

Performance evaluation of carbon dioxide-alkanolamine-water system by equation of state/excess Gibbs energy models

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Abstract. Numerous thermodynamic techniques have been applied to correlate carbon dioxide-alkanolamine-water systems, with varying accuracy and complexity. With advent of high pressure carbon dioxide absorption in industry, the development of high pressure thermodynamic models have become an exigency. Equation of state/excess Gibbs energy models promises a substantial improvement in this field. Many researchers have shown application of these models to high pressure vapour liquid equilibria of said system with good correlation. However, no study shows the range of application of these models in presence of other competitive techniques. Therefore, this study quantitatively describes the range of application of equation of state/excess Gibbs energy models to carbon dioxide-alkanolamine systems. The model uses Linear Combination of Vidal and Michelsen mixing rule for correlation of carbon dioxide absorption in single aqueous monoethanolamine, diethanolamine and methyldiethanolamine mixtures. The results show that correlation of equation of state/excess Gibbs energy models show a transient change at carbon dioxide loadings of 0.8. Therefore, these models are applicable to the above mentioned system for carbon dioxide loadings beyond 0.8 mol/mol and higher. The observations are similar in behaviour for all tested alkanolamines and are therefore generalized for the system.

1. Introduction

Absorption of carbon dioxide in alkanolamines has become a technically and commercially proven technology. A number of alkanolamines have been tested on lab scale and classified for carbon dioxide absorption in industrial environments [1]. These include primary, secondary and tertiary alkanolamines. However, the biggest challenge is to transpire the laboratory based data into an effective industrial value and define the extent of the parametric performance. Therefore, a number of thermodynamic approaches have been proposed for description of vapour liquid equilibria (VLE) of carbon dioxide-alkanolamine-water system. These approaches can be generally classified into three types; namely, semi-empirical models, activity coefficient (G^E) models and equation of state/excess Gibbs energy (EoS/ G^E) models. Semi-empirical models are easy in computation but lack precise theoretical agreement. On the other hand, G^E and EoS/ G^E models are rigorous in nature but require complex simultaneous computations to retrieve specific results. Although similar in theoretical

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development, EoS/ G^E models are an extension of G^E models to high pressure non-ideal VLE. These models have been used in a variety of systems and carbon dioxide-alkanolamine-water system is no exception [2].

Vallée et al. [3] extended electrolyte equation of state [4] to carbon dioxide-diethanolamine (DEA)-water system with good correlation. The model showed low deviation at high loadings/pressure (<20%). However, the low pressure/loadings region was weakly correlated and high deviation from experimental values were observed. Chunxi and Fürst [5] extended the same model to aqueous methyldiethanolamine (MDEA) systems, with similar results. The work of Vrachnos et al. [6] used e-LCVM model to correlate absorption of acid gas in MDEA systems. Figure 1 and 2 present the correlation of their model on logarithmic pressure-solubility plot and linear deviation ratio-solubility plot. The results showed excellent correlation at high pressures/loadings but the correlation was considerably weak at low loading values.

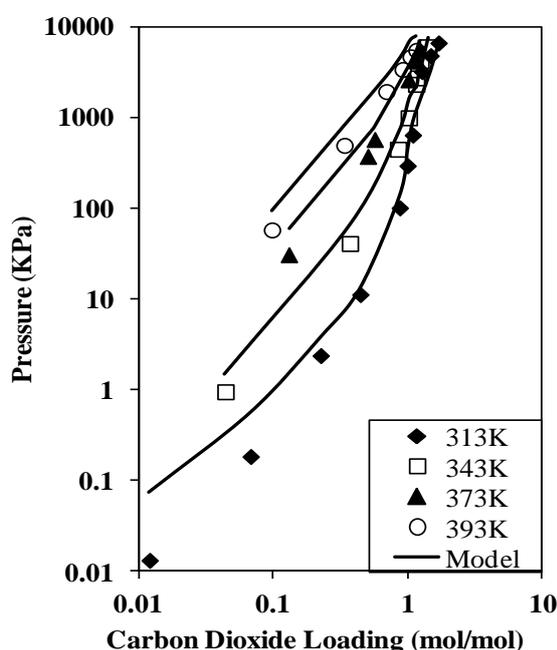


Figure 1. Pressure-Solubility plot for correlation of e-LCVM [6] against experimental data [7] for CO₂-MDEA-H₂O system

