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Isobaric Vapor−Liquid Equilibria for Binary and Ternary Mixtures with Cyclohexane, Cyclohexene, and 2-Methoxyethanol at 100 kPa

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Consistent vapor−liquid equilibria (VLE) data at 100 kPa have been determined for the ternary system cyclohexane + cyclohexene + 2-methoxyethanol and two constituent binary systems: cyclohexane + 2-methoxyethanol and cyclohexene + 2-methoxyethanol. Both binary systems deviate remarkably from ideal behavior presenting a minimum boiling point 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 been also obtained.

Introduction

Cyclohexane/cyclohexene is a mixture of hydrocarbons present in different streams of the petrochemical industry for example in the products of partial catalytic hydrogenation of benzene. Because of their close boiling points extractive or azeotropic distillations are processes potentially suitable for the separation of this hydrocarbon mixture. These distillations require 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 or azeotropic distillations must be based on complete vapor−liquid equilibrium (VLE) data of the mixtures.

The present work was undertaken as a part of thermodynamic research on the separation of cyclohexane and cyclohexene using different solvents. In this work, the behavior of 2-methoxyethanol (widely known by its trade name, methyl cellosolve) as a possible entrainer is investigated since it is recommended as a good entrainer for separating cyclohexane/cyclohexene.[1]

In this work, we measured isobaric VLE data for the ternary system cyclohexane (1) + cyclohexene (2) + 2-methoxyethanol (3) and two constituent binary systems cyclohexane (1) + 2-methoxyethanol (3) and cyclohexene (2) + 2-methoxyethanol (3) at 100 kPa. In a previous work,[2] we reported VLE data for the binary system cyclohexane (1) + cyclohexene (2) at (30, 60, and 101.3) kPa. Thornton and Garner[3] reported an azeotropic behavior for the system cyclohexane + 2-methoxyethanol at 101.3 kPa, but there is no information about cyclohexene + 2-methoxyethanol in the literature. 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(298.15K)				T_b(101.3 kPa)	
	kg·m^{-3}		n_D(298.15 K)		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
2-methoxyethanol (3)	960.02	960.20	1.4006	1.4002	397.37	397.50

[a] Ref 14. [b] Ref 5.

Table 2. Experimental Vapor Pressure (P_i^o) of 2-Methoxyethanol

T/K	P/kPa	T/K	P/kPa
345.94	14.98	381.44	59.94
349.54	17.51	382.64	62.46
352.72	20.02	383.74	64.87
355.49	22.45	384.89	67.49
358.12	25.02	385.95	69.92
360.51	27.53	387.02	72.45
362.72	29.98	388.02	74.99
364.76	32.52	388.98	77.41
366.62	34.91	389.94	79.86
368.51	37.49	390.92	82.45
370.14	39.92	391.85	84.96
371.85	42.51	392.74	87.49
373.35	44.91	393.61	89.96
374.89	47.49	394.47	92.48
376.28	49.96	395.32	94.94
377.65	52.42	396.12	97.48
378.98	54.96	396.96	100.03
380.23	57.48		

Experimental Section

Chemicals. The chemicals cyclohexane ($w \geq 99.8$ %, for residue analysis) and cyclohexene ($w \geq 99.5$ %, puriss. p.a.) were supplied by Fluka, and 2-methoxyethanol anhydrous ($w = 99.8$ %, anhydrous grade) was supplied by Aldrich. 2-Methoxyethanol was dried over 4-Å molecular sieves as soon as the bottles were opened. The reagents were used without further purification after chromatography failed to show any significant impurities. The refractive indexes of the pure components were measured at 298.15 K using an Abbe refractometer Atago 3T, and densities were measured at 298.15 K using an Anton Paar DMA 58 densimeter. Temperature was controlled to ± 0.01 K with a thermostatted 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

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Table 3. Vapor Pressure Parameters

compound	eq [a]	A_i	B_i	C_i	D_i	E_i	ref
cyclohexane (1)	1	14.4184	3166.74	−30.57			[b]
cyclohexene (2)	1	13.1275	2423.40	−71.22			[b]
2-methoxyethanol (3)	1	15.1136	3499.61	−63.89			this work[c]
	2	7.8498	1793.982	236.877			[d]
	3	202.63	−12472	−27.385	$2.64 \cdot 10^{-5}$	2	[e]

