ELSEVIER

Thermochimica Acta 256 (1995) 185–192

thermochimica acta

Excess molar enthalpies of 2,2-dimethyl-3,6-dioxaheptane + *n*-hexane + (*n*-decane or *n*-dodecane) ternary mixtures at 298.15 K

Zhang-Li Jin [1], George C. Benson *, Benjamin C.-Y. Lu

Department of Chemical Engineering, University of Ottawa, Ottawa, Ont. K1N 9B4, Canada

Received 30 August 1994; accepted 5 November 1994

Abstract

Excess molar enthalpies, measured at 298.15 K in a flow microcalorimeter, are reported for the ternary mixtures $x_1(CH_3)_3COCH_2CH_2OCH_3 + x_2C_6H_{14} + x_3C_vH_{2v+2}$, where v is 10 and 12. Smooth representations of the results are described and used to construct constant enthalpy contours on a Roozeboom diagram. The Flory theory provides an excellent correlation of the results.

Keywords: Decane; Dimethyldioxaheptane; Dodecane; Excess molar enthalpy; Hexane; Ternary system

---

1. Introduction

A recent paper [1] from our laboratory reported the excess molar enthalpies of binary mixtures of 2,2-dimethyl-3,6-dioxaheptane (DMDOH) with some *n*-alkanes (C_6, C_7, C_8, C_{10} and C_{12}). That investigation has now been extended to consider ternary mixtures consisting of DMDOH, *n*-hexane and either *n*-decane or *n*-dodecane.

---

* Corresponding author.

[1] Visiting Professor from the Beijing University of Chemical Technology, Beijing, China.

SSDI 0040-6031(94)02175-9

2. Experimental

The samples of DMDOH and the *n*-alkanes were the same as in our earlier work. Details regarding their sources and densities are given in Ref. [1].

Excess molar enthalpies were measured at 298.15 K in an LKB flow microcalorimeter (Model 10700-1) maintained within ±0.002 K of the operating temperature [2,3]. In studying the ternary systems $x_1C_7H_{16}O_2 + x_2C_6H_{14} + x_3C_vH_{2v+2}$, with $v = 10$ and 12, excess molar enthalpies $H^E_{m,1+23}$ were measured for several pseudo-binary systems in which component 1 (DMDOH) was added to a binary mixture of components 2 (*n*-hexane) and 3 (*n*-decane or *n*-dodecane) having a fixed mole ratio 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 $H^E_{m,123}$ of the ternary system was 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 excess molar enthalpies $H^E_{m,1+23}$ at 298.15 K for the addition of DMDOH to a binary mixture of *n*-hexane and *n*-decane to form $x_1C_7H_{16}O_2 + x_2C_6H_{14} + x_3C_{10}H_{22}$, and values of $H^E_{m,123}$ calculated from Eq. (1) using $H^E_{m,23}$ from Ref. [4]

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})
$x_2/x_3 = 0.3502$, $H^E_{m,23}$/(J mol^{-1}) = 11.8								
0.0499	189.1	200.3	0.4001	868.1	875.2	0.6999	773.6	777.2
0.1000	338.0	348.7	0.4501	902.6	909.1	0.7496	692.7	695.7
0.1500	466.5	476.5	0.4999	921.2	927.1	0.7998	594.2	596.6
0.2000	585.1	594.5	0.5501	916.2	921.5	0.8500	459.9	461.6
0.2498	679.8	688.6	0.6001	886.6	891.3	0.9000	327.3	328.5
0.2998	755.5	763.7	0.6499	839.1	843.2	0.9500	164.5	165.1
0.3498	819.1	826.8						
$x_2/x_3 = 1.0641$, $H^E_{m,23}$/(J mol^{-1}) = 14.2								
0.0500	184.0	197.6	0.4002	825.0	833.6	0.7000	715.7	720.0
0.1000	327.9	340.7	0.4497	854.8	862.7	0.7497	638.8	642.3
0.1500	451.5	463.6	0.4999	871.5	878.7	0.8003	540.0	542.8
0.2000	565.0	576.4	0.5500	860.7	867.1	0.8501	421.4	423.5
0.2495	653.2	663.9	0.6000	828.3	834.0	0.9000	292.6	294.0
0.3000	723.4	733.4	0.6498	779.2	784.2	0.9500	141.5	142.2
0.3500	781.2	790.4						
$x_2/x_3 = 3.3044$, $H^E_{m,23}$/(J mol^{-1}) = 9.0								
0.0500	182.7	191.2	0.4003	790.2	795.6	0.6998	656.8	659.5
0.1000	322.0	330.0	0.4499	816.0	820.9	0.7502	582.1	584.4
0.1498	440.4	448.0	0.5002	823.4	827.9	0.8001	486.0	487.8
0.1999	545.6	552.8	0.5499	803.5	807.5	0.8500	379.5	380.9
0.2501	629.1	635.8	0.6004	769.4	772.9	0.9000	259.9	260.8
0.2998	695.9	702.1	0.6499	720.4	723.6	0.9509	124.6	125.1
0.3500	747.8	753.7						

