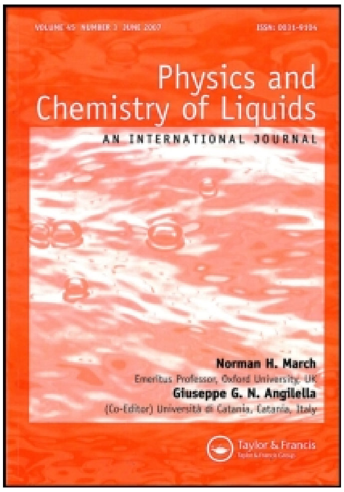

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Phase Equilibria in the Systems Ethyl 1,1-Dimethylethyl Ether Benzene 2,2,4-Trimethylpentane and Benzene 2,2,4-Trimethylpentane at 94.00 kPa

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PHASE EQUILIBRIA IN THE SYSTEMS ETHYL 1,1-DIMETHYLETHYL ETHER + BENZENE + 2,2,4-TRIMETHYLPENTANE AND BENZENE + 2,2,4-TRIMETHYLPENTANE AT 94.00 kPa

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Consistent vapor-liquid equilibria data at 94.00 kPa have been determined for the ternary system ethyl 1,1-dimethylethyl ether + benzene + 2,2,4-trimethylpentane and for its constituent binary benzene + 2,2,4-trimethylpentane, in the temperature range 343 to 370 K. The systems exhibit slight positive deviations from ideal behavior and the system benzene + 2,2,4-trimethylpentane presents an azeotrope. The VLE data have been correlated with the mole fraction using the Redlich-Kister, Wilson, NRTL, UNIQUAC, and Tamir relations. These models, in addition to UNIFAC, allow good prediction of the VLE properties of the ternary system from those of the pertinent binary systems.

Keywords: Vapor-liquid equilibrium; Fuel oxygenating additive; Unleaded gasoline; Ether; ETBE

INTRODUCTION

Recent years have seen the substitution of lead and aromatic octane-enhancers by oxygenates, particularly ethers. MTBE was introduced in

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*Corresponding author. e-mail: hsegura@diq.udec.cl the 1970s and today is the primary oxygenated compound being used to improve the octane rating of gasoline, but it has the drawbacks of easily dissolving in water and of difficult removal from water. These drawbacks are behind the recent decision the state of California to phase out its use within the next years. It is important, then, to research the possible use of other ethers of higher molecular weights, like ETBE, which may be less harmful to the environment. ETBE shows good characteristics for unleaded gasoline formulation including low volatility, high-octane value, and low water solubility.

Phase equilibrium data of oxygenated mixtures are important for predicting the vapor phase concentration that would be in equilibrium with hydrocarbon mixtures, and scarce data are available for multicomponent mixtures that include ETBE.

Vapor-liquid equilibrium (VLE) data for the binary systems ETBE + benzene and ETBE + 2,2,4-trimethylpentane (isooctane) have been reported at 94 kPa by Segura *et al.* [1] and Wisniak *et al.* [2], Clark *et al.* [3] have also reported the vapor pressures at (298, 323) K for a limited range of the liquid phase mole fractions. These two binaries exhibit slight to moderate positive deviations from ideality and do not present azeotropes. Vapor-liquid equilibrium data for the system benzene + isooctane have been reported by Goral and Asmanova [4] at 313.15 K, by Kenny [5] at 298.15 K, by Sieg [6] at 101.32 kPa, and by Weissman and Wood [7] at (308.15, 318.15, 328.15, 338.15 and 348.15) K. According to these sources, the binary system benzene + 2,2,4-trimethylpentane presents positive deviation from ideal behavior. In addition, the systems present an azeotrope rich in benzene, which disappears as temperature increases.

The present work was undertaken to measure VLE data for the system ETBE + benzene + 2,2,4-trimethylpentane at 94.00 kPa, for which isobaric data are not available.

EXPERIMENTAL SECTION

Materials

ETBE (96.0 + mass %) was purchased from *TCI* (*Tokyo Chemical Industry Co. Ltd.*, Japan). Benzene (99.9 mass %) and 2,2,4-trimethylpentane (99.8 mass %) were purchased from Aldrich. ETBE was purified to more than 99.7 + mass % by rectification in a 1-m height -- 30 mm diameter Normschliffgerätebau adiabatic distillation column (packed with 3 × 3 mm stainless steel spirals), working at a 1 : 100 reflux ratio. After this step, gas chromatography failed to show any significant impurity. The properties and purity (as determined by gas liquid chromatography) of the pure components appear in Table I. Appropriate precautions were taken when handling ETBE in order to avoid peroxide formation, and benzene, a human carcinogen.

