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# Excess Enthalpies of 1-Propanol + *n*-Hexane + *n*-Decane or *n*-Dodecane at 298.15 K

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Excess enthalpies, measured at 298.15 K in a flow microcalorimeter, are reported for the ternary systems $C_3H_7OH$ (1) + $C_6H_{14}$ (2) + $C_\nu H_{2\nu+2}$ (3) with $\nu$ = 10 and 12. Smooth representations of the data are used to calculate constant enthalpy contours on a Roozeboom diagram.

## Introduction

The properties of multicomponent mixtures, comprising an alcohol and two or more *n*-alkanes, are of interest in the technology of alcohol-blended gasoline. A recent paper (*1*) from our laboratory reported excess enthalpies for the ternary systems ethanol + *n*-hexane + *n*-decane and ethanol + *n*-hexane + *n*-dodecane. As an extension of that work, we have determined excess enthalpies for the two corresponding systems with ethanol replaced by 1-propanol.

## Experimental Section

Anhydrous 1-propanol, with a stated purity exceeding 99 mol %, was obtained from the Aldrich Chemical Co. Its density, measured at 298.15 K in an Anton-Paar digital densimeter, was 779.74 kg m$^{-3}$. The *n*-hexane, *n*-decane, and *n*-dodecane were the same as used in our previous work (*1*).

Excess molar enthalpies were measured in an LKB flow microcalorimeter (model 10700-1) thermostated at 298.150 ± 0.002 K. Details of this equipment and its operation have been described previously (*2*, *3*). In studying the ternary systems, the excess molar enthalpy $H^E_{m,1+23}$ was measured for several pseudobinary systems, in which component 1 (1-propanol) was added to a binary mixture of components 2 (*n*-hexane) and 3 (*n*-decane or *n*-dodecane) having a fixed mole ratio $x_2/x_3$. These binaries were prepared by weighing. The excess molar enthalpy $H^E_{m,123}$ of the ternary system 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 *n*-alkane mixture. Values of $H^E_{m,23}$ for *n*-hexane + *n*-decane and *n*-hexane + *n*-dodecane were taken from the literature (*4*, *5*). The errors of $H^E_{m,1+23}$ are estimated to be

**Table I. Experimental Results for the Excess Molar Enthalpies, $H^E_{m,ij}$, of $x_1$ $C_3H_7OH$ + (1 − $x_1$) $C_\nu H_{2\nu+2}$ Mixtures at 298.15 K and Their Representations by Equation 2**

| $x_1$ | $H^E_{m,12}$[a]/ (J mol$^{-1}$) | $x_1$ | $H^E_{m,13}$[b]/ (J mol$^{-1}$) | $x_1$ | $H^E_{m,13}$[c]/ (J mol$^{-1}$) |
|---|---|---|---|---|---|
| $\nu$ = 6 | | $\nu$ = 10 | | $\nu$ = 12 | |
| 0.0502 | 344.0 | 0.0500 | 411.1 | 0.0500 | 441.1 |
| 0.0502 | 349.1 | 0.0500 | 411.6 | 0.0998 | 593.6 |
| 0.1001 | 439.8 | 0.1000 | 548.4 | 0.1501 | 678.1 |
| 0.1501 | 501.6 | 0.1000 | 541.2 | 0.2000 | 731.2 |
| 0.1999 | 544.6 | 0.1500 | 621.5 | 0.2500 | 773.0 |
| 0.2501 | 570.4 | 0.2003 | 671.5 | 0.3004 | 796.0 |
| 0.2999 | 584.5 | 0.2500 | 710.2 | 0.3320 | 815.6 |
| 0.3508 | 587.8 | 0.3000 | 742.0 | 0.3499 | 818.5 |
| 0.3992 | 576.6 | 0.3501 | 751.7 | 0.3856 | 819.6 |
| 0.4498 | 558.8 | 0.4001 | 761.7 | 0.4372 | 824.0 |
| 0.5008 | 532.9 | 0.4495 | 756.5 | 0.4878 | 811.3 |
| 0.5499 | 500.4 | 0.5002 | 731.8 | 0.5390 | 785.4 |
| 0.6005 | 462.9 | 0.5495 | 707.3 | 0.5886 | 753.2 |
| 0.6502 | 419.6 | 0.6000 | 672.7 | 0.6366 | 715.7 |
| 0.6990 | 373.2 | 0.6501 | 632.1 | 0.6837 | 667.1 |
| 0.7430 | 329.0 | 0.6999 | 585.0 | 0.7313 | 610.4 |
| 0.8001 | 265.7 | 0.7497 | 525.1 | 0.7782 | 543.0 |
| 0.8281 | 231.4 | 0.8005 | 454.8 | 0.8234 | 469.6 |
| 0.8500 | 205.4 | 0.8500 | 371.2 | 0.8686 | 380.4 |
| 0.8988 | 142.2 | 0.9000 | 270.9 | 0.9130 | 276.0 |
| 0.9500 | 68.9 | 0.9499 | 151.5 | 0.9568 | 153.3 |

