Excess Enthalpies of the Ternary Mixtures 2-Methyltetrahydrofuran + *n*-Octane + (*n*-Decane or *n*-Dodecane) at 298.15 K

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Excess molar enthalpies, measured at 298.15 K in a flow microcalorimeter, are reported for the two ternary systems 2-methyltetrahydrofuran + *n*-octane + *n*-decane and 2-methyltetrahydrofuran + *n*-octane + *n*-dodecane. Smooth representations of the results are described and used to construct constant excess molar enthalpy contours on Roozeboom diagrams. The latter are compared with diagrams obtained when the model of Liebermann and Fried is used to estimate the excess molar enthalpies of the ternary mixtures from the physical properties of the components and the excess molar enthalpies of their binary mixtures.

Introduction

In view of the impending phaseout of methyl *tert*-butyl ether (MTBE) as a gasoline additive, investigation of the thermodynamic properties of other oxygenate + hydrocarbon systems is of interest. Recently, excess molar enthalpies of some binary and ternary mixtures involving 2-methyltetrahydrofuran (MTHF) and various *n*-alkanes were reported.[1,2] As a continuation of those investigations, similar calorimetric measurements at 298.15 K have been made for the two ternary systems formed from MTHF and mixtures of *n*-octane (nC8) with either *n*-decane (nC10) or *n*-dodecane (nC12).

Experimental Section

MTHF was obtained from Aldrich; nC8, nC10, and nC12 were obtained from Sigma. In all cases, the purities stated by the manufacturers were at least 99 mol %. Apart from partial degassing, all of the components were used without further purification. Densities, $\rho/\text{kg·m}^{-3}$, measured at 298.15 K in an Anton−Paar digital densimeter, were 848.10, 698.75, 726.31, and 745.52 for MTHF, nC8, nC10, and nC12, respectively. The result for MTHF is fairly close to that reported recently by De Lorenzi et al.[3] The results for the alkanes are in reasonable agreement with values in the TRC tables.[4]

An LKB flow microcalorimeter (model 10700-1), thermostated at (298.150 ± 0.003) K, was used to measure the excess molar enthalpies H_m^E. Details of the equipment and its operation have been described previously.[5,6]

In our study of the ternary systems, the excess molar enthalpy $H_{m,1+23}^E$ was determined for several pseudo-binary mixtures in which component 1 (MTHF) was added to binary mixtures of components 2 (nC8) and 3 (either nC10 or nC12). For this purpose, binaries with fixed mole ratios, x_2/x_3, were prepared by mass. The excess molar enthalpy $H_{m,123}^E$ of the ternary mixture was then obtained from the relationship

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

where x_1 is the mole fraction of MTHF and $H_{m,23}^E$ is the excess molar enthalpy of the particular binary mixture.
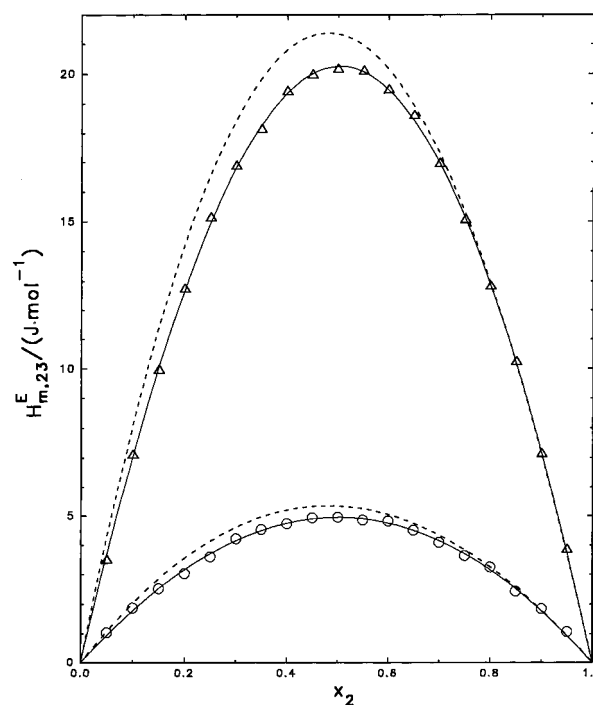

