Excess Enthalpies of 2,2,4-Trimethylpentane + *n*-Alkane Binary Mixtures at 298.15 K

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Excess molar enthalpies, measured at 298.15 K in a microcalorimeter, are reported for the binary systems formed by mixing 2,2,4-trimethylpentane with hexane, heptane, octane, or decane. Smooth representations of the results are described, and a comparison with previously available literature data is presented.

Introduction

The thermodynamic properties of systems formed by mixing the alkylate 2,2,4-trimethylpentane with other hydrocarbons are of practical interest, in view of the use of 2,2,4-trimethylpentane (i.e., isooctane) as a standard reference material in measuring the octane rating or antiknock properties of motor fuels. The present paper reports excess molar enthalpies, measured at 298.15 K, for binary mixtures comprised of 2,2,4-trimethylpentane and a normal alkane, which was either hexane, heptane, octane, or decane.

Experimental Section

HPLC grade 2,2,4-trimethylpentane (TMP), together with hexane (nC6), heptane (nC7), octane (nC8), and decane (nC10), were obtained from Sigma-Aldrich. In all cases, the purities stated by the manufacturer exceeded 99 mol %. Apart from partial degassing, all of the components were used without further purification. Densities, ρ/kg·m^{-3}, measured at 298.15 K in an Anton-Paar digital densimeter, were 687.92, 655.53, 679.94, 698.78, and 726.36, for TMP, nC6, nC7, nC8, and nC10, respectively. These values are in reasonable agreement with values in the literature.[1]

An LKB flow microcalorimeter (Model 10700-1), thermostated at 298.150 ± 0.003 K, was used to measure the excess molar enthalpies H^E_m. Details of the equipment and its operation have been described previously.[2,3] Over most of the mole fraction range, the errors of the excess molar enthalpies and the mole fractions of the mixtures are estimated to be less than 0.5% and 5×10^{-4}, respectively.

Results and Discussion

The experimental results for the excess molar enthalpies, H^E_m, of the four binary mixtures at 298.15 K are listed in Table 1 and plotted in Figure 1. The H^E_m values for the TMP + nC6 system are negative over the entire mole fraction range. The results for the other TMP + alkane binaries are positive; the larger the alkane, the larger the H^E_m value for a fixed value of x_1.

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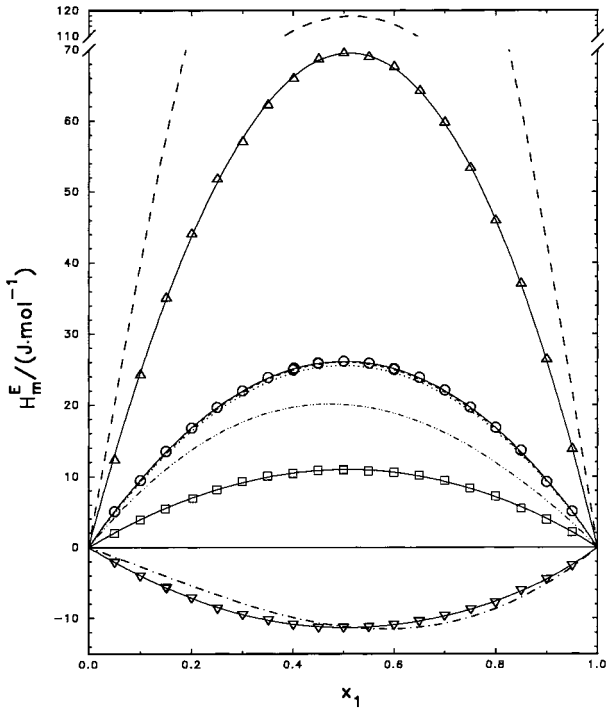

Figure 1. Excess molar enthalpies, H^E_m, for TMP (1) + *n*-alkane (2) at 298.15 K. Experimental results: ▽, nC6; □, nC7; ○, nC8; △, nC10. Curves calculated from the representation of the results by eq 1 with values of the coefficients given in Table 2: —, our results; •—•, nC6;[5] ••—, nC7;[7] •••, nC8;[8] - - -, nC8;[10] — — —, nC12.[4]

The smoothing function

$$H^E_m/J\cdot mol^{-1} = x_1(1 - x_1)\sum_{k=1}^{n} h_k(1 - 2x_1)^{k-1} \qquad (1)$$

was fitted to the results by a least-squares method, with all points weighted equally. Values of the coefficients h_k are listed in Table 2, along with the standard deviation s for each of the representations. Also included in the table are the coefficients, reported recently,[4] for the mixture of TMP with *n*-dodecane (nC12). The curves, shown in Figure 1, were calculated from eq 1 with the coefficients from Table 2.

