MODELING OF CO_2 SOLUBILITY IN AQUEOUS AMINE SOLUTIONS USING HYBRID NEURAL NETWORK

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Abstract

The use of chemical absorption with amine aqueous solutions has become of great interest as potential post-combustion CO_2 removal process. In such processes, knowledge of solution equilibrium conditions is essential and is necessary to design CO_2 treating equipment.

Model of solubility of CO_2 in N-methylidiethanolamine (MDEA) aqueous solution is presented. Model, based on well-known Kent-Eisenberg structure, was combined with neural network. Such combination forms hybrid neural network model. Neural network was used to determine amine protonation equilibrium constant and further was employed in hybrid neural network to predict equilibrium partial pressure of CO_2 over MDEA aqueous solution in different temperatures and for various solution concentrations. Results show very good agreement between model and experimental data.

Keywords: hybrid neural network, CO_2 chemical absorption, MDEA, greenhouse emissions

Introduction

Chemical absorption in amine aqueous solutions is popular method of CO_2 removal from gas streams. It is widely used particularly during natural gas production, in petrochemistry, during ammonia production where among others it reduces risk of pipelines corrosion. Recently it becomes more and more popular as method of removal of CO_2 in context of mitigation of greenhouse emissions.

Primary amines, for example monoethanolamine (MEA), are widely used in foregoing processes. Its popularity is based on low cost and high absorption rate due to fast reaction between primary amine and CO_2 forming carbamates. On contrary tertiary amines, for example methyldiethanolamine (MDEA), reacts slow, due to dominating carbonate formation, but its solutions have high capacity. Recently, solutions of sterically hindered amines are in the focus of research due to relatively high absorption rates and high loading capacities.

In order to design equipment used in described processes, it is necessary to estimate CO_2 solubility in amine solution in different working conditions. In this work, prediction of CO_2 solubility with hybrid neural network model is presented. Model assumptions were verified for MDEA-CO_2-H_2O system, common in industrial processes.

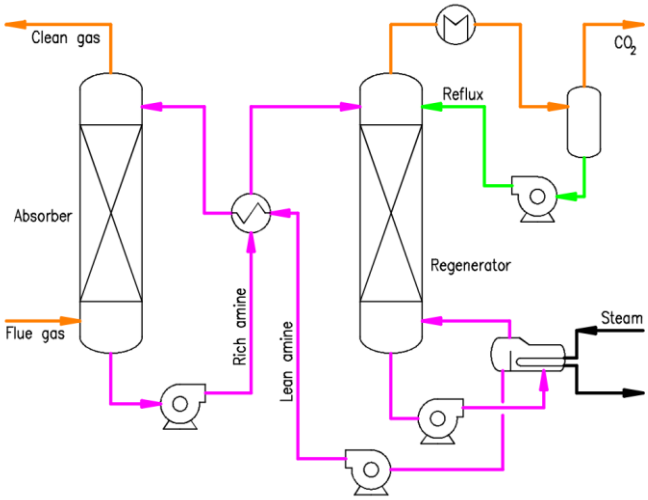

Fig. 1. *Typical flow scheme for amine CO_2 removal process.*

For clarity, typical flow scheme for amine CO_2 removal process is shown on Figure 1. Flue gas is passed through absorber, countercurrent to amine solution. Rich solution from the bottom of the absorber is pre-heated in exchanger by lean amine solution, and fed to regenerator. In regenerator rich solution is further heated by solution vapours and CO_2 is released. Released CO_2 is cooled and

water vapors are separated and fed for further processing. Meanwhile lean amine from the bottom of the evaporator is fed to absorber for reuse.

Model

Chemical equilibrium in MDEA-CO_2-H_2O can be described by four reactions: MDEA protonation (1), the dissociation of carbon dioxide to form bicarbonate (2) and carbonate ions (3), and finally water dissociation (4):

$$H_2O + MDEAH^+ \xleftrightarrow{K_1} H_3O^+ + MDEA \quad (1)$$

$$2H_2O + CO_2 \xleftrightarrow{K_2} HCO_3^- + H_3O^+ \quad (2)$$

$$H_2O + HCO_3^- \xleftrightarrow{K_3} CO_3^{2-} + H_3O^+ \quad (3)$$

$$2H_2O \xleftrightarrow{K_4} H_3O^+ + OH^- \quad (4)$$

Free carbon dioxide concentration in the liquid phase can be estimated by Henry's Law relationship (5):

$$P_{CO_2} = H_{CO_2}[CO_2] \quad (5)$$

The model described in this paper is similar to well-known Kent-Eisenberg model [2]. Kent and Eisenberg used known equilibrium constants $K_{2\text{-}4}$, Henry's constant H_{CO2} and obtained K_1 based on experimental equilibrium data. Having all equilibrium constants, Henry's constant, were able to calculate solution composition and carbon dioxide partial pressure over solution. It is worth mentioning that Kent-Eisenberg model contains simplifications like lack of activity coefficients, but all non-idealities are lumped together in regressed K_1 equilibrium constant. Kent-Eisenberg model, despite the simplicity, correlates the data well.

