Prediction of Equilibrium Solubility of CO$_2$ in Aqueous Alkanolamines Using Differential Evolution Algorithm

M. Kundu$^1$, A. Chitturi$^1$ and S. S. Bandyopadhyay$^2$

$^1$. Chemical Engineering Group, Birla Institute of Technology and Science, Pilani, Rajasthan, India
$^2$. Separation Science Laboratory, Cryogenic Engineering Centre, Indian Institute of Technology, Kharagpur, India

The design of sour-gas treating processes with alkanolamine solvents requires knowledge of the vapour–liquid equilibrium (VLE) of the aqueous acid gas–alkanolamine systems. Representation of the experimental data with a thermodynamically rigorous model is required, so that one can systematically correlate and predict the VLEs of these systems. The modified Clegg–Pitzer equations have been used to correlate and predict the VLE of CO$_2$ in the aqueous N-methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP) systems. Differential evolution (DE), an evolutionary computational technique, has been used for parameter estimation of the developed VLE model in an effort to predict the VLE of CO$_2$ in aqueous MDEA and AMP solutions with a comparable accuracy to that by using the non-traditional simulated annealing (SA) and deterministic technique like Levenberg–Marquardt (LM), if not better. In this work, the DE/rand-best/1/bin strategy has been used for finding near global minimum solutions to the multivariable optimization problem as a part of the numerical solution of the developed model.

Keywords: differential evolution, simulated annealing, VLE, CO$_2$, MDEA, AMP

INTRODUCTION

Removal of acid gas impurities, such as CO$_2$ and H$_2$S, from gas mixtures is very important in natural gas processing, hydrogen purification, treating refinery-off gases, and gas synthesis for ammonia manufacture. Regenerative chemical absorption of the acid gases, into solutions of alkanolamines, is widely used for gas treating. For the rational design of gas treating processes the knowledge of vapour–liquid equilibrium (VLE) of the acid gas over alkanolamine solution is required besides the knowledge of mass transfer and kinetics. The equilibrium solubility determines the minimum circulation rate of the solvent through the absorber, determines the maximum allowable concentration of the acid gases in the regenerated solution to meet the product gas specification, and provides boundary conditions for solving partial differential equations describing mass transfer coupled with chemical reactions. 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. One problem that is encountered in modelling acid gas treating is that the experimenters report statistically different partial pressures of the acid gases at the exactly same conditions (Kundu, 2004). Reliable thermodynamic models can be used confidently to interpolate or extrapolate experimental data, required for process design.
In order to have an understanding of those chemically reacting, multi-component, multiphase systems, a brief discussion about the chemical equilibria, vapour-liquid phase equilibria, thermodynamic framework, and activity coefficient model are included, which ensures an appropriate formulation of the objective function.

The present work requires solving multivariable optimization problem to determine the interaction parameters of the developed VLE model. Among the open literature on modelling VLE of CO2 in single and mixed amine solvents, using the traditional, deterministic techniques, the work of Kent and Eisenberg (1976); Li and Shen (1993); Deshmukh and Mather (1981); Austgen and Rochelle (1991); Li and Mather (1994); Kurzun et al. (1996) are the major ones. Most of the traditional optimization algorithms, like LM, based on gradient methods have the possibility of getting trapped at a local optimum depending upon the degree of non-linearity and initial guess. Unfortunately, none of the traditional algorithms guarantee the global optimal solution, but genetic algorithms (GAs) and SA algorithms are found to have a better global perspective than the traditional methods (Deb, 1996). Moreover, when an optimization problem contains multiple global solutions, just the best global optimum solution may not be the desirable one. It is always prudent to know about other equally good solutions, which correspond to a marginally inferior objective function values but more amenable to be accepted. However, if the traditional methods are used to find multiple optimal solutions, they need to be applied a number of times, each time starting from a different initial guess and hoping to achieve a different optimal solution. Simulated annealing (SA) is a probabilistic optimization technique, which mimics the cooling phenomenon of molten metals to constitute a search procedure (Kirkpatrick et al., 1983). In an effort to predict the VLE of CO2 in aqueous amine solvents with better accuracy, Kundu et al. (2003) and Kundu and Bandyopadhyay (2005, 2006a, 2006b) applied SA successfully besides LM, in parameter estimation. In the present paper, DE algorithms (Price and 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 but have some inherent advantages over GA, like its simple structure, ease of use, speed, and robustness. A relative comparison among these three different optimization algorithms has been made with respect to the VLE prediction accuracy for the aforesaid systems. For (CO2 + MDEA + H2O) system DE performance is comparable to that of SA and LM performance. For (CO2 + AMP + H2O) system, DE seems to predict better than SA and LM predictions. DE has been successfully applied in various fields: dynamic optimization of a continuous polymer reactor, estimation of heat transfer parameters in trickle bed reactor, optimal design of heat exchangers, optimal design of shell and tube heat exchanger, synthesis and optimization of heat integrated distillation systems, expert systems for the optimal design of heat exchangers, etc., but to the best of our knowledge this is the first ever application of DE in phase equilibrium of acid gas + aqueous amine systems.

