



An Electrolyte G^E -EoS Modeling of Solubility of Carbon Dioxide in Aqueous MDEA Solution

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Abstract

Carbon dioxide and hydrogen sulfide are the major contaminants in natural gas and should be separated from natural and flue gases to avoid corrosion in transmission lines and protect environment. The most important method for removing acid gases is the absorption process by alkanolamine solutions. In this study, we applied G^E -EoS approach and using the equation of state with Wong-Sandler mixing rule, we performed vapor-liquid equilibrium calculations for correlation and prediction of the solubility of carbon dioxide in alkanolamine solution. The local composition model plus Wong-Sandler mixing rule is used. In this work, an electrolyte NRTL model was used so that this model is a combination of the NRTL term, a long-range electrolytic model such Debye-Hückel theory, and a Born term. The calculated results are in very good agreement with different experimental data of the CO_2 -MDEA- H_2O systems.

Keywords: Thermodynamic Modeling, G^E -EoS Mixing Rule, MDEA, CO_2

Introduction

Carbon dioxide and hydrogen sulfide are among the most important contaminants of the natural gas in the chemical industry and must be separated from this product to avoid corrosion problems, improve the heating value of natural gas and prevent environmental damages. The most important method for the removal of carbon dioxide is chemical absorption by aqueous alkanolamine solutions. These solutions give weak reactions with acid gases, as they absorb, then in subsequent steps desorption and solvent recovery.

MDEA is a tertiary amine solvent that has better properties such as high loading capacity and high heat degradation resistance and less recovery energy than other types of amines. In addition, MDEA is a relatively cheap chemical and is considered to be the most popular and most widely used amine for use alone or as a blend with other solvents[1]. To design a natural gas sweetening process with alkanolamines, due to the type of process involved in the liquid and gas equilibrium, the use of a suitable thermodynamic model is necessary to predict vapor-liquid equilibrium calculation accurately. In a certain general categorization, three types of models have been proposed for the calculation of the vapor-liquid equilibria of aqueous amine solutions such as semi-empirical, activity coefficient and equation of state.

The first type of model such as the Kent-Eisenberg does not have a basic theoretical background but is more empirical in nature. This model was first used for CO_2 and H_2S capture into MEA and DEA, and MDEA[2]. Another approach is applying the activity coefficient models that are rigorous and precise, especially at low loadings and pressures.



However, they need different equations to account for liquid and vapor phase non-idealities, and, moreover, they need a large number of input parameters. Many researchers have used these models for thermodynamic modeling acid gas removal by alkanolamine. Among this type of model, electrolyte-NRTL[3-4] and electrolyte-UNIQUAC [5], nWilson-NRF[6] and others have been widely used for correlation and prediction of acid gas solubility in alkanolamines. The third type of model is the cubic and non-cubic equations of state (EoS). using EoS approach allows one to calculate the phase equilibrium in both vapor and liquid phases. Many of the mixtures and systems used in different chemical industries exhibit non-ideal behavior. In other words, mixtures of compounds of wide complexity and asymmetry in size and energies are non-ideal systems. It is not appropriate for these types of systems to use conventional mixing rules such as van der Waals or the classical mixing rules, which are applicable in the cubic equation of state such as PR or SRK. Another class of association EoS is statistical association EOS such as CPA [7], SAFT, etc. were used in various complex systems modeling.

A class of mixing rules, named G^E-EoS, has been widely used for the parameters of cubic EoS such as the energy and co-volume parameters by incorporating an activity coefficient model, often a local composition (LC) model like Wilson, NRTL, UNIQUAC, or UNIFAC. The starting point of many but not all G^E-EOS mixing rules is the equality of excess Gibbs energies (g^E) or the excess Helmholtz energies (a^E) obtaining by a cubic EoS with the corresponding excess function using a solution theory such as local composition excess Gibbs functions [8].

