

Thermodynamic modelling of acid gas removal from natural gas using the Extended UNIQUAC model



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ABSTRACT

Thermodynamics of natural gas sweetening process needs to be known for proper design of natural gas treating plants. Absorption with aqueous N-Methyldiethanolamine is currently the most commonly used process for removal of acid gas (CO₂ and H₂S) impurities from natural gas. Model parameters for the Extended UNIQUAC model have already been determined by the same authors to calculate single acid gas solubility in aqueous MDEA. In this study, the model is further extended to estimate solubility of CO₂ and H₂S and their mixture in aqueous MDEA at high pressures with methane as a makeup gas.

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1. Introduction

Natural gas is often recovered from the well at high pressures, around 5–10 MPa. Natural gas is usually contaminated with acid gases (CO₂ and H₂S) [1]. Natural gas sweetening is carried out in order to remove these gases.

In order to avoid extra costs of pressurizing for liquefaction, the sweetening process must be carried out at high pressures, hence, without a pressure drop [2].

Stripping acid gases from natural gas is commonly done by use of aqueous alkanolamines in an absorber-desorber system [1]. In natural gas treatment process, the typical absorber pressure is around 5–10 MPa, but the stripper pressure is between 0.1 and 0.3 MPa. In the absorber, mixtures of acid gas-hydrocarbons, mainly methane, are contacted counter currently with aqueous amines while in the stripper, mixtures of acid gas-amine-water are present as methane and other hydrocarbons are already separated. During

the years different types of amines have been developed and used for specific gas treating applications [3]. Among amines, Methyldiethanolamine (MDEA) is usually preferred for full absorption of H₂S and partial absorption of CO₂ [3]. MDEA can reduce the amount of H₂S and CO₂ to approximately 4 ppmv and 3 mol%, respectively [3]. Representation of the thermodynamic behavior of acid gas removal process from natural gas at operational conditions is important for proper design of natural gas treating plants. The objective of this study is to extend the Extended UNIQUAC model developed earlier by Sadegh et al. [4,5] to describe single and mixed acid gas solubility in aqueous MDEA in presence of methane as a makeup gas (at high pressures).

2. Model description

In this study the Extended UNIQUAC model [6] is developed to describe thermodynamic behavior of the H₂S-CO₂-CH₄-MDEA-H₂O system. The Extended UNIQUAC model is used to calculate activity coefficients in the liquid phase and SRK [7] equation of state is applied for calculation of fugacities in the vapor phase. In the Extended UNIQUAC model the extended Debye – Hückel term is added to the original UNIQUAC [8,9] model in order to allow the model to be used for electrolyte solutions. The model structure has

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already been explained by Sadegh et al. [4,5].

3. Equilibrium calculations

For rigorous modelling of acid gas-alkanolamine system, both physical and chemical equilibrium have to be incorporated in the model.

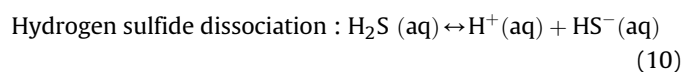
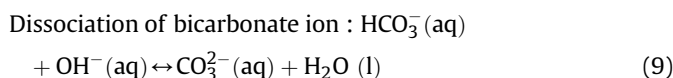
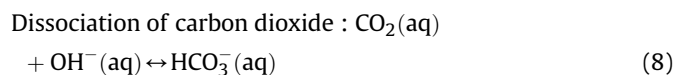
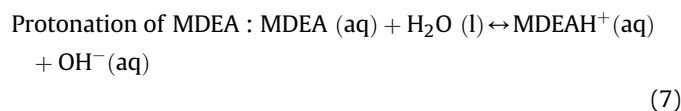
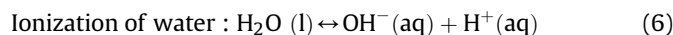
3.1. Physical equilibrium

Molecular species distribute between liquid and vapor phase. The following vapor-liquid equilibria take place in the studied system.



3.2. Chemical equilibrium

Acid gas-alkanolamine system is a reactive system, many reactions occur in the system. The following reactions are considered in this study.



