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Thermochimica Acta 288 (1996) 29–37

thermochimica acta

Excess molar enthalpies of ternary mixtures of an *n*-alkane, ethanol and methyl 1,1-dimethylpropyl ether

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Received 10 April 1996; accepted 9 June 1996

Abstract

Excess molar enthalpies, measured at 298.15 K in a flow microcalorimeter, are reported for $x_1CH_3(CH_2)_vCH_3 + x_2C_2H_5OH + x_3C_2H_5C(CH_3)_2OCH_3$, where v is 5 and 8. Smooth representations of the results are presented and used to construct constant excess molar enthalpy contours on Roozeboom diagrams.

Keywords: Heptane; Decane; Ethanol; Methyl 1,1-dimethylpropyl ether; Excess molar enthalpy; Ternary system

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1. Introduction

The addition of various alcohols and ethers to gasolines has been found to enhance the octane rating and to reduce pollution effects. In this regard, both ethanol (EtOH) and methyl 1,1-dimethylpropyl ether (TAME) have been used as oxygenating agents. Accordingly, the thermodynamic properties of mixtures of these agents with normal alkanes is of practical interest. A previous paper [1] from our laboratory presented the excess molar enthalpies, measured at 298.15 K, for the two ternary systems formed by mixing either *n*-heptane (nC7) or *n*-decane (nC10) with binary mixtures of methyl *tert*-butyl ether (MTBE) and TAME. The present paper reports measurements for the two corresponding systems obtained by replacing the MTBE with EtOH.

2. Experimental

The nC7, nC10 and TAME were the same as used in our previous work [1]. The EtOH was BDH "Aristar" ethanol which was dried over molecular sieves type 3A. Its density,

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PII S0040-6031(96)03046-8

measured at 298.15 K in an Anton-Paar digital densimeter, was 785.21 kg m^{-3}, in reasonable agreement with the literature value 785.09 kg m^{-3} [2].

Excess molar enthalpies H_m^E were determined in an LKB flow microcalorimeter (Model 10700-1) at 298.15 K, maintained within ± 0.002 K. Details of the equipment and the operating procedure have been described previously [3,4].

In studying the ternary systems$x_1CH_3(CH_2)_vCH_3 + x_2C_2H_5OH + x_3C_2H_5C(CH_3)_2OCH_3$ for $v = 5$ and 8, the excess molar enthalpy $H^E_{m,1+23}$ was determined for several psuedo-binary systems in which component 1 (nC7 or nC10) was added to a binary mixture of component 2 (EtOH) and component 3 (TAME), having a fixed mole ratio x_2/x_3. For this purpose, binary mixtures with $x_2/x_3 \approx 0.1, 0.3, 1.0$ and 3.0 were prepared by weighing. The excess molar enthalpy of the ternary system was obtained from the relation

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

where $H^E_{m,23}$ is the excess molar enthalpy of the particular binary mixture of EtOH and TAME. Over most of the mole fraction range of component 1, 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

Table 1 summarizes the experimental values of x_1 and $H^E_{m,ij}$ for the three binary systems nC7(1) + EtOH(2), EtOH(2) + TAME(3) and nC10(1) + EtOH(2). The smoothing function

$$H^E_{m,ij}(x_i, x_j)/(\mathrm{J\ mol^{-1}}) = \left(\frac{x_i x_j}{1 + h_0(x_j - x_i)}\right) \sum_{k=1}^{m} h_k(x_j - x_i)^{k-1} \tag{2}$$

was fitted to each set of results in Table 1 by the method of least squares with all points weighted equally. The values of the coefficients h_k are listed in Table 2, along with the standard deviation s for each representation. Previously, we reported the excess molar enthalpies for the other constituent binaries nC7(1) + TAME(3) [1] and nC10(1) + TAME(3) [5]. The coefficients for the representations of those results are included in Table 2.