Kent and Eisenberg assumed that K_1 depends only on solution temperature but further experimental investigations [3] showed dependences on other solution parameters like amine concentration or carbon dioxide loading. Models, where the expression for equilibrium constant K_1 is modified to contain such parameters are called Extended Kent-Eisenberg models.

Model described in this paper is in fact Extended Kent-Eisenberg model with neural network [4], used to regress unknown K_1 equilibrium constant, instead of using numerical fit like in original model. Such modification allows to omit complex regression function selection and simplifies calculations which don't converge easily due to numerical issues. Structure of hybrid neural network model is shown on Figure 2.

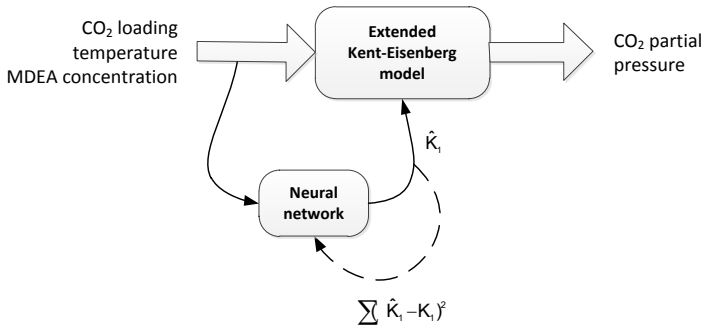

Fig. 2. *Hybrid neural network model structure.*

Neural Network

A Neural Network is an interconnected assembly of simple processing elements, whose functionality is loosely based on the human neuron. The processing ability of the network is stored in the inter-unit connection weights, obtained by a process of learning from a set of training patterns. Neural networks are versatile modelling tool, which in fact, can represent any relationship, regardless its nature. It is required only to properly select network structure and further to train it, using set of patterns describing process.

In this paper neural network was used to model protonation equilibrium constant K_1. Set of patterns containing CO_2 loading, temperature and MDEA concentration as inputs, and experimentally evaluated values of K_1 as output were presented to network. The raw experimental data used during network training were obtained from literature sources: [6]-[13]. Training was carried out until mean squared error between network output and experiment results was acceptable. Further, trained

network was used to predict K_1 and predicted K_1 was introduced to Extended Kent-Eisenberg model. Finally CO_2 partial pressure over solution was calculated.

Following methods [5] were used to improve prediction quality of neural network:

1. Number of training patterns was increased by monotonic spline interpolation of raw experimental data,
2. Neural networks ensemble [14] was employed instead of single network. Actual K_1 value was calculated as average of outputs of 10 networks, which were trained using different training algorithm parameters,
3. Optimal number of hidden neurons, activation function etc. were selected to minimize mean squared network error,
4. Network generalization was improved by cross-validation. Network was tested on independent data set, which wasn't used during training.

Results and conclusions

Quality of hybrid neural network model was verified on various data sets and compared to Kent-Eisenberg model. Results show very good agreement between model and experimental data and significantly surpass Kent-Eisenberg model from which Hybrid Neural Network Model is derived (Figures 3 and 4).

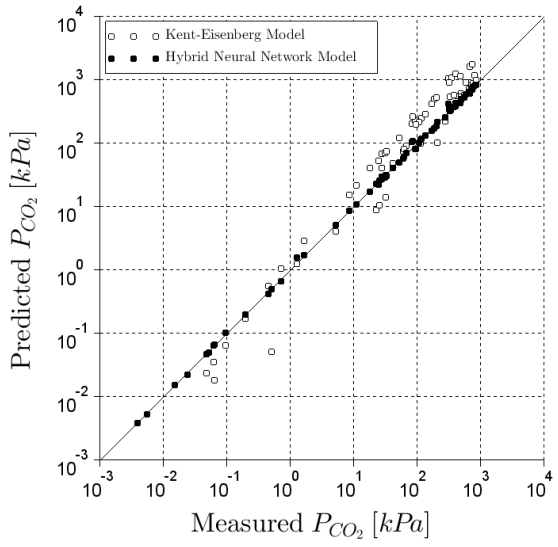

Fig. 3. *Comparison of predicted and measured CO_2 for Kent-Eisenberg and Hybrid Neural Network Model.*

