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Excess molar enthalpies of methyl *tert*-butyl ether + (cyclohexane or 2,3-dimethylbutane) + *n*-decane ternary mixtures at 298.15 K

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Abstract

Microcalorimetric measurements of the excess molar enthalpies at 298.15 K are reported for the ternary mixtures methyl *tert*-butyl ether + (cyclohexane or 2,3-dimethylbutane) + *n*-decane. Smooth representations of the results are presented and used to construct constant enthalpy contours on a Roozeboom diagram. Application of the Flory theory of mixtures to estimate the enthalpies of the ternary mixtures from analyses of data for their constituent binaries is also described.

INTRODUCTION

The use of methyl *tert*-butyl ether (MTBE) as a gasoline-blending agent has led to an increased interest in the thermodynamic properties of mixtures of MTBE with hydrocarbons. A recent paper [1] from our laboratory reported the excess molar enthalpies H_m^E of the ternary system MBTE + *n*-hexane + *n*-decane at 298.15 K. As an extension of that work, similar measurements have been made for the ternary systems MTBE + cyclohexane + *n*-decane, and MTBE + 2,3-dimethylbutane (23DMB) + *n*-decane, in which different C_6-hydrocarbons replace the *n*-hexane used previously.

EXPERIMENTAL

Materials

The MTBE (HPLC grade) used was obtained from the Aldrich Chemical Co. The cyclohexane and 23DMB were Pure Grade materials from the Phillips Chemical Co. All of these materials had stated purities exceeding 99 mol%. The *n*-decane was the same as used in our previous work [1, 2].

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At 298.15 K, the densities of the component liquids were 735.56, 774.04, 657.13 and 726.29 kg m^{-3} for MTBE, cyclohexane, 23DMB and *n*-decane, respectively.

Equipment and technique

The excess molar enthalpies were measured at 298.15 K in a flow microcalorimeter maintained within ± 0.002 K of the nominal operating temperature. The equipment and experimental procedure were the same as in our previous work [1]. In studying the ternary systems, the excess molar enthalpy $H^E_{m,1+23}$ was measured for several pseudo-binary systems in which component 1 (MTBE) was added to a binary mixture of components 2 (cyclohexane or 23DMB) and 3 (*n*-decane) having a fixed mole ratio x_2/x_3. These binaries were prepared by weighing. The excess molar enthalpy $H^E_{m,123}$ was then obtained from the 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. Values of $H^E_{m,23}$ for cyclohexane + *n*-decane and for 23DMB + *n*-decane were taken from the literature [3, 4]. The errors in $H^E_{m,1+23}$ are estimated to be less than 0.5% over most of the MTBE mole fraction range. Errors in the mole fractions of the final ternary mixtures are estimated to be less than 5×10^{-4}.

RESULTS AND DISCUSSION

The values of $H^E_{m,12}$ measured for the binary mixture MTBE + cyclohexane are listed in Table 1. A Redlich–Kister form, representing the data, is given in the footnote of the table, along with its standard deviation s.

TABLE 1

Experimental results for the excess molar enthalpy $H^E_{m,12}$ of $x_1C_5H_{12}O + (1 - x_1)C_6H_{12}$ mixtures at 298.15 K

x_1	$H^E_{m,12}$/ J mol^{-1} [a]	x_1	$H^E_{m,12}$/ J mol^{-1} [a]	x_1	$H^E_{m,12}$/ J mol^{-1} [a]
0.0501	99.1	0.4001	456.6	0.6500	410.4
0.1000	184.9	0.4509	467.5	0.7000	375.4
0.1500	258.1	0.4999	463.6	0.7501	331.8
0.2001	321.3	0.5001	466.7	0.8001	280.6
0.2501	369.9	0.5003	466.0	0.8501	221.1
0.3000	409.5	0.5499	454.3	0.9000	153.5
0.3497	438.1	0.6003	436.8	0.9500	78.8

[a] $H^E_{m,12}/(\mathrm{J\ mol^{-1}}) = x_1(1 - x_1)[1861.87 + 208.86(1 - 2x_1) + 36.21(1 - 2x_1)^2]$; $s = 1.0$.

