Excess Enthalpies of 2,2,4-Trimethylpentane + Hexane + (Octane or Dodecane) at 298.15 K

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Microcalorimetric measurements of excess molar enthalpies, measured at 298.15 K, are reported for the ternary systems 2,2,4-trimethylpentane (1) + hexane (2) + octane (3) and 2,2,4-trimethylpentane (1) + hexane (2) + dodecane (3). Smooth representations of the results are described and used to construct constant-enthalpy contours on Roozeboom diagrams. It is shown that the Flory theory provides a reasonable correlation of the results.

Introduction

Methyl *tert*-butyl ether (MTBE) is widely used as a gasoline additive to enhance the octane rating and to reduce pollution effects. However, there have been some concerns of potential adverse health risks associated with MTBE, and a recent study in California suggested that use of MTBE should be phased out of all gasoline sold in that state. Accordingly, investigation of the thermodynamic properties of hydrocarbon mixtures involving other gasoline additives is of relevance. The present paper reports excess molar enthalpies, measured at 298.15 K, for ternary mixtures comprised of the alkylate 2,2,4-trimethylpentane (TMP), normal hexane (nC6), and either normal octane (nC8) or normal dodecane (nC12).

Experimental Section

The TMP (HPLC Grade), nC6, and nC8 were obtained from Sigma-Aldrich; the dodecane (Pure Grade) was obtained from the Phillips Chemical Co. In all cases, the purities stated by the manufacturers exceeded 99 mol %. Apart from partial degassing, all of the components were used without further purification. The densities, ρ/kg·m^{-3}, measured at 298.15 K in an Anton-Paar digital densimeter, were 687.90, 655.46, 698.69, and 745.34, for TMP, nC6, nC8, and nC12, respectively. These values are in reasonable agreement with values in the literature (TRC, 1988).

Excess molar enthalpies, H^{E}_{m}, were measured in an LKB-Produkter AB (Bromma, Sweden) flow microcalorimeter (Model 10700-1), thermostated at 298.15 K, maintained within ±0.003 K. Details of the equipment and its operation have been described previously (Tanaka et al., 1975; Kimura et al., 1983). In studying the ternary systems, the excess molar enthalpy $H^{E}_{m,1+23}$ was determined for several pseudobinary mixtures in which component 1 (TMP) was added to binary mixtures of components 2 (nC6) and 3 (either nC8 or nC12). For this purpose, binaries with fixed mole ratios x_2/x_3 were prepared by mass. The excess molar enthalpy $H^{E}_{m,123}$ of the ternary mixture was then obtained from the relation

$$H^{E}_{m,123} = H^{E}_{m,1+23} + (1 - x_1)H^{E}_{m,23} \qquad (1)$$

Table 1. Experimental Mole Fractions x_1 and Excess Molar Enthalpies $H^{E}_{m,13}$ for TMP (1) + nC12 (3) at 298.15 K

x_1	$H^{E}_{m,13}$/ J·mol^{-1}	x_1	$H^{E}_{m,13}$/ J·mol^{-1}
0.0500	20.51	0.5502	117.94
0.1001	39.77	0.5997	114.96
0.1500	57.18	0.6502	109.12
0.2001	73.84	0.7001	101.47
0.2499	87.24	0.7501	91.00
0.3003	98.12	0.8001	77.80
0.3498	106.11	0.8506	61.14
0.3998	111.26	0.9000	43.45
0.4499	115.57	0.9500	21.65
0.4998	117.51		

Table 2. Coefficients h_k and Standard Deviations s for the Representation of $H^{E}_{m,ij}$ ($i < j$) by Eq 2 for the Constituent-Binary Mixtures at 298.15 K

component							
i	j	h_1	h_2	h_3	h_4	h_5	s/J·mol^{-1}
TMP	nC12	470.62	−24.85	39.15	6.66	−89.15	0.48
TMP	nC6[a]	−44.61	16.65	1.97			0.12
TMP	nC8[b]	102.1					0.1
nC6	nC8[c]	7.353	2.770	−0.539			0.021
nC6	nC12[d]	156.22	14.58	−11.12			0.10

