results. Relative deviations  $\langle |\Delta p|/p \rangle$  between experimental data [33,34] and calculated values for the  $p$ - $T$ -HLV phase boundaries are found to lie between 4 and 44 %. Although the agreement between experimental and modeled results is poor for the data of Arjmandi et al. [33] at  $\bar{w}_{TBAB} = 0.1$ , the agreement is better for the remaining phase boundaries.

Our model version can be improved by e.g. taking into account the temperature dependence of the activity coefficients. Future research activities will therefore concentrate on the improvement of the model along this line and on its application to other systems like  $H_2O+TBAB+CO_2$ .

## REFERENCES

[1] Paricaud P.; *Modeling the Dissociation Conditions of Salt Hydrates and Gas Semiclathrate Hydrates: Application to Lithium Bromide, Hydrogen Iodide, and Tetra-n-butylammonium Bromide + Carbon Dioxide Systems*. J Phys Chem B. 115 (2011) 288-99.

[2] Davidson, D. W.; Clathrate Hydrates. In *Water, a comprehensive treatise; Vol. 2; Water in crystalline hydrates; aqueous solutions of simple nonelectrolytes*; Franks, F., Ed.; Plenum Press: New York (1973) 140-146.

[3] Shimada, W.; Shiro, M.; Kondo, H.; Takeya, S.; Oyama, H.; Ebinuma, T.; Narita, H.; *Tetra-n-butylammonium bromide-water (1/38)*. Acta Cryst. C 61 (2005) o65-o66

[4] Vu, V. Q.; Suchaux, P.D.; Fürst, W.; *Use of a predictive electrolyte equation of state for the calculation of the gas hydrate formation temperature in the case of systems with methanol and salts*. Fluid Phase Equilibria 194 (2002) 361-370

[5] Masoudi, R.; Tohidi, B.; Danesh, A.; Todd, A. C.; *A new approach in modeling phase equilibria and gas solubility in electrolyte solutions and its applications to gas hydrates*. Fluid Phase Equilib. 215 (2004) 163-174

[6] Ruffine, L.; Trusler, J. P. M.; *Phase behaviour of mixed-gas hydrate systems containing carbon dioxide*. J. Chem. Therm. 42 (2010) 605-611

[7] Zhang, Y.; Zhou, J.; Wang, Z.; Liu, J.; Cen, K.; *Influence of the oxidative/reductive treatments on Pt/CeO<sub>2</sub> catalyst for hydrogen iodide decomposition in sulfur-iodine cycle*. Int. J. Hydrogen Energy 33 (2008) 2211-2217

[8] Duc, N. H.; Chauvy, F.; Herri, J.-M.; *CO<sub>2</sub> capture by hydrate crystallization – A potential solution for gas emission of steelmaking industry*. Energy. Conv. Manag. 48 (2007) 1313-1322.

[9] Li, S.; Fan, S.; Wang, J.; Lang, X.; Liang, D.; J. *CO<sub>2</sub> capture from binary mixture via forming hydrate with the help of tetra-n-butyl ammonium bromide*. Nat. Gas. Chem. 18 (2009) 15-20

[10] Strobel, T. A.; Hester, K. C.; Koh, C.A.; Sum, A. K.; Sloan, E. D.; *Properties of the Clathrates of Hydrogen and Developments in Their Applicability for Hydrogen Storage*. Chem. Phys. Lett. 478 (2009) 97-109

[11] Dyadin, Y. A.; Udachin, K. A.; *Clathrate formation in water Peralkylonium salts systems*. J. Inclusion Phenomena 2 (1984) 61-72

[12] Oyama, H.; Shimada, W.; Ebinuma, T.; Kamata, Y.; Takeya, S.; Uchida, T.; Nagao, J.; Narita, H.; *Phase diagram, latent heat, and specific heat of TBAB semiclathrate hydrate crystals*. Fluid Phase Equilib. 234 (2005) 131-135

[13] Nakayama, H.; *Solid-Liquid and Liquid-Liquid Phase Equilibria in the Symmetrical Tetraalkylammonium Halide–Water Systems*. Bull. Chem. Soc. Jpn. 54 (1981) 3717-3722

[14] Shimada, W.; Ebinuma, T.; Oyama, H.; Kamata, Y.; Takeya, S.; Uchida, T.; Nagao, J.; Narita, H.; *Separation of Gas Molecule Using Tetra-n-butyl Ammonium Bromide Semi-Clathrate Hydrate Crystals*. Jpn. J. Appl. Phys. 42 (2003) L129-L131

