



Thermodynamic Analysis of CO₂ Absorption in Aqueous MDEA-PZ Solution Using ELECNRTL and ENRTL-RK Models

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Carbon capture and storage using chemical absorption is a viable method for reducing CO₂ emissions from the industrial sector. Thermodynamic analysis of MDEA-PZ aqueous alkanolamine solution is of paramount importance to better simulate and improve the efficiency of CO₂ capture processes. In this study, we use the Aspen Plus simulator (V12.1) to compare the theoretical differences and the regression results of the two-liquid activity coefficient models ELECNRTL and ENRTL-RK in terms of CO₂ solubility. The quaternary system CO₂-MDEA-PZ-H₂O vapor-liquid equilibrium (VLE) data found in the open literature are first collected. After excluding anomalous points according to some criteria, 521 confirmed data ranging from 40 °C to 120 °C are then used to regress the binary interaction parameters of molecule-molecule and molecule-electrolyte pairs for both models using the maximum likelihood method. The fitting results show an accuracy enhancement of 34 % for ELECNRTL and 68 % for ENRTL-RK compared to the Aspen default models. The regressed models can be used to improve the accuracy of absorber and stripper simulations in CO₂ capture processes.

1. Introduction

CO₂ capture has become a necessity to limit global warming and achieve the net zero carbon target by 2050. The selection of the process to be used for CO₂ capture depends on several factors, such as the composition of the gas feed and the production flow. For medium to low partial pressures of CO₂ in the gas feed and for very stringent specifications, chemical absorption with alkanolamine solution is largely selected. This type of process has the advantage of liquid chemical reactions that shift the chemical equilibrium between solvent and CO₂ and promote CO₂ solubility. Alkanolamine solvents have several advantages (regenerability, good basicity and stability, etc.) (Li et al., 2020). As a tertiary amine, Methyldiethanolamine (MDEA) has the advantage of good CO₂ absorption capacity and low heat of regeneration (Amann and Bouallou, 2009). However, its reaction kinetics with CO₂ is slow, which can be considered an advantage, especially in the case of H₂S-CO₂ selective absorption. However, for CO₂ capture, this property is a problem that can be solved by adding an "activator". For several years, Piperazine (PZ) has been one of the most successful activators. It is characterized by a very high reaction rate with CO₂, which makes it possible to achieve very strict specifications for CO₂ at the top of the absorber. Several studies on CO₂ absorption in MDEA-PZ solvent have been reported. Moioli et al. (2016) have worked on the thermodynamic modeling of CO₂ absorption in aqueous solutions of MDEA-PZ mixture, using ELECNRTL as the excess model for the liquid phase. Their study shows the influence of the MDEA-PZ molecular interactions on the accuracy of the vapor-liquid equilibrium (VLE) representation. Chen et al. (2009) calculated the essential thermodynamic properties of the CO₂-MDEA-H₂O ternary mixture by regressing the binary parameters of the ENRTL-RK model and some protonated MDEA reference properties. In addition, Dash et al. (2016) carried out an experimental study of CO₂ absorption in the MDEA-PZ chemical solvent and the MDEA-PZ-Sulfolane hybrid solvent. This study shows the positive effect of the addition of Sulfolane on the CO₂ solubility, although this result is highly dependent on the mixture composition and temperature. Also, Bottger et al. measured the CO₂ solubility in a MDEA-PZ solution for a CO₂ loading range of 0.38-1 using different

experimental techniques. Finally, Li et al. (2020) studied the rate-based modelling of CO₂ capture using MDEA-PZ in place of MEA solvent and ELECNRTL as the activity coefficient model. They focused on mass transfer correlations and sensitivity analysis to find the parameters that most influence CO₂ absorption. Aspen Plus introduced a new version of the electrolyte NRTL model called ENRTL-RK. The Aspen team have regressed each of the two models to model carbon capture using MDEA-PZ solvent. However, we believe that their VLE database and the selected number of regressed binary interaction parameters are not sufficient to satisfactorily represent the CO₂-PZ-MDEA-H₂O quaternary system. According to what found in open literature, regression of ENRTL-RK model was never performed for the quaternary system and the Aspen default parameters were used instead (Esmaili et al., 2020). As for ELECNRTL, its regression was done only by few authors and sometimes for other blended amines mixtures (Gonzalez et al., 2023). A direct comparison of the accuracy of the two models for representing the quaternary system has also never been done neither in the literature. For these reasons, the present study aims to compare and to optimize ELECNRTL and ENRTL-RK models in order to better model the VLE of the CO₂-PZ-MDEA-H₂O mixture.

