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Effect of the incorporation of speciation data in the modeling of CO_2–DEA–H_2O system

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ABSTRACT

An electrolyte equation of state based on Redlich Kwong Soave EOS is applied to the representation of the equilibrium properties of the water–CO_2–diethanolamine system in the 298–366.5 K temperature range. In this work we have developed a model which is able to represent the liquid phase speciation as well as the CO_2 solubility in the amine solutions. For this purpose the database used for the parameters determination consists of solubility data as well as Henry's constants and speciation data including experimental concentrations of molecular CO_2 and of carbamate. The need of such speciation data is shown by a comparison of the speciation results obtained and those predicted using models from the literature based only on the data treatment of experimental VLE values.

1. Introduction

The modeling of the equilibrium state associated to the absorption of acid gases in aqueous amine solutions is necessary for the optimization of the absorption units as well as for the optimization of the columns used for the solvent recovery. In the literature, a lot of papers are dealing with the modeling of the solubility of CO_2 or H_2S in various aqueous amine or amine mixtures solutions.

After the use of the quasi-chemical approach of Kent and Eisenberg [1], electrolyte activity coefficient models have been used in the majority of the studies devoted to the modeling of acid gases – aqueous amine solution systems. The e-NRTL model has been used by Austgen et al. [2] to represent the solubility of both CO_2 and H_2S gases in monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) solutions. Since this first paper, the e-NRTL has been applied to the modeling of amine – acid gases systems in other publications such as the recent work of Zhang et al. [3]. Li and Mather [4] have used the Clegg–Pitzer model for the modeling of CO_2 solubility in MDEA-MEA mixtures. An electrolyte extension of UNIQUAC model was also used to modelize the solubility of CO_2 and H_2S in DEA-MDEA mixtures as in the recent work of Al-Rashed and Ali [5]. Since several years, equations of states (EOS) adapted to electrolyte systems have also been applied to the representation of the equilibrium state in acid gases – aqueous amine solutions systems. EOS are more complicated to handle than excess Gibbs energy models but take directly into account the pressure effect and are also well adapted to the calculation of the solubility of non-acid gases such as CH_4. In 1999, the extension of the Redlich Kwong Soave equation of state published by Fürst and Renon [6] was used to calculate the solubility of CO_2 and H_2S in DEA solutions [7]. More recently Nasrifar and Tafazzol [8] used PC-SAFT model for the calculation of the solubility of both CO_2 and H_2S acid gases in solutions of MEA, DEA and MDEA. Other recent papers ([9] and [10]) are reporting the results of the modeling acid gases solubility in various amine solutions with electrolyte equations of states, mPR-CPA and SAFT-VR, respectively.

For the modeling we choose the electrolyte equation of state published by Fürst and Renon [6] because, it presents, as all equations of state the advantage of expressing the VLE equilibrium in a symmetrical way, avoiding the use of Henry's constants. Another advantage is that the number of adjustable ionic parameters of this EOS may be decreased, applying the correlation described in Section 4.

As the amines are chemical solvents, the absorption process combines VLE and chemical equilibrium and produces a lot of ionic and molecular species.

In the Water–DEA–CO_2 system, the chemical equilibria are:

$$CO_2 + 2H_2O = HCO_3^- + H_3O^+ \quad (1)$$

$$HCO_3^- + H_2O = CO_3^{2-} + H_3O^+ \quad (2)$$

$$DEAH^+ + H_2O = DEA + H_3O^+ \quad (3)$$

$$DEACOO^- + H_2O = DEA + HCO_3^- \quad (4)$$

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Nomenclature

a	molar Helmoltz energy
a_0, a_1	parameters of Eq. (19)
a^{SR}	attractive parameter of the Soave EOS
b	covolume
C_i	concentration of the *i* species
D	dielectric constant of the solution
e	protonic charge
Hi	apparent Henry constant
k_{ij}	interaction parameter of the non electrolyte part of the EOS
K	equilibrium constants defined in the mole fraction scale
n	number of moles
N	Avogadro number
P	pressure
rms	root mean square relative deviation
R	ideal gas constant
T	temperature
v	molar volume of the solution
W	interaction parameter
Z	ionic charge
x	molar fraction

