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Vapor–Liquid Equilibria for the Binary Systems *n*-Hexane 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 data at 10, 20, 30, and 40 °C for three branched hydrocarbons in *n*-hexane.

This is the first report in a study of the effect of chain branching on the thermodynamic excess properties of hydrocarbon solutions. It parallels earlier work on the effect of hydrocarbon chain configuration in hydrogen bonding solutions (*3–5*). Pressure–composition data and excess free energies have been reported previously for 2-methylpentane–hexane and 3-methylpentane–hexane at 25 °C (*2*).

Experimental Methods

The vapor pressure apparatus and the experimental methods have been described previously (*6*), but a brief description with modifications will be given. 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 the 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, vacuum pump, McLeod gage, and an external manometer are connected.

Two modifications were made in the equipment for this work: the diameter of the manometers was increased to 10 mm to minimize meniscus error and the manometers were made an integral part of the manifold to eliminate joint trouble.

The sample and reference flasks contain a 50-mL bulb attached to a short condenser above which is connected a stopcock and ball joint. The flasks are disconnected from the manifold for the degassing operation. After the flasks are filled with dry nitrogen, liquid is introduced through the stopcock by a long needle and syringe. A pure liquid of known vapor pressure is placed in the reference flask. The other flasks contain mixtures made by weight from syringes.

The samples are degassed while connected by a flexible tube to the external manifold. The samples are boiled for several minutes under partial vacuum with total reflux in the flask condenser. This pushes all the noncondensibles into the small condenser tube. The flask stopcock is closed and the sample quickly frozen by emmersion into liquid nitrogen. A high vacuum is pulled on the external manifold and the flask stopcock opened again briefly. The degassed flask is attached to the apparatus manifold. When all flasks are degassed and attached, the manifold is suspended in the bath and evacuated. External valves are closed, the flask stopcocks are carefully opened, and the manometers record pressure differences between the sample and reference flasks. The apparatus is agitated in the bath until manometer readings are constant.

The bath is equipped with a large auxiliary heater to hasten temperature changes and a cooling coil to balance the control heater at temperatures below or near room temperature. The temperature in 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, a Leeds and Northrup Mueller bridge, and a null point detector. Both controller and 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 mm with a Scientific Corp. Gaernter cathetometer. Reproducibility was within about 0.03 mm at each meniscus so that overall reading error was less than 0.1 mm and probably within 0.05 mm. 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 about 0.1% was obtained. If a persistent but small change of less than about 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, equipped with a flame ionization detector, contained two 5 ft × $^1/_8$ in. columns in series: one contained 5% SE-30 on Chromosorb with 80/100 mesh, the other 20% SI 550 on Chromosorb P, 80/100 mesh. Temperatures slightly above boiling point were used, and separation was excellent.

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.

To obtain a standard for the work, we ran 2,4-dimethylpentane against water and hexane against 2,4-dimethylpentane. Had hexane been run directly against water, the internal manometer length would have been exceeded. In all subsequent measurements, hexane was used as a standard. It is true that in this sequential use of a standard, accumulative error could occur even though a number of runs were made on the standards for verification. However, in using these data in subsequent calculations, we found there is an advantage in that nonrandom errors tend to cancel. For instance, in nearly ideal solutions for which

$$g^E \simeq Ax_1x_2 \tag{1}$$

A can be approximated by

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

If either P_1 or P_2, the pure component vapor pressures, is the standard which contains the error ΔP, then both numerator and denominator of the logarithmic term contain an error of $2\Delta P$. As this term is not far from one, the errors cancel. On the other hand, small nonrandom pressure errors are significant. For instance, a 0.1-mm nonrandom error in P can cause a maximum error in g^E of about 0.5 cal/mol at 10 °C.

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Table I. Pure Component Vapor Pressures (mmHg)

	10 °C	20 °C	30 °C	40 °C
n-hexane (measd)	75.30	121.00	187.16	279.57
API value	75.81	121.38	187.28	279.64
2-methylpentane (measd)	109.38	171.52	259.16	380.37
API value	109.73	171.66	259.41	380.11
3-methylpentane (measd)	97.44	153.63	233.52	343.65
API value	97.50	153.46	233.08	343.02
2,4-dimethylpentane (measd)	48.15	78.77	122.72	186.31
API value	47.88	78.19	122.80	186.31

