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Excess molar enthalpies of the ternary mixtures: methyl *tert*-butyl ether + 3-methylpentane + (*n*-decane or *n*-dodecane) at 298.15 K

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Abstract

Excess molar enthalpies, measured at 298.15 K in a flow microcalorimeter, are reported for the two ternary mixtures formed by mixing either methyl *tert*-butyl ether with binary mixtures of 3-methylpentane and either *n*-decane or *n*-dodecane. Smooth representations of the ternary results are presented and used to construct constant excess molar enthalpy contours on Roozeboom diagrams. It is found that the Liebermann and Fried model also provided good representation of the ternary results, using only the physical properties of the components and their binary mixtures.

Keywords: Methyl *tert*-butyl ether; 3-Methylpentane; *n*-Decane; *n*-Dodecane; Excess molar enthalpy; Ternary systems; Liebermann–Fried model

1. Introduction

We have reported measurements of excess molar enthalpies at $T = 298.15$ K for ternary mixtures formed by mixing of methyl *tert*-butyl ether with binary mixtures of two hydrocarbons [1–3]. In a recent paper [3], excess molar enthalpies at $T = 298.15$ K for the ternary mixtures formed by mixing methyl *tert*-butyl ether (MTBE) with binary mixtures of 2-methylpentane (2MP), and either *n*-decane (*n*C10) or *n*-dodecane (*n*C12), were presented. To investigate the influence of another isomer of *n*-hexane, similar studies of the analogous ternary systems in which 3-methylpentane (3MP) replaced 2MP used in [3] were made.

2. Experimental

The OmniSol quality MTBE, with 0.995 mole fraction purity, was obtained from the BDH Inc. The 3MP was Research Grade Reagent from the Phillips Chemical Company. The *n*C10 and *n*C12 were obtained from the Aldrich Chemical Company. For the three hydrocarbons, the mole fraction purities, stated by the manufacturers, exceed 0.990. Apart from partial degassing, all of the components were used without further purification. Densities, measured at 298.15 K in an Anton-Paar digital densimeter (Model DMA 02C), were 735.69, 660.30, 726.31, and 745.38 kg m^{-3} for MTBE, 3MP, *n*C10, and *n*C12, respectively. These are comparable with the literature values 735.3 [4], 659.79, 726.35, and 745.18 kg m^{-3} [5].

Excess molar enthalpies H_m^E were determined in an LKB flow microcalorimeter (Model 10700-1) at 298.150 K, maintained at ±0.003 K. Details of the equipment and the operating procedure have been described previously [6,7]. For the ternary systems $x_1C_5H_{12}O + x_2CH_3CH_2CH(CH_3)CH_2CH_3 + x_3CH_3(CH_2)_vCH_3$, with $v = 8$ and 10, the excess molar enthalpy $H^E_{m,1+23}$ was determined for several pseudo-binary systems in which MTBE was added to a binary mixture of components 2 and 3, having a fixed mole ratio x_2/x_3. For this purpose, binary mixtures with $x_2/x_3 \cong 0.3$, 1.0 and 3.0 were prepared by weighing. The excess molar enthalpy of the ternary system was obtained from the

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Table 1
Experimental mole fractions x_1 and excess molar enthalpies $H^E_{m,12}$ for $x_1C_5H_{12}O + (1 - x_1)CH_3CH_2CH(CH3)CH_2CH_3$ binary mixtures at 298.15 K

x_1	$H^E_{m,12}$ (J mol^{-1})	x_1	$H^E_{m,12}$ (J mol^{-1})	x_1	$H^E_{m,12}$ (J mol^{-1})	x_1	$H^E_{m,12}$ (J mol^{-1})
0.0499	57.23	0.3004	263.22	0.5500	310.05	0.7999	199.13
0.0999	108.39	0.3502	285.66	0.5996	300.09	0.8501	157.69
0.1501	159.71	0.3999	301.37	0.6502	286.12	0.8999	109.87
0.2000	201.63	0.4505	311.55	0.7003	263.76	0.9500	53.65
0.2495	233.82	0.4997	314.55	0.7500	234.69		

