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†

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Excess molar enthalpies for the binary and ternary mixtures of cyclohexane, tetrahydropyran, and 1,4-dioxane 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 system are correlated using the Cibulka equation. The capability of the artificial neural network algorithm to model these data is finally studied.

Introduction

Excess thermodynamic properties of liquid mixtures are of great interest to the convenient design of industrial processes and also to provide useful information on molecular interactions required for optimizing thermodynamic model development.[1] Compared to large numbers of data reported in the literature for binary systems, the experimental data for ternary mixtures remain quite scarce. Consequently, we are focusing our current effort on ternary systems. In this article, we report the excess molar enthalpies for the binary and ternary mixtures of cyclohexane, tetrahydropyran, and 1,4-dioxane at 308.15 K and atmospheric pressure. To our knowledge, there was no previous literature information related to the excess molar enthalpy on this ternary system. All reported experimental data have been measured using a Calvet microcalorimeter.[1] The Redlich−Kister equation[2] is used to correlate the experimental binary data. The ternary experimental data are correlated using the Cibulka equation.[3] The capability of the artificial neural network (ANN) algorithm as an alternative method to model these (binary and ternary) data is finally investigated.

Experimental Section

Materials. Purities and suppliers of materials are provided in Table 1.

Experimental Apparatus and Procedure. The experimental enthalpy data were measured at atmospheric pressure by means of a flow calorimeter [Calvet microcalorimeter, type C80 with reversal mixing vessel (made of stainless steel, vessel volume = 12.5 cm^3), Setaram, Lyon, France].[1] The temperature was maintained constant at (308.15 ± 0.02) K. Check measurements on (cyclohexane + benzene) were in good agreement with the data reported by Marsh,[4] within 3 % over the entire range of concentrations. The estimated uncertainties, σ, in mole fractions, x_i, and excess molar enthalpies, h^E, are $\sigma(x_i) = 0.001$ and $\sigma(h^E) = 5\ J \cdot mol^{-1}$, respectively.

Table 1. Purities and Suppliers of Materials

chemical	CAS number	supplier	purity (GC)
cyclohexane	110-82-7	Merck	> 0.99
tetrahydropyran	142-68-7	Fluka	> 0.99
1,4-dioxane	123-91-1	Fluka	> 0.99

To measure experimental molar enthalpy of mixing, $h^E_{m,\phi}$, 1,4-dioxane was added to the binary mixtures composed of cyclohexane and tetrahydropyran, and the calorimetric measurements were then performed. Using the measured calorimetric values for $h^E_{m,\phi}$ and for binary systems, the ternary excess molar enthalpy, $h^E_{m,123}$, can be estimated using the following equation[1]

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

where x_3 represents the mole fraction of 1,4-dioxane in the ternary mixture and $h^E_{m,12}$ is the excess molar enthalpy of the binary mixture of cyclohexane + tetrahydropyran at constant ratio of mole fractions of cyclohexane and tetrahydropyran in their binary mixtures.[1]

Results and Discussion

The experimental excess molar enthalpies for the binary and ternary mixtures of cyclohexane, tetrahydropyran, and 1,4-dioxane are reported in Tables 2 and 3, respectively. As can be observed, the excess molar enthalpies for the binary and ternary systems are positive over the whole range of concentrations. Table 3 also reports experimental molar enthalpy of mixing, $h^E_{m,\phi}$, for the pseudobinary mixtures of the above-mentioned systems.

