

Thermodynamics of CO₂-MDEA using eNRTL with Differential Evolution Algorithm

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Abstract

Carbon dioxide (CO₂) capture by absorption with aqueous alkanolamines is considered as an important technology to reduce CO₂ emissions and to help alleviate global climate change. To understand more the thermodynamics of some of the CO₂-Amines, the NRTL electrolyte model has been used to simulate the behaviour of carbon dioxide absorption by some amines. To determine NRTL interaction parameters of the model, VLE, heat capacity and excess enthalpy data have been used. In this study, carbon dioxide, water and Methyl DiEthanolAmine (MDEA) ternary system are used to calculate eNRTL (electrolyte Non-Random Two Liquid) interaction parameters, and the system was modelled using VLE data available in the literature. Differential evolution algorithm (DE), an evolutionary computational technique, has been used to estimate NRTL parameters model to predict the VLE of CO₂ with MDEA. Differential Evolution algorithm (DE) have been used to compare it with annealing (SA) and deterministic technique like Levenberg–Marquardt (LM) using one set of experimental data for MDEA-H₂O system. Its standard deviation is lower than those of SA and LM algorithms when used to regress the eNRTL binary interactions parameters for MDEA-H₂O

Keywords: Thermodynamics of Electrolytes; CO₂ Capture; MDEA; Differential Evolution; NRTL.

1. Introduction

Differential Evolution (DE) algorithm is a new heuristic approach mainly having three advantages; finding the true global minimum regardless of the initial parameter values, fast convergence, and using few control parameters. DE algorithm is a population based algorithm like genetic algorithms using similar operators; crossover, mutation and selection. However, the success of DE in solving a specific problem crucially depends on appropriately choosing trial vector generation strategies and their associated control parameter values. Employing a trial-and-error scheme to search for the most suitable strategy and its associated parameter settings requires high computational costs. Moreover, at different stages of evolution, different strategies coupled with different parameter settings may be required in order to achieve the best performance. The NRTL-electrolyte model has been used for CO₂ absorption by MDEA where DE has been applied to have a better optimisation of the model.

Scalable simulation, design, and optimization of the CO₂ capture processes start with modeling of the thermodynamic properties, specifically vapor-liquid equilibrium (VLE) and chemical reaction equilibrium, as well as calorimetric properties. Accurate modeling of thermodynamic properties requires availability of reliable experimental data. For the rational gas treating processes

the knowledge of VLE of the acid gas over alkanolamine solution is required besides the knowledge of mass transfer and kinetics. The major problem concerning the VLE measurements of aqueous alkanolamine-acid gas systems, in general, is that lack of consistency and regularity in the numerous published values.

Excess Gibbs energy-based activity coefficient models provide a practical and rigorous thermodynamic framework to model thermodynamic properties of aqueous electrolyte systems, including aqueous alkanolamine systems for CO₂ capture (Chen & Mathias, 2002, Chen, 2006). Austgen *et al.* (1991) and Posey (1996) applied the electrolyte NRTL model (Song & Chen, 2009; Chen & Evans, 1986; Chen *et al.*, 1982) to correlate CO₂ solubility in aqueous MDEA solution and other aqueous alkanolamines.

Kuranov *et al.* (1996) and Kamps *et al.* (2001) used Pitzer's equation correlate the VLE data of the MDEA-H₂O-CO₂ system. Faramarzi *et al.* (2010) used the extended UNIQUAC model (Thomsen, K.; Rasmussen, 1999) to represent VLE for CO₂ absorption in aqueous MDEA, MEA, and mixtures of the two alkanolamines. Arcis *et al.* (2009) also fitted the VLE data with Pitzer's equation and used the thermodynamic model to estimate the enthalpy of solution of CO₂ in aqueous MDEA.

In this work, we used the electrolyte NRTL model as the thermodynamic framework to correlate experimental

data for CO₂ absorption in aqueous MDEA solution. The present work requires solving multivariable optimization problem to determine the interaction parameters of the developed VLE model. In the present paper, DE algorithms (Price & Storn, 1997) have been used for estimation of interaction parameters of the VLE model over a wide range of temperature, CO₂ partial pressure, and amine concentration range. Differential evaluation (DE) is a generic name for a group of algorithms, which is based on the principles of GA (Genetic Algorithm) but have some inherent advantages over GA, like its simple structure, ease of use, speed, and robustness.

We expand the scope of the work of Austgen *et al.* (1991) and Posey⁴ to cover all thermodynamic properties. Much new data for thermodynamic properties and calorimetric properties have become available in recent years, and they cover wider ranges of temperature, pressure, MDEA concentration, and CO₂ loading. The binary NRTL parameters for MDEA-water binary are regressed from the binary VLE, excess enthalpy, and heat capacity data. The binary NRTL parameters for water-electrolyte pairs and MDEA-electrolyte pairs and the standard-state properties of protonated MDEA ion are obtained by fitting to the ternary VLE, heat of absorption, heat capacity, and NMR spectroscopic data.

With the use of the electrolyte NRTL model for the liquid-phase activity coefficients, the PC-SAFT (Gross, J.; Sadowski, 2001, 2002) equation of state (EOS) is used for its ability to model vapor-phase fugacity coefficients at high pressures, which is an important consideration for modeling CO₂ compression, where its parameters used in Zhang and Chen (2010), Gross and Sadowki (2002) and AspenDataBank (2010). The parameters for water and CO₂ are taken from the literature (Gross and Sadowki, 2002; AspenDataBank, 2010). The parameters for MDEA are obtained from the regression of experimental data on vapor pressure, liquid density, and liquid heat capacity.

In this work, Differential Evolution algorithm (DE) have been used to compare it with annealing (SA) and deterministic technique like Levenberg–Marquardt (LM).

