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Excess molar enthalpies of the ternary mixtures: dibutyl ether+2,2,4-trimethylpentane+(*n*-decane or *n*-dodecane)

Zhaohui Wang, Yoshiteru Horikawa, 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 two ternary mixtures $x_1\{CH_3(CH_2)_3\}_2O + x_2(CH_3)_3CCH_2CH(CH_3)_2 + x_3CH_3(CH_2)_vCH_3$, where $v = 8$ and 10. Smooth representations of the results are presented and used to construct constant excess molar enthalpy contours on Roozeboom diagrams. It is shown that good estimates of the ternary enthalpies can be obtained from the Liebermann and Fried model, using only the physical properties of the components and their binary mixtures. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Dibutyl ether; 2,2,4-Trimethylpentane; *n*-Decane; *n*-Dodecane; Excess molar enthalpy; Ternary system; Liebermann–Fried model

1. Introduction

A recent paper [1], from our laboratory, reported excess molar enthalpies at 298.15 K for the ternary systems consisting of di-*n*-butyl ether (DNBE), 2,2,4-trimethylpentane (TMP), together with either *n*-heptane (*n*C7) or *n*-octane (*n*C8). As an extension of that investigation, similar measurements have been made for the analogous systems, in which the *n*C7 and *n*C8 were replaced by *n*-decane (*n*C10) and *n*-dodecane (*n*C12), respectively.

2. Experimental

The components, used for the present measurements, were obtained from Aldrich. The TMP (HPLC Grade) had a stated purity > 99.7 mol%; the DNBE, *n*C10, and *n*C12 had purities of at least 99 mol%. Apart from partial degassing, all of the components were used as received from the manufacturer. Densities, measured at 298.15 K in an Anton-Paar digital densimeter, were 763.99, 688.04, 726.31 and 745.38 kg m^{-3} for DNBE, TMP, *n*C10 and *n*C12, respectively. These are in reasonable agreement with values in the literature [2,3].

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].

For the ternary systems $x_1\{CH_3(CH_2)_3\}_2O + x_2(CH_3)_3CCH_2CH(CH_3)_2 + x_3CH_3(CH_2)_vCH_3$, with $v = 8$ and 10, the excess molar enthalpy $H_{m,1+23}^E$ was determined for several pseudo-binary systems in which DNBE was added to a binary mixture of components 2 and 3, having a fixed mole ratio

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[*] Corresponding author. Tel.: +1-613-562-5800, ext: 6118; fax: +1-613-562-5172.
E-mail address: gbenson@eng.uottawa.ca (G.C. Benson).

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

Component i	j	h_1	h_2	h_3	h_4	h_5	$s(\mathrm{J\,mol^{-1}})$
DNBE	TMP [1]	458.11	22.17	12.51	13.33		0.26
DNBE	*n*C10 [6]	742.66	−15.25	20.29			0.21
TMP	*n*C10 [7]	278.07	−12.38	7.17			0.32
DNBE	*n*C12 [6]	955.57	−66.14	24.40			0.50
TMP	*n*C12 [8]	470.62	−24.85	39.15	6.66	−89.15	0.48

x_2/x_3. For this purpose, binary mixtures with $x_2/x_3 \approx 0.3$, 1.0 and 3.0 were prepared by weighing. The excess molar enthalpy of the ternary system was obtained from the relation

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

where $H^{\mathrm{E}}_{\mathrm{m},23}$ is the excess molar enthalpy of the particular binary mixture of TMP and either *n*C10 or *n*C12. Over most of the mole fraction range of component 1, the errors of $H^{\mathrm{E}}_{\mathrm{m},1+23}$ are estimated to be less than 0.5%. Errors in the mole fractions of the final ternary mixtures are estimated to be less than 5×10^{-4}.