[a] Lam et al. (1974). [b] Lundberg (1964). [c] Hamam et al. (1984a). [d] Hamam et al. (1984b).

where x_1 is the mole fraction of TMP and $H^{E}_{m,23}$ is the excess molar enthalpy of the particular binary mixture. Over most of the mole fraction range, the errors of the excess molar enthalpies and the mole fractions of the final mixtures are estimated to be <0.5% and <5 × 10^{-4}, respectively.

Results and Discussion

Excess molar enthalpies $H^{E}_{m,ij}$ ($i < j$) at 298.15 K, for four of the constituent-binary mixtures of present interest, have been reported previously: TMP (1) + nC6 (2) (Lam et al., 1974); TMP (1) + nC8 (3) (Lundberg, 1964); nC6 (2) + nC8 (3) (Hamam et al., 1984a); nC6 (2) + nC12 (3) (Hamam et al., 1984b). The experimental values for the binary mixture TMP (1) + nC12 (3) at 298.15 K are summarized in Table 1. The smoothing function

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

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Table 3. Experimental Excess Molar Enthalpies $H^{E}_{m,1+23}$ Measured at 298.15 K, for the Addition of TMP to nC6 + nC8 Mixtures to Form TMP (1) + nC6 (2) + nC8 (3), and Values of $H^{E}_{m,123}$ Calculated from Eq 1

x_1	$H^{E}_{m,1+23}{}^{a}$/J·mol^{-1}	$H^{E}_{m,123}$/J·mol^{-1}	x_1	$H^{E}_{m,1+23}{}^{a}$/J·mol^{-1}	$H^{E}_{m,123}$/J·mol^{-1}	x_1	$H^{E}_{m,1+23}{}^{a}$/J·mol^{-1}	$H^{E}_{m,123}$/J·mol^{-1}
$x_2/x_3 = 0.3501$, $H^{E}_{m,23}$/J·mol^{-1} = 1.64								
0.0499	2.66	4.22	0.3997	15.53	16.52	0.7000	13.29	13.78
0.0999	5.53	7.01	0.4487	15.94	16.85	0.7497	11.98	12.39
0.1499	8.12	9.52	0.4994	16.20	17.02	0.7999	10.09	10.42
0.2001	10.25	11.57	0.5501	15.89	16.63	0.8498	7.98	8.22
0.2512	12.08	13.31	0.6003	15.31	15.97	0.9000	5.59	5.76
0.2994	13.58	14.73	0.6504	14.58	15.15	0.9500	2.93	3.02
0.3498	14.80	15.87						
$x_2/x_3 = 0.9964$, $H^{E}_{m,23}$/J·mol^{-1} = 1.84								
0.0500	1.63	3.38	0.3998	7.50	8.61	0.6996	6.17	6.73
0.0999	2.90	4.56	0.4498	7.59	8.60	0.7496	5.45	5.91
0.1498	4.24	5.80	0.4992	7.78	8.70	0.7997	4.50	4.87
0.1998	5.26	6.73	0.5497	7.42	8.25	0.8498	3.65	3.93
0.2497	6.08	7.46	0.5998	7.10	7.84	0.8999	2.38	2.56
0.2998	6.80	8.09	0.6497	6.94	7.59	0.9499	1.30	1.39
0.3500	7.22	8.41						
$x_2/x_3 = 3.0000$, $H^{E}_{m,23}$/J·mol^{-1} = 1.09								
0.0499	−0.22	0.82	0.4004	−1.16	−0.50	0.6998	-1.30	-0.98
0.0999	−0.26	0.72	0.4497	−1.26	−0.66	0.7499	-1.36	-1.09
0.1500	−0.53	0.40	0.4994	−1.60	−1.06	0.7999	-1.17	-0.95
0.1998	−0.58	0.29	0.5502	−1.38	−0.88	0.8498	-0.92	-0.76
0.2494	−0.81	0.01	0.5999	−1.34	−0.90	0.9001	-0.67	-0.56
0.3002	−0.96	−0.19	0.6503	−1.49	−1.11	0.9500	-0.36	-0.31
0.3501	−1.10	−0.39						

