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Application of Differential Evolution Algorithm in VLE of CO_2 Over Aqueous 2-amino-2–methyl-1-propanol

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ABSTRACT

Design of sour-gas treating processes with alkanolamine solvents requires knowledge of vapor-liquid equilibrium (VLE) of the aqueous acid gas – alkanolamine systems. The modified Clegg-Pitzer equation is used to correlate and predict the vapor-liquid equilibrium of the CO_2-AMP-H_2O systems Differential evolution (DE), a computationally stochastic technique, has been used for parameter estimation of the developed model in an effort to predict the VLE of CO_2 in aqueous AMP solutions with a comparable accuracy to that by using simulated annealing (SA) and deterministic technique like Levenberg-Marquardt (LM), if not better. The DE/rand/1/bin strategy has been used here for finding near global minimum solutions to optimization problems.

INTRODUCTION

Removal of acid gas impurities, such as CO_2 and H_2S, from gas mixtures is very important in natural gas processing, hydrogen purification, treating refinery off gases and synthesis gas for ammonia manufacture. Regenerative chemical absorption of the acid gases, into solutions of alkanolamines is widely used for gas treating. Representation of the experimental VLE data with a thermodynamically rigorous model is required, so that one can systematically correlate and predict the vapor-liquid equilibria of these systems. 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 in order to meet the product gas specification, and provides the boundary conditions for solving the partial differential equations describing mass transfer coupled with chemical reactions. In view of this, obtaining the accurate liquid phase interaction parameters of the developed VLE model is significant in order to predict the CO_2 partial pressure over the alkanolamines over a wide range of temperature, partial pressure and amine concentration range.

In order to have an understanding of those chemically reacting, multicomponent, 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 in order to determine the interaction parameters of the developed VLE model.
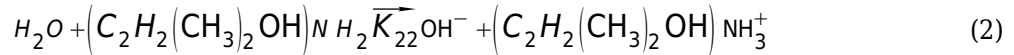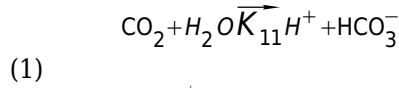

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Among the recent literature on modeling VLE of CO_2 in single and mixed amine solvents, using traditional, deterministic techniques, the work of Kent and Eisenberg (1976), Li and Shen (1993), Deshmukh and Mather (1981), Austgen and Rochelle (1991), Li and Mather (1994) are the major ones. Most of the traditional optimization algorithms, like LM, based on gradient methods have the possibility of getting trapped at 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 (GA's) & 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. Kundu and Bandyopadhyay (2003, 2005, 2006) applied the non-traditional simulated annealing algorithm in modeling VLE of CO_2 in single and mixed amine solvents beside the deterministic technique. In the present work DE has been used for parameter estimation of the developed VLE model. To the best of our knowledge this is the first ever application of DE in phase equilibrium of acid gas + aqueous alkanolamine systems.

MODEL DEVELOPMENT

Chemical Equilibria

In the aqueous phase of the (CO_2 – AMP – H_2O) systems the following chemical equilibria are involved.

$$CO_2 + H_2O \overset{\overrightarrow{K_{11}}}{} H^+ + HCO_3^-$$

(1)

$$H_2O + \left(C_2H_2\left(CH_3\right)_2 OH\right) N H_2 \overset{\overrightarrow{K_{22}}}{} OH^- + \left(C_2H_2\left(CH_3\right)_2 OH\right) NH_3^+ \qquad (2)$$

$$H_2O \overset{\overrightarrow{K_{33}}}{} H^+ + OH^- \qquad (3)$$

Where $K_{11}, K_{22,} K_{33}$ are the equilibrium constants taken from Silkenbäumer *et al* (1998); Li and Shen (1993) and are listed in Table 1. All the equilibrium constants used in the present model have been converted to mole fraction based constants and they are the functions of temperature. The chemical equilibrium constants in this work should adopt the same reference states for each component in equilibrium. The protonated amine dissociation constants were corrected to the pure amine reference state. The correction to the equilibrium constant is related to the infinite dilution activity coefficient of the amine in water.

Vapour-Liquid Equilibria

The vapour-liquid equilibrium of CO_2 over the aqueous alkanolamine solvent, assuming no solvent species in the vapour phase and the vapour phase to be ideal, is given as follows,

$$P_{CO_2} = H_{CO_2}\, x_{CO_2} \gamma_{CO_2}$$

(4)

Where x_{CO_2} is the free acid gas mole fraction in the liquid, γ_{CO_2} is the activity coefficient of free molecular CO_2, which is close to unity here. Henry's law constant is a strong function of temperature and taken from Austgen *et al.* (1991).

