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Modelling of gas clathrate hydrate equilibria using the electrolyte non-random two-liquid (eNRTL) model

Matthias Kwaterski, Jean-Michel Herri*

Centre SPIN, Département GENERIC, École Nationale Supérieure des Mines de Saint-Etienne, France

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ABSTRACT

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Keywords: Modelling Gas hydrate eNRTL model Electrolytes Phase equilibrium CO₂ CH₄ A thermodynamic framework for modelling clathrate hydrate equilibria involving electrolytes is presented. In this framework, the gas phase is described by using the Soave–Redlich–Kwong equation of state, while the gas solubility in the liquid phase is estimated by means of a Henry's law approach. The liquid phase non-idealities are accounted for by using the semi-empirical electrolyte non-random twoliquid (eNRTL) excess Gibbs energy model. The van der Waals and Platteeuw model is used for the hydrate phase.

This three-phase equilibrium model has been implemented in a new Java-based in-house programme. The main focus of the present work is the influence of the electrolytes on the incipient hydrate forming conditions. Therefore, the most recent version of the eNRTL model is thoroughly discussed. The model equations are presented in detail to facilitate future implementation and further development of this model, since the eNRTL modelling approach is quite new in the context of gas hydrate calculations.

The correctness of the programme implementation is rigorously studied and verified by comparing the results with results of selected examples in the literature. At last, calculations are performed on solid-aqueous liquid-gas phase equilibria of selected systems of the type {water+salt+gas}, {water+salt_+salt_+gas}, {water+salt+CH_4+CO_2} and {water+salt_+salt_+cH_4+CO_2} with salt=NaCl, KCl, CaCl₂ and gas=CH₄, CO₂) comprising a gas clathrate hydrate phase. The results are in good agreement with experimental *p*-T-hydrate-liquid-gas phase equilibrium data found in the literature, with average absolute relative deviations between experimental and calculated pressures ranging from 1% to 15%.

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1. Introduction

Gas clathrate hydrates are mixed solid crystalline phases built up by a network of hydrogen bonded water molecules comprising cage-like structural units, each of which can encapsulate a single appropriately sized guest molecule. The guest species stabilise the solid solvent, the thermodynamically metastable host lattice, by interacting with the water molecules through van der Waals forces [1]. Gas hydrates are thermodynamically stable in the ambient or lower temperature region (near the normal freezing point of water) and elevated pressures (typically more than 0.6 MPa) [2,3] and crystallise in the cubic structures I (sI) and II (sII), and the hexagonal structure H (sH). They have the potential for numerous applications in the oil and gas industry and the energy sector as e.g. in gas

* Corresponding author. Tel.: +33 4 77 42 02 92; fax: +33 4 77 49 96 92. *E-mail address*: herri@emse.fr (J.-M. Herri).

http://dx.doi.org/10.1016/j.fluid.2014.02.032 0378-3812/© 2014 Elsevier B.V. All rights reserved. storage and separation, air-conditioning systems or water desalination and treatment [4]. However, they can also cause problems in the oil and gas industry, as e.g. pipeline blockages in drilling applications or gas pipelines [5]. Species capable of forming hydrogen bonds with water molecules like methanol or ethylene glycol as well as water-soluble polymers or electrolytes act as thermodynamic inhibitors with respect to the formation of gas hydrates and can thus be used to prevent hydrate plugs [2].

Due to the electrostatic forces acting between ions the thermodynamic description of electrolyte solutions is significantly more difficult than the treatment of non-electrolyte systems [6,7]. To model electrolyte solutions, an electrolyte equation of state (EOS), especially useful at high pressures, an excess Gibbs energy model [6] or a combination of the two strategies is usually employed. Several electrolyte EOS, like e.g. the Fürst-Renon EOS [8,9], the electrolyte modification [6] of the Trebble-Bishnoi EOS [10,11], or the statistical associating fluid theory with variable range for electrolytes (SAFT-VRE) EOS [12] have been developed. Besides, numerous semi-empirical excess Gibbs energy models have been







proposed [13], as e.g. the model of Bromley [14], the ion-interaction model of Pitzer [15,16], the model of Cruz and Renon [17], the eNRTL-model of Chen et al. [13,18–21], the LIQUAC-model of Li et al. [22] and the MSA-model of Papaiconomou et al. [23].

