Phase Equilibria in the Ternary System Methyl 1,1-Dimethylethyl Ether + **Hexane** + **Octane**

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Vapor-liquid equilibrium at 94 kPa has been determined for the ternary system methyl 1,1-dimethylethyl ether (MTBE) + hexane + octane. The system deviates positively from ideality, and no azeotrope is present. The ternary activity coefficients and the boiling points of the system have been correlated with the composition using the Redlich-Kister, Wilson, NRTL, UNIQUAC, UNIFAC, and Wisniak-Tamir relations. Most of the models allow a very good prediction of the activity coefficients of the ternary system from those of the pertinent binary systems.

Introduction

Ethers are usually added to gasolines in order to improve their combustion and reduce pollution; the commonly used oxygenating additives are methyl 1,1-dimethylethyl ether (MTBE), methanol, and ethanol. MTBE is the primary oxygenated compound being used to improve the octane rating and pollution-reducing capability of gasolines. Phaseequilibrium data of oxygenated mixtures are important for predicting the vapor-phase composition that would be in equilibrium with hydrocarbon mixtures, and the system reported here constitutes an example of such mixtures. Vapor-liquid equilibrium data for the two binary systems methyl 1,1-dimethylethyl ether + hexane and methyl 1,1dimethylethyl ether + octane have already been reported at 94 kPa by Wisniak et al. (1997, 1998), and the two systems present slight to moderate positive deviations from ideality and do not have azeotropic points. Vapor-liquid equilibrium data for the system hexane + octane have been reported by Leslie and Carr (1925) at (12.3, 19.9, 31.1, 47.3, 70.1, and 101.325) kPa, by Kirss et al. (1975) at 328.1 K and by Li et al. (1990) and Weigno et al. (1990) at 298.1 K. According to the data of the last two reports, the system behaves essentially ideal. The present work was undertaken to measure vapor-liquid equilibrium (VLE) data for the ternary system for which no data are available.

Experimental Section

Chemicals. Methyl *tert*-butyl ether (99.93 mass %), hexane (99.57 mass %), and octane (99.80 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.

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

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 %)	<i>n</i> _D (298.15 K)	<i>T</i> /K
methyl 1,1-dimethylethyl ether (99.93)	1.3661 ^a	328.29 ^a
	1.3663 ^b	328.35^{b}
hexane (99.57)	1.3730 ^a	341.84 ^a
	1.37226 ^c	341.89 ^c
octane (99.8)	1.3948 ^a	398.50 ^a
	1.39512^{d}	398.83 ^d

^a Measured. ^b TRC Tables, a-6040. ^c TRC Tables, fa-1460. ^d TRC Tables, fa-1490. ^e TRC Tables, k-1490.

apparatus, about 100 mL of 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 that 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 returned again to the immersion heater. Temperature control is achieved by a Lauda thermometer, model R42/2, provided with a 4-mm diameter Pt-100 temperature sensor, with an accuracy of 0.01 K. The total pressure of the system is controlled by a vacuum pump capable of working under pressures down to 0.25 kPa. The pressure is measured by a Vac Probs pressure transducer with an accuracy of 0.1 kPa. On the average the system reaches equilibrium conditions after 0.5-1 h of operation. Samples, taken by syringing 0.7 μ L 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, injector, and detector temperatures were (338.15, 493.15, and 543.15) K. Very good separation was achieved under these conditions, and calibration analyses using synthetic mixtures were carried out to convert the peak ratio to the mass composition of the

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Table 2.	Experimental Vapor-Liquid Equilibria	Data for Methyl 1,1-Dimethylethyl	Ether (1) + Hexane (2) + Octar	ne (3)
at 94 KPa				

