Extended UNIQUAC model for thermodynamic modeling of CO_2 absorption in aqueous alkanolamine solutions

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ABSTRACT

The extended UNIQUAC model [K. Thomsen, P. Rasmussen, Chem. Eng. Sci. 54 (1999) 1787–1802] was applied to the thermodynamic representation of carbon dioxide absorption in aqueous monoethanolamine (MEA), methyldiethanolamine (MDEA) and varied strength mixtures of the two alkanolamines (MEA–MDEA). For these systems, altogether 13 interaction model parameters are adjusted. Out of these parameters, 11 are temperature dependent.

All the essential parameters of the model are simultaneously regressed to a collective set of data on the single MEA and MDEA systems.

Different types of data are used for modeling and they cover a very wide range of conditions. Vapor–liquid equilibrium (VLE) data for the aqueous alkanolamine systems containing CO_2 in the pressure range of 3–13,000 kPa and temperatures of 25–200 °C are used. The model is also regressed with the VLE and freezing point depression data of the binary aqueous alkanolamine systems (MEA–water and MDEA–water). The two just mentioned types of data cover the full concentration range of alkanolamines from extremely dilute to almost pure. The experimental freezing point depression data down to the temperature of −20 °C are used. Experimental excess enthalpy (H^E) data of the binary MEA–water and MDEA–water systems at 25, 40, 65 and 69 °C are used as well. In order to enhance the calculation of the infinite dilution activity coefficients of MEA and MDEA, the pure alkanolamines vapor pressure data in a relevant temperature range (up to almost 230 °C) are included in the parameter estimation process.

The previously unavailable standard state properties of the alkanolamine ions appearing in this work, i.e. MEA protonate, MEA carbamate and MDEA protonate are determined.

The concentration of the species in both MEA and MDEA solutions containing CO_2 are predicted by the model and in the case of MEA compared to NMR spectroscopic data.

Using only one set of parameters for correlation of different thermodynamic properties, the model has represented the experimental data with good precision.

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1. Introduction

The well established process of chemical absorption into aqueous alkanolamines is considered a prospective option for post-combustion capture of CO_2 from fossil-fueled power plants.

To properly simulate the reversible absorption process, a rate model is needed. However, it is essential to incorporate an accurate thermodynamic model with a rate model to calculate the driving forces for mass transfer correctly.

The problem with thermodynamic modeling of acid gas treating plants is that the vapor–liquid equilibrium (VLE) data reported for these systems are not generally very consistent. Moreover, other indispensable data such as binary VLE of alkanolamine–water system, excess enthalpy data and standard state properties of alkanolamines for both gas and liquid phases are scarce and those available from a handful of sources show discrepancies.

Developing empirical correlations based on the existing data, using excess Gibbs energy based activity coefficient models and application of equations of state which are based on excess Helmholtz energy are three different approaches for thermodynamic modeling of chemical absorption of CO_2.

Correlations could be very precise and calculations are often not cumbersome. Yet, empirical expressions typically fail when being extrapolated to conditions other than what they are based on.

One example is the simple correlation of Kent and Eisenberg [1] for CO_2 solubility in aqueous MEA and diethanolamine (DEA). Gabrielsen et al. [2] presented another very simple correlation for the calculation of the partial pressure and enthalpy of absorption of CO_2 in MEA, DEA and MDEA.

An equation of state can be easily extended to predict the solubility of more than a single gas in the solution; it also can be used to calculate the properties such as density of both liquid and vapor phases. However, the performance of an equation of state to a great extent depends on the mixing rules chosen and an unsuitable choice can lead to erroneous results. Chunxi and Fürst [3], Solbraa [4] and Huttenhuis et al. [5] have used the Fürst and Renon [6] equation of state to represent CO_2 solubility in aqueous MDEA. Solbraa [4] has also applied the Cubic Plus Association (CPA) model proposed by Kontogeorgis et al. [7] for the MDEA system.

Using the electrolyte activity coefficient models is the most common alternative. Posey and Rochelle [8] applied electrolyte NRTL (e-NRTL) model to predict the CO_2 solubility in MDEA solution. This model had been used earlier by Austgen et al. [9,10] for MEA, DEA and mixtures of MDEA with MEA and DEA.

The purpose of the present work is to apply the extended UNIQUAC model [11] to estimate various thermodynamic properties of the alkanolamine systems required for the design of CO_2 capture plants. In addition, the capability of the model to represent different types of thermodynamic properties in a broad range of conditions using only one unique set of parameters is investigated.

Moreover, the standard state Gibbs free energy of formation and enthalpy of formation for the ions that MEA and MDEA form in aqueous CO_2 solutions are calculated. These formerly unavailable properties are required for thermodynamic calculations of MEA and MDEA systems.

