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

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Consistent vapor−liquid equilibria (VLE) at 94.00 kPa has been determined for the ternary system ethyl 1,1-dimethylethyl ether + 2,2,4-trimethylpentane + methylcyclohexane and the two constituent binaries ethyl 1,1-dimethylethyl ether + methylcyclohexane and 2,2,4-trimethylpentane + methylcyclohexane in the temperature range from 343 to 371 K. In addition, vapor pressures have been measured for methylcyclohexane from 331 to 374 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 composition 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. The ethers used mostly, methyl 1,1-dimethylethyl ether (MTBE) and ethyl 1,1-dimethylethyl ether (ETBE), have gained particular favor because of their low Reid vapor pressure (Rvp) and the availability of the feedstock ethanol from renewable resources. MTBE 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. In addition, it is resistant to microbial decomposition. These factors have promoted research on the possible use of ethers of higher molecular weights, less harmful for 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 composition that would be in equilibrium with hydrocarbon mixtures, and scarce data are available for 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 system ETBE + 2,2,4-trimethylpentane (isooctane) have already been reported at 94 kPa by Wisniak et al. (1998); the system presents slight to moderate positive deviations from ideality and does not have an azeotrope. Vapor−liquid equilibrium data for the system isooctane + methylcyclohexane have been reported by Harrison and Berg (1946) at 99 kPa, by Gelus et al. (1949) at 101 kPa, by Sieg (1950) at 101 kPa, and by Bushmakin et al. (1959). According to these sources the binary system isooctane + methylcyclohexane behaves essentially ideally. No data have been reported for the binary system ETBE + methylcyclohexane. The present work was undertaken to measure vapor−liquid equilibrium (VLE) data for the system ETBE + isooctane + methylcyclohexane and some of its constituent binaries, for which data are inaccurate or are not available.

Experimental Section

Materials. ETBE (96.0+ mass %) was purchased from TCI (Tokyo Chemical Industry Co. Ltd., Japan), and methylcyclohexane (99.0 mass %) and isooctane (99.8 mass %) were purchased from Aldrich. All the chemicals were further purified to 99.9+ 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 cromatography) 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 (Bonn, 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

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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,293.15K)		T_b(101.3kPa)/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]
2,2,4-trimethylpentane (99.9+)	1.391 62[a]	1.391 62[d]	372.24[a]	372.39[e]
methylcyclohexane (99.9+)	1.423 28[a]	1.423 10[f]	374.03[a]	374.09[f]

[a] Measured. [b] DIPPR (Daubert and Danner, 1989). [c] Krähenbühl and Gmehling (1994). [d] TRC Tables (1995). [e] Boublík et al. (1984). [f] TRC Tables (1993).

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 total pressure of the system is controlled by a vacuum pump capable of work under vacuum up to 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 ±0.02 kPa. On the 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, 353.15, 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 2−4 and in Figures 1−5, together with the activity coefficients γ_i which were calculated from the following equation (Van Ness and Abbott, 1982):

$$\gamma_i = Py_i/P_i^\circ x_i \tag{1}$$

where P is the total pressure and P_i° is the pure component vapor pressure. In eq 1, also known as modified Raoult's law, 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. (1998) and by Aucejo et al. (1998), 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 2. Experimental Vapor−Liquid Equilibrium Data for the Binary System ETBE (1) + Methylcyclohexane (3) at 94.00 KPa

T/K	x_1	y_1	γ_1	γ_2
371.39	0.000	0.000		1.000
369.46	0.036	0.090	1.164	0.998
367.76	0.072	0.168	1.137	0.997
365.90	0.112	0.248	1.138	0.995
364.63	0.142	0.299	1.118	0.997
363.07	0.180	0.361	1.114	0.997
361.33	0.228	0.425	1.091	1.003
360.36	0.254	0.463	1.094	1.000
359.46	0.281	0.494	1.085	1.004
358.05	0.326	0.544	1.072	1.009
357.13	0.356	0.576	1.069	1.010
355.97	0.399	0.617	1.054	1.016
354.63	0.449	0.662	1.048	1.018
354.10	0.462	0.670	1.045	1.038
352.78	0.517	0.717	1.039	1.034
352.68	0.520	0.720	1.043	1.030
351.54	0.569	0.755	1.033	1.043
350.53	0.613	0.785	1.029	1.052
349.27	0.670	0.822	1.024	1.067
348.05	0.739	0.863	1.012	1.078
346.87	0.795	0.895	1.011	1.098
346.04	0.848	0.924	1.005	1.099
345.57	0.874	0.936	1.003	1.129
344.13	0.958	0.980	1.001	1.154
343.47	1.000	1.000	1.000	

