Vapour-Liquid Equilibrium Prediction of Carbon Dioxide in an Aqueous Alkanolamine Solution Using Deterministic and Stochastic Algorithms

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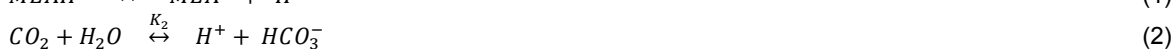kabouche66@yahoo.fr

Carbon dioxide capture by reactive absorption with aqueous alkanolamines has a great importance in reducing CO_2 emissions. The development or the choice of thermodynamic models for (CO_2 + H_2O + alkanolamine) systems presents some specific difficulties. In this work PITZER model have used to correlate and predict the vapour-liquid equilibrium of CO_2 in aqueous monoethanolamine (MEA) solutions, interaction parameters were calculated by using simplex (deterministic algorithm) and genetic algorithms (stochastic algorithm). The solubility of CO_2 in aqueous solutions of 15, 30, 45 and 60 mass % of MEA has been considered over several temperatures and CO_2 partial pressures. The predicted results of vapour-liquid phase equilibrium have been found to be in good agreement with the experimental measurements.

1. Introduction

CO_2 capture by absorption with aqueous alkanolamines solutions is considered as an important technology to reduce CO_2 emissions from fossil-fuel-fired power plants and to help alleviate global climate change (Zhang et al., 2009). Chemical absorption of CO_2 can be used in post-combustion (Athanasios et al., 2014). Kinetic studies of CO_2 by chemical absorption (Molina and Bouallou, 2013) are a key step to give rigorous expression of several parameters that one can cite the very important equilibrium constant. The development of thermodynamic models for (CO_2 + H_2O + alkanolamine) systems is quite complex. The more rigorous models that take into account non-ideality are based on a system of equations for chemical equilibria (Kabouche et al., 2005), phase equilibria, charge, and mass balances. In this work, the fugacity coefficients ϕ were obtained from a truncated virial equation of state and the activity coefficients γ calculated using a Pitzer model in order to correlate and predict the vapour-liquid equilibrium of the (CO_2+H_2O+MEA) system. The required equilibrium constant for chemical reactions were obtained from literature. Two different literature sources giving correlations of the equilibrium constant (as function of temperature) of deprotonation of MEA, hydration of CO_2 and dissociation of carbamate were used in this work to adjust the model cited above.

2. Modelling of phase equilibria

When considering dissolution of CO_2 in aqueous MEA solution, chemical reactions (1) to (5) may take place in the liquid phase:

$$MEAH^+ \overset{K_1}{\leftrightarrow} MEA + H^+ \tag{1}$$

$$CO_2 + H_2O \overset{K_2}{\leftrightarrow} H^+ + HCO_3^- \tag{2}$$

$$HCO_3^- \overset{K_3}{\leftrightarrow} H^+ + CO_3^{2-} \tag{3}$$

$$MEACOO^- + H_2O \overset{K_4}{\leftrightarrow} MEA + HCO_3^- \tag{4}$$

$$H_2O \overset{K_5}{\leftrightarrow} H^+ + OH^- \tag{5}$$

Usually the Henry's law and the equilibrium reaction constants are considered as a function of temperature. The general dependency of these constants to temperature is given by the following equation:

$$ln \left(K_N \ or \ H\right) = \frac{a}{T} + b. \ln T + c.T + d, \quad N = 1 \ to \ 5 \tag{6}$$

The corresponding coefficients for reactions (1) to (5) are summarized in table (1). The molality scale values of the coefficients are given in this Table (1).

Table 1: Coefficients of Eq(6) for the equilibrium constant K_N

Reaction	a	b	c	d	°K	literature
1	-17.3	0	0.05764	-38.846	293-353	(Hamborg and Versteeg,2009)
2	-12092.1	-36.7816	0	235.482	273-498	(Edwards et al,1978)
3	-12431.7	-35.4819	0	220.067	273-498	(Edwards et al,1978)
4	-1545.3	0	0	2.151	293-323	(Aroua et al,1999)
5	-13445.9	-22.4773	0	140.932	273-498	(Edwards et al,1978)
H_{CO_2}	-9624.4	-28.749	0.01441	192.876	273-473	(Rumpf and Maurer,1993)

Another alternative to calculate the equilibrium constants using the parameters of Table 2 is given by the following equation:

$$ln \left(K_N \ or \ H\right) = a + \frac{b}{T} + c. \ln T + d. T + e/T^2 \tag{7}$$

