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Solubility Modeling of Diamines in Supercritical Carbon Dioxide Using Artificial Neural Network

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Abstract: In this paper, ANN and semi-empirical equations has been applied for estimation of solubility in supercritical CO_2 for two diamines (1, 5-naphthalenediamine, and 4, 4'- diamino diphenylmethane). Since solubility in supercritical fluids strongly depends on three variables including temperature, pressure and density of supercritical fluid, these three inputs devoted to the network and semi- empirical equations. In this paper a comparative study between ANN and semi-empirical equation has been done. Results showed accuracy of ANNs is more than other method. ARD for ANNs is 1.5% but semi-empirical equations have ARD about 5% and higher. Accuracy of Jouyban *et al* equations is more than other studied semi-empirical equations.

Key word: Diamines; Solubility; Supercritical carbon dioxide; Semi-empirical equation; artificial neural network (ANN).

INTRODUCTION

In last decade there has been an increasing interest in the use of supercritical fluids as an alternative to the use of organic solvents in many industrial applications, such as in chemical and biochemical reactions, extraction and purification processes, particle production or, more recently in materials and polymer processing. Supercritical fluid technology is becoming increasingly popular in the chemical and pharmaceutical areas (Jafari Nejad, 2010).

In addition to applications in food, petroleum and chemical industries, there are a number of applications in the pharmaceutical industry including, particle size reduction of drugs, preparation of drug-loaded microspheres and micro emulsions (Sara Colussi, 2006). Property estimation procedures are very important in the physicochemical field for development of mathematical models, since design, optimization and advanced control of processes depend on model parameter values obtained from experimental data .The relationship between the physical and thermodynamic properties is highly nonlinear, and consequently an ANN can be a suitable alternative to model the underlying thermodynamic properties (Juan A. Lazzus, 2009).

The empirical models are based on simple error minimization using least squares method and, for most of them; there is no need to use physicochemical properties. Mathematical modeling of solubility data in supercritical fluids could also provide better understanding of the dissolution phenomenon and can be used for solubility prediction at interested pressures and temperatures after measuring a minimum number of experimental data, which could speed up the development of a supercritical fluid process (Jafari Nejad, 2010).

In the method developed in this paper, solubility data of 1, 5–naphtalenediamine (l, 5-NDA) and4, 4'-diamino diphenylmethane (DADPM) at several temperature, pressure and CO_2 density were used to train a neural network and calculation the coefficients of semi-empirical equation.

2. Theory:

2.1. Artificial Neural Network:

The driving force behind the development of the ANN models is the biological neural network, a complex structure, which is the information processing system for a living being. Thus ANN mimics a human brain for solving complex problems, which may be otherwise difficult to solve using available mathematical techniques.

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The advantage of using an ANN model is that it does not require any other data except the input and output data. Once the model has been adequately trained, the input data is sufficient to estimate the output. The other advantage is a single model can be used to get multiple outputs (Kamyar Movagharnejad, 2007).

Numerous types of the artificial neural networks exist such as multi layer perceptron (MLP), radial basis function (RBF) networks and recurrent neural networks (RNN), but each type consists of the same basic features: nodes, layers and connections. The smallest element of a network is the node. Every node receives signal from connection, or link. The signal is then summed together before being applied to transfer function to produce the output. The output signals are then propagated to other nodes until it reaches the output of the network. They have also the ability to accept new sets of experiments and the model can be retrained to extend the range of input parameters (Mèndez-Santiago, 2000).

However, there are a few such as multilayer perceptron and radial basis function that are more popular and find wide applications. A brief description of multilayer perceptron neural network that belongs to the feed forward neural network architecture has been described.

Among different neural network architectures, a multilayer feed forward neural network (MFN) with a single hidden layer has been mathematically proven to be a universal function approximator that is capable of mapping any complicated nonlinear function to an arbitrary degree of accuracy (Cybenco, 1989; Hornik, 1990). This class of networks consists of multiple neuron layers (input, hidden, and output layers) and information moves in only one direction, forward from the input layer, through the hidden layer and to the output layer

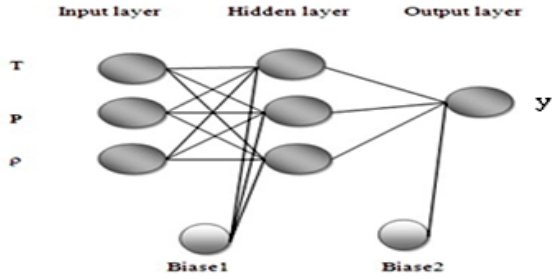

Fig. 1: General topology of an ANN that is used in present work.

Table 1: Data source and range used for development of the ANN & semi-empirical equations.