- [15] Shimada, W.; Ebinuma, T.; Oyama, H.; Kamata, S.; Narita, H.; *Free-growth forms and growth kinetics of tetra-n-butyl ammonium bromide semi-clathrate hydrate crystals*. J. Cryst. Growth 274 (2005) 246-250
- [16] Mohammadi, A. H.; Belandria, V.; Richon, D.; *Use of an artificial neural network algorithm to predict hydrate dissociation conditions for hydrogen+water and hydrogen+tetra-n-butyl ammonium bromide+water systems*. Chem. Eng. Sci. 65 (2010) 4302-4305
- [17] van der Waals, J. H.; Platteeuw, J. C.; *Clathrate solutions*. Adv. Chem. Phys. 2 (1959) 1-57
- [18] Galindo, A.; Gil-Villegas, A.; Jackson, G.; Burgess, A. N.; SAFT-VRE: Phase behavior of electrolyte solutions with the statistical associating fluid theory for potentials of variable range. J. Phys. Chem. B 103 (1999) 10272-10281.
- [19] Chen, C.-C.; Britt, H. I.; Boston, J. F.; Evans, L.B.; *Local Composition Model for Excess Gibbs Energy of Electrolyte Systems*; AIChE J. 28 (1982) 588-596.
- [20] Chen, C.-C., Evans, L. B.; *A Local Composition Model for the Excess Gibbs Energy of Aqueous Electrolyte Systems*; AIChE J. 32 (1986) 444-454.
- [21] Bollas, G. M., Chen, C. C., Barton, P. I.; *Refined Electrolyte-NRTL Model: Activity Coefficient Expressions for Application to Multi-Electrolyte Systems*; AIChE J. 54 (2008) 1608-1624.
- [22] Tumakaka, F.; Prikhodko, I. V.; Sadowski, G.; *Modeling of solid-liquid equilibria for systems with solid-complex phase formation*; 260 (2007) 98-104
- [23] Ewing, M. B. et al.; *IUPAC: A Report of IUPAC Commission I.2 on Thermodynamics. Standard quantities on chemical thermodynamics. Fugacities, activities, and equilibrium constants for pure and mixed phases*; J. Chem. Thermodynamics 27 (1995) 1-16.
- [24] Sloan, E. D.; Koh, C. A.; *Clathrate Hydrates of Natural gases*, 3rd ed., CRC Press, Taylor & Francis Group, Boca Raton, London, New York (2008)
- [25] Soave, G., *Equilibrium constants from a modified Redlich-Kwong equation of state*; Chem. Eng. Sci., 27 (1972) 1197-1203
- [26] Parrish, W. R.; Prausnitz, J. M.; *Dissociation pressure of gas hydrates formed by gas mixtures*. Ind. Eng. Chem. Process Des. Develop.; 11 (1972) 26-35
- [27] McKoy, V., Sinagoglou, O. J.; *Theory of dissociation pressures of some gas hydrates*. J Chem. Phys 38 (1963) 2946
- [28] Herri J.-M., Bouchemoua, A., Kwaterski, M., Fezoua, A., Ouabbas, Y., Cameirao, A., *Gas Hydrate Equilibria for CO<sub>2</sub>-N<sub>2</sub> and CO<sub>2</sub>-CH<sub>4</sub> gas mixtures – Experimental studies and Thermodynamic Modelling*, Fluid Phase Equilibria, 301 (2011) 171-190
- [29] Kwaterski, M.; Herri, J.-M.; *Modelling Gas Hydrate equilibria Using The electrolyte Non-Random Two-Liquid (eNRTL) model*, Proceedings of the 7th International Conference on Gas Hydrates (ICGH 2011), Edinburgh, Scotland, United Kingdom, July 17-21, 2011.
- [30] Belvèze, L. S.; Brennecke, J. F.; Stadtherr, M. A.; *Modeling of Activity Coefficients of Aqueous Solutions of Quaternary Ammonium Salts with the Electrolyte-NRTL Equation*. Ind. Eng. Chem. Res. 43 (2004) 815-825
- [31] Lindenbaum, S.; Boyd, G. E.; *Osmotic and activity coefficients for the symmetrical tetraalkyl ammonium halides in aqueous solution at 25.degree*. J. Phys. Chem. 68 (1964) 911-917
- [32] Lipkowski, J.; Komarov, V. Y.; Radionova T. V. Dyadin, Y. A.; Aladko, L. S.; *The structure of tetrabutylammonium bromide hydrate (C<sub>4</sub>H<sub>9</sub>)NBr · 21/3H<sub>2</sub>O*. J. Supramol. Chem. 2 (2002) 435-439
- [33] Arjmandi, M.; Chapoy, A.; Tohidi, B.; *Equilibrium Data of Hydrogen, Methane, Nitrogen, Carbon Dioxide, and Natural Gas in Semi-Clathrate Hydrates of Tetrabutyl Ammonium Bromide*. J. Chem. Eng. Data 2007, 52, 2153-2158
- [34] Oyama, H., Ebinuma, T., Nagao, J.; Narita, H.; *Phase Behavior Of TBAB Semiclathrate Hydrate Crystal under several Vapor Components*. Proceedings of the 6th International Conference on Gas Hydrates (ICGH 2008), Vancouver, British Columbia, CANADA, July 6-10, 2008.