[a] Ternary term for representation of $H^E_{m,1+23}$ by Eqs. (2) and (3): $H^E_{m,T}/(\text{J mol}^{-1}) = x_1x_2x_3(1469.18 - 12688.40x_1 - 2072.53x_2 + 30846.99x_1^2 + 4449.12x_1x_2 + 1115.45x_2^2 - 21238.51x_1^3)$; $s = 4.7$.

where $H^{E}_{m,23}$ is the excess molar enthalpy of the particular binary mixture. Values of $H^{E}_{m,23}$ for n-hexane + n-decane and for n-hexane + n-dodecane were taken from the literature [4,5]. Over most of the DMDOH mole fraction range, the errors of $H^{E}_{m,1+23}$ 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

The experimental values of $H^{E}_{m,1+23}$ for the two systems are listed in Tables 1 and 2. Also included in these tables are the corresponding values of $H^{E}_{m,123}$ calculated from Eq. (1). Plots of $H^{E}_{m,1+23}$ are shown in Figs. 1 and 2, along with curves for the constituent binaries having either $x_2 = 0$ or $x_3 = 0$. These latter curves were calculated from the representations reported in Ref. [1]. The general characteristics of the

Table 2
Experimental excess molar enthalpies $H^{E}_{m,1+23}$ at 298.15 K for the addition of DMDOH to a binary mixture of n-hexane and n-dodecane to form $x_1C_7H_{16}O_2 + x_2C_6H_{14} + x_3C_{12}H_{26}$, and values of $H^{E}_{m,123}$ calculated from Eq. (1) using $H^{E}_{m,23}$ from Ref. [5]

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})
$x_2/x_3 = 0.3414$, $H^{E}_{m,23}/(\text{J mol}^{-1}) = 31.0$								
0.0499	198.4	227.8	0.4000	936.4	955.0	0.7002	861.6	870.9
0.1000	358.0	385.9	0.4498	976.6	993.6	0.7501	775.7	783.5
0.1502	495.2	521.5	0.4997	1001.5	1017.0	0.8001	660.4	666.6
0.2000	616.1	640.9	0.5500	1006.5	1020.4	0.8500	530.7	535.3
0.2500	722.5	745.8	0.5997	973.9	986.3	0.9001	375.7	378.8
0.2962	807.8	829.6	0.6503	926.4	937.2	0.9500	196.4	198.0
0.3498	881.8	901.9						
$x_2/x_3 = 1.0296$, $H^{E}_{m,23}/(\text{J mol}^{-1}) = 39.4$								
0.0501	187.3	224.7	0.4004	873.7	897.3	0.7002	771.8	783.6
0.1001	336.0	371.5	0.4501	908.2	929.9	0.7498	690.6	700.5
0.1500	464.9	498.4	0.4999	926.4	946.1	0.8000	584.6	592.5
0.2000	578.9	610.4	0.5503	915.6	933.3	0.8500	464.5	470.4
0.2498	675.4	705.0	0.6002	884.5	900.3	0.9001	326.0	330.0
0.3000	758.6	786.2	0.6500	837.1	850.8	0.9500	162.0	163.9
0.3500	822.7	848.3						
$x_2/x_3 = 3.0823$, $H^{E}_{m,23}/(\text{J mol}^{-1}) = 27.1$								
0.0500	184.5	210.2	0.4000	816.4	832.6	0.6997	689.3	697.4
0.1000	326.2	350.6	0.4495	843.8	858.7	0.7502	611.7	618.5
0.1501	448.9	471.9	0.4998	849.7	863.2	0.8000	518.5	523.9
0.1998	552.1	573.8	0.5502	833.7	845.9	0.8500	399.5	403.6
0.2498	644.3	664.6	0.6005	799.8	810.7	0.9000	275.2	277.9
0.3001	716.0	734.9	0.6506	749.7	759.2	0.9500	134.4	135.7
0.3501	772.9	790.5						

