Isobaric Vapor−Liquid Equilibria for Binary and Ternary Mixtures with Cyclohexane, Cyclohexene, and Methyl Isobutyl Ketone at 100 kPa

Beatriz Marrufo,[†] Sonia Loras,*[,‡] and Margarita Sanchotello[‡]

Departamento de Ingeniería Química Básica, Universidad del Zulia, 4011 Maracaibo, Venezuela, and Departamento de Ingeniería Química, Escuela Técnica Superior de Ingeniería, Universitat de València, 46100 Burjassot, València, Spain

Consistent vapor−liquid equilibrium (VLE) data at 100 kPa have been determined for the ternary system cyclohexane + cyclohexene + methyl isobutyl ketone and two constituent binary systems: cyclohexane + methyl isobutyl ketone and cyclohexene + methyl isobutyl ketone. Both binary systems show positive deviations from ideal behavior and do not present an azeotrope. The VLE data have been correlated by the Wilson, UNIQUAC, and NRTL equations. The ternary system does not present an azeotrope and is well predicted from binary interaction parameters. Prediction with the UNIFAC method has also been obtained.

Introduction

Separation of olefins and paraffins is a specific problem in the field of hydrocarbon processing. Because of their close boiling points, it is difficult and expensive to separate them by conventional distillation. Nevertheless, extractive distillation is commonly applied in the petrochemical industry for separation of hydrocarbons. This distillation requires the addition of a solvent known as an entrainer to modify the relative volatility of the mixture to be separated. A number of methods have been reported for the selection of a proper solvent; however, the most accurate solvent selection for extractive distillation must be based on complete vapor−liquid equilibrium (VLE) data of the involved mixtures.

The present work is part of an investigation undertaken to find good entrainers for olefin−paraffin separations by extractive distillation. Specifically, it was desired to find entrainers within the so-called "friendly" solvents, such as alcohols, esters, ketones, and ethers. A cyclohexane−cyclohexene mixture has been chosen to represent the olefin−paraffin mixtures. In previous work,[1,2] the behavior of two solvents as entrainers for separating cyclohexane−cyclohexene was studied: 2-methoxyethanol and morpholine. It was concluded that 2-methoxyethanol was not a good entrainer because it presents two binary homogeneous azeotropes. However, morpholine was a good entrainer since it enhances the relative volatility of cyclohexane to cyclohexene until economically recommended values are reached, but morpholine is not a solvent considered "friendly" due to its toxicity. For this reason, in this paper methyl isobutyl ketone (MIBK) has been selected as a possible entrainer for separating cyclohexane−cyclohexene, since it is a friendly and green solvent.

In this work, we measured isobaric VLE data for the ternary system cyclohexane (1) + cyclohexene (2) + methyl isobutyl ketone (3) and two constituent binary systems, cyclohexane (1) + 2-methyl isobutyl ketone (3) and cyclohexene (2) + methyl isobutyl ketone (3), at 100 kPa. In a previous paper,[3] we reported VLE data for the binary system cyclohexane (1) + cyclohexene (2). Dakshinamurty et al.[4,5] studied the separation of benzene−cyclohexene by extractive distillation using MIBK as the solvent, and isobaric VLE data for the cyclohexane + methyl isobutyl ketone system at atmospheric pressure were reported. However, for the binary system cyclohexene + methyl isobutyl ketone and for the ternary system, no VLE data have been previously published.

Table 1. Denstiy (d), Refractive Index (n_D), and Normal Boiling Point (T_b) of Pure Components

	d(298.15 K)		n_D(298.15 K)		T_b(101.3 kPa)	
	kg·m^{-3}				K	
component	exptl	lit.[a]	exptl	lit.[b]	exptl	lit.[b]
cyclohexane (1)	773.82	773.90	1.4238	1.4235	353.73	353.87
cyclohexene (2)	805.69	806.09	1.4444	1.4438	355.97	356.12
methyl isobutyl ketone (3)	796.03	796.10	1.3942	1.3933	388.78	389.15

[a] Reference 6. [b] Reference 7.

Experimental Section

Chemicals. The chemicals cyclohexane (100 $w \geq 99.8$, for residue analysis) and cyclohexene (100 $w \geq 99.5$, puriss. p.a.) were supplied by Fluka, and methyl isobutyl ketone (100 $w \geq 99.5$, for analysis) was supplied by Acros-Organics. The reagents were used without further purification since impurities are smaller than the detection limit of the analytical method used. The refractive indexes of the pure components were measured at 298.15 K using an Abbe refractometer, Atago 3T, and the densities were measured at 298.15 K using an Anton Paar DMA 58 densimeter. Temperature was controlled to ± 0.01 K with a thermostated bath. The uncertainties in density and refractive index measurements are ± 0.01 kg·m^{-3} and ± 0.0002, respectively. The experimental values of these properties and the normal boiling points are given in Table 1 together with those given in the literature.[6,7]

Apparatus and Procedure. The VLE data and the vapor pressure of the pure compounds were determined using a dynamic-recirculating still (Pilodist VLE 100 D) equipped with a Cottrell circulation pump. This still is capable of handling pressures from (0.25 to 400) kPa and temperatures up to 523 K. The equilibrium temperature was measured with a digital

---

* Corresponding author. Phone: +34 963544317. Fax: +34 963544898. E-mail: sonia.loras@uv.es.
[†] Universidad del Zulia.
[‡] Universitat de València.