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		expe	rimental o	data		activ	ity coeffic/	ients	virial coefficients/cm ³ ·mol ⁻¹				nol ⁻¹	
328.29 0.844 0.064 0.970 0.074 1.004 1.100 1125 1459 3163 1.265 1787 2033 328.23 0.779 0.151 0.864 0.128 0.987 1.176 1.114 1125 1447 3130 1.255 1783 2087 333.10 0.481 0.450 0.599 0.393 0.984 1.068 0.965 1092 1401 3012 1217 1742 2016 333.21 0.754 0.011 0.990 1092 1401 3012 2217 1723 2011 333.410 0.555 0.284 0.770 0.906 0.066 1.001 1.113 1.010 1868 2976 1206 1707 1994 334.10 0.557 0.284 0.781 1.014 1.033 1.388 2976 1206 1707 1994 334.51 0.647 0.437 0.441 1.035 0.391 1079 1382 2960 1201 1706 1983 334.83 0.4070 0.537 <t< th=""><th><i>T</i>/K</th><th><i>x</i>₁</th><th><i>X</i>₂</th><th>y_1</th><th>y_2</th><th>γ1</th><th>Y2</th><th>γ3</th><th>$-B_{11}$</th><th>$-B_{22}$</th><th>$-B_{33}$</th><th>$-B_{12}$</th><th>$-B_{13}$</th><th>$-B_{23}$</th></t<>	<i>T</i> /K	<i>x</i> ₁	<i>X</i> ₂	y_1	y_2	γ1	Y2	γ3	$-B_{11}$	$-B_{22}$	$-B_{33}$	$-B_{12}$	$-B_{13}$	$-B_{23}$
328.94 0.820 0.094 0.917 0.074 1.004 1.103 1.104 1125 1447 3130 1255 1778 2093 331.65 0.662 0.227 0.789 0.198 0.984 1.115 1.078 1104 1418 3055 1231 1746 2042 333.10 0.641 0.599 0.393 0.984 1.016 0.965 1092 1401 3012 1217 1724 2016 333.10 0.677 0.754 0.010 0.966 0.001 1.113 1.010 1086 1382 2982 1208 1710 1988 334.10 0.635 0.284 0.718 0.264 0.991 1.101 0.884 1081 1388 2976 1206 1707 1994 334.30 0.647 0.430 0.090 1.057 0.884 1079 1383 2861 1201 1700 1986 334.87 0.410 0.357 0.451 1.024 0.936 1078 1382 2960 1201 1699 194	328.20	0.844	0.106	0.905	0.089	0.986	1.204	1.150	1125	1459	3163	1265	1799	2107
329.23 0.779 0.151 0.864 0.128 0.987 1.176 1.114 1125 1447 3130 12.55 1783 2087 333.10 0.481 0.450 0.599 0.393 0.984 1.068 0.965 1092 1400 3002 1217 1742 2016 333.21 0.757 0.010 0.906 0.990 1992 1400 3008 1216 1713 2001 333.10 0.657 0.070 0.906 0.065 1.001 1.113 1.010 1864 1390 2988 1210 1713 2001 334.10 0.657 0.441 0.837 0.134 0.985 1.127 1.080 1831 1286 2970 1204 1704 1949 334.51 0.647 0.373 0.641 0.340 1.057 0.984 1079 1382 2961 1201 1699 1985 334.83 0.370 0.541 0.014 0.038 1077 1381 2957 1200 1698 1983 334.8	328.94	0.820	0.094	0.917	0.074	1.004	1.103	1.100	1125	1450	3139	1258	1787	2093
331.65 0.662 0.227 0.789 0.198 0.984 1.115 1.078 1104 H18 3055 1231 1.746 2042 333.10 0.754 0.011 0.969 0.000 1.004 1.109 0.990 1092 1401 3012 1217 1724 2014 333.10 0.567 0.070 0.990 0.0665 1.001 1.084 1392 2988 1210 1.712 2014 334.10 0.557 0.284 0.718 0.264 0.991 1.111 1.010 1.084 1392 2988 1202 1.707 1993 334.57 0.4625 0.168 0.826 0.150 1.000 1.044 0.931 1088 2976 1204 1.704 1993 334.87 0.411 0.435 0.598 0.387 1.015 1.028 0.936 1078 1382 2960 1201 1699 1984 334.87 0.410 0.597 0.387 1.015 1.028 0.936 1077 1383 2957 1200	329.23	0.779	0.151	0.864	0.128	0.987	1.176	1.114	1125	1447	3130	1255	1783	2087
333.10 0.481 0.450 0.599 0.393 0.984 1.068 0.990 1992 1401 3012 1217 1724 2014 333.21 0.757 0.010 1.004 1.103 1.010 1086 1392 2988 1210 1713 2014 334.10 0.555 0.284 0.718 0.264 0.991 1.010 1084 1392 2988 1206 1710 1988 334.30 0.647 0.140 0.837 0.541 1.009 1.057 0.984 1079 1382 2961 1201 1699 1984 334.87 0.441 0.455 0.598 0.387 1.015 1.028 0.396 1078 1382 2961 1201 1699 1984 334.97 0.613 0.145 0.537 0.520 1.024 0.396 1078 1381 2957 1200 1698 1983 334.97 0.613 0.145 0.537 0.220 1.038 1.091 0.374 1391 1864 1893 1374 23	331.65	0.662	0.227	0.789	0.198	0.984	1.115	1.078	1104	1418	3055	1231	1746	2042
