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

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Isobaric vapor−liquid equilibrium (VLE) data at 94.00 kPa have been determined for the ternary system 1-hexene + ethyl 1,1-dimethylethyl ether + benzene and for its constituent binary system 1-hexene + 2,2,4-trimethylpentane (isooctane), in the temperature range 335 to 360 K. According to the experimental results, the system 1-hexene + 2,2,4-trimethylpentane exhibits ideal behavior. The ternary system exhibits slight positive deviations from ideal behavior, and no azeotrope is present. The VLE data have been correlated with the mole fraction using the Redlich−Kister, Wilson, NRTL, UNIQUAC, and Wisniak−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.

Introduction

Methyl *tert*-butyl ether (MTBE) was introduced in the 1970s as an octane replacement for tetraethyllead. It has become the most important component of reformulated gasoline and is currently added to about 30% of the gasoline consumed in the United States. MTBE is soluble in water (0.79 mol % at 298 K),[1] is readily transported in groundwater and surface water systems, has a low taste and odor threshold, and is classified as a possible human carcinogen.[2] These drawbacks are behind the recent decision of the state of California to phase out its use within the next 4 years. It is important then to investigate the possible use of other ethers of higher molecular weight, like ethyl 1,1-dimethylethyl ether (ETBE), which may be less harmful to the environment. ETBE shows good characteristics for unleaded gasoline formulation including low volatility,[3] high octane value,[3] and low water solubility (0.53 mol % at 298 K).[4]

Phase equilibrium data of oxygenated mixtures are important for predicting the vapor-phase concentration that would be in equilibrium with hydrocarbon mixtures, and data are scarce for multicomponent mixtures that include ETBE. The ternary system reported here, for which no data have been published, constitutes an example of such mixtures.

Vapor−liquid equilibrium (VLE) data for the binary systems 1-hexene + ETBE and ETBE + 2,2,4-trimethylpentane (isooctane) have been reported at 94 kPa by Segura et al.[5] and Wisniak et al.[6] For the system ETBE + isooctane, Clark et al.[7] have reported the vapor pressures at (298, 323) K for a limited range of the liquid-phase mole fraction. The two binaries exhibit slightly to moderately positive deviations from ideality and do not present azeotropes. To the best of our knowledge, no VLE data have been reported for the binary system 1-hexene + 2,2,4-trimethylpentane. The present work was undertaken to measure VLE data for the system 1-hexene + ETBE + 2,2,4-trimethylpentane and for the binary system 1-hexene + 2,2,4-trimethylpentane for which isobaric data are not available.

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

component (purity/mass %)	n_D(293.15 K)		T_b(101.3 kPa)/K	
	exptl	lit.	exptl	lit.
1-hexene (99.7+)	1.38806[a]	1.38788[b]	336.61[a]	336.635[b]
ethyl 1,1-dimethylethyl ether (99.9+)	1.37594[a]	1.37564[c]	345.85[a]	345.86[d]
2,2,4-trimethylpentane (99.9+)	1.39162[a]	1.39162[e]	372.24[a]	372.39[f]

[a] Measured. [b] *TRC Tables*,[20] a-2630. [c] DIPPR (Daubert and Danner).[21] [d] Krähenbühl and Gmehling.[22] [e] *TRC Tables*,[20] a-1010. [f] Boublík et al.[23]

Experimental Section

Materials. ETBE (96.0+ mass %) was purchased from TCI (Tokyo Chemical Industry Co. Ltd., Tokyo, Japan), and 1-hexene (97.0 mass %) and 2,2,4-trimethylpentane (99.8 mass %) were purchased from Aldrich. All of the chemicals were further 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 1. Appropriate precautions were taken when handling ETBE in order to avoid peroxide formation.

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

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Table 2. Experimental VLE Data for the Binary System 1-Hexene (1) + 2,2,4-Trimethylpentane (3) at 94.00 kPa

T/K	x_1	y_1	γ_1	γ_3
369.61	0.000	0.000		1.000
365.23	0.075	0.192	1.032	0.993
362.81	0.120	0.284	1.021	0.993
357.90	0.225	0.455	1.000	0.996
354.39	0.308	0.562	0.993	1.003
350.32	0.412	0.677	1.006	0.991
347.23	0.502	0.755	1.008	0.982
343.64	0.622	0.832	0.998	1.004
342.52	0.662	0.855	0.996	1.007
341.10	0.713	0.883	0.998	1.005
339.82	0.761	0.906	0.999	1.009
338.72	0.804	0.926	1.000	1.010
337.43	0.857	0.949	1.000	1.011
336.29	0.905	0.968	1.002	0.998
336.28	0.905	0.968	1.003	0.979
335.18	0.955	0.985	1.001	1.018
334.27	1.000	1.000	1.000	

