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Modeling vapor-liquid equilibrium of CO_2 in aqueous MEA using hybrid genetic based algorithm

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Abstract

The extended UNIQUAC model, and the modified Clegg-Pitzer equation were separately applied to the vapor-liquid equilibrium of CO_2 in aqueous monoethanolamine (MEA) solutions [15 and 30 mass% of MEA has been used over the temperature range of 313 - 393°K], the data results predicting such equilibrium were analyzed and compared. As Hybrid algorithm, the genetic algorithm (GA) and as deterministic model, the Nelder-Mead Simplex (NMS) method was used. In general, these models have been found suitable regarding the adjustments of experimental results of VLE measurement of this work as well as those in the cited literature. However, the UNIQUAC model gives more satisfactory results comparatively to Pitzer model.

Keywords:Alkanolamine; CO_2*; solubility;MEA; Optimzation; Uniquac,*

1. Introduction

Alkanolamines are among the most frequent chemical absorbent used for the removal of carbon dioxide, which can be the consequence of industry activities or just naturally present in gas reservoirs. The gas capture combines chemical reaction with physical absorption of CO2, the acido-basic reaction between carbon dioxide and alkanolamine is reversible making possible the separation of the gas from the absorbent solution (Arcisand al, 2009) [1].

The development of thermodynamic models for (CO2+H2O+alkanolamine) systems is not always an effortless task. Rigorous models that take into account non-ideality are based on adequate equations for phase and chemical equilibria, charge, and mass balances. In literature, some works uses the(γ-φ)approach such as the models of Deshmuk and Mather, 1981 [2], Kuranov and al, 1997 [3], Kundu and al, 2008[4], Faramarzi and al, 2009 [5], Tong and al, 2012[6], and Wagner and al, 2013 [7]. However, these models differ on the choice of the activity model and equation of state. In this work, the extended UNIQUAC model and the modified Clegg-Pitzer equation were used to correlate and predict the vapor-liquid equilibrium of the carbon dioxide in aqueous solution of MEA system. In these models the fugacity coefficients φ were calculated from a truncated virial equation of state.

2. Modeling of phase equilibria

The modeling of phase equilibria in ternary system is based on equations related to chemical reactions in the liquid phase, mass and charge balances, and vapor-liquid equilibria relations. Standard state of acid gas is taken as ideal gas at temperature of reaction, standard state of alkanolamine is considered hypothetically one molar solution at infinite dilution, and standard state of water is supposed pure water on a molality basis.

2.1 Chemical reaction equilibria in aqueous solution of CO_2 and MEA

In the aqueous phase for theCO_2- MEA-H_2O system, chemical reactions (1) to (5) take place in the liquid phase as following:

$$MEAH^+ \overset{K_1}{\leftrightarrow} MEA + H^+ \quad (1)$$

$$CO_2 + H_2O \overset{K_2}{\leftrightarrow} H^+ + HCO_3^- \quad (2)$$

$$HCO_3^- \overset{K_3}{\leftrightarrow} H^+ + CO_3^{2-} \quad (3)$$

$$MEA + HCO_3^- \overset{K_4}{\leftrightarrow} MEACOO^- + H_2O \quad (4)$$

$$H_2O \overset{K_5}{\leftrightarrow} H^+ + OH^- \quad (5)$$

The expressions of equilibrium constants for chemical reactions (1) to (5) are defined as:

$$K_1 = \frac{m_{RR'R''N}m_{H^+}}{m_{RR'R''NH^+}}\frac{\gamma_{RR'R''N}\gamma_{H^+}}{\gamma_{RR'R''NH^+}} \quad (6)$$

$$K_2 = \frac{m_{HCO_3^-}m_{H^+}}{m_{CO_2}}\frac{\gamma_{HCO_3^-}\gamma_{H^+}}{\gamma_{CO_2}} \quad (7)$$

$$K_3 = \frac{m_{CO_3^{2-}} m_{H^+}}{m_{HCO_3^-}} \frac{\gamma_{CO_3^{2-}} \gamma_{H^+}}{\gamma_{HCO_3^-}} \quad (8)$$

$$K_4 = \frac{m_{RR'R''COO^-}}{m_{RR'R''N} m_{HCO_3^-}} \frac{\gamma_{RR'R''COO^-}}{\gamma_{RR'R''N} \gamma_{HCO_3^-}} \quad (9)$$

$$K_5 = m_{OH^-} m_{H^+} \gamma_{OH^-} \gamma_{H^+} \quad (10)$$

2.2 Henry's law and equilibrium constants

Usually the equilibrium reaction constants are given as temperature function, Eq. (11) was used to calculate the equilibrium reaction constants since it gives good results, according to results of previous works Djaballah and Kabouche, 2015 [8].

