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Vapor–Liquid Equilibria for the Binary Systems *n*-Octane with 2-Methylpentane, 3-Methylpentane, and 2,4-Dimethylpentane

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Vapor mole fractions and excess free energies, enthalpies, and entropies are calculated from pressure-composition values measured at 10, 20, 30, and 40 °C for three branched hydrocarbons in *n*-octane. This is the second in a study of the effect of chain branching on the thermodynamic excess properties of hydrocarbon solutions. The previous study involved the same branched hydrocarbons in *n*-hexane.

Experimental Methods

The vapor-pressure equipment used and the experimental methods have been described previously (*2*) with modifications (*3*), but a brief description will be given. The apparatus is a static vapor-pressure device that allows two samples to be run simultaneously over a range of temperatures. The apparatus contains two sample flasks and a reference flask connected by ball joints to a glass manifold containing two manometers which record the pressure difference between a reference liquid and the samples. The entire assembly is suspended in a water bath and can be oscillated to hasten equilibrium. The manometers are read with a cathetometer through a plate-glass wall. The suspended manifold and flask assembly is connected through a convenient valve arrangement to an external manifold to which a nitrogen supply, a vacuum pump, a McLeod gauge, and an external manometer are connected. The sample and reference flasks are disconnected for filling and degassing. After the flasks are first filled with dry nitrogen, the sample components or the reference liquid is introduced into the flasks by a long needle and syringe. The composition of the samples is determined by weighing the syringes. The samples and the reference liquid are degassed by controlled boiling, freezing, and evacuating. After all flasks are reinstalled and the connecting manifold is evacuated, the flasks are opened and the entire apparatus is agitated in the constant-temperature bath until equilibrium is indicated by constant manometer readings.

For vapor pressures below ~100 mmHg, the reference liquid is not used, and direct readings are made. Higher pressures exceed the manometer length, and pressures are determined from the manometer reading and the known vapor pressure of the reference liquid. In this work either *n*-hexane or 2,4-dimethylpentane was used as a reference.

The temperature of the bath is controlled with a Hallikainen Model 1053A thermistor activated controller. Temperatures are measured with a platinum resistance thermometer, Leeds and Northrup Model 8163-B with a Leeds and Northrup Mueller Bridge and null point detector. Both the controller and the thermometer are sensitive to 0.001 °C. Gradients in the bath are just barely detectable, and temperature measurements are made quite near the flasks. Temperatures are believed to be accurate within 0.01 °C.

The mercury manometers were read to 0.01 mmHg with a Scientific Corp. Gaernter cathetometer. Reproducibility was within ~0.03 mmHg at each meniscus so that overall reading error was less than 0.1 mmHg and probably within 0.05 mmHg. The readings were corrected for temperature and gravity. The sample compositions were made by weight, and the calculated value was used. Both before degassing and after the experiment, each sample was analyzed on a chromatograph until reproducibility within ~0.1% was obtained. If a persistent but small change of less than ~0.5% resulted, the composition would be corrected. Larger deviations resulted in discard of the runs. Concentrations are believed accurate to 0.1%. The chromatograph was the same used previously (*3*), and separation was excellent.

Table I. Pure-Component Vapor Pressures (mmHg)

	10 °C	20 °C	30 °C	40 °C
n-octane (measured)	5.40	10.19	18.71	31.67
API	5.64	10.44	18.43	31.07
2-methylpentane (measured)	109.38	171.52	259.16	380.37
API	109.73	171.66	259.41	380.11
3-methylpentane (measured)	97.44	153.63	233.52	343.65
API	97.50	153.46	233.08	343.02
2,4-dimethylpentane (measured)	48.15	78.77	122.72	186.31
API	47.88	78.19	122.80	186.31

The research chemicals were "pure" grade obtained from Phillips Petroleum Co. These were distilled on a Nester–Faust spinning band column to purities equal to or exceeding 99.9% as measured by the chromatograph. The purified materials were stored under nitrogen until used.

