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Excess molar enthalpies of binary mixtures of 1-hexene with some cyclic and aromatic hydrocarbons at 298.15 K

Zhaohui Wang, George C. Benson, Benjamin C.-Y. Lu*

Department of Chemical Engineering, University of Ottawa, Ottawa, Ont., Canada K1N 6N5

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Abstract

Microcalorimetric measurements of excess molar enthalpies, at 298.15 K, are reported for the four binary systems formed by mixing 1-hexene with the cycloalkanes: cyclohexane and methylcyclohexane, and with the aromatic hydrocarcons: benzene and toluene. Smooth Redlich–Kister representations of the results are presented. It was found that the Liebermann–Fried model also provided good representations of the results.

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1. Introduction

The thermodynamic properties of alkene + hydrocarbon mixtures are of interest in view of the use of alkenes to improve the octane ratings of blended gasolines. Recent papers, from our laboratory, reported excess molar enthalpies at 298.15 K for the binary systems formed by mixing 1-hexene (1HX) with either some normal [1] or branched [2] alkanes. As a continuation of those investigations, similar measurements have been made for the binary systems formed by mixing 1HX with the cycloalkanes: cyclohexane (cC6) and methylcyclohexane (MCH), and with the aromatic hydrocarbons: benzene (Bnz) and toluene (Tol).

2. Experimental

The components used for the present measurements, were obtained from the Aldrich Chemical Co. All had stated purities exceeding 99.0 mol%. Apart from partial degassing, the components were used as received from the manufacturer. Densities, measured at 298.15 K in an Anton–Paar digital densimeter, were 668.73, 773.94, 765.11, 873.69, and 862.33 $\mathrm{kg\,m^{-3}}$ for 1HX, cC6, MCH, Bnz and Tol, respectively. These are in reasonable agreement with values in [3].

An LKB flow microcalorimeter (Model 10700-1), maintained at 298.150 ± 0.003 K, was used to measure the excess molar enthalpies H_m^E. Details of the equipment and the operating procedure have been described previously [4,5]. Over most of the mole-fraction range, the errors of the excess molar enthalpies and the mole fractions of the mixtures are estimated to be $<0.005|H_\mathrm{m}^\mathrm{E}|$ and $<5 \times 10^{-4}$, respectively.

3. Results and discussion

Excess molar enthalpies $H_{\mathrm{m},12}^\mathrm{E}$, at $T = 298.15$ K, for the four binary systems:1HX(1) + cC6(2), 1HX(1) + MCH(2), 1HX(1) + Bnz(2), and 1HX(1) + Tol(2) are reported in Table 1 and plotted in Fig. 1. Coefficients h_k for the representations of the results by the Redlich–Kister smoothing function

$$H_{\mathrm{m},12}^\mathrm{E}\ (\mathrm{J\,mol^{-1}}) = x_1(1-x_1)\sum_{k=1}^{m} h_k(1-2x_1)^{k-1} \qquad (1)$$

are listed in Table 2, along with the standard deviations, *s*, of the representations. Plots of these representations are shown as solid curves in Fig. 1.

Previously, excess molar enthalpies of 1HX(1) + Bnz(2) have been reported by Karbalai Ghassemi and Grolier [6].

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* Corresponding author. Tel.: +1-613-562-5800x6097; fax: +1-613-562-5172.

E-mail address: lu@eng.uottawa.ca (B.C.-Y. Lu).

