Thermodynamic models for CO$_2$-H$_2$O-alkanolamine systems, a discussion

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This work adresses the thermodynamic modeling of CO$_2$-H$_2$O-alkanolamine systems. The electrolyte-NRTL model is discussed and applied to the CO$_2$-water-monoethanolamine system.

Keywords: CO$_2$ absorption; Thermodynamics; Modelling; Electrolyte-NRTL

1. Introduction

Despite efforts made, thermodynamic modelling of CO$_2$-H$_2$O-alkanolamine systems still has many unresolved issues. The systems involve a large number of components, both of molecular and ionic character for which both phase and chemical equilibria must be solved. Many of the models available in he literature predict CO$_2$ partial pressure fairly well, but for other properties such as partial pressure of amine, speciation and heat of absorption the predictions often are inadequate. Heat of absorption predictions are important for considering the heat necessary for regeneration, whereas the partial pressure of amine is important for the prediction of amine losses. An rigorous model should be able to predict all these properties adequately.

Throughout the last decades acid gas absorption thermodynamics has been subject to extensive studies. The thermodynamic models proposed can be grouped into three categories. The first and the most simple are the so-called non-rigorous models. These are often models that utilize simple mathematical relations for phase equilibria and fitted chemical equilibrium constants. The Kent-Eisenberg model [1] is an example of such a model, where two of the equilibrium constants are fitted to experimental partial pressures of CO$_2$. This fitting makes the model unsuited for other predictions such as speciation and heat of absorption. However due to it’s simplicity the model has become quite popular, and can be adequate e.g. for early studies of solvents.

More rigorous models can be split into two types, excess Gibbs energy or activity models, and equation of state models. For activity based models the variety is quite
large and the models have varying complexity. Of the simpler models, the Desmukh-
Mather model [2] has been widely used. This model utilizes the extended Debye-Hückel
expression given by Guggenheim [3] to predict all activity coefficients except for water,
which is assumed to behave ideally. Regarding more sophisticated models the electrolyte-
NRTL model (e-NRTL) [4] and the extended UNIQUAC model [5] sticks out. The
e-NRTL model has been applied to amine systems by several authors [6, 7, 8], whereas
the UNIQUAC model has fewer applications [9, 10]. When it comes to equations of state,
the selection is quite small, Solbraa [11], Derks [12] Huttenhuis et al. [13], Vallée et al.
[14] and Chunxi and Furst [15] are among the few that have applied equations of state
to these systems. Many of these have utilized the equation of state presented by Fürist
and Renon [16].

In this work the e-NRTL model as given in the Aspen+ simulation package [21] is
implemented and applied to predicting partial pressures, heats of absorption and specia-
tion. Vapour phase non-idealities are taken into account by utilizing the Peng-Robinson
equation of state. In addition are the revisions to the e-NRTL model made by Bollas et
al. [17] discussed.

2. Fundamental equations

The processes discussed involve both chemical equilibria and multi-component phase
equilibria. The liquid phase comprises both molecular species and ionic species, which
makes the modelling non-trivial. The chemical reactions taking place in the liquid phase
are for a generic amine, $R_1R_2\text{NH}$, given as:

Water ionization:

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

(1)

Dissociation of carbon dioxide:

$$2H_2O + CO_2 \rightleftharpoons H_3O^+ + HCO_3^-$$

(2)

Dissociation of bicarbonate:

$$H_2O + HCO_3^- \rightleftharpoons H_3O^+ + CO_3^{2-}$$

(3)

Dissociation of protonated amine:

$$H_2O + R_1R_2\text{NH}_2^+ \rightleftharpoons H_3O^+ + R_1R_2\text{NH}$$

(4)

Carbamate reversion to bicarbonate:

$$H_2O + R_1R_2\text{NCOO}^- \rightleftharpoons R_1R_2\text{NH} + HCO_3^-$$

(5)

Where the final reaction, only takes place for primary amines, such as MEA.