System	Temperature (K)	Preasure (Bar)	Density of CO_2 (Kg^{-3})	$Y_2 \times 10^5$	No.of Data Point	Reference
DADPM	313.15	110-200	684.38-840.66	3.98-12.78	9	[13]
	323.15	110-200	504.42-784.96	2.05-14.65	9	[13]
	333.15	110-200	357.88-724.09	0.94-16.07	9	[13]
1,5NDA	313.15	110-200	684.38-840.66	0.51-1.30	9	[13]
	323.15	110-200	504.42-784.96	0.26-1.43	9	[13]
	333.15	110-200	357.88-724.09	0.19-1.62	9	[13]

An artificial neural network has to be trained before using it. The learning algorithm is a procedure for modifying the weighting factors and bias weights, and is applied in order to train the network to perform some particular task. During the training, the network is presented with input and output data and it learns to reproduce these output data through an iterative algorithm. Among the available algorithms to train a neural network, the back propagation algorithm is most commonly employed. At the beginning of the training process, initial weights are assigned to the connections randomly. Inputs that are entered into the input layer are propagated forward through the hidden layer of neurons until they reach the output layer. The output thus generated is compared with the actual output. The error is calculated between the predicted and the actual output values and reduced by changing the weights. This process is repeated until some predefined stopping criteria are satisfied. When the training is complete, the network can be used for prediction.

Before using the appropriate propagation method to calculate optimum parameters of ANN, it is necessary to scale outputs and inputs between 0.1 and 0.9 Eq.)1(is used as a linear function for scaling.

$$\text{(Scaled) value} = \text{(Actual) value} \times m + c \quad (1)$$

Adjustable parameters of this equation *(*m and *c)* are tabulated in table 2, produced by two data points: (lowest actual value, 0.1) and (highest actual value, 0.9).

Table 2: Coefficients of Eq (1).

Actual value	Range	m	c
Temperature (K)	313.15-333.15	0.04	-15.55
Pressure (bar)	110-200	0.0088	-1.122
(Kg.m^3)Density	357.88-840.66	0.0016	-0.491
DADPM	0.94-16.07	5287	0.05029
1,5-NDA	0.19-1.62	55946	-0.0062

ANN method can be employed by using appropriate software such as MATLAB. In this work, the MATLAB 7.7.0 m. file editor is used for programming.

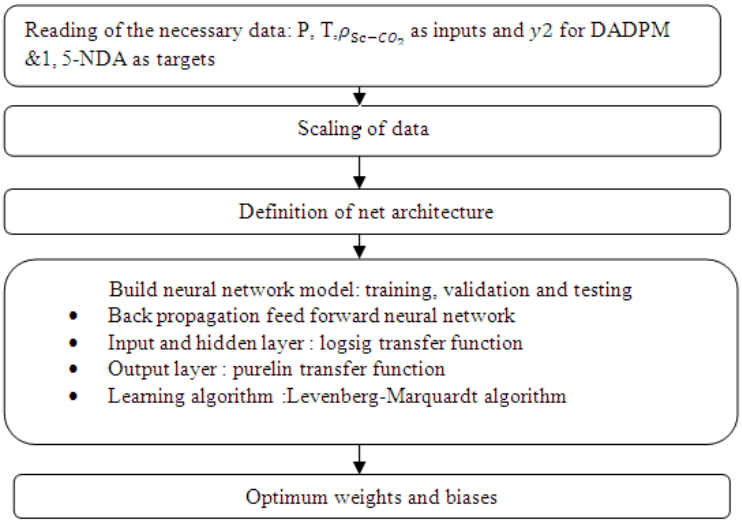

Fig. 2: Flow diagram for the ANN program developed for this work.

ARD and R^2 of1,5- ANN for NDA and DADPM is calculated and showed in table3.

Table 3: Values of ARD and R^2 for 1,5-NDA and DADPM obtained by ANN method.

System	ARD	R^2
1,5-NDA	.0.015	0.996
DADPM	0.013	0.999

2.2. Semi-empirical Equation:

In order to predict solubility of solute in supercritical fluid, several semi empirical equations suggested. In present work four semi-empirical equations is described. Mèndez-Santiago and Teja proposed a density based equation. This model comes from the linear relationship between T ln (y_2P) and ρ which was from the theory of dilute solution.

$$T \ln (y_2P) = A' + B'\rho + C'T$$

Where *A*', *B*' and *C'* are constants, considered as temperature independent, and obtained by a multiple linear regression of solubility experimental data (Mèndez-Santiago, 2000).
Gordillo *et al.* (1999) proposed another empirical model. The model is:

$$\text{Ln } y_2 = D_0 + D_1P + D_2P^2 + D_3PT + D_4T + D_5T^2$$

6 constants exist in this equation (Gordillo, 1999).

Jouyban *et al.* proposed an empirical model. The model is:

$$\text{Ln } y_2 = M_0 + M_1P + M_2P^2 + M_3PT + M_4T/P + M_5 \ln \rho$$

Where M_0 -M_5 are the model constants and ρ is the density of pure SC- CO_2 at different pressures and temperatures (Jouyban, 2000).
Jafarinejad *et al.* (2010) proposed another empirical model. The model is:

$$\text{Ln } y_2 = J_0 + J_1P_2 + J_2T_2 + J_3 \ln \rho$$

Where J_0 - J_3 are the model constants and obtained by least squares method from experimental solubility data, ρ ($kg^{-}m^{-3}$) is the density of pure SC- CO_2 at different pressures (bar) and Temperatures (K) and y_2 is the mole fraction (Jafari, 2010).