Thermodynamic Framework

In CO_2-AMP-H_2O system, two neutral species, AMP and H_2O, and two ionic species, AMPH$^+$ and HCO$_3^-$ in the equilibrated liquid phase have been considered. For simplicity, the free molecular species CO_2 and the ionic species CO_3^{2-}, and OH$^-$ in the liquid phase have been neglected for both

the systems since concentration of these species are very low compared to the other species present in the equilibrated liquid phase. The standard state associated with each solvent is the pure liquid at the system temperature and pressure. The adopted standard state for ionic solutes is the ideal, infinitely dilute aqueous solution (infinitely dilute in solutes and alkanolamines) at the system temperature and pressure. The reference state chosen for molecular solute CO_2 is the ideal, infinitely dilute aqueous solution at the system temperature and pressure.

Thermodynamic expression of equilibrium partial Pressure

The thermodynamic expression for equilibrium partial pressure of CO_2 in aqueous AMP solution is as follows,

$$P_{CO_2} = \frac{(H_{CO_2} K_2 \, x\gamma_{AMPH^+} \, x_{AMPH^+} \gamma_{HCO_3^-}) \, x_{HCO_3^-}}{(K_{11} x_{H_2O} \, x_{AMP} \, \gamma_{H_2O} \, \gamma_{AMP}}$$ (5)

where, $x_n' s$ are the liquid phase mole fractions of the components, based on true molecular or ionic species at equilibrium. K_2 is obtained by mathematical manipulation of K_{22} and K_{33}. The activity coefficient model using modified Clegg-Pitzer equation has been used to derive the activity coefficients of different species present in the equilibrated liquid phase (Li and Mather, 1994). The calculation of the concentration for each component at equilibrim is as follows,

$$C_{HCO_3^-} = C_{AMPH^+} = C_{AMP}^0 \alpha_{CO_2}$$ (6)

$$C_{AMP} = C_{AMP}^0 (1-\alpha)$$ (7)

$$C_{H_2O} = C_{H_2O}^0 - C_{AMPH^+}$$ (8)

Table 1   Temperature Dependence Of The Equilibrium Constants And Henry's Constant.

$$K_{ii} = \exp \left[\frac{A}{(T/K)} + B\ln(T/K) + C(T/K) + D \right]$$

where ii = 11 and 22

$$K_{33} = \exp \left[A + \frac{B}{(T/K)} + \frac{C}{(T/K)^2} + \frac{D}{(T/K)^3} + \frac{E}{(T/K)^4} \right]$$

$$H = \exp \left[A + \frac{B}{(T/K)} + C\ln(T/K) + D(T/K) \right]$$

Reaction	Compd	A	B	C	D	E	Ref
1	CO_2	-7742.6	-14.506	-2.8104e-2	102.28		[c]
2	AMP	-7261.78	-22.4773	0	142.58612		[c]
3	H_2O	39.5554	-9.879e4	0.568827e	-0.14645e1	0.136145e1	[d]
Henry's constant	CO_2	170.7126	-8477.711	-21.95743	0.005781		[a]

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[a] *Austgen* et al., *1991;* [c] *Silkenbäumer* et al., *1998;* [d] *Li and Shen, 1993*

DATA REGRESSION

In this work the experimental solubility data of CO_2 in aqueous AMP in the loading range of 0.03 t0 1.0 mol/mol, temperature in the range 303 - 373 K and the partial pressure of 0.3 to 1000 kPa have been used to estimate the interaction parameters, along with the temperature coefficients relating them by regression analysis. Among the interaction parameters; one is for ion-ion interactions, two are for ion-solvent interactions, and two are for solvent-solvent interactions. The estimated interaction parameters for (CO$_2$ - AMP - H$_2$O) systems along with their temperature coefficients are listed in Table 2. Instead of using binary VLE data, the solvent-solvent interaction parameters in the present work have been derived by regressing the ternary VLE data. The objective function used for optimization is given by,

$$\psi = \sum | \left\{ \left(P_{CO_2} \right)_{cal} - \left(P_{CO_2} \right)_{exp} \right\} ¿ \left(P_{CO_2} \right)_{exp} |$$

(9)

METHOD OF SOLUTION

To estimate the interaction parameters for the present problem Differential Evolution (DE) technique is used. In this work, the DE/rand/1/bin strategy has been used for finding near global minimum solutions to the multivariable optimization problem. The algorithm is as follows,

Step1: Initialize the parameters required for Differential Evolution. Number of population (*NP*)=50, Crossover (*CR*)=0.9, Mutation constant (*F*)=0.8.

Step2: Generate the population randomly between the upper and lower bounds.

Step3: Calculate the objective function value.

Step4: Randomly choose 3 population points a, b, c such that these are not equal and then generate a random number, If this is more than CR then $xm = x(c) + F(x(a) - x(b))$, Where xm is the mutated 'x' and check for bounds. If bounds are violated then generate 'x' randomly between the bounds. Else $xm = x$

Step5: Calculate the objective function for this vector.