3. Results and discussion

Excess molar enthalpies $H^{\mathrm{E}}_{\mathrm{m},ij}(i < j)$, at $T = 298.15\,\mathrm{K}$, for the five constituent-binary systems of present interest, have been reported in our previous papers: DNBE(1) + TMP(2) [1], DNBE(1) + *n*C10(3) [6], TMP(2) + *n*C10(8) [7], DNBE(1) + *n*C12(3) [6], and TMP(2) + *n*C12(3) [8]. Coefficients h_k for the representations of those results by the smoothing function

$$H^{\mathrm{E}}_{\mathrm{m},ij}(\mathrm{J\,mol^{-1}}) = x_i(1 - x_i)\sum_{k=1}^{m} h_k(1 - 2x_i)^{k-1} \quad (i < j) \tag{2}$$

are listed in Table 1, along with the standard deviations s of the representations.

The experimental results for $H^{\mathrm{E}}_{\mathrm{m},1+23}$ and the corresponding values of $H^{\mathrm{E}}_{\mathrm{m},123}$ are summarized in Tables 2 and 3 for $x_1\{\mathrm{CH_3(CH_2)_3}\}_2\mathrm{O} + x_2(\mathrm{CH_3})_3\mathrm{CCH_2CH(CH_3)_2} + x_3\mathrm{CH_3(CH_2)}_v\mathrm{CH_3}$, with $v = 8$

Table 2
Experimental excess molar enthalpies $H^{\mathrm{E}}_{\mathrm{m},1+23}$ at 298.15 K for the addition of DNBE to a binary mixture of TMP and *n*C10 to form $x_1\{\mathrm{CH_3(CH_2)_3}\}_2\mathrm{O} + x_2(\mathrm{CH_3})_3\mathrm{CCH_2CH(CH_3)_2} + x_3\mathrm{CH_3(CH_2)_8CH_3}$, and values of $H^{\mathrm{E}}_{\mathrm{m},123}$ calculated from Eq. (1) using $H^{\mathrm{E}}_{\mathrm{m},23}$ obtained from Eq. (2) with coefficients from Table 1

x_1	$H^{\mathrm{E}}_{\mathrm{m},1+23}$ (J mol^{-1})[a]	$H^{\mathrm{E}}_{\mathrm{m},123}$ (J mol^{-1})
$x_2/x_3 = 0.3335$, $H^{\mathrm{E}}_{\mathrm{m},23} = 51.32(\mathrm{J\,mol^{-1}})$		
0.0500	30.96	79.72
0.1001	57.64	103.83
0.1499	82.10	125.73
0.1981	102.90	144.06
0.2501	118.18	156.67
0.3001	132.19	168.11
0.3504	143.07	176.41
0.3999	150.92	181.72
0.4502	155.51	183.73
0.5005	156.43	182.07
0.5497	156.38	179.49
0.5998	152.13	172.67
0.6496	144.35	162.34
0.6999	133.13	148.53
0.7503	118.94	131.75
0.7998	101.62	111.89
0.8500	81.50	89.20
0.8999	57.93	63.07
0.9500	29.85	32.41
$x_2/x_3 = 0.9994$, $H^{\mathrm{E}}_{\mathrm{m},23} = 69.52(\mathrm{J\,mol^{-1}})$		
0.0500	26.88	92.92
0.1000	49.89	112.45
0.1500	70.90	129.99
0.2000	89.33	144.94
0.2495	102.08	154.25
0.2994	114.33	163.03
0.3504	123.64	168.80
0.3997	130.03	171.76
0.4494	133.87	172.15
0.5002	135.10	169.85
0.5498	134.07	165.37
0.5999	130.02	157.83
0.6502	122.89	147.20

