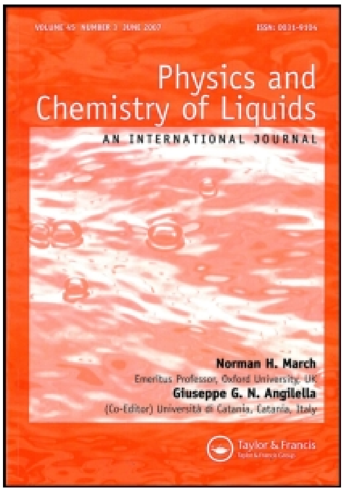

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Phase Equilibria in the Ternary System Methyl 1,1-Dimethylethyl Ether Benzene Toluene

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To cite this Article Reich, Ricardo , Cartes, Marcela , Segura, Hugo and Wisniak, Jaime(2000) 'Phase Equilibria in the Ternary System Methyl 1,1-Dimethylethyl Ether Benzene Toluene', Physics and Chemistry of Liquids, 38: 1, 73 — 87
To link to this Article: DOI: 10.1080/00319100008045298
URL: http://dx.doi.org/10.1080/00319100008045298

Phys. Chem. Liq., 2000, Vol. 38, pp. 73-87
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Printed in Malaysia.

PHASE EQUILIBRIA IN THE TERNARY SYSTEM METHYL 1,1-DIMETHYLETHYL ETHER + BENZENE + TOLUENE

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(Received 20 September 1998)

Consistent vapor-liquid equilibrium data at 94 kPa have been determined for the ternary system methyl 1,1-dimethylethyl ether (MTBE) + benzene + toluene. The results indicate that the system deviates positively from ideality and that no azeotrope is present. The ternary activity coefficients of the system have been correlated with the composition using the Redlich-Kister, Wilson, NRTL, UNIQUAC, and UNIFAC, models. It is shown that most of the models allow a very good prediction of the phase equilibrium of the ternary system using the pertinent parameters of the binary systems. In addition, the Wisniak-Tamir relations were used for correlating bubble-point temperatures.

Keywords: Vapor-liquid equilibrium; fuel oxygenating additives; unleaded gasoline; ethers; aromatics

INTRODUCTION

Ethers are usually added to gasoline as oxygenates to replace lead anti-knock agents, to inhibit the reactivity of combustion emissions and to reduce pollution. The commonly used oxygenating additives

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*Corresponding author. e-mail: rreich@udec.cl are MTBE and light alkanols like methanol and ethanol. MTBE it is the primary oxygenated compound being used 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 gasoline mixtures, for which aromatics may constitute up to 3.5% weight. The system reported here constitutes a particular case of such mixtures.

Vapor–liquid equilibrium (VLE) data for the system methyl 1,1-dimethylethyl ether + benzene have been reported at (323.17, 343.15 and 363.05) K by Jin *et al.* [1] and at 94 kPa by Reich *et al.* [2]. For the system methyl 1,1-dimethylethyl ether + toluene, vapor–liquid equilibrium data have been reported at 363.15 K Plura *et al.* [3] and at 94 kPa by Reich *et al.* [2]. According to these references, the two binary systems present slight to moderate positive deviations from ideality and do not have azeotropes. In addition, many references of experimental VLE data pertaining to the system benzene + toluene can be found in DECHEMA Chemistry Data [4]. Because of problems of thermodynamic consistency, very few of the recopilated systems (as for example, the data of Griswold *et al.* [5]; measured at 393.15 K) allow to conclude that the system behaves like an ideal solution, as commonly classified in textbooks. Kassman and Knapp [6] reported very precise VLE measurements of the system benzene + toluene at 313.15 K and 334.15 K, showing that the system under consideration has an almost constant relative volatility very close to the theoretical ideal value; on the basis of their data the system will be considered ideal in the data treatment that follows in this work. Partial VLE data of simulated gasoline mixtures, which include aromatics and MTBE, have been reported by Wu *et al.* [7] at fixed compositions and temperatures, however, these do not allow a study of specific interactions in solution nor a critical evaluation of the possibility of predicting the VLE of multicomponent unleaded gasoline mixtures from binary contributions.

The present work was undertaken to measure VLE data for the ternary mixture MTBE + benzene + toluene at 94 kPa for which no data have been previously published. It is part of our experimental program to determine the vapor–liquid behavior of gasoline components and oxygenates [2, 8–10].