Step6: Select the least objective function value for next generation.

Step7: *Repeat steps 4 to 6 for all the populations.*

Step8: Repeat steps 4 to 7 until the termination criteria are met.

Step9: Stop.

RESULTS AND DISCUSSION

For (CO$_2$ - AMP - H$_2$O) system the datasets of Kundu *et al* (2003) (2.8 M, 313 K); Seo and Hong (1996) (3.4 M, 333 K); Li and Chang (1994) (3.4 M, 373 K) have been correlated with an average absolute deviation of 8.7 % for the generation of interaction parameters. For (*CO$_2$ + AMP + H$_2$O*) system, two solvent-ion pair interactions, one ion-ion interaction, and two solvent-solvent Margules interaction parameters are determined by regression analysis. The 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 to determine the interaction parameters of the VLE model for this particular system. Average deviation for prediction of VLE data of (*CO$_2$ + AMP + H$_2$O*) system are summarized in Table 3, which also includes the description of VLE prediction accuracy of the same model, having different sets of interaction parameters derived on the basis of different combination of data sets, using three different optimization techniques, LM, SA, DE, when compared with the experimental results of 5 different groups. Fig. 1 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.
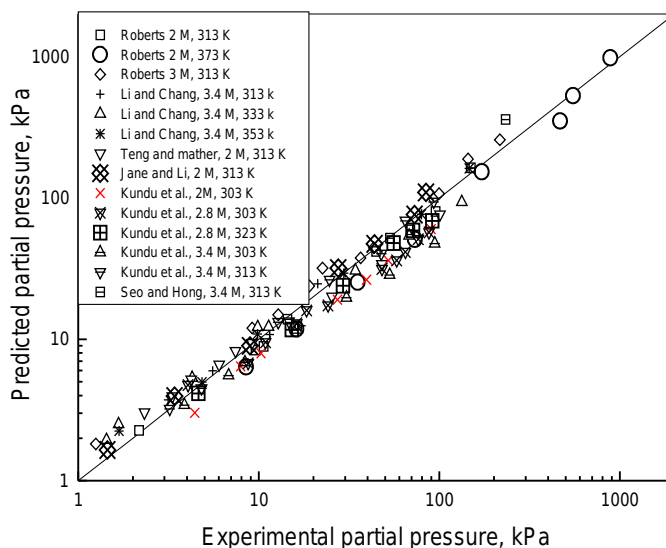

Figure 1 **Comparison Of Model Predicted And Experimentally Measured CO₂ Equilibrium Partial Pressure Over 2 - 3.4 AMP Aqueous Solutions in the Temperature Range 303-373 K.**

Table 2: Estimated interaction parameters for (AMP+CO₂ +H₂O) system

$$B / W/ A = a + b (T)$$

B / W/ A	A	B
B_{MX}	-726.914041	2.04602
W_{1MX}	155.99363	-0.60069
W_{2MX}	240.71317	-0.874055
A_{12}	471.76047	-1.720230
A_{21}	-46.58956	0.139075

Subscripts: 1= AMP, 2 = H_2O, M= $AMPH^+$, X = HCO_3^-

Table 3: VLE Prediction And Comparison Among Different Techniques For (CO₂ + AMP + H₂O) System

Reference	AMP	Temp (K)	Data points	CO_2 Partial pressure range (kPa)	DE [a]AAD% Prediction	SA [a]AAD% Prediction	LM [a]AAD% Prediction
Jane and Li (1997)	2	313	7	1.45-84.2	12.99	20.0	23.5
Roberts (1983)	2 2 3	313 373 313	5 9 14	2.17-95.4 8.5-886 1.25-359	10.86 17.6 20.89	24.2 [corr]10.08 16.04	15.75 [corr]15.8 17.04
Seo and Hong (1996)	3.4	313 353	13	3.94-336	16.19	17.7	19.2
Kundu et al. (2003)	2 2.8 3.4	303 303 323 303 313 323	48	3.2-94	16.53	18.3	19.0
Li and Chang (1994)	3.4	313 333 353	27	1.05-197	23.37	[corr]9.34	[corr]12.55

$$^a\ \text{AAD\%} = \left[\sum_n \left(p_{cal} - p_{exp} \right) / p_{exp} \right] / n \times 100$$

CONCLUSIONS

The modified Clegg-Pitzer equations have been used to correlate and predict the vapor-liquid equilibrium of ($CO_2 + AMP + H_2O$) system, which is of immense significance so far as gas-treating processes are concerned. Differential evolution algorithms have been used for parameter estimation of the developed VLE model. In this work, the DE/rand /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 aforesaid system. For ($CO_2 + AMP + H_2O$) system, DE seems to predict qualitatively better than SA and LM predictions.

ACKNOWLEDGMENT

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