Table 2: Coefficients of equation (7) for the equilibrium constant K_N

Reaction	a	b	c	d	e	°K	literature
1	- 1.73782	- 6092.85	0	0.001157	0	273 - 398	(Hasse et al ,2013)
2	-1,203.01	68,359.6	188.444	- 0.206424	- 4,712,910	273 - 673	(Patterson et al, 1982)
4	- 5.9680	2888.6	0	0	0	293 - 333	(McCann,2012)

3. Thermodynamic Framework

In $(CO_2 - MEA - H_2O)$ system, the existence of neutral specie pure alkanolamine MEA and H_2O, and ionic species – protoned alkanolamine, HCO_3^- and carbamate ion $MEACOO^-$ in the equilibrated liquid phase have been considered. For simplicity, the free molecular species CO_2 and the ionic species CO_3^{-2} and OH^- in the liquid phase have been neglected since concentration of these species are very low compared to the other species present in the equilibrated liquid phase. Several previous workers, one can cite (Posey, 1996), have observed that neglecting the concentration of free molecular CO_2, and OH^- and CO_3^{-2} ions in the liquid phase in this system for CO_2 loading below 1.0 does not result in significant error in the VLE predictions. It is thus assumed that almost all of the dissolved CO_2 is converted into HCO_3^- ions. It is also assumed a physical solubility (Henry's law) relation for the (noncondensible) acid gases and a vapour pressure relation for water. (if the system contains other volatile species, such as hydrocarbons, these can be accounted by additional isofugacity relations based, for example, on Henry's law for sparingly soluble components, or on vapour pressures for condensibles). Thus, the following relation is applied:

$$\phi_{CO_2}. y_{CO_2}. P = H_{CO_2}. \gamma_{CO_2}. m_{CO_2} \tag{8}$$

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. The partial pressure of carbon dioxide is calculated by the following relation (Mondal, 2009):

$$P_{CO_2} = \frac{H_{CO_2}}{\phi_{CO_2}}. \frac{K_1 K_4}{K_2} . \frac{\gamma_{MEAH^+} m_{MEAH^+} \gamma_{MEACOO^-} m_{MEACOO^-}}{(\gamma_{MEA} \ m_{MEA})^2} \tag{9}$$

4. Activity coefficient model

Activity coefficients γ_i of ionic and molecular species i present in solution are calculated using the Pitzer equation as modified by (Edwards et al., 1978).

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

$$-z_i^2\sum_{j\neq w}\sum_{k\neq w}m_j m_k\frac{\beta_{jk}^1}{4I^2}\left[1-(1+2\sqrt{I}+2I)exp(-2\sqrt{I})\right] \tag{10}$$

Where I is ionic strength of the solution, z_i and m_i are charge and molality of species i. A_ϕ is Debye-Huckel limiting slope of osmotic coefficient and β_{ij}^0 and β_{ij}^1 are interaction parameters. A_ϕ is calculated using equation (11) proposed by (Chen et al,1982):

$$A_\phi = -61.44534\,exp\left(\frac{T-273.15}{273.15}\right)+2.864468exp\left[\frac{T-273.15}{273.15}\right]^2+183.5379\,ln\left(\frac{T}{273.15}\right)$$
$$-0.6820223(T-273.15)+7.87595.10^{-4}(T^2-273.15^2)$$
$$+58.95788\left(\frac{273.15}{T}\right) \tag{11}$$

Activity of water is derived from equation (10) using the Gibbs-Duhem equation:

$$ln\,a_w = \frac{M_w}{1000}\left(\frac{2A_\phi I^{1.5}}{1+1.2\sqrt{I}}-\sum_{i\neq w}\sum_{j\neq w}m_i m_j[\beta_{ij}^0+\beta_{ij}^1 exp(-2\sqrt{I})]-\sum_{i\neq w}m_i\right) \tag{12}$$

Where M_w is molecular weight of water.

5. Data regression

In this work, the solubility data of CO_2 in aqueous alkanolamine solutions of various concentrations, in a wide range of CO_2 partial pressure and temperatures and below a CO_2 loading of 1.0 mol CO_2 /mol amine, have been used to estimate the interaction parameters by regression analysis. The data reported by (Aronu et al, 2011) were used to extend the range of application of the model.

The data regressions were carried out at 313 K and 333 K. The objective function (OF) used for optimization is given by:

$$OF = \sum\left|\frac{\left\{(P_{CO_2})_{cal}-(P_{CO_2})_{exp}\right\}}{(P_{CO_2})_{exp}}\right| \tag{13}$$

We investigate the numerical values of interaction parameters that will minimize (OF) the difference between the measured values of equilibrium partial pressure of CO_2 over alkanolamine solutions and the values calculated from the model. The objective function chosen in this work takes care of giving uniform weightage throughout the entire range of partial pressure.

