Journal of the University of Chemical Technology and Metallurgy, 47, 5, 2012, 546-552

A NEURO-FUZZY MODEL FOR ACCURATE PREDICTION OF H_2S SOLUBILITIES IN AQUEOUS SOLVENTS EMPLOYED IN WATER-WASH UNITS OF GAS REFINING PLANTS

Bahman ZareNezhad, Ali Aminian

Ministry of Science, Research and Technology,
Semnan University, Iran
E-mail: prof.b.zarenezhad@gmail.com

Received 30 July 2012
Accepted 15 September 2012

ABSTRACT

A fuzzy network model is presented for accurate prediction of the solubility of H_2S in pure water and aqueous brine solutions over wide ranges of operating conditions. The fuzzy C-means clustering method is used to determine the rule antecedents and the Levenberg-Marquardt method is implemented to calculate the optimal premise parameters. Predictions of the proposed fuzzy model are much more accurate than those obtained through the available thermodynamic models. The presented fuzzy model can be used for accurate design of new water-wash gas sweetening units at the upstream of amine sweetening plants in oil and gas industries.

Keywords: *H_2S , gas sweetening, Neuro-Fuzzy Model, prediction, petroleum.*

INTRODUCTION

At the present, amine solvents are widely used for removing carbon dioxide (CO_2) and hydrogen sulfide (H_2S) from sour natural gases and refinery gaseous streams. Because of higher H_2S content of new exploited reservoirs, it is necessary to optimize the gas sweetening processes to avoid solvent and energy losses. Thus, establishing a sour gas water wash unit using filtered water or aqueous brine solution at the upstream of an amine sweetening unit has been recently found economic justification. The sour gas water wash reduces the H_2S loading, lowers the particulate concentration and allow us to carry out the amine sweetening operations in medium scale units. Therefore accurate prediction of H_2S solubility in pure water and brine solutions are necessary for proper design of sour gas water wash sweetening units.

The most extensive studies of H_2S solubility in aqueous brine solutions (such as NaCl and KCl) are those of Drummond [1], Barrett et al. [2], Suleimenov and Krupp [3], and Xia et al. [4]. Different thermodynamic models have also been presented for correlating the experimental H2S solubility data. However it is not possible to obtain accurate predictions over wide ranges of salt concentrations. Also a considerable computational time is required to determine the model parameters. For example, Carroll and Mather [5] have used Peng-Robinson EOS modified by Vera [5] to predict the solubility of H_2S in pure water. This model underestimates H_2S solubility at low pressure ($P < 10$ bar) and overestimates H_2S solubility at high temperatures ($T > 450$ K). Barta and Bradley [6] developed a semi-empirical model to predict H_2S solubility in aqueous NaCl solution from the Pitzer interaction model. Suleimenov and Krupp [3] have measured H_2S solubility in aqueous NaCl solution up to 593 K and 2.5 M NaCl at 1 atm, but their model can not be used for accurate prediction of H_2S solubilities. Other approaches, i.e. PHREEQC [7]

and SUPCRT92 [8] codes, based on numerical speciation-solubility modeling and thermodynamic equilibrium also proposed for calculating H_2S solubility in H_2S saturated brines and NaCl solutions, respectively.

Duan et al. [9] have developed the most rigorous and most accurate thermodynamic model for prediction of H_2S solubilities in pure water and brines and even in more complex brines such as seawater. However there are significant prediction errors at some ranges of salt concentrations due to several simplifying assumptions made in the model development.

Because of the aforementioned shortcomings in existing thermodynamic models, an artificial fuzzy logic model has been alternatively presented in this work. Fuzzy system is a computation framework based on the concepts of fuzzy sets, fuzzy if-then rules, and fuzzy reasoning. Moreover, the powerful function approximation properties of neural networks [10-15] make them useful for representing nonlinear models. Wang et al. [16] reported the combination of multiobjective hierarchical genetic algorithm and recursive least square method to obtain interpretable Takagi-Sugeno fuzzy models [17] of high accuracy.

The aim of the present work is to develop an integrated fuzzy clustering-fuzzy model for predicting H_2S solubility in pure water and aqueous NaCl brine solutions. For the H_2S-H_2O system, the solubility data from different sources [4,5,18] have been employed. The experimental data for the H_2S – Nacl-H_2O system are those reported by Drummond [1], Barrett et al. [2] and the data of Suleimenov and Krupp [3], which have been used in the present work. The proposed fuzzy model predictions are also compared with those of Duan et al. [9] thermodynamic model and experimental data.