In this work, thermodynamic modeling of the H₂O-MDEA-CO₂ system is performed using G^E-EOS model using the Peng-Robinson, Wong-Sandler, electrolyte Non-Random Two Liquid (PR-WS-eNRTL) at different temperature and concentration. By optimization of the solubility experimental data, the coupling and interaction parameters were obtained.

Thermodynamic models

Chemical equilibria

CO₂ is dissolved into the aqueous phase and a protonation reaction is taking place in the amine solution. Depending on the type of amine used and the system studied, ionic species are produced in the aqueous mixture. The liquid phase chemical reactions for the mixtures were examined in this work as



where the mole fraction-based equilibrium constants for these reactions are defined as

$$K_x = e^{A+B/T+C \ln T} = \prod_i (x_i \gamma_i)^{v_i} \quad (3)$$

where x , γ , and v are mole fraction, activity coefficient, and reaction stoichiometry of the species i , respectively. The coefficients A , B , and C are the numeric constants that are given in the literature [9].

calculated symmetric and asymmetric activity coefficients for water and other species, respectively, are obtained as

$$\gamma_{\text{water}} = \frac{\varphi_{\text{water}}(T, P, x)}{\varphi_{\text{water}}^0(T, P, x_{\text{water}} \rightarrow 1)} \quad (4)$$



$$\gamma_i^* = \frac{\varphi_i(T, P, x)}{\varphi_i^\infty(T, P, x_i \rightarrow 0)} \quad i \neq \text{water} \quad (5)$$

Where the fugacity coefficient of ionic and molecular species are calculated using G^E/EoS equations as follows.

Phase equilibria

The phase equilibrium calculation for the molecular species (CO₂, H₂O, MDEA) is carried out by the equality of the fugacities of each molecular species in the vapor and liquid phase as

$$x_i \varphi_i^l = y_i \varphi_i^v \quad (6)$$

The fugacities of the molecular species are calculated using the PR-WS-eNRTL model, which is extended in this study to electrolyte solutions. Peng-Robinson equation of state (PR EoS) is presented as

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + 2bv - b^2} \quad (7)$$

where T, P, and v are temperature, pressure and molar volume of the system, and R the ideal gas constant. The parameters a and b are given by

$$b = 0.07780 \frac{RT_c}{P_c} \quad (8)$$

$$a(T) = a_c \alpha(T) \quad (9)$$

$$a_c = 0.45724 \frac{(RT_c)^2}{P_c} \quad (10)$$

$$\alpha(T) = 1 + k(1 - T_r^{0.5})^2 \quad (11)$$

$$k = 0.37464 + 1.5422\omega - 0.2699\omega^2 \quad (12)$$

For the extension to mixtures the Wong-Sandler mixing rule is used as

$$a = b \left[\sum_i x_i \frac{a_i}{b_i} - \frac{g^E}{C} \right] \quad (13)$$

$$b = \frac{\sum_i \sum_j x_i x_j (b - \frac{a}{RT})_{ij}}{1 + \frac{g^E}{CRT} - \sum_i x_i \frac{a_i}{b_i RT}} \quad (14)$$

$$(b - \frac{a}{RT})_{ij} = \frac{(b - \frac{a}{RT})_i + (b - \frac{a}{RT})_j}{2} (1 - k_{ij}) \quad (15)$$

where a and b are attractive and co-volume parameters, respectively. g^E is the excess Gibbs energy function that is defined as

$$g_{eNRTL}^E = g_{NRTL}^E + g_{PDH}^E + g_{BORN}^E \quad (16)$$

Model Parameters

The required parameters of the PR-WS-eNRTL model in the VLE calculations of the Water-MDEA-CO₂ system are divided into two types which is explained as follows. The first type is the pure component parameters that were collected from the literatures[9]. The second type is the binary parameters. The model under study has two types of binary parameters that are binary interaction or coupling parameter k_{ij} and binary interaction energy parameter of the



local combination model, i.e. τ_{ij} , in NRTL function. Also, the non-random parameter of the NRTL equation, α , is set to 0.2. The molecule-molecule interaction parameters are obtained through regression of experimental data and all the binary molecule-ion pair and molecule-cation parameters are optimized through regression of the ternary amine–water–CO₂ systems. The temperature-dependent of binary interaction parameters are expressed as

$$k_{ij} = A + \frac{B}{T} \quad \& \quad \tau_{ij} = \frac{A'}{T} \quad (17)$$

The experimental data of the ternary systems used for modeling are given in Table 1.