Calculation of Vapor Compositions

The vapor compositions, activity coefficients, and excess free energies were calculated by the method of Barker (*1*). It was assumed that the excess free energy can be represented by

$$g^E = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2] \qquad (1)$$

from which

$$RT \ln \gamma_1 = x_2^2[A - B(1 - 4x_1) + C(1 - 8x_1 + 12x_1^2)] \qquad (2)$$

$$RT \ln \gamma_2 = x_1^2[A + B(1 - 4x_2) + C(1 - 8x_2 + 12x_2^2)] \qquad (3)$$

Then at low pressure the total pressure can be approximated by

$$P = \gamma_1P_1'x_1 + \gamma_2P_2'x_2 \qquad (4)$$

where

$$P_1' = P_1 \exp[(v_1 - \beta_{11})(P - P_1)/(RT) - P\delta_{12}y_2^2/(RT)] \qquad (5)$$

$$P_2' = P_2 \exp[(v_2 - \beta_{22})(P - P_2)/(RT) - P\delta_{12}y_1^2/(RT)] \qquad (6)$$

$$\delta_{12} = 2\beta_{12} - \beta_{11} - \beta_{22} \qquad (7)$$

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Table II. Measured Pressure and Calculated Vapor Mole Fractions

	10 °C		20 °C		30 °C		40 °C	
x_1	y_1	P, mmHg	y_1	P, mmHg	y_1	P, mmHg	y_1	P, mmHg
n-Octane (1)-2-Methylpentane (2)								
0.1053	0.0070	99.00	0.0081	155.25	0.0095	234.67	0.0108	343.56
0.1856	0.0128	91.28	0.0149	142.98	0.0177	215.90	0.0203	315.69
0.2523	0.0181	84.83	0.0214	132.62	0.0256	200.21	0.0294	292.89
0.3129	0.0237	78.79	0.0281	123.21	0.0337	186.15	0.0389	271.82
0.4189	0.0357	68.18	0.0427	106.45	0.0514	160.79	0.0594	235.16
0.5038	0.0484	59.75	0.0583	93.01	0.0701	140.74	0.0809	205.98
0.5129	0.0500	58.80	0.0602	91.53	0.0724	138.38	0.0835	202.63
0.6047	0.0693	49.41	0.0838	76.87	0.1007	116.55	0.1159	170.93
0.6958	0.0975	39.75	0.1178	62.15	0.1415	94.40	0.1623	139.14
0.7713	0.1336	31.98	0.1609	50.03	0.1928	76.14	0.2202	112.83
0.8381	0.1858	24.63	0.2218	38.96	0.2646	60.08	0.2999	89.75
0.9478	0.4251	12.10	0.4815	20.18	0.5474	32.52	0.5944	50.63
n-Octane (1)-3-Methylpentane (2)								
0.1041	0.0075	88.10	0.0087	138.99	0.0103	211.47	0.0117	311.03
0.1780	0.0135	81.70	0.0157	128.80	0.0186	196.00	0.0213	288.52
0.2963	0.0247	71.60	0.0289	112.71	0.0345	171.31	0.0396	252.40
0.3750	0.0337	64.70	0.0397	101.85	0.0477	154.71	0.0547	228.13
0.4028	0.0373	62.25	0.0440	98.03	0.0531	148.95	0.0608	219.70
0.4930	0.0510	54.46	0.0607	85.58	0.0737	129.83	0.0843	191.82
0.4944	0.0512	54.30	0.0610	85.39	0.0740	129.48	0.0847	191.33
0.6133	0.0774	43.88	0.0928	68.68	0.1130	104.10	0.1289	154.48
0.6899	0.1032	36.75	0.1240	57.40	0.1503	87.55	0.1708	130.20
0.7888	0.1592	26.90	0.1905	42.35	0.2266	66.06	0.2555	99.01
0.8251	0.1923	23.20	0.2289	36.81	0.2692	57.80	0.3020	87.39
0.8940	0.2978	16.20	0.3471	26.38	0.3946	42.51	0.4354	65.29
n-Octane (1)-2,4-Dimethylpentane (2)								
0.1327	0.0200	42.74	0.0223	69.87	0.0255	109.38	0.0277	166.10
0.2156	0.0342	39.54	0.0385	64.61	0.0438	101.05	0.0478	153.63
0.3157	0.0537	35.70	0.0611	58.19	0.0696	91.24	0.0763	138.64
0.3550	0.0623	33.95	0.0712	55.55	0.0812	87.31	0.0891	132.91
0.4343	0.0821	30.89	0.0943	50.50	0.1078	79.35	0.1185	121.06
0.4928	0.0993	28.50	0.1143	46.62	0.1310	73.40	0.1441	112.04
0.4966	0.1005	28.30	0.1157	46.43	0.1327	73.12	0.1459	111.45
0.5470	0.1179	26.36	0.1358	43.15	0.1561	67.98	0.1717	103.65
0.6121	0.1450	23.73	0.1668	38.83	0.1921	61.20	0.2112	93.75
0.7087	2.2002	19.68	0.2287	32.46	0.2635	51.37	0.2890	78.87
0.7875	0.2689	16.01	0.3038	26.80	0.3479	42.85	0.3795	66.32
0.8550	0.3620	12.90	0.4022	21.90	0.4544	35.49	0.4906	55.56
0.8963	0.4493	10.67	0.4916	18.51	0.5466	30.68	0.5838	48.75

