

Hybrid neural network for prediction of CO₂ solubility in monoethanolamine and diethanolamine solutions

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Abstract—The solubility of CO₂ in single monoethanolamine (MEA) and diethanolamine (DEA) solutions was predicted by a model developed based on the Kent-Eisenberg model in combination with a neural network. The combination forms a hybrid neural network (HNN) model. Activation functions used in this work were *purelin*, *logsig* and *tansig*. After training, testing and validation utilizing different numbers of hidden nodes, it was found that a neural network with a 3-15-1 configuration provided the best model to predict the deviation value of the loading input. The accuracy of data predicted by the HNN model was determined over a wide range of temperatures (0 to 120 °C), equilibrium CO₂ partial pressures (0.01 to 6,895 kPa) and solution concentrations (0.5 to 5.0 M). The HNN model could be used to accurately predict CO₂ solubility in alkanolamine solutions since the predicted CO₂ loading values from the model were in good agreement with experimental data.

Key words: Diethanolamine, Monoethanolamine, CO₂ Solubility, Kent-Eisenberg Model, Hybrid Neural Network

INTRODUCTION

The removal of CO₂ from process gas streams is a significant step in various industries such as natural gas and ammonium production, oil refineries as well as petrochemical plants due to two main reasons: minimization of corrosion along gas pipelines and prevention of its emission to the surrounding environment. Amine-based solution technology is the most extensively utilized technique used to strip CO₂ from a gas process stream. In this process, alkanolamine-based solution is usually used to fix CO₂ as non-volatile species. The ultimate CO₂ solubility is one of the most vital factors defining the effectiveness of the absorption solvent. Absorption/stripping with aqueous solutions of alkanolamines has been one of major industrial technologies developed since the 1930s [1]. Primary and secondary amines such as monoethanolamine (MEA) and diethanolamine (DEA) can readily react with CO₂ to form the stable carbamate and show low CO₂ loadings but with high absorption rate. The reaction between CO₂ and aqueous and non-aqueous solutions of tertiary amines such as methyldiethanolamine (MDEA) has been frequently studied for the last two decades [2]. Since they do not form stable carbamate, CO₂ loadings are high but the absorption rates are very low, which tends to curtail their industrial usability. However, sterically-hindered amines are capable of high CO₂ loading with a high absorption rate which are more preferred in industries [3].

Established models are available to analyze the solubility of CO₂ in aqueous solutions of alkanolamines and correlate the equilibrium CO₂ loading. These widely used models are the electrolyte-NRTL [4], Deshmukh-Mather [5] and Kent-Eisenberg [6] models. In this

study, the use of a hybrid neural network (HNN) is proposed. This network combines a regression model derived based on integration of the Kent-Eisenberg model with a neural network. Neural network modeling is essentially “black-box” in nature, no prior knowledge of the process is required, and any existing prior knowledge is not considered. Neural networks are function approximators that work better in practical applications than the conventional (polynomial) function approximations method. A ‘neuron’ takes in a set of inputs, adds them together, subjects them to activation functions and passes the output through a weighted connection to another neuron. The connection weights serve as adjustable parameters set by a ‘training method’. The ability of neural networks to learn non-parametric or structure-free approximation is its strength, albeit this is also considered as its weakness [7]. To overcome this weakness, HNNs are normally developed.

The objective of this study is to predict CO₂ solubility in two single alkanolamine solutions, MEA and DEA, using the proposed HNN model. To date, there is no reported study (to our best knowledge) on development and utilization of the HNN model to determine CO₂ solubility in aqueous solutions of alkanolamines. As such, it is believed that the existence of such a model will greatly aid in the design of CO₂ stripping unit operations.

THEORY

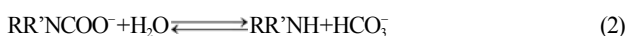
It is well established that absorption of CO₂ by alkanolamine solutions is basically a combination of both physical absorption and chemical reaction. As such, both thermodynamic and kinetics equilibria are important parameters in determining the achievable gas loading (mole CO₂/mole amine) of a particular CO₂ absorption system. The mechanisms for absorption reactions have been proposed by many researchers and Danckwerts and McNeil [8], in particular,

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Table 1. Temperature-dependent equilibrium and Henry's Law constants

	a	b	c	d	Range of validity (°C)	Source
K (DEA)	-3071.15	6.776904	0	-48.7594	0-80	Perrin [16]
K (DEA)	-3417.34	0	0	4.5146	25-120	Austgen et al. [12]
K (MEA)	-3635.09	0	0	2.8898	25-120	Austgen et al. [12]
H _{CO₂}	-6789.04	-11.4519	-0.010454	94.4914	0-250	Edwards et al. [17]