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

Component		h_1 (J mol^{-1})	h_2 (J mol^{-1})	h_3 (J mol^{-1})	h_4 (J mol^{-1})	h_5 (J mol^{-1})	s (J mol^{-1})
i	*j*						
MTBE	3MP	1258.79	−2.27	−44.69	19.76		1.06[a]
MTBE	*n*C10	2000.50	−313.32	110.94	100.36	−87.36	1.20[b]
3MP	*n*C10	162.42	−1.51	−1.63			0.07[c]
MTBE	*n*C12	2279.33	−412.37	254.78	206.70	−214.72	1.10[b]
3MP	*n*C12	298.54	−5.92	−9.38			0.07[d]

[a] This work.
[b] Wang et al. [1].
[c] Hamam and Benson [8].
[d] Hamam et al. [9].

Table 3
Experimental excess molar enthalpies $H^E_{m,1+23}$ at 298.15 K for the addition of MTBE to a binary mixture of 3MP and *n*C10 to form $x_1C_5H_{12}O + x_2CH_3CH_2CH(CH_3)CH_2CH_3 + x_3C_{10}H_{22}$ and values of $H^E_{m,123}$ calculated from Eq. (1) using $H^E_{m,23}$ obtained from Eq. (2) with coefficients from Table 2

x_1	$H^E_{m,1+23}$ (J mol^{-1})	$H^E_{m,123}$ (J mol^{-1})	x_1	$H^E_{m,1+23}$ (J mol^{-1})	$H^E_{m,123}$ (J mol^{-1})	x_1	$H^E_{m,1+23}$ (J mol^{-1})	$H^E_{m,123}$ (J mol^{-1})
$x_2/x_3 = 0.3334$, $H^E_{m,23}$ (J mol^{-1}) = 30.24								
0.0500	80.11	108.84	0.4003	424.16	442.29	0.7000	401.62	410.69
0.1001	152.58	179.79	0.4502	442.65	459.27	0.7501	364.39	371.95
0.1500	216.19	241.89	0.5000	451.73	466.85	0.8000	316.49	322.54
0.2000	273.61	297.80	0.5505	452.16	465.75	0.8499	257.22	261.76
0.2499	327.37	350.05	0.5997	445.60	457.70	0.9006	184.04	187.05
0.3000	370.28	391.45	0.6501	429.52	440.10	0.9500	100.37	101.88
0.3498	397.16	416.82						
$x_2/x_3 = 0.9996$, $H^E_{m,23}$ (J mol^{-1}) = 40.60								
0.0501	71.28	109.85	0.4002	382.55	406.90	0.6998	354.61	366.80
0.1000	138.09	174.63	0.4502	397.73	420.05	0.7502	320.29	330.43
0.1501	194.83	229.34	0.5002	405.08	425.37	0.8001	277.21	285.33
0.1999	247.72	280.21	0.5501	402.20	420.47	0.8503	223.07	229.15
0.2502	295.72	326.16	0.6003	395.62	411.85	0.9002	159.88	163.93
0.3006	327.92	356.32	0.6497	380.60	394.82	0.9500	84.33	86.36
0.3498	358.24	384.64						
$x_2/x_3 = 2.6969$, $H^E_{m,23}$ (J mol^{-1}) = 32.12								
0.0500	66.39	96.90	0.4003	341.52	360.78	0.6999	308.31	317.95
0.1000	124.16	153.07	0.4499	352.83	370.50	0.7500	276.61	284.64
0.1499	178.03	205.34	0.4996	355.70	371.77	0.8007	238.22	244.62
0.2000	225.74	251.44	0.5498	354.21	368.67	0.8495	191.60	196.43
0.2498	262.16	286.26	0.6004	348.74	361.58	0.8998	134.63	137.85
0.3004	295.89	318.36	0.6497	334.22	345.47	0.9500	72.00	73.61
0.3503	320.56	341.43						

Ternary term for representation of $H^E_{m,1+23}$ by Eqs. (3) and (4): $H^E_{m,\mathrm{T}}\,(\mathrm{J\,mol^{-1}}) = x_1x_2x_3(8.60 + 359.39x_1 + 527.27x_2 - 265.30x_1^2 - 2737.25x_1x_2 - 458.76x_2^2$; $s\ (\mathrm{J\,mol^{-1}}) = 2.58$.

