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Excess molar enthalpies of ternary mixtures of *n*-heptane, methyl 1,1-dimethylpropyl ether and 1,2-dimethoxyethane

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Abstract

Excess molar enthalpies, measured at 298.15 K in a flow microcalorimeter, are reported for $x_1CH_3(CH_2)_5CH_3+x_2C_2H_5C(CH_3)_2OCH_3+x_3CH_3O(CH_2)_2OCH_3$. Smooth representations of the results are presented and used to construct constant excess molar enthalpy contours on a Roozeboom diagram. It is shown that good estimates of the ternary enthalpies can be obtained from the Flory theory, using only the physical properties of the components and their binary mixtures. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: 1,2-Dimethoxyethane; Excess molar enthalpy; Heptane; Methyl 1,1-dimethylpropyl ether; Ternary system

1. Introduction

The use of ethers as oxygenating agents in gasoline technology has led to an increased interest in the thermodynamic properties of mixtures composed of hydrocarbons and ethers. A recent paper [1], from our laboratory, reported excess molar enthalpies for the ternary system consisting of *n*-heptane (nC_7) together with methyl 1,1-dimethyethyl ether (MTBE) and 1,2 dimethoxyethane (DME). In an effort to extend that investigation, we have made similar measurements for the analogous system, in which methyl 1,1-dimethylpropyl ether (TAME) replaced the MTBE used previously.

2. Experimental

The materials used in the present work were: pure grade nC_7 (minimum purity 99 mol%) from Phillips Chemical, purum TAME (minimum purity 97 mol%) from Fluka and HPLC Grade DME (minimum purity 99.8 mol%) from Sigma–Aldrich. Densities, measured at 298.15 K in an Anton–Paar digital densimeter, were 679.76, 766.29 and 861.29 kg m^{-3} for nC_7, TAME and DME, respectively. These are in reasonable agreement with values in the literature [2–5].

An LKB flow microcalorimeter, maintained at 298.150±0.003 K, was used to measure the excess molar enthalpies H^E_m. Details of the equipment and the operating procedure have been described previously [6,7].

In studying the ternary system $x_1CH_3(CH_2)_5CH_3+x_2C_2H_5C(CH_3)_2OCH_3+x_3CH_3O(CH_2)_2OCH_3$, the excess molar enthalpy $H^E_{m,1+23}$ was determined for several pseudo-binary systems in which component 1

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(nC$_7$) was added to a binary mixture of component 2 (TAME) and component 3 (DME), 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, respectively, were prepared by weighing. The excess molar enthalpy of the ternary system was obtained from the relation

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

where $H^E_{\mathrm{m},23}$ is the excess molar enthalpy of the particular binary mixture of TAME and DME. Over most of the mole fraction range of component 1, the errors of $H^E_{\mathrm{m},1+23}$ are estimated to be <0.5%. Errors in the mole fractions of the final ternary mixtures are estimated to be $<5\times10^{-4}$.

3. Results and discussion

Excess molar enthalpies $H^E_{\mathrm{m},ij}$ ($i<j$) for the constituent binary mixtures nC$_7$(1)+TAME(2) and nC$_7$(1)+DME(3) have been measured previously [8,9]. In both cases, the function

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

was used to smooth the data. The experimental values of x_2 and $H^E_{\mathrm{m},23}$ for the third constituent binary mixture of present interest, TAME(2)+DME(3), are summarized in Table 1. Eq. (2) was fitted to these results by the method of least squares, with all the points weighted equally. The values obtained for the coefficients h_k are listed in Table 2, along with the standard deviation s of the representation. For convenience, the coefficients for the representations of the two binaries studied previously [8,9] are included in Table 2.