The model parameters are determined based on a large number of data covering the temperature and pressure of the reversible absorption process (both absorption and desorption) and exceeding far beyond. Therefore, these parameters can be used even if the model is applied to other processes such as natural gas purification.
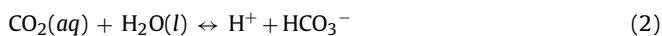
Compared to the previous modeling attempts by other authors, a larger number of properties and a considerably extensive range of conditions are addressed in this work.
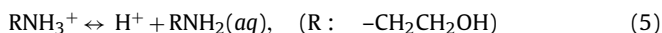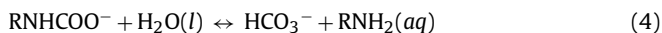
2. Chemical and phase equilibria

2.1. Speciation equilibria

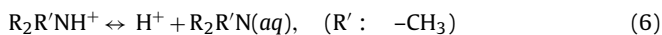CO_2 reacts with alkanolamines in aqueous solutions. The chemical equilibrium reactions considered in this work are:

- Aqueous CO_2 system:

$$H_2O(l) \leftrightarrow H^+ + OH^- \tag{1}$$

$$CO_2(aq) + H_2O(l) \leftrightarrow H^+ + HCO_3^- \tag{2}$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \tag{3}$$

- MEA system:

$$RNHCOO^- + H_2O(l) \leftrightarrow HCO_3^- + RNH_2(aq) \tag{4}$$

$$RNH_3^+ \leftrightarrow H^+ + RNH_2(aq), \quad (R: \quad -CH_2CH_2OH) \tag{5}$$

- MDEA system:

$$R_2R'NH^+ \leftrightarrow H^+ + R_2R'N(aq), \quad (R': \quad -CH_3) \tag{6}$$

The symmetrical convention for water and mole fraction (rational) based asymmetrical convention for all other species is adopted. Based on the symmetrical convention, the activity coefficient of water which is considered to be the only solvent by the model is unity in the pure component state at all temperatures.

The chemical potential of water in the liquid phase is expressed as

$$\mu_w = \mu_w^0 + RT \ln a_w = \mu_w^0 + RT \ln(\gamma_w x_w) \tag{7}$$

where μ_w^0 is the standard state chemical potential for pure liquid water at system temperature and pressure, a_w is the activity, R ($J\,mol^{-1}\,K^{-1}$) the gas constant, T (K) is the temperature and γ_w is the symmetrical activity coefficient of water.

The asymmetrical convention is based on the constraint that the activity coefficient of a solute compound is unity at infinite dilution. The chemical potential for the solute i (all the compounds other than water including alkanolamines) is written as

$$\mu_i = \mu_i^{*,x} + RT \ln(\gamma_i^{*,x} x_i) \tag{8}$$

where $\mu_i^{*,x}$ is the asymmetrical standard state chemical potential for the solute i and $\gamma_i^{*,x}$ is the asymmetrical rational activity coefficient of i. This is a hypothetical ideal state for the pure solute i.

The speciation equilibria can be expressed as

$$-\frac{\Delta G_j^0}{RT} = \sum_i \nu_{i,j} \ln a_i \tag{9}$$

ΔG^0 ($J\,mol^{-1}$) is the variation in the standard state chemical potential caused by the equilibrium reaction j at the certain temperature T (K). a_i is the activity of component i and $\nu_{i,j}$ is the stochiometric coefficient of component i involved in reaction j.

2.2. Vapor–liquid equilibria

For the volatile compounds, the vapor–liquid equilibria can be written as

$$CO_2(g) \leftrightarrow CO_2(aq) \tag{10}$$

$$MEA(g) \leftrightarrow MEA(aq) \tag{11}$$

$$MDEA(g) \leftrightarrow MDEA(aq) \tag{12}$$

$$H_2O(g) \leftrightarrow H_2O(l) \tag{13}$$

For the compounds in the vapor phase, the chemical potential is given by

$$\mu_i^v = \mu_i^{0g} + RT \ln \left(y_i \varphi_i \frac{P}{P_0} \right) \tag{14}$$

where μ_i^{0g} is the standard state chemical potential of the component i in the vapor phase defined as the pure ideal gas at one bar and the temperature T. P_0 is the standard state pressure of one bar. y_i and φ_i are the vapor phase mole fraction and the fugacity coefficient of i and P is the total pressure.

The condition of equilibrium between the aqueous and gas phases is:

$$\mu_i^{aq} = \mu_i^v \tag{15}$$

where μ_i^{aq} and μ_i^v are the chemical potentials of i in the aqueous and the gas phase, respectively.

On the basis of the phase equilibrium condition and also the expressions for the chemical potential (7), (8) and (14) the following expression can be written:

$$-\frac{\Delta G^0}{RT} = \ln \frac{y_i \varphi_i P}{x_i \gamma_i P_0} \tag{16}$$

where

$$\Delta G^0 = \mu_i^{0g} - \mu_i^{0aq} \tag{17}$$

is the chemical potential change due to the transfer of one mole of component i from liquid to the vapor phase. μ_i^0 and γ_i are based on the symmetrical approach for water and asymmetrical approach for the solute species.

The equilibrium equation for speciating compounds should be written in the form of Eq. (9) and Eqs. (10)–(13) should be expressed