[a] Ternary term for representation of $H^{E}_{m,1+23}$ by Eqs. (2) and (3): $H^{E}_{m,T}/(\text{J mol}^{-1}) = x_1x_2x_3(1574.06 - 9094.49x_1 - 5760.91x_2 + 21893.02x_1^2 + 8315.23x_1x_2 + 4465.85x_2^2 - 16785.09x_1^3)$; $s = 4.2$.

sets of curves in both figures are similar to those observed for DMDOH + n-alkane binary mixtures [1]. In particular, the magnitude of the maximum and the skew towards $x_1 = 1$ both increase as the mean chain length of the n-alkane mixture increases.

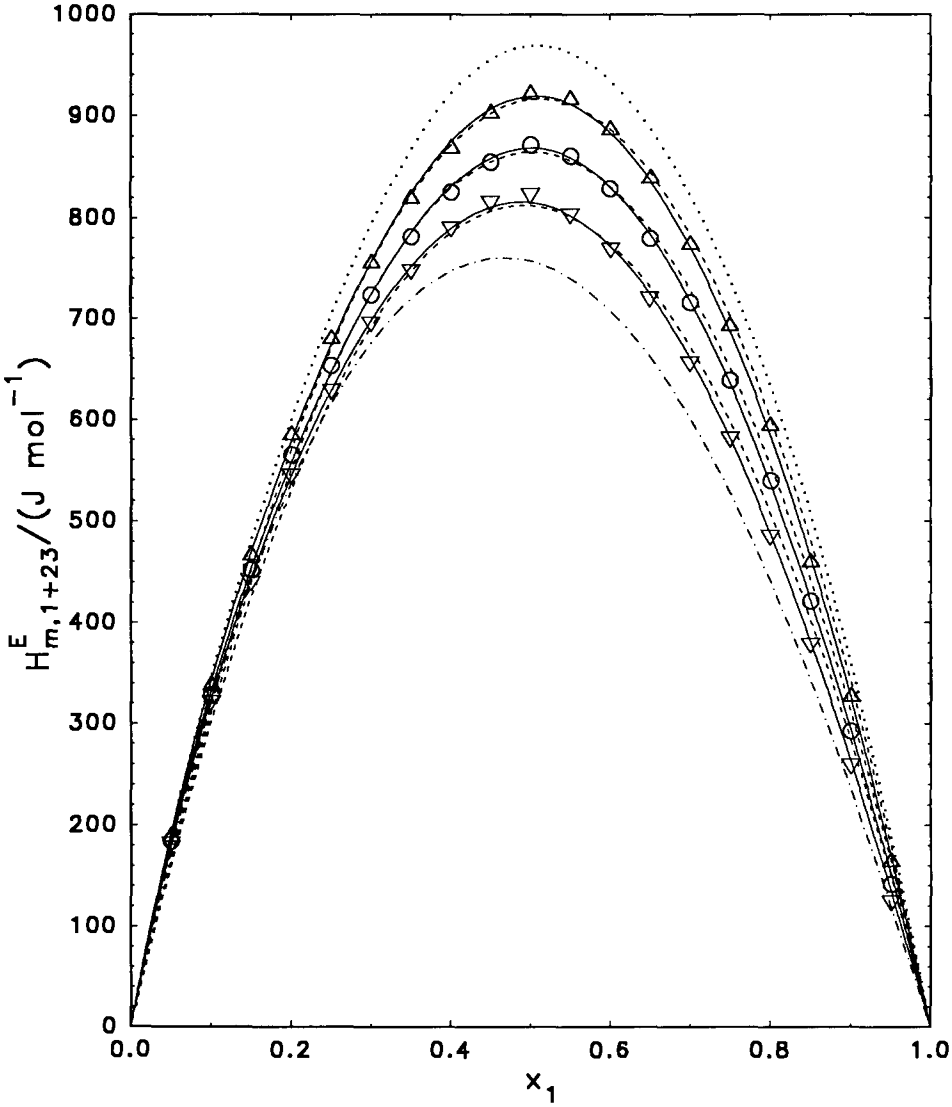

Fig. 1. Excess molar enthalpies $H^E_{m,1+23}$ for $x_1C_7H_{16}O_2 + x_2C_6H_{14} + x_3C_{10}H_{22}$ mixtures at 298.15 K. Experimental results: △, $x_2/x_3 = 0.3502$; ○, $x_2/x_3 = 1.0641$; ▽, $x_2/x_3 = 3.3044$. Curves: · · ·, $x_2 = 0$, from Ref. [1]; – · – ·, $x_3 = 0$, from Ref. [1]; ——, calculated from Eqs. (1)–(3) using the representation of $H^E_{m,T}$ given in the footnote of Table 1; – – –, estimated from the Flory theory.