Regression can be done by several software. In present work, MATLAB 7.7.0 m. file editor is used for programming.
Coefficients of four semi-empirical equation for 1,5-NDA & DADPM is showed in table4.

Table 4: Semi-empirical equations for solubility modeling in supercritical CO_2.

Model no	Model equation	Name
1	$T \ln (y_2 P) = A' + B'\rho + C'T$	Mèndez-Santiago andTeja
2	$\ln y_2 = D_0 + D_1P + D_2P^2 + D_3PT + D_4T + D_5T^2$	Gordillo *et al*
3	$\ln y_2 = M_0 + M_1P + M_2P^2 + M_3PT + M_4T/P + M_5 \ln \rho$	Jouyban *et al*
4	$\ln y_2 = J_0 + J_1P_2 + J_2T_2 + J_3 \ln \rho$	Jafarinejad *et al*

Table 5: Coefficients of four semi-empirical equation for 1,5-NDA & DADPM.

Model no	Constant	1,5-NDA	DADPM
1	A'	-8130	-9056
	B'	2.4	2.7
	C'	13.6	18
2	D_0	13.1122	12.991
	D_1	-0.0479	-0.05
	D_2	-1.84E-04	-0.000224
	D_3	3.66E-04	0.000422
	D_4	-0.1344	-0.1178
	D_5	1.79E-04	7.61E-05
3	M_0	-14.438	-9.45
	M_1	-0.0603	-0.0825
	M_2	-6.14E-06	1.42E-05
	M_3	1.54E-04	1.79E-04
	M_4	-1.4535	-2.2149
	M_5	1.919	1.2776
4	J_0	-38.08	-42.124
	J_1	-7.31E-05	-9.01E-05
	J_2	6.59E-05	6.77E-06
	J_3	5.5467	6.8257

ARD and R^2 of semi-empirical equations for1,5- NDA and DADPM is calculated and showed in table6.

Table 6: ARD and R^2 of semi-empirical equations for1, 5- NDA and DADPM.

Model no	Statistical parameters	NDA	DADPM
1	R^2	0.9847	0.9848
	ARD	0.07	0.1
2	R^2	0.9845	0. 9873
	ARD	0.1	0.14
3	R^2	0.9938	0.9944
	ARD	0.05	0.08
4	R^2	0.9639	0.9688
	ARD	0.14	0.2

RESULT AND DISCUSSION

In this work a comparative study between regression and artificial neural network was done to estimate solubility of NDA&DADPM.

For each method, ARD and R^2 is calculated .This parameters showed accuracy of ANN is more than semi-empirical equations.
In following figures ARD and R^2 of each method is compared.

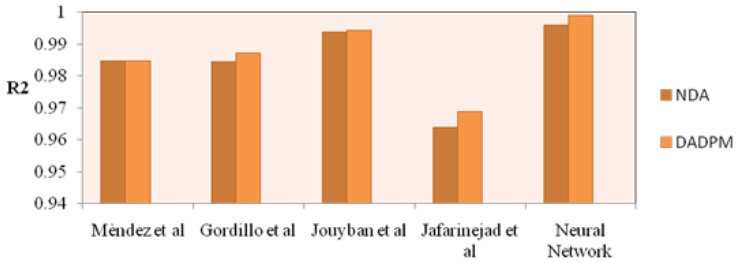

Fig. 3: Comparison between semi-empirical equations and ANN.

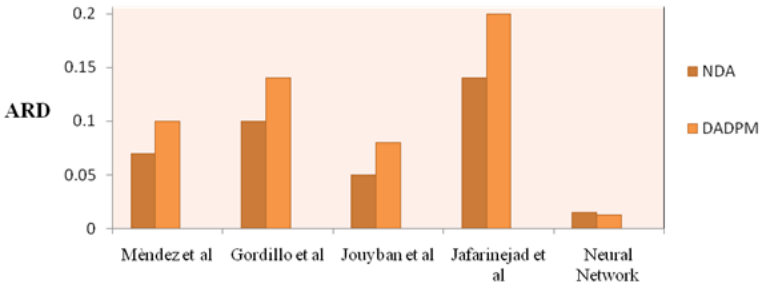

Fig. 4: Comparison between semi-empirical equations and ANN.

Conclusion:

In this work a comparative study between ANN and semi-empirical equation was performed for solubility prediction of 1,5-NDA & DADPM.

Based on result and discussion presented in this study the following conclusion is obtained:

- ANN method can predict solubility in supercritical fluid with more accuracy than semi-empirical equations.
- Semi empirical equations are user-friendly but neural network has special problem, for example: training,…
- Accuracy of Jouyban et al equations is more than other studied semi-empirical equations.

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