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. The accuracy is estimated to be ±0.02 K. The 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 a cathetometer reading); the overall accuracy is estimated to be ±0.03 kPa. On average, the system reaches equilibrium conditions after 2−3 h of 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 of 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 at P = 94.00 kPa are reported in Tables 2 and 3 and in Figures 1−3, together with the activity coefficients γ_i, which were calculated from the equation[8]

$$\gamma_i = \frac{P y_i}{P_i^0 x_i} \tag{1}$$

where P is the total pressure and P_i^0 is the pure-component vapor pressure. In eq 1 the vapor phase is assumed to be an ideal gas and the pressure dependence of the liquid-phase fugacity is neglected. Equation 1 was selected to calculate activity coefficients because the low pressures observed in the present VLE data make these simplifications reasonable. In addition, and as discussed by Reich et al.[9] and by Aucejo et al.,[10] the scarce physical information available for mixtures of ETBE with alkanes does not allow a reliable estimation of second virial coefficients, thus introducing uncertainty in the estimation of vapor-phase corrections.

Table 3. Experimental VLE Data for the Ternary System 1-Hexene (1) + ETBE (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
335.88	0.876	0.070	0.926	0.056	1.004	1.026	0.988
337.30	0.790	0.109	0.872	0.092	1.002	1.032	1.004
337.60	0.666	0.280	0.743	0.236	1.003	1.020	1.084
338.04	0.704	0.195	0.795	0.168	1.001	1.028	1.005
338.87	0.607	0.288	0.706	0.254	1.005	1.024	1.015
339.31	0.473	0.473	0.559	0.419	1.007	1.013	1.069
339.56	0.511	0.393	0.609	0.353	1.008	1.019	1.029
339.95	0.672	0.121	0.808	0.113	1.004	1.046	0.979
340.46	0.414	0.491	0.507	0.452	1.007	1.014	1.088
340.73	0.576	0.223	0.708	0.211	1.002	1.033	1.006
340.98	0.292	0.657	0.364	0.613	1.008	1.011	1.116
341.47	0.315	0.584	0.399	0.556	1.009	1.015	1.084
341.59	0.483	0.318	0.608	0.307	0.999	1.025	1.035
342.33	0.222	0.680	0.290	0.665	1.014	1.014	1.084
342.45	0.387	0.414	0.502	0.410	1.003	1.023	1.040
342.83	0.566	0.121	0.741	0.125	1.001	1.054	0.994
342.84	0.099	0.851	0.133	0.843	1.026	1.011	1.114
343.39	0.121	0.775	0.166	0.785	1.031	1.015	1.073
343.49	0.291	0.506	0.389	0.518	1.001	1.023	1.040
343.55	0.481	0.214	0.640	0.224	0.995	1.044	1.010
344.15	0.205	0.596	0.282	0.622	1.010	1.021	1.070
344.35	0.392	0.305	0.536	0.324	0.998	1.033	1.018
344.97	0.120	0.689	0.170	0.736	1.015	1.019	1.062
345.16	0.305	0.393	0.429	0.427	1.002	1.030	1.022
345.96	0.461	0.124	0.661	0.141	0.997	1.051	0.996
346.14	0.212	0.487	0.306	0.544	0.998	1.027	1.034
346.80	0.369	0.220	0.540	0.255	0.992	1.044	1.012
347.12	0.117	0.582	0.175	0.669	1.005	1.025	1.040
347.57	0.284	0.313	0.422	0.369	0.985	1.036	1.025
348.44	0.200	0.394	0.307	0.477	0.992	1.036	1.022
349.11	0.366	0.123	0.572	0.155	0.990	1.056	1.004
349.17	0.110	0.493	0.174	0.608	1.000	1.032	1.030
349.89	0.280	0.210	0.450	0.271	0.995	1.056	1.002
350.70	0.198	0.298	0.324	0.390	0.990	1.045	1.012
351.78	0.109	0.381	0.184	0.513	0.990	1.041	1.023
353.73	0.182	0.203	0.324	0.294	0.987	1.056	1.005
354.34	0.105	0.285	0.192	0.422	0.997	1.060	1.004
356.07	0.191	0.105	0.366	0.166	0.995	1.076	0.999
357.22	0.105	0.185	0.207	0.302	0.991	1.074	1.002
360.16	0.100	0.104	0.212	0.185	0.983	1.076	1.002