Table 3. Experimental Vapor−Liquid Equilibrium Data for the Binary System Isooctane (2) + Methylcyclohexane (3) + at 94.00 KPa

T/K	x_2	y_2	γ_2	γ_3
371.39	0.000	0.000		1.000
371.26	0.042	0.045	1.021	1.001
371.10	0.108	0.116	1.023	1.000
371.03	0.141	0.149	1.018	1.001
370.96	0.164	0.174	1.019	1.001
370.87	0.203	0.214	1.014	1.002
370.76	0.253	0.265	1.011	1.003
370.70	0.280	0.293	1.013	1.002
370.70	0.283	0.295	1.008	1.004
370.66	0.302	0.315	1.010	1.003
370.56	0.349	0.361	1.009	1.004
370.49	0.385	0.398	1.009	1.004
370.41	0.432	0.445	1.006	1.006
370.32	0.480	0.492	1.005	1.006
370.26	0.521	0.532	1.003	1.008
370.20	0.560	0.571	1.003	1.009
370.05	0.619	0.628	1.003	1.014
370.02	0.670	0.679	1.001	1.013
369.96	0.720	0.727	1.000	1.015
369.90	0.769	0.775	0.999	1.017
369.83	0.822	0.827	0.999	1.019
369.77	0.869	0.872	0.999	1.020
369.72	0.915	0.918	0.999	1.018
369.67	0.960	0.961	0.999	1.027
369.61	1.000	1.000	1.000	

The vapor pressure of methylcyclohexane was measured in the same equipment used for VLE determinations, and the pertinent results are shown in Table 5. The data reported in this table are in good agreement with the correlation suggested by the TRC Tables (1992), as shown in Figure 6, yielding an average percentage deviation of 0.13%. The temperature dependence of pure component vapor pressures P_i° was calculated according to the Antoine equation

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

where the Antoine constants A_i, B_i, and C_i are reported in Table 6. Antoine's equation parameters for ETBE and isooctane were taken from the publications of Reich et al. (1998) and Wisniak et al. (1998), respectively. The parameters of eq 2 for methylcyclohexane were calculated from the fit of the vapor pressure data reported in Table 5, with an average percentage deviation of 0.02%.

