

CO₂ CAPTURE MODELING IN AQUEOUS SOLUTION OF METHYLDIETHANOLAMINE AND HEXYLAMINE

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Abstract: The aim of this work is to establish a thermodynamic model using Non-Random Two-Liquid (NRTL) Electrolyte Aspen Plus™ model, which allows to simulate the CO₂ capture by an aqueous mixture of methyldiethanolamine (MDEA) and hexylamine (HA) with mass concentration of MDEA 37 wt % + HA 3 wt %. CO₂ solubility data in the mixture were obtained by our experiment in different temperatures 298, 313 and 333 K, and were introduced in Aspen Plus™, the binary interaction parameters and electrolyte pairs as well as the parameters of the kinetic constants reaction between CO₂ and aqueous solution with mass concentration MDEA 37 wt % + HA 3wt % + H₂O have been regressed. The average relative deviation on the mole fraction of CO₂ in the liquid phase is estimated. The results obtained show that our model represents the experimental data with an error of 17 %.

Keywords: CO₂ capture, CO₂ solubility, hexylamine (HA), methyldiethanolamine (MDEA), NRTL electrolyte model

INTRODUCTION

The main source of CO₂ is the burning of fossil fuels such as coal, oil and gas in power plants, for transportation 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 industries around the globe (power generation, manufacturing of steel, cement manufacturing). These industries 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 targets of the United Nations Framework Convention on Climate Change (UNFCCC). Increasing Earth temperature 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 CO₂. This technology is based on three main steps:

- CO₂ capture: this is the most important and costly step, CO₂ is captured and compressed.
- CO₂ transport: after being captured, the CO₂ must be transported to the storage place.
- CO₂ storage: CO₂ 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 well represent 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. Many authors have used the Aspen PlusTM electrolyte model for modeling the CO₂ absorption. Zhang *et al.* [2] modeled the CO₂ absorption by the aqueous solution of monoethanolamine (MEA) using the NRTL-electrolyte thermodynamic model to represent the vapor liquid equilibria, Dash *et al.* [3] developed a thermodynamic model for the prediction of the liquid-vapor equilibrium of CO₂ absorption by mixing (AMP + PZ) using the NRTL electrolyte model, the interaction parameters are regressed on all the experimental data, the model developed can predict the heat of absorption, the pH of the charged solution and the volatility of the amine, Hang Li *et al.* (2014) [4] used the Aspen PlusTM NRTL electrolyte model for the calculation of binary parameters, these parameters are regressed on all the experimental data, the developed model can be used to simulate CO₂ absorption by the mixture of piperazine (PZ) and 2-amino-2-methyl-1-propanol (AMP), Hang Li *et al.* (2015) [5] used the same model to represent the equilibrium of CO₂ absorption by 1-methylpiperazine (1MPZ).

EXPERIMENTAL SECTION

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 (Equation 1).

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

Gibbs excess energy is the sum of local interactions $g^{ex,lc}$ and long-distance interactions $g^{ex,LR}$ (Equation 2 and 3).

$$g^{ex} = g^{ex,LR} + g^{ex,lc} \quad (2)$$

$$g^{ex,LR} = - \left(\sum_k x_k \right) \left(\frac{1000}{M_B} \right)^{1/2} \left(\frac{4A_\phi I_x}{\rho} \right) \ln \left(1 + \rho I_x^{1/2} \right) + \frac{Q_e^2}{2kT} \left(\frac{1}{\epsilon} - \frac{1}{\epsilon_w} \right) \left(\frac{\sum_i x_i z_i^2}{r_i} \right) 10^{-2} \quad (3)$$

This last equation takes into account the Pitzer-Debye-Huckel term from the NRTL model and the born term (Equation 4).

$$g^{ex,LC} = \left(\sum_B x_B \right) \left(\frac{\sum_J X_J * G_{JB} * \tau_{JB}}{\sum_k X_k * G_{kB}} \right) + \sum_c x_c \sum_a \left(\frac{X_{a'}}{\sum_{a''} X_{a''}} \right) \frac{\sum_J X_J * G_{JC,a'C}}{\sum_k X_k * G_{kC,a'C}} + \sum_a x \sum_{c'} \left(\frac{X_{c'}}{\sum_{c''} X_{c''}} \right) \frac{\sum_J X_J G_{Ja,C'a} \tau_{Ja,C'a'}}{\sum_k X_k G_{ka,C'a}} \quad (4)$$

