CO_2 capture modeling in aqueous solution of Methyldiethanolamine +Hexylamine

Ammar Mehassouel[(1)], Chakib Bouallou[(2)]

[(1)]*Université d'Ouargla, Faculté des Hydrocarbures, des Energies Renouvelables et des Sciences de la Terre et*

de L'univers, département de production, Algérie

[(2)] *MINES ParisTech, PSL Research University, CES -Centre d'efficacité énergétique des systèmes- 60,*

Boulevard Saint Michel, Paris, France

am_me18@yahoo.fr

Abstract— The aim of this work is to establish a thermodynamic model using NRTL Electrolyte Aspen Plus ™ model, this model allows to simulate the CO_2 capture by an aqueous mixture of Methyldiethanolamine (MDEA) and Hexylamine (HA), CO_2 solubility data in the mixture of Methyldiethanolamine and Hexylamine were obtained by our experiment and were introduced in Aspen Plus™, the binary interaction parameters and electrolyte pairs as well as the parameters of the kinetic constants reaction between CO_2 and aqueous solution with mass concentration MDEA 37wt% + HA 3wt% + H_2O have been regressed. The results obtained shows that our model represents the experimental data with an error of 17%.

Key-Words: Carbon dioxyde capture, modeling, Methyldiethanolamine, Hexylamine

I. INTRODUCTION

The main source of CO_2 (greenhouse gas) is the burning of fossil fuels such as coal, oil and gas in power plants, for transportation, in homes, offices and industry. Fossil fuels provide more than 80% of all energy demands in the world. These large amounts of carbon dioxide are released into the atmosphere by many Major industries around the globe (power generation, manufacturing in steel, cement manufacturing, etc.). These energies currently emit 29 billion tons per year of carbon dioxide [1].

Current trends are leading to temperatures well above 2 ° C by the end of the century. The acceleration of the phenomena with the observation of a greater speed of degradation and change calls for courageous decisions by governments, parliaments and the international community, which together face one of the most serious challenges known for the planet and for humanity. In this context, it is necessary to reduce global greenhouse gas emissions and limit the increase in global average temperature to less than 2 ° C above pre-industrial levels, as stated in the target of the United Nations Framework Convention on Climate Change (UNFCCC). Increasing the temperature of the earth has a negative effect on the environment. For this

reason, it is necessary to act and develop technologies to minimize greenhouse gas emissions; among these promising technologies is the capture and storage of CO_2. This technology is based on three main steps:

- CO_2 Capture: this is the most important and costly step, CO_2 is captured and compressed.

– CO_2 Transport: After capture, the CO_2 must be transported to the place of storage

– CO_2 storage: CO_2 is stored in unutilized coal seams, in oil or gas deposits at the end of exploitation or in deep saline aquifers. In the field of Post-combustion capture, the most usual method is the use of aqueous amine solutions. The choice of the thermodynamic model is essential to represent well the solubility data of the mixture. The NRTL electrolyte model is a model with an activity coefficient that can be used to represent aqueous electrolytic solutions. It calculates the activity coefficients of ionic or non ionic species.

II. ELECTROLYTE NRTL MODEL

This model is suitable for calculating electrolytic system activity coefficients using interaction parameters between different species; the liquid phase activity coefficient of each constituent is calculated from Gibbs excess energy.

$$\ln(\gamma_i) = \frac{1}{RT}\left[\frac{\partial(n_i g^{ex})}{\partial n_i}\right]_{T,P,n_{j\neq i}} \quad (I)$$

Gibbs excess energy is the sum of local interactions $g^{ex,\ lc}$ and long-distance interactions $g^{ex,\ LR}$
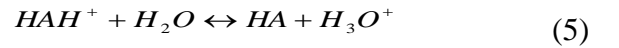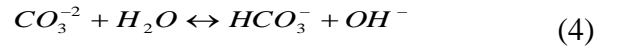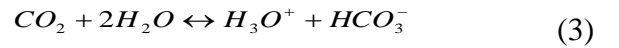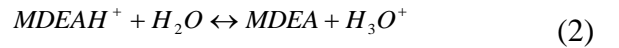
$$g^{ex} = g^{ex.LR} + g^{ex.lc} \quad (II)$$
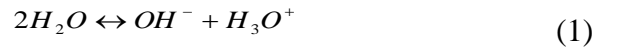
$$g^{ex.LR} = -\left(\sum_k x_k\right)\left(\frac{1000}{M_B}\right)^{1/2}\left(\frac{4A_\varphi I_x}{\rho}\right)\ln\left(1+\rho I_x^{1/2}\right) \quad (III)$$