Correlation of Data. The experimental binary data were correlated using the Redlich−Kister equation[2]

$$h^E_{m,12}/J \cdot mol^{-1} = x(1 - x)\sum_{i=0}^{n} A_i(2x - 1)^i \quad (2)$$

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Table 2. Experimental and Calculated/Predicted Excess Molar Enthalpies, h^E/J·mol^{-1}, for the Binary Mixtures at 308.15 K and Atmospheric Pressure (All the Experimental Data for ANN Were Used for Validation)[a,b,c]

x/mole fraction	exptl h^E/J·mol^{-1}	calcd h^E/J·mol^{-1} using Redlich−Kister equation[2]	AD % using Redlich−Kister equation[2]	predicted h^E/J·mol^{-1} using ANN	AD % using ANN
		x cyclohexane + (1 − x) 1,4-dioxane			
0.101	570	568	0.4	568	0.4
0.204	1050	1052	0.2	1078	2.7
0.288	1333	1335	0.2	1299	2.6
0.408	1565	1561	0.3	1432	8.5
0.506	1620	1620	0.0	1459	9.9
0.606	1574	1579	0.3	1433	9.0
0.705	1435	1432	0.2	1323	7.8
0.803	1150	1149	0.1	1035	10.0
0.900	695	696	0.1	505	27.3
		x cyclohexane + (1 − x) tetrahydropyran			
0.101	157	156	0.6	169	7.6
0.200	294	295	0.3	294	0.0
0.300	412	411	0.2	406	1.5
0.400	490	490	0.0	479	2.2
0.499	526	528	0.4	509	3.2
0.606	519	517	0.4	479	7.7
0.699	461	462	0.2	405	12.1
0.800	355	354	0.3	285	19.7
0.900	198	199	0.5	150	24.2
		x tetrahydropyran + (1 − x) 1,4-dioxane			
0.104	149	150	0.7	160	7.4
0.201	249	249	0.0	264	6.0
0.299	315	315	0.0	325	3.2
0.398	352	352	0.0	348	1.1
0.497	361	362	0.3	342	5.3
0.612	342	342	0.0	306	10.5
0.716	296	295	0.3	252	14.9
0.800	235	235	0.0	198	15.7
0.900	135	135	0.0	125	7.4

[a] AD = |(experimental value − predicted value)/experimental value|. AAD = $(1/M)\sum_{i=1}^{M}$ |(experimental value − predicted value)/experimental value|, where M represents the number of experimental data. [b] Using the ANN algorithm, the ADD for the cyclohexane + 1,4-dioxane mixture, 8.7; ADD for the cyclohexane + tetrahydropyran mixture, 8.7; ADD for the tetrahydropyran + 1,4-dioxane mixture, 7.9. None of these data were used for developing the ANN. The number of adjustable parameters in the ANN equals 13. [c] Using the Redlich−Kister equation,[2] the ADD for the cyclohexane + 1,4-dioxane mixture, 0.2; ADD for the cyclohexane + tetrahydropyran mixture, 0.3; ADD for the tetrahydropyran + 1,4-dioxane mixture, 0.1. All these data were used for developing the Redlich−Kister equation.[2] The number of adjustable parameters in the Redlich−Kister equation[2] equals 18.

Table 3. Measured Molar Enthalpies of Mixing, $h_{m,\phi}^E$/J·mol^{-1}, and Excess Molar Enthalpies, $h_{m,123}^E$/J·mol^{-1}, for the Ternary Mixture of Cyclohexane (1) + Tetrahydropyran (2) + 1,4-Dioxane (3) at 308.15 K and Atmospheric Pressure

x_1	x_2	x_3	$h_{m,\phi}^E$/J·mol^{-1}	$h_{m,123}^E$/J·mol^{-1}
0.183	0.728	0.089	178	448
0.167	0.664	0.169	315	561
0.140	0.559	0.300	440	647
0.120	0.479	0.401	506	683
0.100	0.398	0.502	519	666
0.068	0.271	0.661	486	586
0.060	0.240	0.700	455	544
0.040	0.160	0.799	350	409
0.020	0.081	0.898	191	221
0.449	0.449	0.102	315	789
0.400	0.400	0.200	535	957
0.350	0.350	0.300	684	1054
0.300	0.300	0.399	791	1108
0.250	0.250	0.500	842	1106
0.201	0.201	0.599	818	1030
0.150	0.150	0.700	708	866
0.100	0.100	0.801	558	663
0.050	0.050	0.900	312	365
0.719	0.180	0.101	497	815
0.638	0.160	0.202	817	1100
0.560	0.141	0.299	1025	1273
0.480	0.121	0.399	1187	1400
0.398	0.100	0.503	1265	1441
0.319	0.080	0.600	1220	1361
0.240	0.060	0.700	1095	1201
0.155	0.039	0.807	805	873
0.080	0.020	0.900	477	512