10.1021/je100776x

Table 2. Experimental Vapor Pressure ($P_i°$) of Methyl Isobutyl Ketone

T	P	T	P
K	kPa	K	kPa
343.76	22.45	374.22	65.08
346.51	24.97	375.35	67.44
349.09	27.43	376.56	70.07
351.46	29.98	377.63	72.41
353.65	32.46	378.73	74.98
355.76	35.07	379.78	77.41
357.68	37.44	380.83	79.93
359.54	39.99	381.84	82.44
361.33	42.54	382.84	84.96
362.97	44.96	383.80	87.44
364.61	47.52	384.71	89.85
366.15	50.02	385.67	92.47
367.55	52.44	386.60	95.07
369.05	55.08	387.45	97.46
370.35	57.48	387.82	98.52
371.66	59.96	388.33	99.98
372.96	62.51	388.78	101.33

Hart Scientific thermometer, model 1502A, and a Hart Scientific Pt 100 probe, model AlB0888, calibrated at the Spanish Instituto Nacional de Técnica Aeroespacial. The uncertainty is estimated to be ± 0.02 K. A Pilodist M101 pressure control system was used to measure and control the pressure and the heating power. The measured pressure in the still was (100.0 ± 0.1) kPa. The manometer was calibrated using the vapor pressure of ultrapure water.

In each VLE experiment, the pressure was fixed and held constant by using a vacuum pump, and the heating and stirring systems of the liquid mixture were turned on. The still was operated at constant pressure until equilibrium was reached. Equilibrium conditions were assumed when constant temperature and pressure were obtained for 45 min or longer. To verify equilibrium conditions, the vapor and liquid were analyzed until the variation of the mole fraction of both the liquid and vapor phases was less than 0.001. The sample extractions were carried out with special syringes that allowed withdrawal of small-volume samples.

Analysis. The compositions of the liquid and condensed phases were determined using a Varian CP-3800 gas chromatograph after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 30 m, 0.25 mm i.d. capillary column, CP-Wax 52 CB. The gas chromatography (GC) response peaks were treated with Varian Star No. 1 for Windows. The column, injector, and detector temperatures were 333 K, 473 K, and 493 K, respectively, for all systems. Very good peak separation was achieved under these conditions, and calibration analyses were carried out to convert the peak area ratio to the mass composition of the sample. The average absolute deviation in the mole fraction was usually less than 0.001.

Results and Discussion

Pure Component Vapor Pressures. The pure component vapor pressures for methyl isobutyl ketone, $P_i°$, were determined experimentally using the same equipment as that for obtaining the VLE data. The pertinent results appear in Table 2. The measured vapor pressures were correlated using the Antoine equation

$$\ln P_i°/\text{kPa} = A_i - \frac{B_i}{T/\text{K} + C_i} \quad (1)$$

Table 3. Antoine Coefficients, Eq 1

compound	A_i	B_i	C_i
cyclohexane (1)[a]	14.4184	3166.74	−30.57
cyclohexene (2)[a]	13.1275	2423.40	−71.22
methyl isobutyl ketone (3)	14.1959	3167.41	−58.11

[a] Parameters obtained in ref 3.

Table 4. Experimental Vapor−Liquid Equilibrium Data for the Binary System Cyclohexane (1) + Methyl Isobutyl Ketone (3) at 100.0 kPa

T				
K	x_1	y_1	γ_1	γ_3
386.18	0.019	0.072	1.618	1.005
383.47	0.046	0.168	1.660	1.001
379.36	0.093	0.300	1.615	0.999
375.68	0.141	0.407	1.581	0.998
372.75	0.189	0.486	1.515	1.003
370.20	0.231	0.547	1.489	1.011
367.59	0.284	0.610	1.446	1.016
365.23	0.340	0.662	1.395	1.032
363.35	0.395	0.708	1.351	1.036
361.59	0.449	0.743	1.308	1.062
360.17	0.511	0.770	1.239	1.124
359.40	0.545	0.784	1.208	1.165
358.22	0.602	0.809	1.167	1.227
357.29	0.654	0.832	1.134	1.283
356.32	0.714	0.855	1.097	1.386
355.67	0.769	0.875	1.062	1.515
355.02	0.812	0.895	1.048	1.600
354.41	0.867	0.918	1.025	1.807
353.96	0.917	0.943	1.008	2.047
353.60	0.963	0.972	1.000	2.288
353.41	0.987	0.989	0.998	2.578