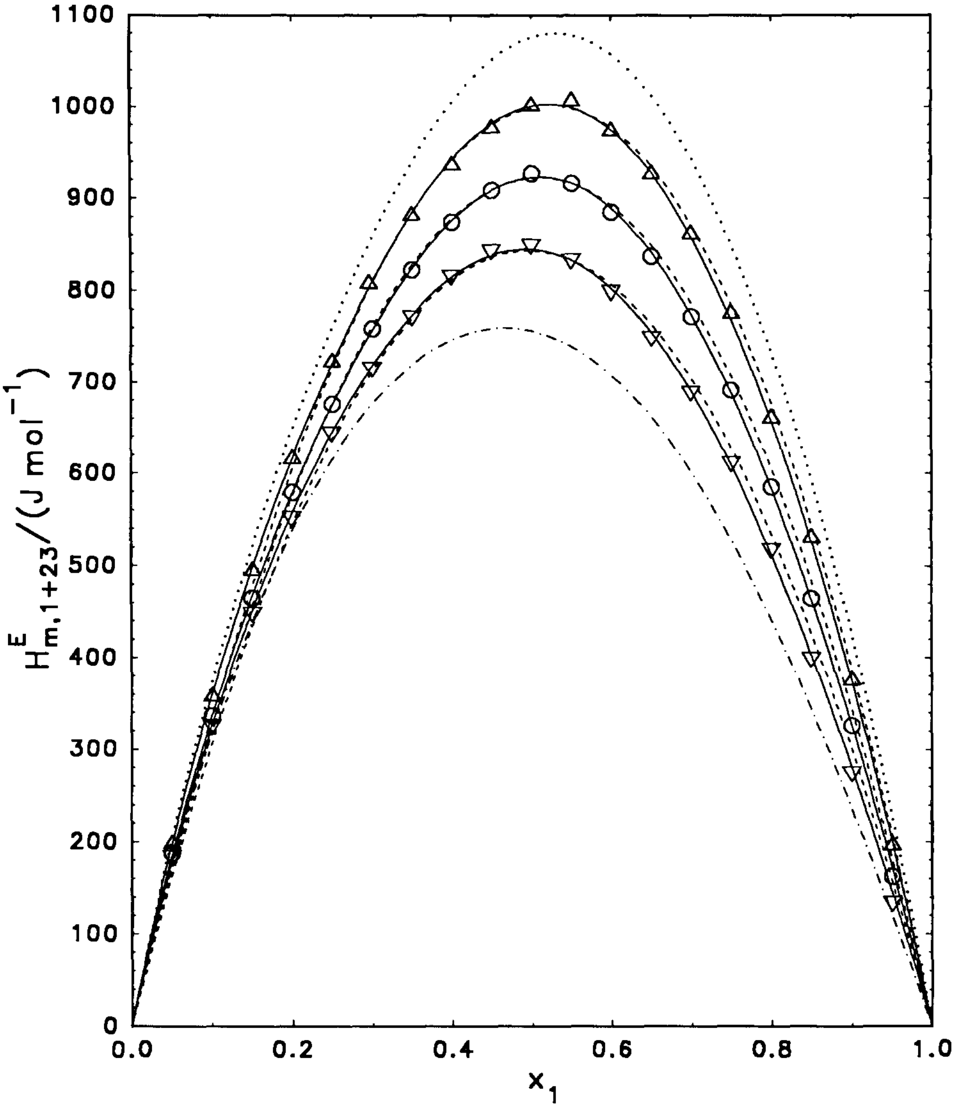

Fig. 2. Excess molar enthalpies $H^E_{m,1+23}$ for $x_1C_7H_{16}O_2 + x_2C_6H_{14} + x_3C_{12}H_{26}$ mixtures at 298.15 K. Experimental results: △, $x_2/x_3 = 0.3414$; ○, $x_2/x_3 = 1.0296$; ▽, $x_2/x_3 = 3.0823$. Curves: · · ·, $x_2 = 0$, from Ref. [1]; – · – ·, $x_3 = 0$, from Ref. [1]; ——, calculated from Eqs. (1)–(3) using the representation of $H^E_{m,T}$ given in the footnote of Table 2; – – –, estimated from the Flory theory.

The values of $H^E_{m,1+23}$ were represented as a sum of binary terms [6] with an added ternary contribution