Table 4. Values of Coefficients of A_i in Equation 2 for the Binary Mixtures of Cyclohexane (1), Tetrahydropyran (2), and 1,4-Dioxane (3)

coefficient	1, 2	1, 3	2, 3
A_0	2112.207	6477.221	1447.017
A_1	303.5701	300.2792	−67.3926
A_2	−230.4609	1437.965	171.029
A_3	0	958.2926	0
A_4	0	−1002.569	0

Table 5. Values of Coefficients of B_i in Equation 3 for the Ternary Mixture of Cyclohexane (1) + Tetrahydropyran (2) + 1,4-Dioxane (3)

coefficient	value
B_0	−375.737343
B_1	−3027.01222
B_2	887.929538

The coefficients A_i were obtained by an unweighted least-squares regression method. Table 4 presents the $A_i$coefficients obtained from eq 2 for three binary systems. In the above equation, n represents number of parameters and x stands for the first component in the binary mixture. The results of the Redlich−Kister equation[2] are reported in Table 2.

Several correlations for ternary excess molar enthalpies are available in the literature. In the present work, the experimental ternary data were correlated using the Cibulka equation[3]

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

The term $h_{m,bin}^E$ is known as the binary contribution to the excess molar enthalpies, which is given by[3]

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

where $h_{m,ij}^E$ is the excess enthalpy calculated from the correlated data of the $i-j$ pair (eq 2) using the ternary mole fractions x_i and x_j. This simplest method assumes that there are no ternary effects; i.e., the ternary excess enthalpy is just a sum of the binary heats of mixing.

The parameters B_i of eq 3 determined by the unweighted least-squares regression method are listed in Table 5. The results of the Cibulka equation[3] are reported in Table 6.

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.[5] 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.[5]

Feed-forward neural networks are the most frequently used and are designed with one input layer, one output layer, and

Table 6. Comparison between Measured and Calculated Values of Excess Molar Enthalpies, $h^E_{m,123}$/J·mol^{-1}, for the Ternary Mixture of Cyclohexane (1) + Tetrahydropyran (2) + 1,4-Dioxane (3) at 308.15 K and Atmospheric Pressure (All the Experimental Data Were Used for Training and Testing Steps in ANN)[a,b]

		measured $h^E_{m,123}$	calcd $h^E_{m,123}$	AD % using	calcd $h^E_{m,123}$	AD % using
x_1	x_2	J·mol^{-1}	J·mol^{-1} using Cibulka equation[3]	Cibulka equation[3]	J·mol^{-1} using ANN	ANN
0.1826	0.728	448	449	0.2	416	7.1
0.1666	0.6643	561	551	1.8	511	8.9
0.1403	0.5594	647	660	2.0	620	4.2
0.1201	0.4789	683	695	1.8	659	3.5
0.0998	0.3978	666	690	3.6	658	1.2
0.0679	0.271	586	593	1.2	574	2.0
0.0601	0.2397	544	552	1.5	537	1.3
0.0402	0.1604	409	415	1.5	406	0.7
0.449	0.4493	790	774	2.0	786	0.5
0.3998	0.4	958	942	1.7	977	2.0
0.35	0.3502	1054	1051	0.3	1082	2.7
0.3002	0.3004	1109	1103	0.5	1120	1.0
0.2499	0.2501	1107	1097	0.9	1101	0.5
0.2005	0.2007	1030	1026	0.4	1026	0.4
0.1499	0.15	867	880	1.5	881	1.6
0.0997	0.0998	664	653	1.7	650	2.1
0.0502	0.0503	365	356	2.5	335	8.2
0.7186	0.1804	816	811	0.6	754	7.6
0.6382	0.1602	1100	1119	1.7	1109	0.8
0.5602	0.1407	1274	1306	2.5	1281	0.5
0.4804	0.1206	1400	1407	0.5	1349	3.6
0.3977	0.0998	1442	1423	1.3	1352	6.2
0.3194	0.0802	1362	1352	0.7	1298	4.7
0.24	0.0603	1202	1179	1.9	1165	3.1
0.1546	0.0388	874	863	1.3	875	0.1

