Experimental Measurements and Correlations of Excess Molar Enthalpies for the Binary and Ternary Mixtures of (Cyclohexane, Tetrahydropyran, and Morpholine) or (Cyclohexane, 1,4-Dioxane, and Morpholine) at 308.15 K and Atmospheric Pressure

Farid B. Belaribi,*,† Atika Dahmoun,† Aomar Dahmani,† Ghénima Boukais-Belaribi,† Amir H. Mohammadi,‡ and Dominique Richon‡

Laboratoire de Thermodynamique et Modélisation Moléculaire, Faculté de Chimie, Université des Sciences et de la Technologie Houari Boumediene, BP 32 El Alia, 16111 Bab Ezzouar, Alger, Algérie, and MINES ParisTech, CEP/TEP - Centre Energétique et Procédés, 35 Rue Saint Honoré, 77305 Fontainebleau, France

Excess molar enthalpies for the binary and ternary systems of (cyclohexane, tetrahydropyran, and morpholine) or (cyclohexane, 1,4-dioxane, and morpholine) have been measured using a Calvet microcalorimeter at 308.15 K and atmospheric pressure. The experimental binary results are correlated using the Redlich−Kister equation. The excess molar enthalpies for the ternary systems are correlated using the Cibulka equation. The capability of an artificial neural network algorithm to model these data is finally studied.

Introduction

Tetrahydropyran, 1,4-dioxane, piperidine, and morpholine, hexacyclic compounds of similar size and shape, differ in only one or two functional groups (NH, O, CH_2) and are of interest to study thermodynamic properties of their cyclohexane-containing mixtures. In our previous studies,[1−3] we have reported experimental excess molar enthalpies for binary and ternary mixtures of these hexacyclic aliphatic compounds. Continuing our investigations, we report here experimental (cyclohexane, tetrahydropyran, and morpholine) and (cyclohexane, 1,4-dioxane, and morpholine) molar excess enthalpies, for ternary systems, and their binaries constituents, at 308.15 K and atmospheric pressure. All reported experimental data have been measured using a Calvet microcalorimeter. The binary and ternary experimental data were correlated using the empirical equations of Redlich−Kister[4] and Cibulka,[5] respectively. The capability of an artificial neural network (ANN) algorithm[6] as an alternative method to model these (binary and ternary) data is finally investigated.

A survey of the open literature shows that few excess molar enthalpy data have been reported for the binary mixtures of both cyclic ethers (1,4-dioxane and tetrahydropyran) with cyclohexane[7−9] but not with morpholine. To our knowledge, there is no literature data for the two ternary systems investigated.

Experimental Section

Materials. Tetrahydropyran, morpholine, and 1,4-dioxane whose CAS numbers are [142-68-7], [110-91-8], and [123-91-1], respectively, were Fluka products. Cyclohexane [110-82-7] was supplied by Merck. All the chemicals were used without further purification. The mole fraction purities were all greater than 0.99.

Experimental Apparatus and Procedure. The experimental enthalpy data were measured at atmospheric pressure by means of a flow calorimeter (Calvet microcalorimeter, model C80, Setaram, France). The temperature was maintained constant at (308.15 ± 0.02) K. The mixtures were prepared by mass using a Mettler PE 160 balance (precision ± 0.1 mg), ensuring a probable uncertainty in the mole fraction less than 10^{-3}. The apparatus and procedures were tested by determining excess enthalpies for the standard system benzene + cyclohexane, and the results were found to differ by less than 3 % from those of Marsh.[10] More details of the apparatus and procedure can be found in previous papers.[11,12]

As in our previous ternary system study,[3] the excess molar enthalpy $H^E_{m,12+3}$ was determined for several pseudobinary mixtures in which component 3 (morpholine) was added to binary mixtures of components 1 (cyclohexane) and 2 (tetrahydropyran or 1,4-dioxane). For this purpose, binaries with fixed mole ratios, x_1/x_2, were prepared by mass. Then, excess molar enthalpy $H^E_{m,123}$ of the ternary mixture was obtained from the following relationship

$$H^E_{m,123} = H^E_{m,12+3} + (1 - x_3)H^E_{m,12} \quad (1)$$

where x_3 represents the mole fraction of morpholine and $H^E_{m,12}$ is the excess molar enthalpy of the particular binary mixture.

Results and Discussion

The experimental excess molar enthalpies, for the binary systems, are reported in Tables 1a and 1b and plotted in Figure 1. For the ternary mixtures, the experimental results are reported in Tables 2 and 3 and plotted in Figures 2 and 3.

Binary Correlation of Data. The experimental binary data were correlated using the Redlich−Kister equation[4]

* Corresponding author. E-mail: f_belaribi@yahoo.com. Tel. and Fax: +(213) 21 248008.
† Université des Sciences et de la Technologie Houari Boumediene.
‡ CEP/TEP - Centre Energétique et Procédés.

10.1021/je9010097
Published on Web 02/12/2010

$$H^{E}_{m,jk}/J \cdot mol^{-1} = x(1 - x)\sum_{i=0}^{n} A_i(2x - 1)^i \qquad (2)$$

where i represents the number of coefficients A_i and x stands for mole fraction of the first component in the binary mixture. The coefficients A_i, obtained by an unweighted least-squares regression method, are summarized in Table 4 together with the standard deviation s.

The results of the correlations are reported in Table 1 and plotted in Figure 1.

