

Excess enthalpies of systems containing unsaturated hydrocarbons by UNIFAC group contribution

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Abstract

The original UNIFAC model is fitted to binary excess enthalpy (H^E) data and tested for its ability to correlate and predict binary H^E in systems containing unsaturated hydrocarbons.

The experimental H^E data have been obtained for seven systems over the whole concentration range at 298.15 K: 1-decene–*n*-decane, 1-heptene–*n*-dodecane, 1-heptyne–*n*-dodecane, 3-heptyne–*n*-dodecane, 1-nonene–4-nonyne, 1-octyne–benzene, 2-octyne–ethylbenzene and for 1-nonene–1-butanol at 313.15 K.

The model represents satisfactory experimental H^E for most binary systems considered. However, in long-chain 1-alkene–*n*-alkane systems, the H^E values are poorly predicted. A significant improvement is observed for H^E prediction in these systems using double values of group surface area.

INTRODUCTION

The original UNIFAC [1] based on vapor–liquid equilibrium (VLE) data is a well established group-contribution model for predicting liquid-phase activity coefficients. However, the prediction of excess enthalpy (H^E) using its interaction parameters leads at most to results which are in qualitative agreement with experiment [2]. The “average” parameters based on both the VLE and H^E data used in modifications of UNIFAC which permit us simultaneously to predict H^E and VLE, have considerably improved the results of predicting H^E [3, 4], but for H^E the best results have been obtained using the group interaction parameters of some UNIFAC modifications based on H^E data only [5, 6].

In order to predict H^E by the original UNIFAC model acceptably well, we constructed a separate UNIFAC group interaction parameter matrix especially suited to H^E within a narrow temperature range. Most attention was paid to the description of H^E in binary systems containing either unsaturated hydrocarbons, *n*-alkenes or *n*-alkynes as one of the com-

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ponents. Such a parameter matrix of the original UNIFAC has been given in refs. 7 and 8. However, the absence of interaction parameters for many groups with double and triple bonds restricts the use of this table.

The excess enthalpies of eight binary systems were measured in order to extend the experimental base of H^E for the above-mentioned systems.

EXPERIMENTAL

Analytical grade 1-alkenes and isomeric alkynes synthesized in our laboratory [9] were fractionally distilled in a 50-plate Teflon bristle-rotor column [10] to purity more than 99.5% as detected by gas chromatography. All measurements were made with freshly purified alkynes. All the substances were stored under an argon atmosphere and protected from light and moisture. *n*-Alkanes, 1-butanol, benzene and ethylbenzene obtained from Reakhim (Kharkov, USSR) in high purity (puriss, p.a. greater than 99%) were used without further purification.

Details of the measurements of excess enthalpies at 298.15 K over the entire composition range of mixtures have been outlined in a previous paper [11]. Errors of determination of H^E and liquid phase mole fraction, X , were estimated to be lower than 2% and 1×10^{-3} , respectively.

Estimation of the UNIFAC interaction parameters on the basis of experimental H^E data was realized using the simplex method, the Nelder-Mead procedure, described in detail by Fredenslund et al. (ref. 1, pp. 79–85) as pointed out in our earlier paper [12].

RESULTS AND DISCUSSION

Table 1 presents the experimental H^E data for the eight binary systems investigated in this work. They were fitted using the equation

$$H^E = X_1 X_2 \sum_{i=1}^n A_i (X_1 - X_2)^{i-1} \quad (1)$$

Table 2 lists the values of coefficients A_i calculated by the least squares method affording the best fit, and the corresponding standard deviations $\sigma(H^E)$.

Table 3 contains the interaction parameters of eleven groups in pairs. In a temperature range of 288 to 323 K the group parameters were assumed to be independent of temperature.

The correlation results given in Table 4 reflect a relative average error ($\delta H^E = \sum_{i=1}^n |H_{\text{exp}}^E - H_{\text{calc}}^E| / H_{\text{exp}}^E \times 100$ (%)), of 28% for all the system sets (274) recalculated using the group interaction parameters obtained and 18% for sets of systems containing unsaturated hydrocarbons (121) among them. Due to the insufficiency of experimental data some interaction parameters were evaluated from one set only. For the other mixtures