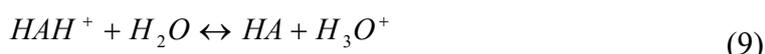
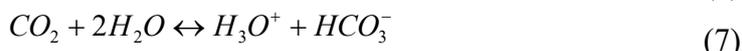
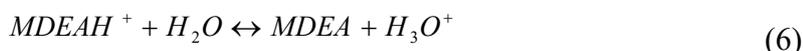
where: the index B representing the molecules, the indices c , c' and c'' the cations and the indices a , a' and a'' the anions.

This equation takes into account local interactions between molecules, anions and cations.

Regression procedure NRTL Model

Aspen PlusTM has inserts for some amine mixtures, for the simulation of CO₂ capture by MDEA, the insert used is EMDEA, because of the addition of a small amount of hexylamine in the solution of MDEA, the insert used for MDEA alone constitutes the thermodynamic basis of this amine mixture, so we considered the EMDEA insert to which we added the equations of the CO₂ reaction with hexylamine, which is a lipophilic primary amine, it is very reactive with CO₂ and which leads to the formation of a carbamat, on the other hand Aspen PlusTM allows to adjust the parameters of this model knowing experimental data equilibrium via a regression module DRS (Data Regression System), the different reactions of CO₂ with the MDEA 37 wt % + HA 3 wt

% mixture are those of the CO₂ reaction with MDEA and the CO₂ reactions with hexylamine which are the dissociation of amine and the conversion of carbamate to bicarbonate (Equation 9 and 10).



The objective function is to have the chosen thermodynamic model adjusted to the experimental data for the solvent MDEA 37 wt % + HA 3 wt %. The default regression method at Aspen PlusTM is the maximum likelihood. In this process, the objective function is given by:

$$F_{obj} = \sum_{n=1}^{NGR} PG_n \sum_{i=1}^{ND_n} \left[\left(\frac{T_{cali} - T_{exp,i}}{\sigma_{T,i}} \right)^2 + \left(\frac{P_{cali} - P_{exp,i}}{\sigma_{P,i}} \right)^2 + \sum_{j=1}^{NC_n-1} \left(\frac{x_{cali,j} - x_{exp,i,j}}{\sigma_{x,i,j}} \right)^2 + \sum_{j=1}^{NC_n-1} \left(\frac{y_{cali,j} - y_{exp,i,j}}{\sigma_{y,i,j}} \right)^2 \right] \quad (11)$$

with F_{obj} the objective function, NGR the number of groups of data, PG_n the weight of the group n , ND_n the number of experimental points in the data group n , NC_n the number of compounds present in the data group n and $\sigma_{z,i}$, the standard deviation at point i for the variable z . Experimental CO₂ absorption data from the MDEA 37 wt % + HA 3 wt % mixture that we obtained [6, 7], were entered in Aspen PlusTM as a data group. A standard deviation can be specified for each experimental point. The equilibrium partial pressure of CO₂ was used instead of the total pressure. A molar fraction of CO₂ 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 shows the standard deviation for each variable, these settings are taken by default by Aspen PlusTM 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 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:

$$k = \exp\left(A + \frac{B}{T}\right) \quad (12)$$

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

$$\tau = A + \frac{B}{T} \quad (13)$$

We estimated the parameters of the kinetic constants of the reactions and those parameters of binary interactions as well as the interactions of the electrolyte pairs between molecule and ionic species. The parameters A and B are estimated by Aspen PlusTM software.

RESULTS AND DISCUSSION

The regression of the various parameters is grouped in Table 2. According to the Table 2, we note that the constants of CO₂ reaction with mixture MDEA 37 wt % + HA3 wt % are very low, that is due to the lipophilic character of hexylamine, so the dissociation in water is low in the first and a small amount of hexylamine in the solution in the second. The binary interaction between hexylamine and CO₂ is very high because hexylamine is primary amine and is very reactive with CO₂ [8], CO₂ react firstly with hexylamine in the mixture of methyldiethanolamine (MDEA) and hexylamine (HA).