Table 2 (*Continued*)

x_1	$H^{E}_{m,1+23}$ (J mol^{-1})[a]	$H^{E}_{m,123}$ (J mol^{-1})
0.6998	113.48	134.35
0.7502	101.26	118.62
0.7998	86.29	100.21
0.8500	68.67	79.10
0.9000	48.55	55.50
0.9500	25.43	28.91
$x_2/x_3 = 2.9987$, $H^{E}_{m,23} = 53.65$(J mol^{-1})		
0.0499	23.54	74.51
0.1000	44.48	92.76
0.1500	63.61	109.21
0.2000	79.67	122.59
0.2498	91.57	131.82
0.3000	102.18	139.73
0.3501	110.52	145.38
0.4001	116.16	148.34
0.4500	119.31	148.82
0.5005	119.75	146.55
0.5505	118.88	143.00
0.6000	114.63	136.09
0.6498	108.55	127.34
0.7000	100.03	116.13
0.7493	89.03	102.48
0.7998	75.60	86.34
0.8499	60.28	68.33
0.8999	42.56	47.93
0.9496	22.74	25.44

[a] Ternary term for representing $H^{E}_{m,1+23}$ by Eqs. (3) and (4): $H^{E}_{m,T}\,(\mathrm{J\,mol^{-1}}) = [x_1x_2x_3/(1 - x_1 + x_2)]\,(40.98 - 1953.74x_1 - 471.70x_2 + 4267.02x_1^2 + 2482.05x_1x_2 - 490.51x_2^2 - 2777.44x_1^3 - 4882.40x_1^2x_2)$; $s(\mathrm{J\,mol^{-1}}) = 0.46$.

and 10, respectively. The results for $H^{E}_{m,1+23}$ in Table 2 are plotted in Fig. 1, and those in Table 3 are plotted in Fig. 2. Also plotted in these figures are curves for the cases $x_2 = 0$ and $x_3 = 0$, calculated from Eq. (2) with the coefficients given in Table 1.

For both systems, the maximum values of $H^{E}_{m,1+23}$ and $H^{E}_{m,123}$ occur near $x_1 = 0.5$. The values of $H^{E}_{m,1+23}$ fall between the results for the two constituent-binaries and at constant x_1, $H^{E}_{m,1+23}$ decreases monotonically as x_2/x_3 increases.

Representation of the values of $H^{E}_{m,1+23}$ was based on the relation

$$H^{E}_{m,1+23} = \left(\frac{x_2}{1 - x_1}\right)H^{E}_{m,12} + \left(\frac{x_3}{1 - x_1}\right)H^{E}_{m,13} + H^{E}_{m,T} \tag{3}$$

Table 3

Experimental excess molar enthalpies $H^{E}_{m,1+23}$ at 298.15 K for the addition of DNBE to a binary mixture of TMP and *n*C12 to form $x_1\{CH_3(CH_2)_3\}_2O + x_2(CH_3)_3CCH_2CH(CH_3)_2 + x_3CH_3(CH_2)_{10}CH_3$, and values of $H^{E}_{m,123}$ calculated from Eq. (1) using $H^{E}_{m,23}$ obtained from Eq. (2) with coefficients from Table 1

x_1	$H^{E}_{m,1+23}$(J mol^{-1})[a]	$H^{E}_{m,123}$(J mol^{-1})
$x_2/x_3 = 0.3335$, $H^{E}_{m,23} = 86.87$(J mol^{-1})		
0.0498	35.51	118.05
0.1000	67.48	145.67
0.1501	96.10	169.93
0.2002	120.20	189.68
0.2501	140.78	205.93
0.2997	155.14	215.98
0.3500	168.48	224.95
0.3999	178.96	231.10
0.4496	185.38	233.19
0.5000	188.13	231.57
0.5480	188.11	227.38
0.6003	183.52	218.24
0.6501	174.77	205.17
0.7003	162.23	188.27
0.7502	145.57	167.27
0.8001	125.24	142.60
0.8492	101.30	114.40
0.9001	71.72	80.40
0.9499	38.35	42.71
$x_2/x_3 = 1.0116$, $H^{E}_{m,23} = 117.69$(J mol^{-1})		
0.0500	28.57	140.37
0.1001	53.24	159.15
0.1500	76.02	176.06
0.2000	96.73	190.88
0.2500	113.25	201.52
0.2999	124.69	207.08
0.3497	135.39	211.92
0.4002	143.20	213.79
0.4513	147.97	212.55
0.4999	149.94	208.80
0.5502	149.15	202.08
0.5997	144.86	191.97
0.6500	137.82	179.01
0.7002	127.69	162.98
0.7497	114.55	144.00
0.8001	98.04	121.57
0.8499	78.47	96.13
0.9001	55.74	67.50
0.9498	29.54	35.45
$x_2/x_3 = 2.9989$, $H^{E}_{m,23} = 91.22$(J mol^{-1})		
0.0499	23.83	110.50
0.1002	46.07	128.15
0.1501	64.85	142.38
0.1999	81.82	154.80
0.2499	93.89	162.31
0.2991	104.47	168.40
0.3501	113.22	172.51
0.4003	119.77	174.48