The results for TAME(2)+DME(3) and their representation by Eq. (2) are plotted in Fig. 1. The maximum value of $H^E_{\mathrm{m},23}/(\mathrm{J\,mol^{-1}}) \approx 407$, occurring near $x_2=0.5$, is $\approx 100\ \mathrm{J\,mol^{-1}}$ larger than that found for MTBE(2)+DME(3) [1]. In both these cases, the curves are nearly symmetric about $x_2=0.5$.

Experimental results for $H^E_{\mathrm{m},1+23}$ and the corresponding values of $H^E_{\mathrm{m},123}$ are listed in Table 3 for the ternary system. In Fig. 2, the values of $H^E_{\mathrm{m},1+23}$ for the three pseudo-binary systems are plotted against x_1, the mole fraction of nC$_7$. Representation of the values of $H^E_{\mathrm{m},1+23}$ was based on the relation

$$H^E_{\mathrm{m},1+23} = \left(\frac{x_2}{1 - x_1}\right)H^E_{\mathrm{m},12} + \left(\frac{x_3}{1 - x_1}\right)H_{\mathrm{m},13} + H^E_{\mathrm{m},T} \qquad (3)$$

This consists of a sum of binary contributions [10], and an added ternary term. The form

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

which was adopted for the latter is similar to the form used by Morris et al. [11], 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 $H^E_{\mathrm{m},1+23}$ in Table 3. In doing this, the values of $H^E_{\mathrm{m},ij}$ for the binary contributions were calculated from Eq. (2) using the appropriate coefficients from Table 2. The resulting form for $H^E_{\mathrm{m},T}$ is given in the footnote of Table 3, along with the standard deviation s for the representation of the values of $H^E_{\mathrm{m},1+23}$.

Table 1
Experimental mole fractions x_2 and excess molar enthalpies $H^E_{\mathrm{m},23}$, at 298.15 K, for TAME(2)+DME(3)

x_2	$H^E_{\mathrm{m},23}$/(J mol^{-1})	x_2	$H^E_{\mathrm{m},23}$/(J mol^{-1})	x_2	$H^E_{\mathrm{m},23}$/(J mol^{-1})	x_2	$H^E_{\mathrm{m},23}$/(J mol^{-1})
0.0501	81.9	0.2998	349.5	0.5499	403.1	0.7502	300.7
0.1000	154.6	0.3506	377.9	0.6000	387.2	0.7999	256.4
0.1500	219.7	0.4000	394.8	0.6005	387.8	0.8501	202.3
0.2000	274.0	0.4501	406.5	0.6494	368.3	0.8998	135.2
0.2501	316.1	0.5012	407.1	0.6997	338.0	0.9499	60.5
0.2997	350.1						

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_1	h_2	h_3	h_4	h_5	h_6	s/(J mol^{-1})
i	j							
nC7	TAME [a]	1176.17	4.48	10.07	−41.00			0.53
nC7	DME [b]	5139.30	179.17	517.85				2.78
TAME	DME	1625.95	84.44	181.17	−152.39	−331.31	400.58	2.09

[a] Tong et al. [8].

[b] Kumaran and Benson [9].