[a] Ternary term for representation of $H^{E}_{m,1+23}$ by eqs 2 and 3: $H^{E}_{m,T}/\mathrm{J\cdot mol^{-1}} = \{x_1x_2x_3/(1 - x_1 + x_2)\}(-300.81 + 1577.35x_1 + 1114.47x_2 - 2643.98x_1^2 - 4418.24x_1x_2 - 1076.27x_2^2 + 1405.52x_1^3 + 4290.70x_1^2x_2 + 2582.66x_1x_2^2)$, s =0.13 J·mol^{-1}.

Table 4. Experimental Excess Molar Enthalpies $H^{E}_{m,1+23}$ Measured at 298.15 K, for the Addition of TMP to nC6 + nC12 Mixtures to Form TMP (1) + nC6 (2) + nC12 (3), and Values of $H^{E}_{m,123}$ Calculated from Eq 1

x_1	$H^{E}_{m,1+23}{}^{a}$/J·mol^{-1}	$H^{E}_{m,123}$/J·mol^{-1}	x_1	$H^{E}_{m,1+23}{}^{a}$/J·mol^{-1}	$H^{E}_{m,123}$/J·mol^{-1}	x_1	$H^{E}_{m,1+23}{}^{a}$/J·mol^{-1}	$H^{E}_{m,123}$/J·mol^{-1}
$x_2/x_3 = 0.3346$, $H^{E}_{m,23}$/J·mol^{-1} = 30.19								
0.0500	14.57	43.25	0.3998	77.26	95.38	0.7009	69.75	78.78
0.1000	27.96	55.13	0.4502	80.20	96.80	0.7501	62.75	70.30
0.1504	40.54	66.19	0.5005	80.84	95.92	0.8001	53.72	59.76
0.1995	51.31	75.48	0.5508	80.94	94.50	0.8499	43.04	47.57
0.2501	60.46	83.10	0.6003	78.95	91.02	0.8998	30.37	33.40
0.3002	67.33	88.46	0.6498	75.26	85.83	0.9500	15.73	17.24
0.3507	73.00	92.61						
$x_2/x_3 = 0.9997$, $H^{E}_{m,23}$/J·mol^{-1} = 39.06								
0.0500	8.78	45.89	0.4001	45.87	69.30	0.6499	43.92	57.59
0.1000	16.84	51.99	0.4497	46.84	68.33	0.7002	40.53	52.24
0.1501	23.89	57.08	0.4500	47.37	68.85	0.7500	36.25	46.02
0.2001	30.48	61.72	0.5001	47.86	67.39	0.7999	30.99	38.81
0.2501	35.69	64.98	0.5008	47.89	67.38	0.8500	24.65	30.51
0.3001	39.48	66.82	0.5500	47.46	65.03	0.9000	17.40	21.31
0.3499	43.15	68.54	0.5996	46.13	61.77	0.9500	8.65	10.61
$x_2/x_3 = 2.9992$, $H^{E}_{m,23}$/J·mol^{-1} = 27.41								
0.0501	3.32	29.35	0.4002	17.01	33.45	0.7002	14.67	22.89
0.0998	6.36	31.03	0.4501	17.32	32.39	0.7500	12.93	19.78
0.1500	9.08	32.38	0.5001	17.82	31.52	0.7999	11.07	16.55
0.2000	11.32	33.25	0.5502	17.42	29.75	0.8502	8.81	12.92
0.2501	13.09	33.64	0.6004	16.81	27.76	0.9000	6.26	9.01
0.3002	14.92	34.10	0.6497	15.90	25.50	0.9499	3.12	4.49
0.3503	16.01	33.82						