The objective function has been optimized by the unconstrained nonlinear minimization Nelder-Mead Simplex method (NMS) and Genetic algorithm (GA) (Kabouche et al., 2012).

6. Results and discussions

Interaction parameters $\beta_{i,j}^0$ and $\beta_{i,j}^1$ are adjusted with experimental data (points) using two different model (Eq. 6 and 7) from the literature to calculate K_1, K_2 and K_4 correlations cited above. Two different kinds of optimization techniques; Deterministic (NMS) and Genetic algorithm (GA) have been used for predicting phase equilibria. For the $(CO_2-MEA-H_2O)$ system, the interaction parameters were determined using solutions of 15, 30, 45 and 60 mass % of MEA at 313 K and 333 K. The literature data has been taken from (Aronu et al., 2011) and model of Eq (9) was used. The equilibrium constants were calculated using two different formula (6) and (7), a discrepancy can be noted in the figures between the curve in solid lines (model of Eq(7)) and the curve in dashed lines (model of Eq(6)), the best results were obtained for the curve in solid lines in figure 1 to 4 using NMS algorithm and figure 8 to 10 using GA algorithm for the temperature 313 K however the results in figures 5 and 6 for temperature 333 K using NMS algorithm and in Figures 7 and 12 for temperature 333 using GA algorithm shows that the model in dashed lines gives the best results. In general the two algorithms give good results using the model of Eq(7) rather than of Eq(6).
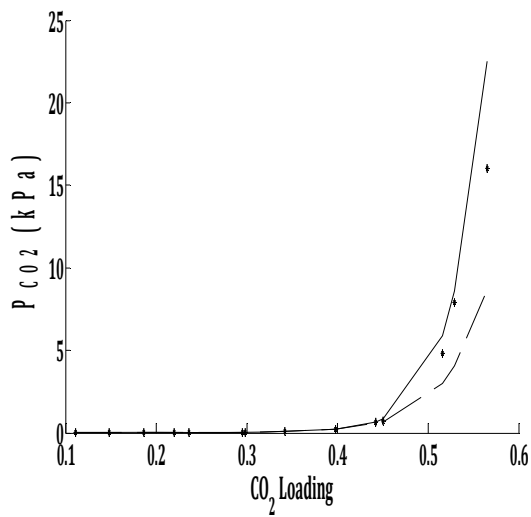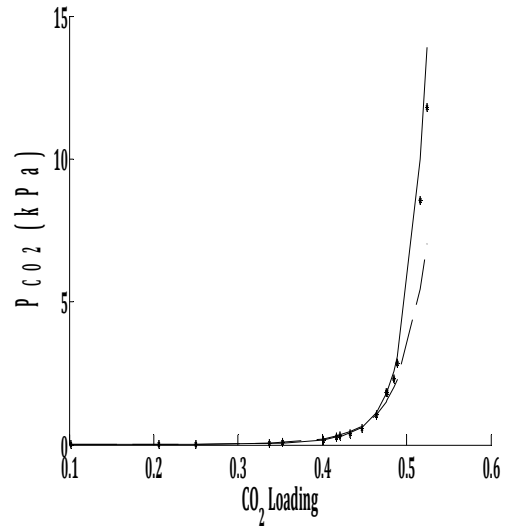
Figure1NMS method %MEA=15, T=313 K
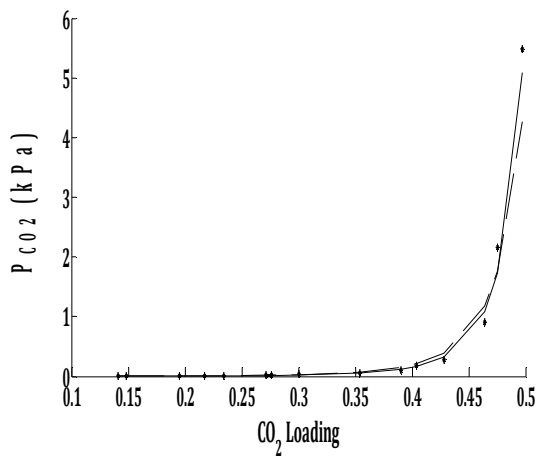