1. EXPERIMENTAL SECTION

1.1. Chemicals

Methyl 1, 1-dimethylethyl ether (99.95 mass %), benzene (99.9 + mass %), and toluene (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 of the pure components (as determined by GLC) appear in Table I. Appropriate precautions were taken when handling methyl 1, 1-dimethylethyl ether, in order to avoid peroxide formation, and benzene, a human carcinogen.

1.2. Apparatus and Procedure

An all glass Fischer LABODEST vapor–liquid-equilibrium apparatus, model 601 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 returned again to the immersion heater. The temperature in the VLE still has been determined with a Systemteknik S1224 digital

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 %)	$n_D(293.15\,K)$	T/K
Methyl 1, 1-dimethylethyl	1.36922[a]	327.85[a]
ether (99.95)	1.3690[b]	328.35[b]
Benzene (99.9 +)	1.50072[a]	353.18[a]
	1.50111[c]	353.21[c]
Toluene (99.80)	1.49688[a]	383.65[a]
	1.49694[c]	383.76[c]

[a] Measured;
[b] TRC Tables, a-6040 [22];
[c] TRC Tables, a-3200 [23].

temperature meter and a Pt100 Ω probe calibrated at the Swedish Statens Provningsanstalt with the IPTS-68 temperature scale. The accuracy is estimated as ±0.2 K. The total pressure of the system is controlled by a vacuum pump capable to work under vacuum up to 0.25 kPa. The pressure is measured with a Fischer pressure transducer calibrated against an absolute mercury-in-glass manometer (22 mm diameter precision tubing with cathetometer reading), the overall accuracy is estimated as ±0.02 kPa. On the average the system reached equilibrium conditions after 1–2 h operation. Samples, taken by syringing 1.0 μL after the system had achieved equilibrium, were analyzed by gas chromatography on a Varian 3400 apparatus provided with a thermal conductivity detector and a Tsp model SP4400 electronic integrator. The column was 3 m long and 0.3 cm in diameter, packed with SE-30. Column, injector and detector temperatures were (343.15, 423.15, 493.15) K, respectively. 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. At least three analyses were made of each composition. Concentration measurements were accurate to better than ±0.001 mole fraction.

2. RESULTS AND DISCUSSIONS

The temperature T and liquid-phase x_i, and vapor-phase y_i mole fraction measurements at $P = 94\,\text{kPa}$ are reported in Table II, together with the activity coefficients γ_i which were calculated from the following equation [11]:

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

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^0 is the pure component vapor pressure, B_{ii} and B_{jj} are the second virial coefficients of the pure gases,

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

	Experimental data				*Activity coefficients*			*Virial coefficients/cm^3 × mol^{-1}*					
T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	$-B_{11}$	$-B_{22}$	$-B_{33}$	$-B_{12}$	$-B_{13}$	$-B_{23}$
372.37	0.038	0.090	0.163	0.175	1.206	1.057	0.975	833	848	1255	829	1015	1024
364.92	0.040	0.298	0.163	0.175	1.212	1.036	0.949	874	891	1326	870	1068	1079
358.75	0.043	0.500	0.163	0.175	1.203	1.027	0.930	911	929	1390	906	1116	1128
353.53	0.046	0.697	0.145	0.465	1.198	1.023	0.915	943	964	1448	939	1159	1172
349.46	0.049	0.883	0.133	0.650	1.212	1.011	0.865	970	993	1496	966	1195	1209
365.52	0.094	0.111	0.124	0.775	1.192	1.060	0.954	871	887	1320	866	1064	1074
362.62	0.094	0.204	0.120	0.858	1.192	1.048	0.939	888	905	1349	883	1086	1097
359.80	0.095	0.302	0.340	0.180	1.168	1.031	0.945	904	923	1379	900	1108	1119
357.25	0.093	0.405	0.317	0.302	1.159	1.027	0.938	920	939	1406	916	1128	1140
355.17	0.093	0.486	0.293	0.406	1.163	1.028	0.921	933	953	1429	929	1146	1158
352.77	0.094	0.583	0.267	0.504	1.176	1.027	0.887	948	969	1457	944	1166	1179
350.21	0.094	0.682	0.254	0.570	1.212	1.032	0.849	965	987	1487	961	1188	1202
348.61	0.095	0.784	0.244	0.636	1.178	1.010	0.864	976	999	1506	972	1203	1217
358.34	0.176	0.112	0.235	0.692	1.136	1.042	0.962	913	932	1394	909	1120	1131
355.74	0.180	0.205	0.221	0.741	1.123	1.026	0.963	929	949	1423	925	1141	1153
353.07	0.184	0.296	0.509	0.146	1.126	1.034	0.959	946	967	1453	942	1163	1176
350.21	0.192	0.394	0.482	0.244	1.139	1.035	0.931	965	987	1487	961	1188	1202
348.04	0.195	0.494	0.461	0.328	1.128	1.032	0.930	980	1003	1514	976	1208	1222
345.86	0.199	0.596	0.451	0.401	1.130	1.029	0.902	995	1019	1541	991	1228	1243
344.26	0.200	0.699	0.428	0.469	1.118	1.016	0.889	1006	1031	1562	1003	1243	1259
350.75	0.284	0.108	0.412	0.527	1.104	1.020	0.984	961	983	1481	958	1184	1197
348.70	0.283	0.208	0.392	0.580	1.104	1.025	0.975	975	998	1505	972	1202	1216
346.76	0.286	0.303	0.656	0.110	1.098	1.031	0.957	988	1013	1529	985	1220	1234
344.54	0.292	0.400	0.619	0.200	1.105	1.029	0.938	1004	1029	1558	1001	1240	1256
342.90	0.291	0.502	0.590	0.276	1.096	1.029	0.943	1016	1042	1579	1013	1256	1272
341.24	0.293	0.603	0.570	0.339	1.094	1.025	0.894	1028	1055	1602	1025	1273	1289
345.22	0.384	0.109	0.538	0.404	1.070	1.014	1.021	999	1024	1549	996	1234	1249
343.42	0.380	0.212	0.516	0.458	1.072	1.050	1.012	1012	1038	1573	1009	1251	1267

