J. Chem. Eng. Data **2004,** *49,* 311−312 **311**

Excess Enthalpies of Binary Mixtures of 1-Hexene with Some *n*-Alkanes at 298.15 K

Zhaohui Wang, George C. Benson,[†] and Benjamin C.-Y. Lu*

Department of Chemical Engineering, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

Excess molar enthalpies, measured at 298.15 K in a flow microcalorimeter, are reported for mixtures of 1-hexene with *n*-heptane, *n*-octane, *n*-decane, *n*-dodecane, and *n*-tetradecane. Smooth Redlich−Kister representations of the results are described. It was found that the Liebermann−Fried model also provided good representations of the data.

Introduction

The use of alkenes to improve the octane ratings of blended gasolines has provided an incentive to study the thermodynamic properties of mixtures of an alkene with various hydrocarbons. The present paper reports excess molar enthalpies, measured at 298.15 K, for binary mixtures of 1-hexene (1HX) with the following normal alkanes: *n*-heptane (nC7), *n*-octane (nC8), *n*-decane (nC10), *n*-dodecane (nC12), and *n*-tetradecane (nC14).

Experimental Section

The 1HX, nC7, nC8, nC10, nC12, and nC14 used in the present work were obtained from the Aldrich Chemical Co. In all cases the purities stated by the manufacturer were at least 99 mol %. Apart from partial degassing, the components were used without further purification. Densities, ρ/kg·m^{-3} at 298.15 K, measured with a precision of 0.03 kg·m^{-3} in an Anton-Paar digital densimeter (model DMA 02C), were 668.73, 680.17, 698.72, 726.30, 745.32, and 759.36 for 1HX, nC7, nC8, nC10, nC12, and nC14, respectively. These results agree within ±0.1% with the corresponding literature[1] values 668.48, 679.46, 698.62, 726.35, 745.18, and 759.20.

An LKB flow microcalorimeter (model 10700-1), thermostated at (298.150 ± 0.003) K, was used to measure the excess molar enthalpies $H^{\mathrm{E}}_{\mathrm{m}}$. Details of the equipment and its operation have been described previously.[2,3] Over most of the mole fraction range, the errors of the excess molar enthalpies and the mole fractions are estimated to be less than 0.5% and 5×10^{-4}, respectively.

Results and Discussion

Excess molar enthalpies, $H^{\mathrm{E}}_{\mathrm{m},12}$, measured at 298.15 K, for the five binary mixtures 1HX (1) + nC7 (2), 1HX (1) + nC8 (2), 1HX (1) + nC10 (2), 1HX(1) + nC12 (2), and 1HX (1) + nC14 (2) are listed in Table 1 and plotted in Figure 1.

The Redlich−Kister smoothing function

$$H^{\mathrm{E}}_{\mathrm{m},12}/\mathrm{J{\cdot}mol^{-1}} = x_1(1 - x_1)\sum_{k=1}^{n} h_k(1 - 2x_1)^{k-1}$$

was fitted to the results in Table 1 by a least-squares method, with all points weighted equally. Values of the coefficients h_k are listed in Table 2, along with the standard deviation *s* for the representation. Plots of those representations are shown as solid curves in Figure 1. For the five systems, the maximum of $H^{\mathrm{E}}_{\mathrm{m},12}$ occurs near $x_1 \approx 0.5$, and the value increases with the alkane chain length.