Table 3 (*Continued*)

x_1	$H^E_{m,1+23}$(J mol^{-1})[a]	$H^E_{m,123}$(J mol^{-1})
0.4500	123.30	173.47
0.4992	124.64	170.32
0.5495	123.66	164.75
0.5995	119.91	156.45
0.6498	113.33	145.27
0.6996	104.65	132.05
0.7495	93.20	116.05
0.7999	79.37	97.62
0.8500	63.20	76.89
0.8998	45.38	54.52
0.9499	24.18	28.75

[a] Ternary term for representing $H^E_{m,1+23}$ by Eqs. (3) and (4): $H^E_{m,T}$ (J mol^{-1}) $= [x_1x_2x_3/(1-x_1+x_2)](6.44 - 2760.44x_1 - 832.99x_2 + 5654.63x_1^2 + 3620.17x_1x_2 - 627.49x_2^2 - 3583.45x_1^3 - 6993.52x_1^2x_2)$; s(J mol^{-1}) $= 0.61$.

which consists of a sum of binary contributions [9], and an added ternary term $H^E_{m,T}$. The form

$$H^E_{m,T} = \left[\frac{x_1x_2x_3}{(1-x_1+x_2)}\right](c_0 + c_1x_1 + c_2x_2 + c_3x_1^2 + c_4x_1x_2 + \cdots) \qquad (4)$$

which was adopted for the latter is similar to the form used by Morris et al. [10], with an extra skewing factor $(1-x_1+x_2)^{-1}$ inserted. The values of the coefficients c_j were adjusted by least-squares analyses in which Eqs. (3) and (4) were fitted to the values of $H^E_{m,1+23}$ in Tables 2 and 3. In doing this, the values of $H^E_{m,ij}$ for the binary contributions were calculated from Eq. (2) using the appropriate coefficients from Table 1. The resulting forms for $H^E_{m,T}$ are given in the footnotes