In addition to the chemical equilibria the distribution of species between the vapour and
the liquid phase must be modelled through the vapour-liquid equilibria (VLE). The stan-
dard VLE problem may be formulated through the thermodynamic equilibrium criteria
at a given temperature and pressure.
\[ \mu_{i}^{vap} = \mu_{i}^{liq} \] (6)

where \( \mu_{i}^{vap} \) and \( \mu_{i}^{liq} \) are the chemical potentials of the species \( i \) in the vapour and liquid phase, respectively. In this case an activity model is used for the liquid phase and an equation of state for the vapour phase. This yields the following working equation for phase equilibrium:

\[ \phi_{i}y_{i}p = \gamma_{i}x_{i}E_{i}\psi_{i} \] (7)

Here \( \gamma_{i} \) and \( \phi_{i} \) are the activity and fugacity coefficients of the species \( i \). \( \psi_{i} \) is a pressure correction factor (Poynting factor), which must be introduced for high pressures in \( G^{E} \)-models. \( E_{i} = \phi_{i}^{sat}p_{i}^{sat} \) for components with a pure component reference state and \( E_{i} = H_{i}^{\infty} \) (Henry’s law coefficient at infinite dilution in water) for components with an infinite dilution reference state, e.g. \( CO_{2} \).

3. Gibbs energy minimization

For the reactions (1) to (5) the equilibrium point is found by minimizing the Gibbs energy of the system, constrained by the material balances. In order to solve this, there are two paths, the stoichiometric and the non-stoichiometric [18]. In the stoichiometric method the mass balance constraints are incorporated through stoichiometric reaction equations, these are solved together with the chemical equilibrium relations (equilibrium constants) as a non-linear root finding problem.

In this work a non-stoichiometric method is used, here the problem is usually formulated as minimizing \( G \), for a fixed \( T \) and \( p \), subject to material balances incorporated through Lagrangian multipliers. The solution procedure used in this work is based on Michelsen and Mollerup [19]. The problem may be formally written as:

\[
\begin{align*}
\text{min } & \quad G(\mathbf{n}) \\
\text{s.t. } & \quad \mathbf{An} = \mathbf{b} \\
& \quad n_{i} \geq 0
\end{align*}
\] (8)

Thus the problem is to express \( G \) as a function of \( \mathbf{n} \) and then seek the composition vector \( \mathbf{n}' \) that minimizes \( G \). \( \mathbf{n} \in \mathbb{R}^{c} \) is the mole number vector, where \( c \) is the number of species in the system and \( m \) the number of elements. \( \mathbf{A} \in \mathbb{R}^{m \times c} \) is the system abundance matrix (mass conservation) and \( \mathbf{b} \in \mathbb{R}^{m} \). The elemental composition vector \( \mathbf{b} \) may be found from the initial mole number vector \( \mathbf{n}^{0} \) through the relation \( \mathbf{b} = \mathbf{An}^{0} \). The equations (8) to (10) form a constrained optimization problem. The most common method for dealing with such problems is by the use of Lagrangian multipliers and the minimization of the so-called Lagrangian (L)

\[ L(\lambda, \mathbf{n}) = G(\mathbf{n}) - \lambda^{T}(\mathbf{An} - \mathbf{b}) \] (11)
where \( \lambda \in \mathbb{R}^m \) is a vector of Lagrangian multipliers. At the minimum it is required that

\[
\frac{\partial L}{\partial n} = \frac{\partial G}{\partial n} - A^T \lambda = \mu - A^T \lambda = 0 \tag{12}
\]

\[
\frac{\partial L}{\partial \lambda} = -(An - b) = 0 \tag{13}
\]

Note that \( \partial G/\partial n \) is recognized as the chemical potential \( \mu \). By recognizing that the Lagrange multipliers represent the chemical potential of the elements, the Gibbs energy may be written as

\[
G_{\text{min}} = n \mu^T = n (A^T \lambda) = b^T \lambda \tag{14}
\]

Which means that the \( m + c \) bodied problem is reduced to a \( m \) bodied problem in terms of \( b \) and \( \lambda \), instead of \( n \) and \( \mu \). By rearranging the equations for the chemical potential an expression for the mole fractions is found.

\[
\mu' = \mu'^0 + \ln \gamma + \ln x \tag{15}
\]

\[
\ln x = A^T \lambda' - \mu'^0 - \ln \gamma \tag{16}
\]

Where the primes indicate that the variables are reduced (divided by \( RT \)). The minimization of Gibbs energy is done by constructing an objective function \( Q \) (dual transformation) that is to be minimized.

\[
Q(n_t, \lambda) = n_t \left( \sum_i x_i - 1 \right) - b^T \lambda \tag{17}
\]

The independent variables of eq. (17) is the total number of moles in the liquid and the elemental chemical potentials, \( \lambda \). The mole fractions are represented by eq. (15). The above equation may be solved for these variables, and the component mole fractions may thereafter be found from eq. (15). The minimization of \( Q \) leads to the following root finding problem

\[
\begin{bmatrix}
  n_t (Ax - b) \\
  \sum_i (x_i - 1)
\end{bmatrix}
\begin{bmatrix}
  \lambda \\
  n_t
\end{bmatrix} = 0 \tag{18}
\]

The final problem is thus a \( m + 1 \) bodied problem instead of a \( c + 1 \) bodied problem and it may be solved by a Newton search. The activity coefficients are updated in an outer loop.