The values of $H^E_{m,ij}$, for the three systems in Table 1, are positive at all x_i and yield curves which are skewed towards low EtOH mole fractions. Van Ness and Abbott [6] have reported $H^E_{m,12}$ for nC7(1) + EtOH(2) at temperatures ranging from 283.15 K to 348.15 K. Interpolation of their data yields $H^E_{m,12}/(\mathrm{J\ mol^{-1}}) = 598.0$ for an equimolar mixture at 298.15 K, which is ~ 0.9% higher than the value estimated from our results. For an equimolar mixture of nC10(1) + EtOH(2) at 298.15 K, $H^E_{m,12}/(\mathrm{J\ mol^{-1}}) = 694.6$ is obtained from the smoothing function reported by Christensen et al. [7]; this is ~ 2.2% higher than the value derived from our results. We are not aware of any directly comparable data for EtOH(2) + TAME(3).

Experimental results for $H^E_{m,1+23}$ and the corresponding values of $H^E_{m,123}$ are listed in Tables 3 and 4 for the two ternary systems. In Fig. 1, the values of $H^E_{m,1+23}$ for the

Table 1
Experimental mole fractions x_i and excess molar enthalpies $H^E_{m,ij}(i < j)$, at 298.15 K, for nC7(1) + EtOH(2), EtOH(2) + TAME(3), and nC10(1) + EtOH(2)

x_i	$H^E_{m,ij}$/ (J mol^{-1})	x_i	$H^E_{m,ij}$/ (J mol^{-1})	x_i	$H^E_{m,ij}$/ (J mol^{-1}	x_i	$H^E_{m,ij}$/ (J mol^{-1})
$x_1CH_3(CH_2)_5CH_3 + (1 - x_1)C_2H_5OH$							
0.0500	135.9	0.2999	489.6	0.5000	590.5	0.7499	554.5
0.1000	242.7	0.3498	525.0	0.5499	602.2	0.8000	519.4
0.1499	324.8	0.4000	553.9	0.6001	605.8	0.8500	468.9
0.1999	391.9	0.4498	575.5	0.6500	601.4	0.9000	401.4
0.2498	445.8	0.4998	591.7	0.7000	583.3	0.9500	300.6
$x_2C_2H_5OH + (1 - x_2)C_2H_5C(CH_3)_2OCH_3$							
0.0498	185.5	0.3489	558.3	0.5486	490.5	0.7991	244.0
0.0995	320.5	0.3989	555.1	0.5990	452.8	0.8495	181.4
0.1494	417.9	0.4487	542.5	0.6488	408.7	0.8996	119.7
0.1993	481.0	0.4987	520.6	0.6989	359.1	0.9498	55.8
0.2490	522.7	0.4987	520.3	0.7490	304.2	0.9498	56.5
0.2990	547.8						
$x_1CH_3(CH_2)_8CH_3 + (1 - x_1)C_2H_5OH$							
0.0500	193.6	0.3001	574.9	0.5001	677.5	0.7499	656.0
0.0999	324.0	0.3501	610.3	0.5500	692.1	0.8000	609.6
0.1500	412.0	0.3997	639.3	0.5999	700.1	0.8499	552.5
0.1999	478.6	0.4497	662.7	0.6500	697.2	0.9000	475.3
0.2498	531.5	0.4998	680.5	0.6999	683.5	0.9500	356.2

nC7 mixtures are plotted against x_1 along with the results for nC7(1) + EtOH(2) from Table 1 and our previously published data for nC7(1) + TAME(3) [1]. A similar plot for the nC10 mixtures is shown in Fig. 2, where the results for nC10(1) + EtOH(2) from Table 1 and our previously published data for nC10(1) + TAME(3) [5] are included. In Figs. 1 and 2, the curves for nC7(1) and nC10(1) with TAME(3) are nearly symmetric about $x_1 = 0.5$. For increasing values of the ratio x_2/x_3, the curves become more skewed towards $x_1 = 1.0$, and in most cases the values of $H^E_{m,1+23}$ for given x_1 tend to increase.