Excess molar enthalpies have been reported previously for three of the present systems. For convenience, coef-

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Table 1. Experimental Mole Fractions, x_1, and Excess Molar Enthalpies, H_m^E, for TMP (1) + *n*-Alkane (2) Mixtures at 298.15 K

x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}
				TMP (1) + nC6 (2)					
0.0502	−2.06	0.2000	−7.10	0.4005	−10.85	0.6000	−10.90	0.7999	−7.74
0.1000	−4.01	0.2507	−8.57	0.4505	−11.23	0.6498	−10.36	0.8500	−6.03
0.1499	−5.62	0.3004	−9.45	0.4999	−11.26	0.7000	−9.61	0.8999	−4.45
0.1508	−5.71	0.3513	−10.20	0.5502	−11.17	0.7512	−8.68	0.9500	−2.50
				TMP (1) + nC7 (2)					
0.0500	2.00	0.2494	8.18	0.4495	10.87	0.6000	10.58	0.7998	7.22
0.0999	3.88	0.2999	9.34	0.4995	10.92	0.6499	10.18	0.8499	5.47
0.1491	5.46	0.3496	10.08	0.5001	11.00	0.7003	9.44	0.9000	3.91
0.2026	6.92	0.4001	10.47	0.5492	10.80	0.7500	8.38	0.9500	2.12
				TMP (1) + nC8 (2)					
0.0500	5.06	0.2998	22.01	0.4498	25.84	0.5998	25.09	0.8002	16.82
0.1000	9.45	0.3498	23.86	0.5002	26.16	0.6503	23.89	0.8501	13.63
0.1500	13.50	0.3997	24.91	0.5507	25.87	0.7000	22.08	0.8999	9.24
0.1997	16.79	0.4013	25.18	0.5998	24.96	0.7503	19.65	0.9500	5.04
0.2498	19.67	0.4495	25.89						
				TMP (1) + nC10 (2)					
0.0501	12.36	0.2500	51.83	0.4504	68.73	0.6506	64.23	0.8500	37.10
0.1001	24.28	0.3000	57.11	0.5002	69.57	0.7002	59.81	0.9000	26.44
0.1501	35.11	0.3499	62.26	0.5502	69.04	0.7501	53.41	0.9500	13.84
0.1999	44.13	0.4002	65.97	0.5999	67.63	0.7996	46.04		

Table 2. Coefficients, h_k, and Standard Deviations, s, for the Representation of H_m^E by Eq 1 for the Binary Mixtures at 298.15 K

component							
1	2	h_1	h_2	h_3	h_4	h_5	s/J·mol^{-1}
TMP	nC6	−45.12	0.30	−2.66	5.02		0.08
TMP	nC7	44.03	−0.80				0.10
TMP	nC8	104.49	−0.032	1.88			0.10
TMP	nC10	278.07	−12.38	7.17			0.32
TMP	nC12[a]	470.62	−24.85	39.15	6.66	−89.15	0.48
TMP	nC6[b]	−44.61	16.65	1.97			0.2
TMP	nC7[c]	80.32	9.04				0.75
TMP	nC8[d]	102.1					0.1
TMP	nC8[e]	103.9					0.1 estd

[a] Peng et al.[4] [b] Lam et al.;[5] Tancrede and Patterson.[6] [c] Mier et al.[7] [d] Grolier,[9] fit of data of Lundberg.[8] [e] Sturtevant and Lyons.[10]

ficients for the representations of the earlier results for TMP + nC6,[5,6] for TMP + nC7,[7] and for TMP + nC8[8−10] are also included in Table 2. Curves calculated from these representations are plotted in Figure 1. In the case of the TMP + nC6 system, it is clear that, although there is good agreement with our curve near $x_1 = 0.5$, there are significant deviations which are positive at lower mole fractions and negative at higher mole fractions. This is probably due to the restricted range $0.34 < x_1 < 0.64$ studied by Lam et al.[5,6] The curve representing the results of Mier et al.[7] for TMP + nC7 is much higher than our results. For an equimolar mixture, their curve indicates $H_m^E(0.5) = \sim 20$ J·mol^{-1}, which is ∼9 J·mol^{-1} larger than the 11 J·mol^{-1} obtained from our curve. Over the entire mole fraction range, Lundberg's curve[8,9] for TMP + nC8 is lower than our curve; that of Sturtevant and Lyons[10] is closer to our results. However, the differences between the three curves are of the same order as the combined estimates of their experimental uncertainties.

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