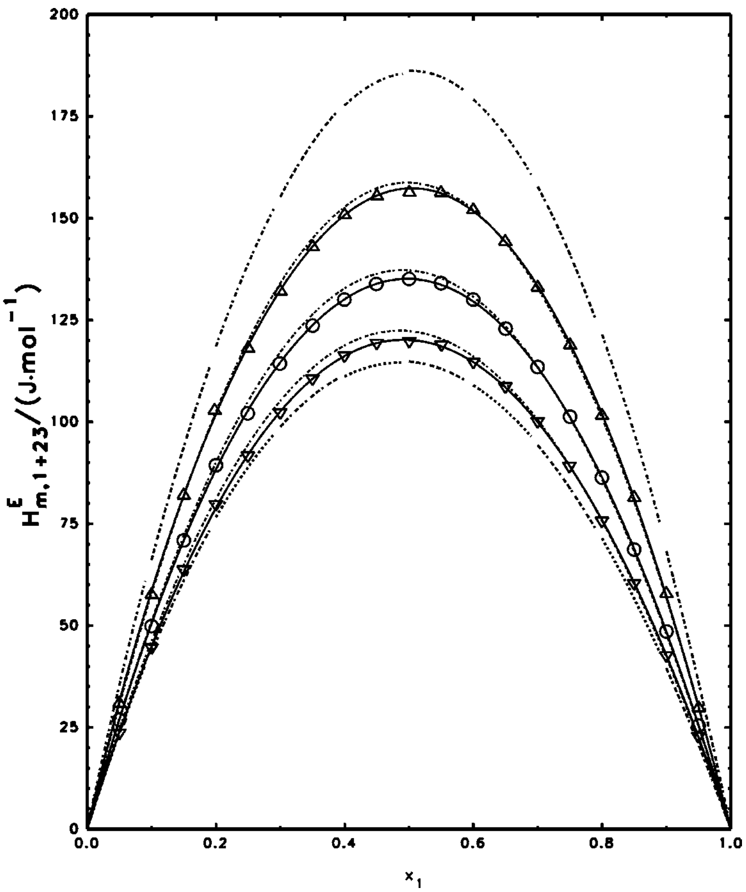

Fig. 1. Excess molar enthalpies, $H^E_{m,1+23}$, for $x_1\{CH_3(CH_2)_3\}_2O + x_2(CH_3)_3CCH_2CH(CH_3)_2 + x_3CH_3(CH_2)_8CH_3$ mixtures at 298.15 K. Experimental results: (Δ)$x_2/x_3 = 0.3335$; (◯)$x_2/x_3 = 0.9994$; (∇)$x_2/x_3 = 2.9987$. Curves: (—) calculated from Eq. (3) with $H^E_{m,T}$ from the footnote of Table 2; (-·-) $x_2 = 0$, Ref. [6]; (· · ·) $x_3 = 0$ Ref. [1]; (- - -) estimated by the Liebermann–Fried model.