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333.90 0.697 0.070 0.906 0.065 1.001 1.113 1.010 1084 1390 2988 1210 1713 2001 334.10 0.647 0.140 0.837 0.134 0.985 1.127 1.080 1083 1388 2970 1206 1707 1998 334.51 0.647 0.373 0.641 0.301 1.009 1.057 0.984 1079 1383 2963 1202 1700 1986 334.83 0.397 0.544 0.357 0.451 1.014 1.035 0.393 1079 1382 2961 1201 1699 1985 334.87 0.411 0.435 0.587 1.014 1.0161 0.878 1077 1380 2957 1200 1688 1983 335.58 0.436 0.440 0.149 1.001 1.012 0.932 1065 1362 2917 1187 1678 1953 336.50 0.533 0.441 0.542 1.024 0.392 1067 1362 2917 1187 1	333.21	0.754	0.011	0.962	0.010	1.004	1.109	0.990	1092	1400	3008	1216	1723	2014
334.10 0.555 0.284 0.718 0.264 0.991 1.101 0.884 1084 1084 1380 2982 1208 1710 1994 334.30 0.647 0.140 0.835 1.127 1.080 1386 2970 1204 1704 1994 334.47 0.647 0.477 0.373 0.641 0.340 1.009 1.057 0.984 1079 1382 2961 1201 1699 1984 334.87 0.410 0.537 0.451 1.014 1.035 0.939 1079 1382 2960 1201 1699 1984 334.95 0.700 0.020 0.944 0.019 1.007 1.096 1.021 1078 1381 2957 1200 1698 1983 335.58 0.436 0.410 0.532 0.140 1.021 1.078 1381 2957 1200 1682 1914 1684 1943 336.60 0.660 0.303 0.382 0.622 1.036 1362 2910 1185 1674 195	333.90	0.697	0.070	0.906	0.065	1.001	1.113	1.010	1086	1392	2988	1210	1713	2001
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334.87 0.441 0.435 0.598 0.387 1.012 1.028 0.936 1078 1382 2960 1201 1699 1984 334.95 0.700 0.020 0.944 0.019 1.007 1.096 1.021 1078 1381 2957 1200 1698 1983 335.58 0.436 0.410 0.597 0.385 1.004 1.061 0.878 1073 1374 2399 1194 1689 1972 336.65 0.252 0.666 0.372 0.620 1.058 0.996 1067 1365 2917 1187 1678 1935 336.66 0.660 0.330 0.932 1.028 1.022 0.932 1064 1362 2909 1185 1674 1950 336.67 0.335 0.533 0.441 0.502 1.021 1.026 0.944 1064 1361 2907 1184 1671 1950 338.02 0.398 0.374 0.591 0.379 1.013 1.061 0.895 1054 1347	334.83	0.397	0.504	0.537	0.451	1.014	1.035	0.939	1079	1382	2961	1201	1699	1985
334.95 0.700 0.020 0.944 0.019 1.007 1.096 1.021 1078 1381 2957 1200 1699 1983 335.58 0.436 0.410 0.597 0.385 1.004 1.061 0.878 1073 1374 2939 1194 1689 1972 336.60 0.660 0.030 0.932 0.022 1.065 1362 2910 1185 1674 1954 336.60 0.660 0.030 0.932 0.028 1.064 1362 2910 1185 1674 1953 336.60 0.660 0.030 0.932 1.022 0.928 1065 1362 2910 1185 1674 1953 336.60 0.212 0.738 0.320 0.673 1.026 0.944 1064 1362 2903 1183 1671 1953 336.02 0.398 0.374 0.591 0.379 1.013 1.061 0.892 1034 1347 2813 1154 1624 1893 340.13 0.500 0.3	334.87	0.441	0.435	0.598	0.387	1.015	1.028	0.936	1078	1382	2960	1201	1699	1984
334.97 0.613 0.145 0.832 0.140 1.013 1.110 0.918 1077 1380 2957 1200 1697 1983 335.58 0.436 0.410 0.597 0.385 1.004 1.061 0.878 1073 1374 2939 1145 1674 1954 336.60 0.660 0.030 0.932 0.028 1.004 1.022 0.932 1065 1362 2910 1185 1674 1954 336.60 0.660 0.030 0.932 0.028 1.002 0.942 1064 1361 2907 1185 1674 1954 336.86 0.212 0.738 0.320 0.673 1.016 0.996 1063 1360 2903 1183 1671 1950 338.02 0.398 0.374 0.591 0.379 1.013 1.061 0.8951 1034 1322 2813 1154 1626 1895 340.30 0.097 0.814 0.168 0.818 1.006 0.981 0.931 1034 1321 <td< td=""><td>334.95</td><td>0.700</td><td>0.020</td><td>0.944</td><td>0.019</td><td>1.007</td><td>1.096</td><td>1.021</td><td>1078</td><td>1381</td><td>2957</td><td>1200</td><td>1698</td><td>1983</td></td<>	334.95	0.700	0.020	0.944	0.019	1.007	1.096	1.021	1078	1381	2957	1200	1698	1983
335.58 0.436 0.410 0.597 0.385 1.004 1.061 0.878 1073 1374 2939 1194 1689 1972 336.55 0.522 0.686 0.372 0.620 1.058 0.996 1065 1362 2917 1185 1674 1959 336.60 0.680 0.309 0.581 0.445 0.542 1.023 1.019 0.881 1064 1362 2909 1185 1674 1953 336.60 0.323 0.533 0.481 0.502 1.026 0.944 1064 1361 2907 1184 1671 1953 338.62 0.212 0.738 0.320 0.673 1.066 0.994 1063 1360 2903 1183 1671 1953 340.13 0.599 0.130 0.812 0.134 1.024 1.015 0.924 1038 1325 2813 1154 1626 1893 340.50 0.530 0.342 0.575 0.380 1.043 1.079 0.900 1034 1321	334.97	0.613	0.145	0.832	0.140	1.013	1.110	0.918	1077	1380	2957	1200	1697	1983
