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

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Consistent vapor−liquid equilibria data at 94 kPa have been determined for the ternary system ethyl 1,1-dimethylethyl ether + cyclohexane + 2,2,4-trimethylpentane and for its constituent binary cyclohexane + 2,2,4-trimethylpentane, in the temperature range 343 to 369 K. According to the experimental results, the systems exhibit 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

Recent years have seen the substitution of lead and aromatic octane-enhancers by oxygenates, particularly ethers. Methyl 1,1-dimethylethyl ether (MTBE) was introduced in 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 of the state of California to phase out its use within the next four years. It is important, then, to research the possible use of other ethers of higher molecular weights, like ethyl 1,1-dimethylethyl ether (ETBE), which may be less harmful to the environment. Among the potential oxygenates, 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. 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 ETBE + cyclohexane and ETBE + 2,2,4-trimethylpentane (isooctane) have been reported at 94 kPa by Segura et al.[1] and Wisniak et al.;[2] for the latter system Clark et al.[3] have also reported the vapor pressures at (298 and 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 cyclohexane + 2,2,4-trimethylpentane have been reported by Battino[4] at (308, 318, 328, 338, and 348) K, by Jain and Yadav[5] at (298, 308, 318, and 328) K, and by Mairs and Swinton[6] at 308 K. According to these sources, the binary system cyclohexane + 2,2,4-trimethylpentane behaves essentially ideally. The present work was undertaken to measure VLE data for the system ETBE + cyclohexane + 2,2,4-trimethylpentane and for the binary system cyclohexane + 2,2,4-trimethylpentane, for which isobaric data are not available.

Table 1. 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_b (101.3 kPa)/K	
	exptl	lit.	exptl	lit.
ethyl 1,1-dimethylethyl ether (99.9+)	1.375 94[a]	1.375 64[b]	345.85[a]	345.86[c]
cyclohexane (99.7+)	1.426 59	1.426 23[d]	353.84[a]	353.95[e]
2,2,4-trimethylpentane (99.9+)	1.391 62[a]	1.391 62[f]	372.24[a]	372.39[e]

[a] Measured. [b] DIPPR (Daubert and Danner[20]). [c] Krähenbühl and Gmehling[21]. [d] *TRC Tables*,[22] fb-2050. [e] Boublík et al.[23] [f] *TRC Tables*,[22] a-1010.

Experimental Section

Materials. ETBE (96.0+ mass %) was purchased from TCI (Tokyo Chemical Industry Co. Ltd., Japan), and cyclohexane (99.0 mass %) and 2,2,4-trimethylpentane (99.8 mass %) were purchased from Aldrich. All the chemicals were further purified to >99.7+ mass % by rectification in a 1 m height by 30 mm diameter Normschliffgerätebau adiabatic distillation column (packed with 3 mm × 3 mm stainless steel spirals), working at a 1 to 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

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Table 2. Experimental Vapor−Liquid Equilibrium Data for the Binary System Cyclohexane (2) + 2,2,4-Trimethylpentane (3) at 94.00 kPa

T/K	x_2	y_2	γ_2	γ_3
369.60	0.000	0.000		1.000
368.83	0.032	0.055	1.036	0.998
367.84	0.073	0.121	1.026	0.998
366.94	0.111	0.179	1.024	0.998
365.61	0.168	0.263	1.031	0.995
364.77	0.204	0.311	1.028	0.997
363.83	0.249	0.367	1.021	0.998
362.78	0.298	0.427	1.023	0.998
361.63	0.356	0.492	1.019	0.998
360.65	0.409	0.545	1.011	1.004
359.68	0.459	0.595	1.012	1.005
358.64	0.515	0.646	1.009	1.012
357.99	0.553	0.680	1.008	1.013
357.71	0.571	0.697	1.009	1.008
357.17	0.602	0.723	1.009	1.010
356.88	0.619	0.735	1.006	1.019
356.29	0.654	0.765	1.008	1.013
355.93	0.677	0.781	1.005	1.023
355.50	0.702	0.800	1.006	1.026
355.46	0.705	0.803	1.007	1.023
355.25	0.721	0.814	1.004	1.028
354.83	0.745	0.833	1.007	1.023
354.19	0.788	0.863	1.005	1.030
354.08	0.800	0.871	1.003	1.032
353.49	0.837	0.897	1.005	1.030
353.28	0.855	0.908	1.002	1.041
352.57	0.894	0.935	1.008	1.037
352.66	0.902	0.939	1.002	1.034
351.96	0.955	0.973	1.001	1.030
351.38	1.000	1.000	1.000	

