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A Mathematical Model Based on Artificial Neural Network Technique for Estimating Liquid Water–Hydrate Equilibrium of Water–Hydrocarbon System

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A mathematical model based on feed-forward artificial neural network technique, which uses a modified Levenberg–Marquardt optimization algorithm, has been developed to estimate the solubility of a pure hydrocarbon hydrate former in pure water being in equilibrium with gas hydrates. More recent and reliable data for three hydrocarbon hydrate formers (methane, ethane, and propane) have been used to train and develop this model. Independent experimental data (not employed in training and testing) have been used to examine the reliability of this technique. The acceptable agreement between the predicted and experimental data demonstrates the capability of the neural network model for estimating the solubility of pure hydrocarbon hydrate formers in pure water being in equilibrium with gas hydrates.

1. Introduction

Gas hydrates are a group of icelike crystalline compounds that are formed through a combination of water and suitably sized guest molecules; however, unlike ice, they may form at temperatures well above the ice point.¹ Knowledge of the liquid water–hydrate (L_W –H) equilibrium is required in the design of gas transportation and storage processes and should be destined for proposed CO₂ sequestration schemes.^{1–4} These factors, and the potential widespread abundance of gas hydrates in the cold subsea, sea floor, and permafrost environments,^{1–4} warrant an understanding of the L_W –H equilibrium. The temperature and pressure dependencies of the pure hydrate former solubility in pure water being in the liquid water–vapor (L_W –V) equilibrium region are different from the corresponding dependencies in the L_W –H equilibrium region.² The L_W –V equilibrium is a strong function of temperature and pressure, whereas the L_W –H equilibrium is a strong function of temperature but a very weak function of pressure.^{1,2,4–17} On the other hand, the pure hydrate former solubility in pure water being in the L_W –V equilibrium region normally increases as the temperature decreases at a given pressure, whereas the corresponding solubility in pure water being in the L_W –H equilibrium region decreases as the temperature decreases at the same pressure.^{1,2,4–17} Literature surveys reveal the availability of few experimental and thermodynamic modeling studies for the L_W –H equilibrium.^{5–13}

The objective of this work is to show the capability of the artificial neural network (ANN) technique for modeling the solubility of pure hydrocarbon hydrate formers in pure water being in equilibrium with gas hydrates. To our knowledge, this method has not previously been reported for estimating the solubility of hydrate formers in pure water being in equilibrium with gas hydrates. Among various ANNs reported in the literature, the feed-forward (back-propagation) neural network (FNN) method with a modified Levenberg–Marquardt optimization algorithm^{18,19} is used, which is known to be effective with regard to representing the nonlinear relationships between variables in complex systems and can be regarded as a large regression method between input and output variables.²⁰ To develop this model, reliable and recently reported data in the literature are used. The developed method is then used to predict independent experimental data (not used in developing this model). It is shown that the results are in acceptable agreement demonstrating the capability of the ANN method to

estimate the solubility of pure hydrocarbon hydrate formers in pure water being in equilibrium with gas hydrates.

2. Artificial Neural Network Model

Artificial neural networks have large numbers of computational units called neurons, that are connected in a massively parallel structure and do not require an explicit formulation of the mathematical or physical relationships of the handled problem.^{21–27} The most commonly used ANNs are the feed-forward neural networks,^{26,27} which are designed with one input layer, one output layer, and hidden layers.^{23–25,27} The number of neurons in the input and output layers is equal to the number of input and output physical quantities, respectively.²⁷ The disadvantage of FNNs is the determination of the ideal number of neurons in the hidden layer(s); few neurons produce a network with low precision and a higher number leads to overfitting and bad quality of interpolation and extrapolation.²⁷ The use of techniques such as Bayesian regularization, along with a Levenberg–Marquardt algorithm,^{18,19} can help overcome this problem.^{21,22,27}

