Prediction of Methane and Ethane Hydrate Phase Equilibria in Porous Media Using Artificial Neural Network

Kamaloddin Momeni
Iran University of Science and Technology
Department of Chemical Engineering
P.O.Box 16844, Tehran, Iran.
ka_momeni@chemeng.iust.ac.ir

Mohammad Taghi Sadeghi
Iran University of Science and Technology
Department of Chemical Engineering
P.O.Box 16844, Tehran, Iran.
sadeghi@iust.ac.ir

Mohammad Ali Fanaei
Ferdowsi University
Department of Chemical Engineering
P.O.Box ------, Mashhad, Iran.
fanaei@ferdowsi.um.ac.ir

ABSTRACT
A few theoretical studies dealing with hydrate–liquid two-phase equilibrium and three-phase equilibrium in porous media is available in the literature. In this paper, an alternate tool, i.e. the artificial neural network (ANN) technique was employed to estimate the temperature of gas hydrate in porous media. The ANN model was applied to the available 359 and 258 sets of data for methane and ethane respectively comprising temperature pressure and pore size. In order to validate the ANN model, the samples were divided into two groups. One containing 289 and 208 samples of methane and ethane that were employed to train the two networks whereas the remaining 70 and 50 other samples were used for validating the model. Moreover, training of the networks was done applying the standard feed forward back propagation algorithm and several structures were tested to obtain the most suitable network for prediction of the equilibrium. The hydrate phase equilibria for binary mixtures of CH₄+water as well as C₂H₆+water in silica pores were predicted. The predictions of this method were in acceptable agreement with independent experimental data, demonstrating the reliability of ANN tool for estimation of the hydrate phase equilibrium in presence of porous media.
sadeghi@iust.ac.ir

1. INTRODUCTION
Clathrate hydrates are solids in which some of the cages formed by the hydrogen-bonded water molecules making up the hydrate lattice are occupied by a small guest-species molecule. Various studies were done concerning formation of the hydrates in pipelines that blocks the flow of gas [1]. Natural gas hydrates exist in the earth’s crust in arctic regions as well as beneath the seafloor around the margins of most continental shelves. Due to increased drilling in the arctic and in the deep ocean waters, natural gas hydrate attract substantial attention for problems they might cause during the drilling and production of oil or natural gas. On the other hand, they represent a potentially huge source of fuel often estimated to be larger than all other sources of fossil fuels [2].

The influence of porous medium on hydrate physical properties, including the kinetics of hydrate accumulation and decomposition, has been intensively studied since the 1960s [3]. A significant part of later works was devoted to the study of the conditions for three-phase equilibrium systems. These consist of water/ice, hydrate and gas placed in porous media with characteristic sizes ranging from a few nanometers to a few tens of nanometers [4, 5, 6]. The calibrated nanosized silica systems used as a model of porous medium stimulated the return of research to the study of the equilibrium properties of hydrates in natural dispersed systems. Moreover, complicated issues such as the effect of a broad distribution of pore sizes, water saturation of a porous medium and space distribution of water in a porous medium were investigated [7].

Handa and Stupin [5] were the first researchers conducting experiments to predict the formation conditions of gas hydrates in sediments. They performed experiments with methane and propane gases in silica sediment with an average pore size of 70°A. More recently, Uchida et al. [8, 9] presented experimental ice melting and clathrate dissociation data for gas hydrates in porous silica. In order to determine the hydrate equilibrium condition in porous media, several researchers have favored continuous heating methods [8, 9], while others have utilized step-heating techniques for data generation [5, 6, 10, 11]. In a series of publications, Wilder et al. [6], Seshradi et al. [11] employed a pressure conceptual model to explain the clathrate equilibrium condition in mesoporous media with a pore size distribution.

The majority of workers to date have employed the equation detailed in the conceptual model of Clennell et al. [12] and Henry et al. [13]. However, this relationship describes clathrate growth in porous media, not dissociation, which is represented by the published experimental hydrate data [14]. In general, there is still no model that can predict the P–T condition for Clathrate hydrate-Liquid water-Vapor (H-Lw-V) equilibrium of gas hydrate in marine sediments accurately [15].

