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Phase Equilibria in the Systems Hexane + Heptane and Methyl 1,1-Dimethylethyl Ether + Hexane + Heptane

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Vapor−liquid equilibrium at 94 kPa has been determined for the systems hexane + heptane and methyl 1,1-dimethylethyl ether (MTBE) + hexane + heptane. The binary system exhibits regular, almost ideal behavior, and no azeotrope is present in the ternary system. The data were correlated by the Redlich−Kister, NRTL, Wilson, UNIQUAC, and Wisniak−Tamir equations and the appropriate parameters are reported. The models allow prediction of the activity coefficients of the ternary system from those of the pertinent binary systems.

In late 1992, the oxy-fuel program was introduced in the U.S. that required that gasoline had to contain 2.7% oxygen by mass in the winter months in areas that where in nonattainment on CO standards. The Reformulated Gasoline Program put stringent requirements on ozone-forming and air toxic emissions. MTBE has been used as a gasoline blending agent since 1979. Now, it is the primary oxygenated compound being used to reformulate gasolines to improve their octane rating and pollution-reducing capability. Unlike most ethers, MTBE minimizes handling and storage concerns associated with peroxide formation and exhibits excellent oxidative stability, resisting peroxide formation without added inhibitors. Phase equilibrium data of oxygenated mixtures are important for predicting the vapor phase composition that would be in equilibrium with hydrocarbon mixtures. Isothermal vapor−liquid data for the system hexane + heptane have been reported at 303.15 K and 323.15 K by Smyth and Engel (1929), at 340.15 K by Beatty and Calingaert (1934), at 323.15 K by Zharov et al. (1971), at (293.15, 303.15, and 413.15) K by Choi et al. (1985), and at 313.15 K by Zielkiewicz (1991). The only data available under isobaric conditions are those of Leslie and Carr (1925) who measured the vapor−liquid equilibrium at (12, 20, 31, 47, 70, 101, and 101.3) kPa. The data of the latter are analyzed in the DECHEMA Data Base and result in activity coefficients at infinite dilution of less than 1 for hexane and larger than 1 for heptane. The present work was undertaken to measure vapor−liquid equilibria (VLE) data for the title systems for which isobaric data are not available or are unreliable. Vapor−liquid equilibrium data for the binary systems methyl 1,1-dimethylethyl ether (1) + hexane (2) and methyl 1,1-dimethylethyl ether (1) + heptane (3) have already been reported at 94 kPa by Wisniak et al. (1997); both systems present small deviations from ideality, and they behave essentially as regular solutions and present no azeotrope.

Experimental Section

Purity of Materials. Methyl *tert*-butyl ether (99.93 mass %), hexane (99.73+ mass %), and heptane (99.57 mass %) were purchased from Aldrich. The reagents were used without further purification after gas chromatography failed to show any significant impurities. The properties and purity (as determined by GLC) of the pure components appear in Table 1.

Table 1. Mole Percent GLC Purities (mass %), Refractive Index n_D at the Na D Line, and Normal Boiling Points T of Pure Components

component (purity/mass %)	n_D(298.15 K)	T/K
methyl 1,1-dimethylethyl ether (99.93)	1.3661[a]	327.75[a]
	1.3663[b]	328.40[b]
hexane (99.73)	1.3730[a]	341.84[a]
	1.37226[c]	341.869[d]
heptane (99.57)	1.3851[a]	371.54[a]
	1.38513[e]	371.553[f]

[a] Measured. [b] TRC Tables, a-6040. [c] TRC Tables, fa-1010. [d] TRC Tables, k1440. [e] TRC Tables, fa-1460. [f] TRC Tables, k1460.