whose parameters A_i, B_i, and C_i are reported in Table 3 together with the Antoine parameters for cyclohexane and cyclohexene obtained in a previous work[3] and were fitted by a nonlinear optimization method to minimize the average relative deviation in pressure (ARDP). The vapor pressures of methyl isobutyl ketone were correlated with an ARDP of 0.09 %. Experimental data are in good agreement with the equation reported by Reid et al.[8] since this equation gives a correlation of the experimental vapor pressures reported in this work with ARDP = 0.97 %.

Binary Systems. The temperature (T) and the liquid-phase (x_i) and vapor-phase (y_i) mole fractions at 100.0 kPa for the systems cyclohexane (1) + methyl isobutyl ketone (3) and cyclohexene (2) + 2-methyl isobutyl ketone (3) are reported in Tables 4 and 5 and plotted in Figures 1 and 2. The activity coefficients (γ_i) were calculated from the following equation[9] assuming nonideality of both the liquid and vapor phases:

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i°} + \frac{(B_{ii} - V_i^{\mathrm{L}})(P - P_i°)}{RT} + \frac{P}{2RT}\sum\sum y_i y_k (2\delta_{ji} - \delta_{jk}) \quad (2)$$

where T and P are the equilibrium temperature and 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^{o} is the pure component vapor pressure, B_{ij} is the cross second virial coefficient, and

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \quad (3)$$

The standard state for the calculation of activity coefficients is the pure component at the pressure and temperature of the

Table 5. Experimental Vapor−Liquid Equilibrium Data for the Binary System Cyclohexene (2) + Methyl Isobutyl Ketone (3) at 100.0 kPa

T/K	x_2	y_2	γ_2	γ_3
386.75	0.018	0.059	1.487	1.002
384.79	0.044	0.136	1.465	0.999
382.14	0.080	0.229	1.441	1.000
379.35	0.123	0.324	1.415	0.998
376.76	0.166	0.403	1.387	1.002
374.30	0.213	0.485	1.381	0.988
372.05	0.258	0.543	1.351	0.998
370.25	0.299	0.592	1.330	0.998
367.94	0.358	0.647	1.288	1.016
365.79	0.422	0.698	1.248	1.035
364.34	0.474	0.733	1.212	1.056
363.04	0.527	0.764	1.177	1.084
361.85	0.582	0.794	1.144	1.115
360.65	0.637	0.819	1.115	1.175
359.70	0.687	0.841	1.090	1.237
358.85	0.740	0.865	1.065	1.303
358.00	0.790	0.888	1.049	1.379
357.29	0.843	0.911	1.029	1.503
356.65	0.893	0.936	1.016	1.623
356.08	0.946	0.964	1.004	1.848
355.77	0.978	0.984	1.001	2.040

solution. Equation 2 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[10] using the molecular parameters suggested by Prausnitz et al.[11] The critical properties of all components were taken from DIPPR.[7]

According to the results, both binary systems show positive deviations from ideal behavior and do not present an azeotrope.

The thermodynamic consistency of the VLE data, for each binary system, has been verified with the Fredenslund test.[12] Pertinent consistency details and statistics are presented in Table 6, and it can be seen that the consistency criterion (AADy < 0.01) was achieved using a three-parameter Legendre polynomial.

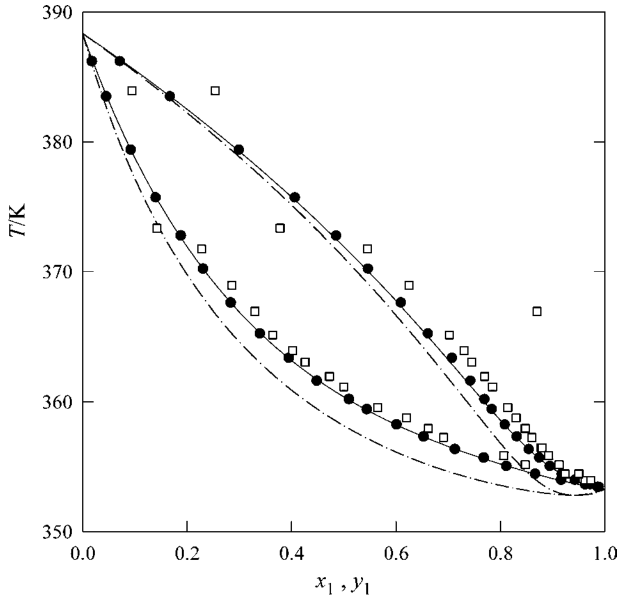

Figure 1. Experimental VLE data for the system cyclohexane (1) + methyl isobutyl ketone (3) at 100.0 kPa: ●, experimental data; □, ref 4; solid line, smoothed data using the NRTL model with the parameters given in Table 7; dotted−dashed line, data predicted by the UNIFAC method.