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

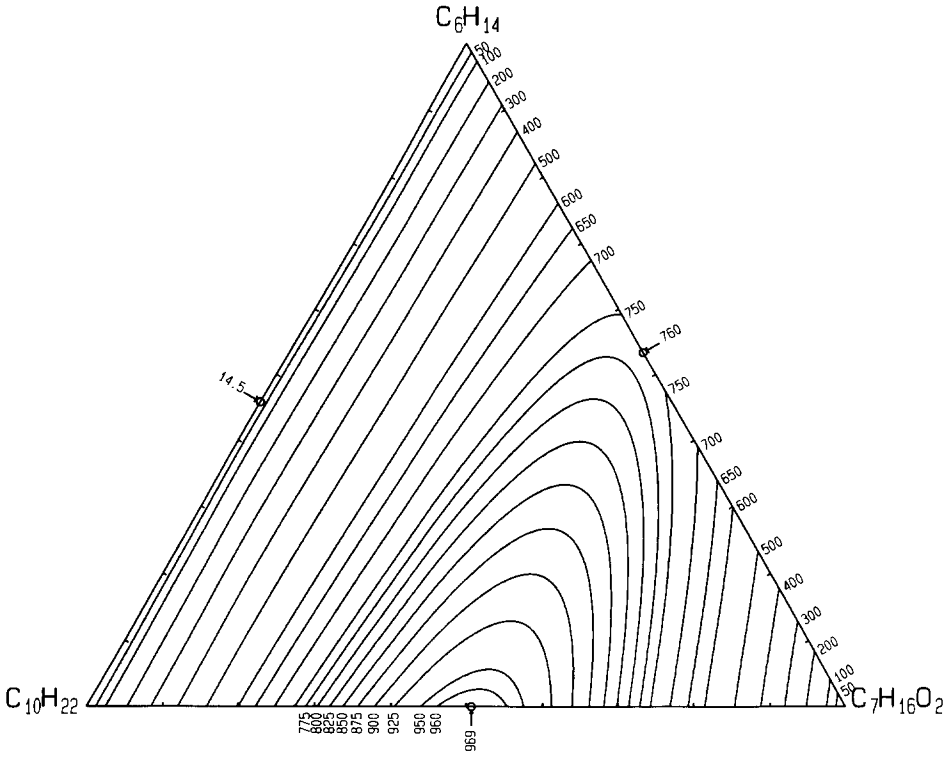

Fig. 3. Contours for constant values of the excess molar enthalpy $H^E_{m,123}/(J\ mol^{-1})$ of $x_1C_7H_{16}O_2 + x_2C_6H_{14} + x_3C_{10}H_{22}$ mixtures at 298.15 K calculated from Eqs. (1)–(3) using the representation of $H^E_{m,T}$ given in the footnote of Table 1.

Following Morris et al. [7], the form

$$H^E_{m,T} = x_1x_2x_3(c_0 + c_1x_1 + c_2x_2 + c_3x_1^2 + c_4x_1x_2 + c_5x_2^2 + c_6x_1^3 + ...) \tag{3}$$

was adopted for the ternary term. For each system, the values of the coefficients c_i were adjusted by least-squares analyses, in which Eqs. (2) and (3) were fitted to the values of $H^E_{m,1+23}$ for the three pseudo-binaries. In doing this, the values of $H^E_{m,12}$ and $H^E_{m,13}$ were calculated from the Redlich–Kister forms reported previously [1]. The resulting representations of $H^E_{m,T}$ are given in the footnotes of Tables 1 and 2, along with their standard deviations s. Curves of $H^E_{m,1+23}$, calculated from these representations, are shown in Figs. 1 and 2.

Some constant $H^E_{m,123}$ contours, calculated from Eqs. (1)–(3), are plotted on the Roozeboom diagrams shown in Figs. 3 and 4. The general characteristics of these are very similar. All of the contours extend to the edges of the triangle. There is no indication of a maximum lying within the triangle, and in both cases, the maximum of $H^E_{m,123}$ is located at the edge of the plot for the constituent binary comprising DMDOH and the longer n-alkane. Contours which terminate only on this edge are skewed towards the (DMDOH + n-hexane) edge.