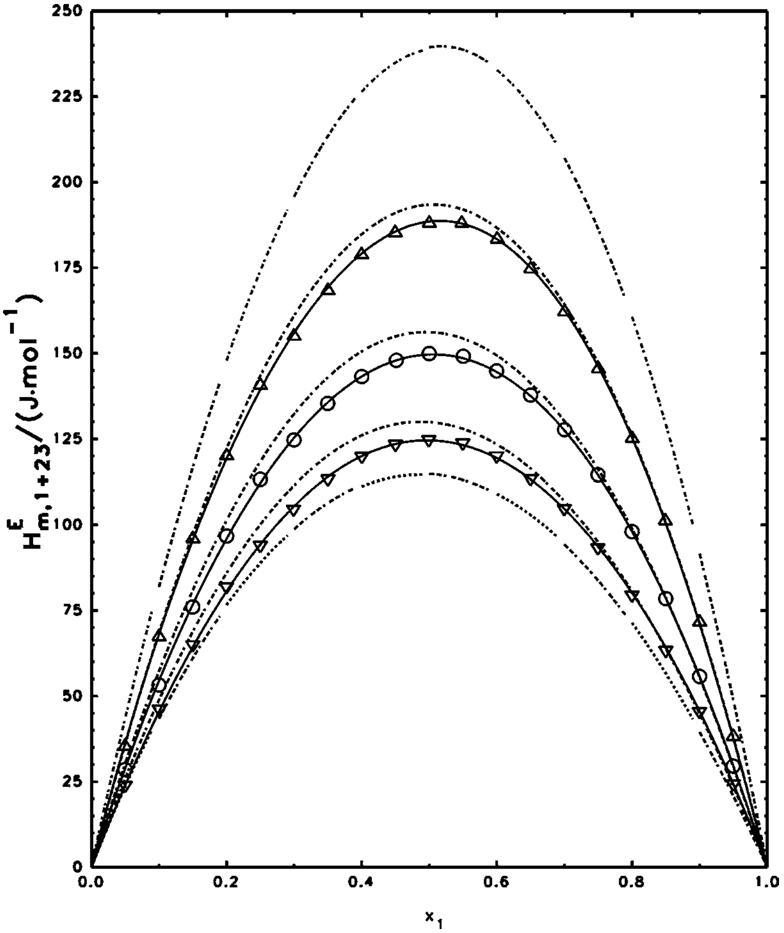

Fig. 2. Excess molar enthalpies, $H^E_{m,1+23}$, for $x_1\{CH_3(CH_2)_3\}_2O + x_2(CH_3)_3CCH_2CH(CH_3)_2 + x_3CH_3(CH_2)_{10}CH_3$ mixtures at 298.15 K. Experimental results: (Δ)$x_2/x_3 = 0.3335$; (○)$x_2/x_3 = 1.0116$; (∇)$x_2/x_3 = 2.9989$. Curves: (—) calculated from Eq. (3) with $H^E_{m,T}$ from the footnote of Table 3; (-·-) $x_2 = 0$, Ref. [6]; (···) $x_3 = 0$ Ref. [1]; (- - -) estimated by the Liebermann–Fried model.

of Tables 2 and 3, along with the standard deviations s for the representation of the values of $H^E_{m,1+23}$.

The solid curves in Figs. 1 and 2 were calculated from Eq. (3) using values of $H^E_{m,T}$ given by the formulae in the footnotes of Tables 2 and 3. It is evident from these, that the representation of the experimental results is quite good.

Some constant $H^E_{m,123}$ contours, calculated from Eqs. (1)–(4), are plotted on the Roozeboom diagrams in part (a) of Figs. 3 and 4. For the nC10 system in Fig. 3(a), there appears to be an internal maximum of 186.0 J mol^{-1}. However, this may not be real, since it is located close to the DNBE(1) + nC10(3) edge of the triangle and is only 0.3 J mol^{-1} higher than the maximum for that constituent-binary. There is no indication of an internal extremum for the nC12 system in Fig. 4(a).

In our earlier work [1] on the enthalpies of the analogous systems containing nC7 and nC8 in place of nC10 and nC12, it was found that the Liebermann–Fried model [11,12] could provide useful estimates of the ternary enthalpies using only the properties of the pure components and interaction parameters derived from the analyses of the excess enthalpies of their constituent-binaries. This approach was investigated for the present systems. Reference can be made to the

