MODELLING GAS HYDRATE EQUILIBRIUM 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 H2O + salt + gas and quaternary H2O + 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, CO2, CH4

NOMENCLATURE

\( A \) – Pitzer-Debye-Hückel constant [\( \text{l} \)]
\( \alpha \) – nonrandomness factor [\( \text{l} \)]
\( \phi \) – Osmotic coefficient [\( \text{l} \)]
\( G \) – Boltzmann kind factor [\( \text{l} \)]
\( G_m \) – Excess molar Gibbs energy [\( \text{J} \cdot \text{mol}^{-1} \)]
\( \gamma \) – Activity coefficient [\( \text{l} \)]
\( I \) – Ionic strength [\( \text{l} \)]
\( m \) – Molality [\( \text{mol} \cdot \text{kg}^{-1} \)]
\( N_{Av} \) – Avogadro’s constant [\( \text{mol}^{-1} \)]
\( N_{exp \_data} \) – Number of experimental data points [\( \text{l} \)]
\( \nu \) – stoichiometric coefficient [\( \text{l} \)]
\( p \) – Pressure [bar, MPa]
\( T \) – Celsius temperature [\( ^\circ \text{C} \)]
\( R \) – Perfect gas constant [\( \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \)]
\( \sigma_{rel} \) – Root mean square deviation (relative) [\( \text{l} \)]
\( \tau \) – Energetic interaction coefficient [\( \text{l} \)]
\( x \) – Mole fraction [\( \text{l} \)]
\( Y \) – Ionic charge fraction [\( \text{l} \)]
\( z \) – Charge number of ionic species [\( \text{l} \)]

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