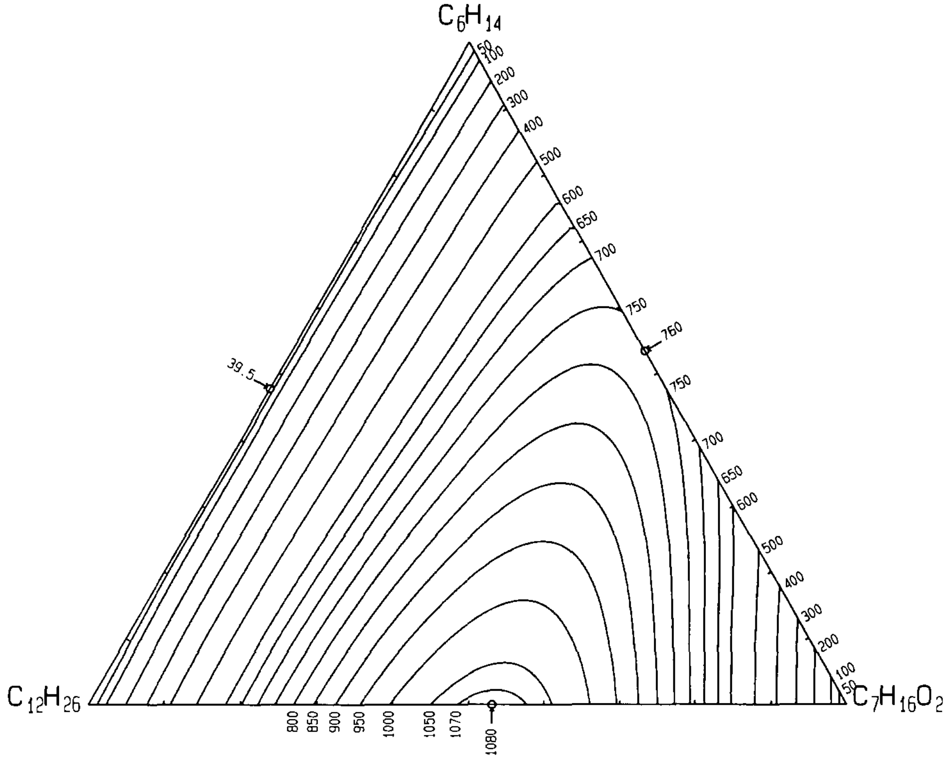

Fig. 4. Contours for constant values of the excess molar enthalpy $H^E_{m,123}/(J\ mol^{-1})$ of $x_1C_7H_{16}O_2 + x_2C_6H_{14} + x_3C_{12}H_{26}$ mixtures at 298.15 K calculated from Eqs. (1)-(3) using the representation of $H^E_{m,T}$ given in the footnote of Table 2.

Previously, for methyl *tert*-butyl ether + *n*-hexane + (*n*-decane or *n*-dodecane) [8], it was found that the Flory theory [9,10], as extended to multi-component mixtures by Brostow and Sochanski [11], provided reasonable estimates of the ternary enthaplies, when only properties of 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 [8] closely, the equations are not reported here.

Values of the characteristic pressures p^*, volumes V^*_m and temperatures T^* were the same as used in the Flory calculations for DMDOH + *n*-alkane binary mixtures (see Table 3 in Ref. [1]). The interchange-interaction energy parameters X_{12} and X_{13} were calculated from the quadratic form in Ref. [1]. For (*n*-hexane + *n*-decane) and (*n*-hexane + *n*-dodecane), the values used for $X_{23}/(J\ cm^{-3})$ were 1.2208 and 2.5204, respectively [8].

The broken curves for $H^E_{m,1+23}$ in Figs. 1 and 2 were estimated from the Flory theory using the values of the parameters outlined above. In view of the fact that no data for the ternary mixtures were used, the agreement between these estimates and the