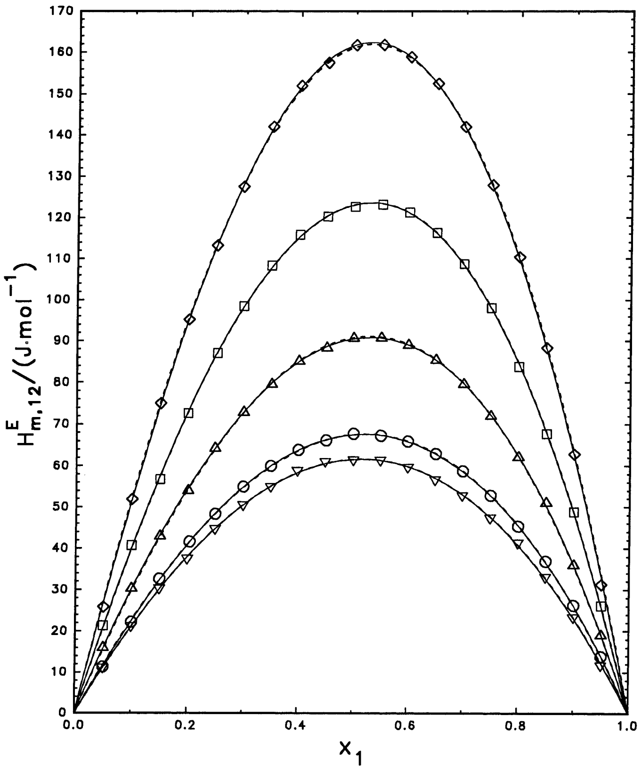

Figure 1. Excess molar enthalpies, $H^{\mathrm{E}}_{\mathrm{m},12}$, for 1HX (1) + *n*-alkane (2) at 298.15 K. Experimental results: ▽, nC7; ○, nC8; △, nC10; □, nC12; ◇, nC14. Curves: —, calculated from the representation of the results by eq 1 using the coefficients in Table 2; - - -, fit of the results by means of the Liebermann−Fried model.

Recent work[4,5] indicates that an extension of the model of Liebermann and Fried[6,7] can be useful in representing the excess enthalpies of binary mixtures and also has the potential for estimating the vapor−liquid equilibria of mixtures and the excess enthalpies of ternary mixtures, from data for the pure components and their binary mixtures. It is therefore of interest to examine how well the Liebermann−Fried model can represent the enthalpies of the present binary systems.

The equations used in this application have been outlined by Wang et al.[5] Values of the Liebermann−Fried

---

* Corresponding author. Telephone: +1-613-562-5800 (6097). Fax: +1-613-562-5172. E-mail: lu@eng.uottawa.ca.

[†] Deceased.

10.1021/je030215z CCC: $27.50

Table 1. Experimental Mole Fractions, x_1, and Excess Molar Enthalpies, $H^{E}_{m,12}$, for Mixtures of 1HX with nC7, nC8, nC10, nC12, and nC14 at 298.15 K

x_1	$\frac{H^{E}_{m,12}}{J \cdot mol^{-1}}$	x_1	$\frac{H^{E}_{m,12}}{J \cdot mol^{-1}}$	x_1	$\frac{H^{E}_{m,12}}{J \cdot mol^{-1}}$	x_1	$\frac{H^{E}_{m,12}}{J \cdot mol^{-1}}$
1HX (1) + nC7 (2)							
0.0500	11.13	0.2998	50.46	0.5498	61.38	0.8000	41.33
0.1000	21.21	0.3500	54.95	0.6000	59.65	0.8499	33.05
0.1499	30.30	0.3984	58.88	0.6496	56.64	0.9000	23.38
0.1998	37.57	0.4492	61.03	0.6992	52.81	0.9500	11.71
0.2496	44.68	0.5005	61.42	0.7497	47.37		
1HX (1) + nC8 (2)							
0.0500	11.36	0.3000	54.95	0.5499	67.25	0.8002	45.33
0.1000	22.25	0.3497	59.97	0.5994	65.86	0.8499	36.91
0.1500	32.65	0.3998	63.87	0.6500	62.90	0.9000	26.29
0.2036	41.61	0.4500	66.13	0.6998	58.72	0.9500	13.89
0.2496	48.28	0.5000	67.70	0.7501	52.79		
1HX (1) + nC10 (2)							
0.0500	16.10	0.2997	72.95	0.5501	90.82	0.7998	62.21
0.1000	30.36	0.3504	79.63	0.5996	89.04	0.8501	51.08
0.1503	43.01	0.3999	85.18	0.6496	85.48	0.9000	36.08
0.2001	54.05	0.4508	88.39	0.7004	79.66	0.9500	19.12
0.2482	64.31	0.4994	90.75	0.7495	72.05		
1HX (1) + nC12 (2)							
0.0501	21.42	0.2994	98.47	0.5505	123.20	0.8001	83.86
0.0999	40.79	0.3494	108.33	0.5998	121.29	0.8503	67.77
0.1500	56.75	0.4001	115.80	0.6501	116.32	0.8999	48.84
0.1999	72.63	0.4503	120.25	0.6999	108.77	0.9500	26.20
0.2521	87.06	0.5001	122.66	0.7499	98.08		
1HX (1) + nC14 (2)							
0.0500	25.84	0.2970	127.49	0.5497	161.77	0.7996	110.41
0.1001	51.92	0.3497	141.99	0.5998	158.83	0.8498	88.32
0.1501	74.99	0.4002	151.93	0.6495	152.44	0.8999	62.85
0.2003	95.19	0.4498	157.48	0.6996	141.90	0.9500	31.24
0.2499	113.18	0.5000	161.71	0.7502	127.83		