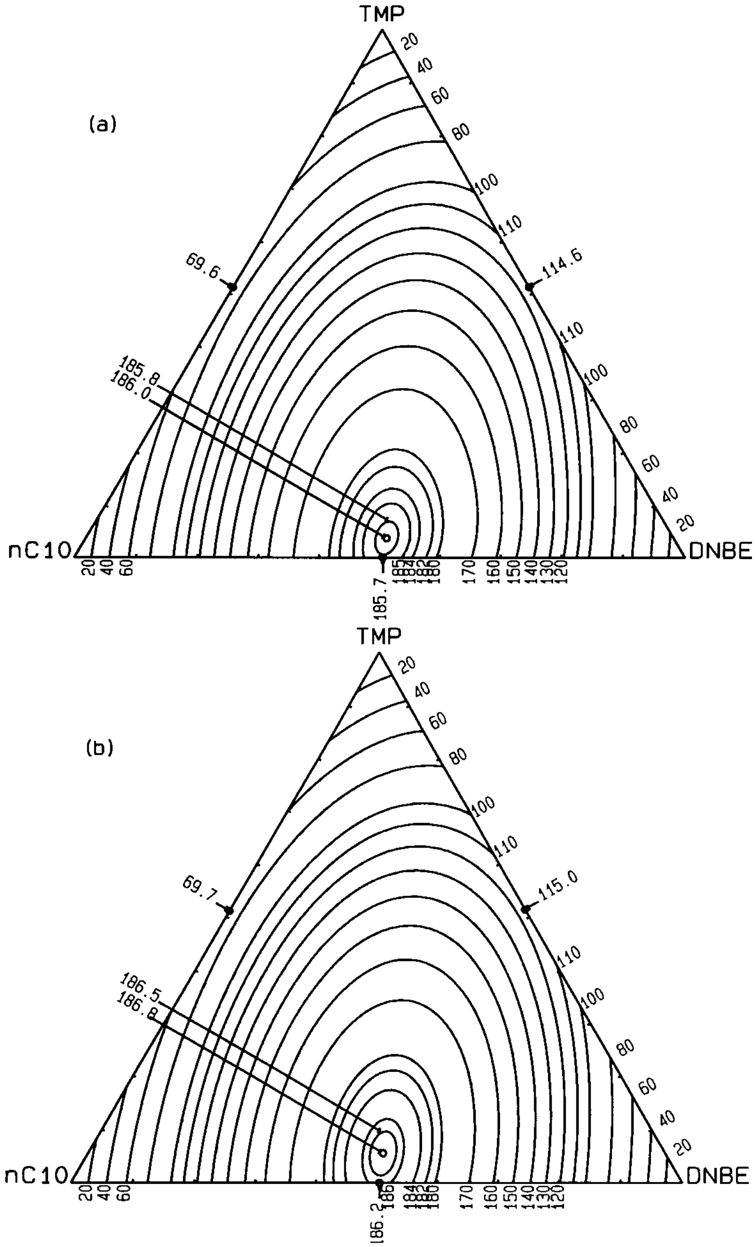

Fig. 3. Contours for constant values of $H^{\mathrm{E}}_{\mathrm{m},123}$(J mol^{-1}) for $x_1\{CH_3(CH_2)_3\}_2O + x_2(CH_3)_3CCH_2CH(CH_3)_2 + x_3CH_3(CH_2)_8CH_3$ mixtures at 298.15 K. Part (a) calculated from the representation of the experimental results by Eqs. (1)–(4) with $H^{\mathrm{E}}_{\mathrm{m},T}$ from the footnote of Table 2; part (b) estimated by the Liebermann–Fried model.

work of Wang et al. [13] for the equations used in this application.

The values of the Liebermann–Fried interaction parameters A_{ij} and A_{ji} for the constituent-binaries are given in Table 4. 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 Refs. [1,6–9]. Also included in the table are