4. The e-NRTL model

As mentioned the activity coefficients are found using the e-NRTL model \[4\]. As most other excess Gibbs energy models for electrolyte solutions it consists of a long-range term
For the long range term the so-called Pitzer-Debye-Hückel equation is used \[20\].

\[
g^{LR,PDH}_{RT} = -\frac{4A_x I_x}{\rho} \ln \left( 1 + \rho \sqrt{I_x} \right) \tag{19}
\]

where \(A_x\) is the Debye-Hückel parameter

\[
A_x = \frac{1}{3} \left( \frac{2\pi N_A d_s}{M_s} \right)^{1/2} \left( \frac{e^2}{4\pi \epsilon_s \epsilon_0 k_B T} \right)^{3/2} \tag{20}
\]

In these equations \(\rho = 14.9 \cdot 10^{-10}\) m is the closest approach parameter, \(I_x\) is the ionic strength, \(N_A\) is the Avogadro number, \(d_s\) is the density of the solvent (mol/m\(^3\)), \(M_s\) is the molar mass of the solvent, \(e\) is the elementary charge, \(\epsilon_s\) and \(\epsilon_0\) are respectively the solvent permittivity and the vacuum permittivity, and \(k_B\) is the Boltzmann constant. All units are SI units. Since the reference state for the Pitzer-Debye-Hückel term generally is taken to be infinite dilution in an aqueous solutions, many authors have added the so-called Born term. This term is meant to correct for the difference between the dielectric constant of water and the mixed solvent \[21\].

\[
g^{LR,Born}_{RT} = \frac{e^2}{8\pi RT \epsilon_0 r_{Born}} \left( \frac{1}{\epsilon_s} - \frac{1}{\epsilon_w} \right) \sum_i \left( x_i z_i^2 \right) \tag{21}
\]

where \(\epsilon_w\) is the static permittivity of water. \(r_{Born}\) is the Born radius (3.0 \cdot 10^{-10} m).

To model the short range interactions Chen proposed a modified NRTL \[22\] term, given here in a mole number explicit form

\[
\frac{n_t G_{SR}}{RT} = \sum_m n_m \left( \frac{\sum_j C_j n_j G_{jm} \tau_{jm}}{\sum_j C_j n_j G_{jm}} \right) + \sum_c n_c |z_c| \left( \sum_a Y_a \frac{\sum_j C_j n_j G_{ja,ca} \tau_{ja,ca}}{\sum_j C_j n_j G_{ja,ca}} \right) + \sum_a n_a |z_a| \left( \sum_c Y_c \frac{\sum_j C_j n_j G_{ja,ca} \tau_{ja,ca}}{\sum_j C_j n_j G_{ja,ca}} \right) \tag{22}
\]

where \(C_j = |z_j|\), is the absolute value of the charge number for ionic species, and \(C_j = 1\) for molecular species. \(Y_a\) and \(Y_c\) are the ionic fractions

\[
Y_a = \frac{n_a |z_a|}{\sum_{a'} n_{a'} |z_{a'}|} \tag{23}
\]

\[
Y_c = \frac{n_c |z_c|}{\sum_{c'} n_{c'} |z_{c'}|} \tag{24}
\]

The \(G\) and \(\tau\) parameters are related through the Boltzmann factor, \(G_{ij} = \exp (-\alpha_{ij} \tau_{ij})\). The parameter structure of the e-NRTL model is not straightforward. From equation
(22) it may be seen that the parameters needed are: \( \tau_{jm}, G_{jm}, \tau_{jc,ac}, G_{jc,ac}, \tau_{ja,ca}, G_{ja,ca} \) where \( j = k = \{m, c, a\} \). In addition the coherent non-randomness parameters must be defined. All of these parameters can not be defined explicitly, some are found from relations and mixing rules given in the e-NRTL theory. The parameters that must be defined explicitly are the electrolyte pair-molecular species interaction parameters; \( \tau_{ca,m}, \tau_{m,ca} \) and the molecular interaction parameters \( \tau_{mm'} \) and \( \tau_{m'm} \). The ternary parameters \( \tau_{ca,ca'}, \tau_{ca',ca}, \tau_{ca,c'a}, \tau_{c'a,ca} \) must also be defined/regressed explicitly, but these are rarely used. In addition the following non-randomness parameters must be defined: \( \alpha_{ca,m}, \alpha_{ca,ca'}, \alpha_{ca,c'a} \) and \( \alpha_{mm'} \). All the other parameters used in the e-NRTL model can be derived from the parameters given above, the relations needed for this is given in the following.