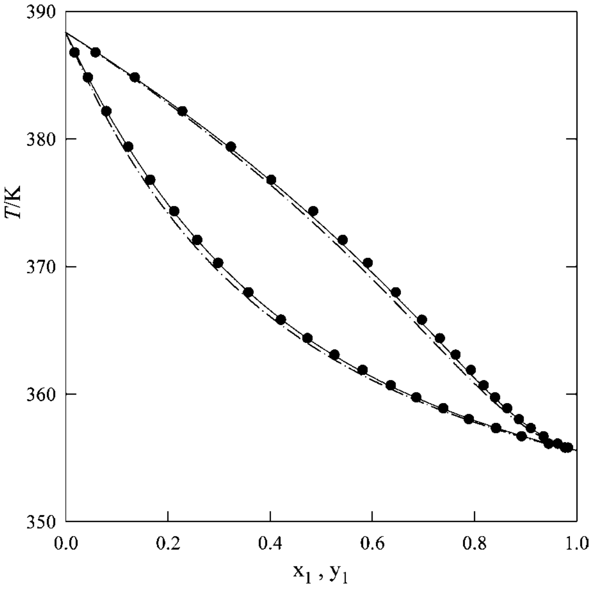

Figure 2. Experimental VLE data for the system cyclohexene (2) + methyl isobutyl ketone (3) at 100.0 kPa: ●, experimental data; solid line, smoothed data using the NRTL model with the parameters given in Table 7; dotted−dashed line, data predicted by the UNIFAC method.

Table 6. Consistency Test Statistics for the Binary Systems

system $i + j$	A_1[a]	A_2[a]	A_3[a]	100·AADy$_i$[b]	AADP[c] kPa
1 + 3	0.6958	0.2032	0.0281	0.273	0.177
2 + 3	0.5250	0.1727	0.0212	0.200	0.400

[a] Legendre polynomial parameters. [b] Average absolute deviation in vapor-phase composition. [c] Average absolute deviation in pressure.

The VLE data for each binary system have been correlated using local composition models (Wilson, NRTL, and UNIQUAC). For the Wilson model, molar liquid volumes of pure components have been estimated with the Rackett equation,[13] and for the UNIQUAC model, volume and surface parameters were taken from DECHEMA.[14] The parameters of these models have been determined by minimizing the following objective function (OF)

$$\mathrm{OF} = \sum_{i=1}^{N} 100\cdot\left(\left|\frac{T_i^{\mathrm{exptl}} - T_i^{\mathrm{calcd}}}{T_i^{\mathrm{exptl}}}\right| + |y_i^{\mathrm{exptl}} - y_i^{\mathrm{calcd}}|\right) \qquad (4)$$

and are reported in Table 7, together with the obtained average deviations of the correlation. An inspection of the results given in that table shows that the three composition models are adequate for the description of the VLE of both binary systems, without any significant difference between them.

The experimental data were compared with those predicted by the UNIFAC contribution method,[12,15] and the quality of the prediction can be observed in Table 7 and Figures 1 and 2. It must be pointed out that this prediction is not too good in the case of the binary system cyclohexane (1) + methyl isobutyl ketone (2), since a minimum boiling azeotrope at $x_1 \approx 0.94$ and $T = 352.8$ K is predicted, and this point has not been found experimentally. Also, in those figures the calculated data using the NRTL model and the VLE bibliographic data[4] are presented.

Ternary System. VLE data for the ternary system cyclohexane (1) + cyclohexene (2) + 2-methyl isobutyl ketone (3) are reported in Table 8 and Figure 3. The activity coefficients (γ_i)

Table 7. Parameters and Correlation Statistics for Different G^E Models for the System Cyclohexane (1) + Cyclohexene (2) + Methyl Isobutyl Ketone (3)

