Estimating Onset of Precipitation of Dissolved Asphaltene in the Solution of Solvent + Precipitant Using Artificial Neural Network Technique

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Abstract: Asphaltene precipitation is traditionally modeled using polymer solution theories or cubic equations of state. We propose another approach based on artificial neural network technique to model onset of precipitation of dissolved asphaltene in the solution of solvent + precipitant. A mathematical model based on feed-forward artificial neural network technique, which takes advantage of a modified *Levenberg–Marquardt* optimization algorithm, has been used to model onset of precipitation of dissolved asphaltene in the solvent + precipitant solution. The experimental data reported in the literature have been used to develop this model. The acceptable agreement between the results of this model and experimental data demonstrates the capability of the neural network technique for estimating onset of precipitation of dissolved asphaltene in the solution of solvent + precipitant.

Keywords: Asphaltene, solvent, precipitant, artificial neural network, modeling, precipitation.

INTRODUCTION

One serious problem that can affect oil production, transportation and processing, is asphaltene precipitation. Asphaltenes are the toluene / benzene soluble fractions that precipitate from oil when an excess (25 to 40 times) of n-heptane / n-pentane is mixed with oil after waiting for at least four hours before filtering [1]. Asphaltene precipitation causes fouling in the reservoir, in the well, in the pipeline and in the production and processing facilities [1-35]. Asphaltene phase behavior has therefore been the subject of numerous theoretical studies [1-35]. The lack of suitable characterization parameters is one of the difficulties encountered in describing the phase behavior of asphaltene-containing systems, because asphaltenes are not well-identified components/ mixtures [1, 7]. They consist of several polar components of aromatic nature with high molecular weights [1, 7]. In the majority of cases, the complexity of the asphaltene fraction leads to the assumption that the asphaltenes can be regarded as one single pseudo-component (monodisperse) [1, 7].

The traditional models reported in the literature typically use polymer solution theories (e.g. Scatchard-Hildebrand [7], Flory-Huggins [7, 36], and Scott-Magat [37] polymer solution theories) to model phase behavior of asphaltene-containing fluids [1, 2, 5, 7, 8, 14, 20-23]. In addition to these models, there are also other models, which are based on cubic equations of state [17, 24]. New thermodynamic models have recently been developed, which can take into account the micellar / aggregation natures of asphaltenes [5, 13, 16, 26-31].

In order to examine the capabilities of the models reported in the literature to predict asphaltene phase behavior in dilute systems, Cimino *et al.* [2, 14] performed some tests (Table **1**) to find onset of precipitation of dissolved asphaltenes in various solutions with different ratios of solvent and precipitant and indicated that the precipitated asphaltene does dissolve in appropriate solvent and the ratio of "solvent mass per asphaltene mass" and "precipitant mass per asphaltene mass" is approximately linear and independent of the asphaltene concentration at onset of asphaltene precipitation [2, 14]. They showed that the capability of colloidal model [25] and traditional Flory-Huggins [36] based models [8, 20] to re-produce the observed behavior is poor, mainly because most of the models reported in the literature assume that the precipitated phase consists of asphaltene only and the presence of non-asphaltene components in the precipitated phase is normally ignored. Cimino *et al*. [2, 14] employed the Flory-Huggins polymer solution theory [36] and assumed that the precipitated phase contains not only asphaltene but also a fraction of non-asphaltene components. They showed that their proposed model [2, 14] can better predict the phase behavior of dissolved asphaltenes in the solutions of solvents and precipitants and none of the literature models is capable of predicting this behavior satisfactorily.

The objective of this work is to show the capability of Artificial Neural Network (*ANN*) technique, as an alternative model, to estimate onset of precipitation of dissolved asphaltene in the solvent + precipitant solutions. To our knowledge, this method has not previously been reported for phase behavior modeling of asphaltene containing systems. Among various *ANN*s models reported in the literature, the *feed-forward* (back propagation) neural network (*FNN*) model along with a modified Levenberg-Marquardt optimization algorithm [40, 41] is used, which is known to be effective to represent the nonlinear relationships between variables in complex systems and can be regarded as a large regression method between input and output variables [42-48]. To develop this model, the experimental data reported by Cimino *et al.* [2, 14] are used. It is shown that the data reported by Cimino *et al.* [2, 14] are well represented by the *ANN* model demonstrating the capability of this technique to estimate