[a] Vapor pressure equations: eq 1, $\ln p^{o}/\text{kPa} = A - B/[(T/\text{K}) + C]$; eq 2, $\log P^{o}/\text{mmHg} = A - B/[(T/°\text{C}) + C]$; eq 3, $\ln P^{o}/\text{Pa} = A + B/(T/\text{K}) + C \ln T/\text{K} + D\,(T/\text{K})^{E}$. [b] Parameters taken from Marrufo et al.[2] [c] Antoine's parameters were calculated from the experimental data in Table 2. [d] Parameters taken from Pick et al.[4] [e] Parameters taken from DIPPR.[5]

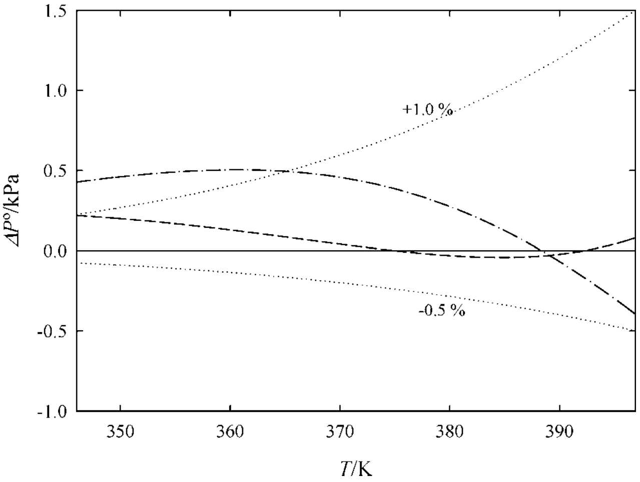

Figure 1. Differences, $\Delta P_i^{o} = P_{i,\text{lit}}^{o} - P_{i,\text{exptl}}^{o}$, obtained for vapor pressures of the 2-methoxyethanol using the parameters given in Table 3. ---, ref 4; −•−, ref 5.

Table 4. Experimental Vapor−Liquid Equilibrium Data for the Binary System Cyclohexane (1) + 2-Methoxyethanol (3) at 100.0 kPa

T/K	x_1	y_1	γ_1	γ_3
391.80	0.012	0.160	4.978	0.998
382.99	0.035	0.387	5.055	0.996
375.57	0.064	0.556	4.757	0.963
363.75	0.119	0.717	4.491	1.012
361.04	0.152	0.766	4.045	0.967
355.47	0.252	0.816	3.041	1.078
354.52	0.284	0.825	2.804	1.114
353.54	0.331	0.832	2.496	1.192
352.80	0.387	0.830	2.177	1.357
352.21	0.466	0.843	1.868	1.475
351.85	0.526	0.847	1.680	1.645
351.55	0.584	0.852	1.536	1.836
351.48	0.630	0.854	1.430	2.042
351.36	0.675	0.860	1.349	2.242
351.17	0.734	0.863	1.252	2.702
351.10	0.779	0.865	1.184	3.215
351.03	0.850	0.868	1.091	4.645
350.99	0.879	0.881	1.041	4.991
351.18	0.934	0.903	1.029	7.725
352.34	0.981	0.954	0.999	12.162

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

T/K	x_2	y_2	γ_2	γ_3
392.57	0.016	0.154	3.811	0.985
383.81	0.050	0.385	3.710	0.988
373.63	0.101	0.588	3.586	0.998
370.16	0.129	0.649	3.384	0.996
366.56	0.161	0.699	3.209	1.015
363.96	0.201	0.734	2.893	1.041
362.46	0.227	0.748	2.719	1.080
360.14	0.285	0.780	2.408	1.117
358.78	0.330	0.797	2.207	1.162
357.80	0.373	0.807	2.032	1.228
356.89	0.427	0.815	1.840	1.336
356.57	0.455	0.820	1.753	1.385
356.03	0.503	0.828	1.626	1.484
355.59	0.546	0.835	1.530	1.587
355.24	0.591	0.849	1.452	1.636
354.94	0.633	0.847	1.364	1.870
354.66	0.679	0.857	1.297	2.022
354.38	0.730	0.861	1.222	2.364
354.19	0.788	0.868	1.147	2.883
354.05	0.836	0.876	1.096	3.522
353.99	0.893	0.893	1.048	4.674
354.30	0.945	0.924	1.015	6.388
354.86	0.975	0.956	1.001	7.967

boiling points are given in Table 1 together with those given in the literature.