					bubble point		
		A_{ij}	A_{ij}		ARDT[a]		
model	system $i + j$	$\mathrm{J \cdot mol^{-1}}$	$\mathrm{J \cdot mol^{-1}}$	α_{ij}	%	$100 \cdot \mathrm{AADy}_1$[b]	$100 \cdot \mathrm{AADy}_2$[b]
Wilson[c]	1 + 2[d]	831.37	−598.78		0.036	0.075	
	1 + 3	44.65	2812.62		0.058	0.330	
	2 + 3	−150.31	2492.32		0.047	0.437	
	1 + 2 + 3[e]				0.124	0.126	0.106
NRTL	1 + 2[d]	−1195.08	1403.45	0.20	0.038	0.072	
	1 + 3	3875.01	−1013.57	0.30	0.050	0.307	
	2 + 3	3883.15	−1458.62	0.30	0.047	0.411	
	1 + 2 + 3[e]				0.112	0.128	0.092
UNIQUAC[f]	1 + 2[d]	−365.51	422.30		0.038	0.070	
	1 + 3	1378.97	−629.93		0.052	0.313	
	2 + 3	1353.01	−722.15		0.048	0.415	
	1 + 2 + 3[e]				0.111	0.123	0.096
UNIFAC[g]	1 + 2[d]				0.062	0.072	
	1 + 3				1.693	1.295	
	2 + 3				0.347		0.620
	1 + 2 + 3[e]				1.070	0.956	0.859

[a] Average relative deviation in temperature. [b] Average absolute deviation in vapor-phase composition. [c] The molar liquid volumes of pure components have been estimated with the Rackett equation.[13] [d] Reference 3. [e] Ternary estimation from binary parameters. [f] Volume and surface parameters from DECHEMA.[14] [g] Calculations based on the original UNIFAC method.[12,15]

Table 8. Experimental Vapor−Liquid Equilibrium Data for the System Cyclohexane (1) + Cyclohexene (2) + Methyl Isobutyl Ketone (3) at 100.0 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
380.48	0.047	0.047	0.150	0.126	1.571	1.405	1.000
370.24	0.048	0.242	0.112	0.467	1.479	1.303	1.013
363.61	0.049	0.440	0.086	0.656	1.314	1.192	1.075
359.36	0.049	0.646	0.069	0.779	1.180	1.082	1.229
355.89	0.050	0.901	0.056	0.911	1.040	1.002	1.857
356.27	0.102	0.799	0.117	0.822	1.052	1.009	1.679
357.59	0.101	0.695	0.126	0.765	1.102	1.039	1.404
359.19	0.099	0.591	0.137	0.708	1.162	1.081	1.243
361.03	0.099	0.490	0.150	0.646	1.221	1.132	1.149
363.31	0.096	0.388	0.167	0.575	1.307	1.195	1.077
366.16	0.096	0.290	0.189	0.484	1.376	1.248	1.039
369.59	0.099	0.194	0.221	0.366	1.434	1.294	1.018
373.73	0.098	0.098	0.255	0.216	1.497	1.354	1.010
368.34	0.196	0.100	0.418	0.181	1.413	1.286	1.032
365.07	0.199	0.198	0.370	0.316	1.341	1.229	1.051
362.75	0.198	0.291	0.328	0.417	1.268	1.173	1.092
360.34	0.197	0.400	0.290	0.513	1.202	1.122	1.163
358.41	0.202	0.507	0.265	0.588	1.130	1.070	1.285
356.34	0.204	0.663	0.234	0.686	1.053	1.014	1.622
355.36	0.202	0.755	0.219	0.750	1.018	1.000	2.038
355.55	0.299	0.604	0.331	0.609	1.034	1.010	1.745
356.82	0.296	0.498	0.356	0.535	1.084	1.036	1.427
358.27	0.296	0.397	0.388	0.456	1.135	1.066	1.295
359.95	0.295	0.290	0.429	0.369	1.204	1.125	1.174
361.99	0.297	0.195	0.478	0.269	1.259	1.153	1.116
365.98	0.284	0.045	0.569	0.078	1.412	1.292	1.032
361.18	0.394	0.100	0.620	0.136	1.261	1.164	1.108
359.13	0.401	0.199	0.563	0.244	1.191	1.109	1.191
357.59	0.401	0.303	0.508	0.340	1.121	1.063	1.331
356.31	0.403	0.402	0.470	0.422	1.068	1.028	1.512
354.81	0.398	0.550	0.424	0.541	1.018	1.004	1.984
355.05	0.499	0.398	0.540	0.396	1.027	1.010	1.795
356.11	0.497	0.298	0.577	0.312	1.070	1.031	1.492
357.33	0.493	0.204	0.620	0.230	1.119	1.072	1.307
359.47	0.498	0.055	0.717	0.070	1.208	1.139	1.162
356.82	0.608	0.100	0.744	0.110	1.106	1.062	1.334
355.72	0.599	0.203	0.684	0.208	1.065	1.024	1.509
354.36	0.600	0.350	0.625	0.340	1.008	1.009	2.051
354.54	0.700	0.199	0.740	0.196	1.019	1.012	1.861
356.18	0.699	0.052	0.811	0.056	1.067	1.052	1.468
354.29	0.800	0.104	0.835	0.102	1.014	1.016	1.932
353.82	0.899	0.053	0.914	0.051	1.001	1.010	2.188

were calculated from eq 2, and the molar virial coefficients were estimated as well as for the binary systems. The ternary data were found to be thermodynamically consistent by the Wisniak and Tamir[16] modification of the McDermott−Ellis test.[17] The test requires that $D < D_{\max}$ for every experimental point, where the local deviation (D) is given by