Figure 1. Excess molar enthalpies, $H_{m,23}^E$, for nC8 (2) + nC10 (3) and nC8 (2) + nC12 (3) at 298.15 K. Experimental results: ○, nC10, present work; △, nC12, Kumaran and Benson.[7] Curves: —, calculated from the representations of the results by eq 2 with values of the coefficients given in Table 2; - - -, fit of results by the Liebermann−Fried model.

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 less than 0.5% and 5×10^{-4}, respectively.

Results and Discussion

Excess molar enthalpies $H_{m,ij}^E$ ($i < j$), at 298.15 K, for four of the five constituent binaries of present interest have been reported previously: MTHF (1) + nC8 (2),[1] MTHF (1) + nC10 (3),[1] MTHF (1) + nC12 (3),[1] and nC8 (2) + nC12 (3).[7] The experimental results for the excess molar enthalpies $H_{m,23}^E$ of nC8 (2) + nC10 (3) at 298.15 K are

Table 1. Experimental Mole Fractions, x_2, and Excess Molar Enthalpies, $H^E_{m,23}$, for nC8 (2) + nC10 (3) Mixtures at 298.15 K

x_2	$H^E_{m,23}$/J·mol^{-1}	x_2	$H^E_{m,23}$/J·mol^{-1}	x_2	$H^E_{m,23}$/J·mol^{-1}	x_2	$H^E_{m,23}$/J·mol^{-1}	x_2	$H^E_{m,23}$/J·mol^{-1}
0.0500	1.039	0.2500	3.616	0.4500	4.941	0.6499	4.524	0.8499	2.446
0.1000	1.881	0.3003	4.232	0.5005	4.961	0.6999	4.111	0.9000	1.857
0.1501	2.529	0.3498	4.548	0.5500	4.866	0.7501	3.654	0.9500	1.075
0.2001	3.048	0.4001	4.745	0.6000	4.832	0.8002	3.257		

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

component		h_1	h_2	h_3	h_4	h_5	h_6	s/J·mol^{-1}
i	j							
nC8	nC10[a]	19.837						0.076
MTHF	nC8[b]	2443.43	−181.55	109.85	−98.50			2.49
MTHF	nC10[b]	2723.73	−429.51	284.04	99.02	−267.95	−432.04	1.88
MTHF	nC12[b]	3011.67	−565.87	190.76	−372.29			3.34
nC8	nC12[c]	81.05	−0.97	−3.15				0.10

[a] Present work. [b] Wang et al.[1] [c] Kumaran and Benson.[7]