$$lnK_N = a + \frac{b}{T} + c.lnT + d.T + \frac{e}{T^2} \quad (11)$$

The related coefficients to this equation for deprotonation of MEA (Eq.1), formation of bicarbonate (Eq. 2) and formation of carbamate (Eq.4) are summarized in Table 1.

Reactions	Reaction1 [7]	Reaction2 [9]	Reaction4 [10]
a	- 1.73782	-1203.01	- 5.9680
b	- 6092.85	68359.6	2888.6
c	0	188.444	0
d	0.001157	- 0.206424	0
e	0	- 4712910	0

The Henry's constant of CO_2 in water is calculated using the following equation given by Rumpf and Maurer, 1993 [11]:

$$ln\,H_{CO_2,w} = \frac{-9624.4}{T} - 28.749\,lnT + 0.01441\,.T + 192.876 \quad (12)$$

2.3 Balance equations in the liquid phase

MEA balance :

$$m_{MEA}^0 = m_{MEACOO^-} + m_{MEAH^+} + m_{MEA} = m_t \quad (13)$$

CO_2 mass balance in the liquid phase:

$$m_{CO_2}^{dis} = m_{MEACOO^-} + m_{HCO_3^-} + m_{CO_3^{2-}} + m_{CO_2} = m_t\alpha \quad (14)$$

The electroneutralityequationis :

$$m_{MEACOO^-} + m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{OH^-} = m_{MEAH^+} + m_{H^+} \quad (15)$$

2.4. Thermodynamic Framework

In $(CO_2 - MEA - H_2O)$ system, there are only four main species, pure alkanolamine MEA, H_2O, HCO_3^- and $MEACOO^-$ in liquid phase at equilibrium state. One can note from literature: the concentration of molecular CO_2, and ionic CO_3^{2-} and OH^- species in the liquid phase are very low compared to the other species present in the equilibrated liquid phase. It was found that not taking into account of the free molecule of CO_2, OH^- and CO_3^{2-} ions in the liquid phase for CO_2 loading below 1 does not lead to a significant error in predictions of vapor-liquid equilibria [12, 13, 14]. Consequently, it is supposed that almost all of the dissolved CO_2 is converted into HCO_3^- ions.

3. Vapor phase equation

It is assumed a physical solubility (Henry's law) relation for the (noncondensible) acid gases and a vapor pressure relation for water. Thus, the following relations apply:

$$\phi_{CO_2}.y_{CO_2}.P = H_{CO_2}.\gamma_{CO_2}.m_{CO_2} \quad (16)$$

Thus :

$$P_{CO_2} = \frac{H_{CO_2}}{\phi_{CO_2}}.\gamma_{CO_2}.m_{CO_2} \quad (17)$$

Where ϕ_{CO_2} is the fugacity coefficient of CO_2, y_{CO_2} is mole fraction, H_{CO_2} is a Henry's constant for the acid gas in pure water, P is the total pressure. MEA is considered as non-volatile compound.

The truncated virial equation of state is used to evaluate pressure of the vapor phase considering the non-ideality for molecular species.

Substitution and arrangements of equilibrium constants equations 6, 7, 9 and balance equations 13-15 with equation 17, the expression for partial pressure of CO_2 may be given by the following relation (Mondal [15]):

$$P_{CO_2} = \frac{H_{CO_2}}{\phi_{CO_2}}.\frac{K_1}{K_2K_4}.\frac{\gamma_{MEAH^+} m_{MEAH^+} \gamma_{MEACOO^-} m_{MEACOO^-}}{(\gamma_{MEA} m_{MEA})^2} \quad (18)$$

4. Activity coefficient model

In this work, two models are applied for modeling solutions containing electrolytes.