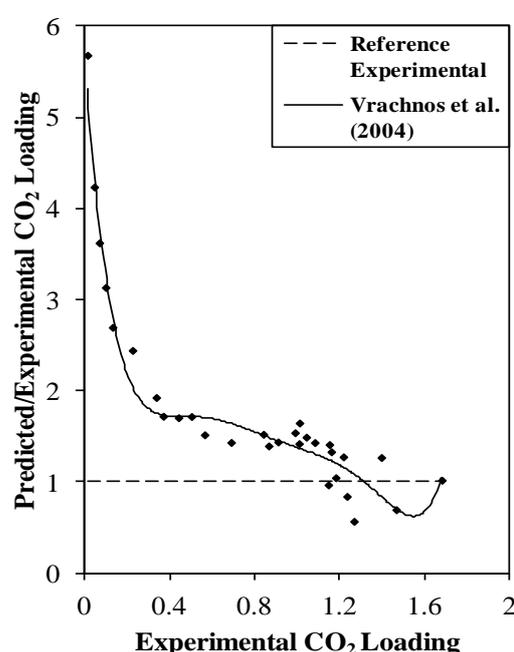


Figure 2. Ratio of Deviation against acid gas loading plot for e-LCVM [6] for CO₂-MDEA-H₂O system

Moreover, Vrachnos et al. [8] extended e-LCVM model to aqueous monoethanolamine (MEA) systems and blends of MEA-MDEA solutions with similar observations. Moreover, various researchers [9,10] have used EoS/ G^E models with varying success for description of CO₂-alkanolamine-H₂O VLE. It is unanimously understood that EoS/ G^E models are applicable to high pressure VLE of the said system due to pure EoS behaviour of EoS/ G^E models at low loadings/pressures [11]. However, the range of application recommended in previous studies remains qualitative. Therefore, it is imperative to understand the model behaviour and develop a general quantitative range for application of EoS/ G^E models to carbon dioxide-alkanolamine-water system. In this study, Linear Combination of Vidal and Michelsen (LCVM) mixing rule [12] has been applied in conjunction with modified translated Peng Robinson EoS [13], original UNIFAC [14] and modified three characteristic parameter correlation (TCPC) electrolyte model [15] for correlation of carbon dioxide solubility in aqueous MEA, DEA and MDEA solutions. The results explain the correlative performance of EoS/ G^E models and quantitatively define their range of application in the aforementioned system.

2. Thermodynamic Framework

LCVM mixing rule was selected for description of carbon dioxide-alkanolamine-water system, due to their superior correlation characteristics [16].

$$\alpha = \left(\frac{\lambda}{A_V} + \frac{1-\lambda}{A_M} \right) \cdot \frac{G^E}{RT} + \frac{1-\lambda}{A_M} \cdot \sum_i x_i \cdot \ln \left(\frac{b}{b_i} \right) + \sum_i x_i \cdot \alpha_i \quad (1)$$

where α defined as a/bRT for all components in the system (where a and b are defined below), λ is the LCVM constant, G^E is the excess Gibbs energy, x_i is the mole fraction of each component. Constants A_V and A_M represent individual Vidal and Michelsen mixing rules' constants.

The translated modified Peng Robinson equation of state was used for description of physical forces.

$$P = \frac{RT}{V+t-b} - \frac{a}{(V+t)(V+t+b)+b(V+t-b)} \quad (2)$$

where P is the pressure, T is the temperature, R is the universal gas constant, V is the volume of the system, a and b are the co-volume parameters and t is the translated volume.

The excess Gibbs energy function was taken as a summative function of short and long range forces.

$$G^E = G_{UNIFAC}^E + G_{TCPC}^E \quad (3)$$

The long range and columbic forces are described by modified Three Characteristic Parameter Correlation (TCPC) electrolytic model.

$$G_{TCPC}^E = \sum_{i=1}^i x_i \left(-z_i^2 A \left[\frac{I^{0.5}}{1+bI^{0.5}} + \frac{2}{b} \ln(1+bI^{0.5}) \right] + \frac{S}{T} \frac{I^{2n}}{v_i} \right) \quad (4)$$

where I is the ionic strength of the components, A is the Debye-Huckel constant, T is the temperature, whereas, b , S and n are fitted constants to the system.