Table III. Constants for the Equation $g^E = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2]$

	10 °C	20 °C	30 °C	40 °C
Octane (1)-2-Methylpentane (2)				
A	110.7448	85.7438	58.6920	39.0481
B	−4.2398	0.8023	−3.8305	−3.0097
C	36.0857	37.3222	21.8454	10.8311
Octane (1)-3-Methylpentane (2)				
A	95.2831	67.3656	50.1011	37.8878
B	−24.7518	−27.3576	−12.8094	−15.7427
C	−13.7939	−9.6536	7.1075	1.3399
Octane (1)-2,4-Dimethylpentane (2)				
A	127.3381	106.6663	77.1298	53.2631
B	−0.5922	12.3576	−0.7784	−5.2112
C	0.8031	0.7608	5.1951	0.8085

The correction for liquid volume was included but is practically negligible at low pressure. The second virial coefficients were estimated as recommended by Prausnitz et al. (*4*). To get initial values of y_1 and y_2 for eq 5 and 6, we used eq 8 to approximate

$$A \simeq 4RT \ln [2P_{x=0.5}/(P_1 + P_2)] \qquad (8)$$

A with eq 2 and 3 terminated after the first constant. Then substituting eq 2, 3, 5, and 6 into eq 4, we used a trial-and-error least-squares procedure to calculate the best values of *A*, *B*, and *C*. After each trial, the vapor compositions were recalculated for eq 5 and 6 by the relation

$$y_1 = \gamma_1 P_1' x_1/P \qquad (9)$$

Results

The vapor pressures of the pure components are given in Table I and compared with values calculated from Antoine's constants given in ref 5. The measured solution pressures are given in Table II along with calculated values of the vapor mole fractions. The constants calculated for eq 1–3 are listed in Table III. Table IV gives two examples of the total output and the error in pressure resulting from the use of the derived equations.

Figures 1–3 show the calculated excess properties at 30 °C. The values of h^E were derived from plots of g^E/T vs. $1/T$ as shown in Figure 4. The degree of precision in g^E is shown by the smooth curves. The maximum error in pressure resulting from a temperature error of 0.01 °C is 0.1 mmHg and usually much less.

Equation 8 would indicate that an error of 0.1 mmHg in pressure could produce a maximum error in g^E of up to 2 cal/mol at 10 °C. Because of the smoothing resulting from the fitting procedure, such an error is very unlikely from random errors. The derived values of h^E and Ts^E are considerably less reliable.