Table 4. Antoine Coefficients (Equation 2)

compound	A_i	B_i	C_i
1-hexene[a]	6.06006	1189.67	43.18
ETBE[b]	5.96651	1151.73	55.06
2,2,4-trimethylpentane[c]	5.88343	1224.46	56.47

[a] Segura et al.[5] [b] Reich et al.[9] [c] Wisniak et al.[6]

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

$$\log(P_i^0/\mathrm{kPa}) = A_i - \frac{B_i}{(T/\mathrm{K}) - C_i} \tag{2}$$

where the Antoine constants A_i, B_i, and C_i are reported in Table 4. Antoine's equation parameters for 1-hexene, ETBE, and 2,2,4-trimethylpentane were taken from the

Table 5. Consistency Test Statistics for the Binary System 1-Hexene (1) + 2,2,4-Trimethylpentane (3) with Ideal Solution Approximation

$100\Delta y^a$	ΔP^b/kPa
0.2	0.13

[a] Average absolute deviation in vapor-phase mole fractions $\Delta y = 1/N\sum_{i=1}^{N}|y_1^{\text{exptl}} - y_1^{\text{calc}}|$ (N = number of data points). [b] Average absolute deviation in pressure $\Delta P = 1/N\sum_{i=1}^{N}|P_1^{\text{exptl}} - P_1^{\text{calc}}|$.

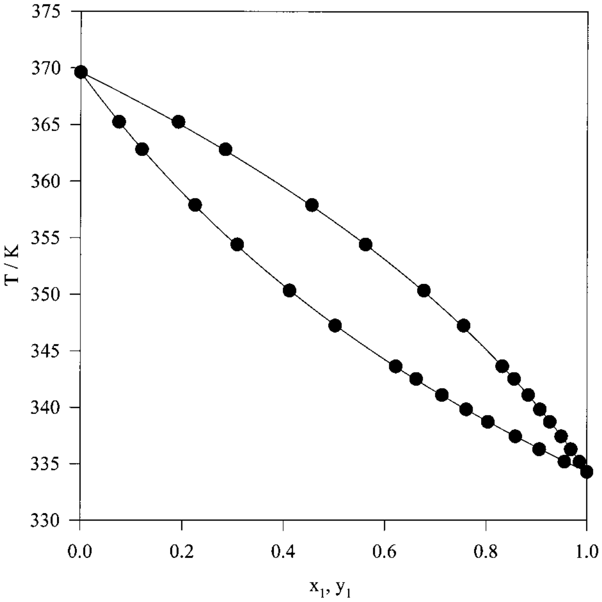

Figure 1. Experimental data for the binary system 1-hexene (1) + 2,2,4-trimethylpentane (3) at 94.00 kPa: (●) experimental data reported in this work; (−−) phase equilibrium predicted by Raoult's law.

publications of Segura et al.,[5] Reich et al.,[9] and Wisniak et al.,[6] respectively. The activity coefficients presented in Tables 2 and 3 are estimated to be accurate within ±2%. The results reported in these tables indicate that the measured systems exhibit moderate positive deviations from ideal behavior and that no azeotrope is present.

The VLE data reported in Table 2 for the binary system 1-hexene (1) + 2,2,4-trimethylpentane (3) were found to be thermodynamically consistent by the point-to-point test of Van Ness et al.,[11] as modified by Fredenslund et al.[12] Consistency criteria ($\Delta y \leq 0.01$) were met using the ideal Raoult's law approximation, for which no activity coefficient correction is needed. Table 5 presents the pertinent deviations. These statistics show that Raoult's law gives a reasonable fit of the data, as indicated by the random distribution of the residuals (Figure 2), and a reasonable fit of the boiling temperatures (Figure 1).

