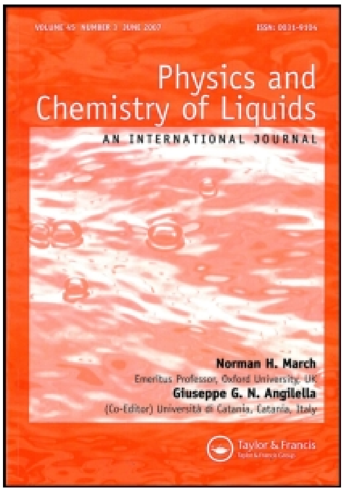

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Phase Equilibria in the Ternary System Methyl 1,1-Dimethylethyl Ether Heptane Octane

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To cite this Article Wisniak, Jaime , Embon, Gabriela , Shafir, Ran , Reich, Ricardo and Segura, Hugo(1998) 'Phase Equilibria in the Ternary System Methyl 1,1-Dimethylethyl Ether Heptane Octane', Physics and Chemistry of Liquids, 37: 1, 51 — 63

To link to this Article: DOI: 10.1080/00319109808032799

URL: http://dx.doi.org/10.1080/00319109808032799

Phys. Chem. Liq., 1998, Vol. 37, pp. 51–63
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Printed in India.

PHASE EQUILIBRIA IN THE TERNARY SYSTEM METHYL 1,1-DIMETHYLETHYL ETHER + HEPTANE + OCTANE

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(Received 24 July 1997)

Vapor-liquid equilibrium at 94 kPa has been determined for the ternary system methyl 1,1-dimethylethyl ether (MTBE) + heptane + 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.

Keywords: Vapor-liquid equilibrium; activity coefficients; ternary systems

1. INTRODUCTION

The Reformulated Gasoline Program of the United States requires that gasoline must fulfill stringent requirements on ozone-forming and air toxic emissions. In order to do so gasoline has to contain 2.7% oxygen by mass in the winter months in areas that are in non-attainment on CO standards. Commonly used oxygenating additives are MTBE, methanol and ethanol. MTBE it is the primary oxygenated compound being used

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to improve the octane rating and pollution-reducing capability of gasolines. Phase equilibrium 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 three binary systems methyl 1,1-dimethylethyl ether (1) + heptane (2), methyl 1,1-dimethylethyl ether (1) + octane (3), and heptane (2) + octane (3) have already been reported at 94 kPa by Wisniak *et al.* [1, 2], the three systems present slight to moderate positive deviations from ideality and do not have azeotropic points. The present work was undertaken to measure vapor-liquid equilibria (VLE) data for the ternary system for which no data are available.

2. EXPERIMENTAL SECTION

2.1. Purity of Materials

Methyl 1,1-dimethylethyl ether (99.93 mass%), heptane (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 I.

2.2. 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, about 100 mL of the solution is heated to its boiling point

TABLE I 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]	328.29[a]
	1.3663[b]	328.35[b]
heptane (99.57)	1.3851[a]	371.54[a]
	1.38513[c]	371.553[c]
octane (99.80)	1.3948[a]	398.50[a]
	1.3952[d]	398.83[d]

[a] Measured. [b] TRC Tables, a-6040 [12]. [c] TRC Tables, fa-1460 [13]. [d] TRC Tables, f-1490 [13].

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 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 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 μL after the system had achieved equilibrium, were analyzed by gas chromatography on a Gow-Mac series 550 P 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 (368.15, 493.15, and 543.15) K. 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.

3. 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 II, together with the activity coefficients γ_i which were calculated from the following equation [3]:

$$\ln \gamma_i = \ln\left(\frac{P y_i}{P_i^0 x_i}\right) + \frac{(B_{ii} - V_i^L)(P - P_i^0)}{RT} + \frac{P}{2RT}\sum\sum y_j\, y_k(2\delta_{ji} - \delta_{jk}) \tag{1}$$

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^0 is the pure component vapor

TABLE II Experimental vapor-liquid equilibria data for methyl 1,1-dimethylethyl ether (1) + heptane (2) + octane (3) at 94 kPa