MODEL USED

Chemical Equilibria

In the aqueous phase of (CO2 + MDEA + H2O) and (CO2 + AMP + H2O) systems the following chemical equilibria are involved:

\[
\begin{align*}
\text{CO}_2 + 2\text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{O}^+ + \text{HCO}_3^- \quad (1) \\
\text{H}_2\text{O} + R'K'NH^- + \text{H}^+ & \rightleftharpoons R'K'N' + \text{NH}_4^+ \quad (2) \\
\text{CO}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \quad (3) \\
\text{H}_2\text{O} + (\text{C}_2\text{H}_4\text{H}_2\text{OH})\text{NH}_3^+ \rightleftharpoons \text{OH}^- + (\text{C}_2\text{H}_4\text{H}_2\text{OH})\text{NH}_4^- \quad (4) \\
\text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{OH}^- \quad (5)
\end{align*}
\]

For MDEA, R, R', and R'' are CH3, C4H9OH, and C6H5OH, respectively; for AMP R, K, and K' are H, H, and C2H5(CH3)2OH, respectively. K1, K2, K3, K4, K5 are the chemical equilibrium constants taken from Austgen and Rochelle (1991); Silkenbaumer et al. (1998); Li and Shen (1993) and are presented in Table 1. All the equilibrium constants used in the present model are mole fraction based after appropriate conversion, wherever necessary (Kundu et al., 2003). Since the present work is limited to low to moderate partial pressure range, the non-ideality of the vapour phase is neglected. In the low to moderate range of CO2 partial pressure the fugacity of CO2 is assumed to be its partial pressure and solubility of CO2 is identical to Henry's constant (KOH). The VLE of CO2 over the aqueous alkanolamine solvent, assuming no amine (solvent) species in the vapour phase, is given as follows:

\[
\ln K_{\text{CO}_2} = R(T)/\text{K}_{\text{CO}_2} - \gamma_{\text{CO}_2}
\]

where \(\gamma_{\text{CO}_2}\) is the free acid gas mole fraction in the liquid phase. Free molecular CO2 concentration in the liquid phase is negligible in comparison to the other species present in the liquid phase below the CO2 loading of 1.0. Henry's law constant is a strong function of temperature and taken from Austgen and Rochelle (1991) and presented in Table 1.

Thermodynamic Framework

In (CO2 + MDEA + H2O) system, two neutral species, MDEA-H and H2O, and two ionic species, MDEA+ and HCO3-, in the equilibrated liquid phase, have been considered. There are four major species, two neutral solvents, AMP and H2O, and two ionic species, AMPH3+ and HCO3-, in the equilibrated liquid phase for the (CO2 + AMP + H2O) system. 2-Amino-2-methyl-1-propanol (AMP), being a sterically hindered primary amine, the AMP-carbamate formed is unstable and it may undergo carbamate reversal reaction (Sartori and Savage, 1983). Yih and Shen (1988) have presumed that sterically hindered amine; AMP cannot form carbamate. Hence, the following alternative reaction was proposed by them for AMP:

\[
R'K'NH^+ + \text{HCO}_3^- \rightleftharpoons R'K'NH_2^+ + \text{CO}_2 \quad (7)
\]

Another alternative mechanism for the bicarbonate formation has been proposed by Chakraborty et al. (1986).

\[
R'K'NH + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons R'K'NH_2^+ + \text{HCO}_3^- \quad (8)
\]

However, Equation (8) is similar to reaction of CO2 with tertiary amines (e.g., MDEA). Hence, the existence of AMP carbamate in the equilibrated liquid phase has been ruled out though it is a primary alkanolamine. Since concentration of free molecular species CO2 and the ionic species CO2- and OH- in the liquid...
where, where 1 = H2O, 2 = AMP/MDEA, M = AMPH+/MDEAH+, X = HCO3−.

Ionic and neutral solutes: γiγi = 1 as xixi → 0, xixi→0, γiγi = 0 where, s refers to any non-aqueous solvent, s refers to ionic or neutral solute. Activity coefficients of all species are assumed to be independent of pressure.

Thermodynamic Expression of Equilibrium Partial Pressure

The thermodynamic expression for equilibrium partial pressure of CO2 in aqueous MDEA solutions is as follows:

\[ P_{CO2} = \left( \frac{K_{CO2} K_2 MDEA \gamma_{MDEA} \gamma_{CO2}}{K_1 \gamma_{H2O} \gamma_{MDEA} \gamma_{CO2}} \right) \]

where, xixi, xixi, xixi 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:

\[ C_{MDEA} = C_{CO2} = C_{MDEA} \gamma_{MDEA} \gamma_{CO2} = C_{AMP} \gamma_{AMP} \gamma_{CO2} \]

Activity coefficients \( \gammai \gammai \) (based on mole fraction scale) for different species present in the liquid phase are calculated from modified Clegg–Pitzer equation in the ‘activity coefficient model’. Similar expression for partial pressure of CO2 in aqueous AMP can also be written.