Neural network technique provides a reliable prediction tool due to its inherent capability of capturing nonlinear functional behaviors. The technique is now being used in many oil and gas applications. These include prediction of hydrate formation conditions for various gas mixtures and inhibitors [16, 17], estimation of water content of natural gas [18], determination of gas hydrate safety margin [19, 20], and prediction of hydrate stability zones of petroleum fluids [21].
A comprehensive literature review shows that the models offered until now are aimed towards prediction of pressure. The models depend on accurate estimation of molar volume of the aqueous phase, contact angle, surface tension, and radius of the pore. Furthermore, earlier ANN models are capable to predict the hydrate phase equilibrium of bulk only. The object of this paper is to develop a model based on neural networks for prediction of the equilibrium dissociation temperature of methane and ethane hydrates inside porous media as well as the bulk. The models are developed aiming to predict the H-L, H-I-V, and high pressure equilibrium conditions that only depend on pore diameter. The results demonstrate that the predictions of the models are in suitable agreement with experimental data.

2. ARTIFICIAL NEURAL NETWORKS

Artificial neurons are similar to their biological counterparts. A neural network consists of numbers of simple processing elements called neurons. Each neuron of the neural network is connected to others via direct communication weights. Many different types of ANNs have been developed. The multilayer feed-forward network with back propagation (BP) learning method is the most popular network in chemical applications [22]. This method was employed to predict the gas hydrate equilibrium condition in this work.

The transfer function was utilized to calculate the input of one node from the output of the others. Several forms have been suggested to describe this function. One of the most commonly used forms is the sigmoid function [23] expressed as following:

$$f(x) = \frac{1}{1 + \exp(-x)}$$

(1)

Where $x$ is the network input variable.

The objective function is the sum of squares of relative deviations between the experimental and calculated values defined by following equation:

$$F = \frac{1}{N} \sum_{i=1}^{N} (T_{exp}(i) - T_{calc}(i))^2$$

(2)

Where $N$ is the number of samples in the data set, $T_{exp}$ represents the experimental target value of temperature and $T_{calc}$ is the calculated value of temperature.

The structures of ANN models used here for methane and ethane hydrates are three-layer feed-forward network with a modified Levenberg-Marquardt training algorithm illustrated in Figure 1. To achieve the lowest value of minimized objective function, a series of sensitivity analyses are conducted on the number of hidden layers and neurons in hidden layer. In fact, the numbers of neurons in hidden layer are varied between 3 and 12. One hidden layer which consists of 10 and 8 neurons in each layer is developed to compute the hydrate equilibrium temperature as a function of pore size and logarithm of pressure for methane and ethane hydrates, respectively. In this study, three types of transfer functions are tested: the exponential-sigmoid, tangent-sigmoid, and linear. With aim of minimum error, consequently, tangent-sigmoid transfer function is used between input and hidden layers and linear transfer function is utilized for hidden layer to output layer, because of the less error that this structure results.

Figure 1. Structure of ANN model for methane and ethane hydrate with 10 and 8 neurons in hidden layer, respectively.

3. INPUT DATA USED IN THE DEVELOPMENT AND TESTING OF THE ANN MODELS

The hydrate phase–equilibrium in porous media data used in this study are obtained from articles listed in Table 1. The data used in this paper are related to silica glass and silica gel porous media. There is no significant difference between those [8]. The predictions of the proposed models are based on the mean pore size. However, the data used here to train and test the models comprises data related to both nominal [24, 25, 26] and mean [2, 4, 8, 9, 27-30] pore size. Nevertheless, there is no significant difference between these two types of data. The ranges of pressure, temperature and number of data utilized in this study are given in Table 1.

4. RESULTS AND DISCUSSIONS

As mentioned above, a wide range of data are reported in literature which have the potential to be employed in this study (see Table 1). The results reported by Handa and Stupin [5] and Smith et al. [10] for methane hydrate differs from those of the other authors [2, 4, 8, 9, 24-30]. According to the discussion by Seshadri et al. [11], Wilder et al. [20] and Zhang et al [25], this discrepancy resulted from the fact that the data of Handa and Stupin [5] and Smith et al. [10] might include the pore size distribution and the initial temperature at which the experiments were started.
Table 1. Ranges of the temperatures, pressures and pores diameter of experimental data and number of data points used in this study.