TABLE 2

Experimental excess molar enthalpies $H^{E}_{m,1+23}$ at 298.15 K for the addition of MTBE to a binary mixture of cyclohexane and n-decane to form $x_1C_5H_{12}O + x_2C_6H_{12} + x_3C_{10}H_{22}$, and values of $H^{E}_{m,123}$ calculated from eqn. (1) using $H^{E}_{m,23}$ from ref. 3

x_1	$H^{E}_{m,1+23}$/J mol^{-1} [a]	$H^{E}_{m,123}$/J mol^{-1}	x_1	$H^{E}_{m,1+23}$/J mol^{-1} [a]	$H^{E}_{m,123}$/J mol^{-1}	x_1	$H^{E}_{m,1+23}$/J mol^{-1} [a]	$H^{E}_{m,123}$/J mol^{-1}
$x_2/x_3 = 0.3313$, $H^{E}_{m,23}/(\mathrm{J\ mol^{-1}}) = 202.5$								
0.0500	74.9	267.3	0.4000	420.3	541.8	0.7002	394.9	455.7
0.1000	147.1	329.4	0.4496	437.4	548.9	0.7501	357.5	408.2
0.1500	211.1	383.3	0.5004	446.5	547.6	0.8001	309.6	350.1
0.2001	268.6	430.6	0.5005	446.0	547.1	0.8501	250.1	280.5
0.2501	319.6	471.5	0.5500	447.7	538.8	0.9004	179.2	199.3
0.3000	360.5	502.3	0.6002	439.2	520.2	0.9500	96.1	106.2
0.3501	394.6	526.2	0.6500	421.9	492.7			
$x_2/x_3 = 1.0032$, $H^{E}_{m,23}/(\mathrm{J\ mol^{-1}}) = 319.1$								
0.0501	72.0	375.1	0.3999	384.8	576.3	0.7002	351.3	447.0
0.1000	139.9	427.0	0.4499	399.3	574.8	0.7500	316.8	396.6
0.1500	199.8	471.0	0.5001	405.7	565.2	0.8002	270.6	334.4
0.2000	250.5	505.8	0.5503	404.6	548.0	0.8500	218.3	266.2
0.2501	296.4	535.7	0.6000	394.8	522.4	0.9000	154.5	186.4
0.3001	333.9	557.3	0.6499	377.6	489.3	0.9500	81.6	97.5
0.3503	362.8	570.1						
$x_2/x_3 = 2.9784$, $H^{E}_{m,23}/(\mathrm{J\ mol^{-1}}) = 292.2$								
0.0500	75.9	353.6	0.3998	381.2	556.6	0.7000	333.3	421.0
0.1000	143.1	406.1	0.4501	392.6	553.3	0.7500	298.4	371.5
0.1500	202.4	450.7	0.4502	392.3	553.0	0.8001	254.2	312.6
0.2000	255.2	489.0	0.5003	398.6	544.6	0.8501	203.7	247.5
0.2500	299.1	518.3	0.5501	394.8	526.3	0.9000	143.1	172.4
0.3001	334.5	539.0	0.6499	362.1	464.4	0.9500	74.4	89.0
0.3502	360.8	550.6						

[a] Ternary term for representation of $H^{E}_{m,1+23}$ by eqns. (2) and (3): $H^{E}_{m,T}/(\mathrm{J\ mol^{-1}}) = x_1x_2x_3(-38.2 - 13140.6x_1 + 735.7x_2 + 41872.6x_1^2 + 5505.0x_1x_2 - 4328.3x_2^2 - 40787.7x_1^3 - 28807.4x_1^2x_2)$; $s = 3.9$.

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 23DMB and n-decane to form $x_1C_5H_{12}O + x_2C_6H_{14} + x_3C_{10}H_{22}$, and values of $H^E_{m,123}$ calculated from eqn. (1) using $H^E_{m,23}$ from ref. 4