4.1. Uniquac model

The extended UNIQUAC thermodynamic model applied to electrolyte systems was considered to calculate the activity coefficients for all species (Thomsen et al [16]).The model consists of three terms: a combinatorial, a residual and the electrostatic term (Debye-Huckel).

The Debye-Huckeltermused in the extended UNIQUAC model is given by the expression:

$$\left(\frac{G^E}{RT}\right)_{D-H} = -x_w M_w \frac{4A}{b^3}\left[ln\left(1+b\sqrt{I}\right) - b\sqrt{I} + \frac{b^2 I}{2}\right] \quad (19)$$

x_w and M_w are the mole fraction and molar mass of water, respectively. The parameter b is equal to 1.5 ($kg^{1/2}$ $mol^{-1/2}$). A is the Debye-Huckelparameter given by:

$$A = \frac{F^3}{4\pi N_A}\left[\frac{d}{2(\varepsilon_0 \varepsilon_r RT)^3}\right]^{(1/2)} \quad (20)$$

Where F (C mol^{-1}) is the Faraday's constant, N_A (mol^{-1}) is Avogadro's number, ε_0 ($C^2 J^{-1} m^{-1}$) is the vacuum permittivity, R (J mol^{-1} K^{-1}) is the gas constant and T(K) is the temperature, d(kg m^{-3}) and $\varepsilon_r$are the density and the relative permittivity of the solution, respectively.

1 (mol/kg H_2O) isthe ionic strength.

The electrostatic part as contributions to the activity coefficients for ions and for water is given by:

$$ln\,\gamma_i^{D-H} = -z_i^2 . A. \frac{I^{\frac{1}{2}}}{\left(1 + b. I^{\frac{1}{2}}\right)} \quad (21)$$

$$ln\,\gamma_w^{D-H} = M_w . 2A. \frac{\left\{1+b.I^{\frac{1}{2}} - \left(1+b.I^{\frac{1}{2}}\right)^{-1} - 2ln\left(1+b.I^{\frac{1}{2}}\right)\right\}}{b^3} \quad (22)$$

The combinatorial and the residual parts as contribution to the activity coefficient of component i are:

$$ln\gamma_i^C = ln\left(\frac{\phi_i}{x_i}\right) + 1 - \frac{\phi_i}{x_i} - \frac{Z}{2} . q_i\left[ln\left(\frac{\phi_i}{\theta_i}\right) + 1 - \frac{\phi_i}{\theta_i}\right] \quad (23)$$

$$ln\gamma_i^R = q_i\left[1 - ln\left(\sum_l \theta_l \Psi_{li}\right) - \sum_l\left(\theta_j \Psi_{ij} / \sum_l \theta_l \Psi_{lj}\right)\right] \quad (24)$$

Where x_i is the mole fraction, ϕ_i is the volume fraction, and$\theta_i$is the surface area fraction of component i.

$\Psi_{ji}$is defined by :

$$\Psi_{ji} = exp\left[-\left(u_{ji} - u_{ii}\right)/T\right] \quad (25)$$

With u_{ji} (interaction parameters) are assumed to be temperature dependent given by :

$$u_{ji} = u_{ji}^0 + u_{ji}^T(T - 298.15) \quad (26)$$

The expression for the solute activity coefficient and for the water activity coefficient is calculated by:

$$ln\,\gamma_i^* = ln\left(\gamma_i^C/\gamma_i^{C,\infty}\right) + ln\left(\gamma_i^R/\gamma_i^{R,\infty}\right) + ln\,\gamma_i^{D-H} \quad (27)$$

$$ln\gamma_w = ln\,\gamma_w^C + ln\,\gamma_w^R + ln\,\gamma_w^{D-H} \quad (28)$$

4.2. Pitzer model

The Pitzerequation(32) is used [17]:

$$ln\,\gamma_i = -A_\phi z_i^2\left(\frac{\sqrt{I}}{1+1.2\sqrt{I}} + \frac{2}{1.2}ln\left(1+1.2\sqrt{I}\right)\right) + 2\sum_{j\neq w} m_j\left(\beta_{ij}^0 + \frac{\beta_{ij}^1}{2I}\left[1 - \left(1+2\sqrt{I}\right)exp\left(-2\sqrt{I}\right)\right]\right) - z_i^2 \sum_{j\neq w}\sum_{k\neq w} m_j m_k \frac{\beta_{jk}^1}{4I^2}\left[1 - \left(1+2\sqrt{I}+2I\right)exp\left(-2\sqrt{I}\right)\right] \quad (29)$$