In the FNN method the input layer of the network receives all the input data and introduces scaled data to the network.²⁷ The data from the input neurons are propagated through the network via weighted interconnections.²⁷ Every neuron i in layer k is connected to every neuron in adjacent layers.²⁷ Neuron i within the hidden k layer performs the following tasks: summation of the arriving weighted inputs (input vector $I_i = [I_{i,1}, \dots, I_{i,N_k-1}]$) and propagations of the resulting summation through a nonlinear activation function, f , to the adjacent neurons of the next hidden layer or to the output neuron(s). Three types of transfer functions are normally used: the exponential sigmoid, the tangent sigmoid, and linear functions.²⁷ In this work, the activation function is a linear function:

$$f(\bar{x}) = \bar{x} \quad (1)$$

where \bar{x} represents a parameter of the linear activation function. A bias term, b , is associated with each interconnection, to introduce a supplementary degree of freedom. The expression of the weighted sum, S , to the i th neuron in the k th layer ($k \geq 2$) is²⁷

$$S_{k,i} = \sum_{j=1}^{N_{k-1}} [(w_{k-1,j,i} I_{k-1,j}) + b_{k,i}] \quad (2)$$

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Table 1. Experimental and Predicted/Calculated Solubility of Methane in Pure Water Being in Equilibrium with Gas Hydrates (Liquid Water–Hydrate Equilibrium), Using Data Taken from (a) Yang,⁵ (b) Servio and Englezos,⁹ and (c) Kim et al.¹¹

temperature, <i>T</i> (K)	pressure, <i>P</i> (MPa)	experimental methane solubility (mole fraction, $\times 10^3$)	Predicted/Calculated Methane Solubility Using the ANN Model		Predicted Methane Solubility Using Thermodynamic Model ^a	
			mole fraction ($\times 10^3$)	AD%	mole fraction ($\times 10^3$)	AD%
(a) Experimental Data from Yang ⁵						
276.19	50.00	1.25 ^b	1.29	3.2	1.40	12.0
277.85	50.81	1.50	1.44	4.0	1.55	3.3
279.85	50.98	1.65 ^c	1.65	0.0	1.74	5.5
280.47	51.26	1.75	1.72	1.7	1.81	3.4
276.36	101.00	1.25	1.30	4.0	1.42	13.6
278.71	101.73	1.50	1.53	2.0	1.63	8.7
280.11	101.88	1.65	1.68	1.8	1.77	7.3
280.65	102.43	1.75	1.74	0.6	1.83	4.6
276.67	127.10	1.25	1.33	6.4	1.44	15.2
278.90	127.22	1.50	1.55	3.3	1.65	10.0
280.39	127.35	1.65	1.71	3.6	1.80	9.1
281.08	127.45	1.75 ^b	1.79	2.3	1.87	6.9
276.91	143.10	1.25	1.35	8.0	1.47	17.6
279.20	143.62	1.50	1.58	5.3	1.68	12.0
280.59	143.25	1.65	1.73	4.8	1.82	10.3
281.65	143.24	1.75	1.86	6.3	1.94	10.9
(b) Experimental Data from Servio and Englezos ⁹						
274.35	3.5	1.170	1.14	2.6	1.26	7.7
275.45	3.5	1.203 ^c	1.23	2.2	1.34	11.4
274.15	5.0	1.190	1.12	5.9	1.25	5.0
277.35	5.0	1.360	1.39	2.2	1.50	10.3
275.25	6.5	1.201	1.21	0.7	1.33	10.7
280.15	6.5	1.567 ^b	1.68	7.2	1.77	13.0
(c) Experimental Data from Kim et al. ¹¹						
276.2	5.0	1.33	1.29	3.0	1.40	5.3
277.9	5.1	1.59	1.45	8.8	1.55	2.5
279.9	5.1	1.75	1.66	5.1	1.75	0.0
280.5	5.1	1.86	1.72	7.5	1.81	2.7
276.4	10.1	1.33 ^c	1.31	1.5	1.41	6.0
278.7	10.2	1.59	1.53	3.8	1.42	10.7
280.1	10.2	1.75	1.68	4.0	1.77	1.1
280.7	10.2	1.86	1.75	5.9	1.84	1.1
276.7	12.7	1.33	1.33	0.0	1.45	9.0
278.9	12.7	1.59 ^b	1.55	2.5	1.65	3.8
280.4	12.7	1.75	1.71	2.3	1.80	2.9
281.1	12.7	1.86	1.79	3.8	1.88	1.1
276.9	14.3	1.33	1.35	1.5	1.46	9.8
279.2	14.4	1.59	1.58	0.6	1.68	5.7
280.6	14.3	1.75	1.73	1.1	1.82	4.0
281.7	14.3	1.88 ^b	1.87	0.5	1.94	3.2