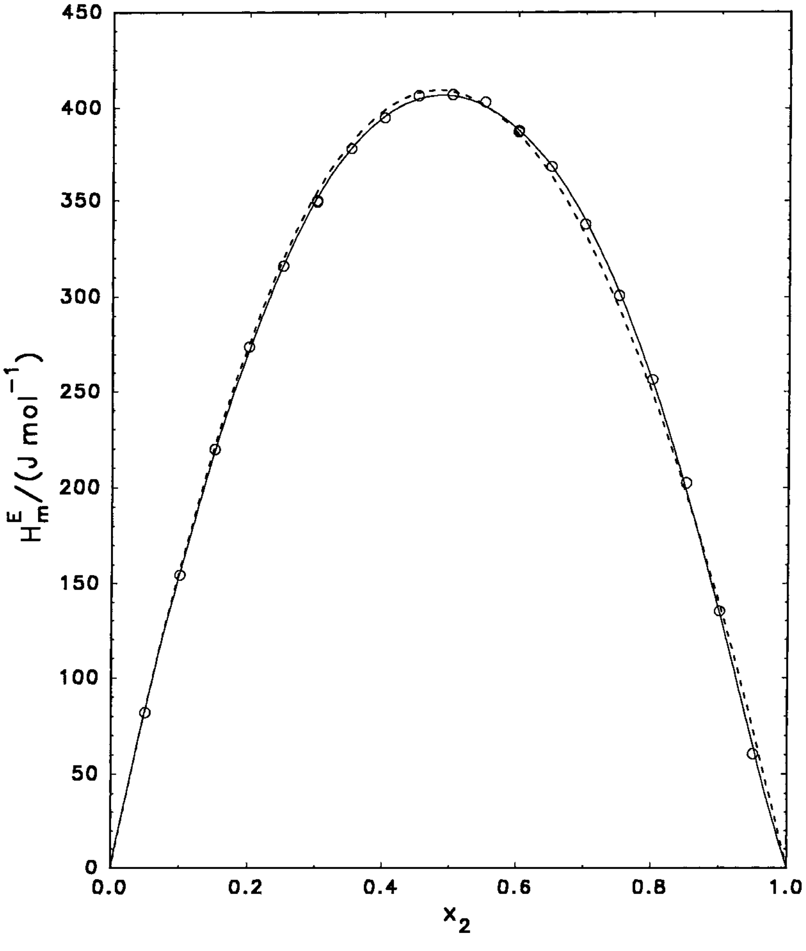

Fig. 1. Excess molar enthalpies, $H^E_{m,23}$, for $x_2C_2H_5C(CH_3)_2OCH_3+(1-x_2)CH_3O(CH_2)_2OCH_3$ at 298.15 K. Experimental results: (○), curves: (———), calculated from Eq. (2) with coefficients from Table 2; and (- - -), estimated by the Flory theory.

Table 3
Experimental excess molar enthalpies $H^E_{m,1+23}$ at 298.15 K for the addition of nC$_7$ to a binary mixture of TAME and DME to form $x_1CH_3(CH_2)_5CH_3+x_2C_2H_5C(CH_3)_2OCH_3+x_3CH_3O(CH_2)_2OCH_3$ 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=0.3333, $H^E_{m,23}$/(J mol^{-1})=316.1								
0.0501	193.4	493.7	0.3999	936.2	1125.9	0.7500	737.0	816.1
0.1000	365.0	649.5	0.4498	960.9	1134.9	0.7999	632.4	695.6
0.1501	520.8	789.5	0.4994	971.1	1129.3	0.8498	499.8	547.3
0.1999	652.2	905.1	0.5501	958.8	1101.1	0.8499	500.3	547.7
0.2500	743.9	981.0	0.6001	933.8	1060.2	0.8999	346.7	378.3
0.3000	826.5	1047.8	0.6501	886.1	996.7	0.9499	163.1	178.9
0.3501	892.0	1097.4	0.6999	822.8	917.7			
x_2/x_3=0.9986, $H^E_{m,23}$/(J mol^{-1})=406.5								
0.0500	136.8	523.0	0.4000	670.4	914.3	0.6997	589.5	711.5
0.1001	257.8	623.6	0.4503	690.9	914.3	0.7498	528.5	630.2
0.1499	365.6	711.2	0.5010	696.0	898.8	0.7998	450.7	532.1
0.1998	459.0	784.3	0.5507	688.6	871.2	0.7999	452.8	534.1
0.2501	529.9	834.7	0.6003	669.6	832.0	0.8500	362.1	423.1
0.3002	592.3	876.7	0.6004	670.7	833.1	0.8999	259.0	299.7
0.3502	636.6	900.7	0.6502	637.2	779.4	0.9499	137.2	157.6
x_2/x_3=2.9979, $H^E_{m,23}$/(J mol^{-1})=302.9								
0.0501	91.8	379.5	0.4001	455.4	637.0	0.6999	400.4	491.3
0.1000	172.7	445.3	0.4503	469.3	635.8	0.7499	358.6	434.4
0.1501	245.9	503.4	0.5008	473.9	625.1	0.8001	307.4	367.9
0.2000	309.5	551.8	0.5496	469.5	605.9	0.8497	246.4	291.9
0.2505	358.0	585.0	0.6006	455.6	576.6	0.9001	171.7	202.0
0.3002	400.6	612.6	0.6501	433.3	539.3	0.9499	80.0	95.2
0.3502	431.9	628.7						