Where I is ionic strength of the solution, z_i and m_i are charge and molality of species i. $A_\phi$is Debye-Huckel limiting slope of osmotic coefficient and β_{ij}^0 and β_{ij}^1 are interaction parameters. $A_\phi$is calculated using the equation proposed by Chen and al [18].

5. Data regression

In this work, the solubility data of CO_2 in aqueous solutions of MEA, in a wide range of CO_2 partial pressure and temperatures and below a carbon dioxide loading of 1.0 mol CO_2/mol amine, have been used to estimate the interaction parameters by regression analysis. The solubility data [6,7,18, 21] were used to extend the range of application of the model.

The data regressions were carried out in the temperature range from (313 to 393) K. The objective function for regression is given by:

$$\Psi = \sum\left|\frac{\left\{\left(P_{CO_2}\right)_{cal} - \left(P_{CO_2}\right)_{exp}\right\}}{\left(P_{CO_2}\right)_{exp}}\right| \quad (30)$$

The numerical values of interaction parameters were investigated by minimizing the difference observed between the measured values of equilibrium partial pressure of CO_2 in alkanolamine solutions and the values predicted by the model (UNIQUAC or Clegg-PITZER).

The objective function has been optimized using a hybrid algorithm (the unconstrained nonlinear minimization/genetic algorithm).

6. Results

UNIQUAC volume parameters r and surface area parameters q for MEA, H_2O, $MEAH^+$, $MEACOO^-$ and HCO_3^- are given in Tab. 2. Interaction parameters $\mathbf{u^0_{ji}}$ and $\mathbf{u^t_{ji}}$ for UNIQUAC model and $\boldsymbol{\beta^0_{i,j}}$ and $\boldsymbol{\beta^1_{i,j}}$ for Pitzer model are adjusted with experimental points using the literature expression of equilibrium constant $\mathbf{K_1}$, K_3 and $\mathbf{K_4}$ correlation cited above.

Table2: The constants of equation (11) (Molality Scale)

Components	r	q	Source
H_2O	0.9200	1.4000	[20]
MEA	4.2800	4.2800	[5]
$MEAH^+$	1.0241	2.5150	[18]
$MEACOO^-$	1.0741	0.1106	[18]
HCO_3^-	9.157	6.3461	[18]

In this work 15% and 30% mass MEA solutions in the temperature range of 313-393K were considered, as well as the experimental data of CO_2 solubility from several workers (Tong et al; 2012, Wagner et al; 2013, Aronu et al; 2011and Ma'mun et al; 2005), and also from of this study have been compared and presented in Figures 1-5.

From Fig. 1-3, one can conclude that the UNIQUAC model show a good ability to predict partial pressure of CO_2 with the experimental data taken from Wagner et al [7] and Aronu et al [18] especially at temperature of 313K and a concentration of 15% mass of MEA. Figure 4, show that the UNIQUAC model provides good results for an aqueous solution of 30 mass% of MEA at 313K as compared to that for a temperature of 393K.

From Fig. 1 one can observe that the Clegg-PITZER Model underestimates the partial pressures of CO_2 for the data of Wagner et al [7] for 15 and 30 mass% solution at 313K comparatively to UNIQUAC model especially when the CO_2 loading is high.