Table 2. Coefficients, h_k, and Standard Deviations, s, for the Representation of $H^{E}_{m,12}$ by Eq 1 for the Binary Mixtures at 298.15 K

component						s
1	2	h_1	h_2	h_3	h_4	$J \cdot mol^{-1}$
1HX	nC7	246.37	−14.39			0.33
1HX	nC8	270.08	−20.36	0.63	−9.71	0.19
1HX	nC10	362.13	−41.43	9.33		0.28
1HX	nC12	492.55	−59.45			0.43
1HX	nC14	647.34	−76.75	−20.30		0.66

Table 3. Values of the Interaction Parameters, A_{ij} and A_{ji}, Standard Deviations, s, and Isobaric Thermal Expansivities, α_p, at 298.15 K for the Liebermann−Fried Model Calculations

component				s	α_p (kK^{-1})	
i	j	A_{ij}	A_{ji}	$J \cdot mol^{-1}$	i	j
1HX	nC7	1.0344	0.9178	0.33	1.411[a]	1.256[b]
1HX	nC8	1.0646	0.8826	0.23	1.411[a]	1.164[b]
1HX	nC10	1.0986	0.8296	0.36	1.411[a]	1.051[b]
1HX	nC12	1.1107	0.7899	0.43	1.411[a]	0.960[b]
1HX	nC14	1.1104	0.7582	0.78	1.411[a]	0.886[c]

[a] Riddick et al.[8] [b] Benson et al.[9] [c] Estimated from density data.[1]

interaction parameters, A_{ij} and A_{ji}, for each of the binary mixtures are given in Table 3. These were obtained by fitting the Liebermann−Fried formula for $H^{E}_{m,ij}$ to the primary experimental results in Table 1. Also included in Table 3 are values of the standard deviations s achieved in the fitting process and values[8,9] of the isobaric thermal expansivities, α_p, of the components, used in evaluating the contributions due to different molecular sizes. It is evident from a comparison of the standard deviations in Tables 2 and 3 that the Liebermann−Fried model provides fits of the experimental data which are very similar to those obtained with the Redlich−Kister forms. This is illustrated in Figure 1, where the Liebermann−Fried values of $H^{E}_{m,12}$ are shown as broken curves and are hardly distinguishable from the solid Redlich−Kister fits.

Literature Cited

(1) *TRC Thermodynamic Tables—Hydrocarbons*; Thermodynamic Research Center, The Texas A&M University System: College Station, TX, 1996; 1961 loose-leaf data sheet 23-2-(5.1201)-a; 1995 loose-leaf data sheet 23-2-(1.10100)-a, page 1; 1976 loose-leaf data sheet 23-2-(1.101)-a, page 2; 1973 loose-leaf data sheet 23-2-(1.101)-d, page 5.

(2) Tanaka, R.; D'Arcy, P. J.; Benson, G. C. Application of a Flow Microcalorimeter to Determine the Excess Enthalpies of Binary Mixtures of Nonelectrolytes. *Thermochim. Acta* **1975**, *11*, 163−175.

(3) Kimura, F.; Benson. G. C.; Halpin, C. J. Excess Enthalpies of Binary Mixtures of *n*-Heptane with Hexane Isomers. *Fluid Phase Equilib.* **1983**, *11*, 245−250.

(4) Peng, D.-Y.; Wang, Z.; Benson, G. C.; Lu, B. C.-Y. Excess Enthalpies and (Vapor + Liquid) Equilibrium for (Oxygenated Additive + *n*-Alkane). *J. Chem. Thermodyn.* **2001**, *33*, 83−93.

(5) Wang, Z.; Peng, D.-Y.; Benson, G. C.; Lu, B. C.-Y. Excess Enthalpies of {Ethyl *tert*-Butyl Ether + Hexane + Heptane, or Octane} at the Temperature 298.15 K. *J. Chem. Thermodyn.* **2001**, *33*, 1181−1191.

(6) Liebermann, E.; Fried, V. Estimation of the Excess Gibbs Free Energy and Enthalpy of Mixing of Binary Nonassociated Mixtures. *Ind. Eng. Chem. Fundam.* **1972**, *11*, 350−354.

(7) Liebermann, E.; Fried, V. The Temperature Dependence of the Excess Gibbs Free Energy of Binary Nonassociated Mixtures. *Ind. Eng. Chem. Fundam.* **1972**, *11*, 354−355.

(8) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Techniques of Chemistry, Volume II, Organic Solvents*, 4th ed.; Wiley: New York, 1986; see page 168.

(9) Benson, G. C.; Luo, B.; Lu, B. C.-Y. Excess Enthalpies of Dibutyl Ether + *n*-Alkane Mixtures at 298.15 K. *Can. J. Chem.* **1988**, *66*, 531−534.

Received for review August 15, 2003. Accepted November 24, 2003. The financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.

JE030215Z