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 Hart Scientific thermometer model 1502A and a Pt 100 probe Hart Scientific 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. Then, samples of liquid and condensate were taken for analysis. The sample extractions were carried out with special syringes that allowed withdrawal of small volume samples (0.5 μL). At least two analyses were made of each liquid and vapor composition.

Analysis. Compositions of the liquid and condensed phases were determined using a Varian CP-3800 gas chromatograph (GC), 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 GC response peaks were treated with Varian Star #1 for Windows. Column, injector, and detector temperatures for the binary systems were (353, 473, and 493) K, respectively, and for the ternary system were (333, 473, and 498) K, respectively. 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.

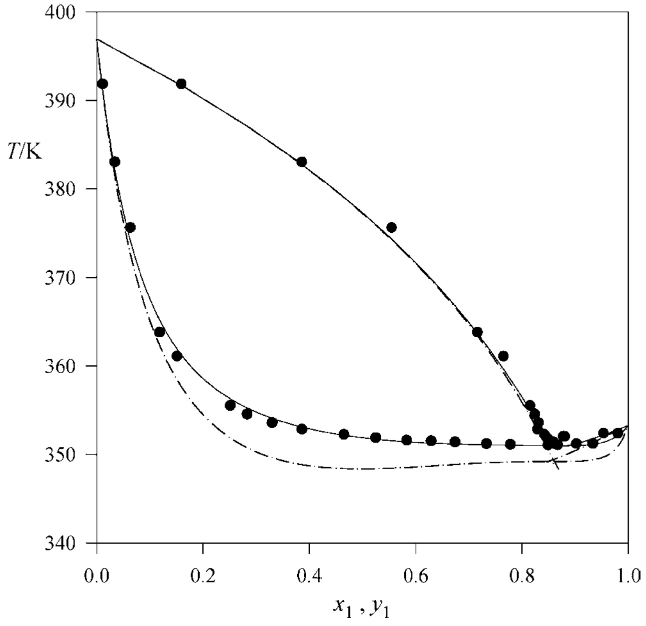

Figure 2. Experimental VLE data for the system cyclohexane (1) + 2-methoxyethanol (3) at 100.0 kPa: ●, experimental data; —, smoothed data using the NRTL model with the parameters given in Table 7; -•-, predicted by the UNIFAC method.

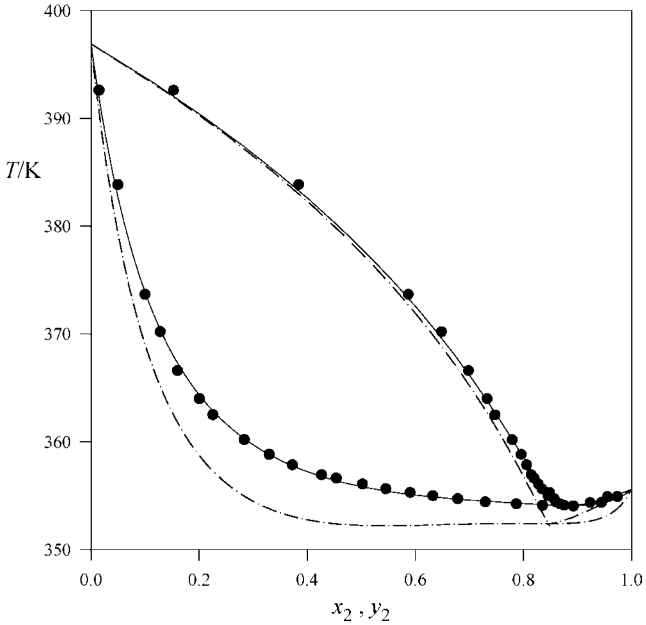

Figure 3. Experimental VLE data for the system cyclohexene (2) + 2-methoxyethanol (3) at 100.0 kPa: ●, experimental data; —, smoothed data using the NRTL model with the parameters given in Table 7; -•-, predicted by the UNIFAC method.