[a] Ternary term for representation of $H^{E}_{m,1+23}$ by Eqs 2 and 3: $H^{E}_{m,T}/\mathrm{J\cdot mol^{-1}} = x_1x_2x_3(104.58 - 1278.14x_1 - 361.32x_2 + 2345.83x_1^2 + 829.88x_1x_2 + 183.55x_2^2 - 1988.26x_1^3)$, s = 0.27 J·mol^{-1}.

was fitted to these results 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 of the representation. For convenience, the coefficients and standard deviations for the representations of $H^{E}_{m,ij}$ for the four other binary mixtures are also included in Table 2.

The experimental results for $H^{E}_{m,1+23}$ and the corresponding values of $H^{E}_{m,123}$ calculated from eq 1 are listed in Tables 3 and 4 against the mole fraction x_1 of TMP. The values of $H^{E}_{m,1+23}$ in Table 3 for the various values of x_2/x_3 are plotted in Figure 1, along with curves for the constituent-binaries having $x_2 = 0$ (Lundberg, 1964) and $x_1 + x_2 = 1$ (Lam et al., 1974). These latter values were calculated

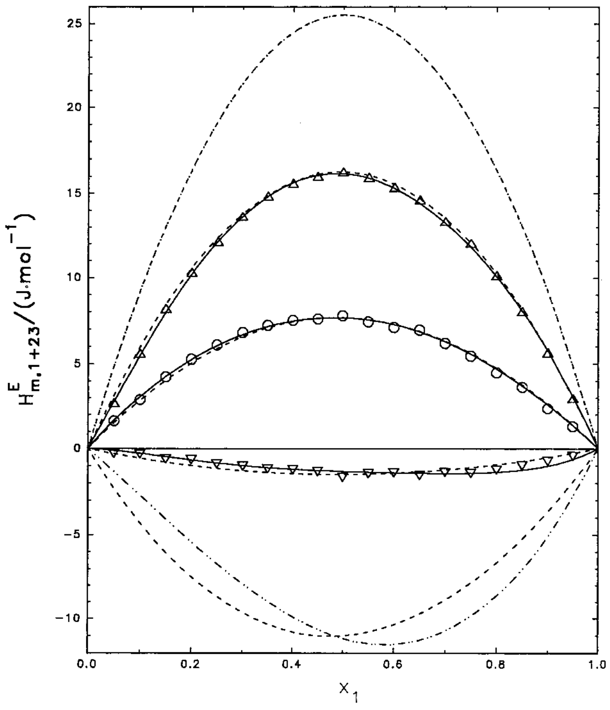

Figure 1. Excess molar enthalpies, $H^E_{m,1+23}$, for TMP (1) + nC6 (2) + nC8 (3) at 298.15 K. Experimental results: △, $x_2/x_3 = 0.3501$; ○, $x_2/x_3 = 0.9964$; ▽, $x_2/x_3 = 3.0000$. Curves: ···, $x_2 = 0$, Lundberg (1964); —··, $x_1 + x_2 = 1$, Lam et al. (1974); —, calculated from the representation of the results by eqs 2−4, using the ternary term $H^E_{m,T}$ given in the footnote of Table 3; - - -, calculated from the Flory theory.