PROPOSED ANFIS MODEL

The proposed neuro-fuzzy model in ANFIS is a multilayer neural network-based fuzzy system as shown in Fig. 1. Assuming that the ANFIS has two inputs x_1 and x_2 and one output, the following rules can be written for a first order Sugeno fuzzy model [17]:

Rule 1 :

If x_1 is A_1 and x_2 is B_1, then $f_1 = p_1 x_1 + q_1 x_2 + r_1$ (1)

Rule 2 :

If x_1 is A_2 and x_2 is B_2, then $f_2 = p_2 x_1 + q_2 x_2 + r_2$ (2)

The proposed ANFIS structure as shown in Fig 1 is described as follows:

Layer 1. This is the input layer where the input nodes, x_1 and x_2 enter the Fuzzy network

Layer 2. The fuzzy part of ANFIS is mathematically incorporated in the form of membership functions (MFs). A membership function $\mu_{Ai}(x)$ can be any continuous and piecewise differentiable function that transforms the input value x into a membership degree, that is to say a value between 0 and 1 [18, 19]. The layer 2 is the fuzzification layer in which each node represents a membership according to the following three parameter Gaussian function:

$$\mu_{Ai}(x) = \exp[-((\frac{x - c_i}{a_i})^2)^{b_i}] \quad (3)$$

Every node i in this layer is an adaptive node with a node function

$$O_{2,i} = \mu_{Ai}(x) \quad \text{for } i = 1,2 \quad \text{or} \quad (4)$$

$$O_{2,i} = \mu_{Bi-2}(x) \quad \text{for } i = 3,4 \quad (5)$$

Where x_1 (or x_2) is the input node i and A_i (or B_{i-2}) is a linguistic lable associated with this node. Therefore $O_{2,i}$ is the membership grade of a fuzzy set (A_1, A_2, B_1, B_2).

As the values of the parameters $\{a_i, b_i, c_i\}$change, the bell-shaped functions vary acccordingly, exhibiting various forms of membership functions on linguistic label A_i. Parameters in this layer are referred to as premise parameters.

Layer 3. Every node in this layer is a fixed node labeled as Π, whose output is the product of all the incoming signals:

$$O_{3,i} = w_i = \mu_{Ai}(x_1) \cdot \mu_{Bi}(x_2) \quad i = 1,2 \quad (6)$$

Every node in this layer computes the multiplication of the input values and gives the product as the output [19]. The membership values represented by $\mu_{Ai}(x_1)$ and $\mu_{Bi}(x_2)$ are multiplied in order to find the firing strength of a rule where the variables x_1 and x_2 have the linguistic values A_i *and* B_i, respectively.

Layer 4. This layer is the normalization layer which normalizes the strength of all rules according to Eq. (7):

$$O_{4,i} = \overline{w}_i = \frac{w_i}{w_1 + w_2} \quad (7)$$

where w_i is the firing strength of the ith rule which is computed in layer 3. Node i of this layer labeled as N computes the ratio of the ith rule's firing strength to the sum of all rules' firing strengths. For convenience, outputs of this layer are called normalized firing strengths [20].

Layer 5. Every node in this layer, labled as an integer value, is an adaptive node with a node function [21]:

$$O_{5,i} = \overline{w}_i f_i = \overline{w}_i (p_i x_1 + q_i x_2 + r_i) \quad (8)$$

where $\overline{w}_i$ is the normalized firing strength from layer 4 and $\{p_i, q_i, r_i\}$ is the parameter set for this node. Parameters in this layer are referred to as consequent parameters

Layer 6. The single node in this layer is a fixed node labeled as $\sum$ which computes the overall output as the summation of all incoming signals:

$$O_{6,i} = \sum_i \overline{w}_i f_i = \frac{\sum_i w_i f_i}{\sum_i w_i} \quad (9)$$

The ANFIS can be trained by a hybrid learning algorithm to identify the membership function parameters [22]. In the forward pass the algorithm uses least squares method to identify the consequent parameters $\{p_i, q_i, r_i\}$ on the layer 5. In the backward pass the errors are propagated backward and premise parameters $\{a_i, b_i, c_i\}$ are updated by gradient descent.