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

Component		h_0	h_1	h_2	h_3	h_4	h_5	h_6	h_7	s
i	j									
nC7	EtOH	0.9566	2370.46	1736.60	525.89	906.38	469.43			1.3
nC7	TAME[a]	0.0	1176.17	4.48	10.07	−41.00				0.5
EtOH	TAME	0.0	2079.01	1052.32	464.50	490.46	162.96	120.09		0.7
nC10	EtOH	0.8608	2719.18	1716.58	1173.74	1270.44	−272.68	552.60	1873.58	1.2
nC10	TAME[b]	0.0	1525.57	166.24	147.24	6.11	−90.84			1.0

[a] Tong et al. [1]; [b] Zhu et al. [5].

Table 3

Experimental excess molar enthalpies $H^{\mathrm{E}}_{\mathrm{m},1+23}$ at 298.15 K for the addition of nC7 to a binary mixture of EtOH and TAME to form $x_1\mathrm{CH_3(CH_2)_5CH_3} + x_2\mathrm{C_2H_5OH} + x_3\mathrm{C_2H_5C(CH_3)_2OCH_3}$, 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 2

x_1	$H^{\mathrm{E}}_{\mathrm{m},1+23}$ [a]/ ($\mathrm{J\,mol^{-1}}$)	$H^{\mathrm{E}}_{\mathrm{m},123}$/ ($\mathrm{J\,mol^{-1}}$)	x_1	$H^{\mathrm{E}}_{\mathrm{m},1+23}$ [a]/ ($\mathrm{J\,mol^{-1}}$)	$H^{\mathrm{E}}_{\mathrm{m},1+123}$/ ($\mathrm{J\,mol^{-1}}$)	x_1	$H^{\mathrm{E}}_{\mathrm{m},1+23}$ [a]/ ($\mathrm{J\,mol^{-1}}$)	$H^{\mathrm{E}}_{\mathrm{m},123}$/ ($\mathrm{J\,mol^{-1}}$)
$x_2/x_3 = 0.1186$, $H^{\mathrm{E}}_{\mathrm{m},23}/(\mathrm{J\,mol^{-1}}) = 335.2$								
0.0500	66.3	384.7	0.4001	369.9	571.0	0.7000	362.0	462.6
0.0998	130.8	432.5	0.4499	385.6	570.0	0.7500	338.1	421.9
0.1500	188.7	473.6	0.4999	392.6	560.2	0.7999	304.6	371.7
0.2000	238.5	506.7	0.5002	394.6	562.2	0.8500	260.5	310.7
0.2500	281.7	533.1	0.5500	395.2	546.0	0.9000	204.0	237.6
0.2999	318.1	552.8	0.6001	391.0	525.1	0.9500	125.8	142.5
0.3502	347.5	565.3	0.6499	380.1	497.5			
$x_2/x_3 = 0.3333$, $H^{\mathrm{E}}_{\mathrm{m},23}/(\mathrm{J\,mol^{-1}}) = 524.3$								
0.0500	77.6	575.7	0.3998	427.7	742.4	0.7001	429.9	587.2
0.1001	151.9	623.8	0.4500	446.8	735.2	0.7501	408.0	539.1
0.1499	218.0	663.8	0.5000	454.7	716.8	0.8000	375.9	480.8
0.1999	276.6	696.2	0.5500	459.1	695.0	0.8500	332.0	410.7
0.2501	326.2	719.4	0.6001	456.8	666.5	0.9000	275.0	327.4
0.3001	367.6	734.6	0.6502	447.2	630.6	0.9500	191.6	217.9
0.3500	401.2	742.0						
$x_2/x_3 = 1.0114$, $H^{\mathrm{E}}_{\mathrm{m},23}/(\mathrm{J\,mol^{-1}}) = 518.3$								
0.0499	94.8	587.2	0.3998	495.7	806.8	0.6497	528.2	709.7
0.1000	184.1	650.5	0.4499	516.9	802.0	0.7020	511.9	666.3
0.1500	260.5	701.0	0.4999	531.2	790.4	0.7500	490.4	620.0
0.1998	326.4	741.1	0.5000	530.5	789.7	0.8000	456.4	560.1
0.2000	326.8	741.4	0.5000	531.4	790.5	0.8500	412.1	489.8
0.2500	382.3	771.0	0.5500	537.2	770.4	0.9000	352.9	404.7
0.3001	429.0	791.7	0.6001	536.5	743.7	0.9500	266.4	292.3
0.3500	466.5	803.4						
$x_2/x_3 = 3.0054$, $H^{\mathrm{E}}_{\mathrm{m},23}/(\mathrm{J\,mol^{-1}}) = 302.3$								
0.0500	113.7	400.8	0.4003	545.2	726.5	0.7000	573.9	664.5
0.1000	214.3	486.3	0.4500	567.3	733.5	0.7501	548.3	623.8
0.1502	299.6	556.4	0.4998	582.3	733.5	0.8000	514.5	574.9
0.2001	370.2	611.9	0.4999	583.0	734.1	0.8500	469.0	514.4
0.2500	428.3	655.0	0.5500	590.8	726.9	0.9000	404.8	435.1
0.2999	476.6	688.2	0.5998	591.0	712.0	0.9501	316.2	331.3
0.3500	515.0	711.5	0.6501	587.8	693.6			