Apparatus and Procedure. An all glass vapor−liquid equilibrium apparatus model 602, manufactured by Fischer Labor-und Verfahrenstechnik (Germany), was used in the equilibrium determinations. In this circulation method apparatus, the solution is heated to its boiling point by a 250 W immersion heater (Cottrell pump). The vapor−liquid mixture flows through an extended contact line which guarantees an intense phase exchange and then enters a separation chamber whose construction prevents an entrainment of liquid particles into the vapor phase. The separated gas and liquid phases are condensed and returned to a mixing chamber, where they are stirred by a magnetic stirrer, and then returned again to the immersion heater. Temperature control is achieved by a 5 mm diameter Pt-100 temperature sensor, with an accuracy of ±0.1 K. The total pressure of the system is controlled by a vacuum pump capable of working under vacuum up to 0.25 kPa. The pressure is measured by a Vac Probs with an accuracy of ±0.1 kPa. On the average the system reaches equilibrium conditions after 1−2 h of operation. Samples, taken by syringing 0.7 μL after the system had achieved equilibrium, were analyzed by gas chromatography on a Gow-Mac series 550P apparatus provided with a thermal conductivity detector and a Spectra Physics Model SP 4290 electronic integrator. The column was 3 m long and 0.2 cm in diameter, packed with SE-30. The column,

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Table 2. Experimental Vapor−Liquid Equilibrium Data for Hexane (2) + Heptane (3) at 94 kPa

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$/ cm^3 mol^{-1}	$-B_{22}$/ cm^3 mol^{-1}	$-B_{12}$/ cm^3 mol^{-1}	G^E/ RT
369.0	0.000	0.000		1.0000				0.000
367.4	0.028	0.063	1.0532	1.0103	1087	1587	1307	0.011
366.0	0.062	0.136	1.0567	1.0052	1098	1604	1320	0.008
364.4	0.103	0.217	1.0486	0.9989	1110	1624	1336	0.004
362.4	0.152	0.300	1.0395	1.0012	1126	1650	1356	0.007
360.0	0.217	0.403	1.0376	0.9952	1146	1682	1381	0.004
357.2	0.301	0.513	1.0288	0.9901	1170	1720	1411	0.002
354.6	0.379	0.601	1.0252	0.9907	1192	1756	1439	0.004
351.8	0.473	0.689	1.0198	0.9921	1218	1797	1471	0.005
348.2	0.602	0.788	1.0128	1.0103	1251	1852	1514	0.012
346.5	0.674	0.837	1.0087	1.0026	1268	1879	1535	0.007
343.6	0.792	0.904	1.0090	1.0257	1296	1926	1571	0.012
341.5	0.887	0.951	1.0092	1.0389	1318	1961	1598	0.012
340.5	0.944	0.976	1.0039	1.0427	1328	1978	1612	0.006
339.7	0.972	0.988	1.0110	1.0521	1337	1992	1622	0.012
339.5	1.000	1.000	1.0000					0.000
γ_i^{∞} [a]			1.04	1.06				

[a] Extrapolated from experimental data according to the method suggested by Wisniak et al. (1996).

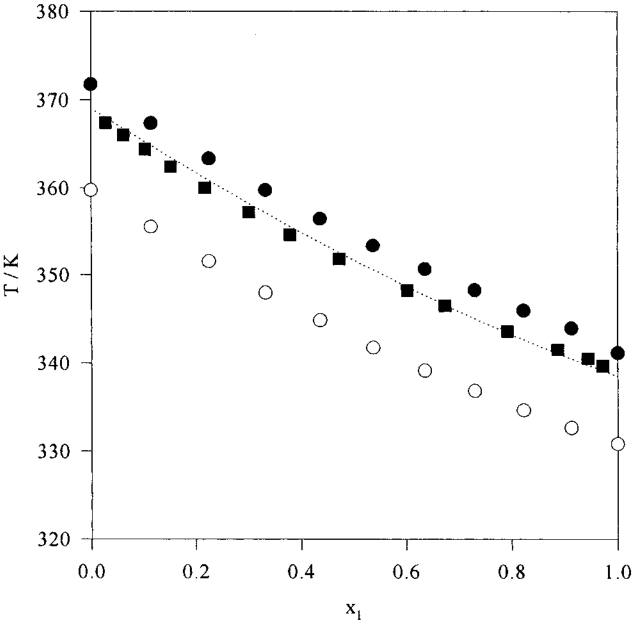

Figure 1. Graphical comparison of bubble-point temperatures of the system hexane (2) + heptane (3) with previously published isobaric data: experimental data of Leslie and Carr (1925) at 70 kPa (●) and 101 kPa (○); this work (■); predicted by the regular solution approximation at 94 kPa from the data of Leslie and Carr (···).