RESULTS AND DISCUSSION

A first order Takagi-Sugeno fuzzy model has been developed for prediction of H_2S solubilities as a function of temperature, pressure, and salt compositions. Solubilities of H_2S in pure water and in 1, 2, 4, 6 M NaCl solutions have been reported with pressure range of 0-200 bar and temperature range of 273 K to 513 K. There are 569 data points of which 398 data points are used for fuzzy model training and 171 data points are used to test the generalization capability of the trained network. The molal concentration, system pressure, and temperature are used as inputs while the output of the fuzzy model is the H_2S solubility in the liquid phase.

Proposed Fuzzy model predictions regarding H_2S solubility in pure water are compared with those predicted by Duan et al. [9] and experimental data as shown in Fig.2. There are some deviations in predicting the solubilities of H_2S, when the thermodynamic model of Duan et al. [9] is used as shown in this figure. At T=393.2 K, the model of Duan underestimates H_2S solubility at pressures above 60 bar, while, at T=453.2 K, Duan model overpredicts the H_2S solubilities at pressures above 40 bar. As shown in Fig. 2, the presented fuzzy model gives accurate predictions over the wide ranges of pressures and temperatures.

The solubility of H_2S is generally increased as the system pressure increases, while an increase in

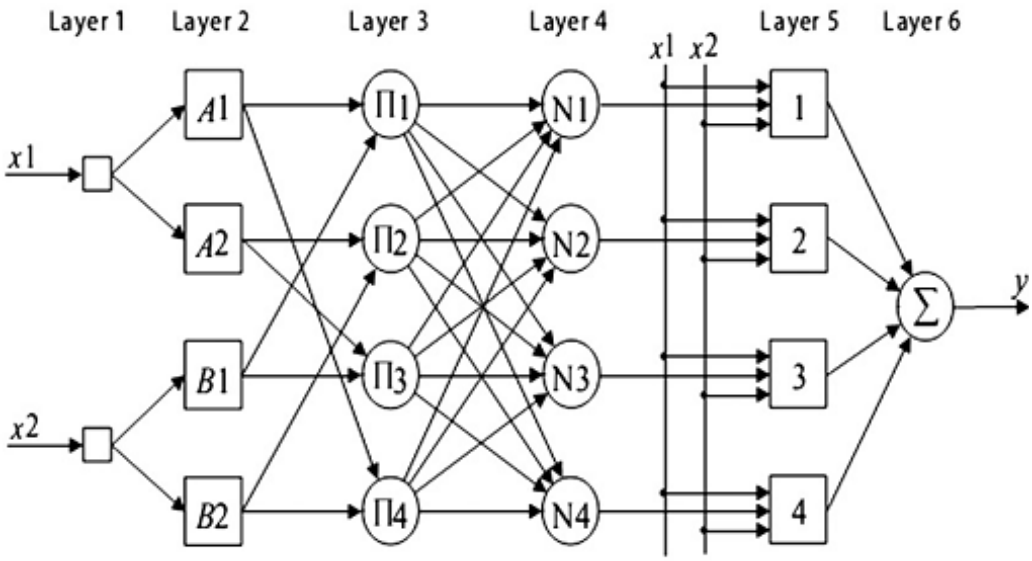

Fig. 1. ANFIS structure for a two input Takagi-Sugeno model with four rules.

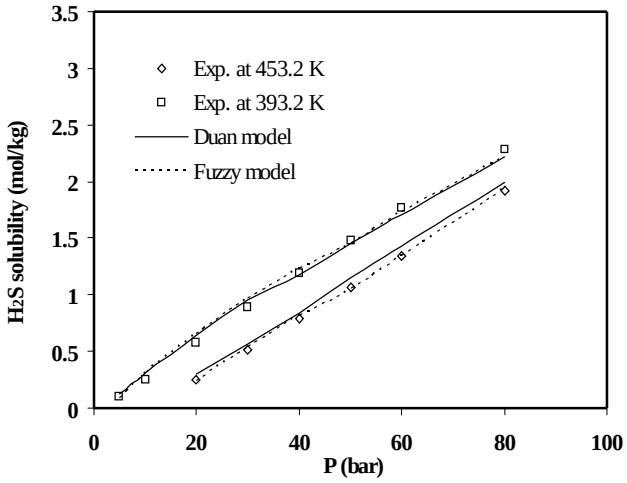

Fig. 2. H_2S solubilities in pure water at 393.2 and 453.2 K (Prediction of fuzzy model vs. experimental data and Duan model).