Ternary Correlation of Data. Several correlations for ternary excess molar enthalpies are available in the literature. In this work, the experimental ternary data were correlated using the empirical equation of Cibulka[5]

Table 1. Experimental and Calculated or Predicted Excess Molar Enthalpies, H^E, for Constituent Binaries of the (a) {Cyclohexane, Tetrahydropyran, and Morpholine}[a] or (b) {Cyclohexane, 1,4-Dioxane, and Morpholine}[b] Ternary System, at 308.15 K and Atmospheric Pressure[c]

(a) x	experimental H^E	calculated H^E(using eq 2)		calculated/predicted H^E(using ANN[6])	
mole fraction	J·mol^{-1}	J·mol^{-1}	100D (using eq 2)	J·mol^{-1}	100D (using ANN)
		x cyclohexane + $(1 - x)$ tetrahydropyran[d]			
0.101	157	156	+0.6	154	+1.9
0.200	294	295	−0.3	294	0.0
0.300	412	411	+0.2	412	0.0
0.400	490	490	0.0	493	−0.6
0.499	526	528	−0.4	530	−0.8
0.606	519	517	+0.4	515	+0.8
0.699	461*	462	−0.2	455	+1.3
0.800	355	354	+0.3	332	+6.5
0.900	198	199	−0.5	190	+4.0
		x cyclohexane + $(1 - x)$ morpholine			
0.100	612	611	+0.2	621	−1.5
0.201	1093*	1095	−0.2	1167	−6.8
0.300	1482*	1481	+0.1	1527	−3.0
0.401	1750	1749	+0.1	1748	+0.1
0.500	1865	1867	−0.1	1864	+0.1
0.600	1825	1826	−0.1	1827	−0.1
0.700	1641	1638	+0.2	1634	+0.4
0.801	1304	1307	−0.2	1320	−1.2
0.900	814	813	+0.1	799	+1.8
		x tetrahydropyran + $(1 - x)$ morpholine			
0.101	163	164	−0.6	173	−6.1
0.199	294	294	0.0	301	−2.4
0.300	396	395	+0.3	394	+0.5
0.401	458	457	+0.2	462	−0.9
0.501	480*	479	+0.2	474	+1.3
0.600	459*	462	−0.6	454	+1.1
0.702	403	402	+0.2	394	+2.2
0.800	306	306	0.0	314	−2.6
0.899	172	171	+0.6	169	+1.7

(b) x	experimental H^E	calculated H^E(using eq 2)		calculated/predicted H^E(using ANN)	
mole fraction	J·mol^{-1}	J·mol^{-1}	100D (using eq 2)	J·mol^{-1}	100D (using ANN[6])
		x cyclohexane + $(1 - x)$ 1,4-dioxane[d]			
0.101	570	568	+0.4	569	+0.2
0.204	1050*	1052	−0.2	1100	−4.5
0.288	1333	1335	−0.2	1333	0.0
0.408	1565	1561	+0.3	1565	0.0
0.506	1620	1620	0.0	1628	−0.5
0.606	1574*	1579	−0.3	1575	−0.1
0.705	1435	1432	+0.2	1426	+0.6
0.803	1150	1149	+0.1	1160	−0.9
0.900	695	696	−0.1	690	+0.7
		x 1,4-dioxane + $(1 - x)$ morpholine			
0.108	124	123	+0.8	129	−3.9
0.201	212	213	−0.5	222	−4.5
0.303	285	284	+0.4	281	+1.4
0.403	323	323	0.0	313	+3.2
0.506	331*	332	−0.3	323	+2.5
0.600	315*	314	+0.3	311	+1.3
0.703	270	271	−0.4	273	−1.1
0.803	207	206	+0.5	209	+1.0
0.905	114	115	−0.9	115	−0.9

[a] Using the ANN algorithm, the AAD for the cyclohexane + tetrahydropyran mixture is 1.8 %; the AAD for the cyclohexane + morpholine mixture is 1.7 %; the AAD for the tetrahydropyran + morpholine mixture is 2.1 %. All of these data were used for developing the ANN,[6] except for the data indicated by stars which were used for validation. Using the Redlich−Kister equation,[4] the AAD for the cyclohexane + tetrahydropyran mixture is 0.3 %; the AAD for the cyclohexane + morpholine mixture is 0.1 %; the AAD for the tetrahydropyran + morpholine mixture is 0.3 %. All of these data were used for developing the Redlich−Kister equation.[4] [b] Using the ANN algorithm, the AAD for the cyclohexane + 1,4-dioxane mixture is 0.8 %; the AAD for the cyclohexane + morpholine mixture is 1.4 %; the AAD for the 1,4-dioxane + morpholine mixture is 2.2 %. All of these data were used for developing the ANN,[6] except for the data indicated by stars which were used for validation. Using the Redlich−Kister equation,[4] the AAD for the cyclohexane + 1,4-dioxane mixture is 0.2 %; the AAD for the cyclohexane + morpholine mixture is 0.1 %; the AAD for the 1,4-dioxane + morpholine mixture is 0.5 %. All of these data were used for developing the Redlich−Kister equation.[4] [c] D = (experimental value − predicted value)/experimental value. AAD = $(1/N)\sum_{i=1}^{N}|$(experimental value,i − predicted value,i)/experimental value,$i|$, where N represents the number of experimental data. [d] From ref 2.