[a] $H^E_{m,12}/(\mathrm{J\ mol^{-1}}) = x_1(1 - x_1)(1 - 0.9839z)^{-1}(2134.1 - 941.2z - 339.8z^2 - 243.2z^3)$; $s$ = 1.5. [b] $H^E_{m,13}/(\mathrm{J\ mol^{-1}}) = x_1(1 - x_1)(1 - 0.9205z)^{-1}(2941.0 - 1853.0z + 312.1z^2 - 689.0z^3 + 705.2z^4)$; $s$ = 2.9. [c] $H^E_{m,13}/(\mathrm{J\ mol^{-1}}) = x_1(1 - x_1)(1 - 0.8809z)^{-1}(3221.1 - 2034.6z + 475.7z^2 - 632.6z^3 + 925.3z^4)$; $s$ = 2.1.

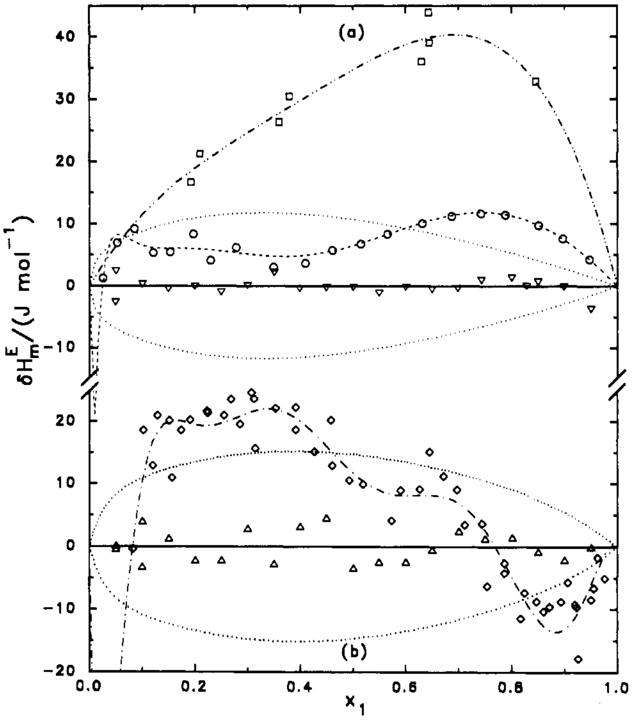

**Figure 1.** Deviations $\delta H^E_m = \{H^E_m(\mathrm{expt}) - H^E_{m,ij}(\mathrm{eq\ 2})\}$ of the excess molar enthalpy at 298.15 K: (a) $x_1$ $C_3H_7OH$ + (1 − $x_1$) $C_6H_{14}$, this work (▽), Brown et al. (*6*) (□) (- ·· -, our smoothing of data), Veselý et al. (*7*) (○) (- - -), ±2% deviation from eq 2 (···); (b) $x_1$ $C_3H_7OH$ + (1 − $x_1$) $C_{10}H_{22}$, this work (△), Christensen et al. (*8*) (◇) (- · -), ±2% deviation from eq 2 (···).