2. Thermodynamic Framework

2.1 Chemical and Phase Equilibrium

Carbon dioxide solubility in aqueous amine solutions is determined by both its physical solubility and the chemical equilibrium for the aqueous phase reactions among CO₂, water, and amines. The equilibrium of CO₂ in vapor and liquid phases is expressed in the following chemical equilibrium



Where it an been expressed in Henry's law by the following formula

$$Py_{CO_2}\phi_{CO_2} = H_{CO_2}x_{CO_2}\gamma_{CO_2}^* \quad (2)$$

where ϕ_{CO_2} the CO₂ fugacity coefficient in the vapor phase, H_{CO_2} the Henry's law constant of CO₂ in the mixed solvent of water and amine, $\gamma_{CO_2}^*$ the unsymmetrical activity coefficient of CO₂ in the mixed solvent of water and amine, P is the system pressure, y_{CO_2} the mole fraction of CO₂ in the vapor phase, and x_{CO_2} the equilibrium CO₂ mole fraction in the liquid phase. Henry's constant in the mixed solvent can be calculated from those of the pure solvents (Van Ness & Abbott, 1979)

$$\ln\left(\frac{H_i}{\gamma_i^\infty}\right) = \sum_A x_A \ln\left(\frac{H_{iA}}{\gamma_{iA}^\infty}\right) \quad (3)$$

H_{iA} The Henry's constant of supercritical component i in pure solvent A , the infinite dilution activity coefficient of supercritical component i in the mixed solvent, γ_{iA}^∞ the infinite dilution activity coefficient of supercritical component i in pure solvent A , and x_A the mole fraction of solvent A , and H_i is the Henry's constant of supercritical component in the mixed solvent. w_A is used instead of x_A in Eq 3 to weigh the contributions from different solvent (Aspen Data bank, 2010). The parameter w_A is calculated using Eq 4:

$$w_A = \frac{x_A(V_{iA}^\infty)^{2/3}}{\sum_B x_B(V_{iA}^\infty)^{2/3}} \quad (4)$$

V_{iA}^∞ represents the partial molar volume of supercritical component i at infinite dilution in pure solvent A , calculated from the Brelvi-O'Connell model (1972) with the characteristic volume for the solute ($V_{CO_2}^{BO}$) and solvent (V_s^{BO}).

The correlation of the characteristic volume for the Brelvi-O'Connell model (V_i^{BO}) is given as follows:

$$V_i^{BO} = v_{1,i} + v_{2,i}T \quad (5)$$

Here, the critical volume, $v_{n,i}$, was used as the characteristic volume for MDEA Zhang & Chen (2011), for CO₂ from Yan and Chen (2010) and for H₂O from Brelvi and O'Connell (1972).

The correlation for Henry's constant is given as follows:

$$\ln H_{ij} = a_{ij} + \frac{b_{ij}}{\ln T + c_{ij} \ln T + d_{ij}T} \quad (6)$$

These parameters can be found in Yan and Chen (2010) for CO₂(solute)-H₂O(solvent) and in Zhang & Chen (2011) for CO₂(solute)-MDEA(solvent)

2.2 Aqueous-Phase Chemical Equilibrium

The processes discussed involve both chemical equilibria and multi-component phase equilibria. The liquid phase comprises both molecular species and ionic species, which makes the modelling non-trivial. The chemical reactions taking place in the liquid phase for MDEA-CO₂-H₂O can be expressed as:

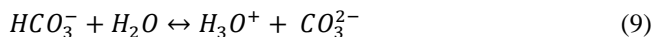
Water ionisation



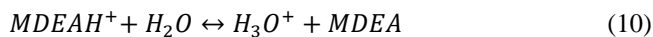
Dissociation of carbon dioxide



Dissociation of bicarbonate



Dissociation of protonated amine



The equilibrium constants of the chemical reactions (8-11) can be expressed as follows:

$$K = \prod(\gamma_i x_i)^{\theta_i} \quad (11)$$

Or another form of the equilibrium constant, K_j , of reaction j , can take place using the reference-state Gibbs free energies, G_j^o , of the participating components

$$-RT \ln K_j = \Delta G_j^o(T) \quad (12)$$

For the aqueous phase reactions, the reference states chosen are pure liquid for the solvents (water and MDEA), and aqueous phase infinite dilution for the solutes (ionic and molecular).

The thermodynamic expression for equilibrium partial pressure of CO_2 in aqueous MDEA solutions is as follows:

$$P_{CO_2} = \frac{(H_{CO_2} K_2 x_{MDEAH^+} \gamma_{MDEAH^+} x_{HCO_3^-} \gamma_{HCO_3^-})}{K_1 x_{H_2O} x_{MDEA} \gamma_{H_2O} \gamma_{MDEA}} \quad (13)$$

Where, x_{ns} are the liquid phase mole fractions of the components, based on true molecular or ionic species at equilibrium.

The calculation of the concentration for each component at equilibrium is as follows:

$$C_{MDEA^+} = C_{HCO_3^-} = C_{MDEA}^0 \alpha_{CO_2} \quad (14)$$

$$C_{MDEA} = C_{MDEA}^0 (1 - \alpha) \quad (15)$$

Activity coefficients γ_i (based on mole fraction scale) for different species present in the liquid phase are calculated from NRTL model.

$$\varphi_{CO_2} \gamma_{CO_2} P = k_{HCO_2} x_{CO_2} \gamma_{CO_2} \exp \left[\frac{v_{CO_2}^{\infty} (P - P_{H_2O}^s)}{RT} \right] \quad (16)$$

Where the final reaction, only takes place for MDEA. In addition to the chemical equilibria the distribution of species between the vapour and the liquid phase must be modelled through the vapour-liquid equilibria (VLE). The standard VLE problem may be formulated through the thermodynamic equilibrium criteria at a given temperature and pressure.

Henry's law constants for CO_2 with water and for CO_2 with MDEA are required. Because of the reaction between CO_2 and amines, it is impossible to get its solubility in amines or MDEA. So for the prediction of the physical

solubility in aqueous MDEA, the CO_2 – N_2O analogy is widely accepted in the literature (Chen & Mathias, 2002; Faramarzi *et al.* 2009). This theory is based on the fact that CO_2 and N_2O are rather similar molecules. The only difference between the molecules is, that N_2O does not chemically (only physically) dissolve in aqueous MDEA. According to the CO_2 – N_2O analogy the Henry's constant (physically dissolved).

So a similar molecular structure of CO_2 is chosen, N_2O , to derive its physical solubility in amines, where their Henry constants are related according to Eq 5.

$$\frac{H_{CO_2, MDEA}}{H_{N_2O, MDEA}} = \frac{H_{CO_2, water}}{H_{N_2O, water}} \quad (17)$$

The solubility of N_2O in pure MDEA was reported by Wang *et al.* (1992). And based on the work of Versteef and van Swaij (1988), we obtained the solubilities of CO_2 and N_2O in water. Then we can use Eq 7 to determine $H_{CO_2, MDEA}$ and its parameters.