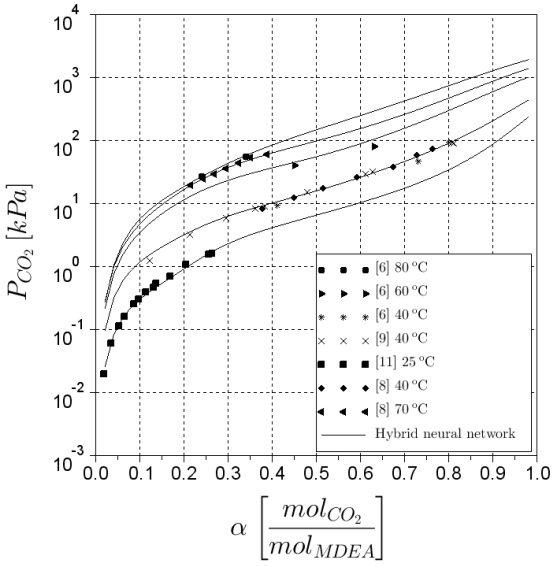

Fig. 4. *Predicted curves for CO_2 partial pressure over 2 mole/dm^3 MDEA solution at various temperatures agree with references.*

Proposed Hybrid Neural Network model can be successfully used to estimate CO_2 solubility over MDEA solutions in various temperatures for different gas loadings and amine concentrations. After slight modifications can be used for other tertiary amine solutions.

Hybrid neural network models perform very well in various fields due to joining *a priori* knowledge with neural network component which serves as a nonparametric approximator of difficult-to-model process parameters. Such combination proved to be reliable and allows to predict modelled process accurately.

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References

[1] P. Bishnoi, G. Rochelle, "Physical and chemical solubility of carbon dioxide in aqueous methyldiethanolamine", *Fluid Phase Equilibrium*, nr 168, pp. 241-258, 2000.

[2] R. Kent, B. Eisenberg, "Better data for amine treating", *Hydrocarbon Processing*, nr 55, pp. 87-90, 1976.

[3] M.Z. Haji-Suleiman, M.K. Aroua, A. Benamor, "Analysis of equilibrium data of CO2 in aqueous solutions of diethanolamine (DEA), methyldiethanolamine (MDEA) and their mixtures using modified Kent Eisenberg model", *Tranpp. IChemE*, vol. 76, pp. 961-968, 1998.

[4] D. Psichogios, L. Ungar, "A Hybrid Neural Network-First Principles Approach to Process Modeling", *AIChE Journal*, vol. 38, nr 10, pp. 1499-1511, 1992.

[5] PP. Geman, E. Bienenstock, R. Doursat, "Neural Networks and the Bias/Variance Dilemma", *Neural Computational*, vol. 4, nr 1, pp. 1-58, 1992.

[6] PP. Ma'mun, R. Nilsen, H. Svendsen, "Solubility of Carbon Dioxide in 30 mass % Monoethanolamine and 50 mass % Methyldiethanolamine Solutions", *Journal of Chemical & Engineering Data*, vol. 50, pp. 630-634, 2005.

[7] B. Si Ali, M.K. Aroua, "Effect of Piperazine on CO_2 Loading on Aqueous Solutions of MDEA at Low Pressure", *International Journal of Thermophysics*, vol. 25, nr 6, pp. 1863-1870, 2004.

[8] R. Sidi-Boumedine et al., "Experimental determination of carbon dioxide solubility data in aqueous alkanoloamine solutions", *Fluid Phase Equilibria*, vol. 218, pp. 85-94, 2004.

[9] PP. Taghipoor, M. Vahidi, M. Goharrokhi, "Prediction and Correlation of CO2 Solubility in MDEA Aqueous Solutions Using the Extended Debye-Hueckel Model", *Journal of Applied Chemical Research*, nr 8, pp. 7-18, 2009.

[10] P.W.J. Derks, Carbon Dioxide Absoprtion in Piperazine Activated N-methyldiethanoloamine, 2006.

[11] J. Bullin, W. Rogers, Collection of VLE Data for Acid Gas-Alkanoloamine Systems using FFT Infrared Spectroscopy, 1995.

[12] B. Lemoine, Yi-Gui Li, R. Cadours, C. Bouallou, D. Richon, "Partial vapor pressure of CO2 and H2S over aqueous methyldiethanoloamine solutions", *Fluid Phase Equilibria*, nr 172, pp. 261-277, 2000.

[13] IChPW, "Badania laboratoryjne wychwytu CO_2 z gazów procesowych", Sprawozdanie Merytoryczne, 2012.

[14] M. Perrone, L. Cooper, "When Networks Disagree: Ensemble Methods for Hybrid Neural Networks", *Artificial Neural Networks for Speech and Vision*, nr 4, pp. 126-142, 1993.