Table 4
Experimental excess molar enthalpies $H^E_{m,1+23}$ at 298.15 K for the addition of MTBE to a binary mixture of 3MP and *n*C12 to form $x_1C_5H_{12}O + x_2CH_3CH_2CH(CH_3)CH_2CH_3 + x_3C_{12}H_{26}$ and values of $H^E_{m,123}$ calculated from Eq. (1) using $H^E_{m,23}$ obtained from Eq. (2) with coefficients from Table 2

x_1	$H^E_{m,1+23}$ (J mol^{-1})	$H^E_{m,123}$ (J mol^{-1})	x_1	$H^E_{m,1+23}$ (J mol^{-1})	$H^E_{m,123}$ (J mol^{-1})	x_1	$H^E_{m,1+23}$ (J mol^{-1})	$H^E_{m,123}$ (J mol^{-1})
$x_2/x_3 = 0.3334$, $H^E_{m,23}$ (J mol^{-1}) = 54.99								
0.0501	83.87	136.10	0.3997	462.71	495.72	0.6992	452.17	468.71
0.0998	163.55	213.05	0.4490	482.38	512.68	0.7493	415.13	428.92
0.1499	225.47	272.22	0.4999	497.45	524.95	0.7999	361.73	372.73
0.1998	286.45	330.45	0.5500	504.30	529.04	0.8503	294.94	303.17
0.2500	348.21	389.45	0.5998	494.92	516.93	0.8966	221.45	227.14
0.3001	399.29	437.78	0.6499	480.89	500.14	0.9499	116.59	119.34
0.3483	430.21	466.05						
$x_2/x_3 = 0.9996$, $H^E_{m,23}$ (J mol^{-1}) = 74.63								
0.0500	77.19	148.09	0.4004	407.90	452.65	0.6998	388.69	411.10
0.1000	141.23	208.40	0.4498	425.27	466.33	0.7498	352.38	371.05
0.1500	209.80	273.24	0.4998	434.04	471.37	0.7998	306.48	321.42
0.1999	261.75	321.47	0.5500	435.20	468.79	0.8500	248.35	259.55
0.2500	314.17	370.15	0.6001	427.23	457.08	0.9041	172.07	179.23
0.2999	354.25	406.50	0.6497	413.00	439.14	0.9500	96.13	99.86
0.3504	380.81	429.29						
$x_2/x_3 = 2.9976$, $H^E_{m,23}$ (J mol^{-1}) = 56.11								
0.0500	69.46	122.77	0.3996	354.21	387.90	0.7000	325.86	342.69
0.1000	129.01	179.51	0.4500	366.10	396.96	0.7499	294.08	308.11
0.1500	185.08	232.78	0.4996	371.38	399.46	0.8000	253.14	264.36
0.1999	232.44	277.34	0.5496	370.31	395.58	0.8496	204.35	212.79
0.2502	271.76	313.83	0.6005	362.88	385.30	0.8999	145.61	151.23
0.3009	303.04	342.27	0.6496	350.32	369.98	0.9500	78.21	81.02
0.3502	333.53	369.99						

Ternary term for representation of $H^E_{m,1+23}$ by Eqs. (3) and (4) $H^E_{m,T}(\mathrm{J\,mol^{-1}}) = x_1x_2x_3(-1876.93 + 3098.73x_1 + 5426.99x_2 - 657.62x_1^2 - 6846.09x_1x_2 - 3610.33x_2^2)$; $s(\mathrm{J\,mol^{-1}}) = 4.25$.

relation

$$H^E_{m,123} = H^E_{m,1+23} + (1 - x_1)H^E_{m,23}, \tag{1}$$

where $H^E_{m,23}$ is the excess molar enthalpy of the particular binary mixture of 3MP and either *n*C10 or *n*C12. Over most of the mole fraction range of component 1, the errors of the excess enthalpies and the mole fractions of the mixtures are estimated to be less than $0.005|H^E_{m,1+23}|$ and less than 5×10^{-4}, respectively.