**Table II. Experimental Excess Molar Enthalpies, $H^E_{m,1+23}$, at 298.15 K for the Addition of 1-Propanol to *n*-Hexane + *n*-Decane Mixtures To Form $C_3H_7OH$ (1) + $C_6H_{14}$ (2) + $C_{10}H_{22}$ (3) and Values of $H^E_{m,123}$ Calculated from Equation 1 Using $H^E_{m,23}$ from Reference 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$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| $x_2/x_3 = 0.3284$; $H^E_{m,23} = 11.5$ J mol$^{-1}$ | | | | | | | | |
| 0.0500 | 399.6 | 410.5 | 0.3997 | 719.5 | 726.4 | 0.7503 | 470.8 | 473.6 |
| 0.1000 | 518.2 | 528.5 | 0.4518 | 706.5 | 712.8 | 0.8000 | 403.5 | 405.7 |
| 0.1500 | 600.0 | 609.7 | 0.5008 | 686.3 | 692.1 | 0.8501 | 322.8 | 324.5 |
| 0.2002 | 653.8 | 663.0 | 0.5500 | 658.0 | 663.2 | 0.9000 | 233.0 | 234.2 |
| 0.2499 | 690.2 | 698.8 | 0.6000 | 621.9 | 626.4 | 0.9500 | 124.8 | 125.4 |
| 0.2998 | 712.0 | 720.0 | 0.6501 | 578.8 | 582.8 | | | |
| 0.3499 | 723.2 | 730.6 | 0.7005 | 529.7 | 533.1 | | | |
| $x_2/x_3 = 0.9912$; $H^E_{m,23} = 14.4$ J mol$^{-1}$ | | | | | | | | |
| 0.0399 | 350.4 | 364.2 | 0.4001 | 679.1 | 687.7 | 0.7501 | 430.3 | 433.9 |
| 0.1000 | 499.3 | 512.2 | 0.4513 | 663.2 | 671.1 | 0.7999 | 365.6 | 368.5 |
| 0.1500 | 567.4 | 579.7 | 0.4996 | 642.8 | 650.0 | 0.8501 | 290.2 | 292.3 |
| 0.1999 | 620.4 | 631.9 | 0.5502 | 614.3 | 620.7 | 0.8984 | 210.1 | 211.6 |
| 0.2500 | 651.9 | 662.7 | 0.6006 | 579.6 | 585.4 | 0.9500 | 109.2 | 109.9 |
| 0.3001 | 675.7 | 685.8 | 0.6505 | 536.8 | 541.8 | | | |
| 0.3499 | 682.4 | 691.7 | 0.7000 | 488.4 | 492.7 | | | |
| $x_2/x_3 = 3.1408$; $H^E_{m,23} = 9.3$ J mol$^{-1}$ | | | | | | | | |
| 0.0501 | 366.5 | 375.3 | 0.3501 | 643.8 | 649.8 | 0.6999 | 437.1 | 439.9 |
| 0.1001 | 473.0 | 481.3 | 0.4018 | 632.5 | 638.0 | 0.7501 | 381.9 | 384.2 |
| 0.1001 | 472.2 | 480.6 | 0.4505 | 618.0 | 623.0 | 0.7997 | 320.5 | 322.3 |
| 0.1489 | 538.6 | 546.5 | 0.5002 | 595.5 | 600.1 | 0.8497 | 250.7 | 252.1 |
| 0.1999 | 588.2 | 595.6 | 0.5494 | 567.3 | 571.5 | 0.8992 | 177.3 | 178.2 |
| 0.2500 | 621.8 | 628.7 | 0.5996 | 525.0 | 528.7 | 0.9501 | 92.2 | 92.7 |
| 0.3000 | 640.4 | 646.9 | 0.6495 | 482.5 | 485.7 | | | |

[a] Ternary term for representation of $H^E_{m,1+23}$ by eqs 3 and 4: $H^E_{m,T}/(\text{J mol}^{-1}) = x_1x_2x_3(1855.1 - 5997.2x_1 - 4936.3x_2 + 4747.0x_1^2 + 10166.1x_1x_2 + 3964.8x_2^2)$; $s = 3.7$.