injector, and detector temperatures were (353.15, 493.15, and 543.15) K for the system hexane + heptane and (333.15, 453.15, and 543.15) K for the system MTBE + hexane + heptane. Very good separation was achieved under these conditions, and calibration analyses were carried out to convert the peak ratio to the mass composition of the sample. The pertinent polynomial fits had a correlation coefficient R^2 better than 0.99. Concentration measurements were accurate to better than ±0.009 mole fraction.

Table 3. Experimental Vapor−Liquid Equilibrium Data for Methyl 1,1-Dimethylethyl Ether (1) + Hexane (2) + Heptane (3) at 94 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
327.6	0.870	0.048	0.935	0.040	1.0076	1.2197	1.2033
328.0	0.856	0.049	0.932	0.040	1.0074	1.1770	1.1647
328.1	0.836	0.061	0.916	0.052	1.0106	1.2319	1.2085
328.2	0.799	0.131	0.878	0.101	1.0113	1.1091	1.1191
328.6	0.816	0.067	0.916	0.049	1.0192	1.0415	1.1404
329.0	0.733	0.177	0.825	0.151	1.0089	1.1910	1.0321
329.2	0.692	0.208	0.797	0.175	1.0268	1.1704	1.0403
329.5	0.744	0.124	0.859	0.104	1.0195	1.1534	1.0266
329.5	0.675	0.215	0.787	0.181	1.0302	1.1572	1.0699
329.7	0.706	0.180	0.805	0.162	1.0005	1.2252	1.0738
329.8	0.682	0.212	0.799	0.168	1.0254	1.0811	1.1191
329.9	0.665	0.229	0.768	0.202	1.0067	1.1998	1.0258
330.2	0.731	0.098	0.876	0.076	1.0356	1.0380	1.0162
330.2	0.637	0.228	0.763	0.196	1.0356	1.1550	1.0801
330.5	0.560	0.362	0.686	0.291	1.0486	1.0678	1.0481
331.3	0.616	0.245	0.736	0.224	0.9984	1.1810	0.9947
331.9	0.685	0.080	0.858	0.072	1.0278	1.1474	0.9917
332.9	0.492	0.342	0.653	0.295	1.0552	1.0614	1.0181
333.5	0.576	0.154	0.764	0.147	1.0361	1.1570	1.0395
333.9	0.367	0.517	0.508	0.456	1.0672	1.0497	0.9802
334.2	0.406	0.429	0.561	0.387	1.0555	1.0628	0.9853
334.2	0.458	0.345	0.623	0.314	1.0387	1.0750	0.9878
334.8	0.442	0.328	0.613	0.308	1.0414	1.0888	1.0342
334.9	0.545	0.125	0.760	0.124	1.0449	1.1390	1.0599
335.2	0.354	0.472	0.507	0.435	1.0611	1.0533	1.0046
335.2	0.468	0.254	0.657	0.249	1.0417	1.1220	1.0047
335.5	0.400	0.364	0.577	0.344	1.0604	1.0712	0.9863
336.6	0.236	0.633	0.361	0.596	1.0898	1.0290	0.9473
337.0	0.328	0.427	0.500	0.415	1.0734	1.0501	0.9707
337.6	0.140	0.783	0.228	0.746	1.1255	1.0101	0.9220
337.7	0.236	0.578	0.374	0.560	1.0947	1.0256	0.9554
338.5	0.391	0.216	0.627	0.230	1.0802	1.0979	0.9608
338.7	0.194	0.616	0.319	0.611	1.1010	1.0171	0.9640
338.7	0.145	0.720	0.240	0.711	1.1052	1.0131	0.9574
338.8	0.360	0.269	0.576	0.286	1.0670	1.0879	0.9758
338.9	0.109	0.787	0.183	0.775	1.1137	1.0035	1.0683
342.0	0.370	0.091	0.655	0.115	1.0774	1.1723	1.0001
342.8	0.123	0.567	0.232	0.639	1.1291	1.0210	0.9423
343.8	0.166	0.425	0.323	0.503	1.1256	1.0397	0.9366
343.9	0.277	0.187	0.531	0.230	1.1080	1.0810	0.9737
344.0	0.204	0.335	0.393	0.404	1.1077	1.0551	0.9617
344.3	0.231	0.286	0.438	0.346	1.0829	1.0507	0.9633
344.4	0.100	0.546	0.202	0.648	1.1502	1.0237	0.9170
345.2	0.129	0.450	0.262	0.552	1.1292	1.0350	0.9270
345.9	0.246	0.161	0.517	0.200	1.1486	1.0307	0.9741
347.2	0.127	0.363	0.277	0.477	1.1487	1.0453	0.9463
348.7	0.134	0.293	0.297	0.406	1.1211	1.0571	0.9669
352.6	0.078	0.272	0.201	0.420	1.1833	1.0580	0.9550
354.6	0.082	0.184	0.230	0.309	1.2219	1.0849	0.9679
355.0	0.045	0.254	0.132	0.431	1.2457	1.0855	0.9500
356.6	0.071	0.149	0.212	0.272	1.2253	1.1191	0.9583
360.1	0.044	0.099	0.153	0.200	1.3136	1.1289	0.9816

