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eNRTL Parameter Fitting Procedure for Blended Amine Systems: MDEA-PZ Case Study

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Abstract

Although chemical absorption is a well-known and established process, design and scale up of equipment are still a challenge. An accurate thermodynamic model will lead to good representation of the system behavior and therefore a more precise design of equipment. The eNRTL model is suitable for amine based processes due to its ability to handle electrolyte systems. However, this model requires that a large number of parameters are fitted against experimental data, usually partial and total pressures. In this work, the blended MDEA (N-methyldiethanolamine) and PZ (Piperazine) system is presented as an example case for showing a new procedure to estimate the eNRTL parameters. The largest system studied is the $MDEA/PZ/CO_2/H_2O$, and the subsystems are formed by suppressing one or more components from the initial mixture, for instance: $MDEA/H_2O$, $PZ/CO_2/H_2O$. The parameter fitting procedure consists of estimating the smaller subsystems' parameters and using them further on to estimate the larger systems. Results show that this procedure gives accurate predictions for all the systems. Moreover, it's possible from the complete model to estimate one of these subsystems without losing accuracy.

Keywords: MDEA, PZ, eNRTL, parameter fitting, PSO

1. Introduction

Great efforts are being done in trying to reduce the costs of carbon capture and storage (CCS) and, hence, making CCS economically viable. For instance, the iCap project aims to reduce the CO_2 capture penalty to about half of what is today [1]. In an absorption post combustion capture process, the stripping section is the most costly unit operation energetically. Research aims at reducing the amount of heat

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needed to regenerate the solvent, which, among can include the development of new solvents (or solvent blends), column packing, modifications and optimization of the capture plant.

A well-known and industrially applied solvent to absorb CO_2 is the mixture between MDEA (N-methyldiethanolamine) and PZ (Piperazine). Literature provides experimental data for vapor liquid equilibrium (VLE) for the complete system (MDEA/PZ/CO_2/H_2O) and its subsystems, namely MDEA/H_2O, PZ/H_2O, MDEA/CO_2/H_2O and PZ/CO_2/H_2O. For example, [2] presents not only experimental data for the MDEA-PZ system, but also the parameters for the eNRTL.

A good representation of the system must be available in order to calculate the performance of the plant. Models for calculating unit operations (for instance, absorbers, strippers, pumps, etc.) are well known and broadly available in commercial simulation software. However, models that accurately predict the properties of a particular (or new) system are not easily found on these softwares.

The development of such models requires experimental data on system properties, in general partial pressures, total pressure and solubility measurements. Upon choosing an activity coefficient equation (e.g. the eNRTL or the extended UNIQUAC), its parameters, frequently temperature dependent, are fitted to the available experimental data.

Sensitivity analyses are usually made to identify the most sensitive parameters to the available set of experimental data, and the optimization is carried on these parameters, while keeping the others constant. For instance, [3] regressed 32 parameters for the MEA system for the UNIQUAC equation using a three step procedure, while [4] fitted only 12 parameters out of 108 for the eNRTL model. Although such methods can lead to good representation, they are very time-consuming.

In this work, a new approach is presented. All the parameters of the activity coefficient model are estimated at once using the particle swarm optimization (PSO) algorithm. Moreover, a procedure for developing a model for blended solutions based on its subsystems is proposed. The activity coefficient model chosen to represent the system was the eNRTL showed in [5]. The vapor phase was calculated using the Peng-Robinson equation of state.

2. The eNRTL framework

In amine-based CO_2 capture, CO_2 reacts with an aqueous amine solution, forming different electrolyte species. Modeling electrolyte systems is challenging and requires models which can cope with the strong non-idealities of the liquid, caused by the presence of cationic and anionic species. The eNRTL model introduced by [5] is suitable for modeling CO_2 capture/acid gas removal process, since it's able to correct the non-ideal behavior of aqueous multicomponent electrolyte systems.

The model features both non-randomness and binary energy parameters. After [4], the non-randomness parameters were fixed at 0.2 for molecule/molecule and water/salt interactions and 0.1 for all others, while the binary energy parameters were assumed to have a temperature dependency as given in equation 1.

$$\tau_{i,j} = a_{i,j} + \frac{b_{i,j}}{T} \tag{1}$$

Where parameters $a_{i,j}$ and $b_{i,j}$ were fitted to experimental data.

3. Regression Procedure

The fitting procedure chosen was to optimize the smallest subsystems and carry these results to the next system level, and finally perform a fine tuning in the complete system. The optimization algorithm used was the particle swarm optimization (PSO).