Table 4. Experimental Vapor−Liquid Equilibrium Data for the Ternary System ETBE (1) + Isooctane (2) + Methylcyclohexane (3) at 94.00 KPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
367.91	0.064	0.051	0.153	0.050	1.161	1.024	0.997
367.34	0.054	0.797	0.120	0.745	1.098	0.998	1.018
366.14	0.100	0.198	0.219	0.181	1.119	1.010	0.997
366.13	0.098	0.299	0.212	0.271	1.107	1.004	0.999
365.82	0.111	0.100	0.240	0.092	1.118	1.023	0.997
365.78	0.103	0.398	0.217	0.357	1.091	1.002	1.006
365.76	0.100	0.494	0.211	0.442	1.094	1.001	1.006
365.70	0.092	0.830	0.193	0.740	1.086	0.999	1.020
365.68	0.096	0.696	0.201	0.620	1.085	0.999	1.017
365.60	0.099	0.600	0.212	0.532	1.113	0.996	1.008
365.47	0.097	0.798	0.206	0.704	1.104	0.995	1.023
363.61	0.165	0.100	0.332	0.085	1.104	1.014	0.997
362.91	0.179	0.202	0.354	0.166	1.106	1.005	0.994
362.50	0.192	0.102	0.377	0.084	1.112	1.009	0.993
362.47	0.189	0.301	0.361	0.245	1.083	1.004	1.005
362.37	0.190	0.403	0.359	0.326	1.073	1.002	1.010
362.36	0.186	0.500	0.352	0.404	1.074	0.999	1.017
362.25	0.183	0.704	0.345	0.567	1.074	1.000	1.020
361.87	0.195	0.602	0.367	0.479	1.084	0.998	1.011
360.79	0.238	0.304	0.429	0.235	1.069	1.001	1.008
359.86	0.269	0.104	0.476	0.079	1.080	1.010	1.001
359.59	0.278	0.049	0.493	0.038	1.088	1.039	0.992
359.58	0.273	0.202	0.479	0.151	1.079	1.006	1.003
359.19	0.276	0.505	0.473	0.371	1.066	1.001	1.023
359.17	0.276	0.407	0.480	0.300	1.081	1.003	1.004
358.87	0.285	0.603	0.481	0.440	1.059	1.003	1.030
357.42	0.343	0.306	0.551	0.214	1.049	1.009	1.019
356.65	0.369	0.200	0.586	0.136	1.063	1.000	1.007
356.46	0.368	0.412	0.577	0.280	1.053	1.008	1.024
356.20	0.374	0.513	0.581	0.345	1.053	1.005	1.039
356.15	0.385	0.106	0.604	0.071	1.066	1.008	1.010
354.52	0.453	0.057	0.666	0.037	1.048	1.019	1.010
354.38	0.449	0.308	0.654	0.197	1.042	1.011	1.030
354.10	0.464	0.195	0.672	0.123	1.044	1.009	1.015
353.69	0.473	0.415	0.673	0.259	1.039	1.011	1.037
353.24	0.494	0.105	0.698	0.065	1.045	1.023	1.026
351.80	0.561	0.192	0.746	0.114	1.028	1.021	1.030
351.70	0.557	0.311	0.738	0.186	1.027	1.031	1.055
351.67	0.563	0.191	0.750	0.113	1.034	1.022	1.016
350.35	0.619	0.105	0.789	0.060	1.029	1.032	1.044
349.80	0.654	0.054	0.814	0.030	1.022	1.022	1.036
349.62	0.654	0.189	0.810	0.106	1.022	1.034	1.048
347.77	0.753	0.102	0.869	0.055	1.008	1.064	1.084
345.89	0.852	0.049	0.926	0.024	1.007	1.049	1.099

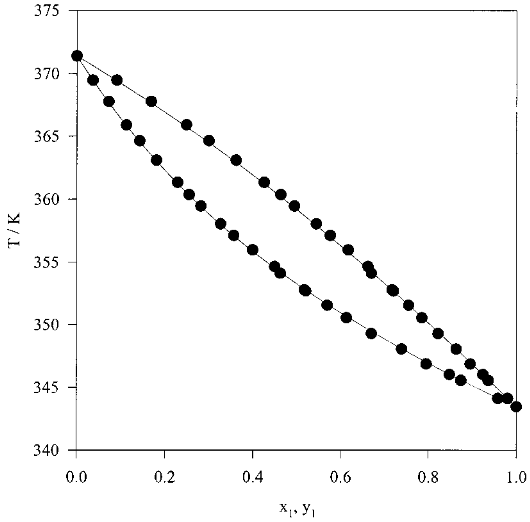

Figure 1. Experimental data for the system ETBE (1) + methylcyclohexane (3) at 94.00 kPa: experimental data (●): smoothed data using the regular model, eq 3, with the *A* parameter given in Table 7 (—).

The activity coefficients reported in Tables 2−4 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. In addition, Figure 5 shows the smoothed trend of the isotherms in the ternary system. No stationary point is observed in Figure 5, indicating that the ternary system does not exhibit azeotropic behavior.