2. Thermodynamic modelling of CO₂ absorption

During the CO₂ absorption, non-independent equilibria occur: the liquid-vapor phase equilibrium (called physical equilibrium) and the chemical equilibrium (liquid reaction equilibrium).

2.1 Chemical Equilibrium

Once CO₂ is absorbed into the MDEA-PZ-H₂O solvent, a series of reactions take place. The global reactions of MDEA-PZ with CO₂ are: (R1) Catalyzed hydration of MDEA - (R2) Bicarbonate formation (with water)



The equilibrium constant of reaction j is related to the reaction standard free enthalpy $\Delta G_{R,j}^0$ and the activity coefficients γ_i through (Eq(1)):

$$K_{eq,j}(T) = \exp\left(-\frac{\Delta G_{R,j}^0(T)}{RT}\right) = \prod_{i=1}^{N_{\text{reactants}}} \left(\frac{\gamma_i(T, \underline{x})}{\gamma_i^\infty(T)} x_{i,true}\right)^{\theta_{i,j}} \quad (1)$$

With $\theta_{i,j}$ the stoichiometric coefficient of species i in reaction j , γ_i^∞ the activity coefficient of species i at infinite dilution in the reference solution and $x_{i,true}$ is the molar fraction of the true species i . In contrast to the term of apparent species which refers only to the molecular species entered by the user in non-dissolvent form, the term of true species includes all the species present in the liquid mixture including ionic dissolved form.

2.2 Physical Equilibrium: Gamma-Phi approach

The thermodynamic phase equilibrium is described by the equality of fugacities of the same component i at the interface of the system phases. To model this equilibrium, we consider the heterogeneous "Gamma-Phi" approach: the vapor phase is modelled by a fugacity coefficient calculated via the RK equation of state, while the liquid phase is modelled by the activity coefficient calculated by an excess Gibbs free energy model. This approach is well suited to represent each phase of the strongly non-ideal system differently: the liquid phase is a solution containing molecular and other ionic species, while the vapor phase contains only molecular species. For the liquid phase, this approach makes it possible to model the different interactions between the different species present in the solution. The resulting ASPEN thermodynamic equations are Eq(2) and Eq(3):

$$\varphi_i^v(T, P, \underline{y}) y_i P = \gamma_i(T, \underline{x}) x_i P_i^{sat}(T) \varphi_i^{sat}(T, P_i^{sat}(T)) \exp\left(\frac{\bar{v}_i^L(T)(P - P_i^{sat}(T))}{RT}\right) \quad (\text{For solvent species}) \quad (2)$$

$$\varphi_i^v(T, P, \underline{y}) y_i P = \gamma_i^*(T, \underline{x}) x_i H_i^{solvent}(T) \quad (\text{For supercritical solute}) \quad (3)$$

With φ_i^v is the vapor fugacity coefficient of component i , y_i and x_i are the vapor and liquid mole fractions of component i , $H_i^{solvent}$ is the Henry constant of the supercritical component i in the mixed solvent, P_i^{sat} is the vapor pressure of the pure component i , γ_i^* is the normalized activity coefficient of the Henry component and \bar{v}_i^L is the molar volume of species i in the liquid phase. The fugacity of the solvent species in the liquid phase is multiplied by the "Poynting factor" to correct for the pressure effect on the liquid fugacity.