**Table III. Experimental Excess Molar Enthalpies, $H^E_{m,1+23}$, at 298.15 K for the Addition of 1-Propanol to *n*-Hexane + *n*-Dodecane Mixtures To Form $C_3H_7OH$ (1) + $C_6H_{14}$ (2) + $C_{12}H_{26}$ (3) and Values of $H^E_{m,123}$ Calculated from Equation 1 Using $H^E_{m,23}$ from Reference 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$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| $x_2/x_3 = 0.3328$; $H^E_{m,23} = 30.6$ J mol$^{-1}$ | | | | | | | | |
| 0.0500 | 430.5 | 459.6 | 0.3502 | 791.6 | 811.5 | 0.7498 | 530.4 | 538.1 |
| 0.0500 | 438.8 | 467.8 | 0.4500 | 781.6 | 798.4 | 0.8001 | 454.4 | 460.5 |
| 0.0999 | 567.6 | 595.2 | 0.5002 | 755.5 | 770.8 | 0.8498 | 368.6 | 373.2 |
| 0.1502 | 651.9 | 677.9 | 0.5515 | 725.2 | 738.9 | 0.9001 | 266.0 | 269.0 |
| 0.1999 | 708.5 | 733.0 | 0.6000 | 690.6 | 702.8 | 0.9499 | 145.8 | 147.3 |
| 0.2499 | 750.4 | 773.3 | 0.6500 | 645.1 | 655.9 | | | |
| 0.2998 | 780.0 | 801.5 | 0.7000 | 592.3 | 601.5 | | | |
| $x_2/x_3 = 0.9845$; $H^E_{m,23} = 39.5$ J mol$^{-1}$ | | | | | | | | |
| 0.0500 | 410.6 | 448.1 | 0.3998 | 720.0 | 743.7 | 0.7504 | 473.1 | 482.9 |
| 0.1001 | 521.1 | 556.7 | 0.4508 | 702.5 | 724.2 | 0.7994 | 407.2 | 415.1 |
| 0.1501 | 602.4 | 635.9 | 0.4997 | 683.3 | 703.0 | 0.8499 | 327.1 | 333.0 |
| 0.2000 | 655.9 | 687.5 | 0.5498 | 655.9 | 673.6 | 0.9002 | 237.5 | 241.4 |
| 0.2501 | 689.9 | 719.5 | 0.5990 | 620.1 | 635.9 | 0.9501 | 128.1 | 130.0 |
| 0.3000 | 716.0 | 743.7 | 0.6503 | 577.9 | 591.7 | | | |
| 0.3500 | 719.5 | 745.1 | 0.7002 | 528.3 | 540.1 | | | |
| $x_2/x_3 = 2.8956$; $H^E_{m,23} = 28.1$ J mol$^{-1}$ | | | | | | | | |
| 0.0495 | 369.4 | 396.1 | 0.3499 | 665.6 | 683.9 | 0.7001 | 479.6 | 488.0 |
| 0.0495 | 365.7 | 392.4 | 0.3998 | 660.8 | 677.6 | 0.7499 | 412.2 | 419.2 |
| 0.1000 | 486.3 | 511.6 | 0.4514 | 654.6 | 670.0 | 0.8001 | 348.3 | 353.9 |
| 0.1501 | 553.8 | 577.6 | 0.5004 | 634.8 | 648.8 | 0.8501 | 275.0 | 279.2 |
| 0.2001 | 608.3 | 630.7 | 0.5494 | 607.4 | 620.1 | 0.9000 | 195.7 | 198.5 |
| 0.2502 | 639.8 | 660.9 | 0.5999 | 571.0 | 582.3 | 0.9499 | 104.2 | 105.6 |
| 0.3000 | 659.2 | 678.9 | 0.6512 | 525.4 | 535.2 | | | |