[a] ADD using Cibulka equation:[3] 1.4. All these data were used for developing the Cibulka equation.[3] The number of adjustable parameters in the Cibulka equation[3] equals 21. [b] ADD using ANN: 2.9. All these data were used for developing the ANN. The number of adjustable parameters in the ANN equals 13.

Table 7. Number of Neurons, Hidden Layers, Parameters, Data, and Type of Activation Function Used in This Algorithm[a]

layer	number of neurons
1	2
2	3
3	1

[a] Number of hidden layers = 1. Number of parameters = 13. Number of data used for training (and testing) = 28. Number of data used for validation = 29. Type of activation function: Exponential sigmoid. Input neurons: mole fractions of cyclohexane (1) and tetrahydropyran (2). Output neuron: $h^E_{m,123}/(RT)$. In developing the ANN, three data corresponding to $h^E_{m,123} = 0$ for pure compounds were also considered.

hidden layers.[5] The number of neurons in the input and output layers equals the number of inputs and outputs, respectively.[5] The accuracy of model representation depends on the architecture and parameters of the neural network.[5]

To develop the ANN, the data sets are generally subdivided into three groups corresponding to the following three steps: training, testing, and validation.[5] 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.[5] 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.[5]

Table 7 reports the summary of the feed-forward ANN used in this work along with number of neurons, hidden layers, parameters, data, and type of activation function. Tables 2 and 6 compare the measured and calculated/predicted values of excess molar enthalpies for the mixture of cyclohexane, tetrahydropyran, and 1,4-dioxane. It should be mentioned that to develop this algorithm the ternary data reported in Table 3 were used for training (and testing). The binary data reported in Table 2 were then used for validation. Considering the ANN developed in this work requires 13 adjustable parameters while the number of these parameters in the Cibulka equation[3] equals 18, the ANN can be regarded as a useful tool for modeling these systems with encouraging results (for the ternary mixture, the ADD value obtained using the Cibulka equation[3] is equal to 1.4, while this value using the ANN is 2.9). As mentioned earlier, the binary data were used for validation of the ANN. In other words, no experimental data reported in Table 2 were used to adjust parameters of ANN, while these data were used to adjust parameters of the Redlich−Kister equation.[2] Again, the ANN provides encouraging results for the binary systems considering the ANN requires 13 adjustable parameters while the number of these parameters in the Redlich−Kister equation[2] equals 15. In the absence of binary data, experimental data on ternary systems can be used to develop an ANN, while both binary and ternary data are required for the Cibulka equation.[3] This can be regarded as one of the advantages of ANN over the Cibulka equation.[3] Of course, by using binary data for adjusting parameters of the ANN, in addition to ternary data, more accurate ANN results for binary systems can be expected. We are fully aware that the ANN procedure was applied to a low number of data, and this procedure would largely gain in accuracy by developing a slightly broader database constituted of well-distributed data. This is a remark to take into account for further works.

Conclusions

We reported experimental excess molar enthalpy data for the binary and ternary mixtures of cyclohexane, tetrahydropyran,

and 1,4-dioxane at 308.15 K and atmospheric pressure, which were measured using a Calvet microcalorimeter.[1] The Redlich−Kister equation[2] was used to correlate the binary data, while the Cibulka equation[3] was employed to correlate the ternary data. A feed-forward artificial neural network algorithm[5] was then used to model satisfactorily the above-mentioned experimental data.

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