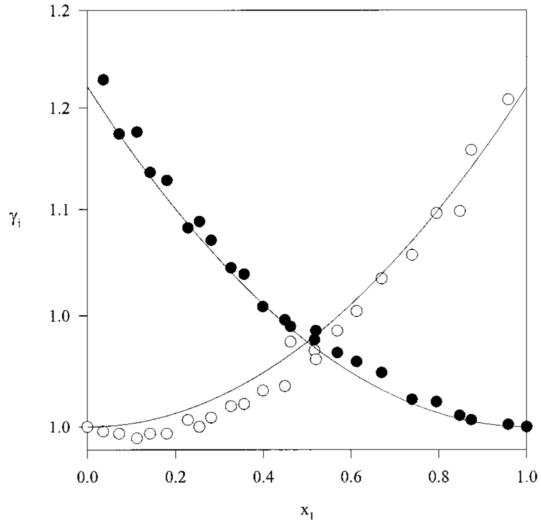

Figure 2. Activity coefficient plot of the system ETBE (1) + methylcyclohexane (3) at 94.00 kPa: experimental data (●); smoothed data using the regular model, eq 3, with the *A* parameter given in Table 7 (—).

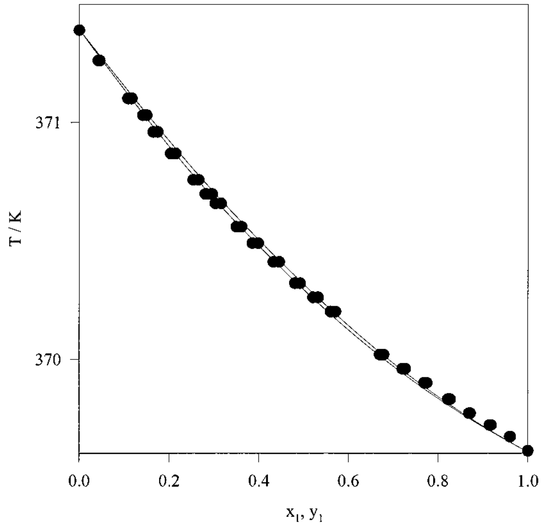

Figure 3. Experimental data for the system isooctane (2) + methylcyclohexane (3) at 94.00 kPa: experimental data (●,○); smoothed data using the regular model, eq 3, with the *A* parameter given in Table 7 (—).

The vapor−liquid equilibria data reported in Tables 2 and 3 for the binary systems ETBE (1) + methylcyclohexane (3) and isooctane (2) + methylcyclohexane (3) were found to be thermodynamically consistent by the point-to-point test of Van Ness et al. (1973), as modified by Fredenslund et al. (1977). Consistency criteria ($\Delta y \leq 0.01$) were met using a one parameter Legendre polynomial, which reduces the functionality of the excess Gibbs energy G^E to the following symmetric relation

$$G^E/RT = Ax_1x_2 \tag{3}$$

Equation 3 is equivalent to the regular solution model or Porter equation (Prigogine and Defay, 1954). Table 7

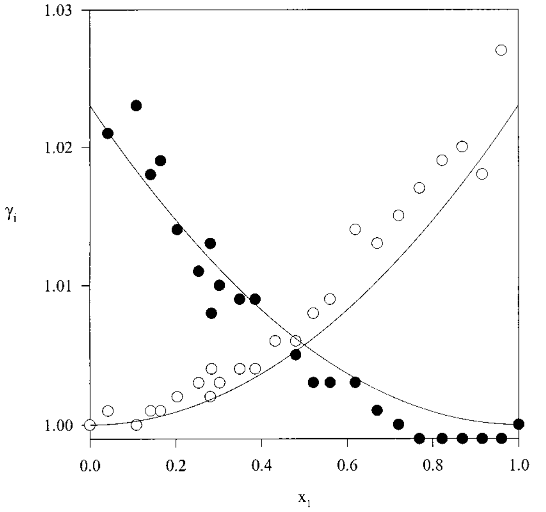

Figure 4. Activity coefficient plot of the system isooctane (2) + methylcyclohexane (3) at 94.00 kPa: experimental data (●,○); smoothed data using the regular model, eq 3, with the *A* parameter given in Table 7 (—).