					Activity coefficients			Virial coefficients $(cm^3 . mol^{-1})$					
T K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	$-B_{12}$	$-B_{13}$	$-B_{23}$	$-B_{11}$	$-B_{22}$	$-B_{33}$
329.45	0.869	0.017	0.981	0.005	0.999	1.187	1.175	1111	2114	2973	1537	1818	2504
331.25	0.790	0.024	0.969	0.008	1.027	1.185	1.079	1096	2082	2924	1514	1791	2464
332.95	0.752	0.032	0.960	0.012	1.014	1.163	1.093	1082	2052	2879	1494	1766	2428
334.75	0.700	0.037	0.948	0.014	1.020	1.146	1.100	1067	2022	2832	1473	1740	2390
336.95	0.637	0.044	0.938	0.017	1.039	1.108	0.989	1050	1985	2776	1448	1709	2345
340.75	0.556	0.053	0.905	0.025	1.028	1.148	1.086	1020	1925	2685	1406	1658	2271
340.95	0.512	0.283	0.836	0.128	1.024	1.098	1.047	1019	1922	2680	1403	1655	2267
342.35	0.520	0.258	0.839	0.126	0.974	1.123	0.899	1008	1900	2648	1388	1637	2241
343.25	0.413	0.548	0.729	0.264	1.039	1.076	0.965	1002	1887	2628	1379	1626	2224
344.85	0.385	0.546	0.717	0.270	1.048	1.047	0.959	990	1863	2592	1362	1605	2195
345.55	0.416	0.349	0.772	0.183	1.025	1.086	0.950	985	1853	2577	1355	1597	2183
345.55	0.431	0.224	0.813	0.119	1.041	1.098	0.991	985	1853	2577	1355	1597	2183
345.85	0.458	0.064	0.862	0.036	1.032	1.155	1.059	983	1848	2570	1352	1593	2178
345.95	0.452	0.035	0.879	0.020	1.062	1.132	0.978	982	1847	2568	1351	1592	2176
346.85	0.386	0.420	0.733	0.228	1.013	1.073	0.976	976	1834	2549	1342	1581	2160
346.95	0.348	0.553	0.695	0.285	1.061	1.014	1.005	975	1833	2547	1341	1580	2158
347.85	0.391	0.240	0.780	0.136	1.034	1.079	1.057	969	1820	2527	1332	1569	2143
348.45	0.419	0.138	0.824	0.079	1.003	1.075	0.987	964	1811	2514	1326	1561	2132
348.65	0.414	0.069	0.846	0.042	1.036	1.129	0.974	963	1809	2511	1324	1559	2129
349.45	0.306	0.598	0.641	0.337	1.042	1.024	0.962	958	1798	2494	1317	1550	2116
349.55	0.314	0.561	0.644	0.327	1.016	1.053	0.997	957	1796	2492	1316	1549	2114
349.95	0.360	0.183	0.781	0.115	1.064	1.126	0.966	954	1791	2484	1312	1544	2107
350.85	0.375	0.074	0.816	0.049	1.043	1.149	1.008	948	1778	2466	1303	1533	2092
352.15	0.355	0.075	0.808	0.051	1.054	1.119	0.974	939	1761	2439	1291	1519	2071
352.55	0.250	0.669	0.555	0.424	1.020	1.039	0.993	937	1755	2432	1287	1514	2064
353.65	0.280	0.474	0.619	0.321	0.984	1.073	0.915	929	1741	2410	1277	1502	2047
353.75	0.275	0.433	0.636	0.289	1.026	1.056	0.954	929	1740	2408	1276	1500	2045