Activity Coefficient Model

The modified Clegg–Pitzer equations have been used to derive the activity coefficients of different species present in the equilibrated liquid phase (Li and Mather, 1994; Kundu et al., 2003; Kundu and Randopyaphany, 2005). Differentiating the expressions for the short-range and long-range force contribution to the excess Gibbs energy one can get activity coefficients for the ions and the neutral species. The expression for the activity coefficient for ionic solutes in the aqueous amine solvent is as follows:

\[ \ln \gamma_{\text{HCO}_3^-} = -z_{\text{HCO}_3^-} A_k \left( \frac{2}{Z} \ln (1 + z_{\text{HCO}_3^-}) + \frac{Z}{2} \left( \frac{x_{\text{HCO}_3^-}}{1 - x_{\text{HCO}_3^-}} \right) \right) + x_{\text{HCO}_3^-} b_{\text{HCO}_3^-} \left( m_i Z_i^2 / Z \right) \]

\[ x_{\text{HCO}_3^-} \left( x_{\text{HCO}_3^-} b_{\text{HCO}_3^-} \left( m_i Z_i^2 / Z \right) \right) \left( \frac{x_{\text{HCO}_3^-}}{1 - x_{\text{HCO}_3^-}} \right) \left( \frac{x_{\text{HCO}_3^-}}{1 - x_{\text{HCO}_3^-}} \right) \left( \frac{x_{\text{HCO}_3^-}}{1 - x_{\text{HCO}_3^-}} \right) - 2x_i x_i (A_{ij} + A_{ij} x_i + x_i (1 - x_i) x_{ij} W_{ij,kl}) \]

where, 1 = H2O, 2 = AMP/MDEA, M = AMPH+ MDEAH+, X = HCO3−. For neutral molecules as for example, water:

\[ \ln \gamma_i = \left( \frac{2A_i \gamma_i}{(1 + z^2)_i} \right) x_i b_{\text{HCO}_3^-} \exp \left( -z_{\text{HCO}_3^-} A_k \left( \frac{2}{Z} \ln (1 + z_{\text{HCO}_3^-}) + \frac{Z}{2} \left( \frac{x_{\text{HCO}_3^-}}{1 - x_{\text{HCO}_3^-}} \right) \right) + x_{\text{HCO}_3^-} b_{\text{HCO}_3^-} \left( m_i Z_i^2 / Z \right) \right) \]

\[ + 2A_{ij} x_i x_i (1 - x_i) + (1 - x_i) x_i (1 - x_i) \left( x_{ij} W_{ij,kl} - x_{ij} (F_i W_{ij,kl}) \right) \]

where, 1 = H2O, 2 = AMP/MDEA, M = AMPH+ MDEAH+, X = HCO3−. Similar expressions for logarithm of activity coefficient can be derived for other molecular and ionic solutes. The function g(x)
in Equation (13) is expressed by:

$$g(x) = 2 [1 - (1 + x) \exp(-x)]x^2$$

where

$$x = (\alpha, \alpha_n^2) = 2f^{1/2}$$

DATA REGRESSION: ESTIMATION OF INTERACTION PARAMETER

In this work, the experimental solubility data of CO$_2$ in aqueous MDEA in the loading range of 0.001–1.0 mol/mol, partial pressure range of 0.01–5500 kPa, concentration ranging from 2.53–4.28 M, temperature range of 298–393 K, and experimental solubility data of CO$_2$ in aqueous AMP and the loading range of 0.03–1.0 mol/mol, concentration range of 2.8–3.4 M, temperature range 303–373 K, and the partial pressure of 0.3–1000 kPa have been used to estimate the interaction parameters by regression analysis. 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 parameters are characteristic of pair interactions of components.

The objective function used for optimization is given by:

$$\Psi = \sum \frac{\left( (CO_2)_{exp} - (CO_2)_{calc} \right)}{(CO_2)_{exp}}$$

Among the interaction parameters for each system; one is for ion–ion interactions, two are for ion–solvent interactions, and two are for solvent–solvent interactions. The estimated interaction parameters along with their temperature dependence and the temperature coefficients, using DE technique for (CO$_2$ + MDEA + H$_2$O) and (CO$_2$ + AMP + H$_2$O) systems are listed in Tables 2 and 3, respectively. The objective function chosen in this work takes care of rendering uniform weightage throughout the entire range of partial pressure (from low to high), provided the data scatter throughout the entire range of partial pressure (from low to high), as claimed by the previous workers, is more or less uniform. In reality, relatively small amounts of solvent–solvent interactions are less significant compared to ion–ion and ion–solvent interactions.