Results

The temperature T and liquid-phase x_i and vapor-phase y_i mole fraction measurements at $P = 94$ kPa are reported in Tables 2 and 3 and Figures 1−3, together with the activity coefficients γ_i which were calculated from the following equation (Van Ness and Abbott, 1982):

$$\ln \gamma_i = \ln\left(\frac{Py_i}{P_i^{\circ}x_i}\right) + \frac{(B_{ii} - V_i^L)(P - P_i^{\circ})}{RT} + \frac{P}{2RT}\sum\sum y_j y_k(2\delta_{ji} - \delta_{jk}) \qquad (1)$$

where T and P are the boiling point and the total pressure, V_i^L is the molar liquid volume of component i, P_i° is the pure component vapor pressure, B_{ii} and B_{jj} are the second virial coefficients of the pure gases, B_{ij} is the cross second virial coefficient, and

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \qquad (2)$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. The pure component vapor pressures P_i° were calculated according to the Antoine equation:

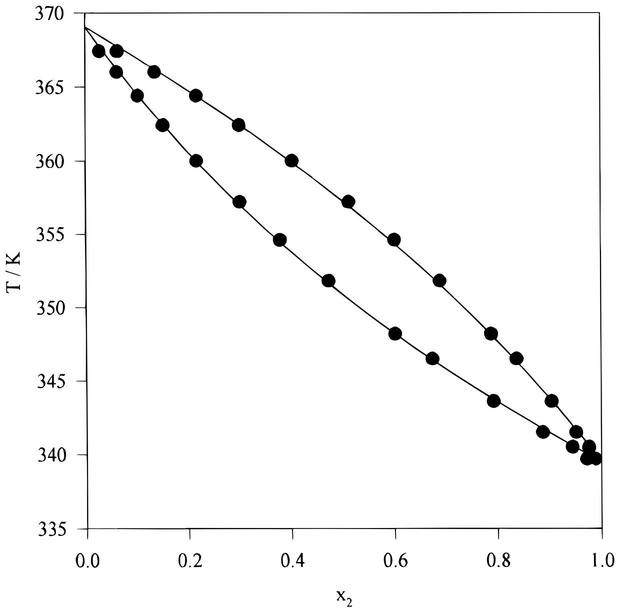

Figure 2. Boiling-point diagram at 94 kPa for the system hexane (2) + heptane (3): experimental data (●); smoothed curve (—).