^a From Mohammadi and Richon.² ^b Data used for validation (the remaining data were used for training). ^c Data used for testing.

where w is the weight parameter between each neuron–neuron interconnection. Using this feed-forward network with a linear activation function, the output, O , of neuron i within hidden layer k is

$$O_{k,i} = S_{k,i} \quad (3)$$

To achieve a better stability, the following scaling rule is applied to solubility of pure hydrocarbon hydrate formers in pure water being in equilibrium with gas hydrates (x) before normalization:

$$x_{\text{Network}} = \log(x_{\text{exp}}) \quad (4)$$

where the subscript “exp” denotes experimental data.

To develop the ANN, the datasets are subdivided into three classes: training, testing, and validation.²⁷ After partitioning the datasets, the training set is used to adjust the parameters. All synaptic weights and biases are first initialized randomly. The network is then trained; its synaptic weights are adjusted by optimization algorithms, until it correctly emulates the input/output mapping, by minimizing the average root-mean-square

error.²⁷ The optimization method chosen in this work was the Levenberg–Marquart algorithm,^{18,19} as mentioned earlier. The testing set is used during the adjustment of the network’s synaptic weights to evaluate the algorithm’s performance on the data not used for adjustment and to stop the adjustment if the error on the testing set increases. Finally, the validation set measures the generalization ability of the model after the fitting process.²⁷

3. Results and Discussion

Among the L_w–H equilibrium data reported in the literature for the solubility of methane in pure water being in equilibrium with gas hydrates, those reported by Yang,⁵ Servio and Englezos,⁹ and Kim et al.¹¹ seem to be the most reliable. These data are reported in Table 1. As can be seen, the temperature range is 274.15–281.7 K, and the pressures are up to 143.62 MPa. Other experimental data reported in the literature^{7,10,12} for methane solubility in pure water being in equilibrium with gas hydrates have not been considered in this work, because they are not consistent with other literature data.^{1,9,11} Limited

Table 2. Experimental and Predicted Solubility of Ethane in Pure Water Being in Equilibrium with Gas Hydrates (Liquid Water–Hydrate Equilibrium), Using Data Taken from (a) Yang⁵ and (b) Kim et al.¹¹

temperature, <i>T</i> (K)	pressure, <i>P</i> (MPa)	experimental ethane solubility (mole fraction, $\times 10^4$) ^b	Predicted Ethane Solubility Using the ANN Model		Predicted Ethane Solubility Using Thermodynamic Model ^a	
			mole fraction ($\times 10^4$)	AD%	mole fraction ($\times 10^4$)	AD%
(a) Experimental Data from Yang ⁵						
277.31	51	4.12	5.00	21.4	4.91	19.2
277.82	101	4.12	5.17	25.5	5.13	24.5
278.46	151	4.12	5.40	31.1	5.42	31.6
(b) Experimental Data from Kim et al. ¹¹						
277.3	10.1	4.37	5.00	14.4	4.90	12.1
277.8	15.1	4.37	5.17	18.3	5.12	17.2
278.5	20.1	4.37	5.42	24.0	5.43	24.3

^a From Mohammadi and Richon.² ^b Experimental solubility data are not temperature-dependent and cannot be considered reliable. Therefore, the pseudo-experimental data generated from the thermodynamic model² were used for training.