Apparatus and Procedure

An all-glass vapor-liquid-equilibrium apparatus model 601, manufactured by Fischer Labor und Verfahrenstechnik (Germany), was used in the equilibrium determinations. In this circulation-method apparatus, the mixture is heated to its boiling point by a 250 W immersion heater. The vapor-liquid mixture flows through an extended contact line (Cottrell pump) 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. The temperature in the VLE still has been determined with a Systemteknik S1224 digital temperature meter, and a Pt 100 Ω probe calibrated at the Swedish Statens Provningsanstält on the IPTS-68. The accuracy is estimated as ± 0.02 K. The

TABLE I Mole % purities (mass %), refractive index n_D at Na D line, and normal boiling points T of pure components

	n_D (293.15 *K*)		T_b (101.3 *kPa*)/*K*	
Component (*purity*/*mass* %)	*exptl.*	*lit.*	*exptl.*	*lit.*
ethyl 1,1-dimethylethyl ether (99.9+)	1.37594[a]	1.37564[b]	345.85[a]	345.86[c]
benzene (99.9+)	1.50113[a]	1.50111[d]	353.20[a]	353.21[d]
2,2,4-trimethylpentane (99.9+)	1.39162[a]	1.39162[e]	372.24[a]	372.39[f]

[a] Measured.
[b] DIPPR (Daubert and Danner [12]).
[c] Krähenbühl and Gmehling [23].
[d] *TRC* Tables [24], a-3200.
[e] *TRC* Tables [24], a-1010.
[f] Boublík *et al.* [25].

total pressure of the system is controlled by a vacuum pump capable of pressures as low as 0.25 kPa. The pressure has been 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 ± 0.03 kPa. On the average the system reaches equilibrium conditions after 2 to 3 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 Thermo Separation Products 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 (323.15, 383.15, 473.15) K respectively, for all the systems. 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.

RESULTS AND DISCUSSION

The temperature T and liquid-phase x_i, and vapor-phase y_i mole fraction measurements for the system benzene (2) + isooctane (3) at $P = 94.00$ kPa are reported in Table II and in Figures 1 to 2, together with the activity coefficients γ_i which were calculated from the following equation [8]:

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - V_i^L)(P - P_i^0)}{\mathrm{R}T} + y_j^2 \frac{\delta_{ij} P}{\mathrm{R}T} \tag{1}$$

where T and P are the boiling point and the total pressure, V_i^L is the molar liquid volume of component i, B_{ii} and B_{jj} are the second virial coefficients of the pure gases, P_i^0 is the vapor pressure, B_{ij} the cross second virial coefficient and

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

TABLE II Experimental vapor-liquid equilibrium data for the binary system benzene (2) + 2,2,4-trimethylpentane (3) at 94.00 kPa

T/K	x_2	y_2	γ_2	γ_3	$-B_{22}/$ $cm^3 \times mol^{-1}$	$-B_{33}/$ $cm^3 \times mol^{-1}$	$-B_{23}/$ $cm^3 \times mol^{-1}$
350.76	0.000	0.000		1.000			
367.62	0.044	0.095	1.336	1.000	875	1695	1215
365.78	0.089	0.181	1.322	1.000	886	1719	1231
364.28	0.131	0.256	1.324	0.993	895	1738	1245
362.18	0.193	0.345	1.283	1.000	908	1767	1264
360.52	0.246	0.417	1.275	1.000	918	1790	1279
359.34	0.287	0.460	1.246	1.014	926	1806	1290
358.25	0.331	0.509	1.234	1.015	933	1822	1301
357.06	0.383	0.558	1.209	1.026	940	1839	1312
355.97	0.433	0.598	1.183	1.049	948	1855	1323
355.17	0.476	0.637	1.174	1.051	953	1867	1331
354.39	0.524	0.669	1.146	1.080	958	1878	1339
353.66	0.575	0.704	1.123	1.106	963	1889	1346
353.01	0.630	0.741	1.100	1.135	968	1899	1353
352.53	0.669	0.765	1.084	1.168	971	1907	1358
352.06	0.722	0.798	1.063	1.213	974	1914	1363
351.70	0.768	0.826	1.046	1.267	977	1919	1367
351.44	0.807	0.850	1.032	1.323	979	1924	1369
351.15	0.857	0.884	1.020	1.394	981	1928	1372
350.94	0.906	0.919	1.009	1.491	982	1931	1375
350.82	0.958	0.960	1.000	1.655	983	1933	1376
350.78	0.974	0.975	1.001	1.673	983	1934	1376
350.77	0.977	0.977	1.000	1.741	983	1934	1376
350.76	1.000	1.000	1.000				