3. Model and Data Used

The Gibbs free energy of solvent s , G_s , is calculated from the ideal gas Gibbs free energy of solvent s , G_s^{ig} , and the Gibbs free energy departure, G_s^{ig-l} , from ideal gas to liquid at temperature T .

$$G_s(T) = G_s^{ig}(T) + \Delta G_s^{ig-l}(T) \quad (18)$$

The ideal gas Gibbs free energy of solvent s , G_s^{ig} , is calculated from the ideal gas Gibbs free energy of formation of solvent s at 298.15 K, $\Delta_f G_{s,298.15}^{ig}$, the ideal gas enthalpy of formation of solvent s at 298.15 K, $\Delta_f H_{s,298.15}^{ig}$, and the ideal gas heat capacity of solvent s , $C_{p,s}^{ig}$.

$$G_s^{ig}(T) = \Delta_f H_{s,298.15}^{ig} + \int_{298.15}^T C_{p,s}^{ig} dT - T * \left(\frac{\Delta_f H_{s,298.15}^{ig} - \Delta_f G_{s,298.15}^{ig}}{298.15} + \int_{298.15}^T \frac{C_{p,s}^{ig}}{T} dT \right) \quad (19)$$

The reference-state properties $\Delta_f G_{s,298.15}^{ig}$ and $\Delta_f H_{s,298.15}^{ig}$ are obtained from AspenDatabank (2010) and regressed from Wagman *et al.* (1982), and Zhang and Chen (2011).

The correlation for the ideal gas heat capacity is given as follows:

$$C_p^{ig} = C_{1i} + C_{2i}T + C_{3i}T^2 + \dots C_{6i}T^5 \quad (20)$$

where $C_{7i} < T < C_{8i}$

The reference-state properties $\Delta_f G_{s,298.15}^{ig}$ and $\Delta_f H_{s,298.15}^{ig}$ can be obtained from Aspen Data bank (2010), Wagman *et al.* (1982), and Zhang & Chen (2011). The ideal heat capacities are obtained from Aspen Data bank, and Zhang & Chen. For water, The Gibbs free energy departure

function is obtained from ASME steam tables. For MDEA, the departure function is calculated from the PC-SFT equation of state.

For molecular solute CO₂, the Gibbs free energy in aqueous phase infinite dilution is calculated from Henry's law :

$$G_i^{\infty,aq}(T) = \Delta_f G_i^{ig}(T) + RT \ln \left(\frac{H_{i,w}}{P^{ref}} \right) \quad (21)$$

where $G_i^{\infty,aq}(T)$ is the mole fraction scale aqueous-phase infinite dilution Gibbs free energy of solute i at temperature T, $\Delta_f G_i^{ig}(T)$ the ideal gas Gibbs free energy of formation of solute i at temperature T, $H_{i,w}$ the Henry's constant of solute i in water, and P^{ref} the reference pressure.

For ionic species, the Gibbs free energy in aqueous-phase infinite dilution is calculated from the Gibbs free energy of formation in aqueous-phase infinite dilution at 298.15 K, the enthalpy of formation in aqueous-phase infinite dilution at 298.15 K, and the heat capacity in aqueous-phase infinite dilution

$$G_i^{\infty,aq}(T) = \Delta_f H_{i,291.15}^{\infty,aq} + \int_{298.15}^T C_{p,i}^{\infty,aq} dT - T * \left(\frac{\Delta_f H_{i,291.15}^{\infty,aq} - \Delta_f G_{i,291.15}^{\infty,aq}}{298.15} + \int_{298.15}^T \frac{C_{p,i}^{\infty,aq}}{T} dT \right) + RT \ln \left(\frac{1000}{M_w} \right) \quad (22)$$

Here, $G_i^{\infty,aq}(T)$ is the mole fraction scale aqueous-phase infinite dilution Gibbs free energy of solute i at temperature T, $\Delta_f G_{i,298.15}^{\infty,aq}$ the molality scale aqueous-phase infinite dilution Gibbs free energy of formation of solute i at 298.15 K, $\Delta_f H_{i,291.15}^{\infty,aq}$ the aqueous phase infinite dilution enthalpy of formation of solute i at 298.15 K, and $C_{p,i}^{\infty,aq}$ the aqueous-phase infinite dilution heat capacity of solute i. The term $RT \ln(1000/M_w)$ is added because $\Delta_f G_{i,291.15}^{\infty,aq}$, as reported in the literature, is based on molality concentration scale while $G_i^{\infty,aq}$ is based on mole fraction scale. The standard-state properties $G_i^{\infty,aq}$, $\Delta_f H_{i,291.15}^{\infty,aq}$ and $\Delta_f G_{i,298.15}^{\infty,aq}$ are available in the literature (Aspen Databank, 2010, Criss & Gobble, 1964) for most ionic species except this of MDEAH⁺ which is calculated from the equilibrium constant in Kamps and Maurer²⁴.

3.1 Heat of Absorption and Heat Capacity

The CO₂ heat of absorption in aqueous MDEA solutions can be derived from an enthalpy balance of the absorption process:

$$\Delta H_{abs} = \frac{n_{Final} H_{Final}^l - n_{Initial} H_{Initial}^l - n_{CO_2} H_{CO_2}^g}{n_{CO_2}} \quad (23)$$

Where ΔH_{abs} , Heat of absorption per mole of CO₂, H_{final}^l , Molar enthalpy of the final solution, $H_{initial}^l$, Molar enthalpy of the initial solution, $H_{CO_2}^g$, Molar enthalpy of gaseous CO₂ absorbed, n_{final} , Number of moles of the final solution, $n_{initial}$, Number of moles of the initial solution and n_{CO_2} , Number of moles of CO₂ absorbed.

To calculate the heat of absorption, enthalpy calculations for the final and initial MDEA-CO₂-H₂O system and for gaseous CO₂ are required. The heat capacity of MDEA-CO₂-H₂O system can be calculated from the temperature derivative of enthalpy. We use the following equation for liquid enthalpy

$$H^l = x_w H_w^l + x_s H_s^l + \sum_i x_i H_i^{\infty,aq} + H^{ex} \quad (24)$$

Here, H^l is the molal enthalpy of the liquid mixture, H_w^l the molar enthalpy of liquid water, H_s^l the molar enthalpy of liquid nonaqueous solvent s, $H_i^{\infty,aq}$ the molar enthalpy of solute a (molecular or ionic) in aqueous-phase infinite dilution, and H^{ex} the molar excess enthalpy. The terms x_w , x_s and x_i represent the mole fractions of water, nonaqueous solvent s, and solute i respectively.

The liquid enthalpy for pure water is calculated from the ideal gas model and ASME Tables EOS for enthalpy departure:

$$H_w^l(T) = \Delta_f H_{w,298.15}^{ig} + \int_{298.15}^T C_{p,w}^{ig} dT + \Delta H_w^{ig \rightarrow l}(T, p) \quad (25)$$

Where $H_w^l(T)$ is the liquid enthalpy of water at temperature T, $\Delta_f H_{w,298.15}^{ig}$ the ideal gas enthalpy of formation of water at 298.15 K, $C_{p,w}^{ig}$ the ideal-gas heat capacity of water, and $\Delta H_w^{ig \rightarrow l}(T, p)$ the enthalpy departure calculated from the ASME Steam Tables EOS.