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

$$g^E = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2] \quad (3)$$

from which

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

$$RT \ln \gamma_2 = x_1^2[A + B(1 - 4x_2) + C(1 - 8x_2 + 12x_2^2)] \quad (5)$$

Then at low pressure the total pressure can be approximated by

$$P = \gamma_1P_1'x_1 + \gamma_2P_2'x_2 \quad (6)$$

where

$$P_1' = P_1 \exp[(v_1 - \beta_{11})(P - P_1)/RT - P\delta_{12}y_2^2/RT] \quad (7)$$

$$P_2' = P_2 \exp[(v_2 - \beta_{22})(P - P_2)/RT - P\delta_{12}y_1^2/RT] \quad (8)$$

$$\delta_{12} = 2\beta_{12} - \beta_{11} - \beta_{22} \quad (9)$$

The correction for liquid volume was included but is practically negligible at low pressure. The second viral coefficients were estimated as recommended by Prausnitz et al. (*7*). To get initial values of y_1 and y_2 for eq 7 and 8, we used eq 2 to evaluate A and eq 4 and 5 terminated after the first constant. Then by substitution of eq 4, 5, 7, and 8 into eq 6, a trial and error least-squares procedure was used to calculate the best values of A, B, and C. After each trial, the vapor compositions were recalculated for eq 7 and 8 by the relation

$$y_1 = \gamma_1P_1'x_1/P \quad (10)$$

Results

The vapor pressures of the pure components are given in Table I and compared with values calculated from the Antoine constants given in API project 44 (*8*). The measured solution pressures are given in Table II along with calculated values of

Table II. Measured Pressure and Calculated Vapor Mole Fractions Pressure (mmHg)

	10 °C		20 °C		30 °C		40 °C	
x_1	y_1	P	y_1	P	y_1	P	y_1	P
			n-Hexane (1)–2-Methylpentane (2)					
0.1006	0.0750	106.67	0.0764	167.40	0.0777	253.61	0.0784	371.51
0.2013	0.1516	103.40	0.1545	162.52	0.1567	246.85	0.1587	361.97
0.2692	0.2054	101.12	0.2093	159.23	0.2122	241.95	0.2152	355.00
0.4135	0.3282	96.31	0.3340	152.25	0.3386	231.55	0.3435	340.57
0.4666	0.3768	94.64	0.3830	149.68	0.3883	227.82	0.3938	335.41
0.5098	0.4177	93.26	0.4243	147.48	0.4302	224.82	0.4359	330.83
0.5560	0.4629	91.66	0.4698	145.00	0.4760	221.40	0.4821	326.42
0.6026	0.5101	89.98	0.5171	142.61	0.5237	217.87	0.5299	321.62
0.7612	0.6836	84.32	0.6897	134.39	0.6930	206.17	0.7016	305.53
0.7929	0.7270	83.00	0.7326	132.50	0.7383	203.52	0.7435	301.80
0.8799	0.8296	80.16	0.8335	128.15	0.8374	197.35	0.8412	293.55
			n-Hexane (1)–3-Methylpentane (2)					
0.0785	0.0646	96.22	0.0656	151.80	0.0662	230.81	0.0668	339.60
0.1295	0.1065	95.20	0.1080	150.24	0.1091	228.81	0.1101	336.74
0.1995	0.1649	93.65	0.1669	148.00	0.1686	225.41	0.1704	332.34
0.3121	0.2621	91.22	0.2651	144.60	0.2679	220.34	0.2709	325.18
0.3992	0.3410	89.48	0.3448	141.90	0.3486	216.52	0.3521	319.55
0.4542	0.3926	88.42	0.3970	140.13	0.4013	213.94	0.4051	316.22
0.4993	0.4361	87.42	0.4408	138.70	0.4456	211.83	0.4495	313.29
0.5475	0.4836	86.33	0.4887	137.11	0.4938	209.77	0.4978	310.30
0.6277	0.5652	84.43	0.5707	134.31	0.5761	205.80	0.5801	305.20
0.7926	0.7435	80.62	0.7482	128.70	0.7528	197.97	0.3563	294.30
0.9169	0.8909	77.63	0.8932	124.57	0.8955	192.10	0.8977	286.03
			n-Hexane (1)–2,4-Dimethylpentane (2)					
0.1279	0.1932	52.20	0.1888	85.02	0.1867	132.05	0.1836	199.63
0.2133	0.3025	54.70	0.2971	88.70	0.2951	137.80	0.2912	208.02
0.3212	0.4271	57.75	0.4214	93.38	0.4195	144.82	0.4153	218.49
0.3984	0.5090	59.87	0.5037	96.71	0.5018	149.92	0.4974	225.74
0.4219	0.5329	60.54	0.5277	97.83	0.5258	151.43	0.5212	227.90
0.4775	0.5876	62.08	0.5828	100.18	0.5808	155.24	0.5765	233.31
0.5392	0.6453	63.76	0.6410	102.77	0.6390	159.22	0.6348	238.94
0.5776	0.6797	64.70	0.6758	104.23	0.6737	161.55	0.6697	242.44
0.6025	0.7013	65.37	0.6977	105.37	0.6957	163.17	0.6918	244.75
0.6251	0.7206	65.95	0.7172	106.32	0.7153	164.55	0.7115	246.71
0.7031	0.7843	68.00	0.7817	109.40	0.7801	169.32	0.7770	254.08
0.8366	0.8847	71.50	0.8836	114.95	0.8829	177.75	0.8810	265.95
0.9100	0.9368	73.42	0.9363	117.40	0.9361	182.11	0.9351	272.20