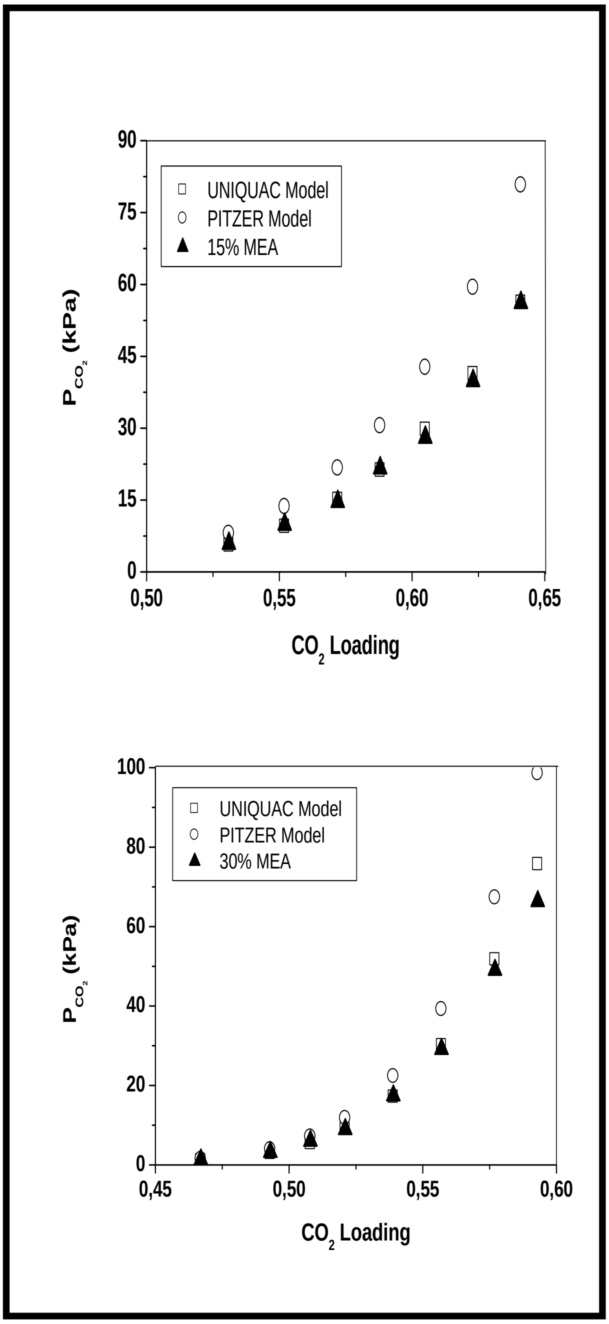

Figure 1. CO_2 partial pressure as function of loading α_c in aqueous 15 and 30 mass% MEA at 313 K, ▲: Experimental data of Wagner et al [7]

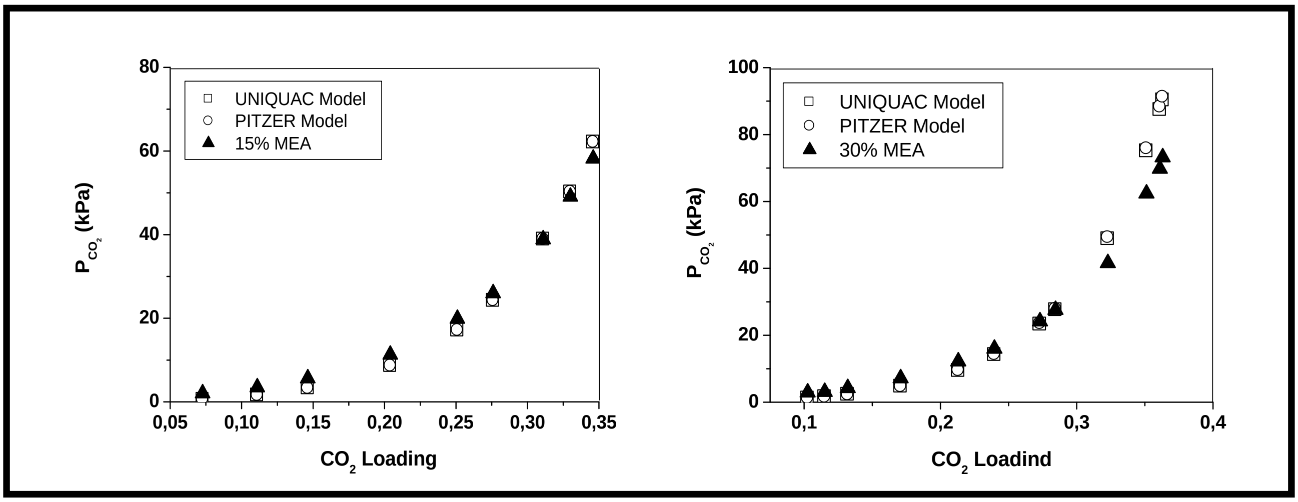

Figure 2. CO_2 partial pressure as function of loadingα ,in aqueous 15 and 30 mass% MEA at 393 K, ▲Experimental data of Wagner et al [7]