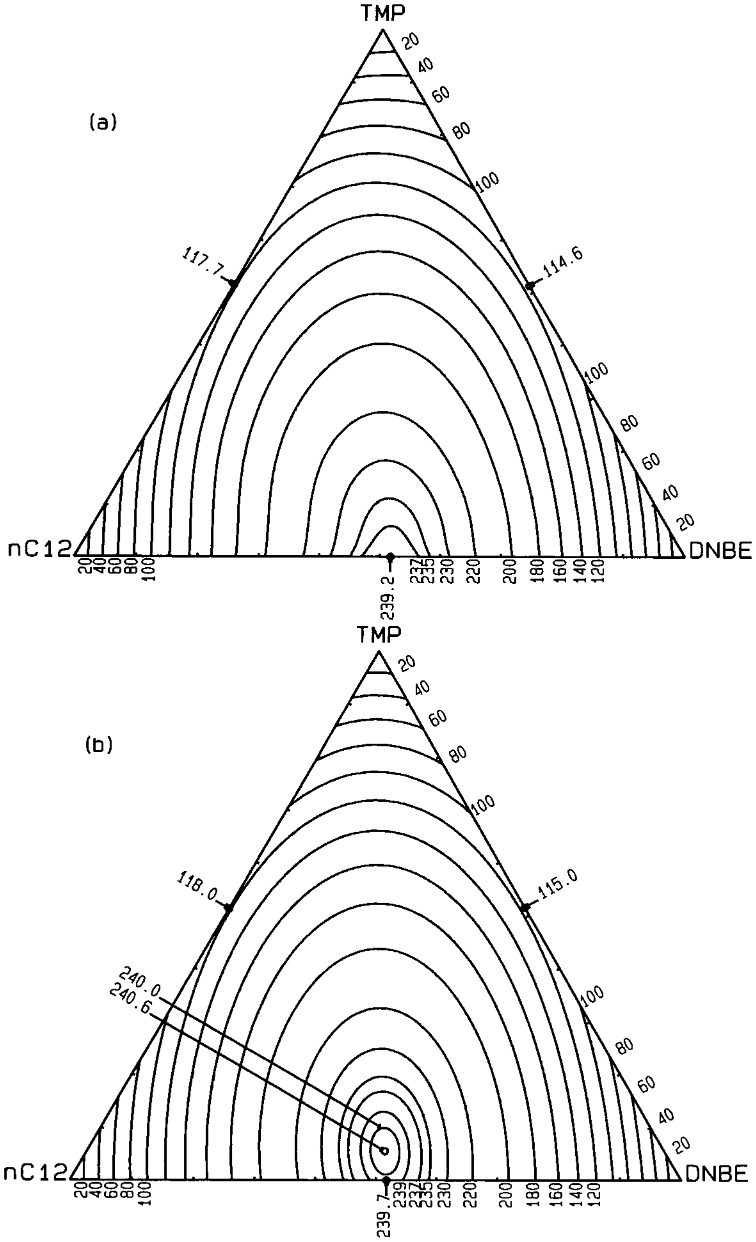

Fig. 4. Contours for constant values of $H^{\mathrm{E}}_{\mathrm{m},123}(\mathrm{J\,mol^{-1}})$ for $x_1\{CH_3(CH_2)_3\}_2O + x_2(CH_3)_3CCH_2CH(CH_3)_2 + x_3CH_3(CH_2)_{10}CH_3$ mixtures at 298.15 K. Part (a) calculated from the representation of the experimental results by Eqs. (1)–(4) with $H^{\mathrm{E}}_{\mathrm{m},T}$ from the footnote of Table 3; part (b) estimated by the Liebermann–Fried model.

values of the standard deviation s achieved in the fitting process, and values of the isobaric expansivity α_p [6,14], used in evaluating the contributions due to different sizes of the molecules.

Estimates of $H^{\mathrm{E}}_{\mathrm{m},1+23}$, derived from the Liebermann–Fried model, are shown as dashed curves in Figs. 1 and 2. It can be seen that, although the fits of the constituent-binaries are very good, there is a

Table 4
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}	$s(\mathrm{J\,mol^{-1}})$	$\alpha_p/k(K^{-1})$	
i	*j*				*i*	*j*
DNBE	TMP	0.9024	1.0137	0.47	1.126 [6]	1.197 [14]
DNBE	*n*C10	0.9509	0.9125	0.59	1.126 [6]	1.051 [6]
TMP	*n*C10	1.0180	0.9268	0.38	1.197 [14]	1.051 [6]
DNBE	*n*C12	0.9811	0.8479	0.68	1.126 [6]	0.960 [6]
TMP	*n*C12	1.0087	0.8958	0.84	1.197 [14]	0.960 [6]

tendency for the model to over-estimate $H^{\mathrm{E}}_{\mathrm{m},1+23}$ for the ternary mixtures. For the 57 points in each of Tables 2 and 3, the root mean square deviations are 1.53 and 4.14 J mol^{-1}, respectively.

Constant $H^{\mathrm{E}}_{\mathrm{m},123}$ contours, estimated on the basis of the model, are shown in the Roozeboom diagrams in part (b) of Figs. 3 and 4. In both of these, the model predicts a relatively small internal maximum close to the $\mathrm{DNBE}(1) + n$-alkane(3) edge of the triangle. Despite the differences between parts (a) and (b) in Fig. 4, it is clear that the Liebermann–Fried model provides useful estimates of $H^{\mathrm{E}}_{\mathrm{m},123}$ for both of the present systems.

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