[a] Ternary term for representation of $H^E_{m,1+23}$ by Eqs. (3) and (4): $H^E_{m,T}/(\mathrm{J\ mol^{-1}})=[x_1x_2x_3/(1-x_1+x_2)](-2120.50+1358.10x_1-3248.75x_2+4849.20x_1^2-3396.39x_1x_2+3146.92x_2^2-7442.90x_1^3)$; $s/(\mathrm{J\ mol^{-1}})=4.7$.

The solid curves in Fig. 2 were calculated from Eq. (3) using values of $H^E_{m,T}$ from the formula in the footnote of Table 3. It is evident from these, that the representation of the experimental results is quite good. Curves calculated from the smooth representations of $H^E_{m,12}$ and $H^E_{m,13}$ are included in Fig. 2 for comparison. In all the cases, the maximum value of $H^E_{m,1+23}$ occurs near x_1=0.5, and at constant x_1 the enthalpies increase with increasing relative content of DME in the mixtures.

Some constant $H^E_{m,123}$ contours, calculated from Eqs. (1)–(4), are plotted on the Roozeboom diagram in Fig. 3. The general characteristics of these are very similar to those found for the system containing MTBE in place of TAME [1]. There is no indication of an internal extremum, and the maximum value of $H^E_{m,123}$ is still located in the edge of the plot for the constituent binary nC$_7$(1)+DME(3).

Previously [1], it was found that the Flory theory [12,13], as applied to multicomponent mixtures [14], provided reasonable estimates of $H^E_{m,1+23}$ for nC$_7$(1)+MTBE(2)+DME(3). The same approach was investigated for the present system containing TAME. Reference can be made to the work of Wang et al. [15] for the equations used in the present application.

The values of the physical properties (molar volume V_m, isobaric expansivity α_p and isothermal compressibility κ_T) and the corresponding Flory characteristic values (pressure p^*, molar volume V^*_m and temperature