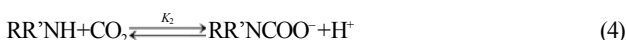
provide important elucidations of chemical reaction rates and equilibria involved in absorption of CO₂ into aqueous amine solutions which form the following basis and equations relevant in our study. The initial reaction is the formation of carbamate ions (for primary and secondary amines):



They are followed by dissociation of protonated alkanolamine:



and formation of carbamate (primary and secondary amines):



Other reactions that occur include dissociation of carbon dioxide and bicarbonate ion as well as ionization of water:



Tertiary amines lack the extra hydrogen atom and do not form carbamate by reaction (4). Primary and secondary amines normally react directly with CO₂ and therefore reaction (5) is not a prerequisite [8]. The equilibrium constants for the above equations are given by the following expressions:

$$K_1 = \frac{[RR'NH][H^+]}{[RR'NH_2^+]} \quad (8)$$

$$K_2 = \frac{[RR'NCOO^-][H^+]}{[RR'NH][CO_2]} \quad (9)$$

$$K_3 = \frac{[HCO_3^-][H^+]}{[CO_2]} \quad (10)$$

$$K_4 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \quad (11)$$

$$K_5 = [H^+][OH^-] \quad (12)$$

The concentration of carbon dioxide in the liquid phase can be estimated from Henry's Law:

$$P_{CO_2} = H_{CO_2}[CO_2] \quad (13)$$

where H_{CO_2} is the Henry's constant for CO₂ and P_{CO_2} the partial pres-

sure of CO₂. The thermodynamic equilibrium constant, K, for the entire chemical reactions and the Henry's constant, H for CO₂ are expressed in the following equation:

$$\ln K \text{ (or } H) = (a/T) + b \ln T + cT + d \quad (14)$$

where a, b, c and d are constants. Values of these constants for overall reaction of alkanolamine with CO₂ and Henry's constant are obtained from previous studies as given in Table 1.

The overall reaction between the alkanolamine and CO₂ is used to calculate solubility (α). Therefore, Eq. (1) can be written as follows:



where

$$K_c = \frac{[RR'NCOO^-][RR'NH_2^+]}{[CO_2][RR'NH]^2} \quad (16)$$

Concentrations of the species can be written in terms of the following measured quantities:

$$[RR'NCOO^-] = m\alpha \quad (17)$$

$$[RR'NH_2^+] = m\alpha \quad (18)$$

$$[RR'NH] = m(1 - 2\alpha) \quad (19)$$

where m is the molarity of alkanolamine and α the CO₂ loading. From (16):

Integrating (13) and (16), we obtain the following:

$$P_{CO_2} = H_{CO_2} \left[\frac{[RR'NCOO^-][RR'NH_2^+]}{K_c[RR'NH]^2} \right] \quad (20)$$

By plugging (16), (17) and (18) into (20), the following equation is obtained:

$$P_{CO_2} = \frac{H_{CO_2}}{K_c} \left[\frac{(m\alpha)(m\alpha)}{[m(1 - 2\alpha)]^2} \right] \quad (21)$$

Eq. (21) can be simplified by eliminating m [8]:

$$P_{CO_2} = \frac{H_{CO_2}}{K_c} \left[\frac{\alpha^2}{(1 - 2\alpha)^2} \right] \quad (22)$$

Once the equilibrium and Henry's constant are known, the solubility of CO₂ can be calculated by substituting these values into Eq. (22).

HYBRID NEURAL NETWORK

1. Artificial Neural Network

Artificial neural networks (ANNs) are essentially an interconnected

set-up of simple processing elements called nodes capable of mimicking human characteristics of problem solving. The processing ability of the network is stored in the inter-unit connection strengths or *weights* [7]. The values of the weights are acquired by a process of training from a set of training pattern (input-output relations). These weights are adapted by one or the other learning rule and correspond to the long-term memory of the neural network. The basic features in neural network are nodes, layers and connections.

2. Hybrid Neural Network

HNNs are constructed from neural networks combined with other components such as first principle model, fuzzy logic or Kalman Filter. The neural networks in a hybrid setup are responsible for learning the difference between the regression model and experimental data. Although the neural network is a semi-parametric estimator, it has the capability of approximating this difference. The hybrid neural network model has internal structures, each part performing a different task.