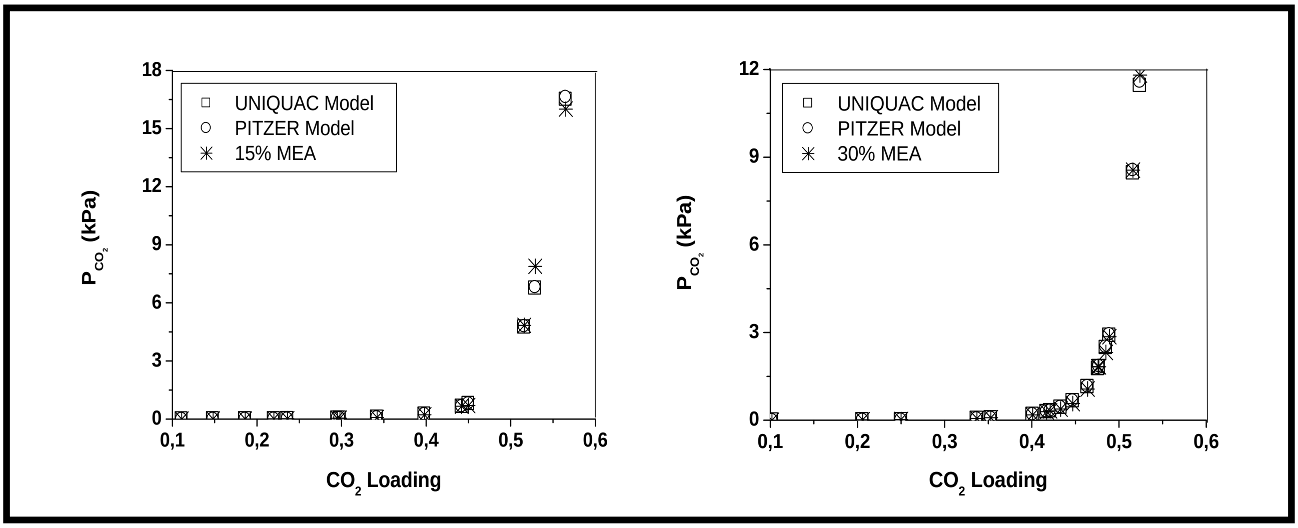

Figure 3. CO_2 partial pressure as function of loadingα , in aqueous 15 and 30 mass% MEAat 313 K*: Experimental data of Aronu et al [18].