Table 1. Estimated interaction parameters derived by the DE technique for (CO$_2$ + AMP + H$_2$O) system $B(a/b _{W} or A) = a + b(T/K)$

<table>
<thead>
<tr>
<th>B or W or A</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{MAX}$</td>
<td>-726.914041233877</td>
<td>2.046016385048488</td>
</tr>
<tr>
<td>$W_{MAX}$</td>
<td>155.9936324496222</td>
<td>-0.60069767840103</td>
</tr>
<tr>
<td>$W_{MIN}$</td>
<td>240.713166719178</td>
<td>-0.87405495529079</td>
</tr>
<tr>
<td>$A_{L}$</td>
<td>471.7604672732886</td>
<td>-1.72023014237471</td>
</tr>
<tr>
<td>$A_{H}$</td>
<td>-46.58596159671227</td>
<td>0.13907473167950</td>
</tr>
</tbody>
</table>

Table 2. Estimated interaction parameters derived by the DE technique for (CO$_2$ + MDEA + H$_2$O) system $B(a/b _{W} or A) = a + b(T/K)$

<table>
<thead>
<tr>
<th>B or W or A</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{MAX}$</td>
<td>745.81258831999431</td>
<td>-2.05272012847313</td>
</tr>
<tr>
<td>$W_{MAX}$</td>
<td>6.16839684502044</td>
<td>-0.0023473249964</td>
</tr>
<tr>
<td>$W_{MIN}$</td>
<td>-0.46316604064298</td>
<td>-0.0514221281018</td>
</tr>
<tr>
<td>$A_{L}$</td>
<td>-0.68748854685858</td>
<td>-0.0293602032959</td>
</tr>
<tr>
<td>$A_{H}$</td>
<td>0.46640372438580</td>
<td>0.02926831991785</td>
</tr>
</tbody>
</table>

The low-loading data are available compared to the moderate/high-loading data, which are of rather poor precision, and possibly of poor accuracy too (Weiland et al., 1993). The present authors think that a higher weighing for the low partial pressure region in the chosen objective function may not be entirely undesirable to predict the low-pressure data with acceptable accuracy using the model, in view of the immense significance of the low-pressure data for gas treating processes.

METHOD OF SOLUTION

Differential evolution (DE) technique is used to estimate the interaction parameters for the VLE model. DE is a stochastic, population-based method. These methods heuristically “mimic” biological evolution, namely, the process of natural selection and the “survival of the fittest” principle. 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 (Equation (11)).

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 a 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 to be 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 of 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. The flow chart for the DE technique is given in Figure 1.

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). The DE/rand-best/1/bin strategy has been adopted here. The general convention used above is DE/x/y/z. DE stands for differential evolution, x represents a string denoting the vector to be perturbed, y is the number of difference vectors considered for perturbation of x, and z stands for the type of crossover being used (exp, exponential; bin, binomial). The perturbation can be either in the best vector of the previous generation or in any randomly chosen vector. Similarly for perturbation either single or two vector differences can be used. In exponential crossover, the crossover is performed on the D (the dimension, i.e., number of variables to be optimized) variables in one loop until it is within the CR bound. In binomial crossover, the crossover is performed on each of the D variables whenever a randomly picked number between 0 and 1 is within
the CR value. DE/rand-best/1/bin strategy has been adopted in the present problem.

Algorithm for Differential Evolution Technique

Step 1: Initialization of the parameters required for DE. Following are the values considered in the present work, population size (NP) = 50, crossover (CR) = 0.9, mutation constant (F) = 0.8.

Step 2: Generation of the population randomly between the upper and lower bounds of the desired parameters.

Step 3: Calculation of the objective function value for all population vectors.

Step 4: Random selection of three population points a, b, c such that these are not equal, followed by the generation of a random number, if the generated random number is less than CR, leading to the mutation according to Equation (18) followed by a crossover. X(c) is now mutated to X(m).

\[ X(m) = X(c) + F(X(a) - X(b)) \] (18)

with a check for bounds of the vector generated from the mutation step. If bounds are violated, then generation of “X” randomly between the bounds; otherwise X(m) = X.

Step 5: If the generated random number is greater than CR, mutation is not necessary, hence, X(m) = X(c).

Step 6: Calculation of the objective function for X(m) vector.

Step 7: Selection of the least objective function value.

Step 8: Repetition of steps 4–6 for all the populations.

Step 9: Repetition of steps 4–7 until the termination criteria are met.

Step 10: Stop.

The termination criteria taken in the present study are of two types. First, if there is no improvement in objective functional value for some generations, and second, the difference in the maximum objective value and minimum objective value in the population is less than 10^{-12}. The hardware platform used was an Intel Pentium IV processor, 1.4 GHz. The developed DE code using MATLAB 7.0 version had to compromise between CPU time and the solution quality. For (CO₂ + MDEA + H₂O) system, sometimes it took 10 000 generations to reach a good quality solution.