$$+\frac{Q_e^2}{2kT}\left(\frac{1}{\varepsilon}-\frac{1}{\varepsilon_w}\right)\left(\frac{\sum_i x_i z_i^2}{r_i}\right)10^{-2}$$

This last equation takes into account the Pitzer-Debye-Huckel term from the NRTL model and the Born term

$$g^{ex.LC} = \left(\sum_B x_B\right)\left(\frac{\sum_J X_J * G_{JB} * \tau_{JB}}{\sum_k X_k * G_{kB}}\right) + \sum_C x_C \sum_a \left(\frac{X_{a'}}{\sum_{a'} X_{a'}}\right)\frac{\sum_J X_J * G_{JC,a'C}}{\sum_k X_k * G_{kC,a'C}} +$$

$$\sum_a x \sum_C \left(\frac{X_{C'}}{\sum_{C'} X_{C'}}\right)\frac{\sum_J X_J G_{Ja,C'a}\tau_{Ja,Ca'}}{\sum_k X_k G_{ka,C'a}} \quad (IV)$$

III. METHODOLOGY

The different CO_2 reactions with the mixture are as follows:

$$2H_2O \leftrightarrow OH^- + H_3O^+ \quad (1)$$

$$MDEAH^+ + H_2O \leftrightarrow MDEA + H_3O^+ \quad (2)$$

$$CO_2 + 2H_2O \leftrightarrow H_3O^+ + HCO_3^- \quad (3)$$

$$CO_3^{-2} + H_2O \leftrightarrow HCO_3^- + OH^- \quad (4)$$

$$HAH^+ + H_2O \leftrightarrow HA + H_3O^+ \quad (5)$$

$$HACOO^- + H_2O \leftrightarrow HA + HCO_3^- \quad (6)$$

The objective function is to have the chosen thermodynamic model adjusted to the experimental data for the solvent MDEA37wt% + HA 3wt%. The default regression method at

Aspen Plus^{TM} is the maximum likelihood. In this process, the objective function is given by:

$$F_{obj} = \sum_{n=1}^{NGR} PG_n \sum_{i=1}^{ND_n} \left[\begin{array}{l} \left(\dfrac{T_{cal,i} - T_{exp,i}}{\sigma_{T,i}}\right)^2 + \left(\dfrac{P_{cal,i} - P_{exp,i}}{\sigma_{P,i}}\right)^2 \\ + \sum_{j=1}^{NC_n-1} \left(\dfrac{x_{cal,i,j} - x_{exp,i,j}}{\sigma_{x,i,j}}\right)^2 + \sum_{j=1}^{NC_n-1} \left(\dfrac{y_{cal,i,j} - y_{exp,i,j}}{\sigma_{y,i,j}}\right)^2 \end{array} \right] \quad (V)$$

With F_{obj} the objective function, NGR the number of groups of data, PGn the weight of the group n, NDn the number of experimental points in the data group n, NC_n the number of compounds present in the data group n and Z, σ i the standard deviation at point i for the variable z. Experimental CO_2 absorption data from the MDEA37wt% + HA3wt% mixture that we obtained [2],[3], were entered in Aspen Plus^{TM} as a data group. A standard deviation can be specified for each experimental point. The equilibrium partial pressure of CO_2 was used instead of the total pressure. A molar fraction of CO_2 in the gas phase of 1 was therefore specified and that in the liquid phase are calculated knowing the experimental data. The standard deviation for each variable is the same. Standard deviations can be given in absolute or relative value. A sufficiently large deviation for the pressure was chosen to improve the temperature estimation, variable for which the uncertainties are much lower than for the pressure. Table 1 below shows the standard deviation for