TABLE 1

Experimental excess enthalpy H^E ($J mol^{-1}$) at 298.15 K for binary systems

| System | x_1 | H^E | System | x_1 | H^E | |
|---|------------------------------|-------|------------------------------|---------------------------------|-----------------------------|-------|
| 1-Decene (x_1)–decane | 0.154 | 19 | 3-Heptyne (x_1)–dodecane | 0.177 | 300 | |
| | 0.228 | 24 | | 0.276 | 440 | |
| | 0.271 | 28 | | 0.400 | 575 | |
| | 0.441 | 38 | | 0.495 | 602 | |
| | 0.477 | 38 | | 0.508 | 605 | |
| | 0.530 | 39 | | 0.600 | 610 | |
| | 0.633 | 35 | | 0.700 | 561 | |
| | 0.724 | 28 | | 0.820 | 376 | |
| | 0.855 | 18 | | 0.870 | 333 | |
| | 1-Heptene (x_1)–dodecane | 0.179 | | 45 | 1-Nonene (x_1)–4-nonyne | 0.176 |
| 0.291 | | 66 | 0.237 | 76 | | |
| 0.425 | | 87 | 0.334 | 93 | | |
| 0.453 | | 92 | 0.403 | 103 | | |
| 0.472 | | 93 | 0.481 | 110 | | |
| 0.548 | | 97 | 0.537 | 114 | | |
| 0.594 | | 95 | 0.643 | 112 | | |
| 0.648 | | 95 | 0.756 | 85 | | |
| 0.758 | | 77 | 0.840 | 59 | | |
| 0.900 | | 37 | 0.156 | 133 | | |
| 1-Heptyne (x_1)–dodecane | 0.095 | 218 | 1-Octyne (x_1)–benzene | 0.204 | 153 | |
| | 0.227 | 429 | | 0.298 | 168 | |
| | 0.388 | 615 | | 0.470 | 166 | |
| | 0.554 | 684 | | 0.522 | 164 | |
| | 0.561 | 692 | | 0.634 | 137 | |
| | 0.696 | 630 | | 0.672 | 120 | |
| | 0.815 | 491 | | 0.855 | 58 | |
| | 0.908 | 273 | | 2-Octyne (x_1)–ethylbenzene | 0.227 | –56 |
| | 0.067 | 168 | | | 0.303 | –63 |
| | 0.102 | 272 | | | 0.365 | –69 |
| 0.130 | 355 | 0.432 | –68 | | | |
| 0.176 | 464 | 0.566 | –64 | | | |
| 0.264 | 638 | 0.678 | –56 | | | |
| 1-Nonene (x_1)–1-butanol ^a | 0.455 | 926 | 0.820 | –33 | | |
| | 0.508 | 1005 | | | | |
| | 0.628 | 1110 | | | | |
| | 0.735 | 1088 | | | | |
| | 0.765 | 1053 | | | | |
| | 0.795 | 1009 | | | | |

^a Measured at 313.15 K.

TABLE 2

Coefficients A_i in eqn. (1) and standard deviations $\sigma(H^E)$ for binary mixtures given in Table 1

| System | A_0 | A_1 | A_2 | A_3 | A_4 | $\sigma(H^E)$ |
|-----------------------|---------|---------|---------|---------|----------|---------------|
| 1-Decene–decane | 155.47 | –0.30 | –112.17 | –1.83 | 171.98 | 0.69 |
| 1-Heptene–dodecane | 378.40 | 130.22 | 37.41 | –94.55 | | 1.15 |
| 1-Heptyne–dodecane | 2705.63 | 746.30 | 313.96 | –424.36 | | 8.23 |
| 3-Heptyne–dodecane | 2426.46 | 509.78 | | | | 15.13 |
| 1-Nonene–4-nonyne | 448.40 | 103.63 | 37.76 | –160.40 | 239.93 | 2.30 |
| 1-Octyne–benzene | 658.88 | –300.01 | 49.13 | –205.00 | 274.08 | 3.45 |
| 2-Octyne–ethylbenzene | –273.82 | 74.07 | | | | 1.42 |
| 1-Nonene–1-butanol | 3936.86 | 2390.40 | 2990.38 | 153.05 | –2259.30 | 9.38 |

TABLE 3
Some UNIFAC group-interaction parameters a_{mn} based on the binary H^E data