To model the Hydrate (H)-Liquid (Lw)-Gas (G)-phase boundary in electrolyte systems, an equation of state and/or activity coefficient approach for the fluid phases is combined with the hydrate model of van der Waals and Platteeuw (vdW-P) [24]. Englezos and Bishnoi [25] e.g. presented an approach to predict the thermodynamic gas hydrate formation conditions in aqueous systems containing light hydrocarbon gases and single or mixed electrolytes using Pitzer's [15] and Meissner's [26] activity coefficient models. Clarke and Bishnoi [6] have developed an electrolyte EOS for mixed salt and mixed solvent systems to describe the Liquid–Vapour- (L–V-) equilibrium in these mixtures. The EOS was also used to model the H-L-V-equilibrium obtained in systems containing additionally one or more of the gases CH₄, CO₂, H₂S and/or C₃H₈ [6]. Hsieh et al. [27] presented an approach for modelling the change in hydrate forming conditions in mixtures with electrolytes and molecular inhibitors. They combined the vdW-P model with the Peng-Robinson-Stryjek-Vera EOS [28], using the first order modified Huron-Vidal (MHV1) mixing rule [29] with two activity coefficient models, the UNIQUAC [30] and the COSMO-SAC [31,32] model. Tse and Bishnoi [33] predicted incipient CO₂ hydrate forming conditions in aqueous solutions of NaCl, KCl and CaCl₂ using three different liquid phase models, the model of Zuo and Guo [34], of Aasberg-Petersen et al. [35] and the eNRTL model [19] investigated here. However, in contrast to this study, Tse and Bishnoi used the Trebble-Bishnoi EOS [10] to describe the gas phase. They concluded that model of Zuo and Guo gave the best result for predicting incipient CO₂ hydrate forming conditions in aqueous electrolyte solutions. Duan and Sun [36] used the Pitzer model [15,37] to predict the pure gas hydrate equilibria of CH₄ and CO₂ in the presence of aqueous electrolyte solutions of NaCl, KCl, CaCl₂ and the mixed salt systems {NaCl+KCl} and {NaCl+CaCl₂}. In the average, the quality of their predictions is better than the one obtained in this study. However, it is has to be pointed out that they use a more advanced ab-initio technique for calculating the Langmuir constants [36]. Moreover, the number of parameters used in the Pitzer model exceeds the number of eNRTL parameters used in this study [36].

Prior to initiating the current study, incipient gas hydrate forming conditions in non-electrolyte aqueous systems were modelled in our research group. The calculations were performed with our inhouse programme named "GasHyDyn" which was created earlier using the object oriented programming language Java. The programme was based on the algorithm proposed by Sloan [38] and its code is available from the second author on request. Up to now, it was successfully used for obtaining Kihara parameters and predicting simple pure and mixed gas hydrate equilibria of carbon dioxide (CO_2) , methane (CH_4) and nitrogen (N_2) in pure water [39] only. The need for extending our in-house programme to enable the treatment of electrolyte systems originated from the attempt to model the thermodynamics of so-called (gas-)semiclathrate hydrates of tetra-n-butylammonium bromide (TBAB). Since in aqueous solution, TBAB dissociates into ions, an electrolyte model was required to describe the liquid phase non-idealities in this system with sufficient accuracy. Belvèze et al. [40] showed that the eNRTLmodel [18,19] does an excellent job in correlating experimental data on the mean molal activity coefficient of TBAB, $\gamma^*_{b,\text{TBAB},\pm}$, in aqueous solution at 298.15 K [41] over a wide range of TBAB concentration (maximum overall molality $\bar{b}_{\text{TBAB,max}} = 27 \text{ mol kg}^{-1}$, residual standard deviation of σ = 0.038 with respect to calculated and measured results on $\ln \gamma_{b, \text{TBAB}, \pm}^*$). Moreover, only two parameters are required for the isothermal description of single

electrolyte solutions with this model [18,19] (e.g. the famous Pitzer model [15] needs three). Hence, we decided to use the eNRTL-model for modelling the isobaric H–L_w equilibrium in the system $\{H_2O+TBAB\}$ and the H–L_w–G-equilibrium in the corresponding gas semi-clathrate hydrate systems.