338.65 0.252 0.686 0.372 0.620 1.058 0.996 0.992 1067 1365 2917 1187 1678 1954 336.60 0.660 0.030 0.932 0.028 1064 1362 2910 1185 1674 1954 336.60 0.335 0.533 0.481 0.542 1.020 1.026 0.944 1064 1361 2907 1184 1673 1953 336.80 0.212 0.738 0.320 0.673 1.066 0.990 1063 1360 2903 1183 1671 1950 338.02 0.398 0.374 0.591 0.379 1.013 1.061 0.895 1054 1347 2871 1172 1655 1930 340.30 0.997 0.814 0.168 0.818 1.004 0.981 1035 1321 2804 1151 1621 1883 340.50 0.350 0.342 0.575 0.380 1.043 1.079 0.900 1034 1320 2800 1151 1621 188	335.58	0.436	0.410	0.597	0.385	1.004	1.061	0.878	1073	1374	2939	1194	1689	1972
336.60 0.660 0.030 0.932 0.028 1.004 1.022 0.932 1065 1362 2910 1185 1674 1954 336.65 0.399 0.581 0.445 0.542 1.023 1.019 0.881 1064 1361 2909 1185 1674 1953 336.66 0.212 0.738 0.320 0.673 1.066 0.990 0.996 1063 1360 2903 1183 1671 1953 336.67 0.338 0.374 0.591 0.379 1.013 1.061 0.895 1054 1347 2871 1152 1624 1893 340.30 0.097 0.814 0.168 0.818 1.106 0.981 0.936 1321 2804 1151 1621 1889 340.50 0.337 0.735 0.236 0.745 1.091 0.982 0.930 1034 1321 2802 1150 1621 1889 340.65 0.533 0.020 0.347 0.994 1.032 1315 2788 1145	336.35	0.252	0.686	0.372	0.620	1.058	0.996	0.996	1067	1365	2917	1187	1678	1959
336.65 0.309 0.581 0.445 0.542 1.023 1.019 0.881 1064 1362 2909 1185 1674 1953 336.70 0.335 0.533 0.481 0.502 1.026 0.944 1064 1361 2903 1183 1671 1953 336.86 0.212 0.738 0.320 0.673 1.066 0.990 0.996 1063 1360 2903 1183 1671 1950 338.02 0.388 0.374 0.591 0.379 1.013 1.061 0.895 1054 1347 2871 1172 1655 1930 340.30 0.097 0.814 0.168 0.818 1.069 0.981 0.981 1036 1321 2804 1151 1621 1889 340.65 0.533 0.420 0.547 1.091 0.982 0.930 1034 1321 2800 1149 1619 1874 341.10 0.204 0.610 0.347 0.999 1.037 0.865 1028 1311 2777 1	336.60	0.660	0.030	0.932	0.028	1.004	1.022	0.932	1065	1362	2910	1185	1674	1954
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	336.65	0.309	0.581	0.445	0.542	1.023	1.019	0.881	1064	1362	2909	1185	1674	1954
336.86 0.212 0.738 0.320 0.673 1.066 0.990 0.996 1063 1360 2903 1183 1671 1950 338.02 0.398 0.374 0.591 0.379 1.013 1.061 0.895 1054 1347 2871 1172 1655 1930 340.30 0.097 0.814 0.168 0.818 1.106 0.981 0.924 1036 1323 2809 1152 1624 1893 340.55 0.374 0.735 0.236 0.745 1.091 0.982 0.930 1034 1321 2802 1150 1621 1889 340.65 0.553 0.020 0.911 0.023 1.041 1.112 0.949 1034 1321 2802 1145 1613 1880 341.14 0.364 0.334 0.585 0.467 0.999 1.037 0.865 1028 1311 2779 1142 1609 1874 342.30 0.275 0.435 0.477 0.994 1.052 0.979 1014 <td< td=""><td>336.70</td><td>0.335</td><td>0.533</td><td>0.481</td><td>0.502</td><td>1.020</td><td>1.026</td><td>0.944</td><td>1064</td><td>1361</td><td>2907</td><td>1184</td><td>1673</td><td>1953</td></td<>	336.70	0.335	0.533	0.481	0.502	1.020	1.026	0.944	1064	1361	2907	1184	1673	1953
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	336.86	0.212	0.738	0.320	0.673	1.066	0.990	0.996	1063	1360	2903	1183	1671	1950
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	338.02	0.398	0.374	0.591	0.379	1.013	1.061	0.895	1054	1347	2871	1172	1655	1930
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	340.13	0.509	0.130	0.812	0.134	1.024	1.015	0.924	1038	1325	2813	1154	1626	1895
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	340.30	0.097	0.814	0.168	0.818	1.106	0.981	0.981	1036	1323	2809	1152	1624	1893