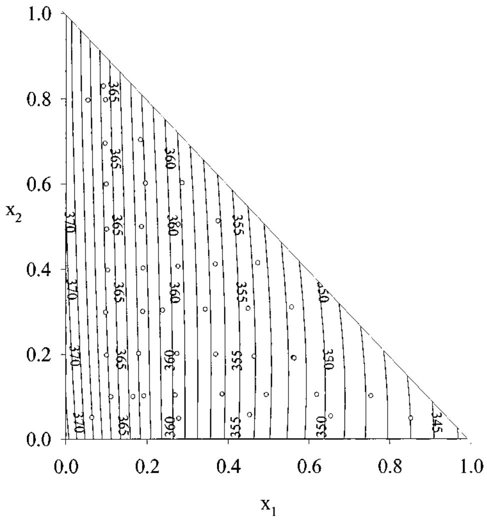

Figure 5. Isotherms for the ternary system ETBE (1) + isooctane (2) + methylcyclohexane (3) at 94.00 kPa: experimental data (○); smoothed with eq 11 and the coefficients given in Table 10 (—).

Table 5. Experimental Vapor Pressure Data $P°$ for Methylcyclohexane

T/K	*P*°/kPa	*T*/K	*P*°/kPa	*T*/K	*P*°/kPa
330.92	24.91	353.78	55.05	367.92	84.97
335.95	29.98	356.54	60.10	369.83	89.88
340.23	34.91	359.09	65.10	371.64	94.70
344.16	40.03	361.47	70.07	372.84	97.98
347.66	45.05	363.74	75.04	374.03	101.33
350.85	50.07	365.92	80.10	374.50	102.68

presents the value of parameter *A* and the pertinent statistics. The statistics show that eq 3 gives a very good fit of the data and a reasonable fit of the activity coefficients, as depicted in Figures 2 and 4. These considerations lead to the conclusion that the systems ETBE (1) + methylcyclohexane (3) and isooctane (2) + methylcyclohexane (3) behave as regular symmetric systems. It should be mentioned that similar conclusions were reported by Wisniak et al. (1998) for the system ETBE (1) + isooctane (2).

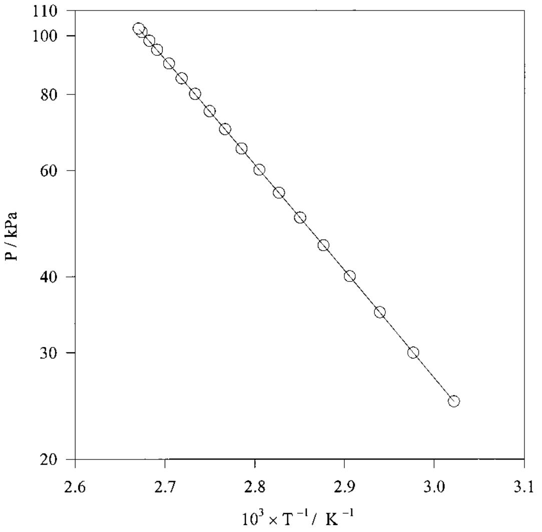

Figure 6. Comparison of vapor pressures of methylcyclohexane with other references: experimental data (○); Antoine's equation with parameters given by TRC Tables (1992) (—).

Table 6. Antoine Coefficients, Equation 2

compound	A_i	B_i	C_i
ETBE[a]	5.966 51	1151.73	55.06
2,2,4-trimethylpentane[b]	5.883 43	1224.46	56.47
methylcyclohexane[c]	6.030 03	1319.03	46.26

[a] Reich et al. (1998). [b] Wisniak et al. (1998). [c] Antoine's parameters were calculated from the experimental data in Table 5.

Table 7. Consistency Test Statistics for the Binary Systems ETBE (1) + Methylcyclohexane (3) and Isooctane (2) + Methylcyclohexane (3)

system	*A*[a]	$100\Delta y$[b]	ΔP[c]/kPa
1 + 3	0.149	0.2	0.24
2 + 3	0.023	0.1	0.02

[a] Zero-order Legendre polynomial (or Porter model) parameter in eq 3. [b] Average absolute deviation in vapor phase mole fractions $\Delta y = 1/N\sum_{i=1}^{N}|y_1^{\text{exptl}} - y_1^{\text{calcd}}|$ (*N*, number of data points). [c] Average absolute deviation in pressure $\Delta P = 1/N\sum_{i=1}^{N}|P_i^{\text{exptl}} - P_i^{\text{calcd}}|$.