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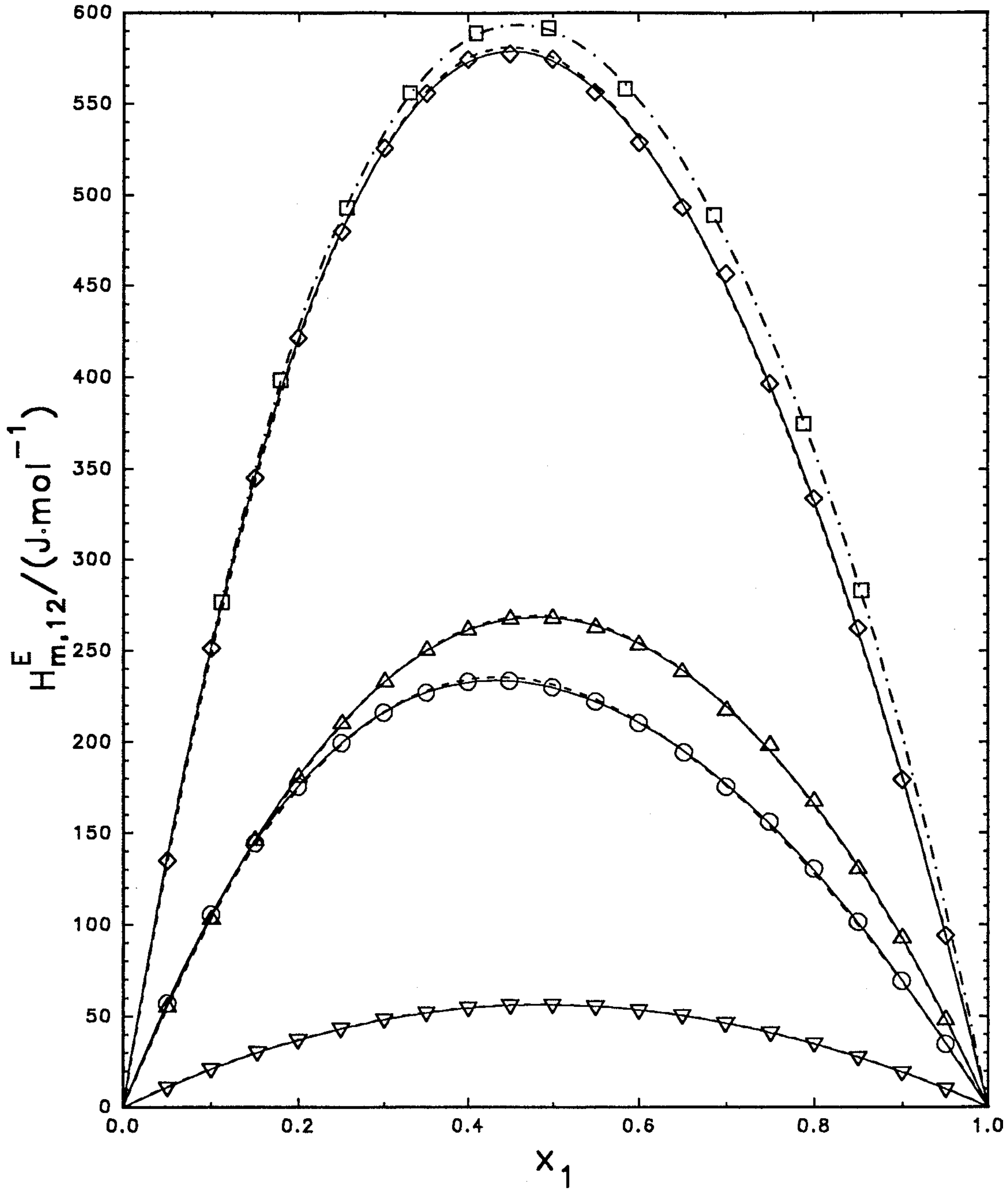

Fig. 1. Excess molar enthalpies, $H^{E}_{m,12}$, for 1HX(1) + cycloalkane(2) and 1HX(1) + aromatic hydrocarbon(2) mixtures at 298.15 K, plotted against mole fraction x_1. Experimental results: (△) Tol; (○) cC6; (▽) MCH; (◇) Bnz; (□) Karbalai Ghassemi and Grolier [6]. Curves: (—) calculated from Eq. (1); (- - -) estimated by the Liebermann–Fried model; (– · –), Karbalai Ghassemi and Grolier [6].

Their results along with their Redlich–Kister representation are plotted in Fig. 1 for comparison. For an equimolal mixture, they are ≈13 J mol^{-1} higher than our curve and the deviations become more evident at higher mole fractions.

Recently [7,8], it was found that the Liebermann–Fried model [9,10] 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. This approach was found to be useful in recent considerations of mixtures involving 1HX with normal [1] and branched alkanes [2]. It is therefore of interest to examine how well the Liebermann–Fried model can represent the results for the present systems. Reference can be made to the work of Wang et al. [8] for the equations used in this application.