| m | n | CH_2 | $\text{C}=\text{C}$ | $\text{HC}\equiv\text{C}$ | $\text{C}\equiv\text{C}$ | ACH | ACCH_2 | CCl_4 | OH | CCOH | CH_2O | CH_3CO |
|---------------------------|---------|---------------|---------------------|---------------------------|--------------------------|--------------|-----------------|----------------|-------------|---------------|-----------------------|------------------------|
| CH_2 | 0 | 259.80 | 456.64 | 501.16 | 93.20 | 170.53 | 59.94 | 981.13 | 600.41 | 264.42 | 585.42 | |
| $\text{C}=\text{C}$ | -145.53 | 0 | 100.66 | 145.08 | -46.96 | 3618.7 | -130.20 | 860.2 | 1263.6 | 86.07 | 201.94 | |
| $\text{HC}\equiv\text{C}$ | 181.46 | 202.65 | 0 | -83.49 | -86.91 | 101.00 | 3.13 | 872.66 | 781.76 | 298.96 | -131.12 | |
| $\text{C}\equiv\text{C}$ | 166.83 | 104.31 | 107.40 | 0 | -191.33 | 243.31 | -179.81 | 690.81 | 657.98 | 211.40 | 147.98 | |
| ACH | 70.99 | 92.66 | 102.68 | 156.50 | 0 | 50.75 | -7.06 | 753.31 | 692.92 | 51.05 | -93.99 | |
| ACCH_2 | -83.62 | -18.44 | 1103.5 | 520.31 | 122.64 | 0 | 21.31 | 698.44 | 718.28 | 522.57 | 281.22 | |
| CCl_4 | -6.20 | 145.54 | 134.72 | 172.52 | 30.03 | 19.52 | 0 | 788.08 | 690.25 | 54.98 | 266.40 | |
| OH | 190.98 | 282.35 | 221.27 | 612.74 | 59.31 | 307.00 | -97.45 | 0 | 0 | 347.95 | 466.68 | |
| CCOH | -82.15 | 51.86 | 317.98 | 611.81 | 28.37 | 48.80 | -131.24 | 0 | 0 | 481.57 | 526.65 | |
| CH_2O | 183.25 | 94.71 | -186.25 | -95.14 | -118.08 | 25.00 | -122.23 | 238.60 | 187.28 | 0 | 88.17 | |
| CH_3CO | 201.20 | 239.76 | 122.99 | -50.45 | 490.06 | 380.10 | -100.09 | 514.14 | 496.30 | 93.83 | 0 | |

containing the same groups the goodness of H^E calculation is uncertain. However for systems which are represented by several data sets the original UNIFAC seems to give the description results of H^E similar to those obtained by model modifications [3, 4, 6].

As a measure of the quality of H^E prediction, together with relative average deviations (δH^E (%)), the mean absolute deviations between the experimental and calculated H^E ($\bar{\Delta}H^E$ (J mol⁻¹)) and those divided by the difference between the highest and lowest experimental H^E values in the data set (norm. ΔH^E (%)) have been used.

The results of H^E prediction for the five binary systems investigated (Table 1) are given in Table 5. The data of the other systems in Table 1 have been used for a_{mn} evaluation.

In particular, the prediction of H^E seems to cause problems for alkene–alkane systems with long-chain molecules. An examination of the results included in Table 6 shows that for these systems it would be advantageous to double the group surface areas (Q_m) in H^E calculations taking into account the recommendation for mixtures containing small groups [17].

TABLE 4

Correlation of excess enthalpy data base by means of the UNIFAC model; group of surface areas (Q_m) are calculated according to Bondi [13] using the original normalization [1]

| System | Number of data sets ^a | Number of data points | δH (%) |
|---|----------------------------------|-----------------------|----------------|
| Alkanes | | | |
| + alkenes | 19 | 152 | 27.5 |
| + 1-alkynes | 10 | 133 | 7.0 |
| + <i>i</i> -alkynes (<i>i</i> = 2, 3, . .) | 7 | 103 | 7.5 |
| + aromatics | 10 | 96 | 4.9 |
| + alkylaromatics | 8 | 59 | 13.3 |
| + CCl ₄ | 5 | 45 | 6.8 |
| + alkanols (OH) | 10 | 122 | 8.4 |
| + alkanols (CCOH) | 10 | 122 | 14.3 |
| + ethers | 3 | 45 | 19.8 |
| + ketones | 7 | 133 | 20.8 |
| Alkenes | | | |
| + 1-alkynes | 2 | 17 | 2.4 |
| + <i>i</i> -alkynes (<i>i</i> = 2, 3, . .) | 3 | 18 | 5.5 |
| + aromatics | 8 | 49 | 7.7 |
| + alkylaromatics | 5 | 35 | 20.4 |
| + CCl ₄ | 6 | 75 | 9.4 |
| + alkanols (OH) | 8 | 90 | 10.5 |
| + alkanols (CCOH) | 8 | 90 | 13.3 |
| + ethers | 2 | 24 | 39.0 |
| + ketones | 3 | 20 | 3.0 |