$$H^{E}_{m,123}/J\cdot mol^{-1} = H^{E}_{m,bin}/J\cdot mol^{-1} + x_1x_2(1 - x_1 - x_2)(B_0 + B_1x_1 + B_2x_2) \quad (3)$$

where $H^{E}_{m,bin}$, known as the binary contribution to the excess molar enthalpy, is given by

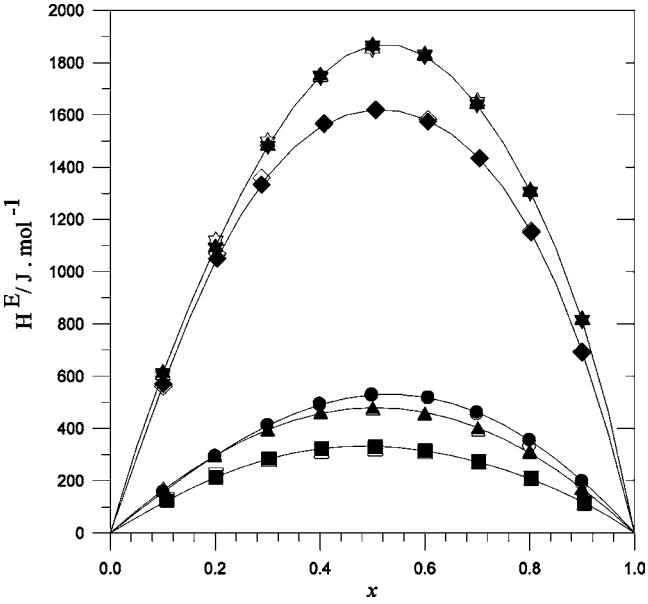

Figure 1. Excess molar enthalpies, $H^E/J\cdot mol^{-1}$, at 308.15 K and atmospheric pressure, for the five binary systems investigated. Solid symbols, experimental data; hollow sysmbols, results using ANN.[6] ★, ☆, {*x* cyclohexane + (1 − *x*) morpholine}; ◆, ◇, {*x* cyclohexane + (1 − *x*) 1,4-dioxane}; ●, ○, {*x* cyclohexane + (1 − *x*) tetrahydropyran}; ▲, △, {*x* tetrahydropyran + (1 − *x*) morpholine}, ■, □; {*x* 1,4-dioxane + (1 − *x*) morpholine}. Solid lines: fit to experimental results using the Redlich−Kister equation.[4]

Table 2. Measured Molar Enthalpies of Mixing, $H^{E}_{m,12+3}$, and Excess Molar Enthalpies, $H^{E}_{m,123}$, for the Ternary Mixture of Cyclohexane (1) + Tetrahydropyran (2) + Morpholine (3) at 308.15 K and Atmospheric Pressure

x_1	x_2	x_3	$H^{E}_{m,12+3}$	$H^{E}_{m,123}$
mole fraction	mole fraction	mole fraction	J·mol^{-1}	J·mol^{-1}
	$x_1/x_2 = 0.25$; $H^{E}_{m,12}/J\cdot mol^{-1} = 296^a$			
0.180	0.719	0.101	251	517
0.160	0.639	0.201	424	661
0.140	0.560	0.300	529	736
0.120	0.480	0.400	597	774
0.100	0.399	0.501	638	786
0.080	0.319	0.601	589	707
0.060	0.240	0.700	530	619
0.020	0.080	0.800	220	250
	$x_1/x_2 = 1$; $H^{E}_{m,12}/J\cdot mol^{-1} = 528^a$			
0.449	0.449	0.102	418	894
0.399	0.401	0.200	688	1111
0.349	0.351	0.300	841	1211
0.299	0.300	0.401	948	1265
0.249	0.250	0.501	1009	1273
0.199	0.200	0.601	974	1185
0.150	0.151	0.701	827	986
0.099	0.100	0.801	611	716
0.050	0.050	0.900	338	391
	$x_1/x_2 = 4$; $H^{E}_{m,12}/J\cdot mol^{-1} = 352^a$			
0.718	0.180	0.102	632	951
0.640	0.160	0.200	1028	1312
0.560	0.140	0.300	1259	1508
0.479	0.120	0.401	1374	1587
0.400	0.100	0.500	1432	1610
0.319	0.080	0.601	1397	1539
0.237	0.060	0.703	1149	1255

[a] The values of $H^{E}_{m,12}$ at specified constant ratios x_1/x_2 were calculated using eq 2.

$$H^{E}_{m,bin} = H^{E}_{m,12} + H^{E}_{m,13} + H^{E}_{m,23} \quad (4)$$

where $H^{E}_{m,jk}$ is the excess enthalpy calculated from the correlated data of the $j-$ pair (eq 2) using the ternary mole fractions x_j and x_k. This simplest method assumes that there are no ternary effects; i.e., the ternary excess enthalpy is just a sum of the binary enthalpies of mixing. The values of $H^{E}_{m,12}$ at three