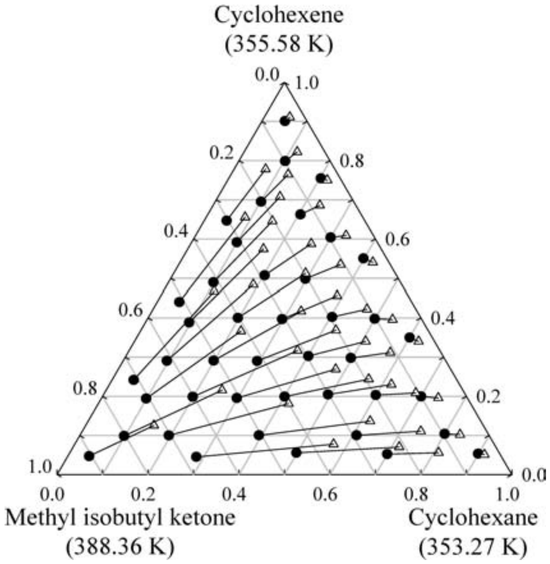

Figure 3. Diagram of VLE for the ternary system cyclohexane (1) + cyclohexene (2) + methyl isobutyl ketone (3) at 100.0 kPa: ●, liquid-phase mole fractions; Δ, vapor-phase mole fractions.

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

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

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

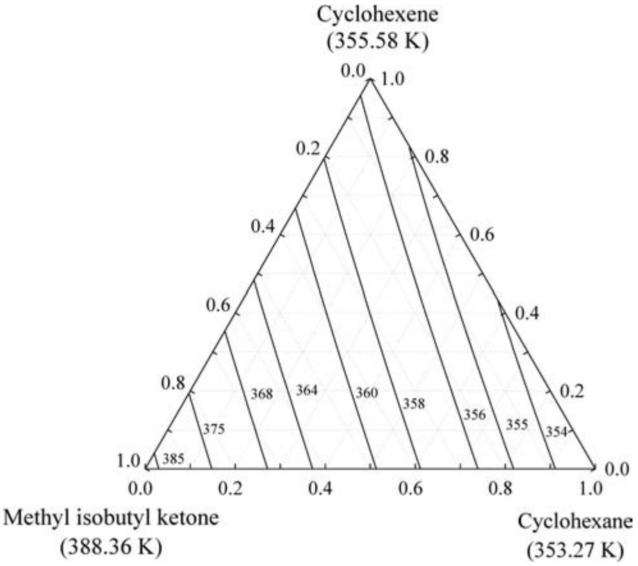

Figure 4. Boiling isotherms (K) for the ternary system cyclohexane (1) + cyclohexene (2) + methyl isobutyl ketone (3) at 100.0 kPa calculated with the NRTL model with the parameters given in Table 7.

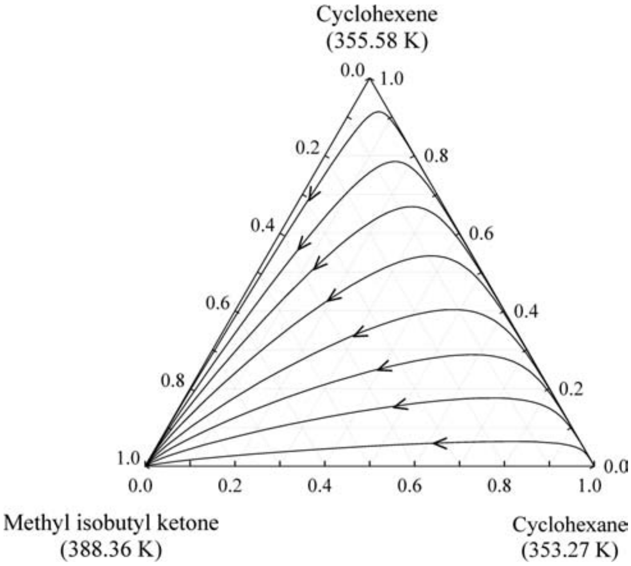

Figure 5. Residue curve map for the ternary system cyclohexane (1) + cyclohexene (2) + methyl isobutyl ketone (3) at 100.0 kPa simulated by Aspen Split using the NRTL model with the parameters given in Table 7.

The errors in the measurements, Δx, ΔP, and ΔT, were as previously indicated. The first and fourth terms in eq 6 are the dominant ones. For each experimental point reported here the value of D was always smaller than the value of $D_{\max}$.