each variable. These settings are taken by default by Aspen Plus^{TM} software

Table 1: Standard deviation for each variable

σ_T (K)	σ_P (%)	σ_x (%)	σ_y (-)
0.2	10%	0.1%	0.0001

The regression of the data is performed considering only the apparent composition water, MDEA and HA. Two groups of parameters were regressed, the group of equilibrium constant parameters and the group of binary interaction parameters between MDEA and Hexylamine (HA), as well as the parameters of the electrolyte pairs between a molecule and ionic species. In the equilibrium model ENRTL, equilibrium constants are related to temperature by the following relation:

$$k = \exp(A + \frac{B}{T}) \quad (VI)$$

On the other hand the binary interactions are related to the temperature according to the relation

$$\tau = a + \frac{b}{T} \quad (VII)$$

We estimated the parameters of the kinetic constants of the reactions (5) and (6). Parameters A and B as well as a and b are estimated by Aspen Plus^{TM} software.

IV.RESULTS

The regression of the various parameters is grouped in the following Table 2:

Table 2: adjusted parameters

parameters	A	B
k_{66}	0.00018	-1000
k_{67}	0.00018	-1000
$\tau_{HA,CO2}$	1.60	9416.64
$\tau_{MDEA,HA}$	1.79	542.67
$\tau_{H2O,HA+,HCO3-}$	8.0009	$1.12*10^{-7}$
$\tau_{HA+,HCO3-,H2O}$	-3.99	$1.12*10^{-7}$
$\tau_{CO2,HA+,HCO3-}$	8.0009	$1.12*10^{-7}$
$\tau_{HA+,HCO3-,CO2}$	-3.99	$1.12*10^{-7}$
$\tau_{MDEA,HA+,HCO3-}$	8.0009	0.000112
$\tau_{,HA+,HCO3-,MDEA}$	-3.99	0.000112
$\tau_{MDEA+,HCO3-,HA+,HCO3-}$	$3.35*10^{5}$	$3.35*10^{5}$
$\tau_{HA+,HCO3-,MDEA+,HCO3-}$	$3.35*10^{5}$	$3.35*10^{-5}$

The interaction parameters are adjusted so as to minimize the error between the experimental data and the model data, the lower the deviation, the better the model can represent the experimental data, and hence the simulation results by the adjusted model. Will be more precise. In the case of the molar fraction, the deviation between the experimental data and the model is written as follows:

$$DEV(X) = \frac{100.\sum_{i=1}^{ND} \frac{|X_{cal,i} - X_{exp,i}|}{X_{exp,i}}}{ND} (\%) \quad \text{(VIII)}$$

For our case, the deviation between the experimental data and the model is of the order of 17%. In the literature [4] found an error of 16.9%, so we can consider that our results are acceptable.

The following fig.1 shows the deviation between the molar fraction of CO_2 in the calculated and experimental liquid phase at different working temperatures 298 K, 313K and 333K. From Fig. 1, it can be said that the model represents well the experimental data.
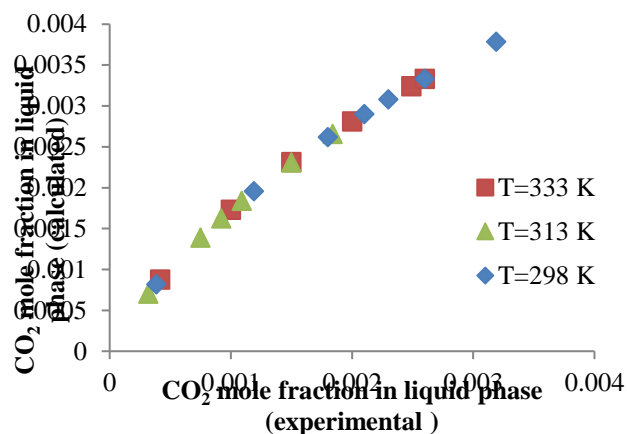

Figure 1: comparison between CO_2 mole fraction in liquid phase experimental and calculated

V.CONCLUSION

The equilibrium data obtained were modeled with the NRTL electrolyte model, the objective function is of the Mximum likelihood type, the different parameters were regressed on all the experimental data. We found an error of 17% that is acceptable, so our model represents well the experimental data.

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