To ensure that the blended system can regress to one of its subsystems, in case one or more species are removed, the common energy interaction parameters were fixed after being fitted against a subsystem's experimental data. As an exception, some parameters were given the default values presented in Aspen plus, namely 0 for water-CO_2 and CO_2-water, 8 for water-salt, -4 for salt-water, 15 for CO_2-salt and -8 for salt-CO_2, for the salt pairs H_3O^+-OH^-, H_3O^+-HCO_3^- and H_3O^+-CO_3^{2-}. The chemical equilibrium constants were taken from literature whenever available; only three reactions from the PZ system were estimated. The reactions considered in this work are the same as in [2] and the values are given in Table 1. All other physical properties were taken from the Aspen plus database.

4. Regression Results

There are plenty of experimental data suitable for parameter estimation regarding the subsystems of the MDEA-PZ-H_2O-CO_2 system. However, data for the MDEA-PZ and MDEA-PZ-H_2O systems are not available in the literature and the parameters related to these subsystems are estimated together with the estimation of the complete system.
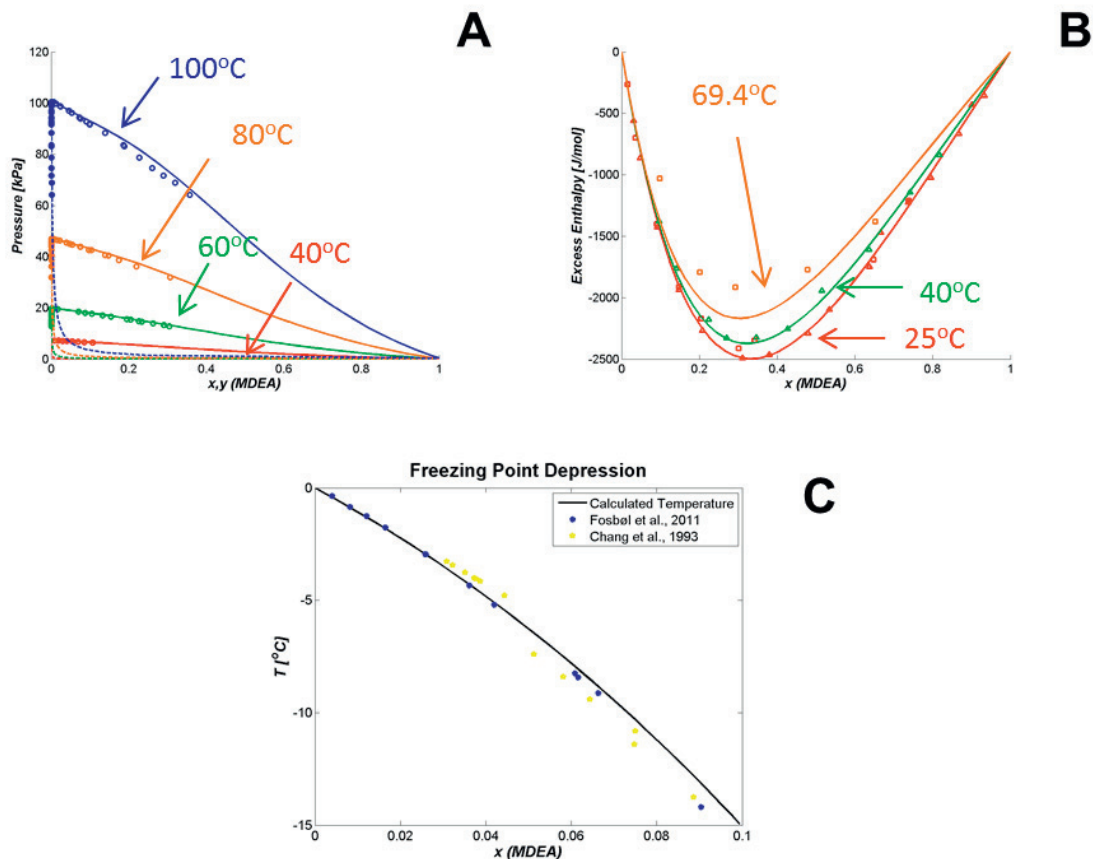

Figure 1: (A) Pxy diagram at 40, 60, 80 and 100° C for MDEA-H2O system: (-) model, (o) from [6]. (B) Excess enthalpy chart at 25, 40 and 69.4° C for MDEA-H2O system: (-) model, ($\triangle$) from [7], ($\square$) from [8]. (C) Freezing point depression plot.

