Iranian Polymer Journal
17 (7), 2008, 483-491

Available online at: http://journal.ippi.ac.ir

Modelling the Solubility of 1,1,1,2-Tetrafluoroethane, 1-Chloro-1,1-difluoroethane, Butane and Iso-butane in LDPE with Artificial Neural Network

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Received 11 September 2006; accepted 7 July 2008

ABSTRACT

The solubility of free monomers in polymer has an effective role in the product quality and on environment in various steps of polymer manufacturing. Therefore, it is important to find confident method to predict the solubility of monomers in polymers. For predicting the solubility of gaseous monomers in polymers, among the various methods used, equations of state are considered as the most effective tools due to the simplicity in their applications. However, the accurate solubility prediction with equations of state needs suitable binary interaction parameters. Unfortunately, these parameters often have unknown temperature and solute composition functionality and therefore, other empirical correlations methods are used. The correlation methods, however, generally consist of equations having several parameters which are to be evaluated from experimental data for each system at a given temperature and this imposes limitation on their applications. Artificial neural network (ANN) can be a powerful alternative tool for predicting gaseous monomers in polymers. In this work, the solubility of 1,1,1,2-tetrafluoroethane (HFC-134a), 1-chloro-1,1-difluoroethane (HCFC-142b), butane and iso-butane in low-density polyethylene (LDPE) has been studied by ANN using back propagation method (BP). It was found that a 2-4-1 architecture can predict the gas solubility satisfactorily.

Key Words:

artificial neural network;
solubility;
back propagation;
prediction;
LDPE.

INTRODUCTION

Solubility of gases is important in many processes especially in molten polymer and in polymer foaming operations [1, 2]. Therefore, experimental and theoretical study of this phenomenon is an interesting subject for most chemical engineers [3,4]. Polymeric foams are widely used because of their special characteristics such as low thermal conductivity, light weight, high impact strength, etc [5, 6]. Gas solubility in polymers can affect these properties as well as their thermodynamic properties [7, 8]. In manufacture of polyvinyl chloride (PVC) the unreacted free mono-

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mers which are soluble in molten polymer are harmful to the environment [9] and also can affect the quality of polyethylene products and their characteristic properties [7]. The prediction of gas solubility in polymers is needed for design and operation purposes in various steps of polymerization processes [7-10].

Many different methods are used to model the solubility of gases in polymers which include molecular simulation methods [8, 11], empirical correlations and equations of state (EOS). Zhong and Masuoka [7] have modeled the solubility of gases in polymers with Peng-Robinson EOS. Peng et al. [9] have studied the gas solubility in polymers with a molecular thermodynamic model and an EOS. They also reviewed the most important investigations on gas solubility in polymers. Wang et al. [1] measured and modeled the solubility of CH_2FCF_3 (HFC-134a), CH_3CClF_2 (HCFC-142b), butane and iso-butane in low-density polyethylene (LDPE). They used the Sanchez-Lacombe (S-L EOS) for modelling the solubility and correlating the temperature variation of Henry's law constant. Solubility of CO_2 and N_2 in polypropylene, high-density polyethylene and polystyrene have been measured and modeled by Sato et al. [5]. In a similar work, Sato et al. [6] have studied the solubility of CO_2 in polyvinyl acetate and polystyrene.

Unfortunately, EOS involves some adjustable binary interaction parameters which are function of temperature and composition [9, 10] also, solubility calculations by an EOS need an iterative method that could be time consuming, tedious and may sometimes pose problems for real time control of an operating plant. Therefore, other calculation methods such as artificial neural network (ANN) which are faster could be more attractive [12, 13]. ANN is a fast and powerful numerical method that can model both linear and non-linear systems and is now widely used in various fields of research and development. Mohanty [12,13] and Urata et al. [14] have used ANN for vapour liquid equilibrium (VLE) calculations; Naik and Bhagwat [15] have used ANN for modelling protein solubility. Jouyban et al. [16] have used ANN for predicting the solubility of anthracene in binary and ternary solvents. There are also some investigations on solubility predictions presented in literature [17-19]. But to our knowledge there is no investigation on application of ANN for predicting the solubility of gases in polymers and especially low density polyethylene (LDPE). As mentioned before, because of ANN advantages it can be considered as an efficient and powerful method for modelling the solubility of gases in molten polymer.