Table 3. Experimental Vapor−Liquid Equilibrium Data for the Ternary System ETBE (1) + Cyclohexane (2) + 2,2,4-Trimethypentane (3) at 94.00 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
344.57	0.841	0.107	0.877	0.096	1.008	1.108	1.110
345.35	0.786	0.116	0.844	0.106	1.011	1.103	1.099
345.68	0.653	0.294	0.709	0.263	1.013	1.072	1.066
345.88	0.683	0.222	0.749	0.203	1.015	1.085	1.075
346.69	0.577	0.319	0.652	0.294	1.022	1.064	1.062
346.91	0.459	0.490	0.530	0.444	1.036	1.041	1.027
347.23	0.678	0.120	0.778	0.114	1.020	1.083	1.068
347.30	0.483	0.416	0.563	0.385	1.032	1.050	1.035
347.87	0.591	0.207	0.693	0.198	1.022	1.068	1.052
348.12	0.384	0.518	0.464	0.484	1.045	1.033	1.036
348.48	0.499	0.301	0.602	0.290	1.030	1.055	1.039
348.53	0.267	0.681	0.339	0.634	1.082	1.017	0.986
348.98	0.288	0.614	0.364	0.584	1.064	1.023	1.011
349.26	0.403	0.397	0.503	0.387	1.043	1.041	1.023
349.49	0.571	0.115	0.707	0.116	1.026	1.068	1.048
349.92	0.201	0.702	0.266	0.679	1.084	1.011	1.041
350.17	0.307	0.492	0.400	0.488	1.057	1.029	1.014
350.19	0.476	0.214	0.607	0.218	1.034	1.055	1.027
350.91	0.382	0.312	0.504	0.321	1.048	1.041	1.016
351.07	0.063	0.887	0.090	0.880	1.130	1.001	1.060
351.09	0.106	0.796	0.149	0.794	1.116	1.006	1.016
351.28	0.208	0.588	0.287	0.597	1.080	1.017	1.006
351.48	0.485	0.111	0.642	0.118	1.032	1.052	1.035
351.86	0.290	0.408	0.395	0.426	1.053	1.029	1.013
352.29	0.400	0.193	0.547	0.208	1.039	1.046	1.023
352.56	0.108	0.687	0.157	0.720	1.098	1.010	1.011
352.93	0.194	0.506	0.277	0.540	1.068	1.018	1.011
353.12	0.317	0.279	0.447	0.305	1.049	1.035	1.012
353.98	0.106	0.597	0.159	0.654	1.091	1.011	1.010
354.17	0.222	0.374	0.328	0.417	1.064	1.024	1.005
354.31	0.365	0.120	0.533	0.137	1.046	1.043	1.018
355.33	0.116	0.486	0.184	0.558	1.101	1.018	0.999
355.42	0.270	0.215	0.410	0.251	1.054	1.032	1.010
356.37	0.184	0.305	0.291	0.363	1.069	1.023	1.006
356.91	0.281	0.108	0.446	0.132	1.053	1.035	1.011
357.27	0.106	0.390	0.174	0.475	1.080	1.019	1.008
358.50	0.145	0.256	0.244	0.324	1.069	1.021	1.005
359.86	0.196	0.096	0.341	0.126	1.060	1.022	1.005
360.63	0.127	0.177	0.229	0.238	1.075	1.022	0.999
363.01	0.110	0.091	0.210	0.131	1.069	1.019	1.001
363.81	0.063	0.138	0.123	0.202	1.069	1.016	1.001
363.90	0.094	0.078	0.185	0.115	1.072	1.018	0.999