RESULTS AND DISCUSSION

Three different kinds of optimization techniques; traditional and gradient based (LM), probabilistic (SA), and evolutionary algorithm (DE) have been used here for predicting phase equilibria. 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.

(CO₂ + MDEA + H₂O) System

For (CO₂ + MDEA + H₂O) system, two solvent–ion pair interactions, one ion–ion interaction, and two solvent–solvent Margules interaction parameters were determined by regression analysis while using SA and DE technique. Li and Mather (1997) derived the Margules interaction parameters by regressing binary (MDEA + H₂O) VLE data. Kundu and Bandyopadhyay (2005) used those solvent–solvent interaction parameters without any further regression. Hence, two solvent–ion pair interactions and one ion–ion interaction parameters were determined by regression analysis while predicting VLE using LM technique. The interaction parameters derived by using SA and LM technique from our previous work (Kundu and Bandyopadhyay, 2005) have been used here to compare the VLE prediction performances of three different techniques.

<table>
<thead>
<tr>
<th>Reference</th>
<th>[MDEA (wt%)]</th>
<th>Temperature (K)</th>
<th>CO₂ partial pressure (kPa)</th>
<th>Data points</th>
<th>AAD% correlation*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jou et al. (1994)</td>
<td>30</td>
<td>298, 313, 333, 393</td>
<td>0.08–5775</td>
<td>54</td>
<td>11.9 – 12.9</td>
</tr>
<tr>
<td>Austig et al. (1991)</td>
<td>23.8</td>
<td>313</td>
<td>6.73–98.8</td>
<td>11</td>
<td>12.0 – 17.0</td>
</tr>
<tr>
<td>Jou et al. (1995)</td>
<td>35.0</td>
<td>313, 373</td>
<td>0.719–263</td>
<td>18</td>
<td>15.8 – 18.9</td>
</tr>
<tr>
<td>Chakera and Meisen (1987)</td>
<td>48.8</td>
<td>413</td>
<td>138–4516</td>
<td>7</td>
<td>15.7 – 17.4</td>
</tr>
<tr>
<td>Dawodu and Meisen (1994)</td>
<td>48.8</td>
<td>373</td>
<td>558–3611</td>
<td>9</td>
<td>7.3 – 10</td>
</tr>
<tr>
<td>Jou et al. (1994)</td>
<td>30</td>
<td>298</td>
<td>0.1–176.95</td>
<td>13</td>
<td>14.3 – 14.3</td>
</tr>
<tr>
<td>Silberkraumber et al. (1998)</td>
<td>31.0</td>
<td>313</td>
<td>12.0–86.8</td>
<td>10</td>
<td>9.38 – 9.38</td>
</tr>
<tr>
<td>Jou et al. (1995)</td>
<td>35.0</td>
<td>373</td>
<td>95.38–191</td>
<td>8</td>
<td>14.52 – 14.52</td>
</tr>
<tr>
<td>Jou et al. (1982)</td>
<td>48.8</td>
<td>393</td>
<td>0.143–5290</td>
<td>9</td>
<td>7.32 – 7.32</td>
</tr>
</tbody>
</table>

* AAD% = \[ \left( \sqrt{\sum_{i=1}^{n} \left( |p_{\text{calc}} - p_{\text{exp}}| / p_{\text{exp}} \right)^2} \right) / n \] × 100
The same data set belonging to the identical conditions of temperature, pressure, and concentration ranges were considered for regression analysis by different techniques, SA and LM, to determine the interaction parameters of the VLE model. DE resulted in a higher correlation and prediction deviations, while using those same data sets for generation of the interaction parameters; hence different combination of data sets are considered in DE technique (in regression analysis) to generate the interaction parameters for (CO2 + MDEA + H2O) system. The temperature coefficients of the interaction parameters have been fitted to the linear/polynomial functionality of temperature with an average regression coefficient of 0.99 ± 0.03 after being estimated by the SA technique at closely spaced interval of temperature. For the LM and DE techniques, the regression analysis was done along with the temperature coefficients relating the interaction parameters.