The objective of this work is to apply the ANN method for modelling the solubility of gases, CH_2FCF_3 (HFC-134a), CH_3CClF_2 (HCFC-142b), butane and iso-butane, in molten LDPE and comparing the results obtained with those obtained by other methods, especially the EOS method.

Artificial Neural Network (ANN)

ANNs are able to provide models even in the case where the information or data are complex. Several kinds of ANNs are available but some of them are more popular. An ANN usually involves one input layer and one output layer. It can also involve some hidden layers too. Each layer is made by some neurons which are connected to neurons located in previous and next layers and have an input, an output and a transfer function. Usually the transfer functions of neurons located in a layer are the same. Sigmoidal function is a popular transfer function that we have used in this investigation and can be expressed as:

$$Y_j = \frac{1}{1+e^{-Sj}} \quad (1)$$

where Y_j is the output from jth neuron and S_j is the input for jth neuron which is produced by outputs of previous layer. S_j is given by:

$$S_j = \sum_{i=1}^{n} (w_{ij} Y_i) + b_j \quad (2)$$

where Y_i s are the outputs of ith neuron from previous layer, w_{ij} presents the weights applied to the connection of neuron ith and jth, and b_j is a bias number. Figure 1 shows the used network. Temperature (K) and pressure (kPa), which are the most important and common parameters are inputs and solubility ($g_{gas}/g_{polymer}$) is the output of the network. Outputs and inputs need to be scaled between 0 and 1 which can be done by a numerical method using a scaling equation in the following form:

$$(\text{Scaled})_{\text{Value}} = (\text{Actual})_{\text{Value}} \times m + c \quad (3)$$

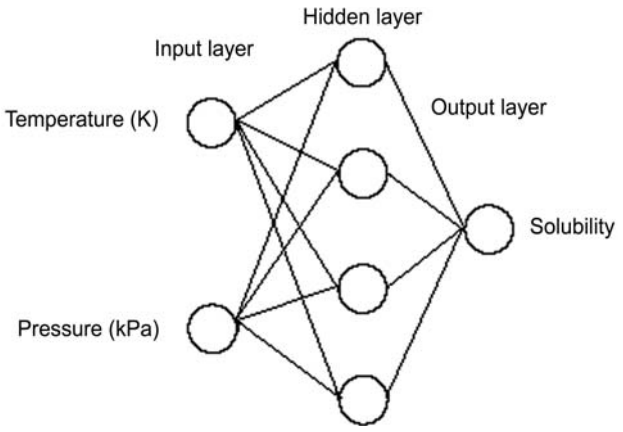

Figure 1. Architecture of designed network (biases are not shown).

where the constant c and m can be evaluated by two points. These 2 points are (lowest value, 0) and (highest value, 1). Table 1 contains the scaling parameters required for eqn (3) for HFC-134a in LDPE system. For other systems we can present a similar table.

There are different methods for predicting the parameters of a network. Back propagation (BP) is a popular propagation method which is used widely [12, 13, 17] and we chose it because of its simplicity. BP method and other propagation methods are explained in the literature [20]. Usually ANN softwares are used for modelling the data, but for having all parameters under control, we did the calculations by producing programmes with MATLAB7, m.file editor.