x_1	$H^E_{m,1+23}$/J mol^{-1} [a]	$H^E_{m,123}$/J mol^{-1}	x_1	$H^E_{m,1+23}$/J mol^{-1} [a]	$H^E_{m,123}$/J mol^{-1}	x_1	$H^E_{m,1+23}$/J mol^{-1} [a]	$H^E_{m,123}$/J mol^{-1}
$x_2/x_3 = 0.3334$, $H^E_{m,23}$/(J mol^{-1}) = 34.2								
0.0500	90.9	123.4	0.3999	449.7	470.3	0.6999	416.2	426.4
0.1000	169.1	199.9	0.4502	467.8	486.6	0.7501	377.3	385.9
0.1500	236.1	265.2	0.5002	479.0	496.1	0.8049	320.1	326.8
0.1999	296.6	324.0	0.5003	474.5	491.7	0.8500	265.4	270.5
0.2511	345.8	371.5	0.5500	476.3	491.7	0.9000	191.7	195.1
0.3000	390.1	414.0	0.6000	467.5	481.2	0.9500	105.3	107.0
0.3502	425.6	447.8	0.6499	444.1	456.1			
$x_2/x_3 = 1.0000$, $H^E_{m,23}$/(J mol^{-1}) = 46.8								
0.0499	91.6	136.0	0.4000	401.3	429.4	0.7002	365.1	379.2
0.1001	156.9	199.0	0.4501	415.3	441.1	0.7479	333.3	345.1
0.1500	216.8	256.5	0.4998	422.4	445.8	0.8000	284.3	293.7
0.2001	267.7	305.1	0.4999	421.6	445.0	0.8502	230.1	237.1
0.2499	307.7	342.8	0.5497	419.3	440.4	0.9000	166.5	171.1
0.3000	349.2	382.0	0.5998	409.7	428.4	0.9500	91.6	94.0
0.3498	379.2	409.6	0.6499	392.0	408.3			
$x_2/x_3 = 3.0080$, $H^E_{m,23}$/(J mol^{-1}) = 35.9								
0.0500	68.3	102.4	0.4001	342.1	363.7	0.7001	301.1	311.9
0.1000	131.1	163.4	0.4501	348.9	368.7	0.7500	272.7	281.7
0.1500	183.1	213.6	0.5000	355.7	373.6	0.8000	230.6	237.7
0.2000	230.6	259.3	0.5000	355.4	373.4	0.8500	186.3	191.7
0.2501	262.8	289.7	0.5498	353.7	369.9	0.9000	129.9	133.5
0.3001	298.2	323.3	0.6003	343.6	358.0	0.9500	70.0	71.8
0.3502	323.8	347.1	0.6498	329.3	341.9			

[a] Ternary term for representation of $H^E_{m,1+23}$ by eqns. (2) and (3): $H^E_{m,T}/(\mathrm{J\ mol^{-1}}) = x_1x_2x_3(3023.2 - 13002.2x_1 - 2318.0x_2 + 29364.6x_1^2 + 10005.3x_1x_2 - 1223.9x_2^2 - 18438.9x_1^3 - 25778.8x_1^2x_2)$; $s = 2.8$.

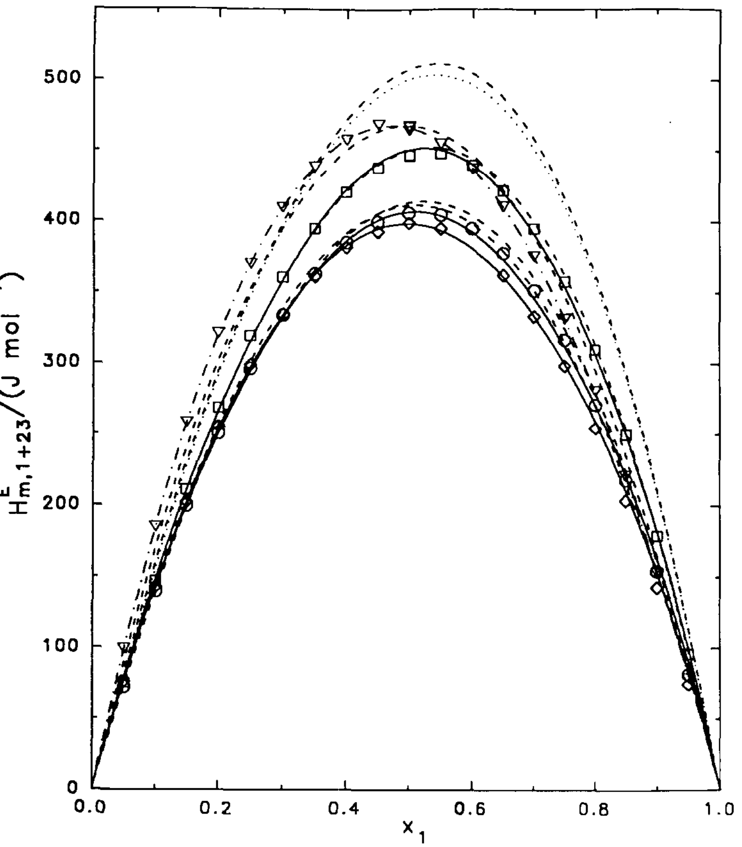

Fig. 1. Excess molar enthalpies $H^E_{m,1+23}$ at 298.15 K for the addition of MTBE to binary mixtures of cyclohexane and n-decane to form $x_1C_5H_{12}O + x_2C_6H_{12} + x_3C_{10}H_{22}$. Experimental results: □, $x_2/x_3 = 0.3313$; ○, $x_2/x_3 = 1.0032$; ◇, $x_2/x_3 = 2.9784$; ▽, $x_3 = 0$. Curves: —·—, $x_3 = 0$, calculated from the representation in the footnote of Table 1; · · ·, $x_2 = 0$, calculated from the representation in ref. 1; ——, calculated from eqn. (2) with $H^E_{m,T}$ from the footnote of Table 2; – – –, calculated from the Flory theory.