Table 3. Experimental (Data from Gaudette and Servio¹³) and Predicted/Calculated Solubility of Propane in Pure Water Being in Equilibrium with Gas Hydrates (Liquid Water–Hydrate Equilibrium)

temperature, <i>T</i> (K)	pressure, <i>P</i> (MPa)	experimental ^b propane solubility (mole fraction, $\times 10^4$)	Predicted/Calculated Propane Solubility Using the ANN Model		Predicted Propane Solubility Using Thermodynamic Model ^a	
			mole fraction ($\times 10^4$)	AD%	mole fraction ($\times 10^4$)	AD%
274.16	0.301	1.440 ^c	1.45	0.7	1.34	6.9
274.23	0.253	1.439	1.46	1.5	1.32	8.3
274.33	0.358	1.546	1.47	4.9	1.54	0.4
275.20	0.302	1.572	1.56	0.8	1.54	2.0
275.20	0.352	1.572	1.56	0.8	1.79	13.9
276.16	0.355	1.642 ^d	1.66	1.1	1.37	16.6

^a From Mohammadi and Richon.² ^b The vapor pressure of the empty hydrate lattice in the thermodynamic model² for propane hydrate was slightly tuned. ^c From Gaudette and Servio.¹³ ^d Data used for testing. ^e Data used for validation (the remaining data were used for training).

information is available for the L_W–H equilibrium of ethane + water system. Yang⁵ and Kim et al.¹¹ measured ethane solubility in pure water being in equilibrium with gas hydrates. These experimental data are reported in Table 2. As can be observed, the temperature range is 277.3–278.5 K, and the pressures are up to 151 MPa. This table also shows that the temperature change has no effect on experimental gas solubility data^{5,11} indicating that the experimental data reported by Yang⁵ and Kim et al.¹¹ for ethane solubility in pure water being in equilibrium with gas hydrates are not reliable. Limited information is also available for propane solubility in pure water being in equilibrium with gas hydrates. Gaudette and Servio¹³ measured these data, which are reported in Table 3. As can be seen, the temperature range is 274.16–276.16 K, and the pressures are up to 0.358 MPa.

The ANN model shown in Figure 1 and detailed in Table 4, with one hidden layer, was used to calculate/predict the logarithm of solubility of pure hydrocarbon hydrate formers in pure water being in equilibrium with gas hydrates, as a function of temperature and carbon number of the hydrocarbon hydrate former (which represents the type of hydrocarbon), because the logarithm of solubility is an approximately linear function of temperature for a given pure hydrocarbon hydrate former. Note that plenty of data should generally be used to develop ANN models, especially for highly nonlinear systems. In our case, where the logarithm of solubility of a pure hydrocarbon hydrate former in pure water being in equilibrium with gas hydrates is an approximately linear function of temperature, few sets of data for training (see the data reported in Tables 1 and 3) can be used to develop the ANN model. However, the greater the amount of data available for training, the more reliable the ANN model results. Having this in mind, one neuron in the hidden layer yielded acceptable results, according to both the accuracy

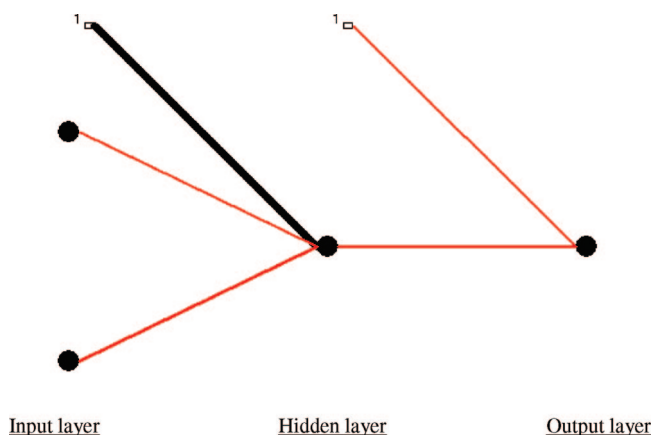


Figure 1. Architecture of the neural network model for predicting/calculating the logarithm of the solubility of pure hydrocarbon hydrate formers in pure water being in equilibrium with gas hydrates, as a function of temperature and carbon number of pure hydrocarbon hydrate former. Label “1” denotes bias, and solid circles represent neurons (the output neuron gives the logarithm of solubility of a pure hydrocarbon hydrate former in pure water being in equilibrium with gas hydrates; the input neurons give the temperature and carbon number of the hydrocarbon hydrate former).

of the fit (minimum value of the objective function) and the predictive power of the neural network.