Table 3. Measured Molar Enthalpies of Mixing, $H^{E}_{m,12+3}$, and Excess Molar Enthalpies, $H^{E}_{m,123}$, for the Ternary Mixture of Cyclohexane (1) + 1,4-Dioxane (2) + Morpholine (3) at 308.15 K and Atmospheric Pressure

x_1	x_2	x_3	$H^{E}_{m,12+3}$	$H^{E}_{m,123}$
mole fraction	mole fraction	mole fraction	J·mol^{-1}	J·mol^{-1}
	$x_1/x_2 = 0.25$; $H^{E}_{m,12}/J\cdot mol^{-1} = 1036^a$			
0.180	0.719	0.101	142	1088
0.159	0.637	0.204	227	1065
0.139	0.556	0.305	266	998
0.119	0.477	0.404	285	912
0.099	0.397	0.504	300	822
0.077	0.318	0.605	301	720
0.059	0.237	0.704	267	578
	$x_1/x_2 = 1$; $H^{E}_{m,12}/J\cdot mol^{-1} = 1619^a$			
0.448	0.447	0.105	249	1698
0.400	0.399	0.201	403	1697
0.351	0.351	0.298	514	1650
0.299	0.298	0.403	587	1554
0.249	0.249	0.502	614	1421
0.198	0.198	0.604	577	1219
0.149	0.149	0.702	519	1001
0.099	0.099	0.802	423	743
	$x_1/x_2 = 4$; $H^{E}_{m,12}/J\cdot mol^{-1} = 1160^a$			
0.719	0.180	0.101	493	1529
0.640	0.160	0.200	828	1750
0.556	0.140	0.304	1022	1829
0.478	0.120	0.402	1152	1841
0.399	0.100	0.501	1188	1764
0.317	0.080	0.603	1134	1593
0.239	0.060	0.701	1005	1350

[a] The values of $H^{E}_{m,12}$ at specified constant ratios x_1/x_2 were calculated using eq 2.

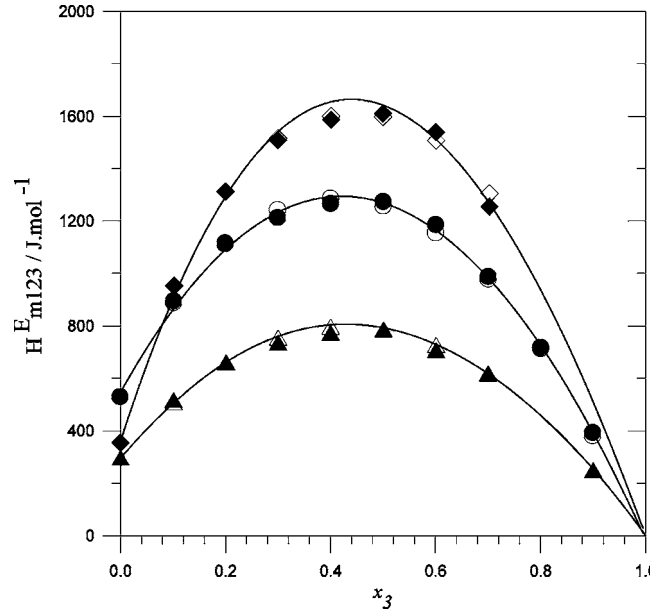

Figure 2. Pseudobinary representation of the experimental and correlated values of the excess molar enthalpies, $H^{E}_{m,123}/J\cdot mol^{-1}$, for the ternary mixtures of {cyclohexane (1) + tetrahydropyran (2) + piperidine (3)}, at 308.15 K and atmospheric pressure. △, ▲, $x_1/x_2 = 0.25$; ○, ●, $x_1/x_2 = 1$; ◇, ◆, $x_1/x_2 = 4$. Solid symbols: experimental data. Hollow symbols: results using ANN.[6] Solid lines: calculated values using the Cibulka equation.[5]

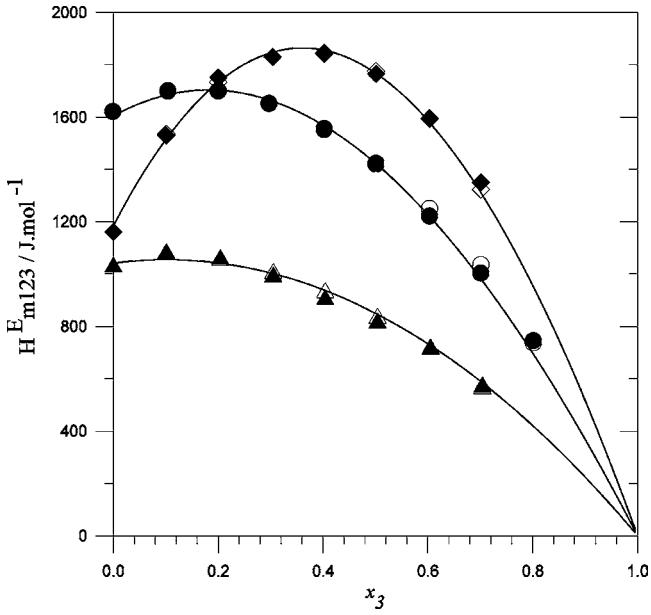

Figure 3. Pseudobinary representation of the experimental and correlated values of the excess molar enthalpies, $H^E_{m,123}$/J·mol^{-}, for the ternary mixtures of {cyclohexane (1) + 1,4-dioxane (2) + morpholine (3)}, at 308.15 K and atmospheric pressure. △, ▲, $x_1/x_2 = 0.25$; ○, ●, $x_1/x_2 = 1$; ◇, ◆), $x_1/x_2 = 4$. Solid symbols: experimental data. Hollow symbols: results using ANN.[6] Solid lines: calculated values using the Cibulka equation.[5]

specified constant ratios x_1/x_2 (approximated ratio values were 0.25, 1, and 4) of mole fractions of cyclohexane and cyclic ether (tetrahydropyran or 1,4-dioxane) in their binary mixtures were interpolated using eq 2. The parameters B_i of eq 3, determined by an unweighted least-squares regression method, are summarized in Table 5.