Liquid enthalpy of the nonaqueous solvent s is calculated from the ideal-gas enthalpy of formation at 298.15 K, the ideal gas heat capacity, the vapor enthalpy departure, and the heat of vaporization:

$$H_s^l(T) = \Delta_f H_{s,298.15}^{ig} + \int_{298.15}^T C_{p,s}^{ig} dT + \Delta H_s^v(T, p) - \Delta_{vap} H_s(T) \quad (26)$$

Here, $H_s^l(T)$ is the liquid enthalpy of solvent s at temperature T, $\Delta_f H_{s,298.15}^{ig}$ the ideal-gas enthalpy of formation of solvent s at 298.15 K, $C_{p,s}^{ig}$ the ideal-gas heat capacity of solvent s, $\Delta H_s^v(T, p)$ the vapor enthalpy departure of solvent s, and $\Delta_{vap} H_s(T)$ the heat of vaporization of solvent s.

The PC-SAFT EOS is used for the vapor enthalpy departure and the DIPPR heat of vaporization correlation is used for the heat of vaporization. The DIPPR equation is:

$$\Delta_{vap} H_i = C_{1i} (1 - T_{ri})^Z \quad (27)$$

Where $Z = C_{2i} + C_{3i} T_{ri} + C_{4i} T_{ri}^2 + C_{5i} T_{ri}^3$ and $T_{ri} = T/T_{ci}$ (T_{ci} is the critical temperature of component i in K). The T_{ci} of MDEA is obtained from Von Niederhausern *et al.* (2006). The correlation parameters are obtained from Zhang & Chen (2011).

Heat of vaporization of MDEA, P_{MDEA}^{*l} , calculated from the vapor Pressure (Antoine Equation, P_{MDEA}^{*l}) using the Clausius-Clapeyron equation, $\frac{d \ln P}{dT} = \frac{\Delta H_{vap}}{RT^2}$.

$$\ln P_{MDEA}^{*,l} = C_1 + \frac{C_2}{T} + C_3 \ln T + \frac{C_4}{T^2} \quad (28)$$

The parameters above, C_n , are regressed using the vapor pressure data (Von Niederhausern *et al.*, 2006; Daubert & Hutchison, 1990; Noll *et al.*, 1998)

The enthalpies of ionic solutes in aqueous phase infinite dilution are calculated from the enthalpy of formation at 298.15 K in aqueous-phase infinite dilution and the heat capacity in aqueous-phase infinite dilution:

$$H_i^{\infty,aq}(T) = \Delta_f H_{i,298.15}^{\infty,aq} + \int_{298.15}^T C_{p,i}^{\infty,aq} dT \quad (29)$$

Where $H_i^{\infty,aq}(T)$ is the enthalpy of solute i in aqueous-phase infinite dilution at temperature T , $\Delta_f H_{i,298.15}^{\infty,aq}$ the enthalpy of formation of solute i in aqueous-phase infinite dilution at 298.15 K, and $C_{p,i}^{\infty,aq}$ the heat capacity of solute i in aqueous-phase infinite dilution.

In this study, $\Delta_f H_{i,298.15}^{\infty,aq}$ and $C_{p,i}^{\infty,aq}$ for MDEAH⁺ are determined by fitting to the experimental phase equilibrium data, the heat of solution data, and the speciation data, together with molality scale Gibbs free energy of formation at 298.15 K, $\Delta_f G_{i,298.15}^{\infty,aq}$, and NRTL interaction parameters.

The enthalpies of molecular solutes in aqueous phase infinite dilution are calculated from Henry's law:

$$H_i^{\infty,aq}(T) = \Delta_f H_i^{ig}(T) - RT^2 \left(\frac{\partial \ln H_{i,w}}{\partial T} \right) \quad (30)$$

Where $\Delta_f H_i^{ig}(T)$ is the ideal gas enthalpy of formation of solute i at temperature T , $H_{i,w}$ Henry's constant of solute i in water. Excess enthalpy, H^{ex} is calculated from the activity coefficient model, NRTL in this case.

3.2 The eNRTL Model

The electrolyte NRTL model consists of three contributions. The first contribution is the long-range contribution represented by the Pitzer-Debye-Hückel expression, which accounts for the contribution due to the electrostatic forces among all ions. The second contribution is an ion-reference-state-transfer contribution represented by the Born expression. In the electrolyte NRTL model, the reference state for ionic species is always infinitely dilute state in water even when there are mixed solvents. The Born expression accounts for the change of the Gibbs energy associated with moving ionic species from a mixed-solvent infinitely dilute state to an aqueous infinitely dilute state. The Born expression drops out if water is the sole solvent in the electrolyte system. The third contribution is a short-range contribution represented by the local composition electrolyte NRTL expression, which accounts for the contribution due to short-range interaction forces among all species. The electrolyte NRTL expression was developed based on the NRTL local composition concept, the like ion repulsion assumption, and the local electroneutrality assumption. The like-ion repulsion assumption stipulates that in the first coordination shell of a cation (anion) the local composition of all other cations (anions) is zero. The local electroneutrality assumption

imposes a condition that in the first coordination shell of a molecular species the composition of cations and anions is such that the local electric charge is zero.

The Pitzer-Debye-Hückel expression for excess Gibbs energy, normalized to a mole fraction of unity for the solvent and zero mole fraction for ions, is given as follows:

$$\frac{g^{ex*,PDH}}{RT} = -(\sum_k X_k) \left(\frac{1000}{M_s} \right)^{1/2} \left(\frac{4A\phi I_x}{\rho} \right) \ln(1 + \rho I_x^{1/2}) \quad (31)$$

Where

$$A_\phi = \left(\frac{1}{3} \right) \left(\frac{2\pi N_0 d}{1000} \right)^{1/2} \left(\frac{e^2}{DKT} \right)^{2/3}$$

$$I_x = \frac{1}{2} \sum_i Z_i^2 x_i$$

The Born expression for excess Gibbs energy is given as follows:

$$\frac{g^{ex*,Born}}{RT} = \frac{e^2}{2kT} \left(\frac{1}{D} - \frac{1}{D_w} \right)^{1/2} \left(\sum_i \frac{x_i Z_i^2}{r_i} \right) * 10^{-2} \quad (32)$$

where D stands for the dielectric constant of the solvent mixture with the same solvent ratio as that in the electrolyte solution. D is a function of the temperature, $D_i(T) = A_i + B_i \left[\left(\frac{1}{T} \right) - \left(\frac{1}{C_i} \right) \right]$ and its parameters are found in Aspen Databank (2010).