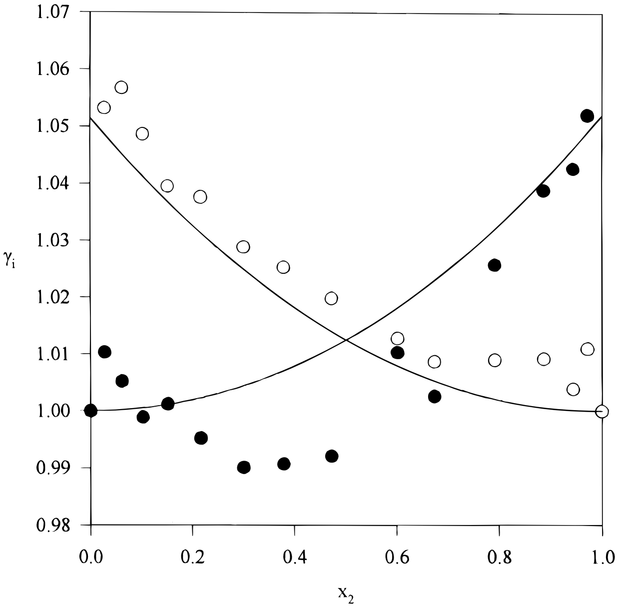

Figure 3. Activity coefficient plot for the system hexane (2) + heptane (3) at 94 kPa: calculated from experimental data (●, ○); smoothed assuming regular solution (—).

Table 4. Antoine Coefficients, Eq 3

compd	A_i	B_i	C_i
methyl 1,1-dimethylethyl ether[a]	5.860 78	1032.99	59.880
hexane[b]	6.001 39	1170.875	48.833
heptane[c]	6.020 23	1263.909	56.718

[a] Reich (1996). [b] TRC Tables, k1440. [c] TRC Tables, k1460.

$$\log(P_i^\circ/\text{kPa}) = A_i - \frac{B_i}{(T/\text{K}) - C_i} \tag{3}$$

where the Antoine constants A_i, B_i, and C_i are reported in Table 4. The molar virial coefficients B_{ii} and B_{ij} were estimated by the method of Hayden and O'Connell (1975) by assuming the association and solvation parameters to be negligible. The last two terms in eq 1 contributed less than 3% to the activity coefficients, and their influence was important only at very dilute concentrations. The calculated activity coefficients are reported in Tables 2 and 3 and are estimated accurate to within ±3%. Table 2 contains also the activity coefficients at infinite dilution calculated by the method suggested by Wisniak et al. (1996).

Figure 1 shows a graphical comparison between bubble-point temperatures measured for the system hexane (2) + heptane (3) in this work and those determined by Leslie and Carr (1925) that are close to the experimental conditions considered in this work. The dashed line corresponds to an interpolation of the data of Leslie and Carr to 94 kPa using a regular solution approximation. Good agreement among these different sets of data is deduced from the figure, although it should be pointed out that the data of Leslie and Carr do not include experimental determination of vapor-phase compositions. As seen from Table 2 and Figure 3, the binary system hexane + heptane behaves essentially ideal, with activity coefficients slightly greater than the unity. In addition, the apparent considerable experimental noise observed can be explained in terms of the almost ideal behavior of the system, as well as the narrow scale of the figure. In fact, the thermodynamic consistency of the system hexane + heptane has been checked using the point-to-point test proposed by Fredenslund et al. (1977), and the consistency criterion are met with a one-parameter Legendre polynomial for which the mean absolute deviation in the vapor phase, MAD(y), is 0.002.