The values of the Liebermann–Fried interaction parameters A_{ij} and A_{ji} for the four binary mixtures are

Table 1
Experimental mole fractions x_1 and excess molar enthalpies $H^{\mathrm{E}}_{\mathrm{m},12}$ ($\mathrm{J\,mol^{-1}}$) for binary mixtures of 1HX(1) with cC6(2), MCH(2), Bnz(2), and Tol(2) at 298.15 K

x_1	$H^{\mathrm{E}}_{\mathrm{m},12}$	x_1	$H^{\mathrm{E}}_{\mathrm{m},12}$	x_1	$H^{\mathrm{E}}_{\mathrm{m},12}$	x_1	$H^{\mathrm{E}}_{\mathrm{m},12}$
1HX(1) + cC6(2)							
0.0500	57.32	0.2996	216.09	0.5501	222.52	0.7998	130.44
0.1001	105.67	0.3501	227.28	0.6001	210.61	0.8500	101.50
0.1501	144.56	0.3996	233.08	0.6518	194.58	0.8999	69.29
0.1997	175.57	0.4491	233.58	0.7001	175.65	0.9500	34.82
0.2498	199.62	0.4998	230.27	0.7498	156.22		
1HX(1) + MCH(2)							
0.0500	10.89	0.3000	48.35	0.5498	55.51	0.7999	35.17
0.1000	21.09	0.3498	52.01	0.5998	53.38	0.8499	27.66
0.1533	30.50	0.4001	54.73	0.6499	50.61	0.8999	19.31
0.1998	37.19	0.4500	56.04	0.6993	46.35	0.9500	10.09
0.2492	43.32	0.4995	56.41	0.7504	41.21		
1HX(1) + Bnz(2)							
0.0500	134.86	0.2999	525.88	0.5495	556.39	0.7999	333.79
0.1000	251.36	0.3502	555.75	0.6005	528.95	0.8500	262.35
0.1499	344.98	0.3999	574.37	0.6500	493.37	0.9001	179.30
0.1996	421.45	0.4495	577.50	0.6999	456.54	0.9499	93.95
0.2501	479.76	0.4998	574.46	0.7500	396.41		
1HX(1) = Tol(2)							
0.0500	55.56	0.3007	233.31	0.5501	263.01	0.8000	167.63
0.1000	103.14	0.3503	250.66	0.6001	253.69	0.8498	130.49
0.1501	146.19	0.3998	261.66	0.6499	238.76	0.9000	92.83
0.2000	180.90	0.4502	267.68	0.7006	217.68	0.9500	48.18
0.2505	210.28	0.4997	268.08	0.7499	198.63		

Table 2
Coefficients h_k and standard deviations s for the representations of the excess molar enthalpies $H^{\mathrm{E}}_{\mathrm{m},12}$ at 298.15 K by Eq. (1)

Component		h_1	h_2	h_3	h_4	h_5	s ($\mathrm{J\,mol^{-1}}$)
1	2						
1HX	cC6[a]	919.40	229.48	121.58	30.00	−63.35	0.60
1HX	MCH[a]	225.46	11.76				0.13
1HX	Bnz[a]	2294.46	428.60	174.69	81.70		2.12
1HX	Bnz[b]	2359.4	348.7	284			1.6
1HX	Tol[a]	1072.58	77.52	33.85			1.16

[a] Present work.
[b] From [6].

given in Table 3. These were obtained by fitting the Liebermann–Fried formula for $H^{\mathrm{E}}_{\mathrm{m},ij}$ to the primary experimental data for the excess molar enthalpies, as given in Table 1. Also included in the table are values of the standard deviations s achieved in the fitting process, and values of the isobaric expansivity α_{p} [11], used in evaluating the contributions due to different sizes of the molecules.

Table 3
Values of the interaction parameters A_{ij} and A_{ji}, standard deviation s and the isobaric thermal expansivity α_{p} at 298.15 K for Liebermann–Fried model calculations

Component		A_{ij}	A_{ji}	s ($\mathrm{J\,mol^{-1}}$)	$\alpha_{\mathrm{p}}/(\mathrm{kK^{-1}})$	
i	j				i	j
1HX	cC6	0.7044	1.1959	1.39	1.411[a]	1.220[b]
1HX	MCH	0.9289	1.0291	0.13	1.411[a]	1.187[c]
1HX	Bnz	0.6738	1.0072	2.70	1.411[a]	1.213[d]
1HX	Tol	0.8456	0.9770	1.35	1.411[a]	1.067[e]

[a] From [11, p. 168].
[b] From [11, p. 90].
[c] From [11, estimated from density data, p.100).
[d] From [11, p. 135].
[e] From [11, p. 137].

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 results which are very similar to those obtained with the Redlich–Kister form. This is illustrated in Fig. 1, where the values of $H^{\mathrm{E}}_{\mathrm{m},12}$, derived from the Liebermann–Fried model, are shown as dashed curves, and are hardly distinguishable from the solid Redlich–Kister fits.

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