The results of the correlations, for the ternary systems cyclohexane + cyclic ether (tetrahydropyran or 1,4-dioxane) + morpholine, are reported in Tables 6 and 7 and plotted in Figures 2 and 3, together with experimental ternary data. The contour lines of constant $H^E_{m,123}$, calculated from Cibulka equation,[5] are plotted in Figures 4 and 5.

As can be observed in Tables 1a and 1b and Figure 1, all the binary mixtures studied are formed endothermally and show symmetric H^E behavior. Cyclohexane + morpholine and 1,4-dioxane + morpholine systems have the largest (1865 J·mol^{-1}) and the lowest (331 J·mol^{-1}) excess enthalpy among the five systems, respectively. The experimental values of excess enthalpy are in the following sequences: morpholine > 1,4-dioxane > tetrahydropyran, for the cyclohexane-containing binary mixtures; cyclohexane > 1,4-dioxane > tetrahydropyran, for the morpholine-containing binary mixtures; and cyclohexane > morpholine, for the tetrahydropyran-containing binary mixtures. As can be observed in Tables 3 and 4 and Figures 2 and 3, the two ternary systems investigated also show an endothermic behavior in the whole range of composition. Also, the calculated $H^E_{m,123}$ values from the Cibulka equation,[5] for the two ternary systems, are almost the same as those calculated from binary contribution, $H^E_{m,bin}$, since the ternary contribution, $H^E_{m,123} - H^E_{m,bin}$, does not exceed 4 %, as can be seen from the last columns of Tables 6 and 7.

Table 5. Values of Coefficients B_i in Equation 3 for the Ternary Systems of Cyclohexane (1) + Cyclic Ether (2) + Morpholine (3)

ternary system	B_0	B_1	B_2	s / J·mol^{-1}
cyclohexane (1) + tetrahydropyran (2) + morpholine (3)	−1292.3	1963.0	39.5	28.9
cyclohexane (1) + 1,4-dioxane (2) + morpholine (3)	−1627.8	−492.9	525.3	22.9

Our experimental excess enthalpy results, for the two binary mixtures of cyclohexane with 1,4-dioxane or tetrahydropyran, were compared to literature data[7,8] in our previous paper.[3] To our knowledge, no excess molar enthalpy data, for the other binary mixtures and for the two ternary systems investigated, were reported in the open literature for comparison.

Artificial Neural Network Algorithm. Artificial neural network algorithms are known to be effective to model complex systems. These models have large numbers of computational units connected in a massively parallel structure and do not require an explicit formulation of the mathematical or physical relationships of the handled problem.[2,3,6] The ANNs are first subjected to a set of training data consisting of input data together with corresponding outputs. After a sufficient number of training iterations, the neural network learns the patterns in the data fed to it and creates an internal model, which it uses to make predictions for new inputs.[2,3,6]

Feed-forward neural networks are the most frequently used and are designed with one input layer, one output layer, and hidden layers.[2,3,6] The number of neurons in the input and output layers equals the number of inputs and outputs, respectively.[2,3,6] The accuracy of model representation depends on the architecture and parameters of the neural network.[2,3,6]

To develop the ANN, the data sets are generally subdivided into three groups corresponding to the following three steps: training, testing, and validation.[2,3,6] 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.[2,3,6]

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 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.[2,3,6]

Tables 8 and 9 report a summary of the feed-forward ANN used in this work along with number of neurons, hidden layers, experimental data, and type of activation function.

Table 4. Values of Coefficients A_i in Equation 2 and Standard Deviation s for the Binary Mixtures of Cyclohexane, Cyclic Ether (Tetrahydropyran or 1,4-Dioxane), and Morpholine

binary system	A_0	A_1	A_2	A_3	A_4	s / J·mol^{-1}
cyclohexane (1) + tetrahydropyran (2)	2112.2	303.6	−230.5	0	0	1.3
cyclohexane (1) + 1,4-dioxane (2)	6477.2	300.3	1438.0	958.3	−1002.6	3.0
cyclohexane (1) + morpholine (2)	7465.9	778.6	−620.0	984.4	2060.9	2.2
tetrahydropyran (1) + morpholine (2)	1917.3	52.1	−106.3	0	0	1.1
1,4-dioxane (1) + morpholine (2)	1327.9	−88.9	−41.4	186.9	0	0.9

Table 6. Comparison Between Measured and Calculated/Predicted Values of Excess Molar Enthalpies, $H^E_{m,123}$, for the Ternary Mixture of Cyclohexane (1) + Tetrahydropyran (2) + Morpholine (3) at 308.15 K and Atmospheric Pressure