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	340.50	0.350	0.342	0.575	0.380	1.043	1.079	0.900	1035	1321	2804	1151	1621	1889
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	340.55	0.137	0.735	0.236	0.745	1.091	0.982	0.930	1034	1321	2802	1150	1621	1889
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	340.65	0.553	0.020	0.911	0.023	1.041	1.112	0.949	1034	1320	2800	1149	1619	1887
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	341.10	0.204	0.601	0.345	0.625	1.056	0.991	0.921	1030	1315	2788	1145	1613	1880
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	341.45	0.364	0.334	0.589	0.367	0.999	1.037	0.865	1028	1311	2779	1142	1609	1874
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	342.30	0.275	0.435	0.470	0.480	1.031	1.015	0.989	1022	1303	2757	1135	1598	1861
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	343.30	0.348	0.294	0.590	0.347	0.994	1.052	0.979	1014	1293	2/31	1127	1585	1845
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	343.95	0.318	0.292	0.570	0.362	1.032	1.086	0.938	1010	1286	2/14	1121	15/6	1835
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	344.30	0.146	0.595	0.282	0.670	1.101	0.976	0.982	1007	1283	2706	1118	1572	1829
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	343.13	0.435	0.099	0.789	0.130	1.009	1.111	0.890	1001	12/4	2084	1111	1501	1010
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	340.33	0.430	0.032	0.647	0.043	1.041	1.092	1.010	991	1201	2001	1002	1544	1790
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	047.00 940 99	0.274	0.200	0.345	0.300	1.030	1.095	0.956	965	1202	2027	1095	1502	1760
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	340.33 950.09	0.129	0.308	0.275	0.045	1.000	0.979	1.003	979	1244	2007	1060	1322	1709
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	251 00	0.115	0.452	0.270	0.030	1.110	0.990	0.934	902	1220	2047	1000	1492	1732
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	259 25	0.340	0.070	0.749	0.103	1.015	1.039	0.989	955	1210	2515	1055	1400	1719
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	252 72	0.228	0.211	0.320	0.343	1.045	1.115	0.939	932	1107	2010	1035	1475	1602
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	356 20	0.103	0.402	0.230	0.020	1.100	1.022	0.935	028	1179	2405	1045	1400	1660
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	357 25	0.189	0.402	0.100	0.321	1.100	1 1 1 1 7	0.940	921	1164	2/09	1027	1492	1646
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	359 11	0.105	0.173	0.433	0.521	1 134	1 029	0.000	910	1148	2371	1015	1401	1622
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	360.25	0.001	0.020	0.230	0.076	1 103	1 174	0.000	903	1130	2348	998	1389	16022
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	364 35	0 191	0.038	0.610	0.075	1 084	1 1 1 9	1 022	879	1106	2268	971	1348	1558
369.55 0.149 0.040 0.530 0.098 1.068 1.076 0.999 850 1066 2173 937 1298 1498 378.85 0.064 0.064 0.289 0.198 1.103 1.089 0.958 801 1001 2017 882 1216 1399 390.90 0.016 0.019 0.090 0.072 1.074 1.023 0.996 745 925 1840 817 1120 1285	365.99	0.122	0.000	0.415	0.283	1 110	1 131	0.974	870	1093	2237	960	1332	1538
378.85 0.064 0.090 0.090 1.003 1.003 0.055 0.055 1005 1.103 1.236 1436 390.90 0.016 0.019 0.090 0.072 1.074 1.023 0.996 745 925 1840 817 1120 1285	369 55	0.122	0.120	0.530	0.008	1 068	1 076	0.999	850	1066	2173	937	1298	1498
390.90 0.016 0.019 0.090 0.072 1.074 1.023 0.996 745 925 1840 817 1120 1285	378.85	0.064	0.064	0.289	0.198	1.103	1.089	0.958	801	1001	2017	882	1216	1399
	390.90	0.016	0.019	0.090	0.072	1.074	1.023	0.996	745	925	1840	817	1120	1285