354.25	0.228	0.676	0.537	0.438	1.033	1.007	0.949	926	1733	2398	1271	1495	2037
355.15	0.234	0.605	0.548	0.409	1.006	1.023	0.923	920	1721	2381	1263	1485	2023
355.45	0.186	0.786	0.462	0.530	1.058	1.010	0.967	918	1718	2375	1260	1482	2018
357.35	0.250	0.369	0.611	0.270	0.991	1.034	1.017	906	1694	2340	1243	1461	1989
358.25	0.265	0.081	0.720	0.067	1.078	1.141	1.029	900	1682	2323	1235	1452	1976
358.55	0.262	0.134	0.703	0.111	1.055	1.131	0.964	898	1679	2318	1233	1448	1971
359.45	0.141	0.784	0.377	0.600	1.028	1.014	0.923	893	1668	2301	1225	1439	1958
361.15	0.109	0.828	0.315	0.662	1.069	1.006	1.009	882	1647	2271	1210	1421	1933
363.35	0.077	0.878	0.233	0.750	1.055	1.006	1.043	869	1621	2233	1192	1399	1901
363.95	0.172	0.330	0.522	0.302	1.047	1.057	0.925	866	1614	2223	1187	1393	1893
366.45	0.160	0.283	0.504	0.280	1.025	1.066	0.929	851	1585	2181	1167	1369	1858
366.75	0.026	0.957	0.089	0.904	1.109	1.008	0.913	849	1582	2176	1164	1366	1854
366.95	0.021	0.967	0.079	0.915	1.223	1.004	1.149	848	1580	2173	1163	1364	1852
368.65	0.075	0.604	0.268	0.600	1.099	1.004	0.918	839	1561	2145	1149	1348	1829
371.35	0.134	0.111	0.503	0.131	1.093	1.109	0.992	824	1532	2103	1128	1323	1794
371.45	0.018	0.769	0.068	0.830	1.093	1.008	0.979	823	1531	2101	1127	1322	1792
373.85	0.112	0.123	0.450	0.157	1.109	1.119	0.971	810	1505	2064	1109	1300	1762
374.65	0.014	0.634	0.062	0.755	1.159	1.019	0.959	806	1497	2052	1103	1293	1752
376.55	0.013	0.555	0.058	0.704	1.138	1.031	0.958	796	1478	2024	1090	1276	1729
377.95	0.035	0.405	0.143	0.537	1.040	1.038	0.951	789	1464	2004	1080	1264	1712
379.15	0.063	0.198	0.287	0.260	1.119	0.998	0.985	783	1452	1987	1071	1254	1698
380.95	0.056	0.167	0.266	0.240	1.126	1.039	0.968	773	1435	1962	1058	1239	1677
381.95	0.036	0.238	0.163	0.357	1.046	1.055	0.980	768	1425	1948	1052	1231	1665
383.45	0.045	0.134	0.219	0.219	1.091	1.105	0.970	761	1411	1928	1041	1219	1648
384.25	0.039	0.141	0.191	0.232	1.091	1.095	0.974	757	1403	1917	1036	1212	1639
386.85	0.027	0.122	0.133	0.208	1.025	1.061	0.994	745	1380	1883	1019	1192	1611
391.45	0.012	0.051	0.069	0.097	1.086	1.072	1.004	723	1339	1824	989	1157	1562
392.45	0.008	0.035	0.048	0.065	1.087	1.006	1.018	719	1330	1812	983	1149	1552

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 were calculated according to the Antoine equation:

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

where the Antoine constants A_i, B_i, and C_i are reported in Table III. The molar virial coefficients B_{ii} and B_{ij} were estimated by the method of Hayden and O'Connell [4] by assuming the association and solvation parameters to be negligible. The last two terms in Equation (1) contributed less than 7% to the activity coefficients, and their influence was important only at very dilute concentrations. The calculated activity coefficients reported in Table II are estimated accurate to within 3% and were found to be thermodynamically consistent as tested by the L-W method of Wisniak [5] and the McDermot-Ellis method [6] modified by Wisniak and Tamir [7]. 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

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

TABLE III Antoine Coefficients, Equation (3)

Compound	A_i	B_i	C_i
methyl 1,1-dimethylethyl ether[a]	5.86078	1032.988	59.876
heptane[b]	6.02023	1263.909	56.718
octane[c]	6.05141	1354.107	63.888

[a]Reich [14]. [b]TRC Tables, k-1490 [12]..

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

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

The errors in the measurements x, P and T were as previously indicated. The first term in Equation (6) was the dominant one. For the experimental points reported here D never exceeded 0.153 while the smallest value of $D_{\max}$ was 0.198.

The activity coefficients for the ternary system were correlated using the following Redlich-Kister expansion [8]:

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

The following relationships can be derived from Equation (7)

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

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

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 Equations (8) and (9) are assumed to be independent of the temperature. Data and constants for the three binary systems have already been reported [1, 2]. 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 C, D_1 and D_2 (Tab. IV) - 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, and somewhat less by the UNIFAC model [9]

TABLE IV Constants for the Redlich-Kister model

A. BINARIES

System	$b_{ij}\times 10^2$	$c_{ij}\times 10^2$	$d_{ij}\times 10^2$	*rmsd*	*% dev*[a]	*max% dev*[b]
MTBE(1) + heptane (2)[c]	7.34	0.08		0.008	3.2	5.9
MTBE (1) + octane (2)[d]	4.25	−0.01		0.008	2.6	4.6
heptane (2) + octane (3)[d]	1.87	−1.00	2.43	0.004	1.3	3.0