The vapor–liquid equilibrium data reported in Table 4 for the ternary system ETBE (1) + isooctane (2) + methylcyclohexane (3) were found to be thermodynamically consistent by the McDermott and Ellis method (1965) as modified by Wisniak and Tamir (1977). 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

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

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

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

Table 8. Constants for the Redlich−Kister Model, Fit, Correlation, and Prediction Statistics

Binary Data

syst	$b_{ij} \times 10^1$	c_{ij}, d_{ij}	rmsd[a]	% dev[b]	max % dev[c]
ETBE (1) + isooctane (2)	1.18	0.00	0.4	0.7	1.3
ETBE (1) + methylcyclohexane (3)	1.49	0.00	0.7	0.7	4.3
isooctane (2) + methylcyclohexane(3)[c]	0.23	0.00	0.1	0.2	0.5

Ternary Data

γ_1/γ_2			γ_1/γ_3		
rmsd	max % dev	% dev	rmsd	max % dev	% dev
1.6	6.0	2.3	1.6	8.1	2.2

VLE Correlations and Predictions

	bubble-point pressures			dew-point pressures		
syst	ΔP^e(%)	$100\Delta y_1$ [f]	$100\Delta y_2$	ΔP (%)	$100\Delta x_1$	$100\Delta x_2$
1 + 2	0.52	0.1	0.1	0.53	0.2	0.2
1 + 3	0.21	0.2		0.31	0.2	
2 + 3	0.05		0.1	0.05		0.1
1 + 2 + 3[g]	0.37	0.3	0.1	0.52	0.3	0.1

[a] Root mean square deviation in activity coefficients $\{\sum_i^N \{\gamma_i^{\text{exptl}} - \gamma_i^{\text{calcd}}\}^2/N\}^{0.5}$ (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 Wisniak et al. (1998). [e] Average percentage deviation in pressure $\Delta P = 100/N\sum_i^N|P_i^{\text{exptl}} - P_i^{\text{calcd}}|P_i^{\text{exptl}}$. [f] Average absolute deviation in mole fraction $\Delta y = 1/N\sum_i^N|y_i^{\text{exptl}} - y_i^{\text{calcd}}|$. [g] Prediction from binary parameters.

Table 9. Parameters and Correlation and Prediction Statistics for Different G^E Models

					bubble-point pressures			dew-point pressures		
model	*ij*	$a_{ij}/(J\cdot\text{mol}^{-1})$	$a_{ji}/(J\cdot\text{mol}^{-1})$	α_{ij}	ΔP^e (%)	$100\Delta y_1$[f]	$100\Delta y_2$	ΔP (%)	$100\Delta x_1$	$100\Delta x_2$
NRTL	1 + 2[d]	261.87	80.47	0.3	0.48	0.1	0.1	0.50	0.2	0.2
	1 + 3	1046.19	−541.19	0.3	0.15	0.2		0.26	0.1	
	2 + 3	1.58	75.45	0.3	0.04		0.1	0.04		0.1
	1 + 2 + 3[g]				0.30	0.3	0.1	0.50	0.3	0.1
Wilson[a]	1 + 2[d]	498.70	−152.23		0.47	0.1	0.1	0.49	0.2	0.2
	1 + 3	−706.76	1239.84		0.13	0.2		0.24	0.1	
	2 + 3	218.03	−9.06		0.00		0.1	0.00		0.1
	1 + 2 + 3[g]				0.15	0.3	0.1	0.28	0.3	0.1
UNIQUAC[b]	1 + 2[d]	−84.50	188.01		0.40	0.2	0.2	0.42	0.2	0.2
	1 + 3	913.11	−716.80		0.13	0.1		0.23	0.1	
	2 + 3	−1.26	−1.22		0.01		0.1	0.00		0.1
	1 + 2 + 3[g]				0.28	0.3	0.2	0.16	0.3	0.2
UNIFAC[c]	1 + 2 + 3[g]				1.50	0.5	0.2	1.44	0.4	0.2

[a] Liquid volumes have been estimated from the Rackett equation (Rackett, 1970). [b] Molecular parameters are those calculated from UNIFAC. [c] Calculations based on original UNIFAC (Fredenslund et al., 1977; Hansen et al., 1991). [d] Data of Wisniak et al. (1998). [e] Average percentage deviation in pressure $\Delta P = 100/N\sum_i^N|P_i^{\text{exptl}} - P_i^{\text{calcd}}|P_i^{\text{exptl}}$ (N, number of data points). [f] Average absolute deviation in mole fraction $\Delta y = 1/N\sum_i^N|y_i^{\text{exptl}} - y_i^{\text{calcd}}|$. [g] Ternary prediction from binary parameters.