The VLE data reported in Table 3 for the ternary system 1-hexene (1) + ETBE (2) + 2,2,4-trimethylpentane (3) were found to be thermodynamically consistent by the McDermott−Ellis method,[13] as modified by Wisniak and Tamir.[14] According to these references, two experimental points a and b are considered to be thermodynamically consistent if the following condition is fulfilled:

$$D < D_{\max} \tag{3}$$

where the local deviation D is given by

$$D = \sum_{i=1}^{N}(x_{ia} + x_{ib})(\ln \gamma_{ia} - \gamma_{ib}) \tag{4}$$

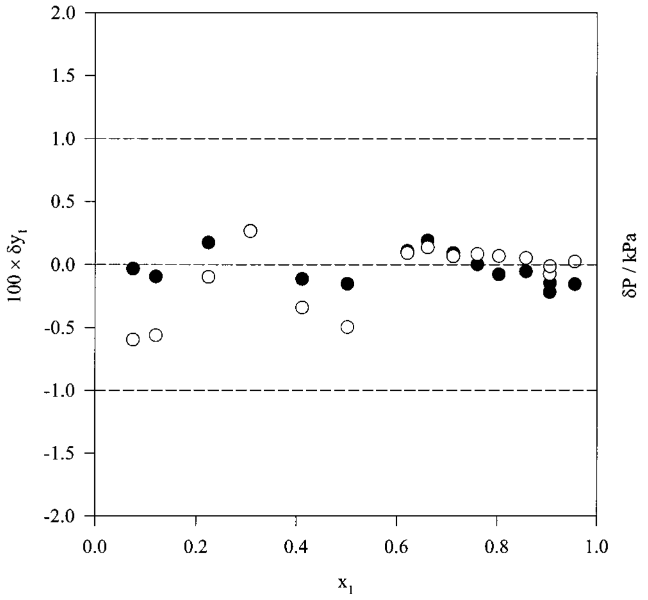

Figure 2. Residual plot of the binary system 1-hexene (1) + 2,2,4-trimethylpentane (3) at 94.00 kPa as predicted by Raoult's law: (○) vapor-phase mole fraction residuals [$100\delta y_1$]; (●) vapor pressure residuals [δP/kPa].

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

$$D_{\max} = \sum_{i=1}^{N}(x_{ia} + x_{ib})\left(\frac{1}{x_{ia}} + \frac{1}{y_{ia}} + \frac{1}{x_{ib}} + \frac{1}{y_{ib}}\right)\Delta x + \sum_{i=1}^{N}(x_{ia} + x_{ib})\frac{\Delta P}{P} + 2\sum_{i=1}^{N}|\ln \gamma_{ib} - \ln \gamma_{ia}|\Delta x + \sum_{i=1}^{N}(x_{ia} + x_{ib})B_j\{(T_a + C_j)^{-2} + (T_b + C_j)^{-2}\}\Delta T \tag{5}$$

The errors in the measurements Δx, ΔP, and ΔT were as previously indicated. The first term in eq 5 was the dominant one. For the experimental points reported here, D never exceeded 0.022, while the smallest value of $D_{\max}$ was 0.023.

The activity coefficients for the ternary system were correlated with the Redlich−Kister expansion[15]

$$\frac{G^E}{RT} = \sum_{i=1}^{3}\sum_{j>i}^{3} x_i x_j[b_{ij} + c_{ij}(x_i - x_j) + d_{ij}(x_i - x_j)^2] + x_1x_2x_3[C + D_1x_1 + D_2x_2] \tag{6}$$

where b_{ij}, c_{ij}, and d_{ij} are the constants for the pertinent ij binary system and C, D_1, and D_2 are ternary constants. All of the constants in eq 6 are assumed to be independent of the temperature, and their pertinent values are reported in Table 6. Data and constants for the binary systems 1-hexene (1) + ETBE (2) and ETBE (2) + 2,2,4-trimethylpentane (3) have already been reported by Segura et al.[5] and by Wisniak et al.[6] In addition, according to experimental results, the binary system 1-hexene (1) + isooctane (3) is ideal and, consequently, its constants for eq 6 are zero. The Redlich−Kister coefficients C, D_1, and D_2 for the ternary mixture were calculated by a Simplex optimization technique. The statistical analysis reveals that ternary constants are not significant, suggesting that the ternary data can be predicted directly from the binary systems. In fact, activity coefficients and equilibrium vapor pressures

Table 6. Constants for the Redlich−Kister Model, Fit, Correlation, and Prediction Statistics