3. Results and discussion

Excess molar enthalpies $H^E_{m,ij}$ $(i < j)$, measured at T = 298.15 K, for four of the constituent binary systems of present interest, have been reported previously: MTBE(1) + *n*C10(3) [1], MTBE(1) *n*C12(3) [1], *n*C10(3) + 3MP(2) [8] and *n*C12(3) + 3MP(2) [9]. Excess enthalpies for the MTBE + 3MP binary measured in this study are listed in Table 1. Coefficients h_k for representing the measured results by the following smoothing function

$$H^E_{m,ij}(\mathrm{J\,mol^{-1}}) = x_i(1 - x_i)\sum_{k=1}^{m} h_k(1 - 2x_i)^{k-1}, \tag{2}$$

where $i < j$ are listed in Table 2, along with the standard deviation, s, of the representation. Also included in Table 2 are the representations of $H^E_{m,ij}$ for the other four constituent-binaries [1,8,9].

The coefficients h_k obtained from the present work together with those reported in the literature for the other four constituent binaries are listed in Table 2.

The experimental results for the two ternary mixtures are reported in Tables 3 and 4, where values of $H^E_{m,1+23}$ are listed against the mole fraction x_1 of MTBE. Also included in those tables are the corresponding values of $H^E_{m,123}$, calculated from Eq. (1), with values of $H^E_{m,23}$ obtained from Eq. (2) using the coefficients reported in Table 2. The results for $H^E_{m,1+23}$ are plotted in Figs. 1 and 2. Also plotted in those figures are the results given in Table 1, corresponding to the cases $x_2 = 0$ [1] and $x_3 = 0$ reported in this work. In all cases, the maximum values of $H^E_{m,1+23}$ and $H^E_{m,123}$ occur near $x_1 = 0.5$. At constant x_1, $H^E_{m,1+23}$ increases as $x_2/(1 - x_1 - x_2)$ increases and the increases are relatively more significant for the mixtures containing *n*C12. The values of $H^E_{m,1+23}$ were represented as a sum of binary terms [10] with an added ternary contribution

$$H^E_{m,1+23} = \left\{\frac{x_2}{1 - x_1}\right\} H^E_{m,12} + \left\{\frac{1 - x_1 - x_2}{1 - x_1}\right\} H^E_{m,13} + H^E_{m,T}. \tag{3}$$

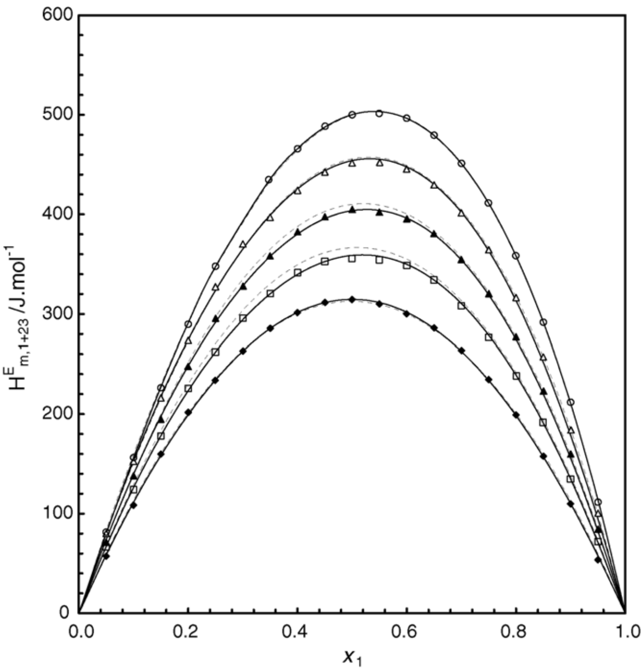


Fig. 1. Excess molar enthalpies, $H^{\mathrm{E}}_{m,1+23}$, for $\{x_1C_5H_{12}O + x_2CH_3CH_2CH(CH_3)CH_2CH_3 + (1 - x_1 - x_2)C_{10}H_{22}\}$ mixtures at the temperature 298.15 K. Experimental results: (○) $x_1 + x_2 = 1$; (△) $x_2/(1 - x_1 - x_2) = 0.3334$; (▲) $x_2/(1 - x_1 - x_2) = 0.9996$; (□) $x_2/(1 - x_1 - x_2) = 2.6969$; (♦) $x_2 = 0$ [1]; (—) calculated from the representation of the results by Eq. (3) with $H^{\mathrm{E}}_{m,\mathrm{T}}$ from the footnote of Table 3; (- - -) estimated by the Liebermann–Fried model.