Table 3. Experimental Excess Molar Enthalpies, $H^E_{m,1+23}$, Measured at 298.15 K, for the Addition of MTHF to nC8 + nC10 Mixtures To Form MTHF (1) + nC8 (2) + nC10 (3) and Values of $H^E_{m,123}$ Calculated from Equation 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}
			$x_2/x_3 = 0.3334$, $H^E_{m,23}$/J·mol$^{-1} = 3.72$					
0.0500	107.01	110.54	0.4004	622.67	624.90	0.7003	596.52	597.63
0.1001	214.90	218.25	0.4502	649.86	651.91	0.7499	543.60	544.53
0.1501	314.62	317.78	0.4999	665.23	667.09	0.8000	473.36	474.10
0.2000	398.13	401.11	0.5503	669.61	671.28	0.8500	385.54	386.10
0.2500	474.00	476.79	0.5999	657.44	658.93	0.9000	279.82	280.19
0.2999	536.67	539.27	0.6504	633.93	635.23	0.9500	153.41	153.60
0.3499	588.22	590.64						
			$x_2/x_3 = 1.0000$, $H^E_{m,23}$/J·mol$^{-1} = 4.96$					
0.0500	109.58	114.29	0.3999	606.85	609.83	0.6999	576.41	577.90
0.1001	212.60	217.06	0.4501	633.28	636.01	0.7499	524.59	525.83
0.1500	308.13	312.35	0.5001	648.11	650.59	0.8000	455.24	456.23
0.2001	389.06	393.03	0.5501	650.57	652.80	0.8500	370.57	371.31
0.2501	463.11	466.83	0.6008	636.28	638.26	0.9000	266.62	267.12
0.3001	526.56	530.03	0.6498	614.35	616.09	0.9500	146.50	146.75
0.3499	575.78	579.00						
			$x_2/x_3 = 2.9952$, $H^E_{m,23}$/J·mol$^{-1} = 3.72$					
0.0500	110.94	114.48	0.3999	592.29	594.52	0.6997	556.25	557.37
0.1000	212.94	216.29	0.4498	616.71	618.76	0.7500	503.86	504.79
0.1501	302.41	305.57	0.5003	629.58	631.44	0.8000	436.77	437.51
0.2001	385.10	388.08	0.5504	628.72	630.39	0.8505	346.20	346.76
0.2501	454.77	457.56	0.6001	617.23	618.72	0.9004	253.45	253.82
0.3000	515.13	517.74	0.6503	592.90	594.20	0.9499	139.70	139.89
0.3501	556.70	559.12						

[a] Ternary term for representation of $H^E_{m,1+23}$ by eqs 4 and 5: $H^E_{m,T}$/J·mol$^{-1} = 71.52x_1x_2x_3$, $s = 1.79$ J·mol^{-1}.

listed in Table 1 and plotted in Figure 1. The smoothing function

$$H^E_{m,ij}/\text{J·mol}^{-1} = x_i(1 - x_i)\sum_{k=1}^{n} h_k(1 - 2x_i)^{k-1} \quad (i < j) \quad (2)$$

was fitted to the 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, for the representation. A curve calculated from this representation is plotted in Figure 1. 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 previously published results for nC8 (2) + nC12 (3)[7] and their representation by eq 2 are also shown in Figure 1 for comparison.

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 MTHF, for the MTHF (1) + nC8 (2) + nC10 (3) and MTHF (1) + nC8 (2) + nC12 (3) ternary systems, respectively. For a

selected value of x_2/x_3 in these tables, the maximum values of $H^E_{m,1+23}$ and $H^E_{m,123}$ occur near $x_1 = 0.5$. For both systems at constant x_1, the enthalpies decrease as x_2/x_3 increases.

To facilitate the graphical presentation of the results, molar enthalpy differences $\Delta H^E_{m,1+23}$, defined by

$$\Delta H^E_{m,1+23} = H^E_{m,1+23} - 2000x_1x_2 \quad (3)$$

are plotted for the two ternary systems in Figures 2 and 3. Included in these figures are curves for the cases $x_2 = 0$ and $x_3 = 0$, calculated from eq 2 using the values of the coefficients given in Table 2.

Following Tsao and Smith[8] the values of $H^E_{m,1+23}$ were represented as a sum of binary terms with an added ternary contribution

$$H^E_{m,1+23} = [x_2/(1 - x_1)]H^E_{m,12} + [x_3/(1 - x_1)]H^E_{m,13} + H^E_{m,T} \quad (4)$$

where values of the $H^E_{m,ij}$ were calculated from the ap-

Table 4. Experimental Excess Molar Enthalpies, $H_{m,1+23}^E$, Measured at 298.15 K, for the Addition of MTHF to nC8 + nC12 Mixtures To Form MTHF (1) + nC8 (2) + nC12 (3) and Values of $H_{m,123}^E$ Calculated from Equation 1