2.2.1 Excess model and activity coefficient

The model of Chen et al. (2009) is considered to calculate the activity coefficients. It is based on the “local composition” concept used previously by other models such as Wilson and Uniquac. This concept assumes two fundamental hypotheses: the first one supposes that the repulsive forces are so strong that a charged species cannot exist in the immediate neighborhood of another species of the same charge. The second hypothesis simply confirms electronic neutrality around a solvent molecule. The model calculates the Gibbs excess energy in the form of two contributions: a local term for the short-range interactions between the different species present in the system and a second term for the long-range interactions between the ions. The first term is calculated by an expression similar to that of NRTL model, including ion-molecule and molecule-molecule interactions (Eq(4)):

$$\frac{G^{E,lc}}{RT} = \sum_m X_m \frac{\sum_j X_j G_{jm} \tau_{jm}}{\sum_j X_j G_{jm}} + \sum_c X_c \left(\sum_a \frac{X_a}{\sum_{a'} X_{a'}} \right) \frac{\sum_j X_j G_{jc,ac} \tau_{jc,ac}}{\sum_k X_k G_{kc,ac}} + \sum_a X_a \left(\sum_c \frac{X_c}{\sum_{c'} X_{c'}} \right) \frac{\sum_j X_j G_{ja,ca} \tau_{ja,ca}}{\sum_k X_k G_{ka,ca}} \quad (4)$$

Where X_j is a modified mole fraction of component j ($j = m$ (molecule), c (cation), a (anion)) and G is a local binary quantity, a function of $\tau_{i,j}$, the binary interaction parameter between species i and j , and α the non-randomness factor. $\tau_{i,j}$ is defined as the difference in interaction energies of species i in the vicinity of species j . Aspen uses T-dependent correlations to compute $\tau_{i,j}$ (Eq(5)) and $\alpha_{i,j}$ (Eq(6)) parameters:

$$\tau_{i,j} = a_{i,j} + \frac{b_{i,j}}{T} + e_{i,j} \ln(T) + f_{i,j} T \quad (5)$$

$$\alpha_{i,j} = c_{i,j} + d_{i,j}(T - 273,15 \text{ K}) \quad (6)$$

The non-randomness factor is generally set to 0.2 for molecule-molecule and molecule-ion pair interactions. The excess term is reduced to the NRTL model in the absence of electrolytes. The new model makes the same assumptions as the NRTL model, such as the regular solution assumption (negligible excess entropy) which remains valid for electrolyte solutions. Developed with the symmetric convention, it is then normalized by the activity coefficients at infinite dilution in water to make it asymmetric.

The second term is expressed by the Pitzer-Debye-Huckel equation, which is a function of the molar composition of the liquid phase and the ionic charge (Eq(7)):

$$\frac{G^{E,PDH}}{RT} = - \left(\sum_k x_k \right) \frac{1000}{M_s} \frac{4A_\phi I_x}{\rho} \ln \left(\frac{1 + \rho I_x^{1/2}}{1 + \rho I_x^{0,1/2}} \right) \quad (7)$$

Where ρ is the “Closest Approach” parameter and A_ϕ the “Debye-Huckel” parameter, which is a function of temperature, solvent density and its dielectric constant, I_x (I_x^0) is the ionic (reference) strength of the solution.

2.2.2 Theoretical differences between ELECNRTL and ENRTL-RK models

Chen's model has been implemented in Aspen under the name of ELECNRTL. This name is given not only to the excess model, but to an entire method for calculating the properties of pure components and mixtures (property method). ENRTL-RK is one of the ELECNRTL model versions created by Aspen. This version corrects some inconsistencies observed with ELECNRTL, especially in the case of liquid-liquid equilibrium of electrolytic solutions with mixed solvent and phase equilibria of non-electrolytic solutions. For example, ENRTL-RK is more consistent with the non-electrolyte version NRTL-RK in calculating the enthalpy of a non-electrolyte organic methanol-benzene mixture. For electrolyte solutions, the difference between the two versions is less important, with a slight advantage for the ENRTL-RK version. Also, the two models do not treat zwitterions (species with positive and negative charges but with zero net charge) in the same way. Since these species are not volatile, ELECNRTL treats them as cations, while ENRTL-RK treats them as molecular solutes in the calculation of solution enthalpy and Gibbs energy. The two models are electrolyte versions of the same basic model (NRTL local term + Pitzer-Debye-Huckel term) using the same asymmetric reference state for ions. Theoretically, the two models also use the same RK equation of state for the vapor phase. However, in the Aspen templates to model CO₂ capture by MDEA-PZ solution, the ENRTL-RK uses PC-SAFT as the equation of state. For the main thermodynamic properties of the solutions (enthalpy, Gibbs energy, etc.), the two models use different calculation methods. Otherwise, both models use the same correlations to calculate certain physicochemical properties (vapor pressure, viscosity, etc.) with different values for the parameters of these correlations. Finally, the optimization of ENRTL-RK was more computationally expensive than that of ELECNRTL owing to the complexity of the ideal gas approach used by ENRTL-RK to calculate the main thermodynamic properties.