Greek letters

α	loading (mol CO_2/mol DEA)
α_{ij}	non random NRTL parameter
α_{LR}	parameter defined in Eq. (11)
σ	diameter
ε_0	vacuum permittivity
γ_i	activity coefficient in the mole fractions scale
ξ_3	function defined in Eq. (13)
Γ	Shielding parameter (defined in Eq. (10))
λ	correlation parameter (Eqs. (25–28))
μ	chemical potential
ν	stoecchiometric coefficient (Eq. (16))
τ	NRTL parameter

Superscripts

(0), (1) and (2)	temperature dependence parameters
L,V	relative to liquid or vapor phases
S	solvated
st	standard state

Subscripts

i,j	relative to ionic species
LR	long-range term
m	relative to molecular species
molec	molecular form of dissolved CO_2
NE	non electrolyte term
k	molecular or ionic species
s	solvated
SR	short-range solvation term
w	water

$$2H_2O = H_3O^+ + OH^- \quad (5)$$

Hence the absorbed CO_2 produces: HCO_3^-, CO_3^{2-}, the carbamate ion noted $DEACOO^-$ and the molecular undissociated CO_2 in the liquid phase, noted $(CO_2)_{molec}$.

It also produces the protonated DEA noted $DEAH^+$.

In almost all studies the calculation of the model parameters are based on a database containing acid gas solubility data over a specific range of experimental conditions (temperature, amine concentration and loading range). However the liquid phase produced by the CO_2 absorption process is a complex one and the use of experimental speciation values in the data treatment seems to be the best way to ensure to get a model with a realistic representation of the liquid phase composition. Such a model could be useful for the determination of the absorption mechanism, where it is necessary to combine mass transfer as well as chemical kinetics in a global modeling where thermodynamics is also involved for the determination of the gas partition at the liquid–gas interface and the equilibrium state for the reactions which may be considered as instantaneous. In this case a thermodynamic model which is able to represent the CO_2 solubility as well as the chemical equilibrium in the liquid phase is required, especially if the kinetics involves loaded solutions.

The model has been already applied to the representation of acid gas absorption in amine solutions in the case of MDEA [11] or in the case of DEA [7] but without considering speciation data, the aim being to get a representation of solubility experimental values.

This explains the need of another fitting procedure to adapt the model to a simultaneous representation of the solubility data and of the speciation ones.

The paper will begin by a short description of the main equations defining the model. Then the database used for the parameter determination will be detailed.

2. Model description

The equation of state published by Fürst and Renon [6], is based on the following expression of the Helmoltz energy:

$$\frac{a-a^{st}}{RT}=\left(\frac{\Delta a}{RT}\right)=\left(\frac{\Delta a}{RT}\right)_{NE}+\left(\frac{\Delta a}{RT}\right)_{LR}+\left(\frac{\Delta a}{RT}\right)_{SR} \quad (6)$$

Where the non-electrolyte part comes from the Redlich–Kwong–Soave equation of state:

$$\left(\frac{\Delta a}{RT}\right)_{NE}=\sum_k x_k \ln\left(\frac{x_k RT}{P^{st}(v-b)}\right)+\frac{a^{SR}}{RT\,b}\ln\left(\frac{v}{v+b}\right) \quad (7)$$

the covolume b of the mixture having an ionic (b_i) as well as a non ionic (b_m) contribution:

$$b=b_m+\sum_i x_i b_i \quad (8)$$

The mixing rule used for the calculation of a^{SR} and b_m is the Wong-Sandler mixing rule [12], the excess energy model being the NRTL one.

The representation of the electrostatic interactions (Long-Range) is made using a MSA term:

$$\left(\frac{\Delta a}{RT}\right)_{LR}=-\frac{\alpha_{LR}^2}{4\pi}\sum_i \frac{x_i Z_i^2 \Gamma}{1+\Gamma\sigma_i}+\frac{\Gamma^3 v}{3\pi N} \quad (9)$$

with

$$4\Gamma^2=\alpha_{LR}^2\sum_i \frac{x_i}{v}\left(\frac{Z_i}{1+\Gamma\sigma_i}\right)^2 \quad (10)$$

and

$$\alpha_{LR}^2=\frac{e^2N}{\varepsilon_0 DRT} \quad (11)$$

The dielectric constant D of the solution takes into account the ion effect using Pottel's expression, as explained in Ref. [6], the