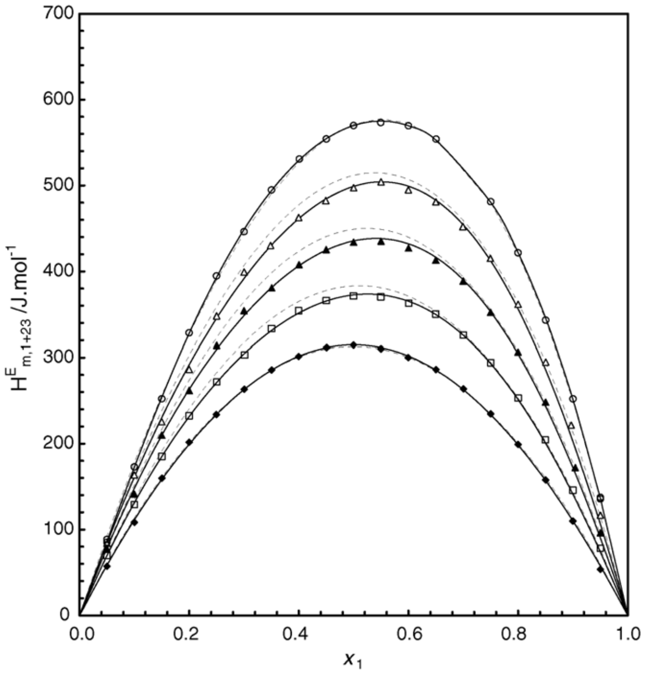


Fig. 2. Excess molar enthalpies, $H^{\mathrm{E}}_{m,1+23}$, for $\{x_1C_5H_{12}O + x_2CH_3CH_2CH(CH_3)CH_2CH_3 + (1 - x_1 - x_2)C_{12}H_{26}\}$ mixtures at the temperature 298.15 K. Experimental results: (○) $x_1 + x_2 = 1$; (△) $x_2/(1 - x_1 - x_2) = 0.3334$; (▲) $x_2/(1 - x_1 - x_2) = 0.9996$; (□) $x_2/(1 - x_1 - x_2) = 2.9976$; (♦) $x_2 = 0$ [1]; (—) calculated from the representation of the results by Eq. (3) with $H^{\mathrm{E}}_{m,\mathrm{T}}$ from the footnote of Table 4; (- - -) estimated by the Liebermann–Fried model.

In the present work, the form

$$H^{\mathrm{E}}_{m,\mathrm{T}}(\mathrm{J\,mol^{-1}}) = x_1x_2(1 - x_1 - x_2)(c_0 + c_1x_1 + c_2x_2 + c_3x_1^2 + c_4x_1x_2 + c_5x_2^2 + \cdots, \qquad (4)$$

which was adopted for the ternary contribution, is similar to that employed by Morris et al. [11]. The values of the coefficients c_i were obtained from least-squares analyses in which Eqs. (3) and (4) were fitted to the values of $H^{\mathrm{E}}_{m,1+23}$ in Tables 3 and 4. The resulting forms for $H^{\mathrm{E}}_{m,\mathrm{T}}$ are given in the footnotes of those two tables, along with the standard deviations, s, for the representations of the values of $H^{\mathrm{E}}_{m,1+23}$. The solid curves for $H^{\mathrm{E}}_{m,1+23}$ in Figs. 1 and 2 were calculated from Eq. (3) using these representations.

Eqs. (1)–(4) were also used to calculate the constant $H^{\mathrm{E}}_{m,123}$ contours plotted on the Roozeboom diagrams in Fig. 3(a) and Fig. 4(a). The general characteristics of these are similar. In both figures, all of the contours extend to the edge of the triangle and there is no indication of an internal maximum.