3. Methods

3.1 Experimental data

To regress the ELECNRTL and ENRTL-RK models, a solid experimental data set is required. VLE data from equilibrium measurements for amine-water system with and without CO₂ must be checked to test their reliability. A database of 951 points was collected from open literature and anomalous points were excluded according to certain criteria: Isotherms of the same amine weight should not intersect – Similar rule to Weiland's one (1993) – Industrial range (CO₂ loadings lower than unity). Also, the data measured at one amine weight are excluded if there are no other data from other authors to compare with. At the end of this sorting phase, 521 validated points constitute the database used.

3.2 Fitting procedure

To perform this optimization, among several possible parameters, it is more reliable and relevant to act on the activity coefficients, more precisely on the $\tau_{i,j}$ (Eq(4)), given the strong non-ideality of the liquid phase. Since our system contains several ionic and molecular species, only the most influencing $\tau_{i,j}$ on the activity coefficients are considered in the regression. These $\tau_{i,j}$ are selected mainly based on the speciation scheme of the system. Also, some interactions were included in the regression because they were regressed by the Aspen team with a limited database. Finally, the Aspen team has regressed only $a_{i,j}$ coefficients (see Eq(5)). In this study, $b_{i,j}$ parameters are also added to take into account the temperature effect. All other binary molecule-ion pair interaction parameters were assumed to be equal to the default values. By default, Aspen uses the maximum likelihood method, where the objective function is a least-squares sum of the error-in-variables including pressure, temperature, and liquid and vapor composition. The optimization results are used to calculate the absolute average deviation *AAD* (%) (Eq(8)) between the experimental CO₂ partial pressures $P_{i,exp}$ and those predicted by the model $P_{i,mod}$ for n data points:

$$AAD = \frac{100}{n} \sum_{i=1}^n \frac{|P_{i,exp} - P_{i,mod}|}{P_{i,exp}} \quad (8)$$

4. Results and discussion

The regression results for the two models are presented and discussed in the following sections.

4.1 ELECNRTL

For ELECNRTL, the default *AAD* (i.e., model before regression) is 32 %. At the end of the regression iterations, the *AAD* deviation drops from 32 % to 21 %. The optimizer seems to be limited at this stage, which can be justified by the dispersion of the database despite the database “cleaning” step. The optimal values of the interaction parameters are reported in Table 1a. The performance of the regressed model is compared with the predictions of the Aspen default model, an example of which is shown in Figure 1a. First, we note that the two models (default and after regression) are physically coherent by showing a strictly increasing function of $P_{CO_2} = f(\text{CO}_2 \text{ loading}, T)$ for each variable at a given amine weight. Second, the cleaning step have clearly led to a consistent dataset though data of Dash et al. (2016) are a little bit less well aligned with the rest of experimental points. The improvement of the model is clearly observed at low loadings (<0.2), where the regressed model better reproduces the experimental data for all reported temperatures. For the mid-high loadings (>0.3), the difference between the two models is less remarkable, since their estimates are good in this range. Compared to the literature, our ELECNRTL regression results are generally equivalent to those found by Moioli et al (2016). This comparison is considered only as qualitative, as our regression database is much larger than theirs, thanks to important complementary sources of experimental data. This may explain why, in this study, the number of interactions required to reach the optimal *AAD* is larger in our study than in Moioli et al. (2016).

The difference between the model predictions and the experimental points can sometimes have other reasons than the values of the binary interaction parameters, namely for example: the experimental measurement error observed both for low loadings and for high temperature data (>100 °C) – The data may not have been measured with exactly the same weight of amines, but they are still grouped together in the same case of amine weights in order to facilitate the comparison of the data. It should be noted that the graphs shown are on a logarithmic scale with respect to the partial pressures of CO₂. A visually small deviation in the mid-high loading range can be as large or even larger in reality than a visually larger deviation in the low loading range. It should also be noted that the conclusions drawn are based solely on the examples of amine weights reported. They may vary more or less for other amine concentrations in the lean solvent.