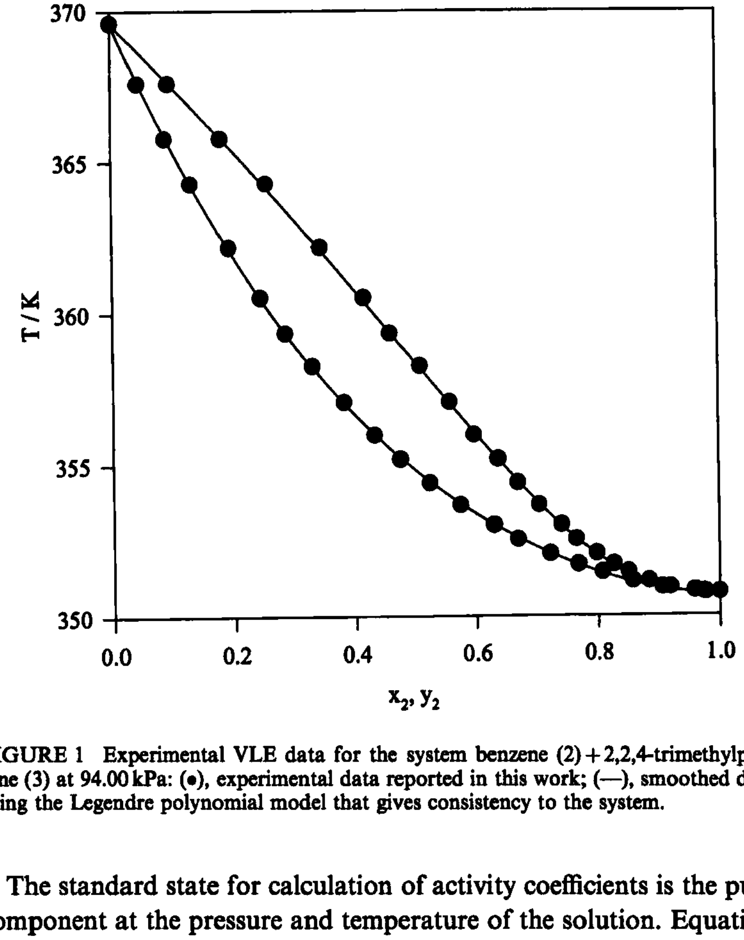

FIGURE 1 Experimental VLE data for the system benzene (2) + 2,2,4-trimethylpentane (3) at 94.00 kPa: (•), experimental data reported in this work; (—), smoothed data using the Legendre polynomial model that gives consistency to the system.

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Equation (1) is valid at low and moderate pressures when the virial equation of state truncated after the second coefficient is adequate to describe the vapor phase of the pure components and their mixtures, and liquid volumes of the pure components are incompressible over the pressure range under consideration. The molar virial coefficients B_{ii} and B_{ij} were estimated by the method of Hayden and O'Connell [9] using the parameters suggested by Prausnitz *et al.* [10]. Liquid volumes were estimated from the correlation proposed by Rackett [11]. Critical properties of both components were taken from DIPPR [12]. The last two terms in Eq. (1), particularly the second one that expresses the correction due to the non ideal behavior of the vapor phase,