[a] Ternary term for representation of $H^{\mathrm{E}}_{\mathrm{m},1+23}$ by Eqs. (2) and (3): $H^{\mathrm{E}}_{\mathrm{m},T}/(\mathrm{J\,mol^{-1}}) = [x_1x_2x_3/(1 - x_1 + x_2)]$ $(4723.09 + 15621.92x_1 - 5825.16x_2 - 50528.70\,x_1^2 - 6841.62x_1x_2 + 6773.26x_2^2 + 36028.20x_1^3 + 28939.76\,x_1^2x_2)$; $s = 5.9$

Representation of the values of $H^{\mathrm{E}}_{\mathrm{m},123}$ was based on the relation

$$H^{\mathrm{E}}_{\mathrm{m},123} = \sum_{i=1}^{2}\sum_{j=i+1}^{3}(x_i + x_j)^2 H^{\mathrm{E}}_{\mathrm{m},ij}\left(\frac{x_i}{x_i + x_j}, \frac{x_j}{x_i + x_j}\right) + H^{\mathrm{E}}_{\mathrm{m,T}} \tag{3}$$

Table 4
Experimental excess molar enthalpies $H^E_{m,1+23}$ at 298.15 K for the addition of nC10 to a binary mixture of EtOH and TAME to form $x_1CH_3(CH_2)_8CH_3 + x_2C_2H_5OH + x_3C_2H_5C(CH_3)_2OCH_3$, and values of $H^E_{m,123}$ calculated from Eq. (1) using $H^E_{m,23}$ obtained from Eq. (2) with coefficients from Table 2