<table>
<thead>
<tr>
<th>References</th>
<th>Species</th>
<th>Pressure, Mpa</th>
<th>Temperature, °K</th>
<th>D, nm</th>
<th>No</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uchida et al. [8, 9]</td>
<td>Methane</td>
<td>1.65 – 9.86</td>
<td>259.7 – 283.7</td>
<td>4 – 102.6</td>
<td>37</td>
</tr>
<tr>
<td>Zhang et al [25, 26]</td>
<td>Methane</td>
<td>0.992 – 3.261</td>
<td>244.2 – 272.2</td>
<td>4 – 15</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>Ethane</td>
<td>0.125 – 1.504</td>
<td>246.15 - 277.15</td>
<td>6 – 15</td>
<td>82</td>
</tr>
<tr>
<td>Anderson et al. [14]</td>
<td>Methane</td>
<td>3.689 – 14.065</td>
<td>271.8 – 287.5</td>
<td>9.2 – 30.6</td>
<td>10</td>
</tr>
<tr>
<td>Smith et al. [24]</td>
<td>Methane</td>
<td>2.20 – 3.88</td>
<td>266.15 – 281.15</td>
<td>30</td>
<td>11</td>
</tr>
<tr>
<td>Aladko et al. [27, 28]</td>
<td>Methane</td>
<td>3.34 – 310</td>
<td>273.60 – 314.95</td>
<td>5.9 – 29.2</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>Ethane</td>
<td>0.402 – 4.59</td>
<td>276.0 – 296.6</td>
<td>10.5 – 29.6</td>
<td>113</td>
</tr>
<tr>
<td>Kang et al. [29]</td>
<td>Methane</td>
<td>2.34 – 9.94</td>
<td>269.65 – 284.25</td>
<td>5.51 – 94.5</td>
<td>15</td>
</tr>
<tr>
<td>Sloan [31]</td>
<td>Methane</td>
<td>0.955 – 527</td>
<td>243.2 – 320.9</td>
<td>Bulk</td>
<td>116</td>
</tr>
<tr>
<td></td>
<td>Ethane</td>
<td>0.022 – 3.316</td>
<td>215.7 – 288.2</td>
<td>Bulk</td>
<td>63</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>References</th>
<th>Species</th>
<th>Pressure, Mpa</th>
<th>Temperature, °K</th>
<th>D, nm</th>
<th>No</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kang et al. [29]</td>
<td>Methane</td>
<td>0.78 – 2.341</td>
<td>238.0 – 277.2</td>
<td>5 – 15</td>
<td>50</td>
</tr>
<tr>
<td>Sloan [31]</td>
<td>Methane</td>
<td>0.955 – 527</td>
<td>243.2 – 320.9</td>
<td>Bulk</td>
<td>116</td>
</tr>
<tr>
<td></td>
<td>Ethane</td>
<td>0.022 – 3.316</td>
<td>215.7 – 288.2</td>
<td>Bulk</td>
<td>63</td>
</tr>
</tbody>
</table>

Table 2. Number of neurons, hidden layers, runs, and data used in this method for estimate the temperature in equilibrium with liquid water and liquid water + ice data (training and test)

<table>
<thead>
<tr>
<th>Species</th>
<th>Phases</th>
<th>Data training</th>
<th>Data testing</th>
<th>No. Run</th>
<th>Structure</th>
<th>%AAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>H-L w-I-V</td>
<td>289</td>
<td>70</td>
<td>1500</td>
<td>2-10-1</td>
<td>0.19</td>
</tr>
<tr>
<td>Ethane</td>
<td>H-L w-I-V</td>
<td>208</td>
<td>50</td>
<td>1500</td>
<td>2-8-1</td>
<td>0.16</td>
</tr>
</tbody>
</table>

\[
%\text{AAD} = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{\text{Experimental value} - \text{Calculated value}}{\text{Experimental value}} \right) \times 100
\]

At higher temperatures, where the equilibrium involves liquid water, the pressures are larger than those for the bulk hydrates, and generally, increase with a decrease in pore diameter [5]. However, at the low temperatures, i.e. lower than quadruple points of each pore size, where the equilibrium involves ice, the pressures are same for the bulk hydrate [25]. The reason of accordance of the low temperature porous media data is that, the equilibrium at low temperatures involves a flat interface removing any capillary effects [25], or due to presence of a hydrate cap covering the pore openings [8].