As we pointed out earlier, an ANN can involve some hidden layers. Usually one hidden layer is enough. Some authors such as Zhang et al. [17] have used the average relative deviation (ARD) for making decision about neurons in hidden layer and we have used the same method.

$$ARD = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{x_i^{exp} - x_i^{cal}}{x_i^{exp}}\right| \quad (4)$$

Average absolute deviation (AAD) is another parameter which shows the error of the network. AAD is expressed as:

$$AAD = \frac{1}{n}\sum_{i=1}^{n}\left|x_i^{exp} - x_i^{cal}\right| \quad (5)$$

RESULTS AND DISCUSSION

First, it is necessary to find the appropriate architecture of the network. Table 2 shows the calculations carried out for optimizing the architecture of the network for HFC-134a in LDPE. It is possible to present such a table for other systems too. We found that a 2-4-1 architecture would be the optimum topology.

The results of using back propagation method (BP) for estimating the weights and biases for HCFC-142b

Table 1. Constants of eqn (3) for HFC-134a in LDPE.

actual value	range	m	c
Temperature (K)	383.15-473.15	0.011111	-4.257222
Pressure (kPa)	335-2256	0.000520	-0.174388
S (g_{gas} / $g_{polymer}$)	0.0053-0.0314	38.314176	-0.203065

Table 2. Effect of neurons in hidden layer and training cycles on ARD (%) for HFC-134a in LDPE.

ARD (%) cycling	Neurons in hidden layer			
	2	3	4	5
1 000	10.52	9.84	11.13	9.24
10 000	1.46	1.39	1.41	1.21
30 000	1.05	0.86	0.83	0.81
100 000	-	0.84	0.76	0.70

Table 3. Weights and biases for solubility of HCFC-142b in LDPE.

neuron	1.1	1.2	3.1	bias
2.1	1.421357	-2.672275	-4.270295	0.180937
2.2	-0.427856	9.049909	8.774585	0.989343
2.3	0.005553	1.569089	-0.069547	1.644769
2.4	-8.689487	10.972274	9.313141	-6.164368
bias	-	-	-7.210884	-

in LDPE system is shown in Table 3, as an example, where neuron 2.1 means the first neuron of second layer, or neuron 3.1 means the first neuron of third layer. Table 3 contains the weights and biases for predicting the solubility without swelling correction. Similar table can be presented for predicting the gas solubility with swelling correction.

Figures 2-5 show the high accuracy of our calculations. The designed network can predict the gas solubility in LDPE without swelling correction as well as with swelling correction. Similar figures can be presented for the other studied systems. In Figures 2-5 circles represent data used for testing the network and black points represent data used for training the network. Tables 4-7 report the results of ANN gas solubility predictions and comparison with experimental data.

The data source was those reported by Wang et al. [1]. In their study the uncertainty of temperature measurement was less than 0.05K, the uncertainty of pressure measurement was less than 0.03% and the uncertainty of solubility measurement was 4.0%, which shows the high quality of the data. Table 8 shows the error of using the designed network. The overall ARD reported in this table can be compared with those reported by Wang et al. [1]. They have used EOS method and confirmed its superiority to similar methods. However, as the results presented in

Table 4. Comparing the results of the 2-4-1 ANN with experimental data for solubility of HFC-134a in LDPE.

T(K)	P(kPa)	Solubility without swelling		Solubility with swelling	
		Experimental	ANN	Experimental	ANN
383.15	335	0.0060	0.0060	0.0061	0.0060
383.15	727	0.0133	0.0133	0.0136	0.0138
383.15	1089	0.0195	0.0201	0.0201	0.0200
383.15	1602	0.0299	0.0298	0.0314	0.0310
4.13.15	373	0.0057	0.0056	0.0057	0.0056
4.13.15	815	0.0126	0.0125	0.0127	0.0126
4.13.15	1226	0.0185	0.0185	0.0192	0.0192
4.13.15	1823	0.0285	0.0288	0.0300	0.0302
443.15	414	0.0054	0.0055	0.0055	0.0054
443.15	903	0.0122	0.0122	0.0125	0.0126
443.15	1364	0.0179	0.0179	0.0187	0.0188
443.15	2038	0.0280	0.0279	0.0296	0.0291
473.15	453	0.0053	0.0054	0.0054	0.0053
473.15	989	0.0121	0.0121	0.0124	0.0124
473.15	1500	0.0178	0.0178	0.0185	0.0186
473.15	2256	0.0279	0.0271	0.0296	0.0292
			AAD=0.0002		AAD=0.0002