Table 2. Adjusted parameters

Parameters	A	B
K ₉	0.00018	-1000
K ₁₀	0.00018	-1000
τ _{HA,CO2}	1.60	9416.64
τ _{MDEA,HA}	1.79	542.67
τ _{H2O,HA+,HCO3-}	8.0009	1.12·10 ⁻⁷
τ _{HA+,HCO3-,H2O}	-3.99	1.12·10 ⁻⁷
τ _{CO2,HA+,HCO3-}	8.0009	1.12·10 ⁻⁷
τ _{HA+,HCO3-,CO2}	-3.99	1.12·10 ⁻⁷
τ _{MDEA,HA+,HCO3-}	8.0009	1.12·10 ⁻⁴
τ _{HA+,HCO3-,MDEA}	-3.99	1.12·10 ⁻⁴
τ _{MDEA+,HCO3-,HA+,HCO3-}	3.35·10 ⁻⁵	3.35·10 ⁻⁵
τ _{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, this model can represent the experimental data, and hence the simulation results by the adjusted model. In the case of the molar fraction, the deviation between the experimental data and the model is written as follows:

$$DEV(X) = \frac{100 \cdot \sum_{i=1}^{ND} |X_{cal,i} - X_{exp,i}|}{ND} (\%) \quad (14)$$

Figure 1 shows the deviation between the molar fraction of CO₂ in the calculated and experimental liquid phase at different working temperatures 298, 313 and 333 K. From Figure 1, it can be said that the model represents well the experimental data. The average deviation between the experimental data and the model is of the order of 17 %. In the literature an error of 16.9 % was reported [9], so we can consider that our results are acceptable.

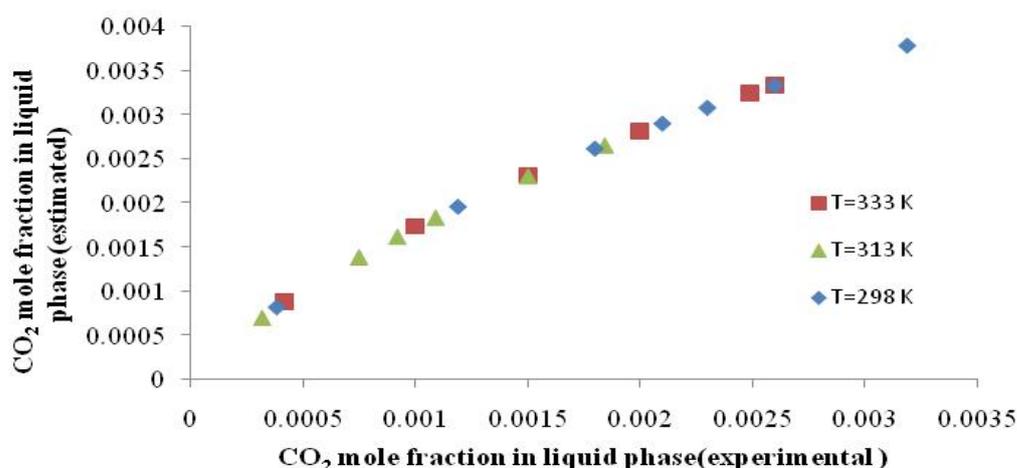


Figure 1. Comparison between CO₂ mole fraction in liquid phase: experimental and estimated

CONCLUSION

The vapor liquid equilibrium data obtained in our previous work [6, 7] were modeled with the Aspen PlusTM NRTL electrolyte model, the objective function is of the maximum likelihood type, the parameters of binary interaction between molecule-molecule and the parameters of pairs interaction between molecule and ionic species were regressed on all the experimental data. The average deviation between molar fraction of CO₂ in liquid phase experimental and calculated is equal to 17 %, which is acceptable, so our model represents well the experimental data.

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