B. TERNARY

System				γ_1/γ_2			γ_1/γ_3		
	$C\times 10^2$	$D_1\times 10^2$	$D_2\times 10^2$	*rmsd* $\times 10^3$	*max dev / %*	*dev/%*	*rmsd* $\times 10^3$	*max dev /%*	*dev/%*
MTBE (1)	0	0	0	8.0	12.6	5.3	7.0	8.8	4.5
+ heptane (2)	2.323	0	0	8.0	12.2	5.2	7.0	8.7	4.5
+ octane (3)	3.368	−5.080	0	8.0	12.2	5.2	7.0	8.8	4.5
	0.749	−1.832	5.204	8.0	12.1	5.2	7.0	8.8	4.6

[a] Percent average deviation. [b] maximum percent deviation. [c] Wisniak *et al.* [1]. [d] Wisniak *et al.* [2].

using only binary parameters, both for bubble point-pressure and dew point pressure calculations, as shown by the statistics and parameters given in Table V. In addition, Table V reports the predictions obtained from the modified UNIFAC model [10], concluding that the binary data allow a good prediction of the ternary system.

The boiling points of the systems were correlated by the equation proposed by Wisniak and Tamir [11]:

$$T/K = \sum_{i=1}^{n} x_i T_i^0/K + \sum_{i,j=1}^{n} \left\{ x_i x_j \sum_{k=0}^{m} C_k (x_i - x_j)^k \right\} \qquad (10)$$
$$+ x_1 x_2 x_3 \{ A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3)]$$

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 [12] for the direct correlation of ternary data, without use of binary data:

$$T/K = \sum_{i=1}^{3} x_i T_i^0 + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2 + \ldots]$$
$$+ x_1 x_3 [A_{13} + B_{13}(x_1 - x_3) + C_{13}(x_1 - x_3)^2 + \ldots]$$
$$+ x_2 x_3 [A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2 + \ldots] \qquad (11)$$

In Equation (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 % average deviation and root mean square deviation (rmsd) and a smaller number of parameters than those for Equation (10). Both equations may require similar number of constants for similar accuracy, but the direct correlation allows as easier calculation of boiling isotherms (Figs. 1 and 2). The various constants of Equations (10) and (11) are reported in Table VI, which also contains information indicating the degree of goodness of

TABLE V Parameters and prediction statistics for different G^E models

Model	*ij*	A_{ij}/ *J mol*$^{-1}$	A_{ji}/ *J mol*$^{-1}$	α_{ij}	*Bubble point pressures* $\Delta P(\%)$	Δy_1	Δy_2	*Dew point pressures* $\Delta P(\%)$	Δx_1	Δx_2
NRTL	1 – 2	–375.85	932.01	0.352	1.76	0.0071	0.0085	1.48	0.0068	0.0095
	1 – 3	–1150.49	1503.98	0.300						
	2 – 3	–1493.86	1886.20	0.300						
[a]Wilson	1 – 2	788.24	−291.11	–	1.74	0.0071	0.0086	1.48	0.0069	0.0097
	1 – 3	1879.95	−1558.65							
	2 – 3	1734.36	−1352.71							
[b]UNIQUAC	1 – 2	–145.97	319.33	–	1.79	0.0072	0.0073	1.40	0.0076	0.0071
	1 – 3	–774.74	982.98							
	2 – 3	–645.40	734.54							
[c]UNIFAC	–	–	–	–	4.12	0.0164	0.0161	2.18	0.0137	0.0160

[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).