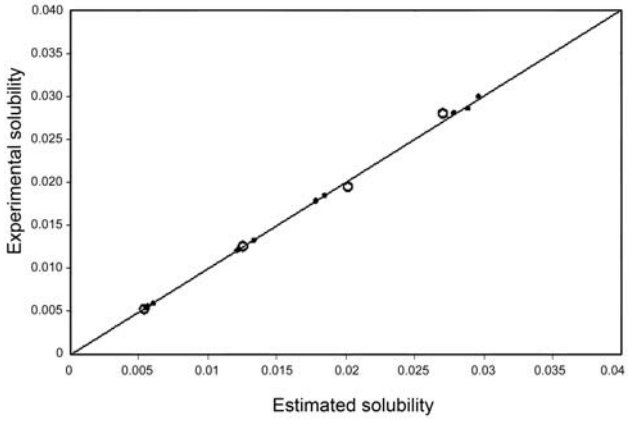

Figure 2. Estimated vs. experimental solubility of HFC-134a in LDPE (g gas/ g polymer) without swelling correction (points: training data, circles: testing data).

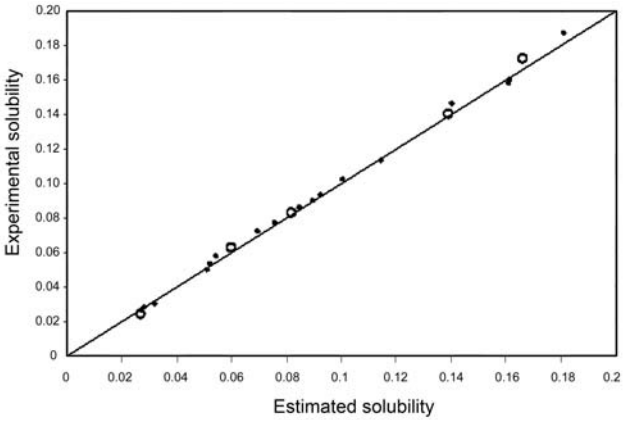

Figure 3. Estimated vs. experimental solubility of iso-butane in LDPE (g gas/ g polymer) with swelling correction (points: training data, circles: testing data).

Table 5. Comparing the results of the 2-4-1 ANN with experimental data for solubility of HCFC-142b in LDPE.

T(K)	P(kPa)	Solubility without swelling		Solubility with swelling	
		Experimental	ANN	Experimental	ANN
383.15	270	0.0191	0.0209	0.0193	0.0213
383.15	436	0.0307	0.0304	0.0313	0.0309
383.15	581	0.0447	0.0431	0.0457	0.0439
383.15	857	0.0703	0.0729	0.0725	0.0750
383.15	1228	0.1120	0.1194	0.1180	0.1187
383.15	1525	0.1540	0.1538	0.1630	0.1613
413.15	324	0.0177	0.0191	0.0179	0.0194
413.15	514	0.0290	0.0266	0.0295	0.0270
413.15	719	0.0405	0.0395	0.0415	0.0403
413.15	1065	0.0635	0.0633	0.0657	0.0662
413.15	1584	0.0989	0.0963	0.1040	0.1025
413.15	2017	0.1340	0.1365	0.1440	0.1499
443.15	388	0.0162	0.0182	0.0164	0.0184
443.15	618	0.0263	0.0252	0.0269	0.0255
443.15	865	0.0368	0.0368	0.0378	0.0376
443.15	1292	0.0569	0.0578	0.0594	0.0610
443.15	1937	0.0884	0.0867	0.0943	0.0930
443.15	2500	0.1190	0.1196	0.1300	0.1305
473.15	451	0.0150	0.0176	0.0152	0.0179
473.15	719	0.0244	0.0240	0.0249	0.0244
473.15	1006	0.0340	0.0339	0.0350	0.0348
473.15	1508	0.0521	0.0515	0.0546	0.0545
473.15	2280	0.0804	0.0805	0.0866	0.0869
473.15	2979	0.1010	0.1103	0.1180	0.1304
			AAD=0.0018		AAD=0.0019