TABLE II (Continued)

	Experimental data				*Activity coefficients*			*Virial coefficients/cm^3 × mol^{-1}*					
T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	$-B_{11}$	$-B_{22}$	$-B_{33}$	$-B_{12}$	$-B_{13}$	$-B_{23}$
341.90	0.384	0.309	0.740	0.093	1.062	1.047	0.978	1023	1050	1593	1020	1266	1283
339.80	0.393	0.406	0.698	0.177	1.066	1.052	0.956	1039	1067	1622	1036	1287	1304
340.75	0.496	0.099	0.669	0.245	1.032	0.998	1.034	1031	1059	1609	1029	1277	1295
339.38	0.492	0.200	0.647	0.302	1.028	1.054	1.007	1042	1070	1628	1039	1291	1309
337.85	0.495	0.300	0.813	0.072	1.027	1.051	0.968	1053	1083	1649	1051	1307	1325
335.67	0.495	0.402	0.772	0.147	1.051	1.074	0.939	1070	1101	1681	1069	1330	1349
337.14	0.590	0.102	0.742	0.209	1.012	1.015	1.081	1059	1089	1659	1057	1314	1333
335.35	0.601	0.198	0.712	0.266	1.009	1.078	1.063	1073	1104	1686	1071	1333	1353
334.15	0.600	0.299	0.853	0.067	1.006	1.086	0.969	1082	1115	1704	1081	1346	1366
333.55	0.691	0.100	0.822	0.130	1.010	0.978	1.095	1087	1120	1713	1086	1353	1373
332.25	0.688	0.206	0.789	0.190	1.011	1.063	1.041	1098	1132	1733	1097	1367	1388
330.45	0.792	0.100	0.896	0.056	1.006	0.953	1.046	1113	1148	1761	1112	1388	1410
329.77	0.792	0.155	0.858	0.120	1.005	1.041	1.042	1119	1154	1772	1118	1396	1418

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:

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

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 [12] assuming the association parameter η to be zero. Critical properties of components were taken from DIPPR [13]. The last two terms in Eq. (1) contributed less than 5% to the activity coefficients, and their influence was important only at very dilute concentrations. The ternary 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 [14] and the McDermot-Ellis method [15] modified by Wisniak and Tamir [16]. According to these references two experimental points a and b are considered thermodynamically consistent if the following condition is fulfilled:

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

where 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, Eq. (3)

Compound	A_i	B_i	C_i
Methyl 1, 1-dimethylethyl ether[a]	5.86078	1032.988	59.880
Benzene[a]	6.08817	1243.256	48.640
Toluene[a]	6.22372	1432.925	43.929

[a] Reich *et al.* [2].

and N is the number of components. The maximum deviation $D_{\max}$ is given by:

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

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 0.045 while the smallest value of $D_{\max}$ was 0.235.