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})
$x_2/x_3 = 0.1127$, $H^E_{m,23}/(J mol^{-1}) = 324.8$								
0.0501	95.8	404.3	0.3810	455.8	656.8	0.7006	427.2	524.5
0.1002	182.2	474.4	0.4508	477.2	655.5	0.7505	391.7	472.7
0.1503	255.9	531.8	0.5007	482.5	644.7	0.8005	347.6	412.4
0.2005	318.7	578.3	0.5007	483.0	645.1	0.8504	291.6	340.2
0.2506	369.1	612.5	0.5510	479.9	625.7	0.9002	225.1	257.5
0.3005	409.0	636.2	0.6007	469.1	598.8	0.9501	133.9	150.1
0.3505	440.7	651.6	0.6508	451.3	564.7			
$x_2/x_3 = 0.3294$, $H^E_{m,23}/(J mol^{-1}) = 522.9$								
0.0500	111.9	608.7	0.4002	535.1	848.7	0.7000	515.6	672.5
0.1000	211.8	682.4	0.4498	553.3	841.1	0.7500	482.5	613.3
0.1500	296.1	740.6	0.4999	558.6	820.1	0.8000	442.0	546.6
0.2002	367.5	785.8	0.4999	562.5	824.0	0.8500	388.0	466.4
0.2499	425.3	817.5	0.5502	558.0	793.2	0.9000	322.5	374.8
0.3000	472.5	838.5	0.5997	550.7	760.0	0.9501	218.3	244.4
0.3502	509.3	849.1	0.6501	539.4	722.3			
$x_2/x_3 = 1.0012$, $H^E_{m,23}/(J mol^{-1}) = 519.6$								
0.0500	135.5	629.1	0.3999	607.1	918.9	0.6999	602.1	758.0
0.1000	251.9	719.5	0.4499	626.4	912.2	0.7500	571.8	701.7
0.1499	346.8	788.5	0.4999	638.8	898.7	0.7999	531.4	635.4
0.2000	425.3	841.0	0.5001	640.3	900.1	0.8507	476.9	554.5
0.2499	488.8	878.6	0.5498	643.3	877.2	0.9000	409.4	461.4
0.2999	539.6	903.3	0.6000	641.5	849.3	0.9500	304.2	330.2
0.3498	578.3	916.2	0.6500	627.8	809.7			
$x_2/x_3 = 2.9997$, $H^E_{m,23}/(J mol^{-1}) = 302.7$								
0.0500	162.7	450.3	0.3999	654.0	835.7	0.7001	660.7	751.4
0.1001	292.1	564.5	0.4496	677.9	844.4	0.7501	630.2	705.8
0.1501	394.1	651.3	0.4998	688.4	839.8	0.8001	591.5	652.1
0.1999	472.7	714.9	0.4999	686.4	837.8	0.8500	542.0	587.4
0.2498	535.4	762.5	0.5500	693.8	830.0	0.9000	468.0	498.2
0.2999	585.9	797.8	0.6000	694.0	815.0	0.9500	362.2	377.3
0.3503	626.3	822.9	0.6500	681.5	787.4			

[a] Ternary term for representation of $H^E_{m,1+23}$ by Eqs. (2) and (3): $H^E_{m,T}/(J\,mol^{-1}) = [x_1x_2x_3/(1 - x_1 + x_2)](5530.48 + 10758.08x_1 - 4038.72x_2 - 45191.81x_1^2 + 12000.78x_1x_2 + 3932.62x_2^2 + 35210.82x_1^3)$; $s = 8.3$

This consists of the sum of binary contributions proposed by Kohler [8], and an added ternary term. The form

$$H^E_{m,T} = \frac{x_1x_2x_3}{1 - x_1 + x_2}(c_0 + c_1x_1 + c_2x_2 + c_3x_1^2 + c_4x_1x_2 + c_5x_2^2 + \ldots) \tag{4}$$

which was adopted for the latter contribution is similar to the form used by Morris et al.