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Table 1. Experimental Values for Mass Fractions of Components in the Synthetic Mixtures of Asphaltene + Solvent + Precipitant at Onset of Asphaltene Precipitation Measured at 298.15 K and 0.1 MPa [14]

Precipitant / Solvent	Mass fraction of component in synthetic mixture at onset of asphaltene precipitation			Precipitant / Solvent	Mass fraction of component in synthetic mixture at onset of asphaltene precipitation		
	Precipitant	Solvent	n-C_5 Asphaltene		Precipitant	Solvent	n-C_7 Asphaltene
n-C_5 / Toluene	0.367	0.621	0.012	n-C_5 / Toluene	0.293	0.694	0.013
	0.369	0.623	0.008		0.294	0.696	0.010
	0.370	0.624	0.006		0.297	0.696	0.007
	0.403	0.594	0.003		0.294	0.703	0.003
n-C_5 / Tetraline	0.477	0.513	0.010	n-C_5 / Tetraline	0.427	0.562	0.011
	0.480	0.513	0.007		0.430	0.562	0.008
	0.480	0.515	0.005		0.445	0.550	0.005
	0.480	0.518	0.002		0.444	0.554	0.002
n-C_7 / Toluene	0.420	0.569	0.011	n-C_7 / Toluene	0.352	0.636	0.012
	0.422	0.570	0.008		0.354	0.637	0.009
	0.423	0.571	0.006		0.355	0.639	0.006
	0.422	0.576	0.002		0.389	0.608	0.003
n-C_7 / Tetraline	0.521	0.470	0.009	n-C_7 / Tetraline	0.481	0.509	0.010
	0.527	0.466	0.007		0.494	0.499	0.007
	0.524	0.471	0.005		0.501	0.494	0.005
	0.524	0.474	0.002		0.525	0.473	0.002
n-C_{10} / Toluene	0.437	0.553	0.010	n-C_{10} / Toluene	0.366	0.622	0.012
	0.440	0.552	0.008		0.407	0.585	0.008
	0.440	0.555	0.005		0.407	0.588	0.005
	0.440	0.558	0.002		0.407	0.591	0.002
n-C_{10} / Tetraline	0.538	0.453	0.009	n-C_{10} / Tetraline	0.492	0.498	0.010
					0.496	0.497	0.007
					0.520	0.475	0.005
					0.542	0.456	0.002

onset of precipitation of dissolved asphaltene in the solutions of solvent + precipitant.

THERMODYNAMIC MODELS TO DETERMINE ONSET OF PRECIPITATION OF DISSOLVED ASPHALTENE IN THE SOLVENT + PRECIPITANT SOLUTION [35]

As mentioned earlier, Cimino *et al.* [2, 14] employed a more correct application of the Flory-Huggins polymer solution theory [36] to represent phase behavior of dissolved asphaltenes in the solvent + precipitant solutions. Different from the previous models based on Flory-Huggins polymer solution theory [36], which assume the precipitated phase forms pure asphaltene, it is assumed that on phase separation, not a pure asphaltene phase nucleates but a phase concentrated in asphaltenes containing also a fraction of solvent [2, 14]. Considering typical asphaltene volume fraction, Φ_a, in oil system (which is estimated in the range of 10^{-2} to 10^{-3} with asphaltene weight percent from 1 to 10 [2, 14]) the oil is assumed safely to be pure maltene (asphaltene free oil), that is $\Phi_a = 0$ [2, 14]. Such an assumption leads to the following final equation [2, 14, 35]:

$$\ln[1-\Phi_a']+\left(1-\frac{V_m}{V_a}\right)\Phi_a'+\chi\Phi_a'^2=0 \quad (1)$$

where the *prime* represents the asphaltene-rich phase and Φ_a' is the volume fraction of asphaltene in asphaltene-rich phase. V_m and V_a are molar volumes of maltene and asphaltene, respectively. χ stands for interaction parameter between asphaltene and maltene and is given by the following equation [2, 8, 14, 35]:

$$\chi = \frac{V_m[(\delta_m-\delta_a)^2]}{RT} \quad (2)$$

where δ_m and δ_a are solubility parameters (the square root of the internal energy of vaporization per molecular volume) for the maltene and the asphaltene, respectively [35]. R and T stand for universal gas constant and temperature respectively.