4.2 ENRTL-RK

In the case of ENRTL-RK, the calculated initial deviation is equal to 85 %. At the end of the regression iterations, the AAD deviation decreases from 85 % to 27 %. The optimal values of the interaction parameters are reported in Table 1b. An example of the regression results is shown in Figure 1b from which the optimization of the model has improved the model accuracy for CO₂ loading greater than 0.1. Also, by comparing the results of the 70 °C isotherm at high loadings (>0.9), we can confirm that the optimal vector also improves the model stability at high pressures, reducing the problems of flash equilibrium calculation in this range. For CO₂ loadings below 0.1, a slight degradation in performance is observed, which decreases at high temperatures.

Table 1: Optimal values of interactions parameters $a_{i,j}$ and $b_{i,j}$ using (1a) ELECNRTL and (1b) ENRTL-RK.

(1a)			(1b)		
Interaction $i - j$	$a_{i,j}$	$b_{i,j}$	Interaction $i - j$	$a_{i,j}$	$b_{i,j}$
MDEA - PZ	21.813	-6926.54	(PZH ⁺ ,HCO ₃ ⁻) - MDEA	-2.4786	
PZ - MDEA	-0.852	-585.81	MDEA - (PZH ⁺ ,HCO ₃ ⁻)	0.5875	
(PZH ⁺ ,PZ(COO ⁻) ₂) - H ₂ O	-7.883	-21.110	(MDEAH ⁺ ,PZ(COO ⁻) ₂) - H ₂ O	-8.597	
H ₂ O - (PZH ⁺ ,PZ(COO ⁻) ₂)	17.792	-24.745	H ₂ O - (MDEAH ⁺ ,PZ(COO ⁻) ₂)	0.467	
(PZH ⁺ ,PZCOO ⁻) - MDEA	-17.288	5431.73	(PZH ⁺ ,PZCOO ⁻) - MDEA	-7.551	
MDEA - (PZH ⁺ ,PZCOO ⁻)	414.42	8287.47	MDEA - (PZH ⁺ ,PZCOO ⁻)	-5.604	
(MDEAH ⁺ ,HCO ₃ ⁻) - H ₂ O	-1.263	-393.96	(MDEAH ⁺ ,HCO ₃ ⁻) - H ₂ O	-1.036	
H ₂ O - (MDEAH ⁺ ,HCO ₃ ⁻)	3.475	-43.93	H ₂ O - (MDEAH ⁺ ,HCO ₃ ⁻)	2.3948	
(MDEAH ⁺ ,PZ(COO ⁻) ₂) - H ₂ O	-4.37	-563.7	(MDEAH ⁺ ,HCO ₃ ⁻) - HPZCOO	6.3	
H ₂ O - (MDEAH ⁺ ,PZ(COO ⁻) ₂)	17.949	-3058.83	HPZCOO - (MDEAH ⁺ ,HCO ₃ ⁻)	10.211	
(MDEAH ⁺ ,PZ(COO ⁻) ₂) - MDEA	-5.911	262.52	(MDEAH ⁺ ,HCO ₃ ⁻) - CO ₂	-0.847	
MDEA - (MDEAH ⁺ ,PZ(COO ⁻) ₂)	4.047	3142.86	CO ₂ - (MDEAH ⁺ ,HCO ₃ ⁻)	0.937	
(HPZCOO,HCO ₃ ⁻) - H ₂ O	-35.90	115.01	(PZH ⁺ ,PZCOO ⁻) - H ₂ O	-9.503	
H ₂ O - (HPZCOO,HCO ₃ ⁻)	-3904.4	3913	H ₂ O - (PZH ⁺ ,PZCOO ⁻)	-22.80	
(PZH ⁺ ,PZCOO ⁻) - PZ	25.175	278.73	H ₂ O - MDEA	2.731	455.51
PZ - (PZH ⁺ ,PZCOO ⁻)	24.548	-293.28			