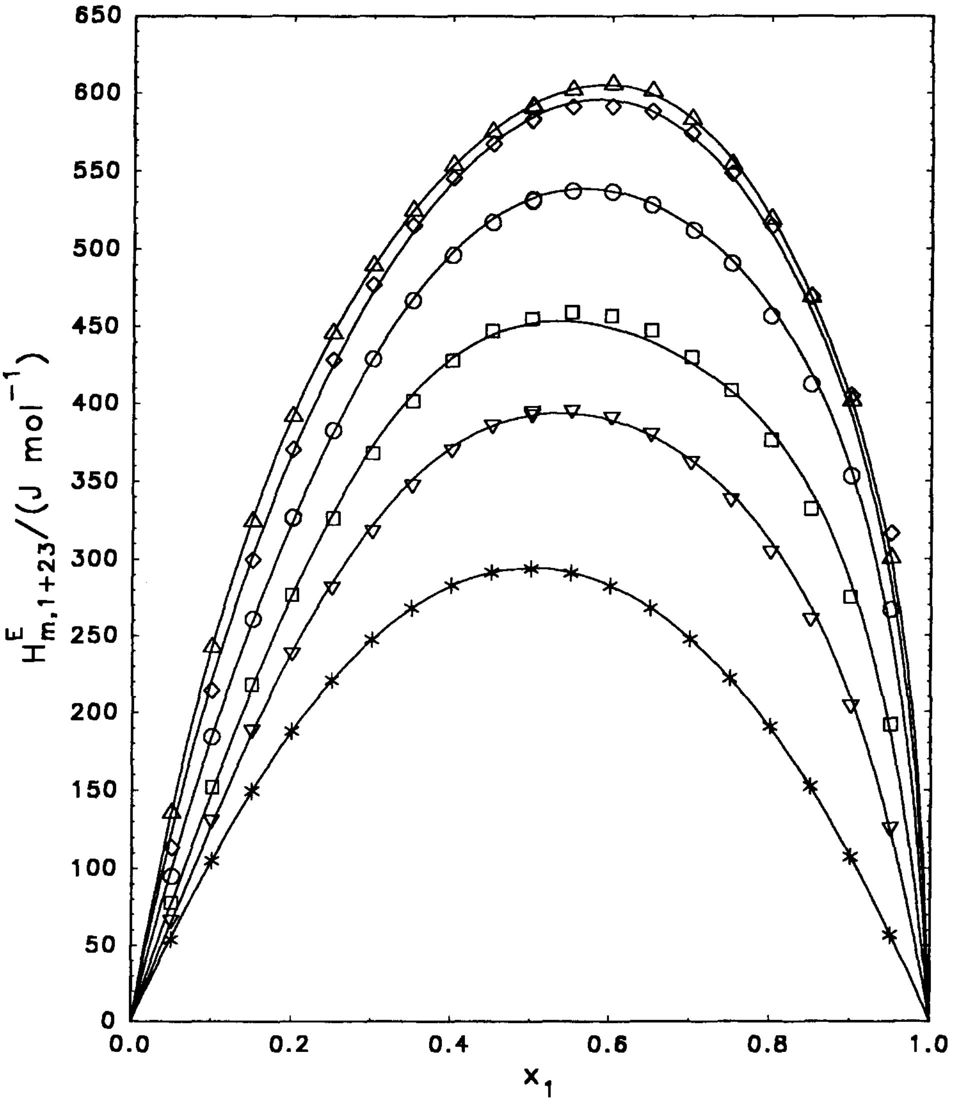

Fig. 1. Excess molar enthalpies, $H^E_{m,1+23}$, for $x_1CH_3(CH_2)_5CH_3 + x_2C_2H_5OH + x_3C_2H_5C(CH_3)_2OCH_3$ mixtures at 298.15 K. Experimental results: *, $x_2 = 0$, nC7(1) + TAME(3) [1]; ▽, $x_2/x_3 = 0.1186$; □, $x_2/x_3 = 0.3333$; ○, $x_2/x_3 = 1.0114$; ◇, $x_2/x_3 = 3.0054$; △, $x_1 + x_2 = 1$, nC7(1) + EtOH(2). Curves: (—) calculated from Eqs. (1)–(3) with $H^E_{m,T}$ from the footnote of Table 3.