Binary Data

system	$b_{ij} \times 10^1$	c_{ij}, d_{ij}	rmsd[a] $\times 10^{-2}$	% dev[b]	max % dev[c]
1-hexene (1) + ETBE (2)[d]	0.45	0.00	0.9	0.5	3.6
1-hexene (1) + 2,2,4-trimethylpentane(3)	0.00	0.00	1.0	0.4	3.5
ETBE (2) + 2,2,4-trimethylpentane (3)[e]	1.18	0.00	0.4	0.7	1.3

Ternary Data

γ_1/γ_2			γ_1/γ_3		
rmsd	max % dev	% dev	rmsd	max % dev	% dev
7×10^{-3}	2.1	0.6	2×10^{-2}	5.9	1.3

VLE Correlation and Predictions

	bubble-point pressures			dew-point pressures		
system	ΔP/%[f]	$100\Delta y$[g]	$100\Delta y_2$	ΔP/%	$100\Delta x_1$	$100\Delta x_2$
1 + 2[d]	0.09	0.1	0.1	0.12	0.1	0.1
1 + 3	0.14	0.2		0.18	0.2	
2 + 3[e]	0.52		0.1	0.53		0.2
1 + 2 + 3[h]	0.27	0.1	0.1	0.29	0.1	0.1

[a] Root-mean-square deviation in activity coefficients $\{\sum_i^N\{\gamma_i^{\text{exptl}} - \gamma_i^{\text{calc}}\}^2/N\}^{0.5}$ (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.[5] [e] Calculated from the data of Wisniak et al.[6] [f] Average percentage deviation in pressure $\Delta P = 100/N\sum_i^N|P_i^{\text{exptl}} - P_i^{\text{calc}}|/P_i^{\text{exptl}}$. [g] Average absolute deviation in mole fraction $\Delta y = 1/N\sum_i^N|y_1^{\text{exptl}} - y_1^{\text{calc}}|$. [h] Prediction from binary parameters.

Table 7. Parameters, Correlation, and Prediction Statistics for Different G^{E} Models

					bubble-point pressures			dew-point pressures		
model	ij	a_{ij}/J·mol^{-1}	a_{ji}/J·mol^{-1}	α_{ij}	ΔP/%[f]	$100\Delta y_1$[g]	$100\Delta y_2$	ΔP/%	$100\Delta x_1$	$100\Delta x_2$
NRTL	1 + 2[d]	−1139.22	1433.47	0.3	0.05	0.1	0.1	0.05	0.1	0.1
	1 + 3	0.00	0.00	0.3	0.14	0.2		0.18	0.2	
	2 + 3[e]	261.87	80.47	0.3	0.48		0.1	0.50		0.2
	1 + 2 + 3[h]				0.30	0.1	0.1	0.30	0.1	0.1
Wilson[a]	1 + 2[d]	−78.13	208.22		0.12	0.1	0.1	0.13	0.1	0.1
	1 + 3	43.24	54.75		0.16	0.2		0.20	0.2	
	2 + 3[e]	498.70	−152.23		0.47		0.1	0.49		0.2
	1 + 2 + 3[h]				0.32	0.1	0.1	0.32	0.1	0.1
UNIQUAC[b]	1 + 2[d]	−146.16	175.08		0.11	0.1	0.1	0.12	0.1	0.1
	1 + 3	−17.52	53.69		0.15	0.2		0.18	0.2	
	2 + 3[e]	−84.50	188.01		0.40		0.2	0.42		0.2
	1 + 2 + 3[h]				0.35	0.2	0.1	0.37	0.2	0.1
UNIFAC[c]	1 + 2 + 3[h]				4.06	1.0	1.4	3.79	0.8	1.4

[a] Liquid volumes have been estimated from the Rackett equation.[24] [b] Molecular parameters are those calculated from UNIFAC. [c] Calculations are based on the original UNIFAC.[17] [d] Data of Segura et al.[5] [e] Data of Wisniak et al.[6] [f] Average percentage deviation in pressure $\Delta P = 100/N\sum_i^N|P_i^{\text{exptl}} - P_i^{\text{calc}}|/P_i^{\text{exptl}}$ (N = number of data points). [g] Average absolute deviation in mole fraction $\Delta y = 1/N\sum_i^N|y_1^{\text{exptl}} - y_1^{\text{calc}}|$. [h] Ternary prediction from binary parameters.