sample. The pertinent polynomial fits had a correlation coefficient R^2 better than 0.99. Concentration measurements were accurate to better than 0.005 mole fraction.

Results

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

$$\ln \gamma_{i} = \ln \left(\frac{Py_{i}}{P_{i}^{0}\mathbf{x}_{i}}\right) + \frac{(B_{ii} - V_{i}^{L})(P - P_{i}^{0})}{RT} + \frac{P}{2RT}\sum y_{j}y_{k}(2\delta_{ji} - \delta_{jk}) \quad (1)$$

where T and P are the boiling point and the total pressure,

Table 3. Antoine Coefficients, Eq 3

compound	A_i	B_i	C_i
methyl 1,1-dimethylethyl ether ^a	5.860 78	1032.988	59.876
hexane ^b	6.000 91	1171.170	48.740
octane ^a	6.051 41	1354.107	63.888

^a Reich et al. (1998). ^b TRC Tables, k-1490.

 $V_i^{\rm L}$ is the molar liquid volume of component *i*, P_i^0 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

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \tag{2}$$

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^0

Table 4.	Constants	for	the	Redlich -	Kister	Model

				A. Binar	ies					
system	n	$b_{ij} imes 1$	0 ² c	$c_{ij} imes 10^2$	$d_{ij} imes 10^2$	rmsd	% dev ^a	max %	6 dev ^b	
$\begin{array}{c} \text{MTBE (1) + he} \\ \text{MTBE (1) + oc} \\ \text{hexane (2) + oc} \end{array}$	exane $(2)^c$ etane $(2)^d$ etane $(3)^e$	8.36 4.61 0.00		0.28 0.07 0.00	0.00 0.00 0.00	0.004 0.007	1.3 2. 2.6 4.		8 7	
B. Ternary										
					γ_1/γ_2			γ_1/γ_3		
system	$C imes 10^2$	$D_1 imes 10^2$	$D_2 imes 10^2$	$rmsd imes 10^3$	max dev/%	dev/%	$rmsd imes 10^3$	max dev/%	dev/%	
MTBE (1) + hexane (2)	0 3.546	0 0	0 0	8.0 8.0	9.7 9.6	4.7 4.6	9.0 9.0	10.3 10.9	4.9 4.9	
+ octane (3)	-2.721	$-11.944 \\ -0.263$	0 21.49	7.0 7.0	9.4 9.3	4.3 4.3	9.0 9.0	11.3 11.6	5.0 5.1	

^{*a*} Percent average deviation. ^{*b*} Maximum percent deviation. ^{*c*} Wisniak et al. (1997a). ^{*d*} Wisniak et al. (1997b). ^{*e*} Calculated assuming ideal behavior in the liquid phase.

 Table 5. Parameters and Prediction Statistics for Different G^E Models

					bubbl	bubble-point pressures		dew-point pressures		sures
model	ij	A_{ij} /J mol $^{-1}$	A_{ij} /J mol ⁻¹	α_{ij}	$\Delta P(\%)$	Δy_1	Δy_2	$\Delta P(\%)$	Δx_1	Δx_2
Redlich-Kister ^a					2.50	0.0103	0.0100	1.45	0.0108	0.0114
	1 - 2	259.30	353.35	0.358						
NRTL	1 - 3	-1150.49	1503.98	0.300	2.14	0.0065	0.0079	2.22	0.0074	0.0083
	2 - 3	0.00	0.00							
	1 - 2	901.71	-244.70							
Wilson ^b	1 - 3	1879.95	-1558.65		2.20	0.0064	0.0077	2.28	0.0073	0.0080
	2 - 3	207.75	-192.35							
	1 - 2	51.36	131.29							
UNIQUAC ^c	1 - 3	-774.74	982.98		2.22	0.0048	0.0052	1.72	0.0062	0.0060
	2 - 3	0.00	0.00							
$UNIFAC^d$					4.31	0.0163	0.0168	4.62	0.0138	0.0147

^{*a*} Parameters have been included in Table 4. ^{*b*} Liquid volumes have been estimated from the Rackett equation. ^{*c*} Molecular parameters are those calculated from UNIFAC. ^{*d*} Calculations based on modified UNIFAC (Larsen, 1987).

were calculated according to the Antoine equation

$$\log (P_i^0/kPa) = A_i - \frac{B_i}{(T/K) - C_i}$$
 (3)

where the Antoine constants A_i , B_i , and C_i are reported in Table 3. The molar virial coefficients B_{ii} and B_{ij} were estimated by the method of Hayden and O'Connell (1975) assuming the association parameter η to be negligible. Critical properties of the pure components were taken from DIPPR (Daubert and Danner, 1989). The last two terms in eq 1 contributed less than 7% to the activity coefficients, and their influence was important only at very dilute concentrations. The ternary activity coefficients reported in Table 2 are estimated accurate to within 3% and 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:

$$D < D_{\max}$$
 (4)

Details of the calculation procedure of D and D_{max} appear in a previous publication (Wisniak, 1996). For the experimental points reported here, D never exceeded 0.145 while the smallest value of D_{max} was 0.184.

The activity coefficients for the ternary system were correlated from the following Redlich–Kister expansion (1948):

$$\frac{G^{E}}{RT} = x_{1}x_{2}[b_{12} + c_{12}(x_{1} - x_{2}) + d_{12}(x_{1} - x_{2})^{2}] + x_{1}x_{3}[b_{13} + c_{13}(x_{1} - x_{3}) + d_{13}(x_{1} - x_{3})^{2}] + x_{2}x_{3}[b_{23} + c_{23}(x_{2} - x_{3}) + d_{23}(x_{2} - x_{3})^{2}] + x_{1}x_{2}x_{3}(C + D_{1}x_{1} + D_{2}x_{2}) \quad (5)$$