Values of g^E are about three times larger than in the hexane system (*3*) but follow the same trend, 2,4-dimethylpentane > 2-methylpentane > 3-methylpentane. Values of h^E follow the

Table IV. Measured and Calculated Properties

x_1	y_1	P_{exptl}, mmHg	P_{calcd}, mmHg	$P_{\text{exptl}} - P_{\text{calcd}}$, mmHg	γ_1	γ_2	g^E, cal/mol	g^E/T, cal/(mol K)
				n-Octane (1)-3-Methylpentane (2) at 40 °C				
0.1041	0.0117	311.030	311.141	−0.111	1.063 17	1.001 45	4.77	0.015 24
0.1780	0.0213	288.520	288.430	+0.089	1.047 09	1.003 94	7.11	0.022 69
0.2963	0.0396	252.400	252.288	+0.111	1.027 88	1.009 67	9.28	0.029 64
0.3750	0.0547	228.130	228.209	−0.079	1.018 76	1.014 21	9.82	0.031 36
0.4028	0.0608	219.700	219.680	+0.020	1.016 12	1.015 88	9.86	0.031 49
0.4930	0.0843	191.820	191.859	−0.039	1.009 36	1.021 36	9.53	0.030 41
0.4944	0.0847	191.330	191.425	−0.095	1.009 27	1.021 45	9.51	0.030 38
0.6133	0.1289	154.480	154.369	+0.111	1.003 81	1.028 26	8.16	0.026 04
0.6899	0.1708	130.200	130.258	−0.058	1.001 82	1.032 05	6.87	0.021 93
0.7888	0.2555	99.010	98.913	+0.096	1.000 49	1.035 87	4.87	0.015 55
0.8251	0.3020	87.390	87.363	+0.027	1.000 25	1.036 91	4.07	0.013 00
0.8940	0.4354	65.290	65.409	−0.119	1.000 03	1.038 23	2.49	0.007 96
				n-Octane (1)-2,4-Dimethylpentane (2) at 10 °C				
0.1327	0.0200	42.700	42.754	−0.014	1.186 29	1.004 11	14.76	0.052 10
0.2156	0.0342	39.540	39.475	+0.064	1.149 40	1.010 82	21.64	0.076 40
0.3157	0.0537	35.700	35.555	+0.144	1.111 45	1.023 17	27.58	0.097 40
0.3550	0.0623	33.950	34.016	−0.066	1.098 35	1.029 31	29.21	0.103 16
0.4343	0.0821	30.890	30.895	−0.005	1.074 77	1.043 97	31.31	0.110 56
0.4928	0.0993	28.500	28.565	−0.065	1.059 68	1.056 81	31.83	0.112 41
0.4966	0.1005	28.300	28.412	−0.112	1.058 76	1.057 70	31.83	0.112 42
0.5470	0.1179	26.360	26.374	−0.014	1.047 35	1.070 28	31.54	0.111 39
0.6121	0.1450	26.730	23.688	+0.041	1.034 54	1.088 59	30.21	0.106 69
0.7087	0.2002	19.680	19.557	+0.122	1.019 27	1.120 27	26.27	0.092 76
0.7875	0.2869	16.010	16.019	−0.009	1.010 31	1.150 46	21.30	0.075 21
0.8550	0.3620	12.900	12.838	+0.061	1.004 80	1.179 72	15.78	0.055 74
0.8963	0.4493	10.670	10.811	−0.141	1.002 46	1.199 29	11.84	0.041 81