Original UNIFAC was used to describe short range molecular forces (activity coefficients).

$$G_{UNIFAC}^E = x_i \cdot \ln \gamma_i^C + x_i \cdot \ln \gamma_i^R \quad (5)$$

where γ_i^C and γ_i^R represent combinatorial and residual forces, respectively. The binary interaction parameters of UNIFAC (BIP) were regressed to ternary experimental data, given in Table 1 for each alkanolamine. The selected experimental data was refined by using a recently developed statistical analysis technique [17].

Table 1. Sources of experimental data for CO₂-alkanolamine-H₂O system

Type of Alkanolamine	Researcher	No. of Data Points	Temperature, T (K)	Pressure, P (KPa)	MDEA Concentration (wt%)
MDEA	Sidi-Boumedine, et al. [18]	46	298.15 – 338.15	113 – 4560	25.73, 46.88
	Chakma and Meisen [19]	76	373.15 – 453.15	103 – 4930	19.8, 48.9
	Jou, et al. [7]	59	298.15 – 393.15	101 – 6630	23.34, 48.9
	Ma'mun, et al. [20]	34	328.15 – 358.15	118 – 813	50
DEA	Lee et al. [21]	160	273.15 – 413.15	217 – 6895	5.25 – 77.6
	Sidi-Boumedine, et al. [18]	15	298.15 – 348.15	110 – 4662	41.78
	Kennard and Meisen [22]	132	373.15 – 478.15	105 – 3747	10 – 30
	Lawson and Garst [23]	30	310.92 – 394.26	121 – 4373	25
MEA	Lee et al. [24]	112	298.15 – 393.15	100 – 7000	6.1 – 30.5
	Tong et al. [25]	48	313.15 – 393.15	101 – 984	30
	Jou, et al. [26]	34	273.15 – 393.15	103 – 6425	30
	Lawson and Garst [23]	14	333.15 – 393.15	127 – 2787	15.25

3. Results and Discussion

Figures 3 to 5 present the correlation of LCVM model in the prediction of carbon dioxide gas loadings in aqueous MDEA, MEA and DEA solutions. The model under-predicted for the values lower than 0.8 mol/mol, whereas the loadings were largely over-predicted for the loadings above 0.8 mol/mol, with a few high temperature values (353-393K) being under-predicted between loadings of 0.8 and 1.0. The over-prediction of the model is attributed to the weak description of physical absorption of carbon dioxide at high pressure.

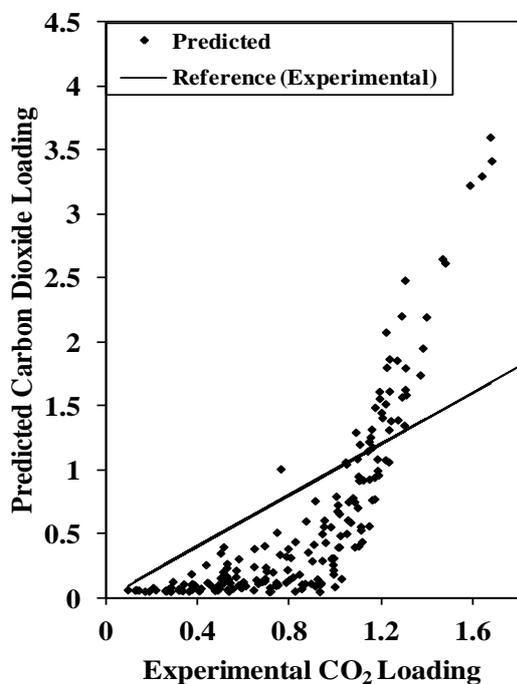


Figure 3. Correlation of CO₂ gas loadings in aqueous MDEA solutions.