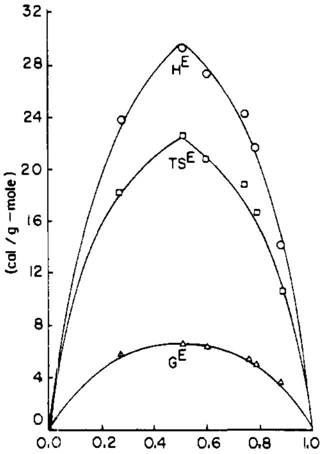

Figure 1. Excess thermodynamic functions for *n*-hexane–2-methylpentane solutions at 20 °C.

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
	Hexane (1)–2-Methylpentane (2)			
A	27.9414	26.0436	21.9668	15.7554
B	−2.08424	−0.6608	−0.4859	2.4452
C	15.3704	15.9080	21.6142	19.8080
	Hexane (1)–3-Methylpentane (2)			
A	24.7905	21.5518	16.6459	13.1362
B	0.83875	0.2861	1.3255	1.3159
C	14.0031	17.7266	20.0780	17.5500
	Hexane (1)–2,4-Dimethylpentane (2)			
A	33.3916	27.3614	25.4331	25.2499
B	0.00485	0.03134	0.7664	1.4538
C	20.9681	20.1062	14.9819	13.4321

the vapor mole fractions. The constants calculated for eq 3–5 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, 2, and 3 show the calculated excess properties at 20 °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 indicating that errors are below the maximum value of 0.5 cal/mol that could result from a

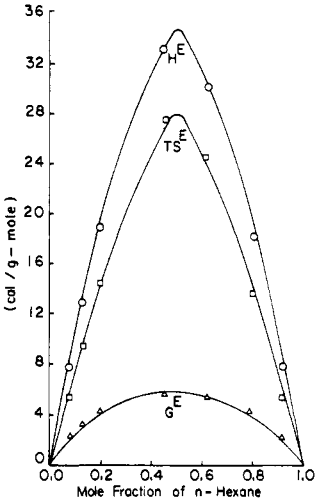

Figure 2. Excess thermodynamic functions for *n*-hexane–3-methylpentane solutions at 20 °C.

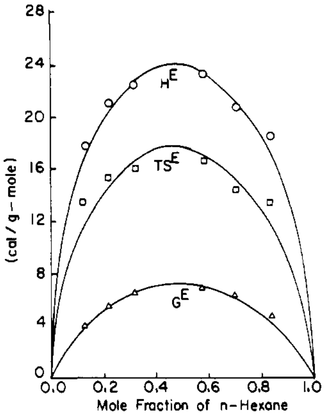

Figure 3. Excess thermodynamic functions for *n*-hexane–2,4-dimethylpentane solutions at 20 °C.

Table IV. Measured and Calculated Properties

x_1	y_1	P_{ex}, mmHg	P_{ca}, mmHg	$P_{ex} - P_{ca}$	γ_1	γ_2	g^E, cal/mol	g^E/T, cal/(g-mol K)
			n-Hexane (1)–2-Methylpentane (2) at 40 °C					
0.1006	0.0784	371.510	371.416	+0.093	1.027 07	1.001 28	2.39	0.007 63
0.2013	0.1587	361.970	361.872	+0.097	1.013 21	1.003 60	3.43	0.010 95
0.2692	0.2152	355.000	355.189	−0.189	1.008 88	1.004 90	3.70	0.011 82
0.4135	0.3435	340.570	340.665	−0.095	1.006 80	1.005 80	3.86	0.012 31
0.4666	0.3938	335.409	335.288	+0.121	1.007 10	1.005 57	3.90	0.012 44
0.5098	0.4359	330.830	330.911	−0.081	1.007 39	1.005 29	3.95	0.012 60
0.5560	0.4821	326.419	326.257	+0.162	1.007 60	1.005 05	4.01	0.012 81
0.6026	0.5299	321.620	321.573	+0.047	1.007 59	1.005 07	4.09	0.013 05
0.7612	0.7016	305.530	305.662	−0.132	1.005 29	1.010 64	4.08	0.013 01
0.7979	0.7435	301.800	301.929	−0.129	1.004 32	1.014 11	3.91	0.012 47
0.8799	0.8412	293.550	293.361	+0.188	1.002 00	1.026 75	3.07	0.009 79
			n-Hexane (1)–2,4-Dimethylpentane (2) at 10 °C					
0.1279	0.1932	52.200	52.234	−0.034	1.051 33	1.002 89	5.02	0.017 72
0.2133	0.3025	54.700	54.714	−0.014	1.033 59	1.006 33	6.76	0.023 87
0.3212	0.4271	57.750	57.732	+0.017	1.021 89	1.010 40	7.86	0.027 77
0.3984	0.5090	59.870	59.859	+0.010	1.017 83	1.012 63	8.21	0.028 99
0.4219	0.5329	60.540	60.504	+0.035	1.017 00	1.013 21	8.27	0.029 20
0.4775	0.5876	62.080	62.026	+0.053	1.015 47	1.014 45	8.34	0.029 45
0.5392	0.6453	63.760	63.706	+0.053	1.014 09	1.015 88	8.33	0.029 41
0.5776	0.6797	64.700	64.744	−0.044	1.013 22	1.016 98	8.27	0.029 20
0.6025	0.7013	65.370	65.414	−0.044	1.012 61	1.017 86	8.21	0.028 98
0.6251	0.7206	65.950	66.019	−0.069	1.012 02	1.018 81	8.13	0.028 72
0.7031	0.7843	68.000	68.080	−0.080	1.009 57	1.023 77	7.69	0.027 16
0.8366	0.8847	71.500	71.468	+0.031	1.004 28	1.042 78	5.86	0.020 70
0.9100	0.9368	73.420	73.238	+0.181	1.001 58	1.062 70	3.89	0.013 73