Results and Discussion

Pure Component Vapor Pressures. The pure component vapor pressures for 2-methoxyethanol (3), P_i°, were determined experimentally in the relevant temperature range for VLE calculations, 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

$$\ln P_i^\circ/\text{kPa} = A_i - \frac{B_i}{T/\text{K} + C_i} \tag{1}$$

whose parameters A_i, B_i, and C_i are reported in Table 3 together with some literature values. The deviations, $\Delta P_i^\circ = P_{i,\text{lit}}^\circ - P_{i,\text{exptl}}^\circ$, calculated by means of the Antoine equation using the constant values of Table 3, have been graphically represented in Figure 1. The mean error was less than 0.2 % with respect to the data reported by Pick et al.[4] and less than 0.8 % with respect to the values reported in DIPPR.[5]

The pure vapor pressures of cyclohexane and cyclohexene were taken from a previous work.[2]

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) + 2-methoxyethanol (3) and cyclohexene (2) + 2-methoxyethanol (3) are reported in Tables 4 and 5 and

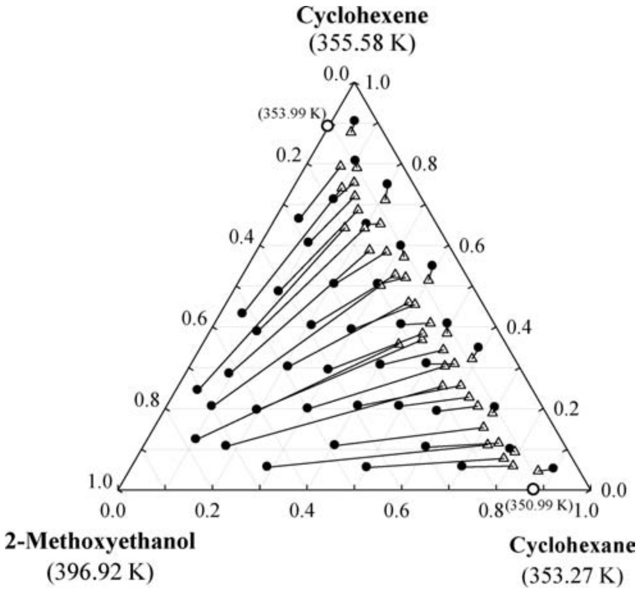

Figure 4. Diagram of VLE for the ternary system cyclohexane (1) + cyclohexene (2) + 2-methoxyethanol (3) at 100.0 kPa: ●, liquid-phase mole fractions; Δ, vapor-phase mole fractions; ○, azeotropes.

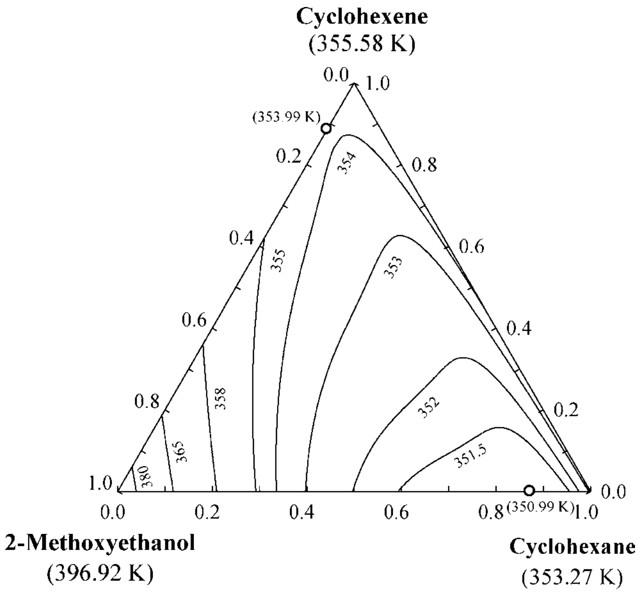

Figure 5. Boiling isotherms (K) for the ternary system cyclohexane (1) + cyclohexene (2) + 2-methoxyethanol (3) at 100.0 kPa calculated with the NRTL model with the parameters given in Table 7: ○, azeotropes.