In the above equation [35, 37-39]

$$\Phi_a = \frac{x_a V_a}{x_a V_a + x_m V_m} \quad (3)$$

or

$$\Phi_a = \frac{w_a/\rho_a}{w_a/\rho_a + w_m/\rho_m} \quad (4)$$

where w_a and w_m are the weight fractions of asphaltene and maltene, respectively and ρ_a and ρ_m represent the mass densities of asphaltene and maltene, respectively. x_a and x_m stand for mole fractions of asphaltene and maltene, respectively.

A similar model based on the Scott-Magat polymer solution theory [37] can also be obtained [35]:

$$\ln[1-\Phi_a']+\Phi_a'+\chi\Phi_a'^2=0 \quad (5)$$

Equation (5) is similar to equation (1) (Considering the ratio $\frac{V_m}{V_a}$ in equation (1) is negligibly small compared to unity, and therefore it may be neglected) [35].

According to the model of Cimino *et al.* [2, 14], δ_a is assumed to be independent of pressure, and Φ_a' is assumed to be constant. The parameters Φ_a' and δ_a are regressed from

Table 2. Experimental Values [14] and the Values Obtained Using the *ANN* Model for (Mass of Precipitant/ Mass of Asphaltene) in Synthetic Mixtures of Asphaltene + Solvent + Precipitant at Onset of Asphaltene Precipitation at 298.15 K and 0.1 MPa

Type of asphaltene	Precipitant	Solvent	Experimental value for (mass of solvent / mass of asphaltene)	Mass of precipitant / mass of asphaltene		AD%*
				Experimental value	Value obtained using the *ANN* model	
n-C5-Asphaltene	n-C5	Toluene	52	31	28**	9.7
			78	46	47**	2.2
			104	62	65**	4.8
			198	134	133**	0.7
	n-C5	Tetraline	51	48	48	0.0
			73	69	68	1.4
			103	96	96	0.0
			259	240	240	0.0
	n-C7	Toluene	52	38	39	2.6
			71	53	53	0.0
			95	71	70	1.4
			288	211	211	0.0
	n-C7	Tetraline	52	58	58	0.0
			67	75	75	0.0
			94	105	105	0.0
			237	262	262	0.0
	n-C10	Toluene	55	44	44	0.0
			69	55	55	0.0
			111	88	88	0.0
			279	220	220	0.0
n-C7-Asphaltene	n-C5	Toluene	53	23	23	0.0
			70	29	30	3.4
			99	42	42	0.0
			234	98	98	0.0
	n-C5	Tetraline	51	39	39	0.0
			70	54	55	1.9
			110	89	87	2.2
			277	222	222	0.0
	n-C7	Toluene	53	29	27	6.9
			71	39	39	0.0
			107	59	63	6.8
			203	130	128	1.5
	n-C7	Tetraline	51	48	47	2.1
			71	71	70	1.4
			99	100	102	2.0
			237	263	262	0.4
	n-C10	Toluene	52	31	34	9.7
			73	51	49	3.9
			118	81	80	1.2
			296	204	204	0.0
	n-C10	Tetraline	50	49	47	4.1
			71	71	73	2.8
			95	104	104	0.0
			228	271	271	0.0

*: Absolute deviation ($AD = \left|\frac{experimental\ value - predicted / calculated\ value}{experimental\ value}\right|$)

**: Validates values. The remaining data in this table were used for training (and testing).

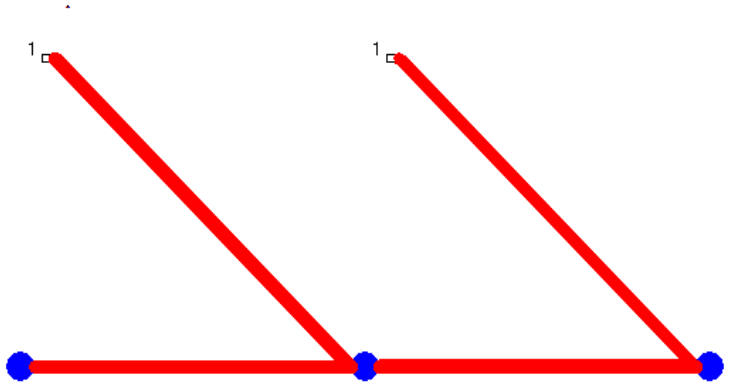

Fig. (1). Architecture of the neural network model used for estimating onset of precipitation of dissolved asphaltene in the solution of solvent + precipitant [1: Bias; ●: Neuron; Output neuron: (mass of precipitant / mass of asphaltene); Input neuron: (mass of solvent / mass of asphaltene).

experimental data on onset of asphaltene precipitation. V_a is calculated from density and molecular weight of asphaltene. For given δ_a, $\Phi_a^{'}$ and temperature, the model only varies with V_m and δ_m.

