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Excess molar enthalpies of the ternary mixture: 2,2,4-trimethylpentane + cyclohexane + *n*-octane

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Abstract

Microcalorimetric measurements of excess molar enthalpies, at 298.15 K, are reported for $x_1(CH_3)_3CCH_2CH(CH_3)_2 + x_2c\text{-}(CH_2)_6 + x_3CH_3(CH_2)_6CH_3$. A smooth representation of the results is 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.

Keywords: 2,2,4-Trimethylpentane; Cyclohexane; *n*-Octane; Excess molar enthalpy; Ternary system

1. Introduction

The thermodynamic properties of multicomponent systems formed by mixing 2,2,4-trimethylpentane (TMP) with other hydrocarbons are of practical interest, in view of the use of TMP (i.e. isooctane) as a standard reference material in measuring the octane rating or antiknock properties of motor fuels. A recent paper [1], from our laboratory, reported excess molar enthalpies for the ternary system consisting of TMP together with *n*-hexane (nC6) and *n*-octane (nC8). As an extension of that investigation, similar measurements have been made for the analogous system, in which cyclohexane (cC6) replaced the nC6 used previously.

2. Experimental

The TMP and nC8 used for the present measurements were the same as in our earlier work [1]. Research grade cC6, with purity exceeding 99.9 mol%, was obtained from the Phillips Chemical Co. Apart from partial degassing, all of the components were used as received from the manufacturers. Densities, measured at 298.15 K in an Anton-Paar digital densimeter, were 687.90, 773.99 and 698.69 kg m^{-3} for TMP, cC6 and nC8, respectively. These are in reasonable agreement with values in the literature [2–4].

An LKB flow microcalorimeter (Model 10 700-1), 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 [5,6].

In studying the ternary system $x_1(CH_3)_3CCH_2CH(CH_3)_2 + x_2c\text{-}(CH_2)_6 + x_3CH_3(CH_2)_6CH_3$, the excess

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molar enthalpy $H^{\mathrm{E}}_{m,1+23}$ was determined for several pseudo-binary systems in which TMP was added to a binary mixture of components 2 and 3, 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 of the ternary system was obtained from the relation:

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

where $H^{\mathrm{E}}_{m,23}$ is the excess molar enthalpy of the particular binary mixture of cC6 and nC8. Over most of the mole fraction range of component 1, the errors of $H^{\mathrm{E}}_{m,1+23}$ 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

Excess molar enthalpies $H^{\mathrm{E}}_{m,ij}$ $(i<j)$, at $T = 298.15$ K, for the three constituent binary systems of present interest, have been reported previously: TMP(1) + cC6(2) [7,8], TMP(1) + nC8(3) [7,8], and cC6(2) + nC8(3) [9]. For convenience, values of the coefficients h_k for representing these results by the function:

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

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

Experimental results for $H^{\mathrm{E}}_{m,1+23}$ and the corresponding values of $H^{\mathrm{E}}_{m,123}$ are listed in Table 2 for the ternary system. In Fig. 1, the values of $H^{\mathrm{E}}_{m,1+23}$ are plotted against x_1, the mole fraction of TMP. Also shown are curves for the constituent binaries having $x_2 = 0$ [8] and $x_3 = 0$ [7]. At constant x_1, the values of $H^{\mathrm{E}}_{m,1+23}$ increase as the ratio x_2/x_3 increases. However, only the results for $x_2/x_3 = 3.0006$ falls between the curves for the constituent binaries. This behavior differs from that observed previously for TMP(1) + nC6(2) + nC8(3) [1].

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

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

which consists of the sum of binary contributions proposed by Kohler [10], and an added ternary term $H^{\mathrm{E}}_{m,T}$. The form

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

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. (1)–(4) were fitted to the values of $H^{\mathrm{E}}_{m,1+23}$ in Table 2. In doing this, the values of $H^{\mathrm{E}}_{m,ij}$ for the binary contributions were calculated from Eq. (2) using the appropriate coefficients from Table 1. The resulting form for $H^{\mathrm{E}}_{m,T}$ is given in the footnote of Table 2, along with the standard deviation s for the representation of the values of $H^{\mathrm{E}}_{m,1+23}$.