x_1	$H_{m,1+23}^E$ [a]/J·mol⁻¹	$H_{m,123}^E$/J·mol⁻¹	x_1	$H_{m,1+23}^E$ [a]/J·mol⁻¹	$H_{m,123}^E$/J·mol⁻¹	x_1	$H_{m,1+23}^E$ [a]/J·mol⁻¹	$H_{m,123}^E$/J·mol⁻¹
			$x_2/x_3 = 0.3336$, $H_{m,23}^E$/J·mol⁻¹ = 14.96					
0.0500	113.07	127.29	0.4000	663.46	672.44	0.7001	656.35	660.84
0.1000	224.73	238.20	0.4502	697.59	705.82	0.7499	600.05	603.79
0.1499	322.85	335.57	0.5002	716.84	724.32	0.8000	526.89	529.88
0.2000	420.57	432.54	0.5496	724.35	731.09	0.8501	432.24	434.48
0.2500	497.63	508.85	0.5999	716.64	722.63	0.9000	312.22	313.72
0.3000	570.87	581.34	0.6500	692.46	697.70	0.9500	171.92	172.67
0.3499	625.85	635.58						
			$x_2/x_3 = 1.0001$, $H_{m,23}^E$/J·mol⁻¹ = 20.26					
0.0501	110.23	129.48	0.4001	634.44	646.60	0.6997	616.05	622.13
0.1001	215.26	233.49	0.4502	664.24	675.38	0.7498	561.81	566.88
0.1500	316.20	333.42	0.5001	681.25	691.38	0.7998	490.28	494.34
0.1999	402.92	419.13	0.5502	685.38	694.49	0.8500	401.42	404.46
0.2501	479.93	495.13	0.5998	676.43	684.54	0.9000	292.10	294.13
0.2999	546.64	560.83	0.6497	653.92	661.02	0.9499	156.49	157.50
0.3499	599.44	612.61						
			$x_2/x_3 = 3.0030$, $H_{m,23}^E$/J·mol⁻¹ = 15.13					
0.0501	110.92	125.29	0.3999	605.37	614.45	0.7001	574.56	579.10
0.1000	214.41	228.03	0.4471	630.85	639.22	0.7500	520.76	524.54
0.1500	302.20	315.06	0.5002	646.15	653.71	0.8000	455.07	458.10
0.1999	391.54	403.65	0.5501	647.31	654.12	0.8500	369.68	371.95
0.2500	464.45	475.80	0.6001	637.15	643.20	0.9000	267.78	269.29
0.3001	524.82	535.41	0.6498	613.56	618.86	0.9500	144.89	145.65
0.3500	567.76	577.60						

[a] Ternary term for representation of $H_{m,1+23}^E$ by eqs 4 and 5: $H_{m,T}^E$/J·mol⁻¹ = $x_1x_2x_3(371.87 - 1224.11x_1 - 271.01x_2 + 1334.65x_1^2)$, $s = 2.23$ J·mol⁻¹.
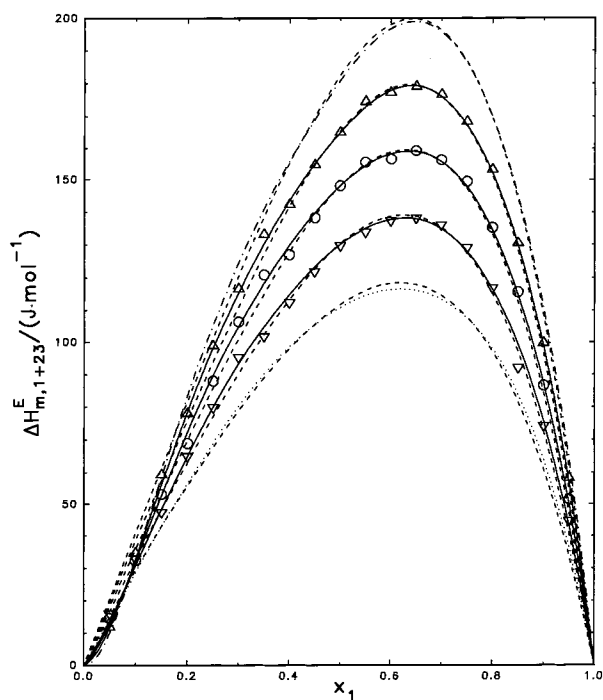