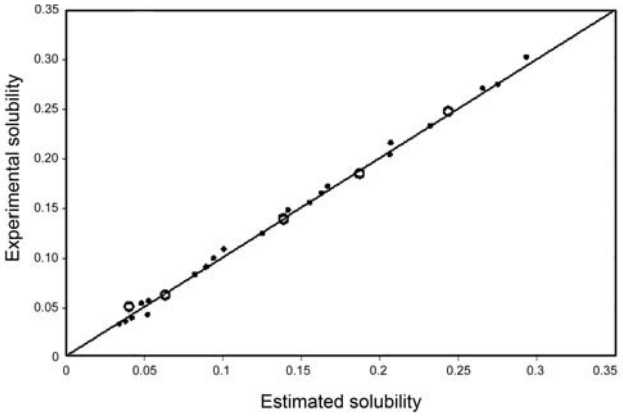

Figure 4. Estimated vs. experimental solubility of butane in LDPE (g gas/ g polymer) without swelling correction (points: training data, circles: testing data).

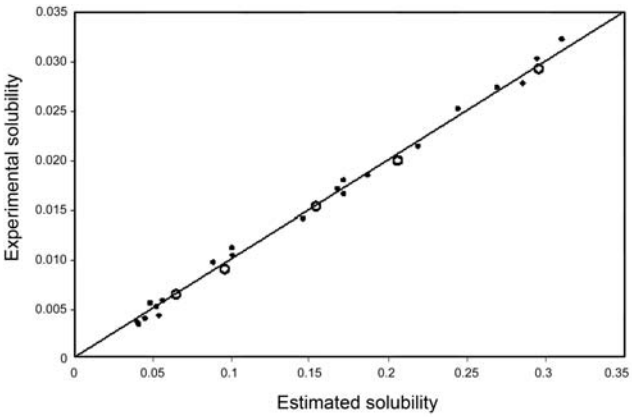

Figure 5. Estimated vs. experimental solubility of butane in LDPE (g gas/ g polymer) with swelling correction (points: training data, circles: testing data).

Table 6. Comparing the results of the 2-4-1 ANN with experimental data for solubility of butane in LDPE.

T(K)	P(kPa)	Solubility without swelling		Solubility with swelling	
		Experimental	ANN	Experimental	ANN
383.15	373	0.0415	0.0521	0.0420	0.0539
383.15	521	0.0620	0.0637	0.0632	0.0644
383.15	805	0.1080	0.1010	0.1110	0.1001
383.15	1077	0.1710	0.1666	0.1790	0.1711
383.15	1193	0.2030	0.2064	0.2130	0.2185
383.15	1386	0.2750	0.2750	0.2920	0.2954
383.15	1455	0.3020	0.2934	0.3220	0.3102
413.15	529	0.0382	0.0422	0.0389	0.0450
413.15	?752	0.0559	0.0529	0.0572	0.0560
413.15	1192	0.0989	0.0938	0.1030	0.1008
413.15	1632	0.1550	0.1555	0.1650	0.1714
413.15	1837	0.1840	0.1870	0.1990	0.2059
413.15	2203	0.2470	0.2435	0.2730	0.2690
413.15	2347	0.2700	0.2657	0.3020	0.2942
443.15	698	0.0352	0.0382	0.0360	0.0396
443.15	1005	0.0531	0.0483	0.0550	0.0481
443.15	1624	0.0902	0.0897	0.0957	0.0886
443.15	2260	0.1380	0.1385	0.1520	0.1538
443.15	2601	0.1640	0.1627	0.1840	0.1868
443.15	3185	0.2150	0.2072	0.2510	0.2440
443.15	3447	0.2320	0.2326	0.2770	0.2854
473.15	871	0.0326	0.0343	0.0344	0.0408
473.15	1266	0.0495	0.0405	0.0516	0.0520
473.15	2075	0.0827	0.0820	0.0891	0.0959
473.15	2923	0.1240	0.1251	0.1400	0.1453
473.15	3427	0.1470	0.1416	0.1700	0.1672
			AAD=0.0037		AAD=0.0040