The ternary activity coefficients reported in Table 3 were found to be thermodynamically consistent as tested by the $L-W$ method of Wisniak (1993) and the McDermot−Ellis method (1965) modified by Wisniak and Tamir (1977). According to these references two experimental points *a* and *b* are considered thermodynamically consistent if the following condition is fulfilled:

$$D < D_{\max} \tag{4}$$

The local deviation D is given by

$$D = \sum_{i=1}^{N}(x_{ia} + x_{ib})(\ln \gamma_{ia} - \ln \gamma_{ib}) \tag{5}$$

where N is the number of components and the maximum deviation $D_{\max}$ is

$$D_{\max} = \sum_{i=1}^{N}(x_{ia} + x_{ib})\left(\frac{1}{x_{ia}} + \frac{1}{y_{ia}} + \frac{1}{x_{ib}} + \frac{1}{y_{ib}}\right)\Delta x + \sum_{i=1}^{N}(x_{ia} + x_{ib})\frac{\Delta P}{P} + 2\sum_{i=1}^{N}|\ln \gamma_{ib} - \ln \gamma_{ia}|\Delta x + \sum_{i=1}^{N}(x_{ia} + x_{ib})B_j\{(T_a + C_j)^{-2} + (T_b + C_j)^{-2}\}\Delta T \tag{6}$$

The errors in the measurements Δx, ΔP, and ΔT were as previously indicated. The first term in eq 6 was the dominant one. For the experimental points reported here D never exceeded 0.062 while the smallest value of $D_{\max}$ was 0.218.

In Table 3, an inversion of the deviation of heptane (3) can be appreciated from Raoult's law; deviations are positive ($\gamma_3 > 1$) at low temperatures and become negative ($\gamma_3 < 1$) at higher temperatures. This experimental result is in good agreement with the data of Lee et al. (1994), who found the same behavior in the system methyl 1,1-dimethylethyl ether (1) + heptane (3) between 318.15 K and 338.15 K. In our previous work (Wisniak et al., 1997) we have measured the system methyl 1,1-dimethylethyl

Table 5. Parameters and Deviations between Experimental and Calculated Values for the Redlich−Kister Expansion, Eqs 7−9

			γ_1/γ_2			γ_1/γ_3		
case	D_1	D_2	max dev (%)	av dev (%)	rmsd	max dev (%)	av dev (%)	rmsd
a	0.0000	0.0000	12.86	3.93	0.01	12.39	5.54	0.01
b	0.0500	0.0585	12.77	3.93	0.01	11.89	5.57	0.01

Binary Constants

ij	b_{ij}	c_{ij}	d_{ij}
1−2	0.0831	0.0053	0.0054
1−3	0.0693	0.0043	0.0190
2−3	0.0231	0.0016	−0.0041

[a] Considering only binary constants. [b] Including optimized ternary constants.

ether (1) + heptane (3) at 94 kPa, the aforementioned inversion was masked by a rapid variation of the bubble-point temperature from 366 K to 326 K, although data suggest negative deviations for heptane (3) in the concentrated range and positive deviations are evident for the same component in the dilution range.

The activity coefficients for the ternary system were correlated from the following Redlich−Kister expansion

$$\frac{G^E}{RT} = x_1x_2[b_{12} + c_{12}(x_1 - x_2) + d_{12}(x_1 - x_2)^2] + x_1x_3[b_{13} + c_{13}(x_1 - x_3) + d_{13}(x_1 - x_3)^2] + x_2x_3[b_{23} + c_{23}(x_2 - x_3) + d_{23}(x_2 - x_3)^2] + x_1x_2x_3(C + D_1x_1 + D_2x_2) \quad (7)$$

$$\ln\frac{\gamma_1}{\gamma_2} = (b_{13} + b_{23})x_3 + (b_{12} + Cx_3)(x_2 - x_1) - c_{13}x_3(x - 2x_1) + c_{12}[2x_1x_2 - (x_1 - x_2)^2 - c_{23}x_3(2x_2 - x_3) + D_1x_1x_3(2x_2 - x_1) - d_{13}x_3(x_3 - 3x_1)(x_1 - x_3) + D_2x_3x_2(x_2 - 2x_1) + d_{12}(x_2 - x_1)[(x_2 - x_1)^2 - 4x_1x_2] - d_{23}x_3(x_2 - x_3)(3x_2 - x_3) \quad (8)$$