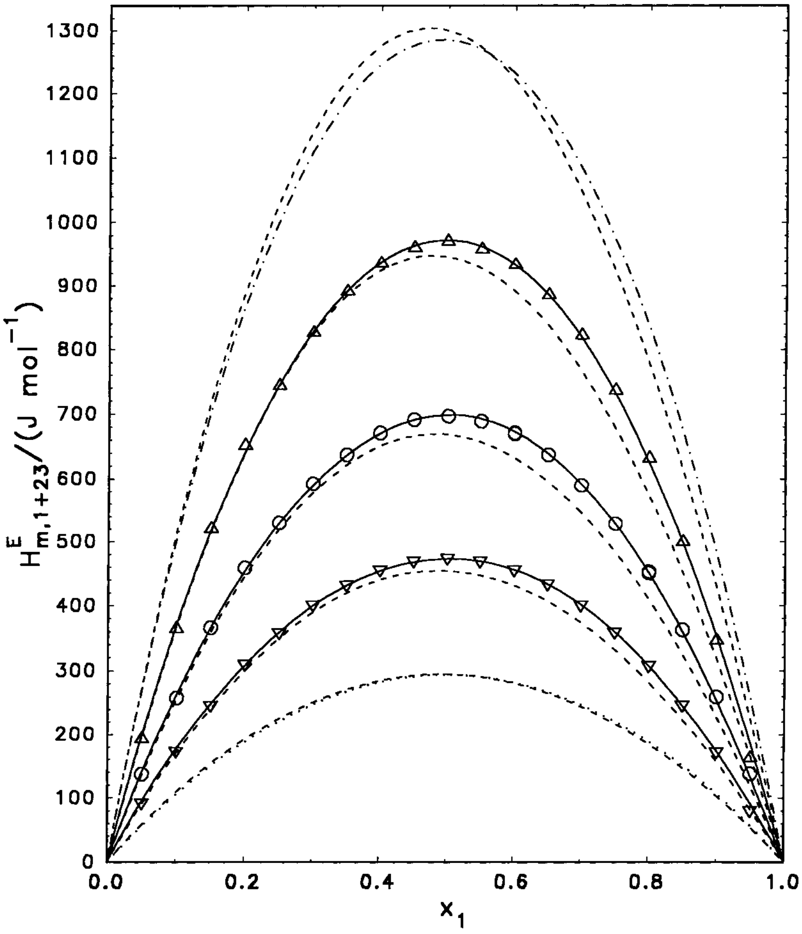

Fig. 2. Excess molar enthalpies, $H^E_{m,1+23}$, for $x_1CH_3(CH_2)_5CH_3+x_2C_2H_5C(CH_3)_2OCH_3+x_3CH_3O(CH_2)_2OCH_3$ mixtures at 298.15 K. Experimental results: (△), $x_2/x_3=0.3333$; (○), $x_2/x_3=0.9986$; (▽), $x_2/x_3=2.9979$. Curves: (– • –), $x_2=0$, Kumaran and Benson [9]; (———), calculated from Eqs. (3) and (4) with $H^E_{m,T}$ from the footnote of Table 3; (· · ·), $x_3=0$, Tong et al. [8]; and (- - -), estimated by the Flory theory.

Table 4

Physical properties and parameters [a] used in Flory theory calculations at 298.15 K for $x_1CH_3(CH_2)_5CH_3+x_2C_2H_5C(CH_3)_2COCH_3+x_3CH_3O(CH_2)_2OCH_3$

Component	V_m/(cm^3 mol^{-1})	α_p/(kK^{-1})	κ_T/(T Pa^{-1})	p^*/(MPa)	V^*_m/(cm^3 mol^{-1})	T^*/K	Ref.
nC$_7$	147.45	1.256	1460.6	431.9	113.60	4648.1	[16]
TAME	133.4	1.22	1329.0	456.1	103.32	4714.8	[17]
DME	104.64	1.267	1115.1	572.5	80.49	4628.5	[1]

[a] Interchange-energy parameters X_{ij}/(J cm^{-3}): $X_{12}=10.1217$, Tong et al. [8]; $X_{13}=48.6502$, Benson et al. [1]; $X_{23}=16.3052$.