The solid curves in Fig. 1 were calculated from Eqs. (1)–(4) using values of $H^{\mathrm{E}}_{m,T}$ given by the formula in the footnote of Table 2. It is evident from these, that

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

Component		h_1	h_2	h_3	h_4	h_5	s (J mol^{-1})
i	j						
TMP	cC6[a]	722.6	98.8	−33.7			0.8
TMP	nC8[a]	102.1					0.1
cC6	nC8[b]	1029.63	−349.37	275.56	−101.55	−205.01	0.7

[a] Grolier [8] fit of Lundberg [7] data.

[b] Ref. [9].

Table 2
Experimental excess molar enthalpies $H^{E}_{m,1+23}$ at 298.15 K for the addition of TMP to a binary mixture of cC6 and nC8 to form $x_1(CH_3)_3CCH_2CH(CH_3)_2 + x_2$c-$(CH_2)_6 + x_3CH_3(CH_2)_6CH_3$ 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	$H^{E}_{m,1+23}$ [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})
$x_2/x_3 = 0.3332$, $H^{E}_{m,23}$ (J mol^{-1}) = 168.4								
0.0500	2.97	162.9	0.3992	14.89	116.1	0.7003	12.25	62.7
0.1000	5.76	157.3	0.4505	15.21	107.7	0.7500	10.57	52.7
0.1501	8.45	151.6	0.5000	15.19	99.4	0.8000	8.61	42.3
0.2000	10.54	145.3	0.5493	14.90	90.8	0.8505	6.80	32.0
0.2495	11.97	138.3	0.5496	14.93	90.8	0.9001	4.60	21.4
0.2997	12.87	130.8	0.6001	14.26	81.6	0.9500	2.34	10.8
0.3500	14.18	123.6	0.6500	13.27	72.2			
$x_2/x_3 = 1.0001$, $H^{E}_{m,23}$ (J mol^{-1}) = 257.4								
0.0500	4.91	249.5	0.4009	23.21	177.4	0.7000	19.86	97.1
0.0999	9.10	240.8	0.4499	23.93	165.5	0.7500	17.53	81.9
0.1501	12.76	231.5	0.4999	23.75	152.5	0.8001	14.78	66.2
0.1999	16.04	222.0	0.5496	23.74	139.7	0.8500	11.64	50.2
0.2499	18.34	211.4	0.6004	22.90	125.8	0.9000	7.70	33.4
0.2985	20.43	201.0	0.6502	21.56	111.6	0.9500	3.56	16.4
0.3500	21.92	189.2						
$x_2/x_3 = 3.0006$, $H^{E}_{m,23}$ (J mol^{-1}) = 238.7								
0.0500	12.84	239.6	0.4001	65.25	208.4	0.6997	56.15	127.8
0.1000	24.76	239.6	0.4499	66.55	197.8	0.7507	49.73	109.2
0.1500	35.45	238.3	0.5000	67.68	187.0	0.8000	42.17	89.9
0.1995	43.72	234.8	0.5002	68.01	187.3	0.8499	33.28	69.1
0.2503	51.37	230.3	0.5496	66.98	174.5	0.8999	22.50	46.4
0.3001	57.21	224.3	0.5995	64.76	160.3	0.9499	11.54	23.5
0.3505	62.19	217.2	0.6507	61.26	144.6			

[a] Ternary term for representation of $H^{E}_{m,1+23}$ by Eqs. (1)–(4): $H^{E}_{m,T}$ (J mol^{-1}) $= [x_1x_2x_3/(1-x_1+x_2)]\,(-505.26 + 3371.65x_1 + 1407.54x_2 - 5688.78x_1^2 - 10714.75x_1x_2 - 2556.27x_2^2 + 2792.31x_1^3 + 10282.35x_1^2x_2 + 4834.54x_1x_2^2)$; s (J mol^{-1}) = 0.39.

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 diagram in part (a) of Fig. 2. There is no indication of an internal extremum, and the maximum value of $H^{E}_{m,123}$ is located in the edge of the plot for the constituent binary cC6(2) + nC8(3).

Previously [1], it was found that the Flory theory [12,13], as applied to multicomponent mixtures [14], provided reasonable estimates of $H^{E}_{m,123}$ for TMP(1) + nC6(2) + nC8(3). The same approach was investigated for the present system containing cC6. 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 T^*) are summarized in Table 3. As indicated in the last column, these were taken from previous publications [16–18].

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_{ij}, given in the footnote of Table 3, were obtained by fitting the Flory formula for $H^{E}_{m,ij}$ to the smooth representations of the excess molar enthalpies of each of the three constituent binary systems, using Eq. (2) and the coefficients given in Table 1.