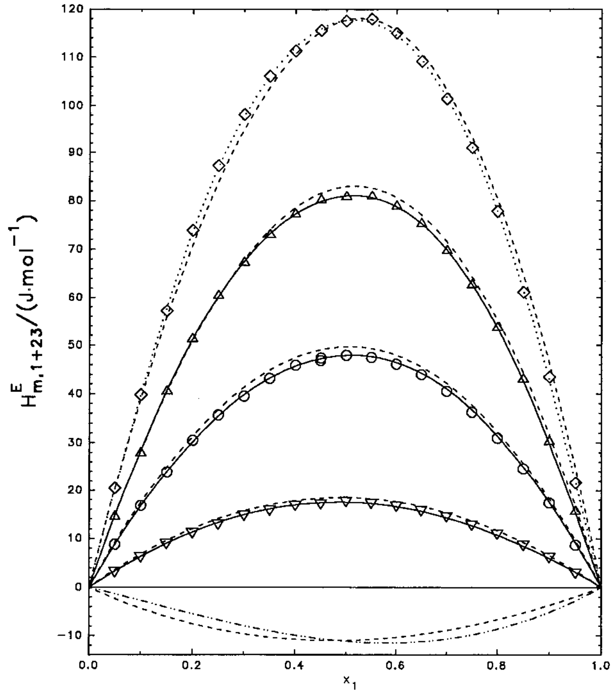

Figure 2. Excess molar enthalpies, $H^E_{m,1+23}$, for TMP (1) + nC6 (2) + nC12 (3) at 298.15 K. Experimental results: ◇, $x_2 = 0$; △, $x_2/x_3 = 0.3346$; ○, $x_2/x_3 = 0.9997$; ▽, $x_2/x_3 = 2.9992$. Curves: ···, $x_2 = 0$; —··, $x_1 + x_2 = 1$, Lam et al. (1974); —, calculated from the representation of the results by eqs 2−4, using the ternary term $H^E_{m,T}$ given in the footnote of Table 4; - - -, calculated from the Flory theory.

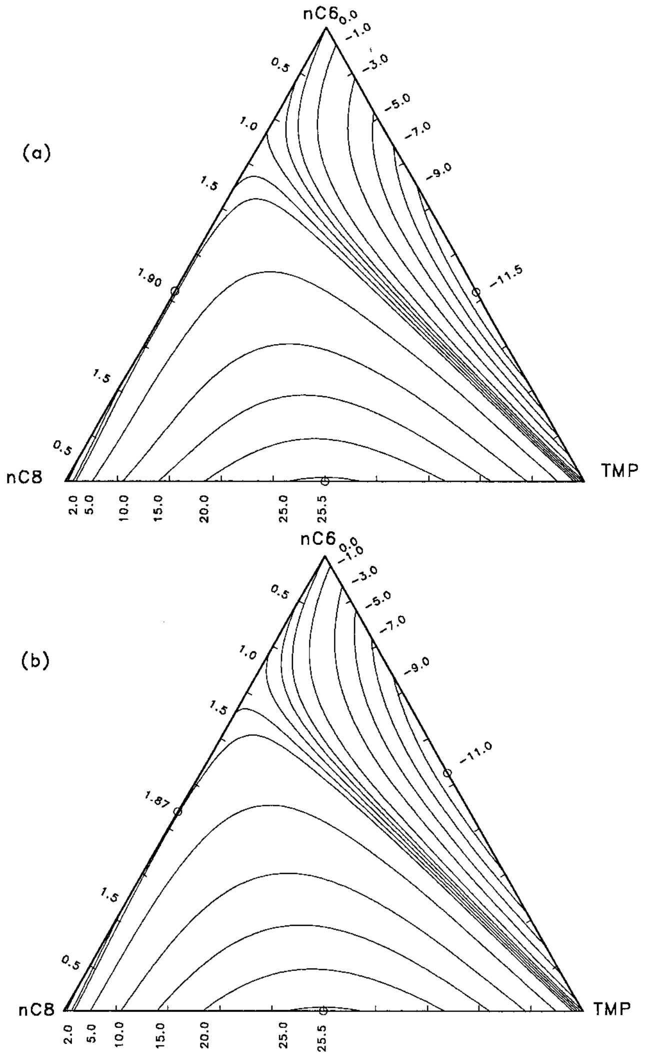

Figure 3. Contours for constant values of $H^E_{m,123}/J\cdot mol^{-1}$ for TMP (1) + nC6 (2) + nC8 (3) at 298.15 K: (a) calculated from the representation of the experimental results by eqs 1−4 with $H^E_{m,T}$ from the footnote of Table 3; (b) calculated from the Flory theory.

from eq 2 using the values of the coefficients given in Table 2. The results for the mixtures contaning nC12 are plotted in Figure 2, along with the values of $H^E_{m,13}$ given in Table 1 for TMP (1) + nC12 (3) and with curves for the two constituent-binaries, calculated from eq 2.