Figure 2. Excess molar enthalpy differences, $\Delta H_{m,1+23}^E$, for MTHF (1) + nC8 (2) + nC10 (3) at 298.15 K. Experimental results: $\triangle$, $x_2/x_3 = 0.3334$; $\bigcirc$, $x_2/x_3 = 1.0000$; ∇, $x_2/x_3 = 2.9952$. Curves: ·—·, $x_2 = 0$, Wang et al.[1]; ···, $x_3 = 0$, Wang et al.[1]; —, calculated from the representation of the results by eq 4, using the ternary term $H_{m,T}^E$ given in the footnote of Table 3; - - -, estimated by means of the Liebermann–Fried model.

Figure 3. Excess molar enthalpy differences, $\Delta H_{m,1+23}^E$, for MTHF (1) + nC8 (2) + nC12 (3) at 298.15 K. Experimental results: $\triangle$, $x_2/x_3 = 0.3336$; $\bigcirc$, $x_2/x_3 = 1.0001$; ∇, $x_2/x_3 = 3.0030$. Curves: ·—·, $x_2 = 0$, Wang et al.[1]; ···, $x_3 = 0$, Wang et al.[1]; —, calculated from the representation of the results by eq 4, using the ternary term $H_{m,T}^E$ given in the footnote of Table 4; - - -, estimated by means of the Liebermann–Fried model.

propriate smoothing functions. The form

$$H_{m,T}^E/\text{J·mol}^{-1} = x_1x_2x_3(c_0 + c_1x_1 + c_2x_2 + c_3x_1^2 + c_4x_1x_2 + c_5x_2^2 + ...) \quad (5)$$

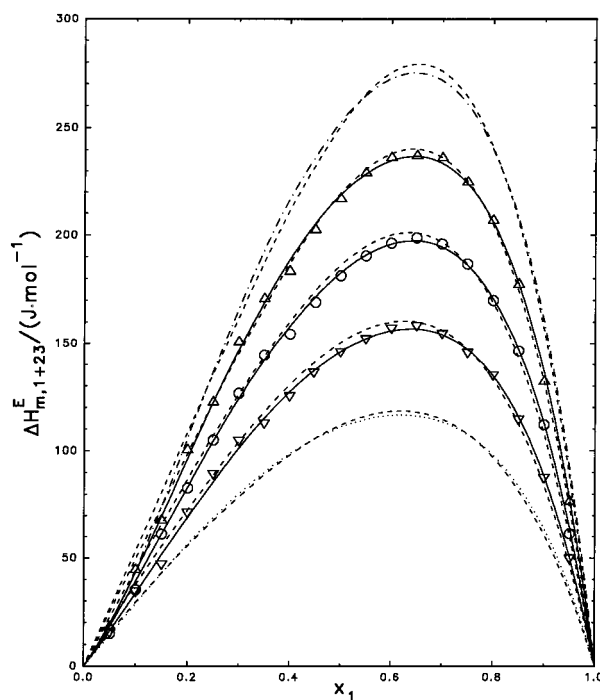adopted for the ternary contribution is similar to that used