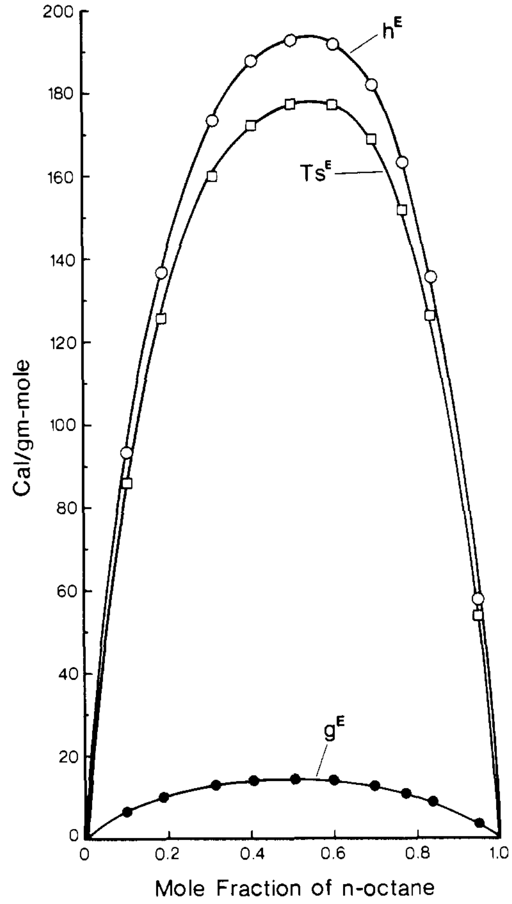

Figure 1. Excess thermodynamic functions for *n*-octane–2-methylpentane solutions at 30 °C.

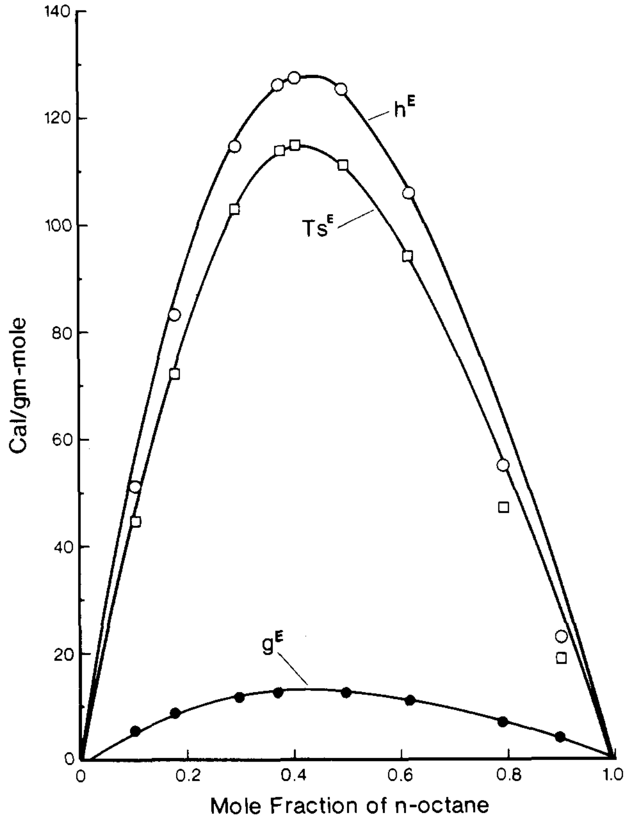

Figure 2. Excess thermodynamic functions for *n*-octane–3-methylpentane solutions at 30 °C.

same trend as g^E in this work but do not in the hexane systems. Values of h^E in the hexane solutions are only about one-sixth those in the octane solutions, and it is possible that the inherent error of deriving h^E from the slope of g^E/T is as large as the differences in the former systems.