x_1	x_2	x_3	experimental $H^E_{m,123}$	calculated $H^E_{m,123}$(using the Cibulka equation[5])		calculated $H^E_{m,123}$(using ANN[6])		
mole fraction	mole fraction	mole fraction	J·mol^{-1}	J·mol^{-1}	100D^a (using the Cibulka equation[5])	J·mol^{-1}	100D^b (using ANN[6])	100Δ
0.180	0.719	0.101	517	506	+2.1	508	+1.7	2.4
0.160	0.639	0.201	661	661	0.0	660	+0.2	3.0
0.140	0.560	0.300	736	760	−3.3	755	−2.6	3.1
0.120	0.479	0.400	774*	804	−3.9	797	−3.0	3.0
0.100	0.399	0.501	786	793	−0.9	787	−0.1	2.7
0.080	0.319	0.601	707	729	−3.1	727	−2.8	2.4
0.060	0.240	0.700	619	617	+0.3	617	+0.3	1.9
0.020	0.080	0.900	250	254	−1.6	248	+0.8	0.7
0.449	0.449	0.102	894	859	+3.9	888	+0.7	0.9
0.399	0.401	0.200	1111	1085	+2.3	1114	−0.3	1.5
0.349	0.351	0.300	1211*	1226	−1.2	1241	−2.5	1.8
0.299	0.300	0.401	1265	1279	−1.1	1285	−1.6	2.0
0.249	0.250	0.501	1273	1246	+2.1	1256	+1.3	2.0
0.199	0.200	0.601	1185	1131	+4.6	1153	+2.7	1.9
0.150	0.151	0.701	986	948	+3.9	977	+0.9	1.7
0.099	0.100	0.801	716	698	+2.5	712	+0.6	1.2
0.050	0.050	0.900	391	390	+0.3	379	+3.1	0.7
0.718	0.180	0.102	951	926	+2.6	953	−0.2	0.2
0.640	0.160	0.200	1312*	1289	+1.8	1313	−0.1	0.0
0.560	0.140	0.300	1508	1533	−1.7	1515	−0.5	0.3
0.479	0.120	0.401	1587	1654	−4.2	1600	−0.8	0.5
0.400	0.100	0.500	1610	1647	−2.3	1597	+0.8	0.6
0.319	0.080	0.601	1539	1513	+1.7	1507	+2.1	0.7
0.238	0.060	0.703	1255	1264	−0.7	1305	−4.0	0.7

[a] The AAD using the Cibulka equation[5] is 2.2. All of these data were used for developing the Cibulka equation.[5] [b] The AAD using ANN[6] is 1.4. All of these data were used for developing the ANN,[6] except for the data indicated by stars which were used for validation. $\Delta = |(H^E_{m,123} - H^E_{m,bin})/H^E_{m,123}|$ (calculated using the Cibulka equation[5]).

Table 7. Comparison between Measured and Calculated/Predicted Values of Excess Molar Enthalpies, $H^E_{m,123}$, for the Ternary Mixture of Cyclohexane (1) + 1,4-Dioxane (2) + Morpholine (3) at 308.15 K and Atmospheric Pressure

x_1	x_2	x_3	experimental $H^E_{m,123}$	calculated $H^E_{m,123}$(using the Cibulka equation[5])		calculated $H^E_{m,123}$(using ANN[6])		
mole fraction	mole fraction	mole fraction	J·mol^{-1}	J·mol^{-1}	100D^a (using the Cibulka equation[5])	J·mol^{-1}	100D^b (using ANN[6])	100Δ
0.180	0.719	0.101	1088	1054	+3.1	1087	+0.1	1.7
0.159	0.637	0.204	1065	1041	+2.3	1060	+0.5	2.7
0.139	0.556	0.305	998	1001	−0.3	1011	−1.3	3.3
0.119	0.477	0.404	912*	936	−2.6	938	−2.9	3.5
0.099	0.397	0.504	822*	845	−2.8	840	+2.2	3.4
0.080	0.318	0.605	720	730	−1.4	723	+0.4	3.2
0.059	0.237	0.704	578	582	−0.7	570	+1.4	2.6
0.448	0.447	0.105	1698	1688	+0.6	1697	+0.1	2.0
0.400	0.399	0.201	1697	1698	−0.1	1698	−0.1	3.1
0.351	0.351	0.298	1650	1662	−0.7	1649	+0.1	3.6
0.299	0.298	0.403	1554	1568	−0.9	1550	+0.3	3.7
0.249	0.249	0.502	1421	1422	−0.1	1417	+0.3	3.5
0.198	0.198	0.604	1219	1220*	−0.1	1248	−2.4	3.1
0.149	0.149	0.702	1001	976*	+2.5	1033	−3.2	2.6
0.099	0.099	0.802	743	690	+7.1	735	+1.1	1.9
0.719	0.180	0.101	1529	1521	+0.5	1534	−0.3	1.6
0.640	0.160	0.200	1750	1727	+1.3	1733	+1.0	2.2
0.560	0.140	0.304	1829	1840	−0.6	1829	0.0	2.4
0.478	0.120	0.402	1841	1859	−1.0	1844	−0.2	2.2
0.399	0.100	0.501	1764	1775	−0.6	1775	−0.6	2.0
0.319	0.080	0.603	1593	1584	+0.6	1595	−0.1	1.7
0.239	0.060	0.701	1350	1301*	+3.6	1323	+2.0	1.3

[a] The AAD (absolute average deviation) using the Cibulka equation[5] is 1.5. All these data were used for developing the Cibulka equation.[5] [b] The AAD using ANN[6] is 0.9. All of these data were used for developing the ANN[6] except the star marked data. $\Delta = |(H^E_{m,123} - H^E_{m,bin})/H^E_{m,123}|$ (calculated using the Cibulka equation[5]).

Tables 1a, 1b, 6, and 7 compare the measured and calculated/predicted values of excess molar enthalpies for the binary and ternary mixture of cyclohexane, tetrahydropyran (or 1,4-dioxane), and morpholine. The results are plotted in Figures 1 to 3.