$$\ln\frac{\gamma_1}{\gamma_3} = (b_{13} + D_2x_2{}^2 + Cx_2)(x_3 - x_1) + x_2(b_{12} + b_{23}) + c_{23}x_2(2x_3 - x_2) + c_{13}[6x_1x_3 - (1 - x_2)^2] + c_{12}x_2(2x_1 - x_2) + D_1x_1x_2(2x_3 - x_1) + d_{23}x_2(3x_3 - x_2)(x_2 - x_3)[8x_1x_3 - (1 - x_2)^2] + d_{12}x_2(x_2 - 3x_1)(x_2 - x_1) \quad (9)$$

where b_{ij}, c_{ij}, and d_{ij} are constants for the pertinent binary and C, D_1, and D_2 are ternary constants. All the constants in eqs 8 and 9 are assumed to be independent of the temperature. It should be mentioned that the expressions corresponding to eqs 8 and 9 in the book of Hala et al. (1967) are in error. Data and constants for the binary systems methyl 1,1-dimethylethyl ether (1) + hexane (2) and methyl 1,1-dimethylethyl ether (1) + heptane (3) have already been reported (Wisniak et al., 1997). The ternary Redlich−Kister coefficient was obtained by a Simplex optimization technique. The differences between the values of the root mean square deviation for the activity coefficient for the two cases—with and without the ternary constants D (Table 5)—are statistically not significant, suggesting that ternary data can be predicted directly from the binary systems. In fact, equilibrium vapor pressures were correlated very well by the NRTL, Wilson, and UNIQUAC models (Walas, 1985) using only binary parameters, both for bubble-point pressure and dew-point pressure calculations, as shown by the statistics and parameters given in Table 6. In addition, Table 6 reports the predictions obtained from the modified UNIFAC model (Larsen, 1987), concluding a good fit of the ternary system.

The boiling points of the systems were correlated by the equation proposed by Wisniak and Tamir (1976):

$$T/\mathrm{K} = \sum_{i=1}^{n} x_iT_i{}^\circ/\mathrm{K} + \sum_{i,j=1}^{n}\{x_ix_j\sum_{k=0}^{n}C_k(x_i - x_j)^k\} + x_1x_2x_3\{A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3)\} \quad (10)$$

In this equation n is the number of components ($n = 2$ or 3), $T_i{}^\circ$ is the boiling point of the pure component i, and m is the number of terms in the series expansion of $(x_i - x_j)$. C_k are the binary constants where A, B, C, and D are ternary constants. The following equation, of the same structure, has been suggested by Tamir (1981) for the direct correlation of ternary data, without use of binary data:

$$T/\mathrm{K} = \sum_{i=1}^{3} x_iT_i{}^\circ + x_1x_2[A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x^2)^2 + \ldots + x_1x_3[A_{13} + B_{13}(x_1 - x_3) + C_{13}(x_1 - x_3)^2 + \ldots] + x_2x_3[A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2 + \ldots] \quad (11)$$

In eq 11 coefficients A_{ij}, B_{ij}, and C_{ij} are not binary constants, they are multicomponent parameters determined directly from the data. Direct correlation of $T(x)$ for ternary mixtures can be very efficient, as reflected by a lower percent average deviation and root mean square deviation (rmsd) and a smaller number of parameters than

Table 6. Parameters and Prediction Statistics for Different G^E Models

					bubble-point pressures			dew-point pressures		
model	*ij*	A_{ij}/J mol^{-1}	A_{ji}/J mol^{-1}	α_j	ΔP/%	Δy_1	Δy_2	ΔP/%	Δx_1	Δx_2
	1−2	259.30	353.35	0.358						
NRTL	1−3	−375.85	932.01	0.352	0.73	0.0056	0.0074	1.30	0.0063	0.0096
	2−3	647.23	−385.56	0.300						
	1−2	901.71	−244.70							
Wilson[a]	1−3	788.24	−291.11		0.77	0.0058	0.0066	1.26	0.0064	0.0087
	2−3	−1024.03	1827.06							
	1−2	51.36	131.29							
UNIQUAC[b]	1−3	−145.97	319.33		0.65	0.0052	0.0048	1.03	0.0062	0.0065
	2−3	420.40	−356.41							
UNIFAC[c]					1.54	0.0101	0.0137	1.70	0.0093	0.0137