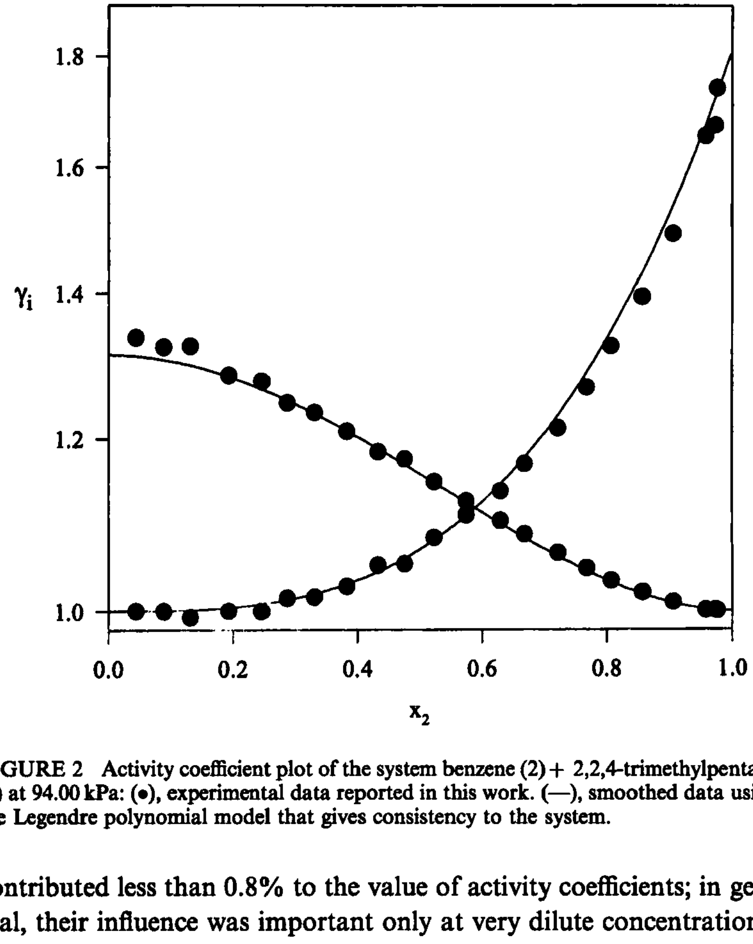

FIGURE 2 Activity coefficient plot of the system benzene (2) + 2,2,4-trimethylpentane (3) at 94.00 kPa: (•), experimental data reported in this work. (—), smoothed data using the Legendre polynomial model that gives consistency to the system.

contributed less than 0.8% to the value of activity coefficients; in general, their influence was important only at very dilute concentrations.

The equilibrium properties an activity coefficients of the ternary system ETBE (1) + benzene (2) + isooctane (3) at 94 kPa are reported in Table III. For this system γ_i were calculated from the following equation [8]:

$$\gamma_i = \frac{y_i P}{x_i P_i^0} \tag{3}$$

In Eq. (3) the vapor phase is assumed to be an ideal gas and the pressure dependence of the liquid phase fugacity is neglected. Equation (3) was selected to calculate activity coefficients of the ternary system because the low pressures observed in the present VLE

TABLE III Experimental vapor-liquid equilibrium data for the ternary system ETBE (1) + benzene (2) + 2,2,4-trimethylpentane (3) at 94.00 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
344.73	0.835	0.114	0.871	0.103	1.002	1.097	1.106
345.27	0.784	0.116	0.839	0.109	1.011	1.114	1.123
345.63	0.643	0.307	0.692	0.280	1.006	1.075	1.169
345.79	0.678	0.221	0.738	0.208	1.011	1.100	1.130
346.42	0.572	0.326	0.635	0.308	1.011	1.087	1.144
346.69	0.692	0.115	0.778	0.116	1.016	1.144	1.120
346.80	0.463	0.485	0.519	0.449	1.011	1.050	1.240
346.95	0.476	0.423	0.538	0.403	1.013	1.075	1.182
347.28	0.602	0.208	0.684	0.209	1.009	1.125	1.115
347.64	0.381	0.517	0.440	0.496	1.013	1.060	1.238
347.80	0.504	0.305	0.580	0.309	1.005	1.112	1.139
348.10	0.266	0.683	0.319	0.645	1.037	1.027	1.374
348.22	0.286	0.614	0.340	0.593	1.024	1.047	1.291
348.34	0.413	0.394	0.484	0.401	1.006	1.098	1.152
348.69	0.586	0.118	0.703	0.128	1.019	1.160	1.085
348.96	0.318	0.486	0.379	0.498	1.005	1.084	1.181
349.04	0.195	0.707	0.239	0.690	1.030	1.032	1.348
349.09	0.484	0.219	0.587	0.241	1.016	1.156	1.096
349.56	0.218	0.585	0.266	0.604	1.010	1.072	1.222
349.60	0.387	0.317	0.474	0.349	1.011	1.142	1.106
349.86	0.104	0.798	0.133	0.791	1.046	1.020	1.418
350.07	0.293	0.413	0.361	0.454	1.004	1.123	1.143
350.10	0.061	0.888	0.082	0.875	1.087	1.006	1.552
350.38	0.111	0.693	0.139	0.721	1.008	1.053	1.288
350.64	0.204	0.505	0.254	0.556	0.998	1.105	1.165
350.65	0.497	0.115	0.633	0.136	1.019	1.189	1.063
351.02	0.402	0.208	0.517	0.247	1.017	1.179	1.070
351.29	0.111	0.600	0.141	0.663	0.994	1.086	1.191
351.49	0.302	0.302	0.393	0.361	1.016	1.171	1.076
351.92	0.209	0.402	0.273	0.478	1.005	1.148	1.095