Table 1. Sources of experimental data for the CO₂-MDEA-H₂O system

Author	T (K)	%wt_MDEA	Loading	Data Point
B. Lemoine[10]	297.7	23.63	0.0171 - 0.2625	13
S. Ma'mun[11]	328.15 , 343.15 , 358.15	50	0.1658 - 0.8133	34
D. M. Austgen[12]	313.15	23.4 , 4.9	0.006015 - 0.84	14
R. Sidi-Boumedine[13]	298.07 , 313.15 , 348.17	25.73 , 46.88	0.008 - 1.303	77
Rogres et al[14]	313.15 , 323.15	23 , 50	0.000249 - 0.1177	- 34
G. Kuranov[15]	313.15 , 333.15 , 373.15 , 393.15 , 413.15	18.84 , 19.2 , 31.12	0.105 - 1.316	78
Kamps[16]	313.15 , 353.15 , 393.15	23.8-32.1 , 48.78	0.126 - 1.24	33
Overall	297.7-413.15	18.84-50	0.000249-1.303	283

Table 2. PR-WS-eNRTL binary parameters for the CO₂-MDEA-H₂O system

k_{ij}	A	B	τ_{ij}	A'
H ₂ O-CO ₂	4.061	-558.680	H ₂ O-CO ₂	-123.603
H ₂ O-MDEA	0.501	36.481	H ₂ O-MDEA	8.981
H ₂ O-MDEAH ⁺	0.535	26.566	H ₂ O-(MDEAH ⁺ ,HCO ₃ ⁻)	62.405
CO ₂ -MDEA	0	0	CO ₂ - H ₂ O	-18.429
CO ₂ -MDEAH ⁺	-8.494	3518.992	CO ₂ -MDEA	0
MDEA- MDEAH ⁺	0.069	854.865	CO ₂ -(MDEAH ⁺ ,HCO ₃ ⁻)	-21.672
MDEAH ⁺ -HCO ₃ ⁻	6.611	-2170.486	MDEA- H ₂ O	156.163
			MDEA- CO ₂	0
			MDEA-(MDEAH ⁺ ,HCO ₃ ⁻)	-2026.86
			(MDEAH ⁺ ,HCO ₃ ⁻)- H ₂ O	1024.421
			(MDEAH ⁺ ,HCO ₃ ⁻)- CO ₂	-0.406
			(MDEAH ⁺ ,HCO ₃ ⁻)- MDEA	21.937

* $k_{ij} = k_{ji}$, $k_{\text{anion-(molecule)}} = 0$

Results and discussion

The parameters of the PR-WS-eNRTL model were fitted using the experimental data of solubility of carbon dioxide gas in the MDEA solution, which is shown in Table 1. For optimization of the adjustable parameters, the following objective function is used.

$$\%AAD = \frac{100}{NP} \times \sum_{i=1}^{NP} \frac{|P_{exp} - P_{cal}|}{P_{exp}} \quad (18)$$



Table 2 demonstrates the optimum values of the binary interaction parameters of the PR-WS-eNRTL model in all temperatures and amine concentrations. Figures 1 and 2 demonstrate the results of the correlation for the CO₂-MDEA-H₂O system using the experimental data from Sidi-Boumedine et al. [13] and Bhairi [17], respectively. As shown, the present model shows excellent agreement with experiment at a wide range of temperature and pressure and alkanolamine concentrations.