Estimates of $H^{E}_{m,1+23}$, based on the values of the parameters in Table 3, are plotted as broken curves in

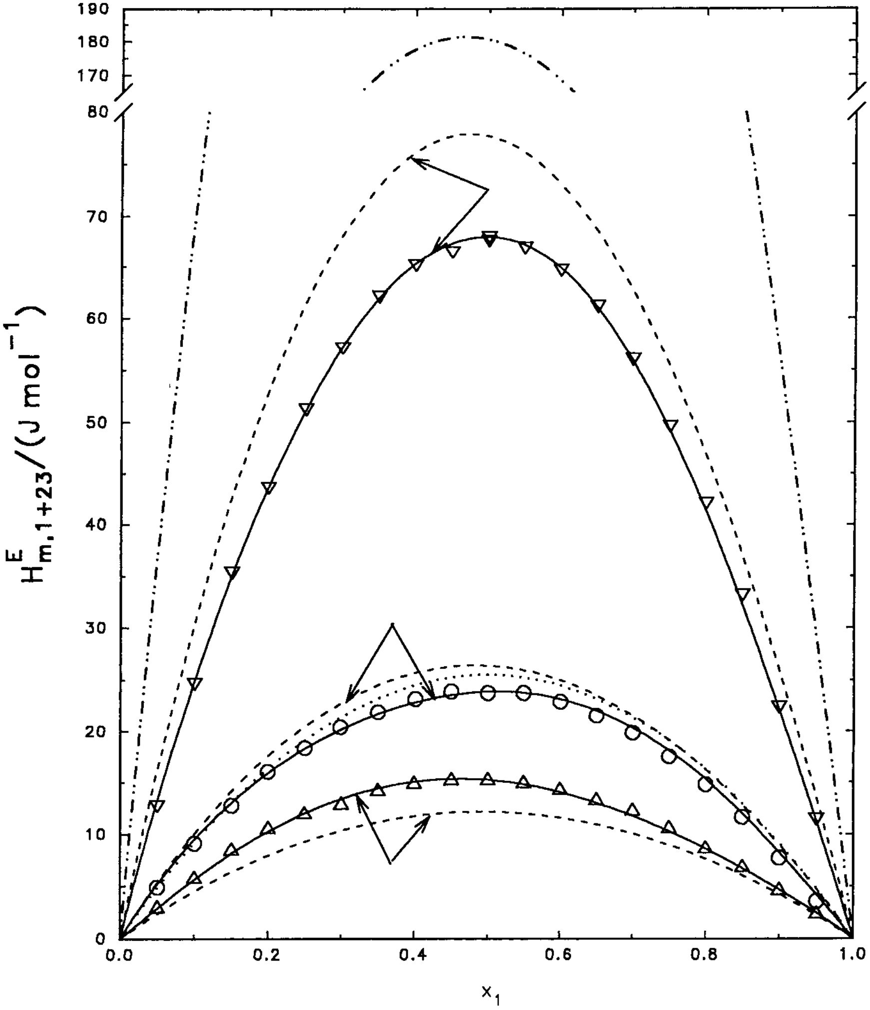

Fig. 1. Excess molar enthalpies, $H^E_{m,1+23}$ for $x_1(CH_3)_3CCH_2CH(CH_3)_2 + x_2c\text{-}(CH_2)_6 + x_3CH_3(CH_2)_6CH_3$ mixtures at 298.15 K. Experimental results: (Δ) $x_2/x_3 = 0.3332$; (○) $x_2/x_3 = 1.0001$; (▽) $x_2/x_3 = 3.0006$. Curves: (····), $x_2 = 0$, Lundberg [7]; (-··), $x_3 = 0$, Lundberg [7]; (—), calculated from Eqs. (1)–(4) with $H^E_{m,T}$ from the footnote of Table 2; (- - - -), estimated by the Flory theory.

Table 3
Physical properties and parameters[a] used in Flory theory calculations at 298.15 K for $x_1(CH_3)_3CCH_2CH(CH_3)_2 + x_2c\text{-}(CH_2)_6 + x_3CH_3(CH_2)_6CH_3$

Component	V_m ($cm^3\ mol^{-1}$)	α_p ($k\ K^{-1}$)	κ_T ($T\ Pa^{-1}$)	p^* (MPa)	V^*_m ($cm^3\ mol^{-1}$)	T^* (K)	References
TMP	166.098	1.197	1542.1	383.2	129.083	4759.5	[16]
cC6	108.751	1.220	1140.0	532.0	84.229	4714.8	[17]
nC8	163.50	1.164	1302.4	436.8	127.695	4827.0	[18]

[a] Interchange-energy parameters X_{ij} ($J\ cm^{-3}$): $X_{12} = 6.1196$; $X_{13} = 0.7604$; $X_{23} = 10.5254$.