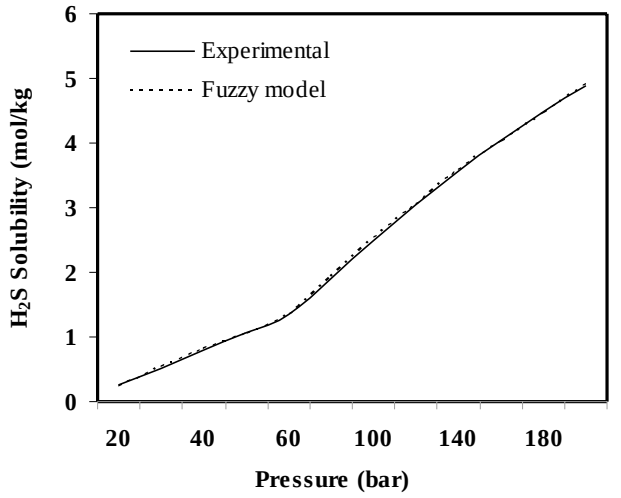

Fig. 3. H_2S solubility in pure water at 453.2 K (Prediction of fuzzy model vs. experimental data).

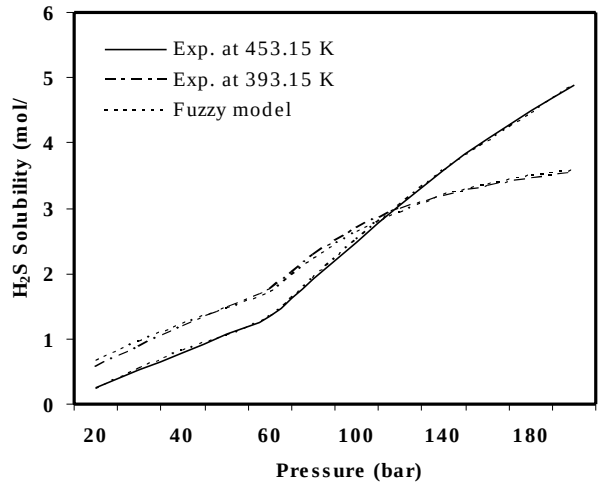

Fig. 4. Comparison between H_2S solubility in pure water at 393.15 and 453.2 K.

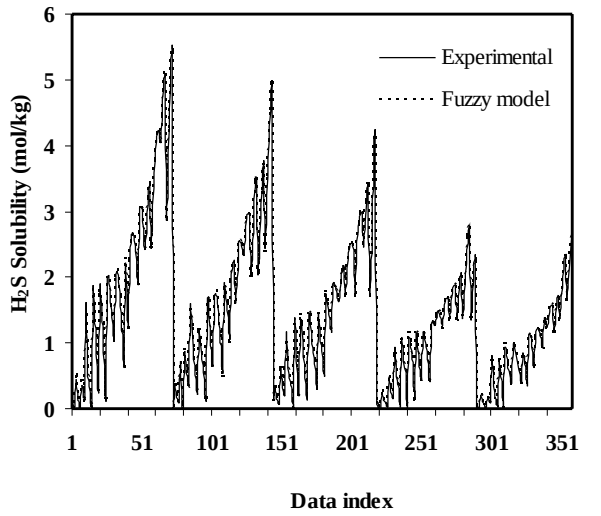

Fig. 5. Training performance of the proposed fuzzy model.