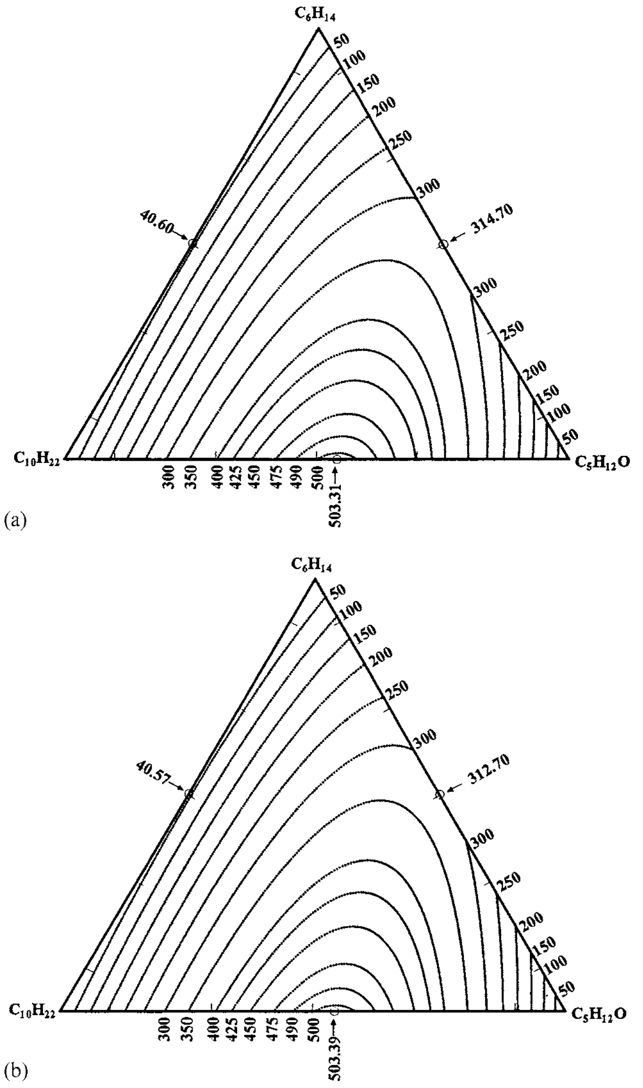
Recent work [12] indicates that an extension of the model of Liebermann and Fried [13,14] can be useful in representing the excess enthalpies of binary mixtures and also has the potential for estimating the enthalpies of ternary mixtures from data for the pure components and their binary mixtures. It is therefore of interest to examine how well the Liebermann–Fried model can represent the enthalpies of the present ternary systems.

The values of the Liebermann–Fried interaction parameters, A_{ij} and A_{ji}, for all the five constituent binaries are given in Table 5. These were obtained by fitting the Liebermann–Fried formula for $H^{\mathrm{E}}_{m,ij}$ to the experimental results reported in Table 1 for the MTBE + 3MP binary, as well as those evaluated from the literature values for the other four binaries [1,8,9]. Also included in Table 5 are values of the standard deviations, s, achieved in the fitting process, and values [1,9,15] of the isobaric thermal expansivities α_{p}, used in evaluating the contributions due to different sizes of the molecules.

Estimates of $H^{\mathrm{E}}_{m,1+23}$, derived from the Libermann–Fried model, are shown as dashed curves in Figs. 1 and 2. In both cases, the model predicts correctly the order of the three experimental curves and their positions relative to the curves for the two constituent binaries. The root mean square deviations for the 57 points in Tables 3 and 4 are 2.58 and 4.25 J mol^{-1}, respectively.

Constant $H^{\mathrm{E}}_{m,123}$ contours, estimated on the basis of the Liebermann–Fried model, are shown on the Roozeboom diagrams in Fig. 3(b) and Fig. 4(b). A comparison of the two parts in each figure indicates that the model provides useful estimates of $H^{\mathrm{E}}_{m,123}$ for both of the present mixtures.