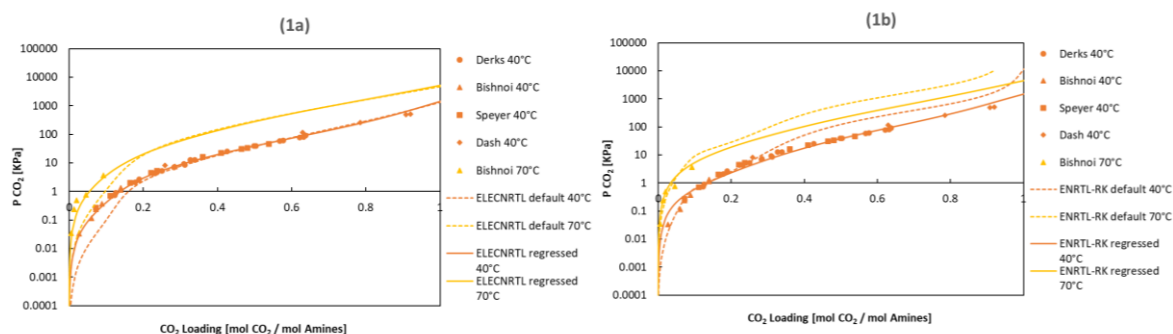


Figure 1: Measured and predicted solubility of CO₂ in aqueous 48 % MDEA-5 % PZ solution using (1a) ELECNRTL and (1b) ENRTL-RK models

4.3 Comparison of the two models

After the comparison of the pre- and post-optimization results for each model separately, it is now important to compare the results of the optimized models together. Figure 2 illustrates this comparison for the same amine weight of 48 % MDEA-5 % PZ. For the 40 °C isotherm, ELECNRTL shows a better behaviour in the low loading range while the two models have an overall identical performance at medium and high loadings. For the 70 °C isotherm, and despite the slight differences observed between the curves of the two models, it is difficult to say which model is more accurate in this range due to the lack of experimental data. In terms of regressed parameters required to get the optimal AAD (see Tables 1a and 1b), and although ENRTL-RK rely less on $b_{i,j}$ parameters due to regression numerical problems, the two models involve the same number of pairs and have

equivalent values of the Akaike information criterion (the difference between the number of estimated parameters and the value of the maximum-likelihood function).

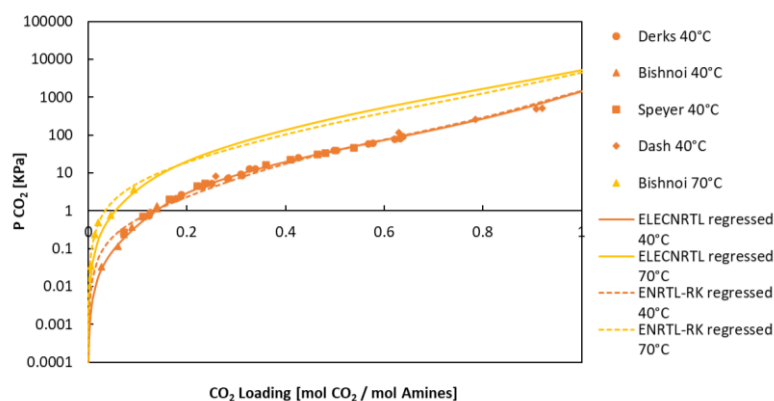


Figure 2: Comparison of regressed ELECNRTL and ENRTL-RK models predictions of CO₂ solubility in aqueous 48 % MDEA-5 % PZ solution

5. Conclusion

The optimization of the ELECNRTL and ENRTL-RK models to represent the vapor-liquid equilibrium of the CO₂-PZ-MDEA-H₂O system has allowed the two models to reach equivalent final accuracies (about 20 %), despite their differences in theory and solubility profiles. With a larger database, the regression results of ELECNRTL are generally equivalent to those found in some previous works while the regression results of ENRTL-RK are new. With the other physicochemical properties set to Aspen default values, the optimal values of interactions parameters found in this study can be used directly in Aspen Plus to improve the accuracy of rate-based carbon capture simulations. Finally, a perspective of the current work is to consider CO₂ absorption heat data in the regression database for further improvement of stripping performance predictions.

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