352.60	0.113	0.487	0.149	0.583	0.995	1.131	1.122
353.20	0.384	0.115	0.533	0.152	1.028	1.222	1.036
353.31	0.297	0.211	0.410	0.275	1.018	1.203	1.052
353.60	0.207	0.302	0.289	0.394	1.020	1.196	1.048
354.11	0.112	0.399	0.157	0.517	1.004	1.169	1.066
355.68	0.292	0.111	0.438	0.160	1.031	1.238	1.026
355.77	0.207	0.206	0.307	0.293	1.019	1.221	1.032
356.16	0.110	0.297	0.165	0.426	1.021	1.216	1.032
358.47	0.108	0.204	0.176	0.323	1.034	1.252	1.015
358.50	0.187	0.112	0.309	0.180	1.048	1.266	1.016
361.49	0.103	0.106	0.185	0.187	1.042	1.277	1.009

data makes these simplifications reasonable. In fact, as discussed before, vapor phase corrections may be neglected in the system benzene (2) + isooctane (3). In addition, and as discussed by Reich *et al.* [13] and by Aucejo *et al.* [14], the scarce physical information available for mixtures of ETBE with alkanes does not allow a reliable estimation of their second virial coefficients, thus introducing uncertainty in the estimation of vapor phase corrections.

The temperature dependence of the pure component vapor pressure P_i^0 was calculated using the Antoine equation

$$\log(P_i^0/\mathrm{kPa}) = A_i - \frac{B_i}{(T/K) - C_i} \tag{4}$$

where the Antoine constants A_i, B_i, and C_i are reported in Table IV. The activity coefficients presented in Tables II and III are estimated accurate to within ± 2%. The results reported in these tables indicate that the measured systems exhibit moderate to positive deviations from ideal behavior. In addition, Figure 1 suggests the possibility of an azeotrope for the system benzene (2) + 2,2,4-trimethylpentane (3) at 94 kPa ($x_2^{Az} \sim 0.98$, $T \sim 350.76\,\mathrm{K}$). Due to the experimental error of our determinations, this supposition has not been proved in a definite manner, although the evidence points to the existence of the azeotrope. Our experimental measurements of the boiling temperatures of benzene with traces of 2,2,4-trimethylpentane ($x_2 > 0.99$) show a small depression in the bubble temperature, although inside the range of experimental error. In addition, according to the data of Weissman and Wood [7] and Sieg [6], the azeotrope of the system benzene (2) + 2,2,4-trimethylpentane disappears at atmospheric pressure (for $x_2 = 1$). The evolution of the azeotrope in temperature coincides well with our estimation of the azeotropic point at 94 kPa.

The VLE data reported in Table II for the binary system benzene (2) + 2,2,4-trimethylpentane (3) were found to be thermodynamically

TABLE IV Antoine coefficients, Eq. (4)

Compound	A_i	B_i	C_i
ETBE[a]	5.96651	1151.73	55.06
Benzene[b]	6.08817	1243.26	48.64
2,2,4-trimethylpentane[c]	5.88343	1224.46	56.47

[a] Reich *et al.* [26].
[b] Segura *et al.* [1].
[c] Wisniak *et al.* [2].

consistent by the point-to-point test of Van Ness *et al.* [15], as modified by Fredenslund *et al.* [16]. Consistency criteria ($\Delta y \leq 0.01$) were met using a three-parameter Legendre polynomial and considering fugacity corrections. Consistency statistics are presented in Table V, according to which it is possible to conclude a very good fit of the data and activity coefficients as shown in Figure 2. In addition, as shown in Figure 3, the consistency model allows a fair prediction of the isothermal data reported by Sieg [6], yielding an average deviation of 0.3 K in bubble temperature.

The vapor-liquid equilibrium data reported in Table III for the ternary system ETBE (1) + benzene (2) + 2,2,4-trimethylpentane (3) were found to be thermodynamically consistent by the McDermott – Ellis method [17], as modified by Wisniak and Tamir [18]. According to these references, two experimental points *a* and *b* are considered thermodynamically consistent if the following condition is fulfilled

$$D < D_{\max} \tag{5}$$

where the local deviation D is given by

$$D = \sum_{i=1}^{N} (x_{ia} + x_{ib})(\ln \gamma_{ia} - \ln \gamma_{ib}) \tag{6}$$

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

$$\begin{aligned} D_{\max} &= \sum_{i=1}^{N} (x_{ia} + x_{ib}) \left(\frac{1}{x_{ia}} + \frac{1}{y_{ia}} + \frac{1}{x_{ib}} + \frac{1}{y_{ib}} \right) \Delta x \\ &\quad + \sum_{i=1}^{N} (x_{ia} + x_{ib}) \frac{\Delta P}{P} + 2 \sum_{i=1}^{N} |\ln \gamma_{ib} - \ln \gamma_{ia}| \Delta x \\ &\quad + \sum_{i=1}^{N} (x_{ia} + x_{ib}) B_j \{ (T_a + C_j)^{-2} + (T_b + C_j)^{-2} \} \Delta T \end{aligned} \tag{7}$$

TABLE V Consistency test statistics for the binary system cyclohexane (2) + 2,2,4-trimethylpentane (3)

$100 \times \Delta y$[a]	ΔP[b]$/kPa$
0.19	0.11

[a] Average absolute deviation in vapor phase mole fractions $\Delta y = 1/N \sum_{i=1}^{N} |y_1^{exptl} - y_1^{calc}|$ (N: number of data points).