[a] Ternary term for representation of $H^E_{m,1+23}$ by eqs 3 and 4: $H^E_{m,T}/(\text{J mol}^{-1}) = x_1x_2x_3(-1252.7 + 33198.2x_1 + 8596.7x_2 - 78880.3x_1^2 - 112649.7x_1x_2 - 9200.4x_2^2 + 51959.0x_1^3 + 129996.0x_1^2x_2 + 88705.0x_1x_2^2)$; $s = 4.9$.

less than 0.5% over most of the range of propanol mole fractions. Errors in the mole fractions of the final ternary mixtures are estimated to be less than 5 × 10$^{-4}$.

## Results and Discussion

Measurements of the excess molar enthalpies, $H^E_{m,ij}$, for the binary systems formed by mixing 1-propanol with each of the three *n*-alkanes are summarized in Table I. Representations of these results by the skewed Redlich–Kister form

$$H^E_{m,ij}/(\text{J mol}^{-1}) = x_i(1 - x_i)(1 + h_o z)^{-1}\sum_{k=1}^{n} h_k z^{k-1} \quad (2)$$

$$z = 1 - 2x_i \text{ and } j > i$$

and the standard deviations, $s$, of these representations are given in the footnotes of the table. Values of $H^E_{m,12}$ for 1-propanol + *n*-hexane at 298.15 K have been reported previously by Brown et al. (*6*) and by Veselý et al. (*7*). The

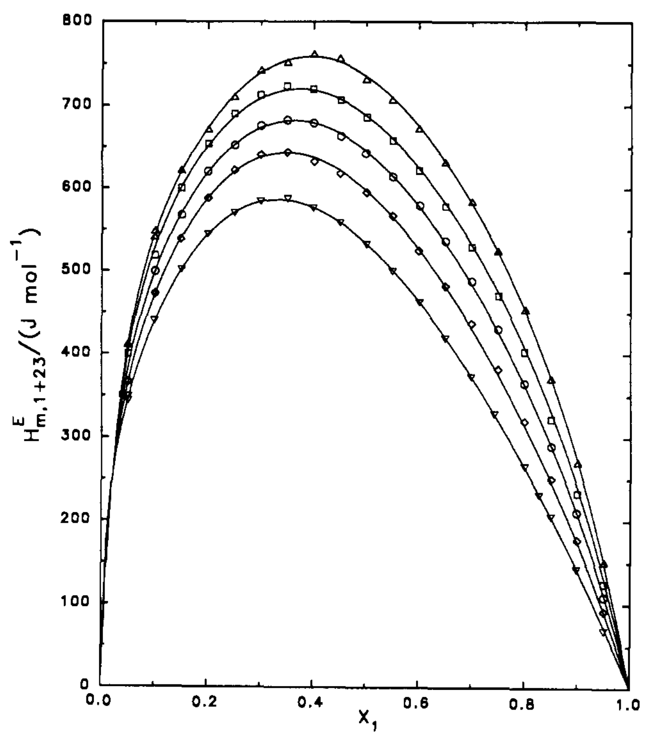

**Figure 2.** Excess molar enthalpies, $H^E_{m,1+23}$, of $C_3H_7OH$ (1) + $C_6H_{14}$ (2) + $C_{10}H_{22}$ (3) at 298.15 K. Experimental results: (▽) $x_3 = 0$; (◇) $x_2/x_3 = 3.1408$; (○) $x_2/x_3 = 0.9912$; (□) $x_2/x_3 = 0.3284$; (△) $x_2 = 0$. Curve: (—) calculated from eqs 3 and 4 using the forms given in the footnotes of Tables I and II.