by Morris et al.[9] Values of the parameters c_i were obtained from least-squares analyses in which eqs 4 and 5 were fitted to the experimental values in Tables 3 and 4. The resulting representations of $H_{m,T}^E$ are given in the footnotes of the tables, along with the standard deviations s of the fits. The solid curves for $\Delta H_{m,1+23}^E$ in Figures 2 and 3
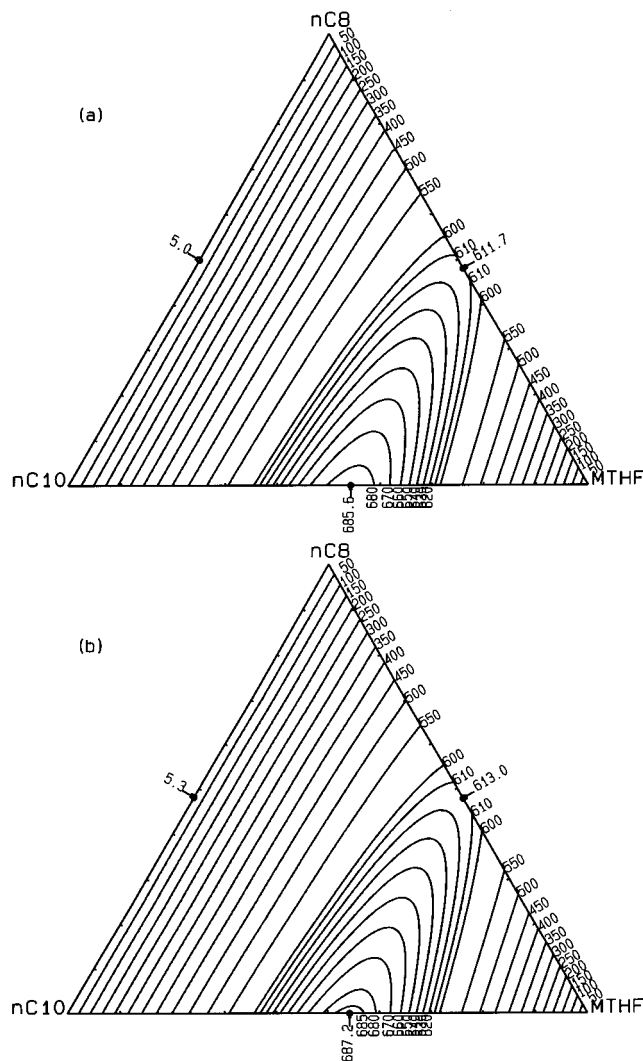
Figure 4. Contours for constant values of $H^E_{m,123}$/J·mol^{-1} for MTHF (1) + nC8 (2) + nC10 (3) at 298.15 K: (a) calculated from the representation of the experimental results by eqs 1 and 4 with $H^E_{m,T}$ from the footnote of Table 3; (b) estimated by means of the Liebermann–Fried model.

Figure 5. Contours for constant values of $H^E_{m,123}$/J·mol^{-1} for MTHF (1) + nC8 (2) + nC12 (3) at 298.15 K: (a) calculated from the representation of the experimental results by eqs 1 and 4 with $H^E_{m,T}$ from the footnote of Table 4; (b) estimated by means of the Liebermann–Fried model.

were calculated from eqs 3–5, using these representations.

Equations 1 and 4 were also used to calculate the constant $H^E_{m,123}$ contours plotted on the Roozeboom diagrams in Figures 4a and 5a. The general characteristics of these are similar, and there is no indication of an internal extremum.

Recent work[10,11] indicates that an extension of the model of Liebermann and Fried[12,13] can be useful in representing the excess enthalpies of binary mixtures and also has the potential for estimating the 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 ternary systems.