\[
G_{cm} = \frac{\sum n_a G_{ca,m}}{\sum n_{a'} n_{a'}}; \quad \alpha_{cm} = \frac{\sum n_a \alpha_{ca,m}}{\sum n_{a'} n_{a'}}
\]

\[
G_{am} = \frac{\sum n_c G_{ca,m}}{\sum n_{c'} n_{c'}}; \quad \alpha_{am} = \frac{\sum n_c \alpha_{ca,m}}{\sum n_{c'} n_{c'}}
\]

\[
\tau_{ma,ca} = \tau_{am} - \tau_{cam} + \tau_{mca}
\]

\[
\tau_{mc,ac} = \tau_{cm} - \tau_{cam} + \tau_{mca}
\]

The activity coefficients are found by differentiating the expression for the total excess Gibbs energy

\[
RT \ln \gamma = \frac{\partial G_{\text{tot}}^E}{\partial n_i} = \frac{\partial}{\partial n_i} \left( n_t g_{\text{SR}}^{E,S} + n_t g_{\text{LR}}^{L,R,DH} + n_t g_{\text{LR}}^{L,R,Born} \right)
\]

While differentiating one should note that the compositional dependency of the density and the dielectric constant in equations (19), (20) and (21) is disregarded. This assumption is very common for the treatment of the long-range term. There are also some assumptions made for the differentiation of the short range term. This is addressed in the next section.

4.1. The refined e-NRTL model

In the model referred above the cationic and anionic charge fractions, \( Y_c \) and \( Y_a \) and the composition dependent parameters in eqs. (25) and (26) are held constant during the differentiation in eq. (29). In reality, these are composition dependent variables, and they must therefore be accounted for in the differentiation. The incorporation of these dependencies will change the equations for the activity coefficients and thus have large impact on the model. These changes will only have an effect for systems with multiple cations and/or anions. For simpler systems, there will be no change to the equations. Due to this the e-NRTL model as presented does not fulfill the Gibbs-Duhem equation for multi-ionic systems. This gives inconsistencies if both the expression for excess Gibbs energy and the activity coefficients are used in the same model. In a recent paper by Bollas et al. \[17\] this was discussed and the model equations of the so-called "Refined electrolyte-NRTL model" were given. In the same paper it was stated that this refined model gave more accurate predictions of the non-idealities in electrolyte systems. Because of this, and the need for a consistent thermodynamic model, our group is currently investigating this refined model for amine systems.
5. Modeling results and discussion

Figures 1(a), 1(b) and 1(c) show the predictions from the implemented electrolyte-NRTL/Peng-Robinson model along with experimental data. All interaction parameters and physical properties are taken from the simulation package Aspen+ [21]. Equilibrium and Henry’s constants are taken from Austgen [6]. The heat of absorption is calculated using a modified Gibbs-Helmholtz equation, \( -\frac{\Delta H}{R} = \frac{\partial \ln P_{CO_2}}{\partial (1/T)} \).

The figures show that the model is able to predict partial pressure of CO\(_2\) fairly well. Also the species concentrations are predicted reasonably well compared to NMR data from Jakobsen et al. [23] and Böttinger et al. [24]. As for the heat of absorption
predictions, they are not accurate. However, the heat of absorption is in this work found by using a quite simple method, later extensions will aim at finding the heat of absorption by also incorporating the excess term. In the further work the refined model, somewhat analog to that of Bollas et al. [17] will be basis for the calculations.

6. Conclusion

The e-NRTL model has become popular for amine-water-CO$_2$ systems. However there are some inconsistencies in the model for multi-ionic systems. The effect of these inconsistencies are currently being explored for the systems in discussion. The original e-NRTL model has been implemented and has been used to predict partial pressure of CO$_2$, speciation and heat of absorption.

REFERENCES