The following relationships can be derived from from eq 5

$$\ln \frac{\gamma_1}{\gamma_2} = (b_{13} - b_{23})x_3 + (b_{12} + Cx_3)(x_2 - x_1) - c_{13}x_3(x_3 - 2x_1) + c_{12}[2x_1x_2 - (x_1 - x_2)^2] - c_{23}x_3(2x_2 - x_3) + D_1x_1x_3(2x_2 - x_1) - d_{13}x_3(x_3 - 3x_1)(x_1 - x_3) + D_2x_3x_2(x_2 - 2x_1) + d_{12}(x_2 - x_1)[(x_2 - x_1)^2 - 4x_1x_2] - d_{23}x_3(x_2 - x_3) (3x_2 - x_3) (6)$$

$$\ln \frac{\gamma_1}{\gamma_3} = (b_{13} + D_2 x_2^2 + C x_2)(x_3 - x_1) + x_2(b_{12} - b_{23}) + c_{23} x_2(2x_3 - x_2) + c_{13}[6x_1x_3 - (1 - x_2)^2] + c_{12} x_2(2x_1 - x_2) + D_1 x_1 x_2(2x_3 - xx) + d_{23} x_2(3x_3 - x_2)(x_2 - x_3) + d_{13}(x_1 - x_3)[8x_1x_3 - (1 - x_2)^2] + d_{12} x_2(x_2 - 3x_1)(x_2 - x_1)$$
(7)

where b_{ij} , c_{ij} , and d_{ij} are the constants for the pertinent ij binary and C, D_1 , and D_2 are ternary constants. All the constants in eqs 6 and 7 are assumed to be independent of the temperature. Data and constants for two of the binary systems have already been reported (Wisniak et al., 1977,



Figure 1. Isothermals for the ternary system MTBE (1) + hexane (2) + octane (3) at 94 kPa from 328 K to 378 K, every 10 K. Coefficients from eq 9.

1998), and the system hexane (2) + octane (3) was assumed to be ideal. The ternary Redlich-Kister coefficient was obtained by a Simplex optimization technique, and the results indicated that terms such as d_{ij} were null. 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 C, D_1 , and D_2 (Table 4)—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 (the binary parameters have been reported by Wisniak et al. (1997a,b)), and somewhat less by the UNIFAC model (Fredenslund et al., 1977; Larsen et al., 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 5. The boiling points of the systems were correlated by the equation proposed by Wisniak and Tamir (1976):

$$T/\mathbf{K} = \sum_{i=1}^{n} x_i T_i^0 / \mathbf{K} + \sum_{i,j=1}^{n} \{ x_i x_j \sum_{k=0}^{m} C_k (x_i - x_j)^k \} + x_1 x_2 x_3 \{ A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3) \}$$
(8)

In this equation *n* is the number of components (n = 2 or 3), T_i^0 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:

$$T/\mathbf{K} = \sum_{i=1}^{3} x_i T_i^0 + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2 + \dots] + x_1 x_3 [A_{13} + B_{13}(x_1 - x_3) + C_{13}(x_1 - x_3)^2 + \dots] + x_2 x_3 [A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2 + \dots]$$
(9)

In eq 9 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 % average deviation and root-mean-square deviation



Figure 2. Three-dimensional graph $T-x_1-x_2$.

Table 6.Coefficients in Correlation of Boiling Points,Eqs 10 and 11, Average Deviation, andRoot-Mean-Square Deviations in Temperature, rmsd(*TI*K)

A. Eq 10 (Fit from Binary Constants)

	-			-							
Α	A B C		max	dev/K ^a	avg dev/K ^b	rmsd ^c					
52.210	-82.334	0	1	.41	0.54	0.09					
	Binary Constants										
s	ystem		C_0	C_1	C_2	C_3					
MTBE (1)	+ hexane (2)) ^d -9	.2092	3.39392	-12.0157						
MTBE (1)	+ octane (2)	e -65	.0826	21.8543	-13.3961	28.4200					
hexane (2) + octane (3)	$f^{f} - 41$.4730	16.5117	-7.4023	2.8684					
		B. Ea	11 (Di	rect Fit)							

	D. Eq II (Direct III)									
ij	A_{ij}	B_{ij}	C_{ij}	$\max {\rm dev}/{\rm K}^a$	avg dev/K ^b	rmsd ^c				
1-2	-4.482	6.810	0.094							
1 - 3	-63.093	38.802	-32.608	0.99	0.25	0.05				
2-3	-36.603	21.129	0.496							

^{*a*} Maximum deviations. ^{*b*} Average deviations. ^{*c*} rmsd (*T*/K): rootmean-square deviation, { $\Sigma(T_{exptl} - T_{obsd})^2$ }^{0.5}/*N*. ^{*d*} Wisniak et al. (1997a). ^{*e*} Wisniak et al. (1997b). ^{*f*} Calculated assuming ideal behavior in the liquid phase.