As can be observed, thermodynamic models require considerable efforts to find an appropriate relationship for fitting experimental data, which can be eliminated by using artificial neural network technique.

ARTIFICIAL NEURAL NETWORK MODEL

The most commonly used *ANN*s are the feed-forward neural networks [42-48], which are designed with one input layer, one output layer and hidden layers [44-46, 48]. The number of neurons in the input and output layers equals to the number of inputs and outputs physical quantities, respectively [48]. In a *FNN* model, the ideal number of neurons in the hidden layer(s) should be determined; few neurons produce a network with low precision and a higher number leads to overfitting and bad quality of interpolation and extrapolation [48]. The use of techniques such as Bayesian regularization, along with a *Levenberg–Marquardt* algorithm [40, 41], can help overcome this problem [42, 43, 48].

In the *FNN* model, the input layer of the network receives all the input data and introduces scaled data to the network [48]. The data from the input neurons are propagated through the network *via* weighted interconnections [48]. Every *i* neuron in a *k* layer is connected to every neuron in adjacent layers [48]. The *i* neuron within the hidden *k* layer performs the following tasks: summation of the arriving weighted inputs (input vector $I_i = [I_{i,1},\ldots I_{i,Nk-1}]$) and propagations of the resulting summation through an activation function, *f*, to the adjacent neurons of the next hidden layer or to the output neuron(s). In this work, the activation function is a linear function:

$$f(x) = x \quad \text{where} \quad x \in [0,1] \tag{6}$$

where *x* stands for parameter of linear activation function. A bias term, *b*, is associated with each interconnection in order to introduce a supplementary degree of freedom. The expression of the weighted sum, *S*, to the i^{th} neuron in the k^{th} layer ($k \geq 2$) is [48]:

$$S_{k,i} = \sum_{j=1}^{N_{k-1}} \left[(w_{k-1,j,i} I_{k-1,j}) + b_{k,i} \right] \tag{7}$$

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

$$O_{k,i} = S_{k,i} \tag{8}$$

To develop the *ANN*, the data sets are generally subdivided into 3 classes: training, testing and validation [48]. After partitioning the data sets, 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 algorithm, until it correctly emulates the input/output mapping, by minimizing the average root mean square error [48]. The optimization method chosen in this work was the *Levenberg - Marquart* algorithm [40, 41], as mentioned earlier. The testing set is used during the adjustment of the network's synaptic weights to evaluate the algorithms performance on

Table 3. Number of Neurons, Hidden Layers, Parameters, Data and Type of Activation Function Used in this Method

Layer	Number of neurons
1	1
2	1
3	1

- Number of hidden layers = 1.
- Number of parameters = 4.
- Number of data used for training (and testing) = 40.
- Type of activation function: linear.
- Input neurons: (mass of solvent/ mass of asphaltene).
- Output neuron: (mass of precipitant/ mass of asphaltene).

Table 4. Experimental Values [14] and the Values Obtained Using the *ANN* Model for Mass Fraction of Precipitant in Synthetic Mixtures of Asphaltene + Solvent + Precipitant at Onset of Asphaltene Precipitation at 298.15 K and 0.1 MPa