experimental results is very good. For the 57 points of the system containing decane in Table 1, the standard deviation between the estimated and experimental values of $H^{\mathrm{E}}_{\mathrm{m},123}$ is 13.8 J mol^{-1} and the mean absolute relative deviation is 3.3% For the 57 points of the dodecane system in Table 2, the corresponding deviations are 13.4 J mol^{-1} and 2.8%. Thus for the present type of systems, it appears that the Flory treatment can provide estimates of the enthalpies within less than 5%.

Acknowledgement

The financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.

References

[1] Z.-L. Jin, G.C. Benson and B.C.-Y. Lu, Thermochim. Acta, submitted.
[2] R. Tanaka, P.J. D'Arcy and G.C. Benson, Thermochim. Acta, 11 (1975) 163.
[3] F. Kimura, G.C. Benson and C.J. Halpin, Fluid Phase Equilib., 11 (1983) 245.
[4] K.N. Marsh, J.B. Ott and M.J. Costigan, J. Chem. Thermodyn., 12 (1980) 343.
[5] J.B. Ott, K.N. Marsh and R.H. Stokes, J. Chem. Thermodyn., 13 (1981) 371.
[6] C.C. Tsao and J.M. Smith, Chem. Eng. Prog. Symp. Ser. No. 7, 49 (1953) 107.
[7] J.W. Morris, P.J. Mulvey, M.M. Abbott and H.C. Van Ness, J. Chem. Eng. Data, 20 (1975) 403.
[8] L. Wang, G.C. Benson and B.C.-Y. Lu, Thermochim. Acta, 213 (1993) 83.
[9] P.J. Flory, J. Am. Chem. Soc., 87 (1965) 1833.
[10] A. Abe and P.J. Flory, J. Am. Chem. Soc., 87 (1965) 1838.
[11] W. Brostow and J.S. Sochanski, J. Mater. Sci., 10 (1975) 2134.