temperature leads to a decrease in H_2S solubility as shown in Figs. 2 and 3. Solubility of a gas in typical solvents usually falls with rising temperature. However, at higher temperatures, approaching the critical temperature of the solvent, the solubility of a gas usually rises with temperature [23], as illustrated in Fig.4. As shown in this Figure, the trend of solubility data at different operating conditions are well predicted by the proposed Fuzzy model. According to the Table 1, the fuzzy model can represent the experimental solubility data at different NaCl concentrations accurately with the mean AAD% (average absolute deviation percent) of about 2.43% according to the following equation:

$$AAD(\%) = \frac{100}{N}\sum_{i=1}^{N}\frac{\left|\left(m_{H_2S}^{exp}\right)_i - \left(m_{H_2S}^{pred}\right)_i\right|}{\left(m_{H_2S}^{exp}\right)_i} \qquad (10)$$

where N is the number of data points and $\left(m_{H_2S}^{exp}\right)$ and $\left(m_{H_2S}^{pred}\right)$ are the experimental and predicted H_2S solubility respectively. It should be noted that the Duan thermodynamic model prediction accuracy deteriorates at high pressures and temperatures (T>500 K and P>100 bar) such that the AAD% between Duan model predictions and experimental data is as high as about 7%. Fuzzy model training performance is shown in Fig. 5. The trained Fuzzy model is validated by the testing data set. Fig. 6 represents the validation results of the proposed fuzzy network model,

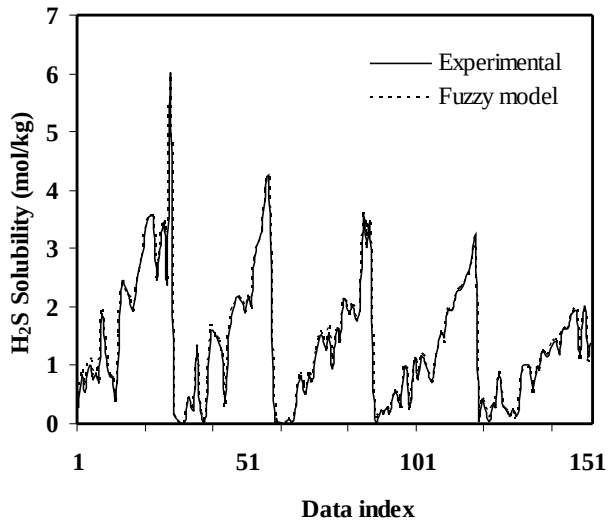

Fig. 6. Testing performance of the proposed fuzzy model.

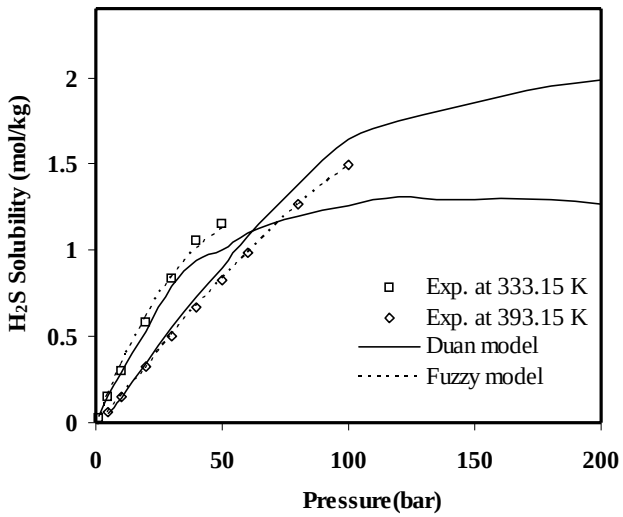

Fig. 8. H_2S solubility in 4M NaCl solution at 333.15 and 393.15 K (Comparison between Fuzzy model and Duan model).

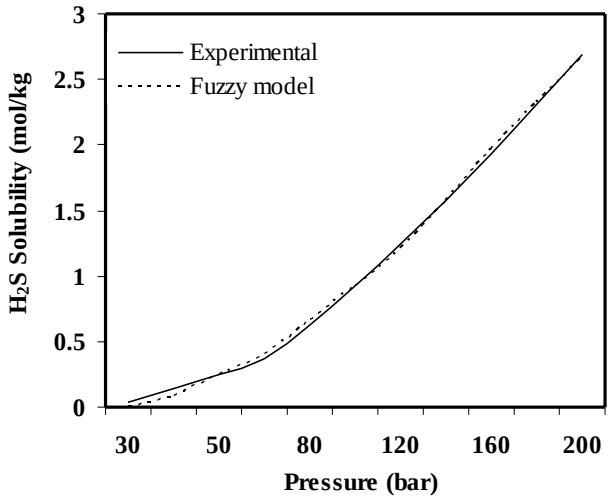

Fig. 7. H_2S solubility in 6M NaCl solution at 513.15 K (Proposed fuzzy model Predictions vs. experimental data).