Considering not all the experimental data in Tables 1a, 1b, 6, and 7 were used to develop the ANN, it can be regarded as a useful tool for modeling these systems with encouraging results with respect to the Cibulka equation,[5] as shown in Tables 6 and 7. In general, only experimental data on ternary

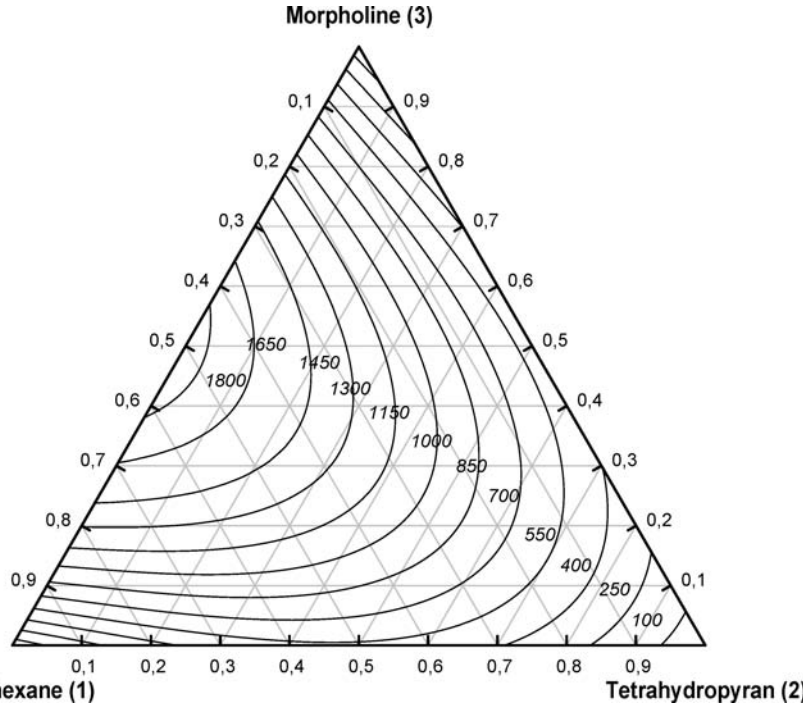

Figure 4. Curves of constant ternary excess molar enthalpy, $H^{E}_{m,123}$/J·mol^{-1}, calculated using the Cibulka equation,[5] for the cyclohexane (1) + tetrahydropyran (2) + morpholine (3) system, at 308.15 K and atmospheric pressure.

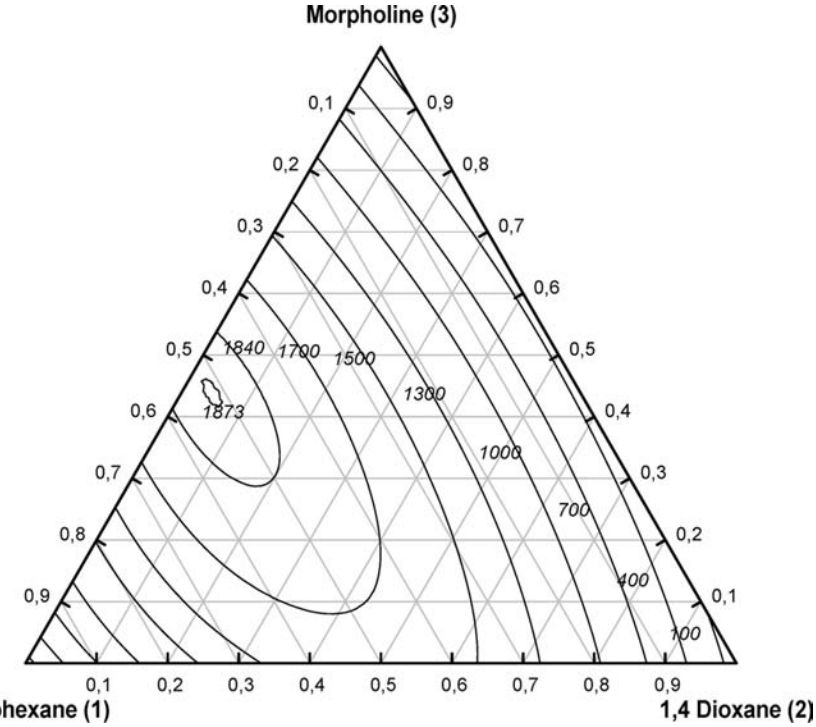

Figure 5. Curves of constant ternary excess molar enthalpy, $H^{E}_{m,123}$/J·mol^{-1}, calculated using the Cibulka equation,[5] for the cyclohexane (1) + 1,4-dioxane (2) + morpholine (3) system, at 308.15 K and atmospheric pressure.

systems are normally sufficient to develop reliable ANN, while both binary and ternary data are required for the Cibulka equation.[5] This can be regarded as one of the advantages of ANN over the Cibulka equation.[5]

Conclusions

We reported experimental excess molar enthalpy data for the binary and ternary mixtures of cyclohexane, cyclic ether (tetrahydropyran or 1,4-dioxane), and morpholine, at 308.15 K and atmospheric pressure, which were measured using a Calvet microcalorimeter. All the binary mixtures are formed endothermally and show symmetric H^{E} behavior. Cyclohexane + morpholine and 1,4-dioxane + morpholine systems have the largest and the lowest excess enthalpies among the five systems, respectively. The Redlich−Kister equation[4] was used to correlate the binary data. The ternary systems investigated also show an endothermic behavior in the whole range of compositions. The Cibulka equation[5] was employed to correlate the ternary data.