Figure 2 NMS method % MEA=30, T=313 K

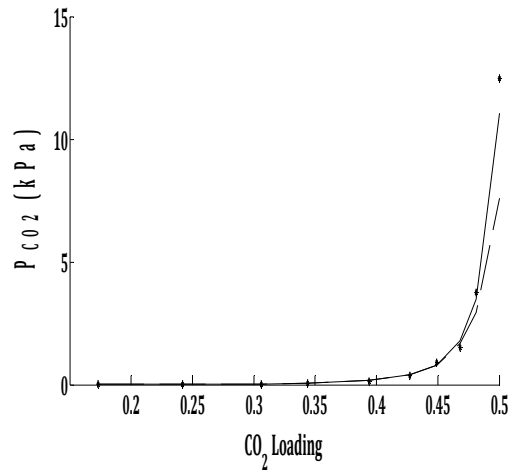*Figure 3: NMS method %MEA = 45, T = 313 K*

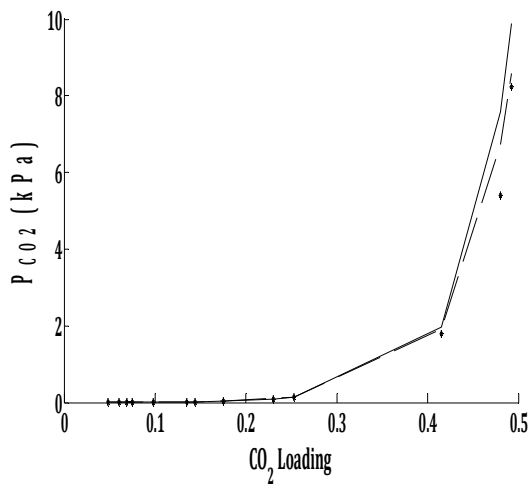*Figure 4: NMS method % MEA = 60, T = 313 K*

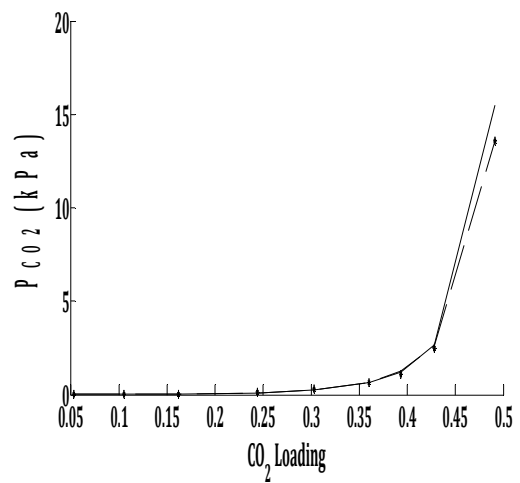
Figure 5: NMS method %MEA = 15, T = 333 K
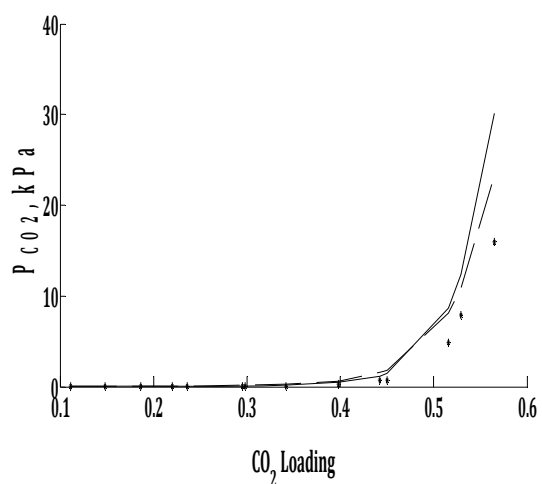