For the entire data used in this study, to provide a reliable model of ANN, training of the neural networks is performed with 359 and 258 sets of data for methane and ethane hydrate, respectively. In order to validate the ANN model, the samples are divided into two groups. The first group containing 289 and 208 samples of methane and ethane hydrates, respectively, is employed to train the two networks, whereas the second group including the remaining other 70 and 50 samples are used to validate the model. The errors presented in Table 2 for methane and ethane hydrates are the average of the errors obtained from 5 runs of the models. In each run, the training and testing data were selected from the whole data randomly. To take better results from models, two styles of normalization tested. Once temperature and pressure are normalized and tested with 1/T and ln (P), respectively. Thereafter, they are compared with the result of relationships indicated in Eqs. (4) and (5). Despite these styles did not have significant variation, the latter normalization style has better results.

\[
T_{\text{Normal}} = \frac{T_{\text{max}} - T_{\text{exp}}}{T_{\text{max}} - T_{\text{min}}} T (^\circ \text{K})
\]

\[
P_{\text{Normal}} = \frac{(\ln (P)_{\text{max}} - \ln (P)_{\text{exp}})}{(\ln (P)_{\text{max}} - \ln (P)_{\text{min}})} P (\text{atm})
\]

As discussed above, we considered the methane and ethane hydrate equilibrium conditions in H-Lw-V and H-I-V phase combinations together with high pressure equilibrium of ethane hydrate (H-Lw-LwH equilibrium). Figure 2 illustrates the results obtained from predictions of ANN model compared with experimental data for methane hydrate equilibrium in porous media by various pore diameters. Figure 2(a) shows a comparison between predictions of ANN model for 4, 6, 10 and 15 nm pore diameters and experimental data. The results presented in this plot show that the P-T condition for H-I-V equilibrium of methane hydrate in narrow pores is the same that in bulk system. Figure 2(b) show the methane hydrate equilibrium dissociation temperature predicted by ANN model within a wide range of pressures. It is clear that the predictions of this model agree well with the experimental data for methane hydrate.

Figure 3(a) contains a plot of this model and experimental data presented in Table 1 for the ethane hydrate. Note that the data for each pore size separate into two distinct portions. The portions which take place on top of the bulk H-I-V equilibrium line (under quadruple points of each pore size) involve ice. The data which take place above the bulk H-Lw-V equilibrium line (upper quadruple points of each pore size) correspond to equilibrium involving water. Figure 3(b) shows a similar plot for
experimental data reported by Aladko et al. [27] for ethane hydrate at pressure up to 1GPa and prediction of the proposed model. The percent average absolute deviations (%AAD) between experimental and calculated values obtained from these models are listed in Table 2. There exists satisfactory agreement between the predictions of the ANN models and experimental data for both methane and ethane hydrates.

Figure 2 (a). Hydrate phase boundary of methane (H-LW-V and HI-V equilibriums) in the porous media with 4, 6, 10, 15 nm pore diameters as compared to bulk in low temperatures.

Figure 2. (b) Hydrate phase boundary of methane in the porous media with 10.5, 18.8, 29.6 nm pore diameters as compared to bulk in high temperatures.

Figure 3 (a). Hydrate phase boundary of ethane (H-LW-V and HI-V equilibriums) in the porous media with 6, 10 and 15 nm pore diameters as compared to bulk in low temperatures.

Figure 3 (b). Hydrate phase boundary of ethane (H-LW-LHC ethane equilibrium) in the porous media with 10.5 and 29.6 nm pore diameters.

Figure 4(a) and 4(b) show the calculated hydrate dissociation temperatures from the ANN models towards the hydrate dissociation temperatures used in developing these models, which used for methane and ethane hydrate, respectively. As observed, very little scatter are obtained around the 45° line. These indicate a good agreement between the measured and calculated results.

Figure 4 (a). Calculated methane hydrate equilibrium temperature from ANN model versus data of learning sets reported in Table 1.

Figure 7 (b). Calculated ethane hydrate equilibrium temperature from ANN model versus data of learning sets reported in Table 1.
5. CONCLUSION

In this work, two feed-forward ANN method were developed for estimating methane and ethane hydrate equilibrium temperatures as function of pressure and pore diameter of porous media as well as the bulk. The percent absolute deviations obtained from these models (0.19% for methane and 0.16% for ethane) show that the difference between models predictions and validation data was very small confirming the ability of ANN tool to accurately predict the hydrate equilibrium temperatures in porous media.

6. REFERENCES