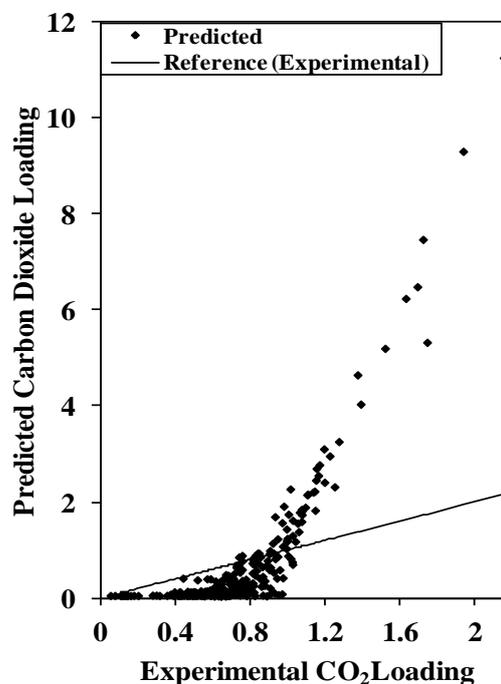


Figure 4. Correlation of CO₂ gas loadings in aqueous MEA solutions.

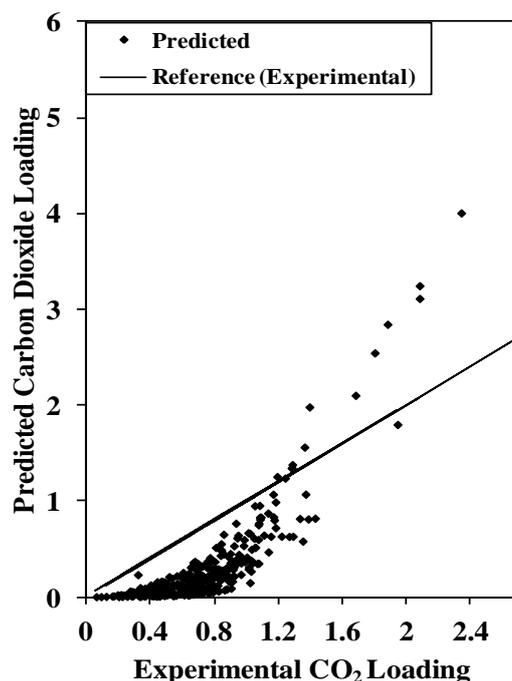


Figure 5. Correlation of CO₂ gas loadings in aqueous DEA solutions.

It is interesting to note that all figures show similar trends and the behaviour of the model is reverted around the loading values of 0.8. Thus, the loading value of 0.8 acts as a pinch point for the solubility correlation via EoS/G^E models. Theoretically, at higher loadings (at high pressures), the physical solubility of carbon dioxide in aqueous alkanolamines solutions is appreciable. However, these equilibrium absorption values are considerably lower than observed reactive dissolution at lower loadings (at low pressures) experimentally. Therefore, LCVM over-predicts the carbon dioxide loadings taking the reactive dissolution into consideration by its molecular and electrolytic equilibria. This effect is further worsened by large number of available experimental data points at low loadings (< 0.8), which heavily channels the regression of UNIFAC BIP to lower loadings. Therefore, the UNIFAC BIP should be regressed to either loadings lower than 0.8 or greater than 0.8 for adequate correlation. This would result in weak prediction of values on the other end. It is therefore, recommended that EoS/G^E model can be used for high pressure/loading data, as other comparative thermodynamic techniques are weak in correlation in this region [27], as done by previous researchers[3, 5, 6, 8] and shown in Figures 1 and 2. Moreover, it explains the qualitative statements by other researchers [27,28] that EoS/G^E models are applicable for higher CO₂ loadings. However, the current study quantitatively states that EoS/G^E models are applicable above carbon dioxide loadings of 0.8 in carbon dioxide loaded aqueous alkanolamine solutions.

4. Conclusions

The performance of EoS/G^E model has been evaluated for carbon dioxide absorption in aqueous MEA, DEA and MDEA solutions. The model showed similar performance in all tested alkanolamines and exhibited a transition in correlation characteristics at carbon dioxide loadings of 0.8 mol/mol. It defines the quantitative lower application limit for EoS/G^E models for the system, which have been previously reported by various researchers in qualitative terms. Thus, EoS/G^E models are suitably applicable to carbon dioxide loadings of 0.8 mol/mol and above for correlation of VLE in carbon dioxide solubility in aqueous MEA, DEA and MDEA solutions.

5. References

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