of the ternary system were predicted well by the Redlich−Kister equation when using only the binary constants, as shown in Table 6, where C, D_1, and D_2 are zero. Equilibrium vapor pressures and VLE mole fractions were also well predicted for the ternary system using the NRTL, Wilson, and UNIQUAC models (Walas)[16] but somewhat less by the UNIFAC model[12,17] using parameters from previous fits to the binaries. Table 7 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 equation proposed by Wisniak and Tamir[18]

$$T/\text{K} = \sum_{i=1}^{n} x_i T_i^0/\text{K} + \sum_{j>i=1}^{n} \{x_i x_j \sum_{k=0}^{m} C_k (x_i - x_j)^k\} + x_1 x_2 x_3 \{A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3)\} \quad (7)$$

where 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, whereas A, B, C, and D are ternary constants. Tamir[19] has suggested the following equation, of the same structure, for the direct correlation of ternary data, without the use of binary data:

$$T/\text{K} = \sum_{i=1}^{3} x_i T_i^0 + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2 + ...] + x_1 x_3 [A_{13} + B_{13}(x_1 - x_3) + C_{13}(x_1 - x_3)^2 + ...] + x_2 x_3 [A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2 + ...] \quad (8)$$

where the coefficients A_{ij}, B_{ij}, and C_{ij} are not binary constants but multicomponent parameters determined directly from the data. Direct correlation of $T(x)$ for ternary mixtures can be very efficient, as reflected by a lower percentage average deviation and root-mean-square deviation (rmsd) and a smaller number of parameters than those required for eq 8. Although both equations may require a similar number of constants for similar accuracy, the direct

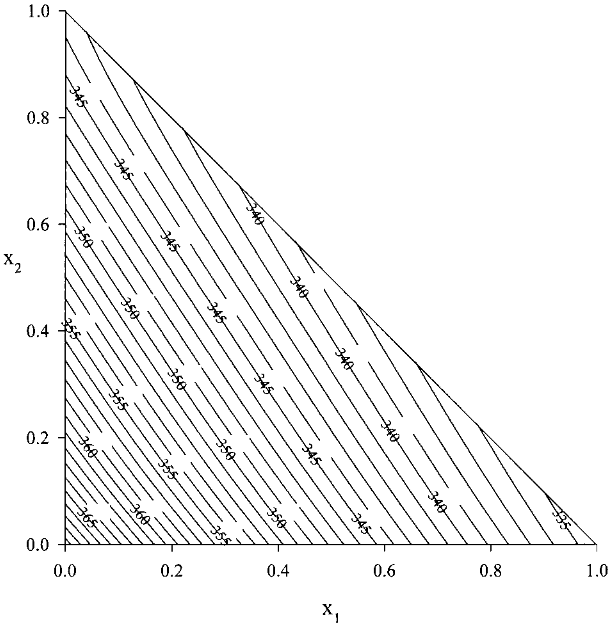

Figure 3. Boiling temperatures for the ternary system ETBE (1) + cyclohexane (2) + 2,2,4-trimethylpentane (3) at 94.00 kPa: (−−) smoothed with eq 8 and the coefficients given in Table 8.

Table 8. Coefficients in Correlation of Boiling Points, Equations 7 and 8, Average Deviation, and Root-Mean-Square Deviations in Temperature

Equation 7 (Fit from Binary Constants)

A	*B*	*C*	*D*	max dev/K[a]	avg dev/K[b]	rmsd[c]
6.3245	−1.0254	−7.5976		0.21	0.06	0.09

Binary Constants

system	C_0	C_1	C_2
1 + 2[d]	−2.4360	0.7850	−0.5020
1 + 3	−18.2337	5.4589	−2.2702
2 + 3[e]	−14.0624	3.0841	−5.1931

Equation 8 (Direct Fit)

ij	A_{ij}	B_{ij}	C_{ij}	max dev/K[a]	avg dev/K[b]	rmsd[c]
1−2	−1.9186	0.5853	−1.4134	0.12	0.04	0.05
1−3	−16.6293	2.9707	−2.2223			
2−3	−14.0183	3.8859	−7.1610			

[a] Maximum deviations. [b] Average deviations. [c] rmsd (T/K): root-mean-square deviation, $\{\sum(T_{\mathrm{exptl}} - T_{\mathrm{calc}})^2/N\}^{0.5}$. [d] Data taken from Segura et al.[5] [e] Data taken from Wisniak et al.[6]

correlation will allow an easier calculation of the boiling isotherms (Figure 3). The various constants of eqs 7 and 8 are reported in Table 8, together with information regarding the quality of the correlation. It is clear that for the ternary system in question a direct fit of the data gives a better fit.

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