Table 6. Consistency Test Statistics for the Binary Systems

system $i + j$	A_1[a]	A_2[a]	A_3[a]	A_4[a]	$100 \cdot \mathrm{AAD}y_i$[b]	AADP[c]/kPa
cyclohexane (1) + 2-methoxyethanol (3)	2.0348	0.4111	0.1090	0.1264	0.309	1.144
cyclohexene (2) + 2-methoxyethanol (3)	1.7573	0.4546	0.1281	0.1192	0.449	0.448

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

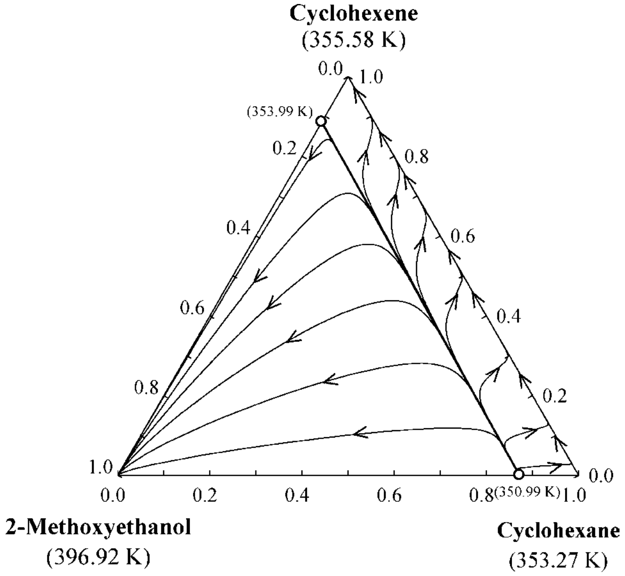

Figure 6. Residue curve map for the ternary system cyclohexane (1) + cyclohexene (2) + 2-methoxyethanol (3) at 100.0 kPa simulated by Aspen split using the NRTL model with the parameters given in Table 7. ○, azeotropes.

plotted in Figures 2 and 3. The activity coefficients γ_i were calculated from the following equation[6] assuming nonideality of both liquid and vapor phases

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

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

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

The standard state for the calculation of activity coefficients is the pure component at the pressure and temperature of the 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[7] using the molecular parameters suggested by Prausnitz et al.[8] Critical properties of all components were taken from DIPPR.[5]

According to the results, both binary systems deviate remarkably from ideality and present a minimum boiling temperature azeotrope at $x_1 \approx 0.88$ and $T = 350.99$ K for the system cyclohexane (1) + 2-methoxyethanol (3) and at $x_2 \approx 0.89$ and $T = 353.99$ K for the system cyclohexene (2) + 2-methoxyethanol (3).

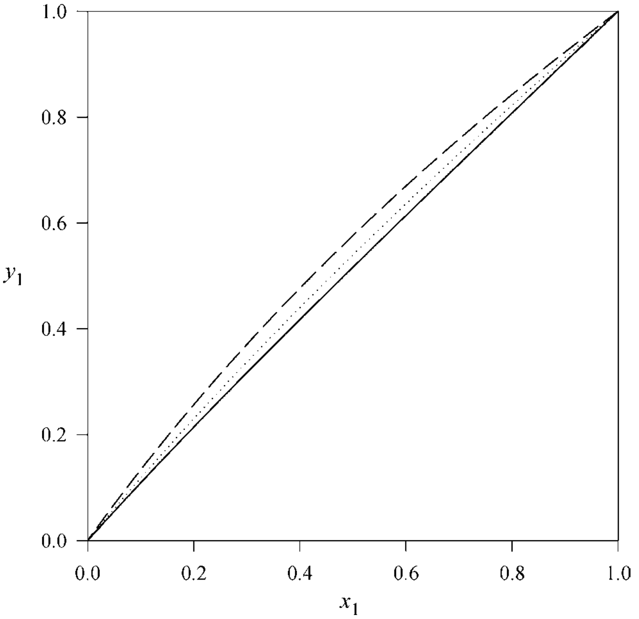

Figure 7. VLE data plotted on a solvent-free basis for the system cyclohexane (1) + cyclohexene (2) + 2-methoxyethanol (3) at 100.0 kPa. Continuous line[2] for $x_3 = 0.00$. Dotted line for $x_3 = 0.10$, and dashed line for $x_3 = 0.70$, calculated using the NRTL model with the parameters given in Table 7
.