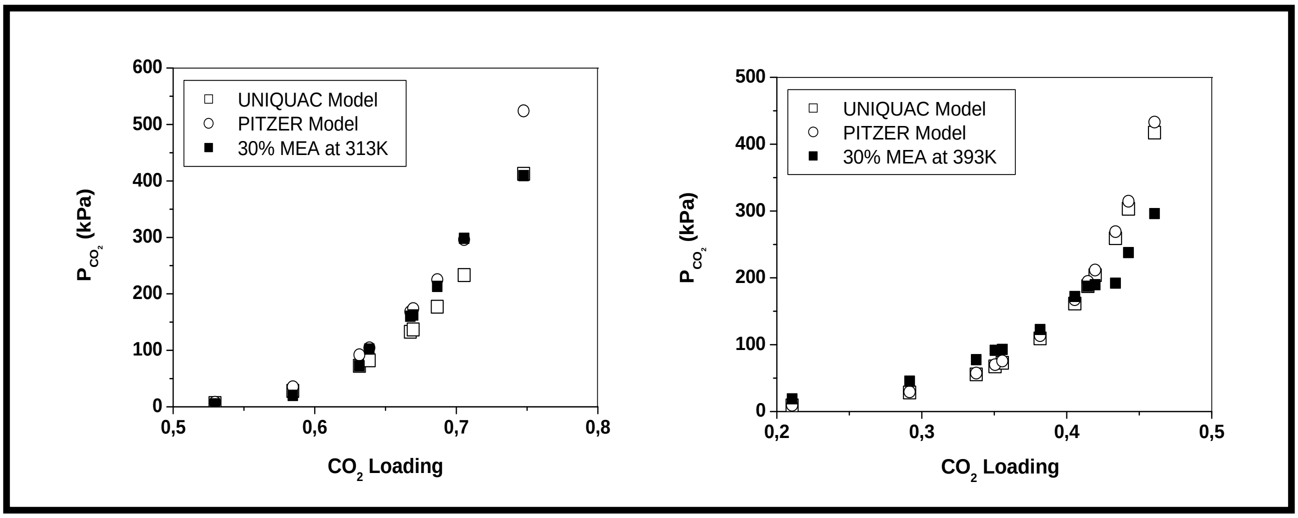

Figure 4. CO_2 partial pressure as function of loadingα , in aqueous 30 mass% MEAat 393 K;■ Experimental data of Tong et al [6].

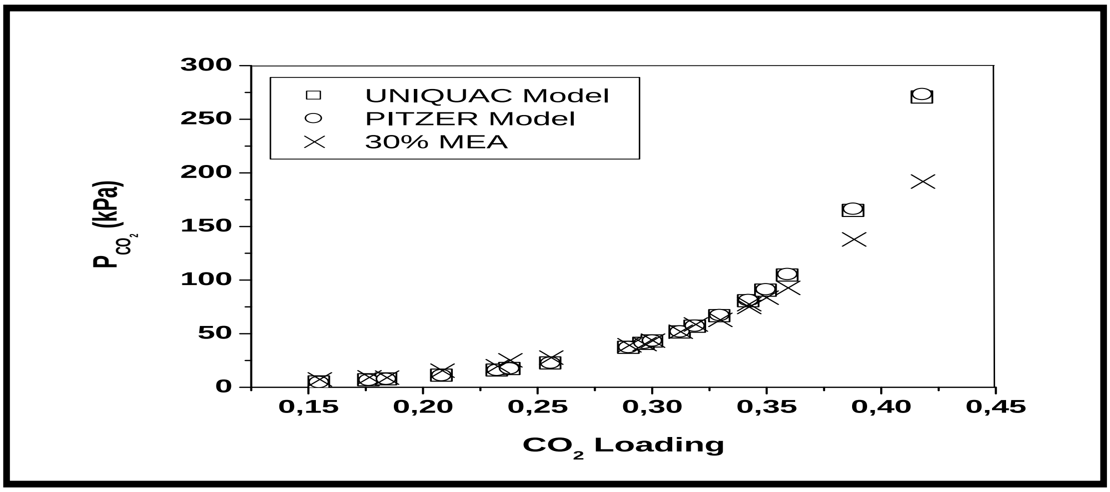

Figure 5. CO_2 partial pressure as function of loadingα_c in aqueous 30 mass% MEAat 393 K;× : Experimental data of Ma'mun et al [21].

7. Conclusion

Two thermodynamic models were considered to correlate solubility data from literature. The extended UNIQUAC thermodynamic model and modified Clegg-PITZER model were applied to molecular and ionic species described by equilibrium relationships of equations 1 to 5 for calculating activity coefficients, these coefficients may be calculated by the accurate knowledge of interaction parameters values. The solubility data regression uses complex optimization method (hybrid method) following the steps of the algorithm given by (Kabouche et al, 2011) [22]. The fugacity coefficient was calculated using the Virial equations of state. As conclusion, in this work, the models give good correlation particularly when the loading is low. However the UNIQUAC model gives the more suitable results comparatively to PITZER model. As Hybrid algorithm, the genetic algorithm (GA) and as deterministic model, the Nelder-Mead Simplex (NMS) method was used. In general, the optimization models used in this work gives good approximations compared with experimental data for system (CO_2 + H_2O + MEA) at 313 K and 333 K considering the solubility of CO_2 in aqueous solutions of 15 and 30 mass % of MEA especially for low values of CO_2 loading for modified Clegg-Pitzer model and good approximations were given by extended UNIQUAC model.

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