4.1. MDEA-H₂O Subsystem

The parameters for the MDEA-H_2O system were estimated using VLE data from [6], excess enthalpy data from [7] and [8] and freezing point depression data from [9] and [10]. The absolute average relative deviations (AARD) were 0.013%, 4.6% and 7.3% for total pressure, excess enthalpy and freezing point depression, respectively. The results for the estimation of this subsystem are presented in Figure 1.

The model is able to represent well the pressure, excess enthalpy and freezing point depression of the MDEA-H_2O system. For the freezing point depression some data points from [9] were excluded from the regression due to disagreement with [10]. Even so, there is still some scatter between the sources. This is also observed in the excess enthalpy data at 25ºC. At 69.4ºC the model presents a higher deviation from the experimental data than at the other temperatures.

Table1: Chemical equilibrium constants in molar basis. $\ln(K) = a + b/T + c*\ln(T) + d*T$, T in K.

Reaction[1]	a	b	c	d	Source
2	132.899	-13445.9	-22.4773	0	[4]
3	231.465	-12092.1	-367816	0	[4]
4	216.049	-12431.7	-35.4819	0	[4]
5[3]	-60.0245	-1974.4	7.5329	0	[4]
6[3]	-15.44	-2000.6	0	0.019635	[31][2]
7	135.269	71.115	-24.6573	0.02154	This work
8	-134.782	197.85	20.8197	-0.00922	This work
9	-69.255	27.857	-0.4289	0.01302	This work

[1]For ease, the numbering of reactions follows [2].
[2]Regressed from experimental data form [31].
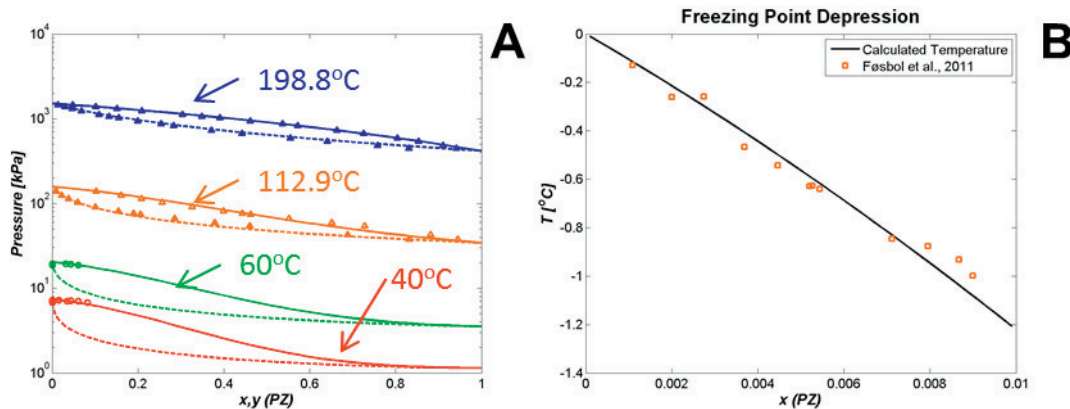[3]Asymmetric reference state for the amine.

Figure 2: (A) Pxy diagram at 40, 60, 112.9 and 198.8ºC for PZ-H2O system: (-) model, (o) from [12], ( ) from [11]. (B) Freezing point depression plot.

4.2. PZ-H₂O Subsystem

For the estimation of the PZ-H_2O subsystem, experimental VLE data from [11] and [12] and freezing point depression data from [13] were used.

The AARD was 0.025% and 9.0% for total pressure and freezing point depression, respectively. The results are shown in Figure 2.Both pressure and freezing point depression are well represented by the model. The AARD is higher for the freezing point depression due to more scattered experimental data.