A comparison of the measured excess molar enthalpies obtained in the work for the ternary system containing 3MP with those reported in [3] for the ternary system containing



(a)

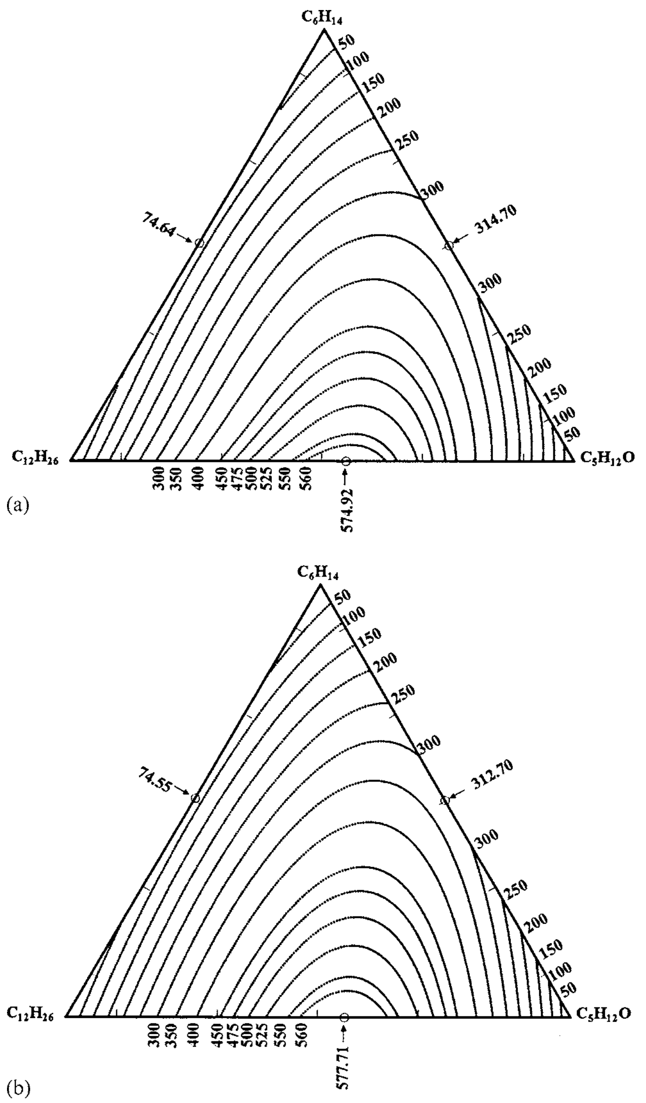
(b)

Fig. 3. Contours for constant values of $H^E_{m,123}$ for $\{x_1C_5H_{12}O + x_2CH_3CH_2\text{-}CH(CH_3)CH_2CH_3 + (1 - x_1 - x_2)C_{10}H_{22}\}$ mixtures at the temperature 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) estimated by the Liebermann–Fried model.

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		A_{ij}	A_{ji}	s(J mol^{-1})	α_p (kK^{-1})	
i	j				i	j
MTBE	3MP	0.8895	0.8955	2.43	1.423[a]	1.396[b]
MTBE	nC10	0.9949	0.6952	1.95	1.423[a]	1.051[c]
3MP	nC10	1.0597	0.8958	0.07	1.396[b]	1.051[c]
MTBE	nC12	1.0107	0.6468	3.50	1.423[a]	0.960[c]
3MP	nC12	1.0727	0.8505	0.14	1.396[b]	0.960[c]

[a] Wang et al. [1].
[b] Hamam et al. [9].
[c] Benson et al. [15].



(a)

(b)

Fig. 4. Contours for constant values of $H^E_{m,123}$ for $\{x_1C_5H_{12}O + x_2CH_3CH_2\text{-}CH(CH_3)CH_2CH_3 + (1 - x_1 - x_2)C_{12}H_{26}\}$ mixtures at the temperature 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) estimated by the Liebermann–Fried model.

2MP indicates that the differences are rather moderate. However, there are differences between the Libermann and Fried model parameters for the MTBE-3MP and the MTBE-2MP binaries. Previously, the Liebermann–Fried model parameters A_{ij} and A_{ji} were successfully applied for the prediction of binary and ternary vapor–liquid equilibria (VLE) for mixtures containing MTBE with hydrocarbon [16]. The newly acquired values expand the available list of these parameters, useful in further VLE predictions.

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