Labor und Verfahrenstechnik (Germany), was used in the equilibrium determinations. In this circulation-method apparatus, the mixture is heated to its boiling point with 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 with 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 to be ±0.02 K. The total pressure of the system is controlled with 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 to be ±0.03 kPa. On the average, the system reaches equilibrium conditions after 2 to 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. The column, injector, and detector temperatures were (323.15, 383.15, and 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 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 following equation (Van Ness and Abbott[7]):

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

where P is the total pressure and P_i° 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.[8] and by Aucejo et al.,[9] 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.

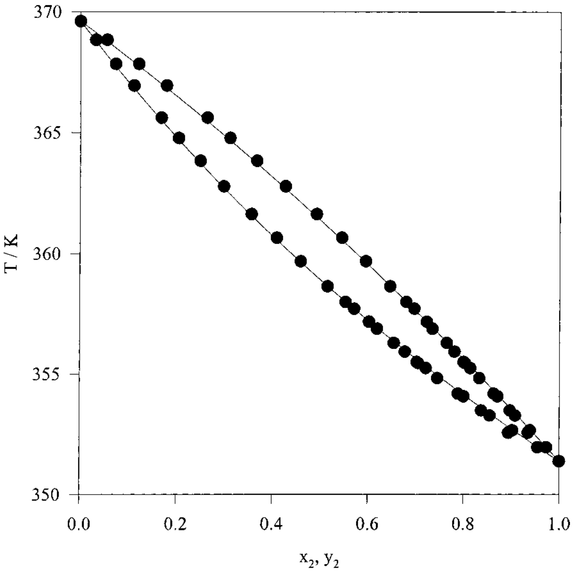

Figure 1. Experimental data for the system cyclohexane (2) + 2,2,4-trimethylpentane (3) at 94.00 kPa: (●) experimental data reported in this work; (—) smoothed data using the regular model, eq 3, with the *A* parameter given in Table 5.

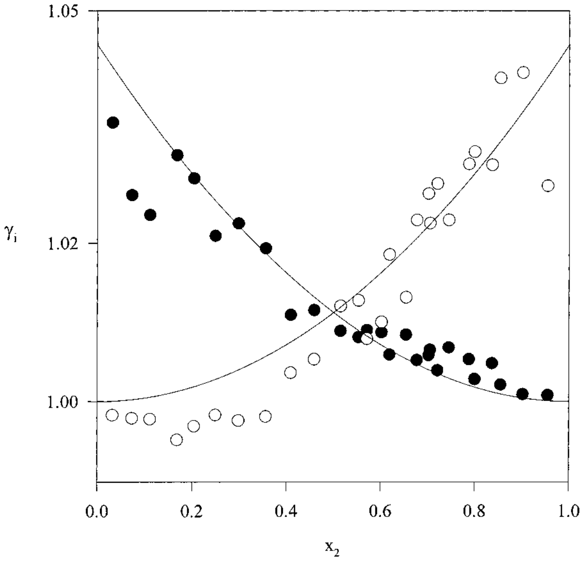

Figure 2. Activity coefficient plot of the system cyclohexane (2) + 2,2,4-trimethylpentane (3) at 94.00 kPa: (●, ○) experimental data reported in this work; (—) smoothed data using the regular model, eq 3, with the *A* parameter given in Table 5.