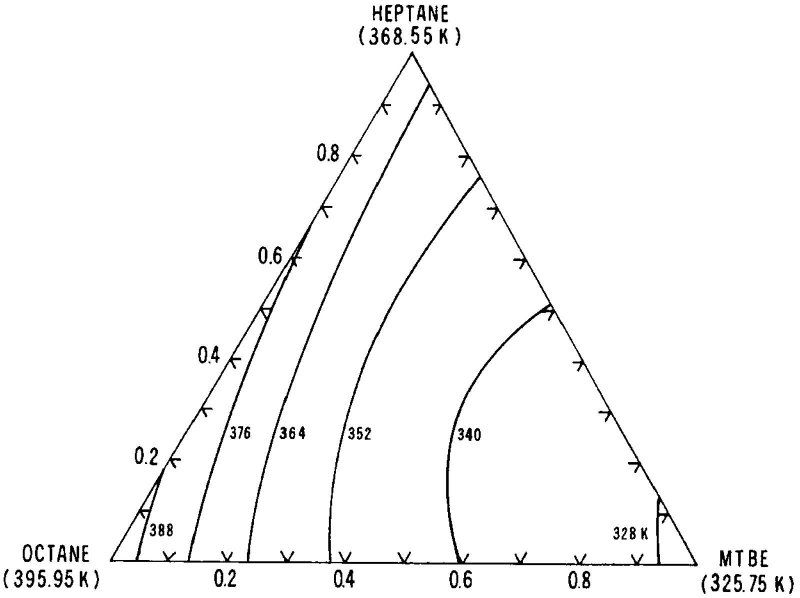

FIGURE 1 Isothermals for the ternary system MTBE (1) + heptane (2) + octane (3) at 94 kPa from 344 K to 366 K, every 12 K. Coefficients from Equation (11).

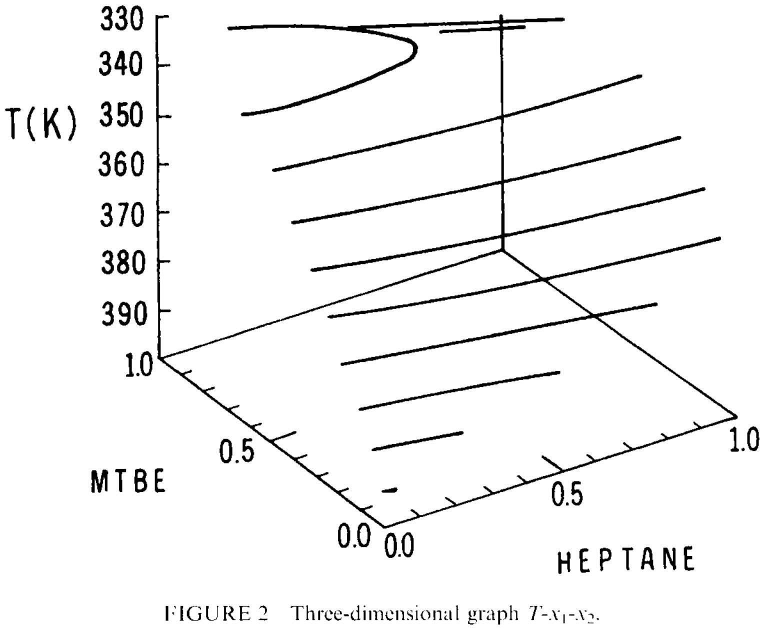

FIGURE 2 Three-dimensional graph T-x_1-x_2.

TABLE VI Coefficients in correlation of boiling points, equations (10) and (11), average deviation and root mean square deviations in temperature, rmsd (T/K)

A. Equation (10)(fit from binary constants)

A	*B*	*C*, *D*	*max dev/K*[a]	*avr dev/K*[b]	*rmsd*[c]
−147.8173	103.4212	0	6.60	2.20	0.30

BINARY CONSTANTS

System	C_0	C_1	C_2	C_3
MTBE (1) + heptane (2)[d]	−30.1335	12.7723	−7.46950	-
MTBE (1) + octane (2)[e]	−65.0826	21.8543	−13.3961	28.4200
heptane (2) + octane (3)[e]	−9.54589	5.92320		

B. Equation 11 (direct fit)

ij	A_{ij}	B_{ij}	C_{ij}	*max dev/K*[a]	*avr dev/K*[b]	*rmsd*[c]
1 − 2	−31.116	11.628	3.6329	1.80	0.40	0.06
1 3	−70.155	34.462	−3.0611			
2 3	−10.814	8.668	−11.4567			

[a] Maximum deviations. [b] Average deviations. [c] rmsd (T/K): Root mean square deviation, $\{\sum(T_{\text{expt}} - T_{\text{calc}})^2\}^{0.5}/N$. [d] Wisniak *et al.* [1]. [e] Wisniak *et al.* [2].

the correlation. It is clear that for the ternary system in question a direct fit of the data gives a much better fit.

Acknowledgement

Yehudit Reizner helped in the experimental part. This work was partially financed by FONDECYT, Chile, project No. 1960583.

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