[9], 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 values of $H^E_{m,123}$ in Tables 3 and 4. In doing this, the values of $H^E_{m,ij}$ for the binary contributions were calculated from Eq. (2) using the parameters in Table 1. The resulting representations of $H^E_{m,T}$ are given in the footnotes of Tables 2 and 3, along with their standard

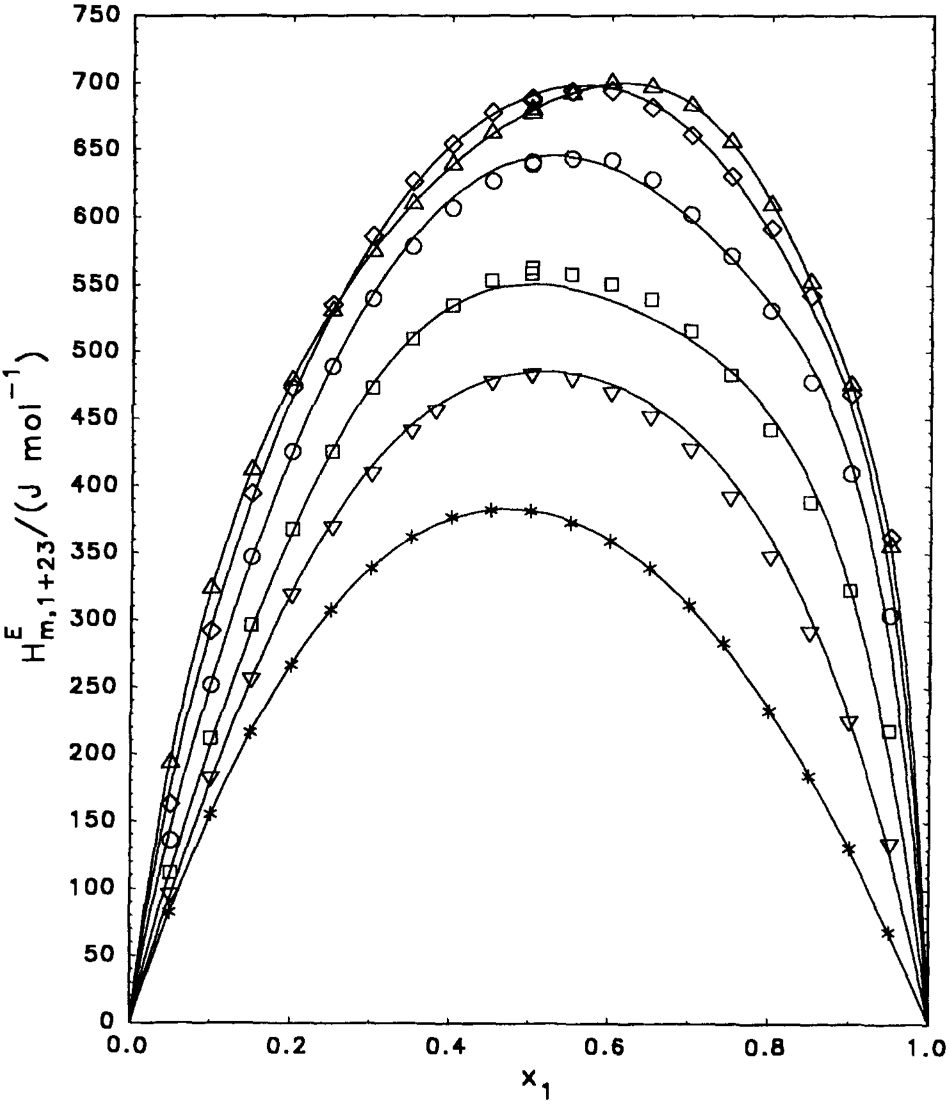

Fig. 2. Excess molar enthalpies, $H^E_{m,1+23}$, for $x_1CH_3(CH_2)_8CH_3 + x_2C_2H_5OH + x_3C_2H_5C(CH_3)_2OCH_3$ mixtures at 298.15 K. Experimental results: ∗, $x_2 = 0$, nC10(1) + TAME(3) [5]; ▽, $x_2/x_3 = 0.1127$; □, $x_2/x_3 = 0.3294$; ○, $x_2/x_3 = 1.0012$; ◇, $x_2/x_3 = 2.9997$; △, $x_1 + x_2 = 1$, nC10(1) + EtOH(2). Curves: (—) calculated from Eqs. (1)–(3) with $H^E_{m,T}$ from the footnote of Table 4.

deviations s. Curves of $H^E_{m,1+23}$, calculated from Eq. (1) using these representations, are shown in Figs. 1 and 2. It is evident from these, that the representations of the experimental results are quite good, even including the crossing of some of the curves for different values of x_2/x_3.