VLE data for the ternary systems have been estimated by using the Wilson, NRTL and UNIQUAC models with the binary interaction parameters obtained from the regression of binary data and also are predicted by the UNIFAC method. Table 7 lists the mean absolute deviations between experimental and calculated temperatures and vapor-phase mole fractions of the components. The three models represent the data successfully. Thus, the models can be used to calculate boiling points from liquid-phase compositions at the system pressure. As an example, boiling isotherms calculated with the NRTL model are presented in Figure 4.

Solvent Effects. Several methods are available for determining the product distribution in a distillation of multicomponent mixtures. One of the most widely practiced methods is the analysis of the residue curve map.[18] In Figure 5, residue curves simulated by Aspen Split v2006 using the NRTL model with the experimental parameters reported in Table 7 are shown. As can be seen in this figure, there are three singular points (nodes and saddles): three pure component vertices. Cyclohexane is an unstable node (where residue curves begin), cyclohexene is a saddle (where residue curves are deflected), and methyl isobutyl ketone is a stable node (where residue curves terminate). Therefore, cyclohexane could be obtained as an overhead product (unstable node), and methyl isobutyl ketone could be obtained as a bottom product (stable nodes), as was to be expected according to the boiling points of the three pure components. The actual compositions of the final products obviously will depend on the number of plates and feed, reflux, and reboil ratios, etc. In this case the residue curve map gives little valuable information.

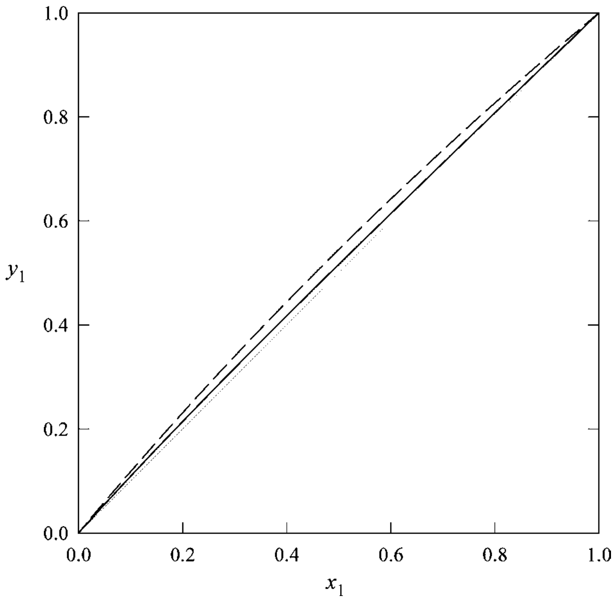

Figure 6. VLE data plotted on a solvent-free basis for the system cyclohexane (1) + cyclohexene (2) + methyl isobutyl ketone (3) at 100.0 kPa calculated using the NRTL model with the parameters given in Table 7: continuous line,[3] $x_3 = 0.00$; dashed line, $x_3 = 0.70$.

A more useful method in this case is the study of the solvent influence on the phase behavior of the ternary mixture on a solvent-free basis. As can be observed in Figure 6, methyl isobutyl ketone enhances the relative volatility of cyclohexane to cyclohexene ($\alpha_{12} = 1.070$);[3] for instance, $\alpha^{S}_{12} = 1.197$ for $x_3 = 0.70$ and $\alpha^{S}_{12} = 1.212$ for $x_3 = 0.80$ (α^{S}_{12} is the relative volatility in the presence of the solvent and has been calculated using the NRTL model with the parameters given in Table 7). To know whether this value of α^{S}_{12} is enough to consider extractive distillation as an economic separation process in this case, there is an economic rule of thumb[19] that gives some orientations to determine whether the extractive distillation with a specific solvent can be economically viable on the basis of the variation of the relative volatility. According to this rule, the separation of cyclohexane/cyclohexene by extractive distillation using a determined entrainer could be a process with good economic probability from a value of $\alpha^{S}_{12} = 1.20$, and the economic probability is high from a value of $\alpha^{S}_{12} = 1.33$. Attending to the achieved values of α^{S}_{12} with a composition of $x_3 = 0.80$ using methyl isobutyl ketone and morpholine[2] as entrainers, it can be concluded that morpholine is a better solvent than methyl isobutyl ketone, since morpholine requires less quantity for the same separation. On the other hand, methyl isobutyl ketone is considered a friendly solvent and morpholine is not. In this sense, methyl isobutyl ketone is a more advisible entrainer than morpholine. Therefore, to study the economic viability of the separation of cyclohexane/cyclohexane by extractive distillation using a defined entrainer, the flow relation feed/solvent and the materials safety data sheets must be taken into account.

Conclusions

Consistent VLE data at 100.0 kPa have been determined for the binary systems cyclohexane (1) + methyl isobutyl ketone (3) and cyclohexane (2) + methyl isobutyl ketone (3) and the ternary system cyclohexane (1) + cyclohexane (2) + methyl isobutyl ketone (3). The Wilson, NRTL, and UNIQUAC models correlated the binary systems well and yielded a good estimation for the ternary system, without any remarkable difference.