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

$$\log(P_i^o/\text{kPa}) = A_i - \frac{B_i}{(T/\text{K}) - C_i} \qquad (2)$$

where the Antoine constants A_i, B_i, and C_i are reported in Table 4. Antoine's equation parameters for ETBE, cyclohexane, and 2,2,4-trimethylpentane were taken from the publications of Reich et al.,[8] Segura et al.,[1] and Wisniak et al.,[2] respectively.

The activity coefficients presented in Tables 2 and 3 are estimated to be accurate to 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.

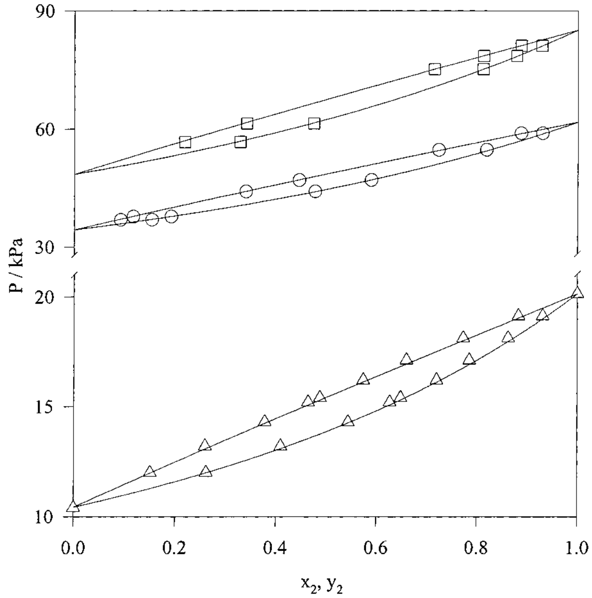

Figure 3. Prediction of isothermal VLE data for the system cyclohexane (2) + 2,2,4-trimethylpentane (3): (□) experimental data of Battino[4] at 348.15 K; (○) experimental data of Battino[4] at 338.15 K; (△) experimental data of Mairs and Swinton[6] at 308.15 K; (—) predicted from the regular model, eq 3, with the *A* parameter given in Table 5.

Table 4. Antoine Coefficients, Eq 2

compound	A_i	B_i	C_i
ETBE[a]	5.966 51	1151.73	55.06
cyclohexane[b]	6.069 03	1259.10	43.97
2,2,4-trimethylpentane[c]	5.883 43	1224.46	56.47

[a] Reich et al.[8] [b] Segura et al.[1] [c] Wisniak et al.[2]

Table 5. Consistency Test Statistics for the Binary System Cyclohexane (2) + 2,2,4-Trimethylpentane (3)

A[a]	$100\Delta y$[b]	ΔP[c]/kPa
0.039	0.1	0.20

[a] Zeroth order Legendre polynomial (or Porter model) parameter in eq 3. [b] 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). [c] Average absolute deviation in pressure $\Delta P = (1/N)\sum_{i=1}^{N}|P^{\text{exptl}} - P^{\text{calc}}|$.

The VLE data reported in Table 2 for the binary system cyclohexane (2) + 2,2,4-trimethylpentane (3) were found to be thermodynamically consistent by the point-to-point test of Van Ness et al.,[10] as modified by Fredenslund et al.[11] Consistency criteria ($\Delta y \le 0.01$) were met using a one-parameter Legendre polynomial, which reduces the functionality of the excess Gibbs energy G^E to the symmetric relation

$$\frac{G^E}{RT} = Ax_1x_2 \qquad (3)$$

Equation 3 is equivalent to the regular solution model or symmetric Porter equation.[12] Table 5 presents the value of parameter *A* and the pertinent deviations. The statistics show that eq 3 gives a very good fit of the data and a reasonable fit of the activity coefficients, as shown in Figure 2. In addition, as shown in Figure 3, the regular model allows a good prediction of the isothermal data reported by Battino[4] and by Mairs and Swinton,[6] exhibiting an average percentage deviation of 0.2% in vapor pressure. It