(rmsd) and a smaller number of parameters than those for eq 8. Both equations may require a similar number of constants for similar accuracy, but the direct correlation allows an easier calculation of boiling isotherms (Figures 1 and 2). The various constants of eqs 8 and 9 are reported in Table 6, 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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Literature Cited

- Daubert, T. E.; Danner, R. P. Physical and Thermodynamic Properties of Pure Chemicals. Data Compilation, Taylor & Francis: Bristol, PA, 1989.
- Fredenslund, A.; Gmehling, J.; Rasmussen, P. Vapor-Liquid Equilibria Using UNIFAC; Elsevier: Amsterdam, 1977.
- Hayden, J.; O'Connell, J. A. A Generalized Method for Predicting Second Virial Coefficients. *Ind. Eng. Chem. Process Des. Dev.* 1975, 14, 209–216.
- Kirso, K.; Kudryatseva, L. S.; Eisen, O. Liquid–Vapor Equilibrium in 1-Hexene-Hexane-Octane, Benzene-1-Heptene-Heptane, 1-Heptene-Heptane-Toluene Ternary Systems and in the Corresponding Binary Systems at 55 °C. *Eesti NSV Tead. Akad. Toim., Geol.* 1975, 24, 15–22.
- Larsen, B.; Rasmussen, P.; Fredenslund, Aa. A Modified UNIFAC Group-Contribution-Model For the Prediction of Phase Equilibria and Heats of Mixing Ind Eng. Chem. Res **1987**, 26 2274–2286
- and Heats of Mixing. Ind. Eng. Chem. Res. **1987**, 26, 2274–2286. Leslie, E. H.; Carr, A. R. Vapor Pressure of Organic Solutions. Ind. Eng. Chem. **1925**, 17, 810–817.

- Li, J.-D.; Li, Y.-G.; Chen, J.; Lu, J.-F.; Teng, T. Activity Coefficient Data and Their Correlation for Tributyl Phosphate-Hydrocarbon and Uranyl Nitrate Tributyl Phosphate Complex-Hydrocarbon Solutions Measured by Head-Space Gas Chromatography at 25 °C. *Fluid Phase Equilib.* 1990, *58*, 307–318.
 McDermott, C.; Ellis, S. R. M. A Multicomponent Consistency Test. *Chem. Eng. Sci.* 1965, *20*, 293–296.
- Rackett, H. G. Equation of State for Saturated Liquids. J. Chem. Eng. Data 1970, 15, 514–517.
- Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* 1948, 40, 345-348. Reich, R.; Cartesa, M.; Wisniak, J.; Segura, H. Phase Equilibria in
- the Systems Methyl 1,1-Dimethylethyl Ether + Benzene and + Toluene. J. Chem. Eng. Data **1998**, 43, 299–303.
- Tamir, A. New Correlations for Fitting Multicomponent Vapor-Liquid Equilibria Data and Prediction of Azeotropic Behavior. Chem. Eng. *Sci.* **1981**, *36*, 1453–1465. *TRC-Thermodynamic Tables-Hydrocarbons*; Thermodynamics Re-
- search Center, The Texas A&M University System: College Station, TX, extant 1996; fa-1490, 1990; k-1490, 1990.
- TRC-Thermodynamic Tables-Non-Hydrocarbons, Thermodynamics Research Center, The Texas A&M University System: College Station, TX, extant 1996; a-6040, 1963.
- Van Ness, H. C.; Abbott, M. M. Classical Thermodynamics of Nonelectrolyte Solutions; McGraw-Hill Book Co.: New York, 1982.
- Weigno, S.; Qin, A. X.; McElry, P. J.; Williamson, A. G. (Vapour + Liquid) Equilibria of (*n*-Hexane + *n*-Hexadecane), (*n*-Hexane +

n-Octane) and (n-Octane + n-Hexadecane). J. Chem. Thermodyn. **1990**, 22, 905-914.

- Wisniak, J. A New Test for the Thermodynamic Consistency of Vapor-
- Liquid Equilibrium. *Ind. Eng. Chem. Res.* **1993**, *32*, 1531–1533. Wisniak, J. Phase Equilibria in the Systems Methyl Methanoate + 1-Bromopropane, Ethyl Methanoate + Cyclohexane, and Ethyl Methanoate + 1-Bromopropane + Cyclohexane. J. Chem. Eng. Data **1996**, *41*, 468–473.
- Wisniak, J.; Tamir, A. Correlation of the Boiling Point of Mixtures. Wisniak, J.; Talini, A. Contration of the Louing - Line *Chem. Eng. Sci.* **1976**, *31*, 631–635. Wisniak, J.; Tamir, A. Vapor–Liquid Equilibria in the Ternary System
- Wisniak, J., Tahin, A. Vapor Enquid Equinibra in the Fernary System Water–Formic Acid–Acetic Acid and Water–Acetic Acid–Propionic Acid. J. Chem. Eng. Data 1977, 22, 253–260.
 Wisniak, J.; Magen, E.; Shachar, M.; Zeroni, I.; Reich, R.; Segura, H. Isobaric Vapor–Liquid Equilibria in the Systems Methyl 1,1-Distribution build build build build build.
- Dimethylethyl Ether + Hexane and + Heptane. J. Chem. Eng. Data **1997a**, *42*, 243–247.
- Wisniak, J.; Embon, G.; R. Shafir, R.; Segura, H.; Reich, R. Isobaric Vapor-Liquid Equilibria in the Systems Methyl 1,1-Dimethylethyl Ether + Octane and Heptane + Octane. J. Chem. Eng. Data 1997b, *42*, 1191–1194.

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