The experimental results for $H^E_{m,1+23}$ and the corresponding values of $H^E_{m,123}$ are listed in Tables 2 and 3 for the two ternary systems. The values of $H^E_{m,1+23}$ are plotted in Figs. 1 and 2. The results for $H^E_{m,12}$ from Table 1 can be identified with $H^E_{m,1+23}$ for the case $x_3 = 0$, and are included in Fig. 1 for comparison.

$H^E_{m,1+23}$ was represented as a sum of binary terms [5] with an added ternary contribution

$$H^E_{m,1+23} = \left(\frac{x_2}{1-x_1}\right)H^E_{m,12} + \left(\frac{x_3}{1-x_1}\right)H^E_{m,13} + H^E_{m,T} \tag{2}$$

where values of $H^E_{m,ij}$ were calculated from the appropriate smoothing functions as given either in Table 1 or in the literature [1, 6]. Following Morris et al. [7], the form

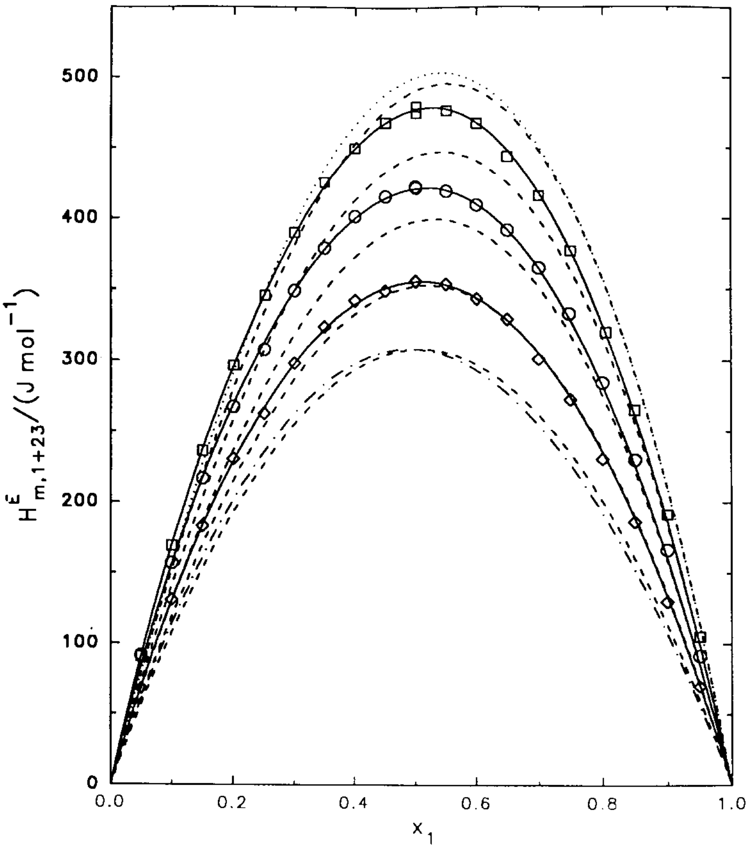

Fig. 2. Excess molar enthalpies $H^E_{m,1+23}$ at 298.15 K for the addition of MTBE to binary mixtures of 23DMB and n-decane to form $x_1C_5H_{12}O + x_2C_6H_{14} + x_3C_{10}H_{22}$. Experimental results: □, $x_2/x_3 = 0.3334$; ○, $x_2/x_3 = 1.0000$; ◇, $x_2/x_3 = 3.0080$. Curves: —·—, $x_3 = 0$, calculated from the representation in ref. 6; · · ·, $x_2 = 0$, calculated from the representation in ref. 1; ——, calculated from eqn. (2) with $H^E_{m,T}$ from the footnote of Table 3; – – –, calculated from the Flory theory.

$$H^E_{m,T} = x_1x_2x_3(c_0 + c_1x_1 + c_2x_2 + c_3x_1^2 + c_4x_1x_2 + c_5x_2^2 + \ldots) \tag{3}$$

was adopted for the ternary term. Values of the parameters c_i were obtained from least-squares analyses in which eqns. (2) and (3) were fitted to the experimental results for the ternary systems. These representations are given in the footnotes of Tables 2 and 3, along with their standard deviations s; curves calculated from them are shown in Figs. 1 and 2.