The values of $H^E_{m,1+23}$ were represented as a sum of binary terms (Tsao and Smith, 1953) with an added ternary contribution

$$H^E_{m,1+23} = [x_2/(1 - x_1)]H^E_{m,12} + [x_3/(1 - x_1)]H^E_{m,13} + H^E_{m,T} \tag{3}$$

where the values of the $H^E_{m,ij}$ were calculated from the appropriate smoothing functions. The form

$$H^E_{m,T}/J\cdot mol^{-1} = [x_1x_2x_3/\{1 + b(x_2 - x_1)\}](c_0 + c_1x_1 + c_2x_2 + c_3x_1^2 + c_4x_1x_2 + c_5x_2^2 + c_6x_1^3 + \cdots) \tag{4}$$

which was adopted for the ternary contribution, is similar to that used by Morris et al. (1975) with the possibility of an extra skewing factor $[1 + b(x_2 - x_1)]^{-1}$ inserted. In the case of the nC8 system $b = 1$ was used, while for the nC12 system $b = 0$ was found to be more appropriate. Values of the parameters c_i were obtained from least-squares analyses in which eqs 3 and 4 were fitted to the experimental values in Tables 3 and 4. The resulting representations of $H^E_{m,T}$ are given in the footnotes of the tables, along with

Table 5. Parameters Used in Flory Calculations at T = 298.15 K for [TMP (1) + nC6 (2) + nC8 (3)][a]and [TMP (1) + nC6 (2) + nC12 (3)][b]

component	p^*/J·cm^{-3}	V^*_m/cm^3·mol^{-1}	T^*/K	ref
TMP	383.2	129.08	4759.5	Treszczanowicz and Benson, (1988)
nC6	424.2	99.52	4436.1	Benson et al. (1988)
nC8	436.8	127.70	4827.0	Benson et al. (1988)
nC12	445.2	184.40	5351.4	Benson et al. (1988)

[a] Interchange energy parameters X_{ij}/J·cm^{-3}: $X_{12} = -0.1637$; $X_{13} = 0.7604$; $X_{23} = 0.3675$. [b] Interchange energy parameters X_{ij}/J·cm^{-3}: $X_{12} = -0.1637$; $X_{13} = 3.5227$; $X_{23} = 2.5083$.