In this research, the neural network model is combined with the regression model derived based on the Kent-Eisenberg model [6]. Fig. 1 illustrates the general structure of the neural network model used in our study. In essence, all signals disseminate in a forward direction through the network layers with no self-connections. Each node receives signals from connection and then summed together before being applied to a transfer function to create an output. The hidden layers as well as the number of neurons in each layer may vary from one to any finite number depending on the user specification [7]. The output signals are subsequently propagated to other nodes until the output of the network is reached. Fig. 2 shows the training scheme of HNN used in this study.

3. Modelling Methodology

Activation functions used in this work are *purelin*, *logsig* and

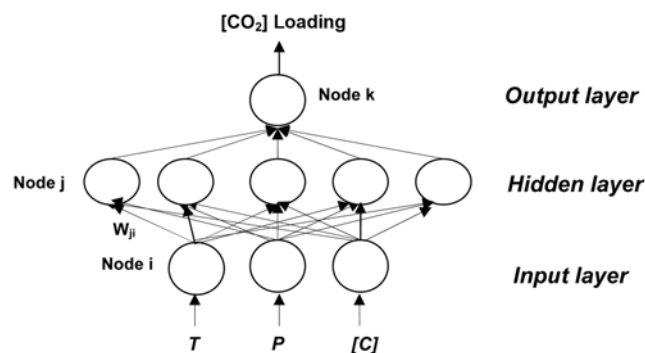


Fig. 1. General structure of neural network model used in this study.

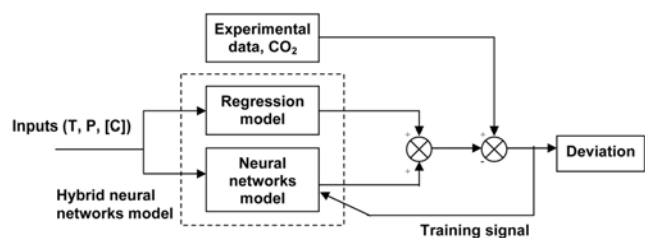


Fig. 2. Training scheme of HNN for prediction of CO₂ solubility in aqueous solutions of alkanolamine.

tansig. *Purelin* is a linear transfer function and used in the output layer. *Logsig* is one of the sigmoid transfer functions that takes an input value between plus minus infinity and then provides the output into the range from 0 to 1. *Tansig* uses a hyperbolic tangent transfer function with values from -1 to $+1$. The training data are scaled from 0 to 1 before using it for training with neural networks. Training is conducted until the mean square error (MSE) obtained is less than a minimum value. The number of training cycles required to achieve this error is approximately 50 epochs. MSE value is defined as the average of the square of the differences between the actual output (experimental values) and the neural network model output (predicted values) [7]. The optimum configurations of the neural networks are stipulated after trial and error based on the minimum MSE obtained during the training process. Validation of the network is subsequently conducted to ensure that network is able to generalize to other sets of data other than the training data.

The input data for HNN are temperature, partial pressure of CO₂ and concentration of alkanolamine solutions, whereas the output is CO₂ loading. The data are divided into three parts: training, testing and validation. Each of them is scaled from 0 to 1 prior to being used to obtain the HNN model. In this study, different hidden nodes for each alkanolamine solution are determined by trial and error method to validate the trained HNN model and they are found to provide satisfactory performance. As can be seen in Fig. 2, the difference in values of the output (CO₂ loading) between the experimental data and data obtained from combination of the model and neural network is the deviation value that is used to train the HNN. After training, testing and validation utilizing different number of hidden nodes, it is found that a neural network with a 3-15-1 configuration provides the best model to predict the deviation value of the loading input. The raw experimental data used to determine the experimental CO₂ gas loading in DEA (0.5 to 8 M; 0 to 120 °C) are obtained from Lee et al. [9]. For CO₂ gas loading in MEA, raw experimental data are obtained from Park et al. [10] (1.63 M; 40 °C), Daneshvar et al. [11] (2 M; 30 to 70 °C), Austgen et al. [12] and Shen and Li [13] (2.5 M; 40 °C) and Jou et al. [14].

MODELLING RESULTS AND DISCUSSION

Our model is developed based on the Kent and Eisenberg [6] model, the simplest among the available models as it basically adjusts the values of the equilibrium constants that best fit the experimental data, where the activity coefficient is neglected. However, it is unable to determine the concentrations of all liquids phase species, ionic or molecular, since separation requires an accurate representation of activity coefficients, which is not provided by the model. To develop an easier prediction method, the HNN model is used because the network is able to learn with many data collections as well as to generalize a function, especially when the training data points are limited.