Type of asphaltene	Precipitant	Solvent	Mass fraction of asphaltene	Mass fraction of solvent	Mass fraction of precipitant		
					Experimental value	Value obtained using the *ANN model*	*AD%*
n-C5-Asphaltene	n-C5	Toluene	0.012	0.621	0.367	0.336*	8.4
			0.008	0.623	0.369	0.376*	1.9
			0.006	0.624	0.370	0.390*	5.4
			0.003	0.594	0.403	0.399*	1.0
	n-C5	Tetraline	0.010	0.513	0.477	0.480	0.6
			0.007	0.513	0.480	0.476	0.8
			0.005	0.515	0.480	0.480	0.0
			0.002	0.518	0.480	0.480	0.0
	n-C7	Toluene	0.011	0.569	0.420	0.429	2.1
			0.008	0.570	0.422	0.424	0.5
			0.006	0.571	0.423	0.420	0.7
			0.002	0.576	0.422	0.422	0.0
	n-C7	Tetraline	0.009	0.470	0.521	0.522	0.2
			0.007	0.466	0.527	0.525	0.4
			0.005	0.471	0.524	0.525	0.2
			0.002	0.474	0.524	0.524	0.0
	n-C10	Toluene	0.010	0.553	0.437	0.440	0.7
			0.008	0.552	0.440	0.440	0.0
			0.005	0.555	0.440	0.440	0.0
			0.002	0.558	0.440	0.440	0.0
n-C7-Asphaltene	n-C5	Toluene	0.013	0.694	0.293	0.299	2.0
			0.010	0.696	0.294	0.300	2.0
			0.007	0.696	0.297	0.294	1.0
			0.003	0.703	0.294	0.294	0.0
	n-C5	Tetraline	0.011	0.562	0.427	0.429	0.5
			0.008	0.562	0.430	0.440	2.3
			0.005	0.550	0.445	0.435	2.2
			0.002	0.554	0.444	0.444	0.0
	n-C7	Toluene	0.012	0.636	0.352	0.324	8.0
			0.009	0.637	0.354	0.351	0.8
			0.006	0.639	0.355	0.378	6.5
			0.003	0.608	0.389	0.384	1.3
	n-C7	Tetraline	0.010	0.509	0.481	0.470	2.3
			0.007	0.499	0.494	0.490	0.8
			0.005	0.494	0.501	0.510	1.8
			0.002	0.473	0.525	0.524	0.2
	n-C10	Toluene	0.012	0.622	0.366	0.408	11.5
			0.008	0.585	0.407	0.392	3.7
			0.005	0.588	0.407	0.400	1.7
			0.002	0.591	0.407	0.408	0.2
	n-C10	Tetraline	0.010	0.498	0.492	0.471	4.3
			0.007	0.497	0.496	0.514	3.6
			0.005	0.475	0.520	0.518	0.4
			0.002	0.456	0.542	0.542	0.0

*: Obtained using validation step.

the data not used for adjustment and stop the adjusting if the error on the testing set increases. Finally, the validation set measures the generalization ability of the model after the fitting process [48].

RESULTS AND DISCUSSION

The experimental data of Cimino *et al.* [14] are reported in Table **1**. Table **2** reports the values for (mass of solvent / mass of asphaltene) and (mass of precipitant / mass of asphaltene), which have been used to developed the *ANN* method. The model shown in Fig. (**1**) and detailed in Table **3** with one hidden layer was used to calculate (mass of precipitant/ mass of asphaltene) as a function of (mass of solvent/ mass of asphaltene). It should be mentioned that plenty of data should generally be used for developing *AAN* models, especially for highly non-linear systems. In our case, where the (mass of precipitant/ mass of asphaltene) is approximately linear function of (mass of solvent/ mass of asphaltene), few sets of data for training can be used to develop the *ANN* model. However, the more data for training, the more reliable *ANN* model results. Having this mind, one neuron in the hidden layer yielded acceptable results according to both the accuracy of the fit (minimum value of the objective function) and the predictive power of the neural network.

Tables **2** and **4** show the results obtained using the *ANN* model developed in this work along with the absolute deviations (*AD*). As can be seen in Table **4**, the results obtained using the *ANN* model for mass of precipitant in the solution of solvent + precipitant required to precipitate asphaltene are in acceptable agreement with the experimental data [14] reported in the literature. The results show less than 12% absolute deviation and the average absolute deviation (*AAD*) among all the experimental and estimated data is less than 2 %. The deviations may be attributed to unreliability of some experimental data [14], as it is known that measuring onset of asphaltene precipitation, especially in dilute systems is one of the most difficult problems of oil analyses [32]. It should finally be mentioned that in the *ANN* model developed in this work, three parameters of the four parameters approach zero indicating that this *ANN* model is approximately equivalent to a linear function.

CONCLUSIONS

A feed-forward artificial neural network model with one hidden layer that takes advantage of a modified *Levenberg–Marquardt* optimization algorithm [40, 41], was developed for estimating onset of precipitation of dissolved asphaltenes in the solutions of solvent + precipitant. This model has one output neuron (mass of precipitant/ mass of asphaltene), one input neurons (mass of solvent/ mass of asphaltene) and one neuron in the hidden layer and uses a linear activation function. It was shown the experimental data reported in the literature [14] are well represented using this *ANN* model.

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