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

Binary Data

system	$10b_{ij}$	c_{ij}, d_{ij}	10^{-2} × rmsd[a]	% dev[b]	max % dev[c]
ETBE (1) + cyclohexane (2)[d]	1.49	0.00	0.7	0.6	2.7
ETBE (1) + 2,2,4-trimethylpentane (3)[e]	1.18	0.00	0.4	0.7	1.3
cyclohexane (2) + 2,2,4-trimethylpentane(3)	0.39	0.00	0.1	0.4	1.2

Ternary Data

γ_1/γ_2			γ_1/γ_3		
rmsd	max % dev	% dev	rmsd	max % dev	% dev
10^{-2}	2.7	1.2	2×10^{-2}	5.8	1.4

VLE Correlations and Predictions

	bubble-point pressures			dew-point pressures		
system	ΔP/%[f]	$100\Delta y_1$[g]	$100\Delta y_2$	ΔP/%	$100\Delta x_1$	$100\Delta x_2$
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	0.22		0.1	0.23		0.1
1 + 2 + 3[h]	0.29	0.2	0.2	0.24	0.2	0.2

[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.[1] [e] Calculated from the data of Wisniak et al.[2] [f] Average percentage deviation in pressure $\Delta P = 100/N\sum_i^N|P_i^{\text{exptl}} - P_i^{\text{calc}}|/P_i^{\text{exptl}}$. [g] Average absolute deviation in mole fraction $\Delta y = 1/N\sum_i^N|y_i^{\text{exptl}} - y_i^{\text{calc}}|$. [h] Prediction from binary parameters.

can then be concluded that the system cyclohexane (2) + 2,2,4-trimethylpentane (3) behaves as a symmetric system. It should be mentioned that similar conclusions were reported by Wisniak et al.[2] for the system ETBE (1) + 2,2,4-trimethylpentane (2) and by Segura et al.[1] for the system ETBE (1) + cyclohexane (2).

The vapor−liquid equilibrium data reported in Table 3 for the ternary system ETBE (1) + cyclohexane (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 thermodynamically consistent if the following condition is fulfilled

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

where the local deviation D is given by

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

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

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

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 0.018 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]

$$\frac{G^{\text{E}}}{RT} = \sum_{i=l}^{3}\sum_{j>i}^{3}x_ix_j[b_{ij} + c_{ij}(x_i - x_j) + d_{ij}(x_i - x_j)^2] + x_1x_2x_3[C + D_1x_1 + D_2x_2] \tag{7}$$

where b_{ij}, c_{ij}, and d_{ij} are the constants for the pertinent ij binary and C, D_1, and D_2 are ternary constants. All the constants in eq 7 are assumed to be independent of the temperature. Data and constants for the binary system ETBE (1) + cyclohexane (2) and ETBE (1) + 2,2,4-trimethylpentane (3) have already been reported by Segura et al.[1] and by Wisniak et al.[2] The Redlich−Kister coefficients for the binaries cyclohexane (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 6. Analysis of the correlation indicated that the binary constants c_{ij} and d_{ij} are negligible, which is consistent with the previous discussion about eq 3. In addition, 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, activity coefficients and

Table 7. Parameters and 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]	219.19	225.30	0.3	0.10	0.2	0.2	0.12	0.2	0.2
	1 + 3[e]	261.87	80.47	0.3	0.48	0.1		0.50	0.2	
	2 + 3	116.12	0.39	0.3	0.22		0.1	0.23		0.1
	1 + 2 + 3[h]				0.25	0.2	0.2	0.22	0.2	0.2
Wilson[a]	1 + 2[d]	263.49	268.22		0.13	0.1	0.1	0.14	0.1	0.1
	1 + 3[e]	498.70	−152.23		0.47	0.1		0.49	0.2	
	2 + 3	−249.21	890.39		0.08		0.2	0.09		0.2
	1 + 2 + 3[h]				0.25	0.2	0.1	0.23	0.2	0.1
UNIQUAC[b]	1 + 2[d]	459.79	−333.41		0.09	0.2	0.2	0.08	0.2	0.2
	1 + 3[e]	−84.50	188.01		0.40	0.2		0.42	0.2	
	2 + 3	58.83	−13.94		0.11		0.1	0.16		0.1
	1 + 2 + 3[h]				0.20	0.2	0.2	0.20	0.2	0.1
UNIFAC[c]	1 + 2 + 3[h]				0.67	0.8	0.5	0.41	0.6	0.4