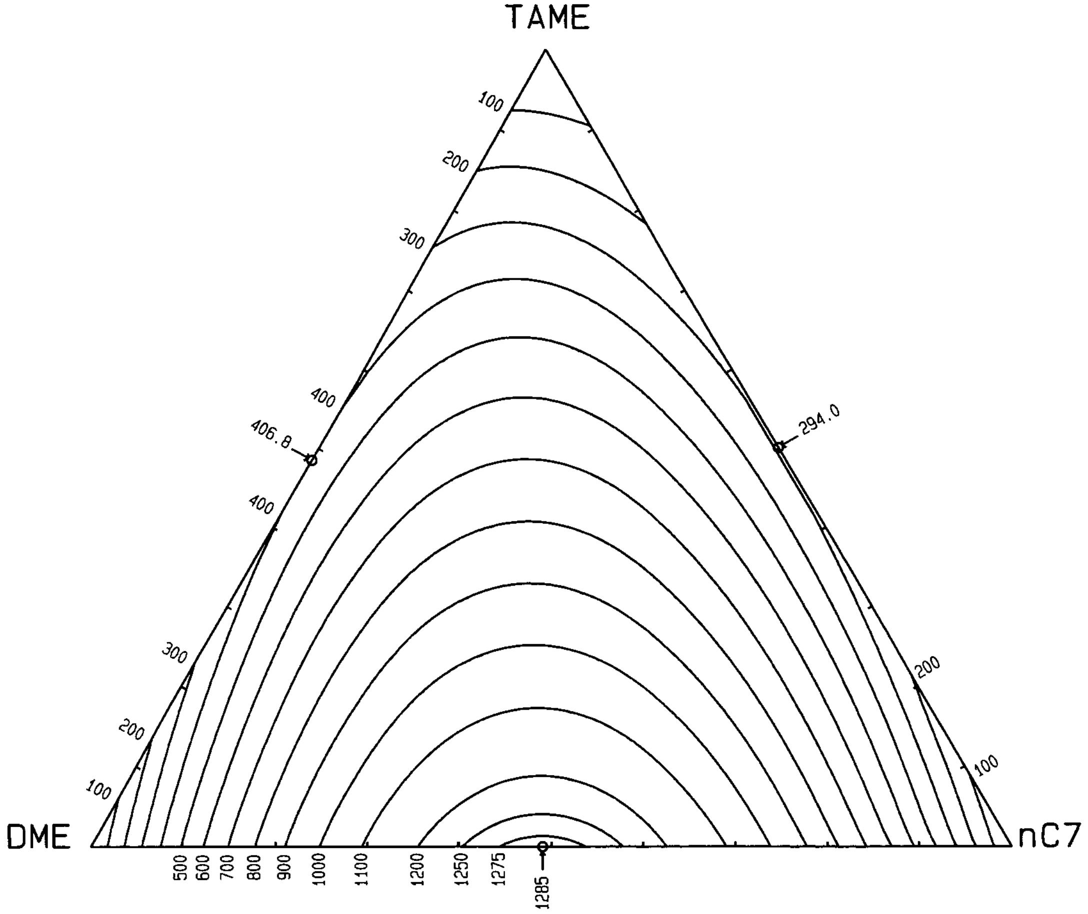

Fig. 3. Contours for constant values of $H^E_{\mathrm{m},123}$/(J mol^{-1}) for $x_1\mathrm{CH_3(CH_2)_5CH_3}+x_2\mathrm{C_2H_5C(CH_3)_2OCH_3}+x_3\mathrm{CH_3O(CH_2)_2OCH_3}$ at 298.15 K obtained from the representation of the experimental results by Eqs. (3) and (4) with $H^E_{\mathrm{m},T}$ from the footnote of Table 3.

T^*) are summarized in Table 4. As indicated in the last column, these were taken from previous publications [1,16,17].

In evaluating s_i/s_j, the ratio of molecular surface areas of contact per segment between components i and j, it was assumed that the molecules were spherical. The values of the interchange energy parameters X_{12} and X_{13} were taken from previous publications [8,17]. The value of X_{23} was obtained by fitting the Flory formula for $H^E_{\mathrm{m},23}$ to the smooth representation of the results for TAME(2)+DME(3) by Eq. (2).

Estimates of $H^E_{\mathrm{m},23}$ and $H^E_{\mathrm{m},1+23}$, derived from the values of the parameters in Table 4, are plotted as broken curves in Figs. 1 and 2. In the case of TAME(2)+DME(3), there is a fairly good agreement with the smooth representation of the experimental results. For the three pseudo-binary mixtures, the Flory theory tends to underestimate the experimental results for x_1>0.4. The mean absolute relative deviation of the 60 values of $H^E_{\mathrm{m},123}$ in Table 3 amounts to 4.0%.