Tables 1–3 show the predicted/calculated solubility values using the ANN model developed in this work, along with the absolute deviation (AD) values. As can be seen in Table 1, the results obtained using the ANN model for methane solubility in pure water being in equilibrium with gas hydrates show an absolute deviation of AD < 9%, and the average absolute deviation (AAD) among all the experimental and predicted data is 3.4%. The maximum AD and AAD values between the experimental data and predicted data using the ANN model for

Table 4. Number of Neurons, Hidden Layers, Parameters, Data, and Type of Activation Function Used in This Model

parameter	value
number of neurons	
layer 1	2
layer 2	1
layer 3	1
number of hidden layers	1
number of parameters	5
number of data used for training (and testing)	44
type of activation function	linear
input neurons	temperature and carbon number of hydrocarbon hydrate former (representing the type of hydrocarbon)
output neuron	logarithm of solubility of hydrocarbon hydrate former being in equilibrium with gas hydrates

ethane solubility in pure water being in equilibrium with gas hydrates are 31% and 22%, respectively, as mentioned in Table 2. The deviations are attributed to the experimental data,^{5,11} which are not temperature-dependent and cannot be considered to be reliable data. Because of the unreliability of the experimental data,^{5,11} for the ethane + water system, the pseudo-experimental data generated from a previously reported thermodynamic model² were used to train the ANN model. Table 3 shows that, using the ANN model, the maximum AD value between the experimental and predicted data for propane solubility in pure water being in equilibrium with gas hydrates is <5% and the AAD value is equal to 1.6%.

Tables 1–3 also show the predicted/calculated solubility values using the thermodynamic model,² along with the absolute deviations. Generally, the AD values obtained using the thermodynamic model² are greater than the AD values obtained using the ANN model. This was expected, because none of the parameters of this thermodynamic model² were adjusted. A detailed description of this thermodynamic model is given elsewhere.² Briefly, it is based on the equality of fugacity concept, which uses the solid solution theory of van der Waals–Platteeuw²⁸ to calculate the fugacity of water in the hydrate phase, whereas the activity coefficient and Henry's law approaches are used to calculate the fugacities in the liquid water phase.² In this thermodynamic model,² the parameters were set to those reported in the literature and none of them were adjusted, as mentioned previously. The capability of this thermodynamic model² to predict the solubility of a pure hydrocarbon hydrate former in pure water being in equilibrium with gas hydrates was successfully examined using some selected experimental data from the literature for the methane + water and ethane + water systems.² It was urged that, in addition to the quality of the experimental data reported in the literature, the deviations of this thermodynamic model² could be attributed to the model parameters, such as the vapor pressures of the empty hydrate lattice, the Langmuir constants, and Henry's law values, which may not be very accurate for pure heavy hydrocarbon hydrate formers.² In Tables 1–3, some of the experimental data were not accessible at the time that this thermodynamic model² was developed. As can be observed, the predictions of this thermodynamic model² for the solubility of methane in pure water being in equilibrium with gas hydrates exhibit an AD value of <18% and the AAD value among all the experimental and predicted data is 7.3%. The maximum AD value between the experimental and predicted data for the ethane + water system is <32% and the AAD value is <22%. The deviations are attributed to experimental data,^{5,11} which are not