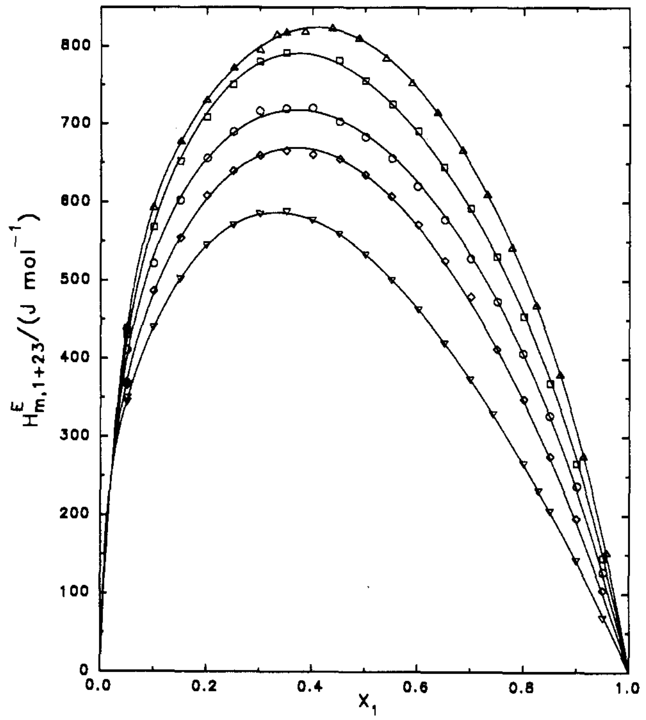

**Figure 3.** Excess molar enthalpies, $H^E_{m,1+23}$, of $C_3H_7OH$ (1) + $C_6H_{14}$ (2) + $C_{12}H_{26}$ (3) at 298.15 K. Experimental results: (▽) $x_3 = 0$; (◇) $x_2/x_3 = 2.8956$; (○) $x_2/x_3 = 0.9845$; (□) $x_2/x_3 = 0.3328$; (△) $x_2 = 0$. Curve: (—) calculated from eqs 3 and 4 using the forms given in the footnotes of Tables I and III.

system 1-propanol + n-decane has also been studied (8) but at a somewhat elevated pressure, 170 kPa. Deviations of these earlier data from the representations of our results are plotted in Figure 1. Apart from the relatively large deviations of the values from Brown et al. (6), there is agreement between our results and the previously published data within ~3% over most of the mole fraction range.

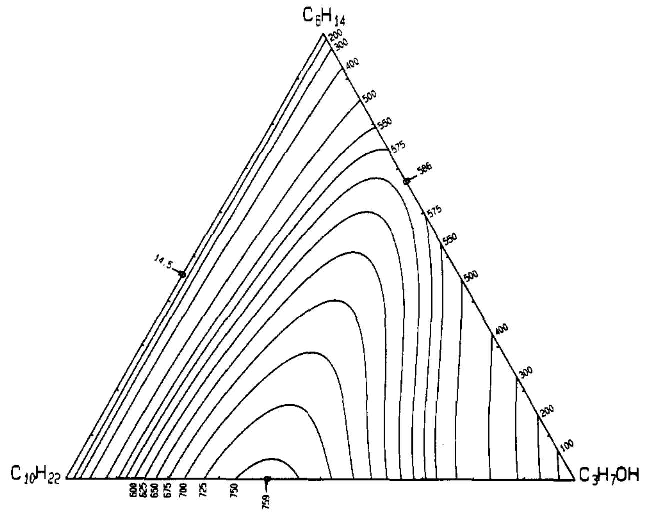

**Figure 4.** Constant $H^E_{m,123}$/(J mol$^{-1}$) contours for $C_3H_7OH$ (1) + $C_6H_{14}$ (2) + $C_{10}H_{22}$ (3) at 298.15 K, calculated from the representation of our experimental results by eqs 3 and 4 with forms from the footnotes of Tables I and II.