[b] Average absolute deviation in pressure $\Delta P = 1/N \sum_{i=1}^{N} |P^{exptl} - P^{calc}|$.

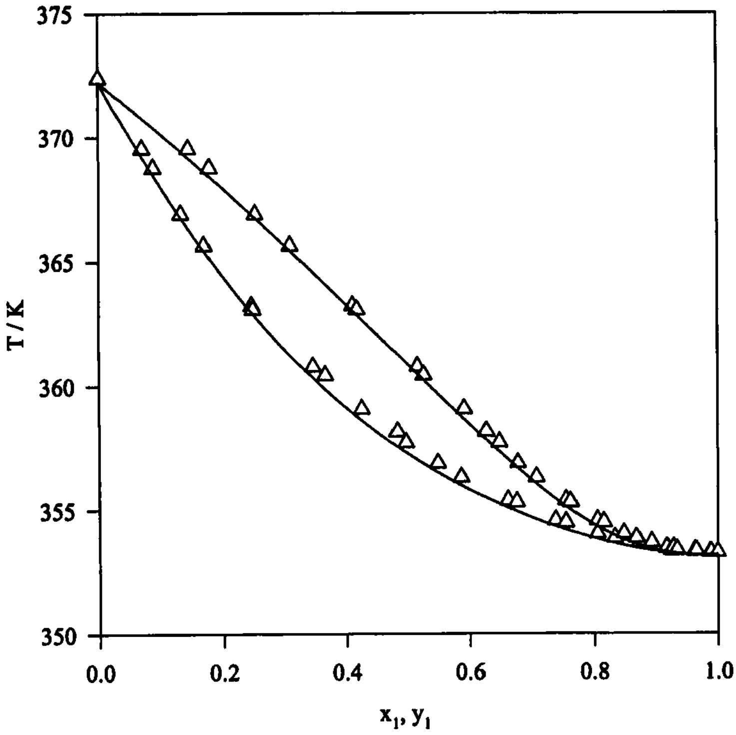

FIGURE 3 Prediction of isobaric VLE data for the system benzene (2)+2,2,4-trimethylpentane (3): (Δ), experimental data of Sieg [6] at 101.32 kPa; (—), predicted from the model that gives consistency to the data measured in this work.

The errors in the measurements Δx, ΔP and ΔT were as previously indicated. The first term in Eq. (7) was the dominant one. For the experimental points reported here D never exceeded the maximum value 0.023, for which the local value of $D_{\max}$ was 0.032. In addition, the smallest calculated value of $D_{\max}$ for the present ternary data was 0.023.

The activity coefficients for the ternary system were correlated with the Redlich-Kister expansion [19]

$$\frac{G^E}{RT} = \sum_{i=1}^{3}\sum_{j>i}^{3} x_i x_j \left[b_{ij} + c_{ij}(x_i - x_j) + d_{ij}(x_i - x_j)^2\right] + x_1 x_2 x_3 [C + D_1 x_1 + D_2 x_2] \quad (8)$$

where b_{ij}, c_{ij} and d_{ij} are the constants for the ij binary, and C, D_1 and D_2 are ternary constants. All the constants in Eq. (8) are assumed to be temperature-independent. In addition, and by the reasons explained before, *no vapor phase correction is considered for constituent binaries* in the data treatment of the ternary system. Data and constants for the binary systems ETBE (1) + benzene (2) and ETBE (1) + 2,2,4-trimethylpentane (3) have been calculated from the data reported by Segura *et al.* [1], and by Wisniak *et al.* [2]. The Redlich-Kister coefficients for the binaries benzene (2) + 2,2,4-trimethylpentane (3) and the values of the constants C, D_1 and D_2 for the ternary mixture, were obtained by a Simplex optimization technique; the results are shown in Table VI. The ternary constants C, D_1 and D_2 were not statistically significant, suggesting that the ternary data can be predicted directly from the binary systems. In fact, as shown in Table VI, equilibrium vapor pressures and vapor phase mole fractions of the ternary system were predicted very well by the Redlich-Kister equation when using only the binary constants, where C, D_1 and D_2

TABLE VI Constants for the Redlich-Kister model, fit, correlation and prediction statistics. system ETBE (1)+benzene (2)+2,2,4-trimethylpentane (3) at 94.00 kPa