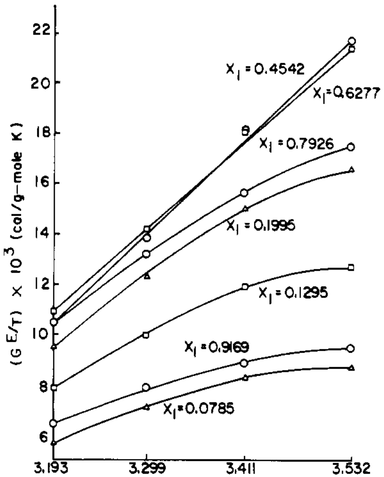

Figure 4. g^E/T vs. $1/T$ for *n*-hexane–3-methylpentane at various hexane mole fractions.

0.1-mm random pressure error. The derived values of h^E and Ts^E are considerably less reliable.

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_1, P_2	vapor pressures of components 1 and 2, mmHg
v	molar volume, mL
x	mole fraction in liquid
y	mole fraction in vapor

Greek Letters

β	virial coefficients
δ	defined by eq 9
γ	activity coefficient

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Infinite Dilution Activity Coefficients for Selected Binary Mixtures of Hydrocarbons, Alcohols, and Ketones

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Infinite dilution activity coefficients are determined in a gas–liquid partition chromatograph of a new design. Data are reported for 2-pentanone and 1-pentanol as solutes in 1-methylnaphthalene and phenanthrene, 2-nonanone in phenanthrene, and various hydrocarbons in 2-nonanone and 1-hexadecanol. Temperatures observed include 60, 120, and 180 °C.

Infinite dilution activity coefficients of solutes in pure solvents are of much interest in solution thermodynamics. They define boundary conditions in the integration of the Gibbs–Duhem equation and are the most sensitively reflective of the departures of the solutes from ideal solution behavior. Schreiber and Eckert (*4*) showed that the real solution behavior in the complete composition range can be described on the basis of data on the infinite dilution activity coefficients only.

The experimental apparatus and procedure of this work have been described (*5*). Briefly the apparatus is a gas–liquid partition chromatograph of a new design for the accurate determination of the gas–liquid vaporization equilibrium ratio K of the solute at infinite dilution over a wide temperature range. The infinite dilution activity coefficient γ^∞ is calculated from the K^∞ value. K_a^∞ is defined as the limit of y_a/x_a as x_a approaches zero, where y_a and x_a are mole fractions of component a in the vapor and liquid, respectively.

Table I. Chemicals Used in This Work

substance	source	% purity
helium	Airco (purified, grade 4.5)	99.9/95
n-hexane	Phillips, Research Grade	99.96
1-pentanol	Eastman	99
1-hexadecanol	Baker Chemicals[a]	99
2-pentanone	Aldrich	97
2-nonanone	Aldrich	99.5
benzene	Phillips, Research Grade	99.9
toluene	Phillips, Research Grade	99.4
ethylbenzene	Phillips, Research Grade	99.9
n-propylbenzene	Aldrich	98
p-xylene	Phillips, Research Grade	99.9
naphthalene	Fisher, certified	99+
1-methylnaphthalene	Aldrich[a]	99
phenanthrene	Eastman[b]	99

[a] Purified by fractional distillation. [b] Recrystallized in ether.

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