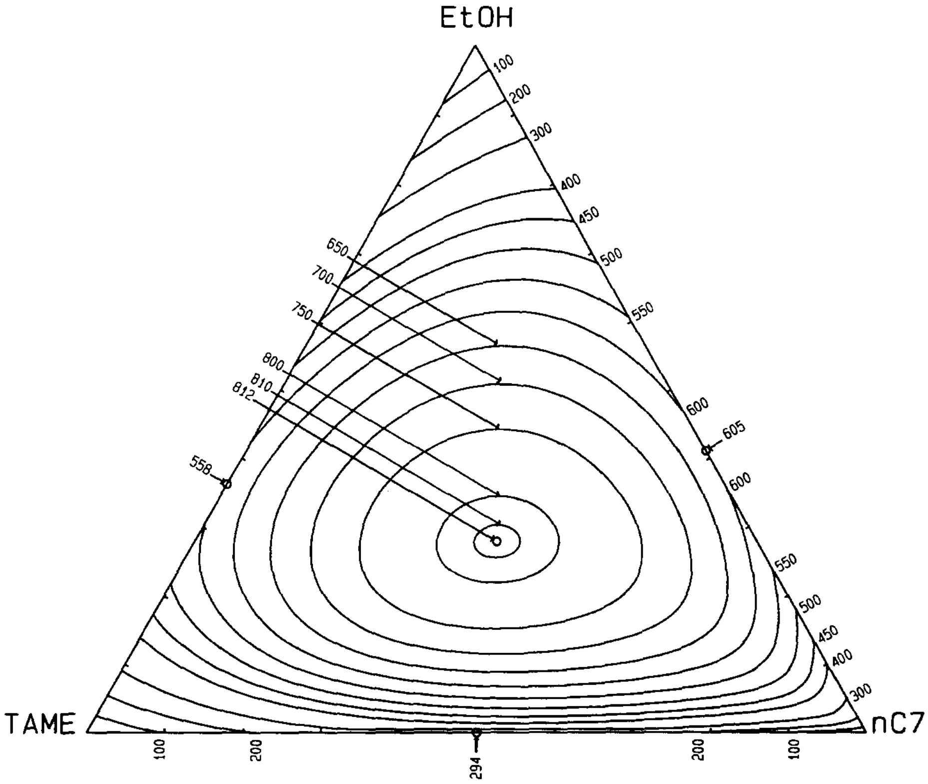

Fig. 3. Contours for constant values of $H^E_{m,123}/(J\cdot mol^{-1})$ for $x_1CH_3(CH_2)_5CH_3 + x_2C_2H_5OH + x_3C_2H_5C(CH_3)_2OCH_3$ at 298.15 K obtained from the representation of the experimental results by Eq. 3 with $H^E_{m,T}$ from the footnote of Table 3.

Some constant $H^E_{m,123}$ contours, calculated from Eqs. (3) and (4), were plotted on Roozeboom diagrams. The general characteristics of these are very similar, and only that for the nC7 system is shown in Fig. 3. For both systems, there is an internal maximum near the centroid of the triangle. This corresponds to $H^E_{m,123}/(J\ mol^{-1}) = 812$ for the nC7 system and 928 for the nC10 system. This differs from the behavior of the systems in our previous investigation [1], in which MTBE was used instead of EtOH. In that case, there was no indication of an internal maximum for either the nC7 or nC10 systems.

Acknowledgement

The authors are indebted to the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support of this work.

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