Figs. 3 and 4 show the comparison between predicted and experimental CO₂ loading in MEA and DEA, respectively. It is obvious that HNN modelling provides accurate predicted CO₂ loading judging by absence of significant outliers, that is, the plotted values remain close to the curve of CO₂ loading_{predicted} = CO₂ loading_{experimental}. To further quantify the accuracy of our model, the absolute mean percentage error values (MPE) between the predicted and experimental

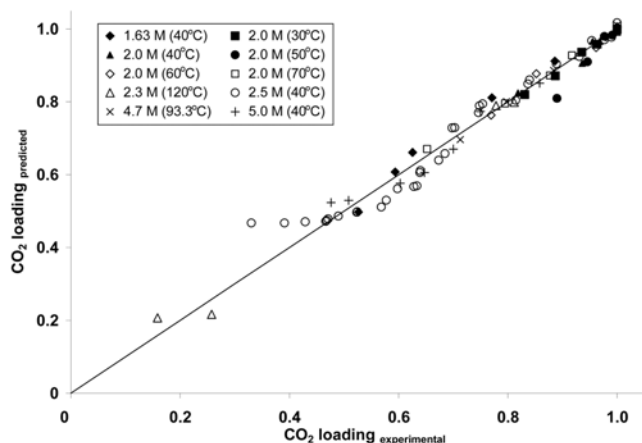


Fig. 3. Comparison between predicted and experimental CO₂ loading in MEA.

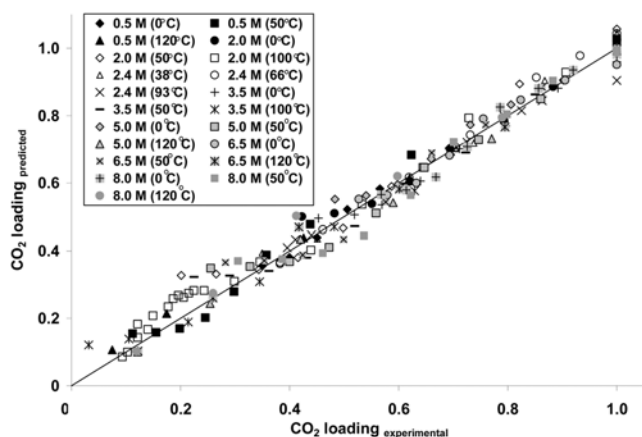


Fig. 4. Comparison between predicted and experimental CO₂ loading in DEA.

values are calculated using the following equation:

$$\text{MPE} = \frac{1}{n} \sum_{i=1}^n \frac{|(\text{CO}_2 \text{ loading})_{\text{ex. perimental}} - (\text{CO}_2 \text{ loading})_{\text{predicted}}|}{(\text{CO}_2 \text{ loading})_{\text{ex. perimental}}} \times 100\% \quad (23)$$

Using Eq. (23), we found that the MPE values for MEA (1.63 to 5.0 M; 40 to 120 °C) and DEA (0.5 to 8.0 M; 0 to 120 °C) data are 4.10 and 16.77%, respectively. We surmise that discrepancies between experimental and predicted CO₂ loading from HNN model exist, because at the time the data are used for training, the model provides different weights and bias that affect the network output. Nonetheless, our MPE values are relatively small (especially for MEA) and certainly comparable to other similar models such as the one reported by Park et al. [15] where they use a modified Kent-Eisenberg model to predict CO₂ solubility in 30 wt% MEA and DEA

(40 to 80 °C) that yields MPE values from 7.7 to 14.9%. It is suggested that for future usage, better results can be obtained by using different activation or transfer functions.

CONCLUSIONS

An HNN model was developed based on Kent-Eisenberg model in combination with a neural network. The HNN methodology used to predict the solubility of CO₂ in single MEA and DEA solutions was described. A neural network with a 3-15-1 configuration provided the best model to predict the deviation value of the loading input. The HNN model could be used to accurately predict CO₂ solubility in alkanolamine solutions (especially MEA) since the predicted CO₂ loading values from the model were in good agreement with experimental data. The MPE values for MEA (1.63 to 5.0 M; 40 to 120 °C) and DEA (0.5 to 8.0 M; 0 to 120 °C) data were 4.10 and 16.77%, respectively.

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