Some enthalpy contours corresponding to constant values of $H^E_{m,123}$ are plotted on the Roozeboom diagrams shown in Figs. 3 and 4. Previously, for the MTBE + n-hexane + n-decane system [1], the maximum of $H^E_{m,123}$ was located on the edge of the triangle in the constituent MTBE + n-decane binary. In Fig. 3, where n-hexane has been replaced by its branched isomer 23DMB, the maximum of $H^E_{m,123}$ has increased only slightly and although it

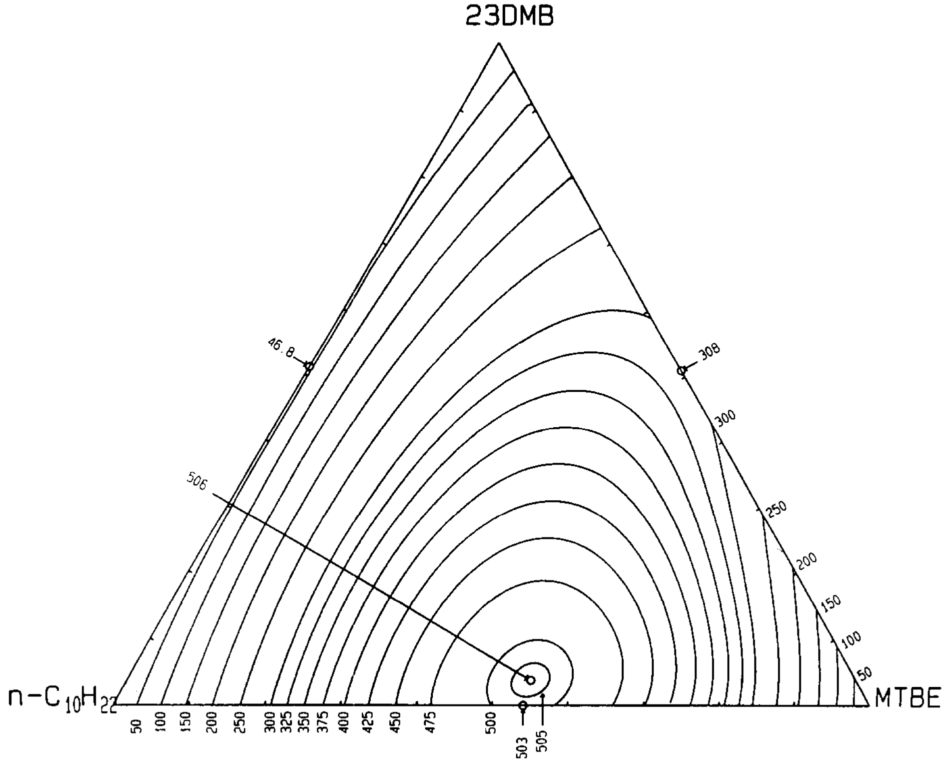

Fig. 3. Contours for constant values of the excess molar enthalpy $H^{E}_{m,123}/(\mathrm{J\ mol^{-1}})$ of the MTBE + 23DMB + n-$C_{10}H_{22}$ system at 298.15 K, calculated from eqns. (1) and (2) using $H^{E}_{m,T}$ from the footnote of Table 3.

is located inside the triangle, it is still fairly close to the edge. However, for the system with cyclohexane (Fig. 4), the maximum of $H^{E}_{m,123}$ has increased by about 70 J mol^{-1}, and is more centrally located in the triangle.