	Binary data (parameters for Eq. (8))					
System	$b_{ij} \times 10^1$	$c_{ij} \times 10^1$	$d_{ij} \times 10^2$	*rmsd*[a] $\times 10^{-2}$	*%dev*[b]	*max %dev*[c]
1+2[d]	1.46	0.00	0.00	1.2	0.9	5.2
1+3[e]	1.18	0.00	0.00	0.4	0.7	1.3
2+3	4.24	1.36	2.13	0.1	0.4	1.2

	VLE correlations and predictions					
	Bubble-point pressures			*Dew-point pressures*		
System	$\Delta P/\%$[f]	$100 \times \Delta y_1$[g]	$100 \times \Delta y_2$	$\Delta P/\%$	$100 \times \Delta x_1$	$100 \times \Delta x_2$
1+2[d]	0.12	0.2	0.2	0.16	0.2	0.2
1+3[e]	0.52	0.1	–	0.53	0.2	–
2+3	0.27	–	0.2	0.32	–	0.2
1+2+3[h]	0.33	0.3	0.2	0.33	0.2	0.2

[a] Root mean square deviation in activity coefficients $\{\sum_i^N\{\gamma_i^{exptl} - \gamma_i^{calc}\}^2/N\}^{0.5}$ (N: number of data points).

[b] Average percentage deviation in activity coefficients.

[c] Maximum percentage deviation in activity coefficients.

[d] Calculated from the data of Segura *et al.* [1].

[e] Calculated from the data of Wisniak *et al.* [2].

[f] Average percentage deviation in pressure $\Delta P = 100/N\sum_i^N |P_i^{exptl} - P_i^{calc}|/P_i^{exptl}$.

[g] Average absolute deviation in mole fraction $\Delta y = 1/N\sum_i^N |y_i^{exptl} - y_i^{calc}|$.

[h] Prediction from binary parameters.

TABLE VII Parameters, correlation and prediction statistics for different G^E models

		$a_{ij}/$	$a_{ji}/$		Bubble-point pressures			Dew-point pressures		
Model	*ij*	$J \times mol^{-1}$	$J \times mol^{-1}$	α_{ij}	$\Delta P/\%$[f]	$100 \times \Delta y_1$[g]	$100 \times \Delta y_2$	$\Delta P/\%$	$100 \times \Delta x_1$	$100 \times \Delta x_2$
NRTL	1+2[d]	92.84	314.46	0.3	0.14	0.2	–	0.18	0.2	–
	1+3[e]	261.87	80.47	0.3	0.48	0.1	–	0.50	0.2	–
	2+3	3584.12	−1559.14	0.3	0.23	–	0.2	0.28	–	0.2
	1+2+3[h]				0.61	0.2	0.2	0.61	0.2	0.2
Wilson[a]	1+2[d]	320.98	341.04		0.27	0.1	–	0.27	0.1	–
	1+3[f]	498.70	−152.23		0.47	0.1	–	0.49	0.2	–
	2+3	1013.26	916.76		0.24	–	0.2	0.26	–	0.2
	1+2+3[h]				0.56	0.1	0.1	0.50	0.1	0.1
UNIQUAC[b]	1+2[d]	33.99	−23.45		0.30	0.1	–	0.29	0.1	–
	1+3[e]	−151.71	241.45		0.44	0.1	–	0.46	0.2	–
	2+3	−320.61	797.38		0.22	–	0.2	0.27	–	0.2
	1+2+3[h]				0.65	0.1	0.1	0.61	0.1	0.1
UNIFAC[c]	1+2+3[h]				1.00	0.8	1.2	0.89	0.5	1.1

[a] Liquid volumes have been estimated from the Rackett equation [11].

[b] Molecular parameters are those calculated from UNIFAC [21].

[c] Calculations based on original UNIFAC [16,21].

[d] Calculated from the data of Segura *et al.* [1] neglecting vapor phase corrections.

[e] Calculated from the data of Wisniak *et al.* [2] neglecting vapor phase corrections.

[f] Average percentage deviation in pressure $\Delta P = 100/N \sum_i^N |P_i^{exptl} - P_i^{calc}|/P_i^{exptl}$ (*N*: number of data points).

[g] Average absolute deviation in mole fraction $\Delta y = 1/N \sum_i^N |y_i^{exptl} - y_i^{calc}|$.

[h] Ternary prediction from binary parameters.

are zero. Equilibrium vapor pressures and VLE mole fractions were also well predicted for the ternary system using the NRTL, Wilson, and UNIQUAC models [20], but somewhat worse by the UNIFAC model [16, 21] using parameters previously fitted to the binaries. Table VII reports results of the pertinent bubble-point pressure and dew point pressure calculations, together with statistics and parameters. From these results it can be concluded again that the binary contributions allow a good prediction of the ternary system.