In this preliminary study we aim at testing the suitability of the overall thermodynamic framework implemented in our in-house programme for describing H-L_w-G-phase equilibria of systems involving conventional gas hydrates in the presence of electrolytes. The main objective of this study is to take into account the influence of electrolytes on gas hydrate equilibria. Therefore, the first part of this article is devoted to the thorough presentation of the eNRTL model and the testing of the correctness of our programme code. Both the previous [19] and the updated version of the single-solvent multicomponent eNRTL-model [21] were implemented. Since different types of activity coefficients will be needed in the modelling of semi-clathrate hydrate equilibria, it is important to present the relevant model equations in detail. Indeed, the quality of a gas hydrate model, and particularly the values for the Kihara parameters, do strongly depend on the code itself (values of the Kihara parameter for a given gas differ widely among different authors [38,39,42,43]). Therefore it is necessary to test and ensure the reliability of the code of the eNRTL model in particular and the overall modelling framework of our in-house programme in general. In the second part, the new programme was used to predict incipient gas hydrate formation conditions in aqueous electrolyte systems with one or two of the salts sodium chloride (NaCl), potassium chloride (KCl) or calcium chloride $(CaCl_2)$ and the gases CH_4 and/or CO_2 .

2. Modelling approach

2.1. Hydrate-liquid-gas equilibrium

Thermodynamic equilibrium between the gas hydrate phase (H) and the aqueous liquid phase (L_w) under incipient hydrate formation conditions, when being in simultaneous equilibrium with a gas phase (G), can be expressed by

$$\Delta_{\beta}^{\rm H}\mu_{\rm W} = \Delta_{\beta}^{\rm L_{\rm W}}\mu_{\rm W} \tag{1}$$

where $\Delta_{\beta}^{H}\mu_{w} \equiv \mu_{w}^{H} - \mu_{w}^{\circ,\beta}$ denotes the difference in the chemical potential of water in the gas hydrate phase and the pure (index °) solid solvent phase, i.e. the empty metastable hydrate lattice (index β). Similarly, $\Delta_{\beta}^{L_{w}}\mu_{w} \equiv \mu_{w}^{L_{w}} - \mu_{w}^{\circ,\beta}$ designates the chemical potential difference of water in the liquid and the empty hydrate phase. It should be pointed out that the way for expressing the equilibrium condition in Eq. (1) differs from the way it is usually found in the literature, firstly because minuend and subtrahend are reversed as it was also done by Ballard and Sloan [44] (i.e., $\mu_{w}^{\pi} - \mu_{w}^{\circ,\beta}$ instead of $\mu_{w}^{\circ,\beta} - \mu_{w}^{\pi}$ with $\pi = H, L_{w}$), and secondly, because the nomenclature is adopted from the notation as recommended by the IUPAC Commission I.2. [45]. Since the presence of water in the gas phase was neglected in a good approximation, the condition involving the chemical potential of water in this phase was not considered.

2.2. The thermodynamic description of the hydrate phase

The clathrate hydrate phase is described by means of the ideal solid solution theory of van der Waals and Platteuuw [24]. In this statistical thermodynamic model, the chemical potential difference $\Delta^{\rm H}_{R}\mu_{\rm W}$, expressed on a molar basis, is given by

$$\frac{\Delta_{\beta}^{\mathrm{H}}\mu_{\mathrm{W}}}{RT} = \sum_{i \in S_{\mathrm{cav}}} \nu_{i} \ln \left(1 - \sum_{j \in S_{\mathrm{g}}} \theta_{ji}^{\mathrm{H}} \right)$$
(2)

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