The experimental solubility data used for regression analysis by DE, SA, and LM, to estimate the interaction parameters, along with their correlation deviations have been summarized in Table 4. The deviation of correlation varies in the range from 7.3 to 15.8% by SA, 10 to 40% by LM whereas 7.52 to 14.52% by DE technique. In the DE technique, the average absolute deviation between all the experimental and correlated CO2 partial pressure was 10.8%. The fitted interaction parameters derived by DE (presented in Table 2), SA and LM technique (taken from Kundu and Bandyopadhyay, 2005) for CO2–MDEA–H2O ternary system have been used to predict some solubility data, which were not used for regression (correlation). The prediction results using DE technique are summarized in Table 5. Table 5 also presents a description of VLE prediction accuracy of the same model using three different optimization techniques, LM, SA, and DE, when compared with the experimental results of seven different groups. Figure 2 is a typical parity plot showing some of the predicted results. On a relative assessment of using the LM and the SA algorithms for parameter estimation, it was found earlier by Kundu et al. (2003) and Kundu and Bandyopadhyay (2005) that use of the SA algorithm resulted in a relatively better accuracy in correlation and prediction of VLE of (CO2 + MDEA + H2O) and (CO2–AMP–H2O) system for most of the cases. In the present work, it has been found that (Table 5), both SA and DE techniques have shown a comparable VLE prediction accuracy for (CO2 + MDEA + H2O) system, which is better than LM for some data sets, considered earlier by Kundu and Bandyopadhyay (2005). Figure 2 shows the typical parity plot showing some of the predicted results for this system. It is to be mentioned that the predicted CO2 partial pressures using DE technique are in excellent agreement with the data set of Kuranov et al. (1996) for 4.13 M MDEA solution over a temperature range of 298–413 K.

![Figure 2](image-url)  
Figure 2. Comparison of DE predicted and experimentally measured CO2 equilibrium partial pressure over 23.4–48.8 wt% (1.985–4.28 M) MDEA aqueous solutions in the temperature range of 298–413 K.

The comparison of DE predicted and experimentally measured CO2 equilibrium partial pressure over 23.4–48.8 wt% (1.985–4.28 M) MDEA aqueous solutions in the temperature range of 298–413 K.

Table 5. VLE prediction and comparison among different techniques for (CO2 + MDEA + H2O) system

<table>
<thead>
<tr>
<th>Reference</th>
<th>MDEA wt%</th>
<th>Temperature (K)</th>
<th>Data points</th>
<th>CO2 partial pressure range (kPa)</th>
<th>AAD% prediction*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jou et al. (1994)</td>
<td>50.0</td>
<td>313, 335, 393</td>
<td>41</td>
<td>0.494–5775</td>
<td>26</td>
</tr>
<tr>
<td>Austgen and Rochelle (1991)</td>
<td>23.8</td>
<td>313</td>
<td>11</td>
<td>6.73–98.8</td>
<td>16.15</td>
</tr>
<tr>
<td>Jou et al. (1995)</td>
<td>55.0</td>
<td>313</td>
<td>10</td>
<td>0.719–100</td>
<td>36.6</td>
</tr>
<tr>
<td>Davoud and Meisen (1994)</td>
<td>48.8</td>
<td>373</td>
<td>9</td>
<td>558–3611</td>
<td>29.73</td>
</tr>
<tr>
<td>Macgregor and Mather (1991)</td>
<td>23.8</td>
<td>313</td>
<td>4</td>
<td>1.17–588</td>
<td>10.42</td>
</tr>
<tr>
<td>Jou et al. (1982)</td>
<td>23.8</td>
<td>313</td>
<td>3</td>
<td>3.28–101</td>
<td>30.66</td>
</tr>
<tr>
<td>Jou et al. (1982)</td>
<td>48.8</td>
<td>313, 343, 373</td>
<td>34</td>
<td>200–4000</td>
<td>26.63</td>
</tr>
<tr>
<td>Chakma and Meisen (1987)</td>
<td>48.8</td>
<td>373</td>
<td>12</td>
<td>463–3600</td>
<td>26.28</td>
</tr>
<tr>
<td>Kundu (2004)</td>
<td>23.8</td>
<td>303, 313, 323</td>
<td>24</td>
<td>1–100</td>
<td>19.69</td>
</tr>
<tr>
<td>Kundu (2004)</td>
<td>23.8</td>
<td>313</td>
<td>19</td>
<td>1–100</td>
<td>20.75</td>
</tr>
<tr>
<td>Lemoine et al. (2000)</td>
<td>23.6</td>
<td>298</td>
<td>13</td>
<td>0.02–1.636</td>
<td>36.63</td>
</tr>
<tr>
<td>Kuranov et al. (1996)</td>
<td>47</td>
<td>313–413</td>
<td>29</td>
<td>39–4460</td>
<td>13.31</td>
</tr>
</tbody>
</table>

* AAD% = \[\frac{1}{n} \sum_{i=1}^{n} \frac{p_{\text{cal}} - p_{\text{exp}}}{p_{\text{exp}}} \times 100\]