The local-composition electrolyte NRTL expression for excess Gibbs energy is given as follows:

$$g^{ex,lc} = \sum_m X_m \frac{\sum_j X_j G_{jm} \tau_{jm}}{\sum_k X_k G_{km}} + \sum_c X_c \sum_{a'} \left(\frac{X_{a'}}{\sum_{a''} X_{a''}} \right) \frac{\sum_j X_j G_{jc,a} \alpha_{jc,a,c}}{\sum_k X_k G_{kc,a,c}} + \sum_a X_a \sum_{c'} \left(\frac{X_{c'}}{\sum_{c''} X_{c''}} \right) \frac{\sum_j X_j G_{ja,c} \alpha_{ja,c,a}}{\sum_k X_k G_{ka,c,a}} \quad (33)$$

Where

$$G_{jm} = \exp(-\alpha_{jm} \tau_{jm})$$

$$G_{jc,ac} = \exp(-\alpha_{jc,ac} \tau_{jc,ac})$$

$$G_{ja,ca} = \exp(-\alpha_{ja,ca} \tau_{ja,ca})$$

$$G_{ja,ca} = \exp(-\alpha_{ja,ca} \tau_{ja,ca})$$

$$G_{cm} = \frac{\sum_a X_a G_{ca,m}}{\sum_{a'} X_{a'}}$$

$$G_{am} = \frac{\sum_c X_c G_{ca,m}}{\sum_{c'} X_{c'}}$$

$$\alpha_{cm} = \frac{\sum_a X_a \alpha_{ca,m}}{\sum_{c'} X_{c'}}$$

$$\alpha_{am} = \frac{\sum_c X_c \alpha_{ca,m}}{\sum_{c'} X_{c'}}$$

$$\tau_{mc,ac} = \tau_{cm} - \tau_{ca,m} + \tau_{m,ca}$$

$$\tau_{ma,ca} = \tau_{am} - \tau_{ca,m} + \tau_{m,ca}$$

The variables τ_{cm} and τ_{am} are computed accordingly from G_{cm} and G_{am} . It is worth mentioning that the first term on the right-hand side of Eq 33 represents the short-range interaction contribution where the molecular species are the local center and the second and third terms account for the short-range interaction contributions where cations and anions are the local center, respectively.

In NRTL model, the binary interaction parameters for molecule-molecule binary, molecule-electrolyte binary, and electrolyte-electrolyte binary systems are required for liquid phase activity coefficients calculations. Here, electrolytes are defined as cation and anion pairs.

We set all molecule-molecule and electrolyte-electrolyte binary parameters to zero, unless specified otherwise, and molecule-electrolyte binary parameters to 8 and -4 as reported in NRTL model¹². The non-randomness factor (α) is fixed at 0.2, but it can be variable from 0.1 to 0.9. The calculated thermodynamic properties of the electrolyte solution are dominated by the binary NRTL parameters associated with the major species in the system. The calculated thermodynamic properties of the electrolyte solution are dominated by the binary NRTL parameters associated with the major species in the system. In other words, the binary parameters for the water-MDEA binary, the water-(MDEAH⁺, HCO₃⁻) binary, the water-(MDEAH⁺, CO₃²⁻) binary, and the MDEA-(MDEAH⁺, HCO₃⁻) binary systems determine the calculated thermodynamic properties. These binary parameters, in turn, are identified from fitting to available experimental data.

After proper consideration of unsymmetrical convention for the solutes and ionic species, the complete excess Gibbs energy expression of the electrolyte NRTL model is given as follows:

$$g^{ex*} = g^{ex,PDH} + g^{ex*,Born} + g^{ex*,lc} \quad (34)$$

The activity coefficient for any species i , ionic or molecular, solute or solvent, is derived from the partial derivative of the excess Gibbs energy with respect to the mole number of species i :

$$\ln \gamma_i = \frac{1}{RT} \left[\frac{\partial (n_i g^{ex*})}{\partial n_i} \right]_{T,P,n_{i \neq j}} \quad (35)$$

Where n_t is the total mole number for all species in the system.

4. Data Regression

At first all available experimental data from different authors were used for regression analysis to obtain the interaction parameters, which resulted in a large average correlation deviation. Then a lot of equilibrium curves were

made at the same temperatures and the same initial amine concentrations but from the different authors and some sets of data, which were far away from most of the data, were discarded. Finally, the combination of data useful for generating a correlation to obtain a set of interaction parameters has been identified. Since the adjustable interaction parameters are characteristic of pair interactions of components of the solution and are independent of solution composition, the fitted parameters are valid outside the range of concentrations over which they were fitted.

4.1 Differential Evolution Algorithm

DE is a stochastic, population-based method (Storn, 1997). These methods heuristically “mimic” biological evolution, namely, the process of natural selection and the “survival of the fittest” principle.

Differential evolution (DE) technique is used to estimate the interaction parameters for the VLE model. An adaptive search procedure based on a “population” of candidate solution points is used. “NP” denotes the population size. In a population of potential solutions within an n -dimensional search space, a fixed number of vectors are randomly initialized, then evolved over time to explore the search space and to locate the minima of the objective function. “D” denotes the dimension of each vector, which is actually the number of optimum parameters to be estimated of the proposed objective function ψ (Eq 36)

$$\psi = \sum_{i=1}^c \sum_{j=1}^n \left| \frac{P_{CO_2}^{cal} - P_{CO_2}^{exp}}{P_{CO_2}^{exp}} \right|^2 \quad (36)$$

n is the number of experimental data, and c is the number of components in the mixture, respectively.

The main operation in DE is the NP number of competitions, which are to be carried out to decide the next generation population. Generations or iterations involve a competitive selection that drops the poorer solutions. From the current generation population of the vectors, one target vector is selected. Among the remaining population vectors, DE adds the weighted weight factor is denoted by F , and is specified at the starting) difference between two randomly chosen population vectors to third vector, called trial vector (randomly chosen), which results in a “noisy” random vector. This operation is called recombination (mutation). Subsequently, crossover is performed between the trial vector and the noisy random vector (perturbed trial vector) to decide upon the final trial vector or offspring of this generation. For mutation and crossover to be carried out together, a random number is generated which is less than the CR crossover constant). If the random number generated is greater than CR, then the vector taken for mutation (trial vector) is kept copied as it is; as an offspring of this generation (mutation is not compulsory). This way no separate probability distribution has been used which makes the scheme completely self-organizing. Finally, the trial vector replaces the target vector for the next generation

population, if, and only if it yields a reduced value the objective function than in comparison to the objective function based on target vector. In this way, all the NP number of vectors of the current generation is selected one by one as target vectors and checked whether the trial vector (offspring) to create the population of the next generation should replace them or not. The control parameters of the algorithm are: number of parents (NP), weighing factor or mutation constant (F), crossover constant (CR). There is always a convergence speed (lower F value) and robustness (higher NP value) trade-off. CR is more like a fine tuning element. High values of CR like CR = 1 give faster convergence if convergence occurs.