The boiling points of the systems were correlated by the following equation proposed by Tamir [22],

$$\begin{aligned} T/K = \sum_{i=1}^{3} x_i T_i^0 &+ x_1x_2[A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2 + \cdots] \\ &+ x_1x_3[A_{13} + B_{13}(x_1 - x_3) + C_{13}(x_1 - x_3)^2 + \cdots] \\ &+ x_2x_3[A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2 + \cdots] \end{aligned} \tag{9}$$

where the coefficients A_{ij}, B_{ij} and C_{ij} are multicomponent parameters determined directly from the data. The various constants of Eq. (9) are reported in Table VIII, together with information regarding the quality of the correlation. In addition, Figure 4 shows the isotherms of the ternary system as calculated from Eq. (8). Inspection of Figure 4 reveals that no additional stationary points appear in boiling temperature, indicating that the ternary system breaks the azeotrope of the constituent binary benzene (2)+2,2,4-trimethylpentane (3).

TABLE VIII Coefficients in correlation of boiling points, Eq. (9), average deviation and root mean square deviations in temperature, rmsd (T/K)

ij	A_{ij}	B_{ij}	C_{ij}	*Max dev/ K*[a]	*Avg dev/ K*[b]	*rmsd*[c]
1+2[d]	−3.176850	1.502234	−0.725882			
1+3	−13.602111	0.363286	−3.808850	0.17	0.06	0.05
2+3	−21.297318	4.527827	−1.671940			

[a] Maximum deviations.
[b] Average deviations.
[c] rmsd (T/K): Root mean square deviation, $\{\sum(T_{exptl} - T_{calc})^2/N\}^{0.5}$.

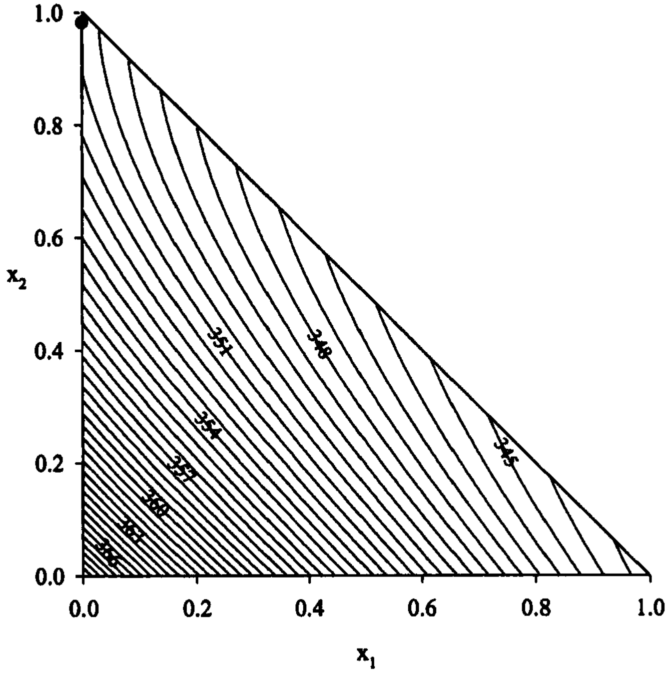

FIGURE 4 Isotherms for the ternary system ETBE (1) + benzene (2) + 2,2,4-trimethylpentane (3) at 94.00 kPa: (—), smoothed with Eq. (9) and the coefficients given in Table VIII. (•), binary azeotrope for the system benzene (2) + 2,2,4-trimethylpentane (3).

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LIST OF SYMBOLS

A_i	Antoine's equation parameter, Eq. (4)
B_i	Antoine's equation parameter, Eq. (4)
B_{ii}	pure component second virial coefficient $cm^3 \times mol^{-1}$
B_{ij}	cross second virial coefficient $cm^3 \times mol^{-1}$
C_i	Antoine's equation parameter, Eq. (4); parameters in Eq. (9)
G^E	excess Gibbs energy $J \times mol^{-1}$
P	absolute pressure kPa

P^0	pure component vapor pressure kPa
R	universal gas constant J × mol × K^{-1}
T	absolute temperature K
V	volume cm^3 × mol^{-1}
x, y	mole fractions of the liquid and vapor phases

Greek Letters

δ_{ij}	parameter defined in Eq. (2) cm^3 × mol^{-1}
γ	activity coefficient

Superscripts

E	excess property
L	pertaining to the liquid phase

Subscripts

i,j	component i, j respectively

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