According to the results, methyl isobutyl ketone enhances the relative volatitility of cyclohexane to cyclohexene until economically recommended values are obtained. Therefore, it can be concluded that methyl isobutyl ketone could be a good entrainer for the separation of cyclohexane/cyclohexene by extractive distillation. This separation process is especially attractive since methyl isobutyl ketone is a friendly solvent.

Literature Cited

(1) Marrufo, B.; Loras, S.; Sanchotello, M. Isobaric Vapor−Liquid Equilibrium for Binary Mixtures of Cyclohexane, Cyclohexene, and 2-Methoxyethanol at 100 kPa. *J. Chem. Eng. Data* **2010**, *55*, 62–68.

(2) Marrufo, B.; Loras, S.; Sanchotello, M. Isobaric Vapor−Liquid Equilibrium for Binary Mixtures of Cyclohexane, Cyclohexene, and Morpholine at 100 kPa. *Fluid Phase Equilib.* **2010**, *296*, 178–183.

(3) Marrufo, B.; Aucejo, A.; Loras, S.; Sanchotello, M. Isobaric Vapor−Liquid Equilibrium for Binary Mixtures of 1-Hexene + n-Hexane and Cyclohexane + Cyclohexene at 30, 60 and 101.3 kPa. *Fluid Phase Equilib.* **2009**, *279*, 11–16.

(4) Dakshinamurty, P.; Rao, G. J. R.; Acharya, M. V. R.; Rao, C. V. Vapour−Liquid Equilibria: Cyclohexane−Methyl Isobutyl Ketone & Benzene−Methyl Isobutyl Ketone. *J. Sci. Ind. Res.* **1957**, *16B*, 340–345.

(5) Dakshinamurty, P.; Rao, G. J. R.; Acharya, M. V. R.; Rao, C. V. Ternary Vapour−Liquid Equilibria in the System: Benzene + Cyclohexane + Methyl Isobutyl Ketone. *Chem. Eng. Sci.* **1958**, *9*, 69–73.

(6) NIST Standard Reference Database 85, NIST/TRC Table Database, WinTable, Version 2004.

(7) Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals. Data Compilation*; Taylor & Francis: Bristol, PA, 1989.

(8) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.

(9) Van Ness, H. C.; Abbott, M. M. *Classical Thermodynamics of Nonelectrolyte Solutions*; McGraw-Hill: New York, 1982.

(10) Hayden, J.; O'Connell, J. A Generalized Method for Predicting Second Virial Coefficients. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209–216.

(11) Prausnitz, J.; Anderson, T.; Grens, E.; Eckert, C.; Hsieh, R.; O'Connell, J. *Computer Calculation for Multicomponent Vapor−Liquid and Liquid−Liquid Equilibria*; Prentice Hall: Englewood Cliffs, NJ, 1980.

(12) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor−Liquid Equilibria Using UNIFAC. A Group Contribution Method*; Elsevier: Amsterdam, 1977.

(13) Rackett, H. G. Equation of State for Saturated Liquids. *J. Chem. Eng. Data* **1970**, *15*, 514–517.

(14) Gmehling, J.; Onken, U. *Vapor−Liquid Equilibrium Data Collection*; DECHEMA: Frankfurt, Germany, 1977.

(15) Hansen, H. K.; Rasmussen, P.; Fredenslund, A.; Schiller, M.; Gmehling, J. Vapor−Liquid Equilibria by UNIFAC Group Contribution. 5. Revision and Extension. *Ind. Eng. Chem. Res.* **1991**, *30*, 2352–2355.

(16) Wisniak, J.; Tamir, A. Vapor−Liquid Equilibria in the Ternary System Water−Formic Acid−Acetic Acid and Water−Acetic Acid−Propionic Acid. *J. Chem. Eng. Data* **1977**, *22*, 253–260.

(17) McDermott, C.; Ellis, S. R. M. A Multicomponent Consistency Test. *Chem. Eng. Sci.* **1965**, *20*, 293–296.

(18) Doherty, M. F.; Malone, M. F. *Conceptual Design of Distillation Systems*; McGraw-Hill: New York, 2001.

(19) Brix-Berg. http://www.brix-berg.com (accessed Nov 15, 2010).

Received for review July 26, 2010. Accepted October 26, 2010. Financial support from the Ministerio de Ciencia y Tecnología of Spain, through Project No. CTQ2007-61400/PPQ), the FEDER European Program, and the Conselleria de Cultura, Educació i Esport (Generalitat Valenciana) of Valencia is gratefully acknowledged. B.M. has been funded by a grant from La Universidad del Zulia, Venezuela.

JE100776X