The activity coefficients for the ternary system were correlated from the following Redlich-Kister expansion [17]:

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

The following relationships can be derived from Eq. (7)

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

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

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. (8) and (9) are assumed to be independent of the temperature. Data and constants for two of the binary systems were calculated from the data of Reich *et al.* [2] and the liquid phase of the system benzene (2) + toluene (3) was assumed to be ideal. The ternary Redlich-Kister coefficients were obtained using 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 and compositions were correlated very well by the NRTL and Wilson models (the pertinent binary parameters were calculated from the data of Reich *et al.* [2] assuming ideal behavior for the benzene (2) + toluene (3) binary pair in the liquid phase), and somewhat less, by the modified UNIFAC model [18, 19] 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. It can be concluded 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 [20];

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

In the 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 considered 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 [21] for the direct correlation of ternary data, without use of binary data:

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

TABLE IV Constants for the Redlich-Kister model (parameters expressed in $\log_{10}$)

A. Binary systems

System	$b_{ij} \times 10^2$	$c_{ij} \times 10^2$	$d_{ij} \times 10^2$	*rmsd*	*% dev* [a]	*max % dev* [b]
MTBE (1) + Benzene (2) [c]	5.57	−1.11	1.01	0.005	1.8	4.8
MTBE (1) + Toluene (3) [c]	6.14	0.40	3.76	0.008	3.5	13.09
Benzene (2) + Toluene (3) [c]	0.00	0.00	0.00	—	—	—

B. Ternary system

System [d]	$C \times 10^2$	$D_1 \times 10^2$	$D_2 \times 10^2$	*rmsd* × 10^2	$\frac{(\gamma_1/\gamma_2}{max\ dev/\%)}$	*dev/%*	*rmsd* × 10^2	$\frac{(\gamma_1/\gamma_3}{max\ dev/\%)}$	*dev/%*
MTBE (1) +	0.00	0.00	0.00	1.0	10.1	2.4	2.0	21.2	8.9
Benzene (2) +									
Toluene (3)	−12.97	34.61	37.50	1.0	12.9	2.0	2.0	17.67	8.0

[a] Percent average deviation.

[b] Maximum percent deviation.

[c] Calculated from the data of Reich *et al.* [2].

[d] Calculated assuming ideal behaviour in the liquid phase.

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

Model	*ij*	A_{ij}/ J mol^{-1}	A_{ij}/ J mol^{-1}	α_{ij}	*System*	*Bubble-point pressures*			*Dew-point pressures*		
						ΔP(%)	$\Delta y_1 \times 10^2$	$\Delta y_2 \times 10^2$	ΔP(%)	$\Delta x_1 \times 10^2$	$\Delta x_2 \times 10^2$
[a] WILSON	1 – 2	82.85	389.51		1 + 2	0.28	0.25	0.25	0.41	0.26	0.26
	1 – 3	8.84	437.73		1 + 3	0.31	0.35	—	0.92	0.60	—
	2 – 3	− 139.12	222.95		2 + 3	0.00	—	0.00	0.00	—	0.00
					1 + 2 + 3	1.01	0.66	0.50	1.08	0.63	1.02
NRTL	1 – 2	− 732.88	1197.31	0.3	1 + 2	0.28	0.24	0.24	0.40	0.26	0.26
	1 – 3	219.26	217.06	0.3	1 + 3	0.30	0.34	—	0.92	0.60	—
	2 – 3	0.00	0.00	0.3	2 + 3	0.00	—	0.00	0.00	0.00	—
					1 + 2 + 3	1.09	0.68	0.50	1.04	0.62	1.02
[b] UNIQUAC	1 – 2	− 60.13	− 60.67		1 + 2	0.85	4.43	4.43	4.72	4.03	4.03
	1 – 3	− 62.40	− 236.81		1 + 3	2.23	2.66	—	6.57	4.24	—
	2 – 3	22.14	22.04		2 + 3	0.03	—	0.27	0.28	—	0.34
					1 + 2 + 3	2.52	3.85	3.18	6.09	4.46	2.80
[c] UNIFAC					1 + 2 + 3	3.10	1.68	0.56	1.51	1.25	0.69

[a] Liquid volumes have been estimated from the Rackett equation [24]).

[b] Molecular parameters are those calculated from UNIFAC.

[c] Calculations based on modified UNIFAC [19].