Bisulfide ion dissociation reaction ($\text{HS}^- (\text{aq}) \leftrightarrow \text{H}^+ (\text{aq}) + \text{S}^{2-} (\text{aq})$) is excluded for modelling work of this study because the amount of sulfide ion is very small and negligible [5].

4. Evaluation of model parameters

All adjustable model parameters belong to the UNIQUAC term and there is no adjustable parameter in Debye – Hückel term and SRK EoS. The adjustable model parameters are: UNIQUAC volume parameter (r_i), surface area parameter (q_i) and binary interaction parameters between species “i” and “j” (u_{ij}). The binary interaction parameters are symmetric ($u_{ij} = u_{ji}$) and temperature dependent.

$$u_{ij} = u_{ij}^0 + u_{ij}^T (T - 298.15) \quad (11)$$

Values of u_{ij}^0 and u_{ij}^T are adjusted to the experimental data. The values of u_{ij}^0 and u_{ij}^T for the binary interaction parameter between species that have a low possibility of coexistence in the solution has been set to 10^{10} and 0, respectively. The assigned values keep the ineffective parameters away from the regression process.

Evaluated experimental vapor-liquid equilibrium data (total pressure and acid gas partial pressure) were regressed in order to find the optimum values of model adjustable parameters. The model parameters were optimized to obtain the minimum of the objective function (S):

$$S = \sum_{\text{VLEdata}} \left[\frac{P_{\text{calc}} - P_{\text{exp}}}{w(P_{\text{exp}} + 0.01 \text{ bar})} \right]^2 \quad (12)$$

In equation (12), “calc” and “exp” are calculated and experimental values, respectively. P (in bar) is either the solution total pressure or acid gas partial pressure. w is the weight given to vapor-liquid equilibria data and it set to 0.05. This value was chosen based on the accuracy of the regressed data. 0.01 bar is added to the denominator of the VLE term in order to avoid giving too much weight to low pressure data.

5. Model parameters

5.1. Single acid gas-CH₄-MDEA-H₂O systems

The modelling of the CO₂-CH₄-MDEA-H₂O and the H₂S-CH₄-MDEA-H₂O quaternary systems was started by determining model parameters for the CH₄-H₂O binary subsystem.

Methane dissolves only physically in the water. Vapor-liquid equilibrium should be taken into account to obtain methane physical solubility in water. To model the CH₄-H₂O system, the binary parameter for interaction between CH₄ and H₂O has been fitted to the binary VLE data for CH₄-H₂O system. The volume and surface area parameters, r and q , for methane and water were respectively taken from Addicks et al. [10] and Abrams and Prausnitz [8]. The values of the adjusted UNIQUAC parameters required for modelling CH₄-H₂O mixture are shown in Table 1. The determined parameter sets for the CH₄-H₂O system were then combined with the parameter sets of ternary acid gas-MDEA-H₂O from Sadegh et al. [4,5] work to form a model for quaternary acid gas-CH₄-MDEA-H₂O system. The behavior of the quaternary acid gas-CH₄-MDEA-H₂O system can be well predicted by the combined model and there is no need to adjust any additional parameter.

5.2. Mixed acid gas-CH₄-MDEA-H₂O system

Mixed acid gas system can be modeled based on the parameters for single acid gases. When CO₂ and H₂S are both present, the additional HCO₃⁻-HS⁻ and CO₃²⁻-HS⁻ interaction parameters are required compared to single acid gas systems. The H₂S-CO₂ interaction parameter was found to have no effect on modelling the mixed acid gas system. This interaction parameter was set to a large value which indicates no contribution to the excess Gibbs energy function. The parameters for the interactions HCO₃⁻-HS⁻ and

Table 1
 $u_{ij}^0 = u_{ji}^0$ and $u_{ij}^T = u_{ji}^T$ parameters required for calculating UNIQUAC energy interaction parameters.

Pair	$u_{ij}^0 = u_{ji}^0$	$u_{ij}^T = u_{ji}^T$
CH ₄ -H ₂ O	44.16483	1.4836
HCO ₃ ⁻ -HS ⁻	494.76	0.2494
CO ₃ ²⁻ -HS ⁻	262.13	3.685

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