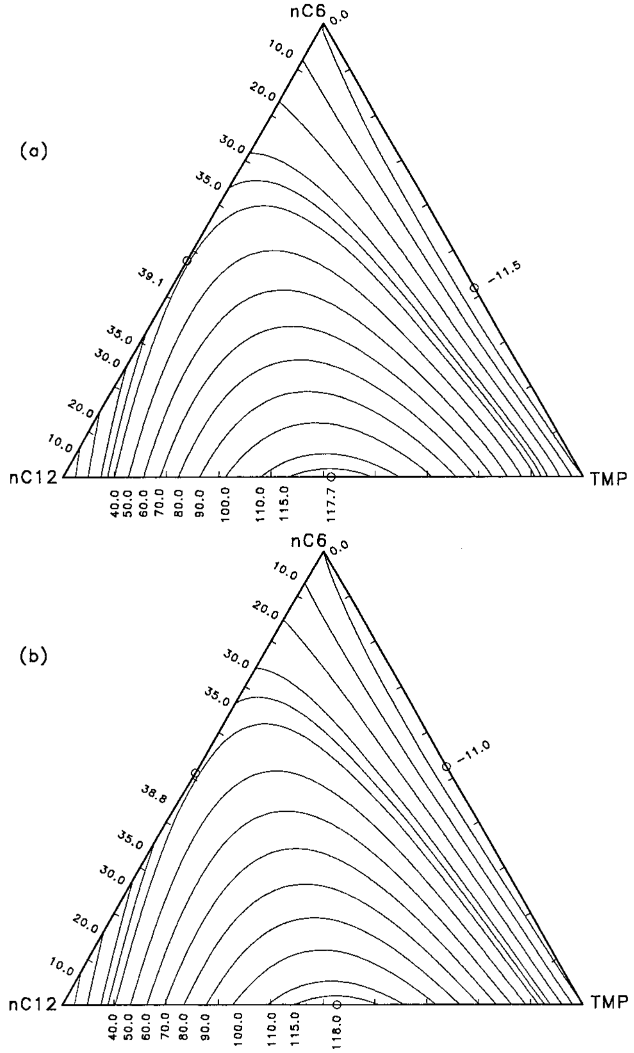

Figure 4. Contours for constant values of $H^{E}_{m,123}$/J·mol^{-1} for TMP (1) + nC6 (2) + nC12 (3) at 298.15 K: (a) calculated from the representation of the experimental results by eqs 1−4 with $H^{E}_{m,T}$ from the footnote of Table 4; (b) calculated from the Flory theory.

the standard deviations s of the fits. The solid curves for $H^{E}_{m,1+23}$ in Figures 1 and 2 were calculated from eq 3, using these representations. For both systems, the curves of $H^{E}_{m,1+23}$ for a fixed value of x_2/x_3 are approximately symmetric about $x_1 = 0.5$, and for a fixed value of x_1 the values of $H^{E}_{m,1+23}$ increase with an increase in the relative content of nC8 or nC12 in the binary mixture.

Equations 1−4 were also used to calculate the constant $H^{E}_{m,123}$ contours plotted on the Roozeboom diagrams in Figures 3a and 4a. The general characteristics of these are similar. However, the change from nC8 to nC12 leads to a marked reduction to the area of negative values of $H^{E}_{m,123}$.

Previously, we have found that the Flory theory (Flory, 1965; Abe and Flory, 1965), as applied to ternary mixtures by Brostow and Sochanski (1975), could provide reasonable estimates of the ternary excess molar enthalpies for mixtures containing alkanes and ethers, when only the properties of the pure components and their binary mixtures were used. The equations for the treatment have been outlined by Wang et al. (1993). The values of the parameters for applying this approach to the present systems are summarized in Table 5. The characteristic pressures p^*, molar volumes V^*_m, and temperatures T^* were taken from our previous publications, as indicated in the last column of the table. In evaluating s_i/s_j, the ratio of the molecular surface areas of contact per segment between components i and j, it was assumed that the molecules were spherical. The values of the interchange parameters X_{ij} are given in the footnotes of Table 5. These were obtained by fitting the Flory formula for $H^{E}_{m,ij}$ to the smooth representations of the excess molar enthalpy of each of the constituent-binaries by eq 1 using the coefficients given in Table 2.

The Flory estimates of $H^{E}_{m,1+23}$ are shown as dashed curves in Figures 1 and 2. The root-mean-square deviations for the 57 experimental points in Table 3 and the 59 points in Table 4 are 0.2 and 1.2 J·mol^{-1}, respectively. Constant $H^{E}_{m,123}$ contours estimated on the basis of the Flory theory are shown in Figures 3b and 4b. The overall characteristics of these are very similar to those derived from the smooth representations of the experimental results. It is clear from the comparison of the two parts of Figures 3 and 4 that the Flory theory provides useful estimates of $H^{E}_{m,123}$ for both of the present systems, without requiring the direct investigation of the excess enthalpies of any ternary mixtures.

Supporting Information Available:

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