4.3. MDEA-H_2O-CO_2 Subsystem

The loaded MDEA subsystem was estimated using partial pressures of CO_2 from [14], [15], [16], [17] and [18], total pressure data [19] and [20] and fixing the parameters obtained from the estimation of the binary MDEA-H_2O system. A total of 52 parameters were estimated. The model was estimated within a wide range of temperatures and amine weight percentages, from 40 to 140ºC and 5 to 50 weight percent respectively. The examples in Figure 3 show that there is a good agreement between the experimental data and the model. The total AARD was 16.9 %.
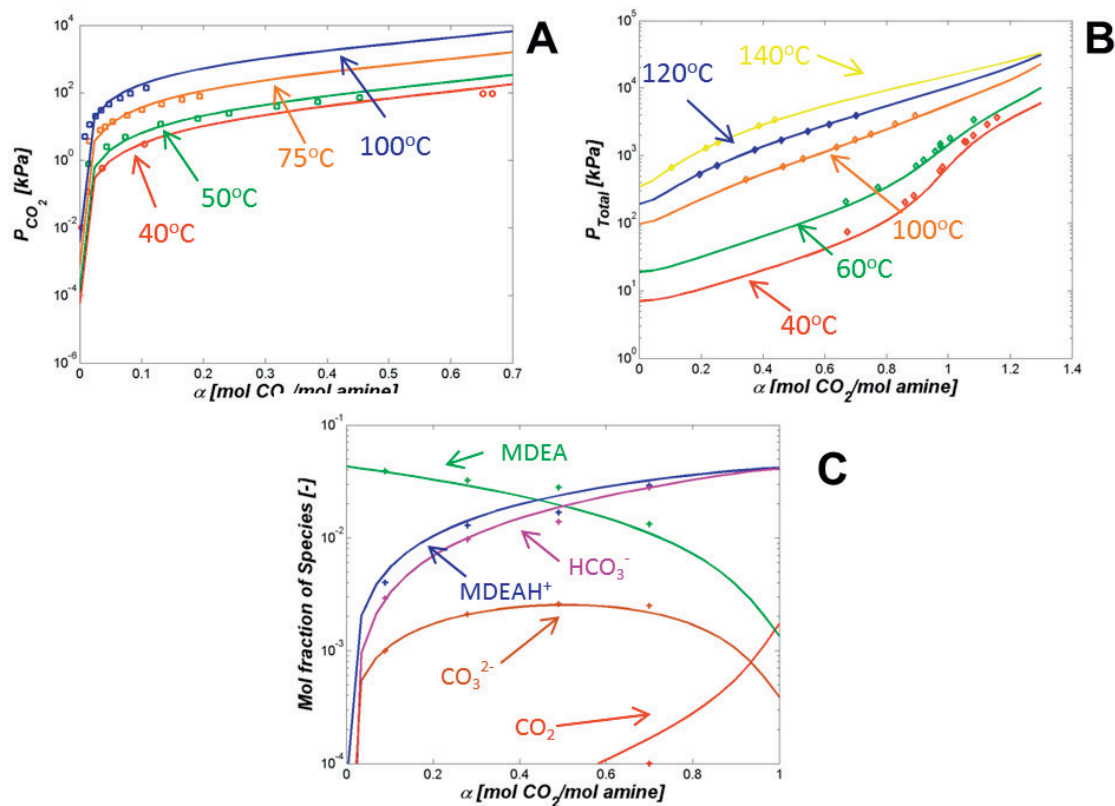

Figure 3: (A) Partial pressure of CO_2 for 50 wt. % MDEA at 40, 50, 75 and 100ºC: (-) model, (o) from [14], (□) from [16]. (B) Total pressure for 25.49 wt. % MDEA at 40, 60, 100, 120 and 140ºC: (-) model, ( ) from [19]. (C) Speciation for 23 wt. % MDEA at 20ºC.

Both partial pressures of CO_2 and total pressure were in good agreement with the experimental data. Moreover, speciation data from [21] were compared to the model predictions. Although these data were not used in the optimization procedure, the model predictions are in very good agreement with the data.