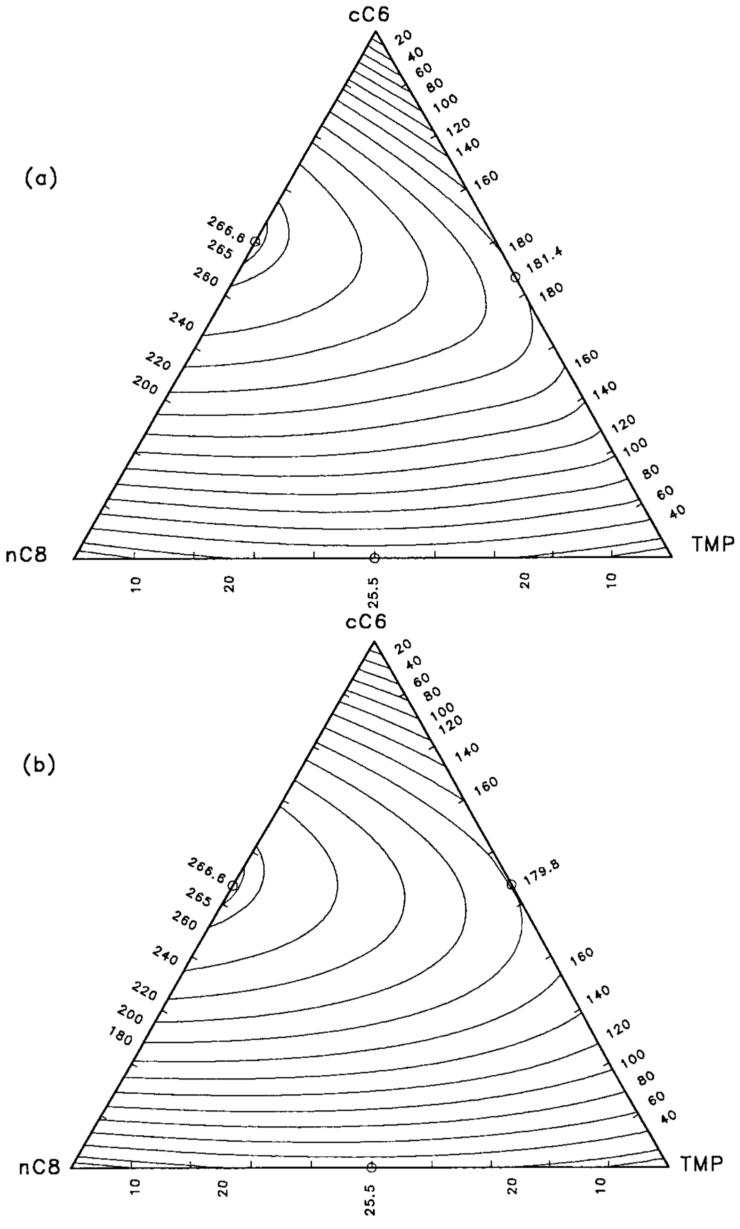

Fig. 2. Contours for constant values of for $H^{E}_{m,123}$ (J mol^{-1}) $x_1(CH_3)_3CCH_2CH(CH_3)_2 + x_2c\text{-}(CH_2)_6 + x_3CH_3(CH_2)_6CH_3$ at 298.15 K: (a) calculated from the representation of the experimental results by Eqs. (1)–(4) with $H^{E}_{m,T}$ from the footnote of Table 2; (b) calculated from the Flory theory.

Fig. 1. For the three pseudo-binary mixtures, the Flory theory provides reasonable predictions of their relative order and positions with respect to the curves for the two constituent binaries. For the 59 experimental points in Table 2, the root mean square deviation between the estimated and observed values of $H^{E}_{m,1+23}$ is 5.0 J mol^{-1}.

Constant $H^{E}_{m,123}$ contours, estimated on the basis of the Flory theory, are shown on the Roozeboom diagram in Fig. 2b. As found previously [1] for

TMP(1) + nC6(2) + nC8(3), it is clear from a comparison of Fig. 2a and b, that the Flory theory again provides useful estimates of $H^{\mathrm{E}}_{m,123}$, without requiring the direct investigation of any ternary mixtures.

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