The same data set belonging to the identical conditions of temperature, pressure, and concentration ranges were considered for regression analysis by different techniques, SA and LM, to determine the interaction parameters of the VLE model. DE resulted in a higher correlation and prediction deviations, while using those same data sets for generation of the interaction parameters; hence different combination of data sets are considered in DE technique (in regression analysis) to generate the interaction parameters for (CO2 + MDEA + H2O) system. The temperature coefficients of the interaction parameters have been fitted to the linear/polynomial functionality of temperature with an average regression coefficient of 0.99 ± 0.03 after being estimated by the SA technique at closely spaced interval of temperature. For the LM and DE techniques, the regression analysis was done along with the temperature coefficients relating the interaction parameters.
same data set belonging to the identical conditions of temperature, pressure, and concentration ranges were not considered for regression analysis by different techniques, LM, SA, and DE in determining the interaction parameters of the VLE model for this particular system. The interaction parameters derived on the basis of same data sets for three optimization techniques resulted in relatively higher correlation and prediction deviation for any one or two of the techniques. Hence, different combinations of data sets were considered for three different techniques to generate the interaction parameters for (CO$_2$ + AMP + H$_2$O) system; which may lead to minimum possible correlation and prediction deviations. The experimental solubility data used for regression analysis by DE, SA, and LM, to estimate the interaction parameters, along with their correlation deviations have been summarized in Table 6. The deviation of correlation varies in the range from 5.67%-15.5% by DE, 9.34–16.0% SA, and 11.0–15.32% by the LM technique. The average absolute deviation between all the experimental and correlated CO$_2$ partial pressure was 8.77% by the DE technique. The fitted interaction parameters derived by DE (presented in Table 3), SA, and LM techniques (taken from Kundu et al., 2003) for (CO$_2$ + AMP + H$_2$O) ternary system have been used to predict some solubility data, which were not used for regression (correlation). The prediction results using DE technique are summarized in Table 7. Table 7 also presents a description of VLE prediction accuracy of the same model using three different optimization techniques, LM, SA, DE, when compared with the experimental results of five different groups. Figure 3 is a typical parity plot showing some of the predicted results for this system. It has been found that the prediction accuracy using DE technique for (CO$_2$ + AMP + H$_2$O) system is better than both SA and LM when compared on the basis of the same data sets considered by Kundu et al. (2003) for their relative assessment on VLE prediction accuracy using SA and LM techniques. Figure 4

### Table 6. Experimental solubility data used in the regression analysis to estimate the interaction parameters and the correlation deviations for (CO$_2$–AMP–H$_2$O) system

<table>
<thead>
<tr>
<th>Reference</th>
<th>[AMP] wt%</th>
<th>Temperature (K)</th>
<th>CO$_2$ partial pressure (kPa)</th>
<th>Data points</th>
<th>AAD% correlation*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teng and Mather (1989)</td>
<td>18.0</td>
<td>313,343</td>
<td>0.3–500</td>
<td>24</td>
<td>16.0</td>
</tr>
<tr>
<td>Roberts (1983)</td>
<td>18.0</td>
<td>373</td>
<td>8.5–866</td>
<td>9</td>
<td>10.08</td>
</tr>
<tr>
<td>Kundu et al. (2003)</td>
<td>25.0</td>
<td>313</td>
<td>3.25–91.5</td>
<td>8</td>
<td>7.28</td>
</tr>
<tr>
<td>Seo and Hong (1996)</td>
<td>30.0</td>
<td>333</td>
<td>5.9–336</td>
<td>6</td>
<td>0.57</td>
</tr>
<tr>
<td>Li and Chang (1994)</td>
<td>30.0</td>
<td>373</td>
<td>1.12–71.2</td>
<td>9</td>
<td>15.5</td>
</tr>
<tr>
<td>Teng and Mather (1989)</td>
<td>18.0</td>
<td>343</td>
<td>2.43–434.6</td>
<td>9</td>
<td>10.03</td>
</tr>
</tbody>
</table>

* $\text{AAD}\% = \frac{\sum (p_{\text{cal}} - p_{\text{exp}})}{n} \times 100$

### Table 7. VLE prediction and comparison among different techniques for (CO$_2$ + AMP + H$_2$O) system

<table>
<thead>
<tr>
<th>Reference</th>
<th>[AMP] wt%</th>
<th>Temperature (K)</th>
<th>CO$_2$ partial pressure range (kPa)</th>
<th>Data points</th>
<th>AAD% prediction*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jane and Li (1997)</td>
<td>18.0</td>
<td>313</td>
<td>1.45–84.2</td>
<td>7</td>
<td>12.99</td>
</tr>
<tr>
<td>Roberts (1983)</td>
<td>18.0</td>
<td>313</td>
<td>2.17–95.4</td>
<td>5</td>
<td>10.86</td>
</tr>
<tr>
<td>Kundu et al. (2003)</td>
<td>25.0</td>
<td>303</td>
<td>1.2–359</td>
<td>48</td>
<td>16.53</td>
</tr>
<tr>
<td>Li and Chang (1994)</td>
<td>30.0</td>
<td>313</td>
<td>1.05–197</td>
<td>27</td>
<td>23.37</td>
</tr>
</tbody>
</table>

* $\text{AAD}\% = \frac{\sum (p_{\text{cal}} - p_{\text{exp}})}{n} \times 100$
CONCLUSIONS

The modified Clegg-Pitzer equations have been used to correlate and predict the VLE of (CO2 + AMP + H2O) and (CO2 + MDEA + H2O) systems, which are of immense significance as far as gas-treating processes are concerned. The present work requires solving a multivariable optimization problem. DE algorithms have been used for parameter estimation of the developed VLE model. In this work, the DE/rand-best/1/bin strategy has been used. A relative comparison among different traditional and non-traditional optimization algorithms has been made with respect to the VLE prediction accuracy for the aforementioned systems. For the (CO2 + MDEA + H2O) system DE performance is comparable to that of SA, and better than LM performance. For (CO2 + AMP + H2O) system, DE seems to predict qualitatively better than SA and LM predictions.