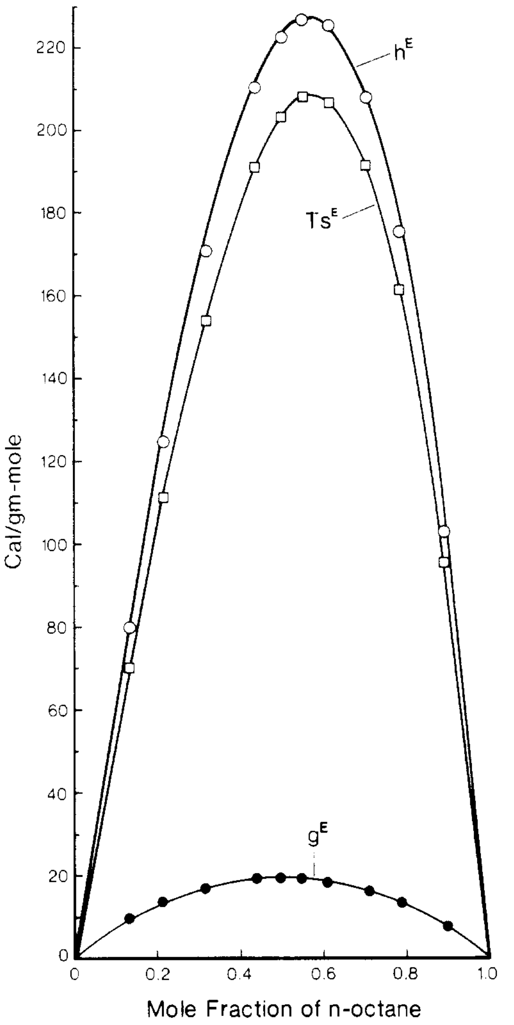

Figure 3. Excess thermodynamic functions for *n*-octane–2,4-dimethylpentane solutions at 30 °C.

Glossary

A, *B*, *C*	constants in expansions of g^E
g^E	excess Gibbs free energy, cal/mol
h^E	excess enthalpy, cal/mol
P	total pressure, mmHg
P_{exptl}, P_{calcd}	experimental and calculated values of the total pressure, mmHg
P_1, P_2	vapor pressures of components 1 and 2, mmHg
v	molar volume in mL
x	mole fraction in liquid
y	mole fraction in vapor

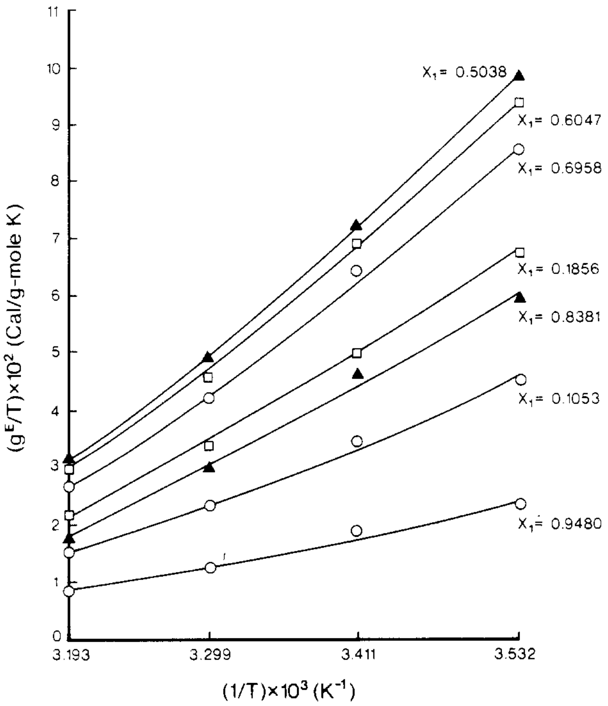

Figure 4. g^E/T vs. $1/T$ for *n*-octane–2-methylpentane at various octane mole fractions.

Greek Letters

β	virial coefficients
δ	defined by eq 9
γ	activity coefficient

Literature Cited

(1) Barker, J. A. *Aust. J. Chem.* **1953**, *6*, 207.
(2) Davison, R. R.; Smith, W. H.; Chun, K. W. *AIChE J.* **1967**, *13*, 590.
(3) Ho, Chun L.; Davison, R. R. *J. Chem. Eng. Data* **1979**, *24*, 293.
(4) Prausnitz, J. M.; Eckert, C. A.; Orye, R. V.; O'Connell, J. P. "Computer Calculations for Multicomponent Vapor-Liquid Equilibria"; Prentice-Hall: Englewood Cliffs, NJ, 1967; p 18.
(5) Zwolinski et al. API Research Project 44, Thermodynamic Research Center, Texas A & M University, College Station, TX.

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