For each individual $x_{i,G}$ in the current generation G, DE generates a new trial individual $x'_{i,G}$ by adding the weighted difference between two randomly selected individuals $x_{r1,G}$ and $x_{r2,G}$ to a third randomly selected individual $x_{r3,G}$. The resulting individual $x'_{i,G}$ is crossed-over with the original individual, $x_{i,G}$. The fitness of the resulting individual, referred to as perturbed vector $u_{i,G+1}$, is then compared with the fitness of $x_{i,G}$. If the fitness of $u_{i,G+1}$ is greater than the fitness of $x_{i,G}$, $x_{i,G}$ is replaced with $u_{i,G+1}$, otherwise $x_{i,G}$, remains in the population as $u_{i,G+1}$. Differential Evolution is robust, fast, and effective with global optimization ability. It does not require that the objective function is differentiable, and it works with noisy, epistatic and time-dependent objective functions. Pseudocode of DE shows:

1. *Input* : $D, G_{max}, NP \geq 4, F \in (0,1), CR \in [0,1]$, and *initial bounds* : $\vec{x}^{(lo)}, \vec{x}^{(hi)}$
2. *Initialise* : $\forall i \leq NP \wedge \forall j \leq D : x_{i,j,G=0} = \vec{x}^{(lo)} + rand_j[0,1] \cdot (\vec{x}^{(hi)} - \vec{x}^{(lo)})$
 $i = \{1,2, \dots, NP\}, \{1,2, \dots, D\}, G = 0, rand_i[0,1] \in [0,1]$
3. *While* $G < G_{max}$
 - $\forall i \leq NP$
 4. *Mutate and Recombine*
 - 4.1 $r_1, r_2, r_3 \in \{1,2, \dots, NP\}$, randomly selected, except : $r_1 \neq r_2$
 - 4.2 $j_{rand} \in \{1,2, \dots, D\}$, randomly selected once each i
 - 4.3 $\forall j \leq D, u_{j,i,G+1} = \{x_{j,r3,G} + F \cdot (x_{j,r1,G} - x_{j,r2,G})$
if $(rand_j [0,1] < CR \vee j = j_{rand})$
 $x_{j,i,G}$ otherwise
 5. *select*
 $x_{i,G+1} = \{\vec{u}_{i,G+1} \text{ if } f(\vec{u}_{i,G+1}) \leq f(\vec{u}_{i,G})$

$$\{x_{i,G} \text{ otherwise}$$

$$G = G + 1$$

There are some versions for optimization by mean differential evolution and two standard versions of DE, one of them, DERand1Bin, is chosen for optimization of eNRTL parameters.

It is recommended to set the number of parents NP to 10 times the number of parameters (e.g. For a binary mixtures such as MDEA-H₂O, we need two interaction parameters $\tau_{MDEA,H2O}$ and $\tau_{H2O,MDEA}$, then NP should be equal to 20 in this special case), to select weighting factor F=0.8, and crossover constant CR=0.9. It has been found recently that selecting F from the interval [0.5, 1.0] randomly for each generation or for each difference vector, a technique called dither, improves convergence behaviour significantly, especially for noisy objective functions. It has also been found that setting CR to a low value, e.g. CR=0.2 helps optimizing separable functions since it fosters the search along the coordinate axes. On the contrary this choice is not effective if parameter dependence is encountered, something which is frequently occurring in real-world optimization problems rather than artificial test functions. So for parameter dependence the choice of CR=0.9 is more appropriate. Another interesting empirical finding is that raising NP above, say, 40 does not substantially improve the convergence, independent of the number of parameters. Different problems often require different settings for NP, F and CR.

4.2 The strategy adopted

Different strategies can be adopted in DE algorithm depending upon the type of problem for which DE is applied. The strategies can vary; based on the vector to be perturbed, number of difference vectors considered for perturbation, and finally the type of crossover used (Babu, 2004)²⁸.

The DE algorithm is a population based algorithm like genetic algorithms using the similar operators; crossover, mutation and selection. The main difference in constructing better solutions is that genetic algorithms rely on crossover while DE relies on mutation operation. This main operation is based on the differences of randomly sampled pairs of solutions in the population.

The algorithm uses mutation operation as a search mechanism and selection operation to direct the search toward the prospective regions in the search space. The DE algorithm also uses a non-uniform crossover that can take child vector parameters from one parent more often than it does from others. By using the components of the existing population members to construct trial vectors, the recombination (crossover) operator efficiently shuffles information about successful combinations, enabling the search for a better solution space.

An optimization task consisting of D parameters can be represented by a D-dimensional vector. In DE, a population of NP solution vectors is randomly created at the start. This

population is successfully improved by applying mutation, crossover and selection operators. The main steps of the DE algorithm are given below:

- **Initialization**
- **Evaluation**
- **Repeat**
 - Mutation
 - Recombination
 - Evaluation
 - Selection
- **Until** (*termination criteria are met*)

5. RESULTS AND DISCUSSION

Only, the eNRTL parameters (Tables 1-2) have been regressed using differential evolution algorithm, the rest of the data have been taken from the literature. Table 3 summarizes the model parameters and sources of the parameters used in the thermodynamic model. Most of the parameters can be obtained from the literature. A lot of results can be plotted but we confined ourselves a few of them to show the modeling compared to the experimental and sometimes compared to eNRTL without DE algorithm. Figure 1 shows the comparison for the experimental total pressure data and the calculated results from the model. Figure 1 shows the model also provides excellent representation of the heat capacity data.

Figure 1 shows the comparison of the experimental data from Kim *et al.* (2008) with the model eNRTL-DE for MDEA-H₂O system. For both temperatures, as the mole fraction of MDEA increases the total pressure of the system decreases.

Figure 2 shows an increase in heat capacity as the temperature increases at different MDEA mole fraction. It shows a very good fit of the model with the experimental data.

The excess enthalpy fit is given in Figure 3. Both the experimental excess enthalpy data from Posey⁹ and those of Maham *et al.* (1997, 2000) are represented very well. It shows also a better fit for eNRTL-DE model. Figure 4 shows the model predictions for water and MDEA activity coefficients at 313, 353, and 393°K. While the water activity coefficient remains relatively constant, the model suggests that the MDEA activity coefficient varies strongly with MDEA concentration and temperature, especially in dilute aqueous MDEA solutions, and figure 4 shows the predicted activity coefficients of water and MDEA.