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 0.024.

The activity coefficients for the ternary system were correlated with the Redlich−Kister (1948) expansion

$$G^E/RT = \sum_{i=1}^{3}\sum_{j>i}^{3} x_i x_j [b_{ij} + c_{ij}(x_i - x_j) + d_{ij}(x_i - x_j)^2] + x_1 x_2 x_3 [C + D_1 x_1 + D_2 x_2] \quad (7)$$

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) + isooctane (2) have already been reported by Wisniak et al. (1998). The Redlich−Kister coefficients for the binaries ETBE (1) + methylcylcohexane (3) and isooctane (2) + methylcyclohexane (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 8. Analysis of the correlation indicated that the binary constants c_{ij} and d_{ij} are not needed, in good agreement with the previous discussion about eq 7. In addition, the ternary constants C, D_1, and D_2 were statistically not significant, suggesting that the ternary data can be predicted directly from the binary systems. In fact, activity coefficients and 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 8 where C, D_1, and D_2 are zero. Equilibrium vapor pressures and VLE compositions were also well predicted for the ternary system using the NRTL, Wilson, and UNIQUAC models (Walas, 1985) but somewhat worse by the UNIFAC model (Fredenslund et al., 1977; Hansen et al., 1991) using parameters previously fitted to the binaries. Table 9 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 data allow a good prediction of the ternary system.

Table 10. Coefficients in Correlation of Boiling Points, Equations 10 and 11, Average Deviation, and Root Mean Square Deviations in Temperature, rmsd (*T*/K)

Equation 10 (Fit from Binary Constants)

A	−7.1897	*C*	11.2026	avg dev/K[b]	0.09
B	11.1494	max dev/K[a]	0.23	rmsd[c]	0.07

	binary constants		
syst	C_0	C_1	C_2
1 + 2[d]	−14.0624	3.0841	−5.1931
1 + 3	−16.8057	6.8454	−2.7868
2 + 3	−0.8534	0.3200	0.0779

Equation 11 (Direct Fit)

ij	A_{ij}	B_{ij}	C_{ij}	max dev[a]/K	av dev[b]/K	rmsd[c]
1−2[d]	−15.5030	4.9457	1.0087	0.21	0.05	0.04
1−3	−17.2334	6.7167	−1.5593			
2−3	−1.8495	0.2050	−0.1456			

[a] Maximum deviations. [b] Average deviations. [c] rmsd (*T*/K): Root mean square deviation, $\{\sum(T_{\mathrm{exptl}} - T_{\mathrm{calcd}})^2/N\}^{0.5}$. [d] Data taken from Wisniak et al. (1998).

The boiling points of the systems were correlated by the equation proposed by Wisniak and Tamir (1976)

$$T/K = \sum_{i=1}^{n} x_i(T_i^\circ/\mathrm{K}) + \sum_{i,j=1}^{n}\{x_ix_j\sum_{k=0}^{m} C_k(x_i - x_j)^k\} + x_1x_2x_3\{A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3)\} \quad (8)$$

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 (1981) has suggested the following equation, of the same structure, for the direct correlation of ternary data, without use of binary data:

$$T/K = \sum_{i=1}^{3} x_iT_i^\circ + x_1x_2[A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2 + ...] + x_1x_3[A_{13} + B_{13}(x_1 - x_3) + C_{13}(x_1 - x_3)^2 + ...] + x_2x_3[A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2 + ...] \quad (9)$$

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 (Figure 5). The various constants of eqs 8 and 9 are reported in Table 10, together with information regarding 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 better fit.

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