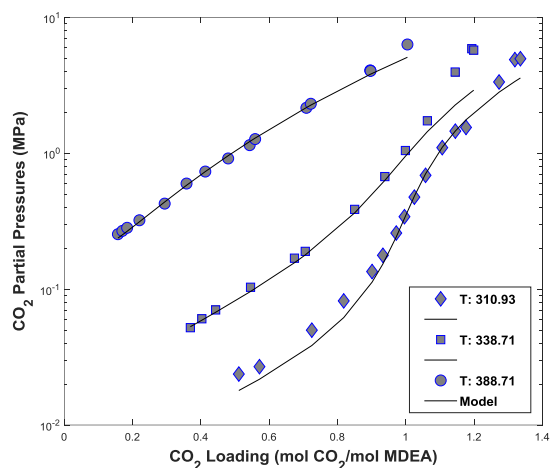


Fig.1 Calculated partial pressure of CO₂ versus its gas loading at different temperatures using PR-WS-eNRTL model for the CO₂-H₂O- MDEA (20 wt%) system and comparison with experiment [17].

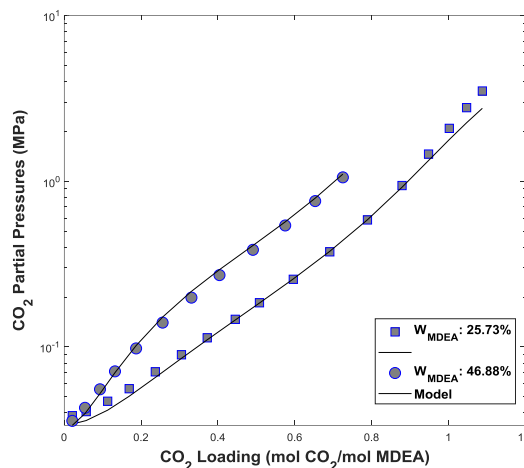


Fig.2 Calculated partial pressure of CO₂ versus its gas loading at different MDEA concentrations using PR-WS-eNRTL model for the CO₂-H₂O- MDEA system at temperature of 348 K[13].

Table 3- Sources of Experimental Data for CO₂-MDEA-H₂O System

Author	Data Point	This work	ENRTL[3]	UMR-PRU[2]
Correlation				
B. Lemoine[10]	13	24.41	-	-
S. Ma'mun[11]	34	4.68	-	17.7
D. M. Austgen[12]	14	20.9	-	28.4
R. Sidi-Boumedine[13]	77	11.05	19.2	26.9
Rogres et al[14]	34	16.66	-	29.1
G. Kuranov[15]	78	11.15	18.23	26.1
Kamps[16]	33	18.15	23.1	29.4
<i>overall</i>		12.91	19.48	26.01
Prediction				
Chakma[18]	33	34.03	-	32.9
Bhairi[17]	99	18.44	21.7	36.2
S. Rho[19]	58	27.22	29.64	-
Xu[20]	65	18.48	31.7	20.7
Dawodu	12	19.44	-	14.7
M. K. Park[21]	30	32.72	29.64	42.2
MacGeroger	5	26.59	-	29.4
D. Silkenbäumer[22]	11	14.05	15.92	32.1
<i>overall</i>	596	23.1	26.6	31.16



Conclusions

The G^E -EoS model, PR-WS-eNRTL was successfully applied to the CO₂-MDEA-H₂O system using 14 adjustable parameters. In this work, we used simplified assumptions to reduce the number of parameters and increasing accuracy. The 283 experimental data within temperature range of 297–413 K, 18–50 wt% amine concentration, and 0.0003-1.31 gas loading were used for the correlation model and the other experimental data (about 313) were used to evaluate the model prediction as shown in Table 3. The correlated results showed a very good agreement with experiment so that the predicted results showed the accuracy of the present model. The calculated results were obtained by the present eNRTL[3] were compared with those results were obtained by UMR-PRU[2] that showed a relatively large improvement.

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