4.4. PZ-H₂O-CO₂ Subsystem

Using the parameters estimated from the PZ-H$_2$O subsystem, the 124 remaining parameters for the loaded PZ subsystem were estimated using CO$_2$ partial pressure data from [12], [22], [23], [24] and [25] and total pressure data given by [26]. In addition to the eNRTL parameters, the chemical equilibrium constants for three reactions had to be estimated, resulting in 12 more parameters. The total AARD was 24.9%. Figure 4 shows some results of the estimation.
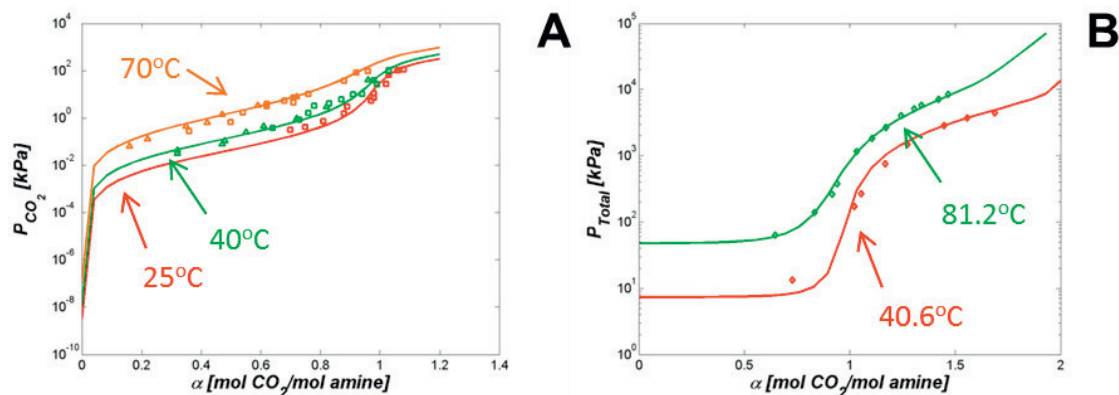

Figure 4: (A) Partial pressure of CO$_2$ for 5.11 wt. % PZ at 25, 40 and 70°C: (-) model, (□) from [23], ( ) from [22]. (B) Total pressure for 14.66 wt% MDEA at 40.6, 81.2°C: (-) model, ( ) from [26].
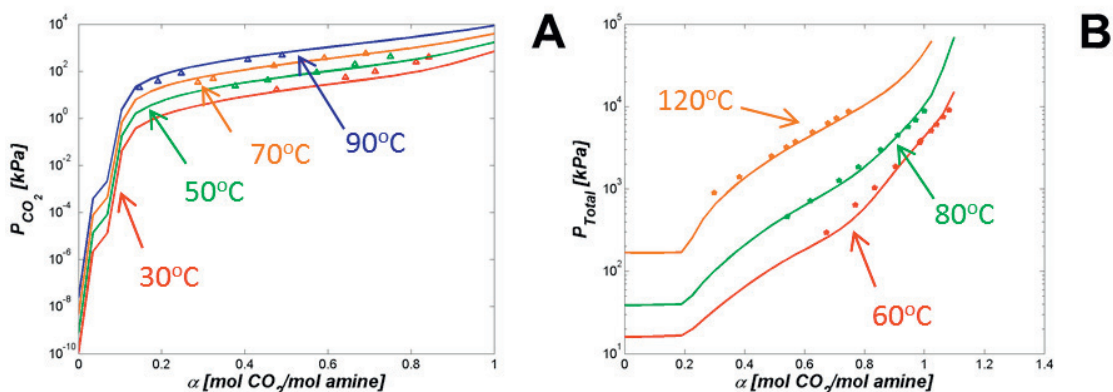

Figure 5: (A) Partial pressure of CO$_2$ for 32.46 wt. % MDEA and 5.87 wt% PZ at 30, 50, 70 and 90°C: (-) model, ( ) from [28]. (B) Total pressure for 44.19 wt. % MDEA and 8.45 wt. % PZ at 60, 80 and 120°C: (-) model, (*) from [30].

4.5. MDEA-PZ-CO₂-H₂O

The parameters estimated in the previous sections were used in the estimation of the blended MDEA/PZ system. As a consequence, only 100 parameters out of 312 were left to estimate. CO$_2$ partial pressure data from [27], [28], [29], and total pressure data from [26] and [30] were used for the final

estimation. With a few outliers in the low pressure region, the model was able to represent the system. Figure 5 shows some results of the estimation. The total AARD was 26.2%.

The parameters for the complete system can be obtained by getting in contact with the authors.

5. Conclusion

A procedure for parameter estimation in blended amine systems for CO_2 capture was proposed, developing the model from the smallest subsystems to the larger ones, using the $MDEA/PZ/CO_2/H_2O$ as study case. The procedure is based on the local composition feature of the eNRTL model, and provides a total model that does not lose the power of prediction in case of removing one of the components from the system (for instance, reducing from $MDEA/PZ/CO_2/H_2O$ to $MDEA/CO_2/H_2O$). The subsystems with available data in the literature were estimated with reasonable accuracy, leading to a good representation of the complete system.

For further development of the method, speciation data can be used when estimating the chemical equilibrium constants. Additionally, heat of reaction predictions should be compared to experimental data, in order to have an accurate design of the process.

Acknowledgements

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