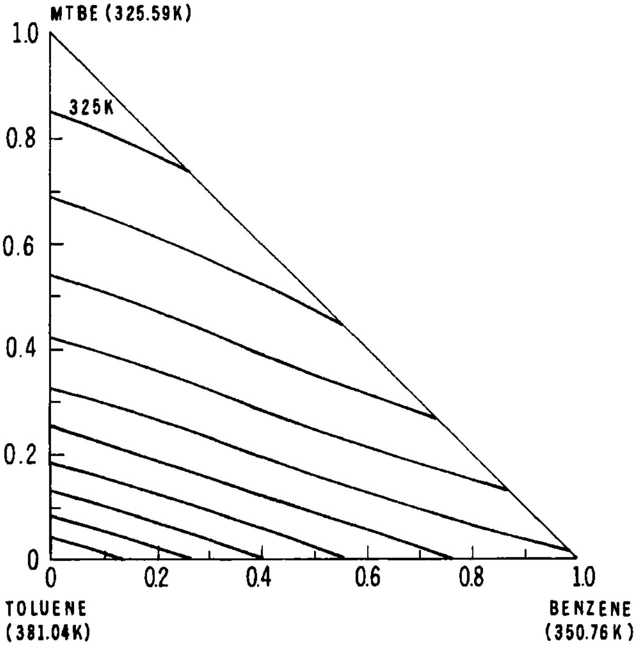

FIGURE 1 Isothermals for the ternary system MTBE (1) + benzene (2) + toluene (3) at 94 kPa from 325 K to 365 K, every 5 K. Coefficients from Eq. (11).

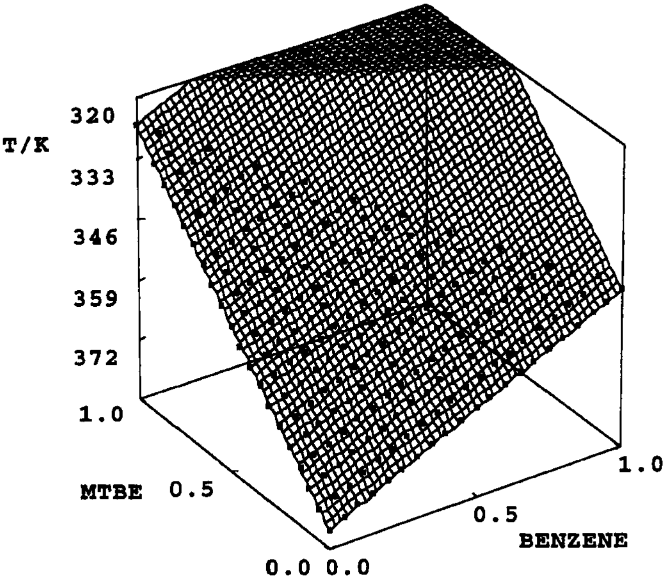

FIGURE 2 Three-dimensional graph T-x_1-x_2.

TABLE VI Coefficients in correlation of boiling points Eqs. (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]
– 34.597	12.482	0	0.80	0.32	0.06

System	C_0	*Binary constants* C_1	C_2	*max dev* /*K* [a]
MTBE (1) + Benzene (2)[d]	– 15.0509	13.6307	11.3331	1.17
MTBE (1) + Toluene (3)[a]	– 45.1567	24.9083	–12.0349	0.35
Benzene (2) + Toluene (3)[e]	– 12.4484	2.4253	– 0.7796	–

B. Equation 11 (*direct fit*)

ij	A_{ij}	B_{ij}	C_{ij}	*max dev*/*K* [a]	*avr dev*/*K* [b]	*rmsd*[c]
1–2	– 16.166	8.352	2.467	0.35	0.13	0.03
1 - 3	–46.605	30.619	–10.695			
2–3	–14.597	–0.803	–0.246			

[a] Maximum deviation.

[b] Average deviation.

[c] rmsd (T/K): Root mean square deviation, $\{\sum(T_{\mathrm{expt}} - T_{\mathrm{calc}})^2\}^{0.5}/N$.

[d] Calculated from the data of Reich *et al.* (1998).

[e] Calculated assuming ideal behaviour in the liquid phase.

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 % average deviation and root mean square deviation (rmsd) and a smaller number of parameters than those for Eq. (10). Both equations may require similar number of constants for similar accuracy, but the direct correlation allows an easier calculation of boiling isotherms (Figs. 1 and 2). The various constants of Eqs. (10) and (11) are reported in Table VI, 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.

Acknowledgement

This work was financed by FONDECYT, Chile, project No. 1960583.

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