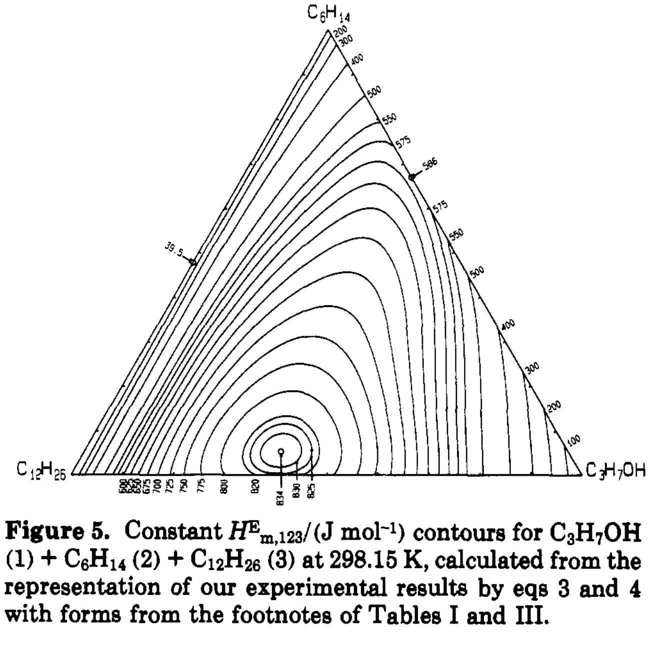

**Figure 5.** Constant $H^E_{m,123}$/(J mol$^{-1}$) contours for $C_3H_7OH$ (1) + $C_6H_{14}$ (2) + $C_{12}H_{26}$ (3) at 298.15 K, calculated from the representation of our experimental results by eqs 3 and 4 with forms from the footnotes of Tables I and III.

The experimental results for $H^E_{m,1+23}$ and the corresponding $H^E_{m,123}$ are listed in Tables II and III for the two ternary mixtures. The values of $H^E_{m,1+23}$ are plotted in Figures 2 and 3, along with the results for the binary systems having $x_2 = 0$ or $x_3 = 0$. In all cases, the maximum values of $H^E_{m,1+23}$ and $H^E_{m,123}$ occur near $x_1 = 0.4$, and for comparable $x_2/x_3$, the values of the maxima are larger for the mixture containing n-dodecane. For both systems at a constant value of $x_1$, the enthalpies increase as the ratio $x_2/x_3$ decreases. This behavior is closely similar to that found previously for the ethanol systems (1). However, for a given $x_1$ and n-alkane mixture, $H^E_{m,1+23}$ is somewhat larger for the 1-propanol system.

The values of $H^E_{m,1+23}$ were represented as a sum of binary terms (9) with an added ternary contribution:

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

Following Morris et al. (*10*), the relation

$$H^{E}_{m,T}/(\mathrm{J\ mol^{-1}}) = x_1x_2x_3(c_0 + c_1x_1 + c_2x_2 + c_3x_1^2 + c_4x_1x_2 + c_5x_2^2 + c_6x_1^3 + c_7x_1^2x_2 + c_8x_1x_2^2 + c_9x_2^3) \quad (4)$$

was adopted for the ternary term. Least-squares analyses, in which eqs 3 and 4 were fitted to the experimental values of $H^{E}_{m,1+23}$, led to the forms given for $H^{E}_{m,T}$ in the footnotes of Tables II and III, where the standard deviations, $s$, of the representations are also indicated. Curves obtained from these representations are shown in Figures 2 and 3.

Some contours, corresponding to constant values of $H^{E}_{m,123}$, are plotted in Figures 4 and 5. These are very similar to those obtained previously for the ethanol systems (*1*). The main difference is the occurrence of a maximum located inside the triangular plot for the 1-propanol + *n*-hexane + *n*-dodecane system.

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**Registry No.** 1-Propanol, 71-23-8; *n*-hexane, 110-54-3; *n*-decane, 124-18-5; *n*-dodecane, 112-40-3.