[a] Liquid volumes have been estimated from the Rackett equation. [b] Molecular parameters are those calculated from UNIFAC. [c] Calculations based on modified UNIFAC (Larsen, 1987).

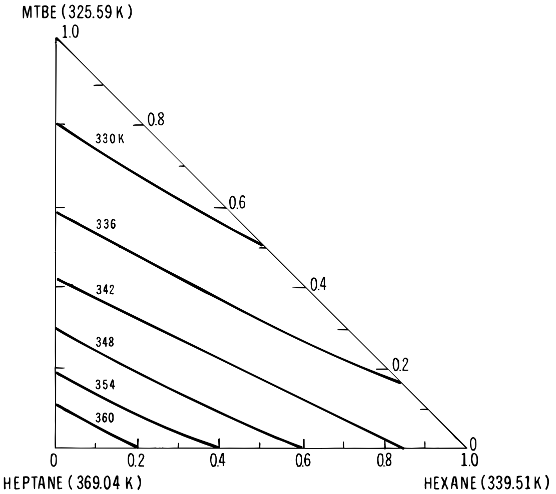

Figure 4. Isothermals for the ternary system MTBE (1) + hexane (2) + heptane (3) at 94 kPa from 329.15 K to 349.15 K, every 5 K. Coefficients from eq 11.

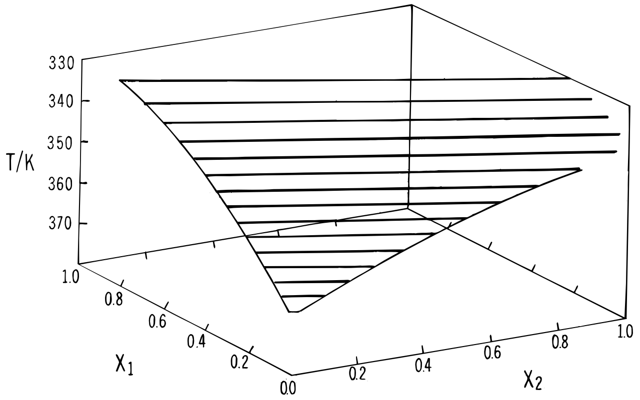

Figure 5. Three-dimensional graph $T-x_1-x_2$.

Table 7. Coefficients in Correlation of Boiling Points, Eqs 10 and 11, Average Deviation, and Root Mean Square Deviations in Temperature, rmsd (*T*/K)

Equation 10 (Fit from Binary Constants)

A	B	C	max dev/K	av dev/K	rmsd
−5.6455	−59.5313	43.3700	0.59	0.28	0.045

Binary Constants

system[a]	C_0	C_1	C_2
hexane (2) + heptane (3)	−11.1203	3.2231	−12.9263

Equation 11 (Direct Fit)

ij	A_{ij}	B_{ij}	C_{ij}	max dev /K	av dev /K	rmsd
1−2	−9.1890	0.4072	3.6329	0.43	0.10	0.02
1−3	−32.7744	14.9164	−3.0611			
2−3	−12.5428	4.8090	−11.4567			

[a] The constants for the other binaries have been reported by Wisniak et al. (1996).

those for eq 10. Both equations may require a similar number of constants for similar accuracy, but the direct correlation allows an easier calculation of boiling isotherms (Figures 4 and 5). The various constants of eqs 10 and 11 are reported in Table 7, which also contains information indicating the degree of goodness of the correlation. It is clear that for the ternary system in question a direct fit of the data gives a much better fit.

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