Figure 5 shows the species distribution as a function of CO₂ loading for a 23wt% MDEA solution at 293°K. The calculated concentrations of the species are consistent with the experimental NMR measurements from Jakobsen *et al.* (2005).

Figures 6 show comparisons of the model correlations and the experimental data of Mathonat (1995) for the integral heat of CO₂ absorption in aqueous MDEA solution at 313K. The calculated values are in good agreement with

the experimental data. Also shown in Figure 6 are the predicted differential heats of CO₂ absorption.

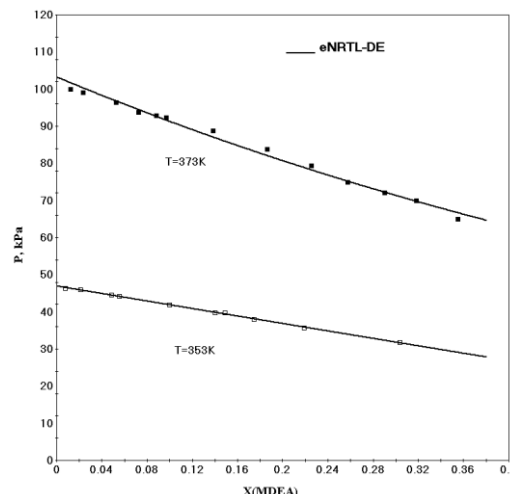


Figure 1 : Comparison of the experimental data from Kim *et al.* with the model eNRTL-DE for MDEA-H₂O system.

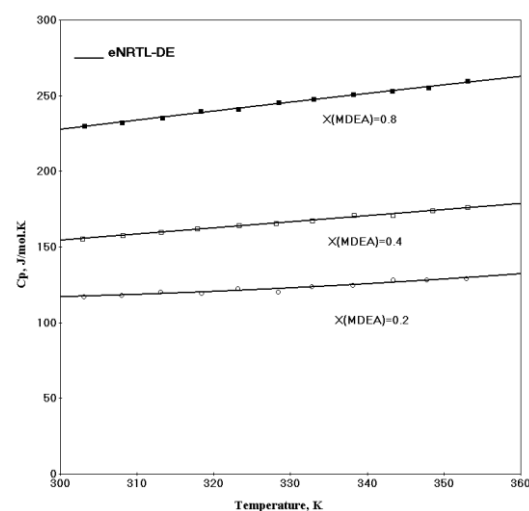


Figure 2 : Comparison of the experimental (MDEA-H₂O) data from Chen *et al.* with the model eNRTL-DE for MDEA-H₂O system.

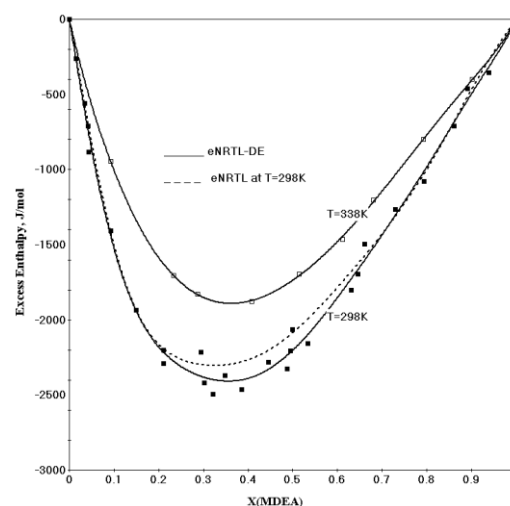


Figure 3 : Comparison of the experimental data from Posey with the model eNRTL-DE for MDEA-H₂O.

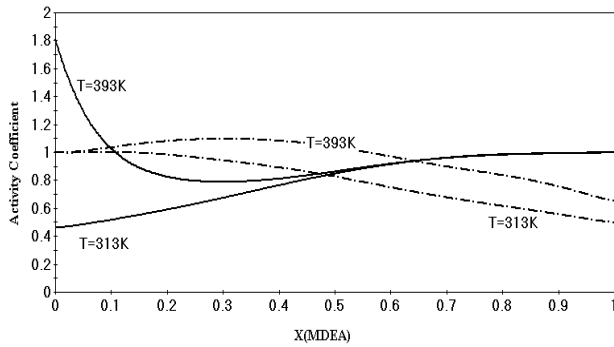


Figure 4 : Model predictions of MDEA and H₂O activity coefficients : (——) H₂O activity coefficients and (-.-.-) MDEA activity coefficients.

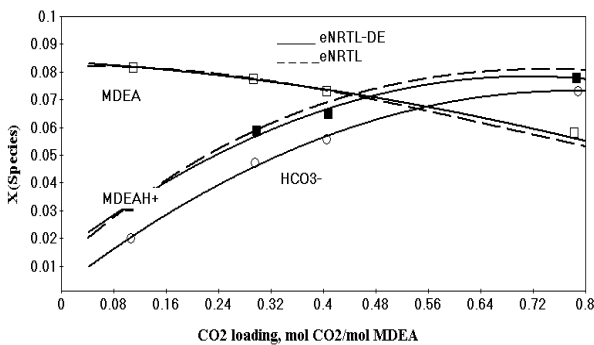


Figure 5 : Comparison of the experimental data for some species concentration in MDEA-CO₂-H₂O system at T=293K and MDEA concentration 23 wt%.

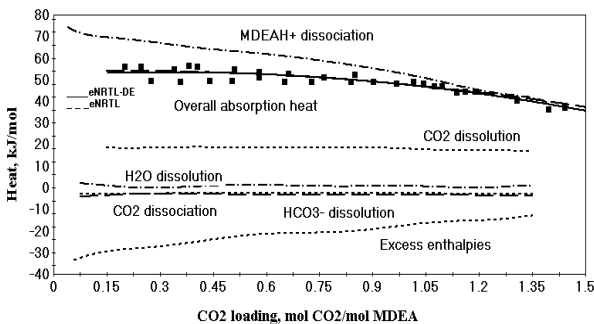


Figure 6 : Heat of reaction of the different components in 30 wt% MDEA solution at T=313K.

5.1 eNRTL parameters : Results

LM is a non-linear least-squares method, which uses a steepest descent method and cannot guarantee a global optimum solution; limited by the degree of non-linearity and initial guess. SA is a generic probabilistic meta-algorithm locating a good approximation to the global optima of a given objective function in a search space. The main driving force behind SA is to occasionally allow for wrong-way movement (uphill moves for minimization) saving the method from becoming stuck at local optima. DE maintains a pool of solutions rather than just one. New

candidate solutions are generated not only by “mutation” (as in SA), but also by “combination” of two solutions from the pool. It ensures to have a better global perspective of the solution than the other two techniques discussed.