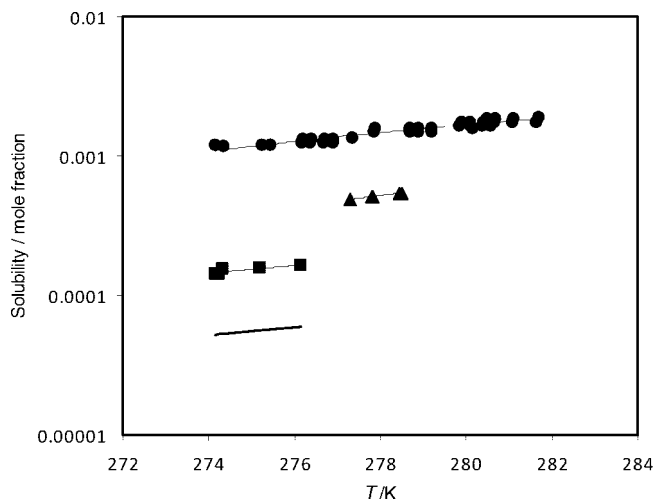


Figure 2. Estimated solubility of pure hydrocarbon hydrate formers in pure water being in equilibrium with gas hydrates. Symbols represent experimental data reported in Tables 1–3, whereas lines represent estimated values using the ANN model (from top to bottom: methane, ethane, propane, and isobutane (the latter in this group is the heaviest simple hydrocarbon hydrate former)).

temperature-dependent and cannot be considered reliable, as mentioned previously. For the propane + water system, AAD = 8% and the maximum AD value between the experimental and predicted data is <17%. For this system, the vapor pressure of the empty hydrate lattice in the thermodynamic model² was slightly tuned, because it can be regarded as one of the deviation sources in the thermodynamic model.² This parameter is consistent with initial data on the liquid water/ice–vapor–hydrate equilibrium, and, because the experimental conditions go far below the initial hydrate formation region, the assumptions that are evidently valid at the initial hydrate formation conditions may be invalid elsewhere, as mentioned by Sloan and Koh.¹

Using the ANN model, the solubility of isobutane (which is the the heaviest pure hydrocarbon hydrate former) in pure water being in equilibrium with gas hydrates, for which there are no experimental data in the literature, was predicted. These data, along with the predictions of the ANN model for methane, ethane, and propane are shown in Figure 2. As can be observed, the ANN model predicts the true behavior of solubilities of the pure hydrocarbon hydrate formers in pure water being in equilibrium with gas hydrates (the solubility decreases by increasing the carbon number of the pure hydrocarbon hydrate former and increases by increasing the temperature), demonstrating the capability of the ANN technique to model the L_w–H equilibrium of water + hydrocarbon systems.

4. Conclusions

A feed-forward artificial neural network model with one hidden layer, which uses a modified Levenberg–Marquardt optimization algorithm,^{18,19} was developed to estimate the solubility of pure hydrocarbon hydrate formers in pure water being in equilibrium with gas hydrates. This model has one output neuron (the logarithm of the solubility of a pure hydrocarbon hydrate former in pure water being in equilibrium with gas hydrates), two input neurons (temperature and the carbon number of the hydrocarbon hydrate former, the latter of which represents the type of hydrocarbon), and one neuron in the hidden layer, taking advantage of a linear activation function. The model was trained and developed using more recent and reliable data that have been reported in the literature, and its predictions were successfully compared with some independent

experimental data (not used to develop the artificial neural network model) and the results of a previously reported thermodynamic model² for three hydrate formers: methane, ethane, and propane. The study showed a need to generate reliable experimental data for the liquid water–hydrate equilibrium, especially for the systems that contain heavy hydrocarbon hydrate formers.

Nomenclature

Parameters

I = input vector
 N = number of feed inputs
 M = number of experimental data
 O = output
 P = pressure
 S = weighted sum
 T = temperature
 b = bias
 f = activation function
 w = weight parameter between each neuron–neuron interconnection
 \bar{x} = parameter of activation function
 x = mole fraction in the liquid phase

Abbreviations

AAD = average absolute deviation, which is defined as

$$\text{AAD} = \frac{1}{M} \sum_i^M \left| \frac{\text{experimental value} - \text{predicted/calculated value}}{\text{experimental value}} \right|$$

AD = absolute deviation, which is defined as

$$\text{AD} = \left| \frac{\text{experimental value} - \text{predicted/calculated value}}{\text{experimental value}} \right|$$

ANN = artificial neural network

FNN = feed-forward (back propagation) neural network

H = hydrate

L = liquid

V = vapor

Subscript

W = water

exp = experimental data

i = index

j = index

k = layer

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