The equations used in this application have been outlined by Wang et al.[11] Values of the Liebermann–Fried interaction parameters, A_{ij} and A_{ji}, for each of the binary mixtures are given in Table 5. These were obtained by fitting the Liebermann–Fried formula for $H^E_{m,ij}$ to the primary experimental results in Table 1 and those reported by Wang et al.[1] and by Kumaran and Benson.[7] Also included in Table 5 are values of the standard deviations s achieved in the fitting process and values[3,14] of the
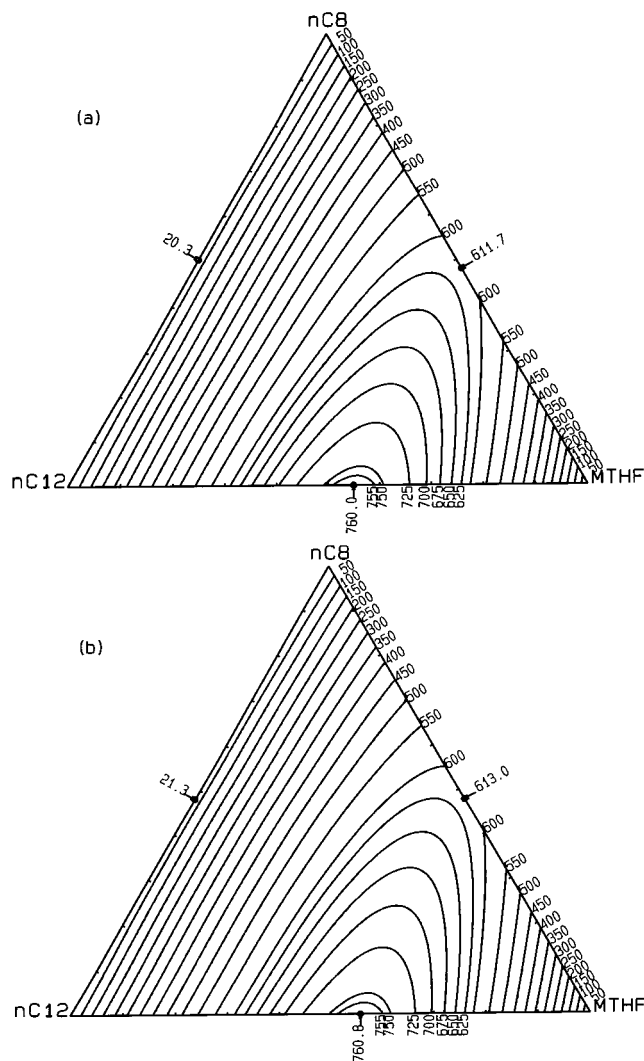
Table 5. Values of the Interaction Parameters, A_{ij} and A_{ji}, Standard Deviations, s, and Isobaric Thermal Expansivities, α_p, at 298.15 K for Liebermann–Fried Model Calculations

component				s	α_p (kK^{-1})	
i	j	A_{ij}	A_{ji}	J·mol^{-1}	i	j
MTHF	nC8	0.8884	0.7423	2.80	1.215^a	1.164^b
MTHF	nC10	0.9416	0.6652	3.38	1.215^a	1.051^b
nC8	nC10	0.9901	1.0027	0.33	1.164^b	1.051^b
MTHF	nC12	0.9804	0.6070	5.74	1.215^a	0.960^b
nC8	nC12	0.9970	0.9764	1.09	1.164^b	0.960^b

^{a} Estimated from the density data of De Lorenzi et al.[3] ^{b} Benson et al.[14]

isobaric thermal expansivities α_p of the components, used in evaluating the contributions due to different molecular sizes.

Using the values of the parameters given in Table 5, $H^E_{m,1+23}$ and $H^E_{m,123}$ were calculated for the present mixtures. The resulting values of $H^E_{m,1+23}$ for the ternary mixtures and of $H^E_{m,ij}$ for the constituent binaries were used to plot the dashed curves in Figures 1–3. It can be seen from these that, although the deviations of the fits of the data for some of the constituent binaries are relatively

significant, the Liebermann−Fried model provides useful estimates of the enthalpies of both ternary systems. The mean absolute relative deviations between the 57 experimental and estimated values of $H^E_{m,1+23}$ in both Tables 3 and 4 amount to 0.74 and 0.97%, respectively.

Constant $H^E_{m,123}$ contours were also estimated on the basis of the Liebermann−Fried model and are shown in parts b of Figures 4 and 5. The overall characteristics of these are very similar to those in parts a, which were derived from the representations of the experimental data for the ternary mixtures. This again indicates that the Liebermann−Fried model provides useful estimates of the ternary enthalpy behavior without requiring the direct investigation of the excess enthalpies of any ternary mixtures.

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