[a] Liquid volumes have been estimated from the Rackett equation.[24] [b] Molecular parameters are those calculated from UNIFAC. [c] Calculations based on original UNIFAC.[17] [d] Data of Segura et al.[1] [e] Data of Wisniak et al.[2] [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 $\Delta y = 1/N\sum_i^N|y_i^{\text{exptl}} - y_i^{\text{calc}}|$. [h] Ternary prediction from binary parameters.

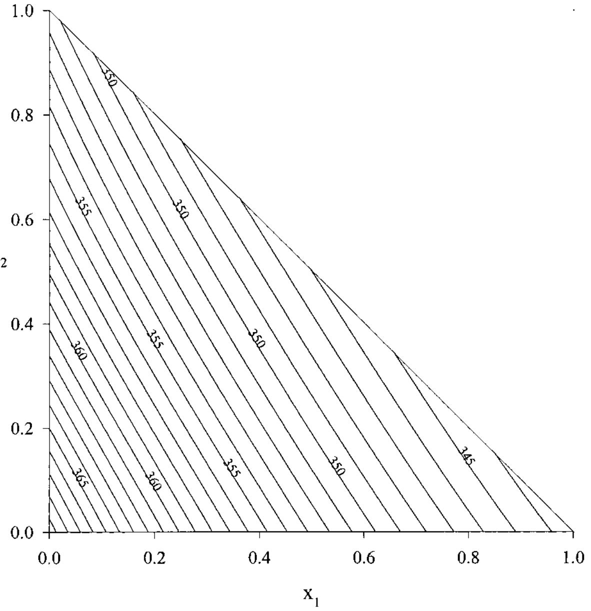

Figure 4. Isotherms for the ternary system ETBE (1) + cyclohexane (2) + 2,2,4-trimethylpentane (3) at 94.00 kPa: (—) smoothed with eq 9 and the coefficients given in Table 8.

Table 8. Coefficients in Correlation of Boiling Points, Eqs 8 and 9, Average Deviation, and Root Mean Square Deviations in Temperature, rmsd(*T*/K)

Equation 8 (Fit from Binary Constants)

A	*B*	*C*	*D*	max dev[a]/K	avg dev[b]/K	rmsd[c]
−0.9735	−2.4878	2.6262		0.17	0.05	0.04

Binary Constants

system	C_0	C_1	C_2
1 + 2[d]	−5.9208	1.4841	−0.8225
1 + 3	−14.0624	3.0841	−5.1931
2 + 3	−6.2314	0.3716	−0.5230

Equation 9 (Direct Fit)

ij	A_{ij}	B_{ij}	C_{ij}	max dev[a]/K	avg dev[b]/K	rmsd[c]
1 + 2[d]	−5.7227	2.3172	−2.0470	0.08	0.02	0.02
1 + 3	−14.8675	3.1860	−2.1490			
2 + 3	−6.3011	0.8752	2.2491			

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

equilibrium vapor pressures of the ternary system were predicted very 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 a somewhat worse prediction was given by the UNIFAC model (Fredenslund et al.[11] Hansen et al.[17]) using parameters previously fitted 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]

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

where *n* is the number of components (*n* = 2 or 3), T_i° 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 use of binary data:

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

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 correlation will allow an easier calculation of the boiling isotherms, as shown in Figure 4. The various constants of eqs 8 and 9 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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