Table 8. Number of Neurons, Hidden Layers, Experimental Data, and the Type of Activation Function Used in This Algorithm[a]

layer	number of neurons
1	2
2	5
3	1

[a] Number of hidden layers = 1; number of data used for training (and testing) = 46; number of data used for validation = 8; type of activation function, tangent sigmoid; input neurons, mole fractions of cyclohexane (1) and tetrahydropyran (2); output neuron, $H^{E}_{m,123}/(RT)$. In developing the ANN,[6] three data corresponding to $H^{E}_{m,123} = 0$ for pure compounds were also considered.

Table 9. Number of Neurons, Hidden Layers, Experimental Data, and the Type of Activation Function Used in This Algorithm[a]

layer	number of neurons
1	2
2	5
3	1

[a] Number of hidden layers = 1; number of data used for training (and testing) = 41; number of data used for validation = 11; type of activation function, tangent sigmoid; input neurons, mole fractions of cyclohexane (1) and 1,4-dioxane (2); output neuron, $H^{E}_{m,123}/(RT)$. In developing the ANN,[6] three data corresponding to $H^{E}_{m,123} = 0$ for pure compounds were also considered.

Also, the calculated $H^{E}_{m,123}$ values from the Cibulka equation,[5] for the two ternary systems, are almost the same as those calculated from the binary contribution. A feed-forward artificial neural network algorithm[6] was then used to model satisfactorily the aforementioned experimental data with respect to the Cibulka equation.[5] Furthermore, the ANN presented here has shown good predictive power for both ternary and binary systems.

Acknowledgment

F.B.B. and G.B.-B. would like to thank the Algerian Ministry for the Higher Education and Scientific Research, and the Faculty of Chemistry of the University of Sciences and Technology Houari Boumediene (USTHB), for the opportunity to work as visiting scientists at CEP/TEP.

Literature Cited

(1) Hamoudi, Z.; Belaribi, F. B.; Ait-Kaci, A.; Belaribi-Boukais, G. Experimental and Predicted Excess Molar Enthalpies for 1,4-Dioxane+ Octane + Cyclohexane at 303.15K. *Fluid Phase Equilib.* **2006**, *244*, 62–67.

(2) Boukais-Belaribi, G.; Mohammadi, A. H.; Belaribi, F. B.; Richon, D. Excess Molar Enthalpies for the Binary and Ternary Mixtures of Cyclohexane, Tetrahydropyran and 1,4-Dioxane at 308.15 K and Atmospheric Pressure: Experimental Measurements and Correlations. *J. Chem. Eng. Data* **2009**, *54*, 2513–2516.

(3) Belaribi, F. B.; Boukais-Belaribi, G.; Mohammadi, A. H.; Richon, D. Excess Molar Enthalpies for the Binary and Ternary Mixtures of Cyclohexane, Tetrahydropyran and Piperidine at 308.15 K and Atmospheric Pressure: Experimental Measurements and Correlations. *J. Chem. Eng. Data* **2010**, *55*, 303−307.

(4) Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40/2*, 345–348.

(5) Cibulka, I. Estimation of excess volume and density of ternary liquid mixtures of non electrolytes from binary data. *Collect. Czech. Chem. Commun.* **1982**, *47*, 1414–1419.

(6) Chapoy, A.; Mohammadi, A. H.; Richon, D. Predicting the Hydrate Stability Zones of Natural Gases Using Artificial Neural Networks. *Oil Gas Sci. Technol.* **2007**, *62/5*, 701–706.

(7) Moelwyn-Hughes, E. A.; Thorpe, P. L. The Physical and Thermodynamic Properties of Some Associated Solutions. I. Dielectric Constants and Heats of Mixing. *Proc. R. Soc.* **1964**, *277A*, 423–436.

(8) Brocos, P.; Calvo, E.; Bravo, R.; Pintos, M.; Amigo, A.; Roux, A. H.; Roux-Desgranges, G. Heat capacities, excess enthalpies, and volumes of mixtures containing cyclic ethers. 3. Binary systems {Tetrahydrofuran, Tetrahydropyran, 1,4-Dioxane, or 1,3-Dioxolane + Cyclohexane or Toluene}. *J. Chem. Eng. Data* **1999**, *44*, 67–72.

(9) Lafuente, C.; Cea, P.; Dominguez, M.; Royo, F. M.; Urieta, J. S. Excess molar enthalpies of cyclic ethers with cyclohexane or chlorocyclohexane. *J. Solution Chem.* **2001**, *30* (9), 795–805.

(10) Marsh, K N. Excess enthalpy and excess volume of binary mixtures containing cyclohexane, benzene and tetrachloromethane. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1973**, *1*, 1–3.

(11) Zehioua, R.; Coquelet, C.; Soo, C. B.; Richon, D.; Meniai, A. H. Experimental and predicted excess molar enthalpies of some working pairs for absorption cycles. *Thermochim. Acta* **2009**, *495*, 72–80.

(12) Dahmani, O.; Ait-Kaci, A. Chaleurs de mélanges à 298.15 K du système ternaire cyclohexane (1) + benzene (2) + 1-chlorobutane (3). *J. Therm. Anal.* **1994**, *42*, 963–971.

Received for review November 27, 2009. Accepted January 14, 2010.

JE9010097