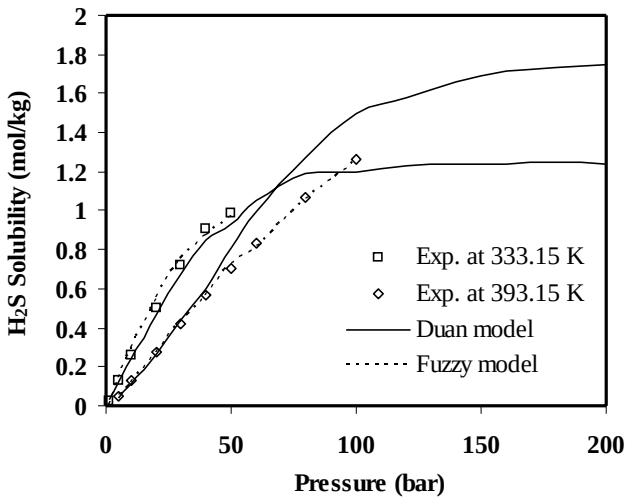

Fig. 9. H_2S solubility in 6M NaCl solution at 333.15 and 393.15 K (Comparison between Fuzzy model and Duan model).

from which it can be observed that the testing errors for all the testing data set are nearly zero. This clearly indicates the effectiveness and the reliability of the proposed model for H_2S solubility predictions.

Fig. 7 represents the comparison between the experimental data and the result of fuzzy model for 6M NaCl brine solution at 513.15 K. As shown, the proposed fuzzy model can reproduce the experimental data at high temperatures very accurately.

Proposed fuzzy model solubility predictions are compared with those of Duan model and experimental data regarding 4M and 6 M NaCl aqueous solutions at two different temperatures of 333.15 and 393.15 K in Figs. 8 and 9, respectively. As shown in these Figures the proposed Fuzzy Network Model solubility predictions are in excellent agreement with experimental data, while there are significant deviations between Duan thermodynamic model predictions and measured data especially at higher pressures. As shown in Fig 10, the proposed Fuzzy model predictions are in excellent agreement with all measured values over wide ranges of operating variables such that the presented Fuzzy model outperforms the available thermodynamic models.

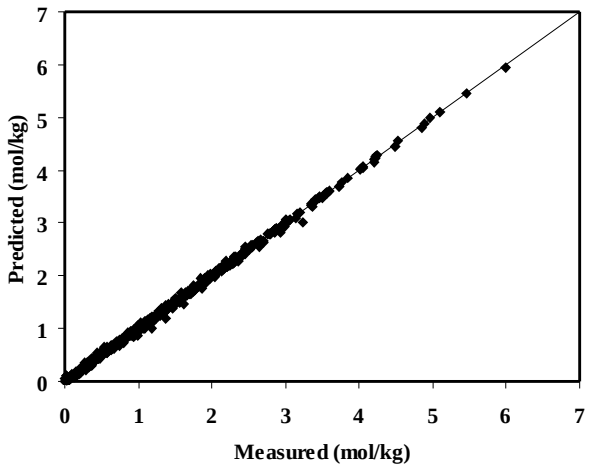

Fig. 10. Comparison of the proposed Fuzzy model predictions with all measured H_2S solubilities in aqueous solutions.

Table 1. Deviations between proposed fuzzy model predictions and experimental data.

System	AAD(%)
Pure water	2.64
1M NaCl	1.69
2M NaCl	1.81
4M NaCl	2.83

CONCLUSIONS

H_2S solubilities in pure water and aqueous brine solutions are determined by using a fuzzy network model. Optimal fuzzy model is obtained according to fuzzy clustering followed by Levenberg-Marquardt algorithm. The genetic algorithm is used to initialize the consequent parameters of the rules. The mean least square method is then implemented to obtain the optimal sequence of consequent parameters. The suggested fuzzy network is tested against the independent set of brine concentrations not used during the network training. Predictions of the proposed fuzzy model are much more accurate than those obtained through the available thermodynamic models. The presented fuzzy model can be used for accurate design of water wash gas sweetening units at the upstream of amine sweetening plants in oil and gas industries.

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