Constant $H^E_{\mathrm{m},123}$ contours, estimated on the basis of the Flory theory, are shown on the Roozeboom diagram in Fig. 4. As found previously [1] for $n\mathrm{C_7}$(1)+MTBE(2)+DME(3), it is clear from a comparison with Fig. 3, that the Flory theory provides useful estimates of $H^E_{\mathrm{m},123}$, without requiring the direct investigation of any ternary mixtures.

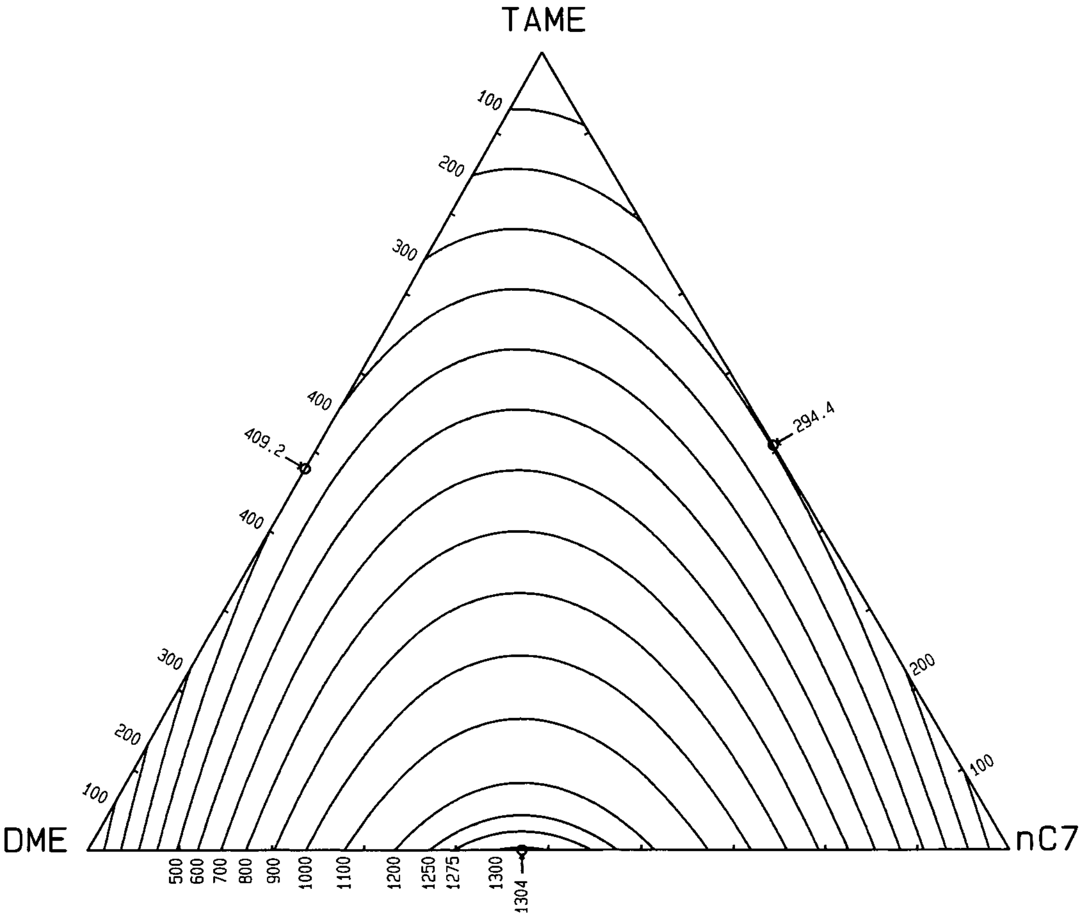

Fig. 4. Contours for constant values of $H^{E}_{m,123}$/(J mol^{-1}) for $x_1CH_3(CH_2)_5CH_3$+$x_2C_2H_5C(CH_3)_2OCH_3$+$x_3CH_3O(CH_2)_2OCH_3$ at 298.15 K estimated by the Flory theory.

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