Table 7. Comparing the results of the 2-4-1 ANN with experimental data for solubility of iso-butane in LDPE.

T(K)	P(kPa)	Solubility without swelling		Solubility with swelling	
		Experimental	ANN	Experimental	ANN
383.15	380	0.0301	0.0334	0.0305	0.0321
383.15	709	0.0611	0.0586	0.0626	0.0600
383.15	944	0.0869	0.0861	0.0901	0.0898
383.15	1119	0.1080	0.1096	0.1130	0.1144
383.15	1383	0.1500	0.1533	0.1580	0.1609
383.15	1525	0.1750	0.1747	0.1870	0.1808
413.15	501	0.0280	0.0284	-	-
413.15	976	0.0558	0.0516	0.0577	0.0544
413.15	1326	0.0792	0.0792	0.0832	0.0816
413.15	1571	0.0963	0.0970	0.1020	0.1005
413.15	2032	0.1330	0.1309	0.1460	0.1403
413.15	2240	0.1560	0.1556	0.1720	0.1659
443.15	639	0.0260	0.0269	0.0266	0.0271
443.15	1258	0.0511	0.0484	0.0535	0.0521
443.15	1731	0.0724	0.0726	0.0772	0.0755
443.15	2048	0.0864	0.0869	0.0933	0.0925
443.15	2765	0.1250	0.1191	0.1400	0.1388
443.15	3025	0.1410	0.1418	0.1600	0.1611
473.15	795	0.0240	0.0266	0.0246	0.0268
473.15	1542	0.0474	0.0486	0.0499	0.0511
473.15	2142	0.0669	0.0678	0.0721	0.0696
473.15	2535	0.0784	0.0775	0.0860	0.0848
			AAD=0.0016		AAD=0.0021

Tables 4-7 indicate, the designed ANN used in this work has a better performance than Wang et al. EOS method and by increasing the number of neurons in hidden layer it is possible to obtain better accuracy.

Table 8. Comparing the error (ARD %) of designed ANN with S-L Equation of State.

Gas	S-L Equation of state	ANN (with swelling)		ANN (without swelling)		
		ARD overall (%)	ARD test (%)	ARD overall (%)	ARD test (%)	Data points [1]
HFC-134a	3.0	0.85	1.65	0.92	2.19	32
HCFC-142b	5.1	4.16	4.35	4.08	3.51	48
Butane	7.2	6.05	4.68	4.61	4.85	52
Iso-butane	3.5	2.66	3.88	2.83	5.25	43

CONCLUSION

Solubility of gases in molten polymer can affect the properties of products and a fast and powerful method for predicting the gas solubility in polymers can be useful in polymer processing. In this work, we have studied the solubility of four gases in low density polyethylene (LDPE) by using artificial neural network (ANN). The results have indicated that ANN with a 2-4-1 architecture can give accurate gas solubility predictions compared with the experimental data and EOS method.

However, ANN has some disadvantages, namely, it requires a large amount of high quality data to train the network but after training it is a fast, powerful and efficient method for gas solubility predictions.

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