TABLE 4 (continued)

| System | Number of data sets ^a | Number of data points | δH (%) |
|--|----------------------------------|-----------------------|----------------|
| 1-Alkynes | | | |
| + <i>i</i> -alkynes (<i>i</i> = 2, 3, . . .) | 1 | 17 | 5.3 |
| + aromatics | 3 | 26 | 16.1 |
| + alkylaromatics | 2 | 18 | 40.8 |
| + CCl ₄ | 3 | 42 | 62.7 |
| + alkanols (OH) | 6 | 66 | 18.0 |
| + alkanols (CCOH) | 6 | 66 | 18.2 |
| + ethers | 2 | 26 | 4.3 |
| + ketones | 1 | 8 | 17.9 |
| <i>i</i>-Alkynes (<i>i</i> = 2, 3, . . .) | | | |
| + aromatics | 1 | 12 | 9.9 |
| + alkylaromatics | 2 | 15 | 42.2 |
| + CCl ₄ | 4 | 49 | 5.6 |
| + alkanols (OH) | 3 | 19 | 15.9 |
| + alkanols (CCOH) | 3 | 19 | 16.0 |
| + ethers | 2 | 29 | 44.4 |
| + ketones | 1 | 10 | 6.2 |
| Aromatics | | | |
| + alkylaromatics | 4 | 39 | 5.3 |
| + CCl ₄ | 2 | 30 | 1.4 |
| + alkanols (OH) | 7 | 154 | 12.3 |
| + alkanols (CCOH) | 7 | 154 | 9.1 |
| + ethers | 5 | 17 | 19.1 |
| + ketones | 2 | 41 | 84.5 |
| Alkylaromatics | | | |
| + CCl ₄ | 3 | 22 | 42.3 |
| + alkanols (OH) | 5 | 69 | 14.4 |
| + alkanols (CCOH) | 5 | 69 | 9.6 |
| + ethers | 3 | 24 | 203.3 |
| + ketones | 3 | 61 | 212.8 |
| CCl₄ | | | |
| + alkanols (OH) | 6 | 84 | 66.5 |
| + alkanols (CCOH) | 6 | 84 | 66.6 |
| + ethers | 6 | 56 | 13.2 |
| + ketones | 4 | 70 | 77.9 |
| Alkanols (OH) | | | |
| + ethers | 5 | 91 | 27.5 |
| + ketones | 7 | 116 | 7.4 |
| Alkanols (CCOH) | | | |
| + ethers | 5 | 91 | 27.8 |
| + ketones | 6 | 100 | 13.1 |
| Ethers + ketones | 9 | 105 | 10.6 |

^a Most of the experimental data have been taken from refs. 14, 15 and 16.

TABLE 5

Results of H^E prediction for some binary systems investigated

| System | $\bar{\Delta}H^E$ (J mol ⁻¹) | norm. ΔH^E (%) | δH^E (%) |
|-------------------------------|--|------------------------|------------------|
| 1-Decene– <i>n</i> -decane | 13 | 32 | 42 |
| 1-Heptene– <i>n</i> -dodecane | 19 | 20 | 22 |
| 1-Heptyne– <i>n</i> -dodecane | 50 | 7 | 11 |
| 3-Heptyne– <i>n</i> -dodecane | 116 | 19 | 23 |
| 1-Nonene–1-butanol | 107 | 10 | 17 |

TABLE 6

Results ^a of prediction of binary H^E data for some 1-alkene–alkane systems using single (I) and double (II) Q_m values

| System | Temp (K) | Source of data | I | | | II | | |
|-----------------------|----------|----------------|-------------------|--------------------|--------------|-------------------|--------------------|--------------|
| | | | $\bar{\Delta}H^E$ | norm. ΔH^E | δH^E | $\bar{\Delta}H^E$ | norm. ΔH^E | δH^E |
| 1-Dodecene–octane | 298.15 | [15] | 27 | 36 | 49 | 2 | 3 | 4 |
| 1-Hexene–dodecane | 293.15 | [14] | 57 | 42 | 45 | 14 | 10 | 11 |
| 1-Dodecene–dodecane | 298.15 | [15] | 29 | 32 | 44 | 16 | 18 | 30 |
| 1-Octene–hexadecane | 298.15 | [14] | 68 | 42 | 54 | 28 | 17 | 23 |
| 1-Octene–hexadecane | 323.15 | [14] | 20 | 20 | 21 | 10 | 9 | 9 |
| 1-Decene–hexadecane | 298.15 | [15] | 46 | 39 | 48 | 9 | 8 | 10 |
| 1-Dodecene–hexadecane | 298.15 | [15] | 56 | 42 | 57 | 14 | 10 | 14 |

^a $\bar{\Delta}H^E$ (J mol⁻¹); norm. ΔH^E (%); δH^E (%).

Taking into account the results given in ref. 8 it is believed that the new group interaction parameters can now be applied to ternary and higher systems. It also enables us to predict H^E for mixtures of relatively unstable substances containing unsaturated bonds. In our laboratory, they are mostly used to study natural aromatic compounds. Evaluation of the interaction between some key components of aromatics in binary systems is now in progress.

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