Previously, for MTBE + n-hexane + n-decane [1], it was found that the Flory theory [8, 9], as extended by Brostow and Sochanski [10], provided reasonable estimates of the ternary enthalpies when only data for the pure components and their binary mixtures were used. The same approach was investigated for the present systems. Because the treatment follows our previous work closely, only the primary data and the results of the calculations are reported here. The component properties [1, 11–13] and parameters are summarized in Table 4, where the notation is the same as defined in ref. 1. The results of the calculations of $H^{E}_{m,1+23}$ are shown as broken curves in Figs. 1 and 2. For the 58 points of the cyclohexane system (given in Table 2), the standard deviation between the estimated and experimental values of $H^{E}_{m,123}$ is 8.8 J mol^{-1}, and the mean absolute relative deviation is 2.2%. For the 60 points of the 23DMB system (given in Table 3), the corresponding deviations are 18.5 J mol^{-1} and 5.1%. Although these deviations are larger

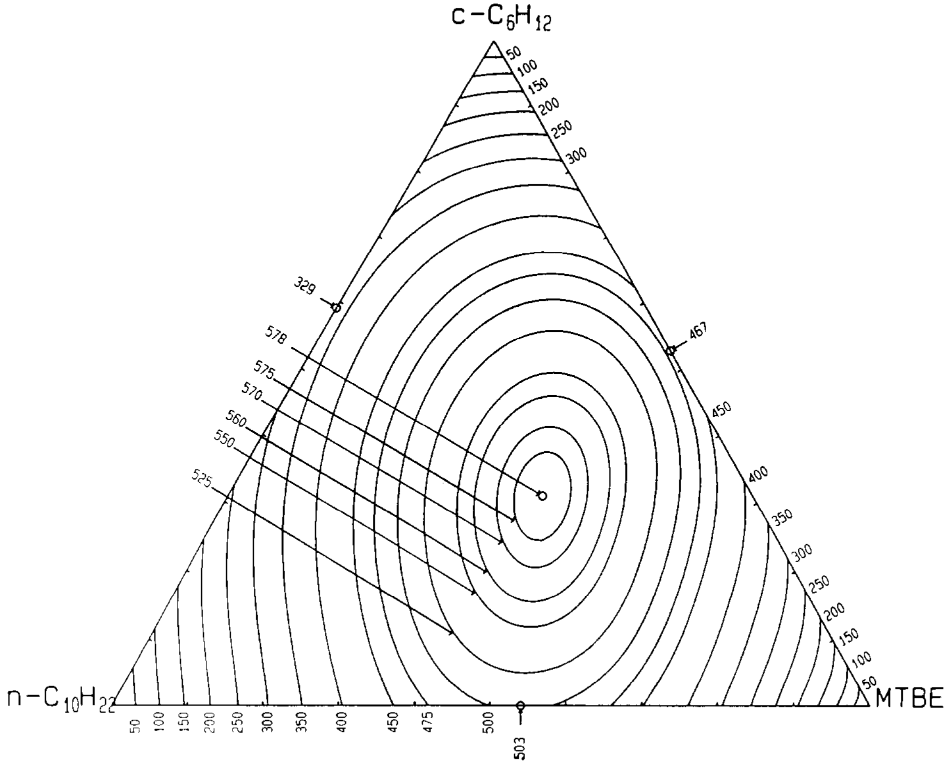

Fig. 4. Contours for constant values of the excess molar enthalpy $H^{E}_{m,123}/(J\ mol^{-1})$ of the MTBE + c-C_6H_{12} + n-$C_{10}H_{22}$ system at 298.15 K, calculated from eqns. (1) and (2) using $H^{E}_{m,T}$ from the footnote of Table 2.

TABLE 4

Component properties and parameters used in Flory calculations for the systems $x_1C_5H_{12}O + x_2C_6H_{12} + x_3C_{10}H_{22}$ [a] and $x_1C_5H_{12}O + x_2C_6H_{14} + x_3C_{10}H_{22}$ [b] at 298.15 K

Component	V_m/ $cm^3\ mol^{-1}$	α_p/ kK^{-1}	κ_T/ TPa^{-1}	P^*/ $J\ cm^{-3}$	V^*/ $cm^3\ mol^{-1}$	T^*/ K	Ref.
$C_5H_{12}O$ (MTBE)	119.82	1.423	1690.6	442.9	90.20	4385.0	1
C_6H_{12}	108.75	1.220	1140.0	532.0	84.23	4715.0	11
C_6H_{14} (23DMB)	131.16	1.391	1790.2	405.3	99.16	4430.2	12
$C_{10}H_{22}$	195.94	1.051	1109.6	447.0	155.75	5091.4	13

Interchange interaction parameters $X_{ij}/(J\ cm^{-3})$: [a] $X_{12} = 20.1640$; $X_{13} = 18.7764$; $X_{23} = 12.4736$. [b] $X_{12} = 12.3507$; $X_{13} = 18.7764$; $X_{23} = 2.3015$.

than those found previously for MTBE + n-hexane + n-decane, it appears that the Flory treatment can provide estimates of the enthalpies of the present systems within less than 10%.

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