Figure 6: NMS method % MEA = 30, T =333 K
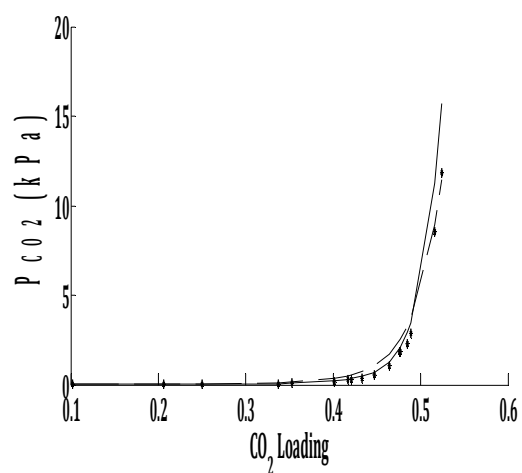
Figure 7: GA method %MEA = 15, T = 313 K
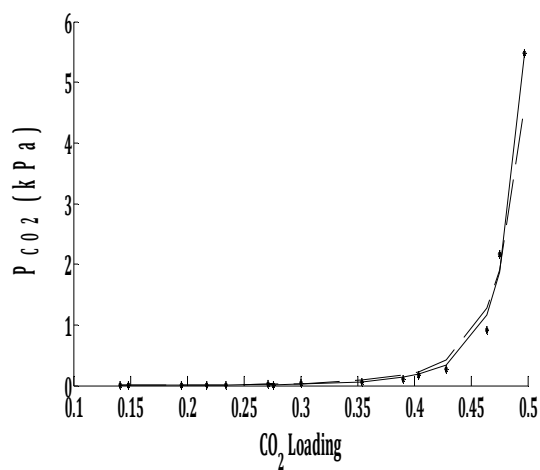
Figure 8: GA method % MEA = 30, T = 313 K
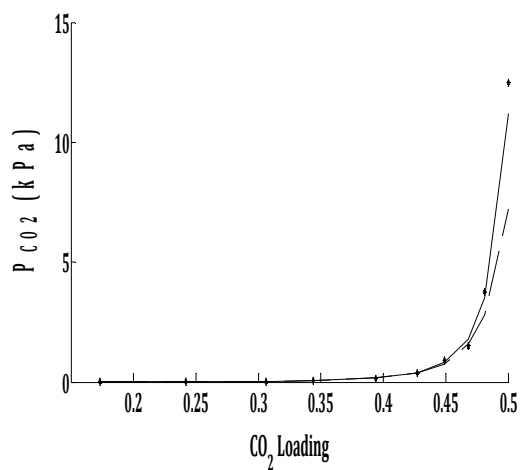
Figure 9: GA method %MEA = 45, T = 313 K

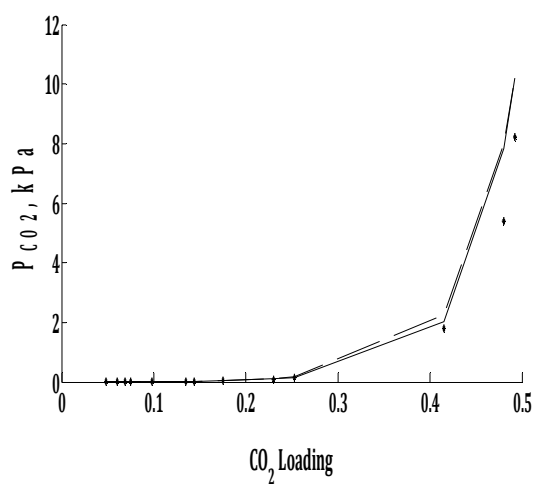Figure 10: GA method % MEA = 60, T = 313 K
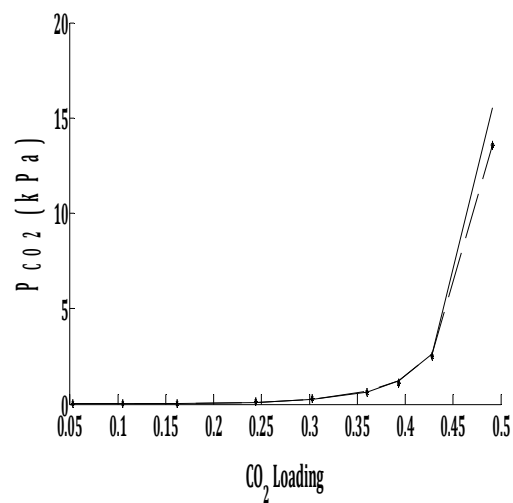
Figure 11: GA method %MEA = 15, T = 333 K

Figure 12: GA method % MEA = 30, T = 333 K

7. Conclusion

In this work, a thermodynamic model was used to correlate solubility data (Aronu et al, 2011) considering the effect of MEA deprotonation, hydration of CO_2 and dissociation of carbamate equilibrium constants. The thermodynamic model is based on PITZER equations from Eq(10) to Eq(12). The model was applied to molecular and ionic species generated by the equilibrium reactions of equations A to E for calculating activity coefficients after regression of solubility data (using optimization methods). The fugacity coefficient is calculated using the virial equations. Finally, in this work, two models for calculating the equilibrium constants were considered; in general the results show that the model in Eq(7) gives the best results. As stochastic algorithm, the genetic algorithm (GA) is used and as deterministic model, the Nelder-Mead Simplex (NMS) method is used. The two optimization models used in this work give a quite good approximations to the experimental data for system (CO_2 + H_2O + alkanolamine) at 313 K and 333 K considering the solubility of CO_2 in aqueous solutions of 15, 30, 45 and 60 mass % of MEA.

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