Table 3 summarizes the model parameters, sources of the parameters and the type of data used in the thermodynamic model. Most of the parameters can be obtained from the literature. The remaining parameters are determined by fitting to the experimental data. For MDEA-H₂O binary only, the standard deviations are compared using DE algorithm and Levenberg–Marquardt (LM) algorithms (Table 1). It is clear that DE presents lower σ than LM and SA.

Table 1 : eNRTL parameters (τ) for the MDEA-H₂O using Differential Evolution Algorithm ($\alpha = 0.2$)

$$\tau = a + \frac{b}{T}$$

where T is the temperature in K and σ is the standard deviation.

Par.	$i-j$	Value	σ (eNRTL-DE)	σ (eNRTL-LM)	σ (eNRTL-SA)
a_{ij}	MDEA-H ₂ O	-1.3781	0.0129	0.0566	0.1472
a_{ji}	H ₂ O-MDEA	12.153	0.0469	0.1641	0.1078
b_{ij}	MDEA-H ₂ O	-316.46	5.3898	22.97	10.378
b_{ji}	H ₂ O-MDEA	-1237.9	8.7256	45.70	9.6247

a_{ij}	CO ₂ -H ₂ O	10.064*	-	-	-
a_{ji}	H ₂ O-CO ₂	10.064*	-	-	-
b_{ij}	CO ₂ -H ₂ O	-3268.135*	-	-	-
b_{ji}	H ₂ O-CO ₂	-3268.135	-	-	-

Table 2 : eNRTL parameters molecule-electrolyte binaries (τ) for the MDEA-H₂O-CO₂ system with DE ($\alpha = 0.2$)

Parameter	i	j	Value	σ
τ_{ij}	H ₂ O	(MDEAH ⁺ , HCO ₃ ⁻)	6.2699	0.0981
τ_{ji}	(MDEAH ⁺ , HCO ₃ ⁻)	H ₂ O	-7.8856	0.0194
τ_{ij}	H ₂ O	(MDEAH ⁺ , CO ₃ ²⁻)	17.2754	0.0367
τ_{ji}	(MDEAH ⁺ , CO ₃ ²⁻)	H ₂ O	-0.1982	0.0653
τ_{ij}	MDEA	(MDEAH ⁺ , HCO ₃ ⁻)	11.3765	0.0762
τ_{ji}	(MDEAH ⁺ , HCO ₃ ⁻)	MDEA	-3.1299	0.0492

6. CONCLUSIONS

The electrolyte eNRTL model has been successfully applied with Differential Evolution algorithm to calculate the interaction parameters and to correlate the experimental data on thermodynamic properties of MDEA-H₂O-CO₂ system. The model has validated a lot of experimental data, but more research needs to be carry out to compare eNRTL-DE with eNRTL-LM and eNRTL-LM for all the interactions parameters. The model can be used to support process modeling and simulation of the CO₂ capture process with MDEA.

Table 3 : Parameters estimated in modeling with their sources and the type of data regressed.

Parameters	Component	Source	Type of Data required in regression and their sources
$\Delta_f G_{298.15}^{ig}$	H ₂ O, MDEA, CO ₂	Aspen Databank	
$\Delta_f H_{298.15}^{ig}$	H ₂ O, MDEA, CO ₂	Aspen Databank	
C_P^{ig}	H ₂ O, CO ₂ MDEA	Aspen Databank Regression	Data (Liquid heat capacity of MDEA) Regression (Maham et al, Chen et al, Zhang et al)
$\Delta_f G_{298.15}^{\infty,aq}$	H ₃ O ⁺ , OH ⁻ , HCO ₃ ⁻ , CO ₃ ²⁻ MDEAH ⁺	Aspen Databank Regression	Data (VLE, excess enthalpy, heat capacity, and species concentration from NMR spectra for the MDEA-H ₂ O-CO ₂ system) Regression (Kuranov et al, Kamps et al, Ermatchkov et al, Mathonat, Weiland et al, Jackobsen et al)
$\Delta_f H_{298.15}^{\infty,aq}$	H ₃ O ⁺ , OH ⁻ , HCO ₃ ⁻ , CO ₃ ²⁻ MDEAH ⁺	Aspen Databank Regression	Data (VLE, excess enthalpy, heat capacity, and species concentration from NMR spectra for the MDEA-H ₂ O-CO ₂ system) Regression (Kuranov et al, Kamps et al, Ermatchkov et al, Mathonat, Weiland et al, Jackobsen et al)
$C_P^{\infty,aq}$	H ₃ O ⁺ , OH ⁻	Aspen Databank Criss and Cobble Regression	Data (VLE, excess enthalpy, heat capacity, and species concentration from NMR spectra for the MDEA-H ₂ O-CO ₂ system) Regression (Kuranov et al, Kamps et al, Ermatchkov et al, Mathonat, Weiland et al, Jackobsen et al)
$\Delta_{vap}H$	MDEA	Regression	Heat of vaporization of MDEA, calculated from the vapor Pressure (Antoine Equation) using the Clausius-Clapeyron equation
Antoine Equation	MDEA	Regression	Data (Vapor pressure of MDEA, heat of vaporization of MDEA, calculated from the vapor pressure using the Clausius-Clapeyron equation) Regression (Daubert et al, Noll et al, VonNiederhausern et al)
Dielectric Constant	MDEA	Criss and Cobble	
Henry's Constant	CO ₂ in H ₂ O CO ₂ in MDEA	Yan and Chen Zhang & Chen	
NRTL-Electrolyte Binary Parameters	CO ₂ -H ₂ O binary MDEA-H ₂ O binary MDEA-H ₂ O-CO ₂ Molecule-Electrolyte Binaries	Regression ^{1-DE} Regression ^{2-DE} Regression ^{3-DE}	Data 1. Solubility of CO ₂ in pure water 2. VLE, excess enthalpy, and heat capacity for the MDEA-H ₂ O and CO ₂ -H ₂ O binaries 3. VLE, excess enthalpy, heat capacity, and species concentration from NMR spectra for the MDEA-H ₂ O-CO ₂ system Regression 1. Yan & Chen 2. (Xu et al, Voutsas et al, Kim et al, Posey, Maham et al, Chiu and Li, Chen e al, Zhang et al) 3. (Kuranov et al, Kamps et al, Ermatchkov et a, Mathonat, Weiland et al, Jackobsen et al)

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