ACKNOWLEDGEMENTS

The financial support by the Department of Science and Technology (DST) and Centre for High Technology (CHT), New Delhi, India, are gratefully acknowledged. The authors are grateful to Professor A. E. Mather, University of Alberta, Canada, for providing some important experimental VLE data for CO2 in aqueous MDEA and AMP solutions.

REFERENCES


NOMENCLATURE

\[ \alpha_{\text{DE}} \] Deybe-Huckel parameter on a mole fraction basis
\[ \alpha_{\text{SA}} \] interaction parameter between neutral molecules
\[ B_c \] ion-\text{ion} interaction parameter
\[ C^T_{\text{H2O}} \] initial concentration of species
\[ D_i \] cationic fraction
\[ F_{\text{H2O}} \] Henry’s law constant for CO2, kPa
\[ I \] ionic strength on a molar concentration basis
\[ I_{\text{w}} \] ionic strength on mole fraction basis
\[ K_1, K_2, K_3 \] thermodynamic chemical equilibrium constants
\[ p_{\text{CO2}} \] partial pressure of CO2, Pa or kPa
\[ T \] absolute temperature, K
\[ W \] interaction parameter between neutral and ionic species
\[ Z \] valency of an ion

Greek Symbols

\[ \alpha \] Pitzer universal constant in Equation (16)
\[ \alpha_{\text{CO2}} \] liquid phase loading of CO2, kmol CO2/kmol amine
\[ \gamma \] activity coefficient
\[ \psi \] objective function for regression

Subscripts

\[ a, x \] anion
\[ c, M \] cation
\[ n, n' \] neutral solvent species
\[ \text{cal} \] calculated value
\[ \text{ex} \] experimental value
\[ s \] solvent
\[ i \] ionic or neutral solute
\[ w \] water solvent

Note in Equation (11) \( \alpha \) is to be written as \( \alpha_{\text{CO2}} \), which is liquid phase loading of CO2, kmol CO2/kmol amine same as used in Equation (10).

Greek Symbols

\[ \alpha \] Pitzer universal constant in Equation (16)
\[ \alpha_{\text{CO2}} \] liquid phase loading of CO2, kmol CO2/kmol amine
\[ \gamma \] activity coefficient
\[ \psi \] objective function for regression

Subscripts

\[ a, x \] anion
\[ c, M \] cation
\[ n, n' \] neutral solvent species
\[ \text{cal} \] calculated value
\[ \text{ex} \] experimental value
\[ s \] solvent
\[ i \] ionic or neutral solute
\[ w \] water solvent

Note in Equation (11) \( \alpha \) is to be written as \( \alpha_{\text{CO2}} \), which is liquid phase loading of CO2, kmol CO2/kmol amine same as used in Equation (10).

NOMENCLATURE

\[ \alpha_{\text{DE}} \] Deybe-Huckel parameter on a mole fraction basis
\[ \alpha_{\text{SA}} \] interaction parameter between neutral molecules
\[ B_c \] ion-\text{ion} interaction parameter
\[ C^T_{\text{H2O}} \] initial concentration of species
\[ D_i \] cationic fraction
\[ F_{\text{H2O}} \] Henry’s law constant for CO2, kPa
\[ I \] ionic strength on a molar concentration basis
\[ I_{\text{w}} \] ionic strength on mole fraction basis
\[ K_1, K_2, K_3 \] thermodynamic chemical equilibrium constants
\[ p_{\text{CO2}} \] partial pressure of CO2, Pa or kPa
\[ T \] absolute temperature, K
\[ W \] interaction parameter between neutral and ionic species
\[ Z \] valency of an ion

Greek Symbols

\[ \alpha \] Pitzer universal constant in Equation (16)
\[ \alpha_{\text{CO2}} \] liquid phase loading of CO2, kmol CO2/kmol amine
\[ \gamma \] activity coefficient
\[ \psi \] objective function for regression

Subscripts

\[ a, x \] anion
\[ c, M \] cation
\[ n, n' \] neutral solvent species
\[ \text{cal} \] calculated value
\[ \text{ex} \] experimental value
\[ s \] solvent
\[ i \] ionic or neutral solute
\[ w \] water solvent

Note in Equation (11) \( \alpha \) is to be written as \( \alpha_{\text{CO2}} \), which is liquid phase loading of CO2, kmol CO2/kmol amine same as used in Equation (10).