The thermodynamic consistency of the VLE data, for each binary system, has been verified with the Fredenslund test.[9] Pertinent consistency details and statistics are presented in Table 6.

The VLE data for each binary system have been correlated using local composition models (Wilson, NRTL, and UNIQUAC) and predicted by the UNIFAC contribution method.[9,10] The parameters of these models have been determined minimizing the following objective function (OF)

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

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. However, it must be pointed out that the deviations obtained for the prediction with UNIFAC are quite larger.

Ternary System. VLE data for the ternary system cyclohexane (1) + cyclohexene (2) + 2-methoxyethanol (3) are reported in Table 8 and Figure 4. The activity coefficients γ_i 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[11] modification of the McDermott−Ellis test[12] ($D < D_{\max}$ at all data points).

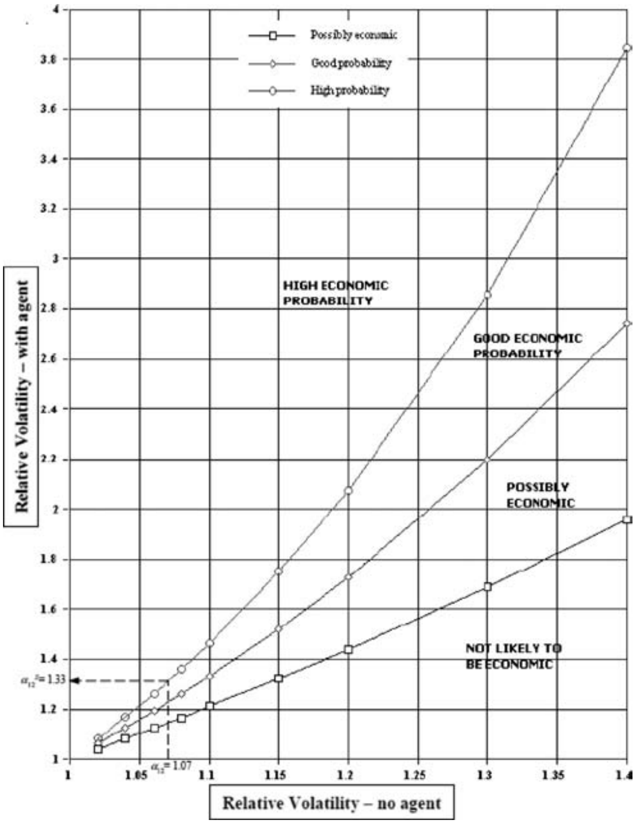

Figure 8. Economic rule-of-thumb for extractive distillation.[2]

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 5.

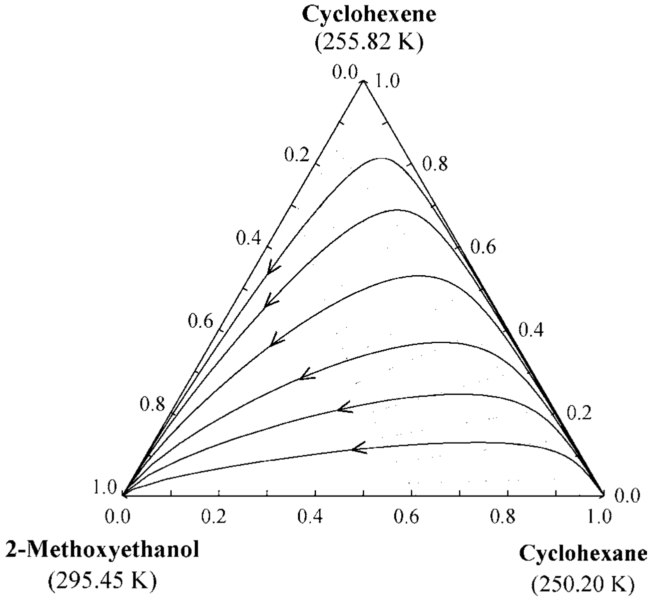

Figure 9. Residue curve map and liquid−liquid immiscibility region for the ternary system cyclohexane (1) + cyclohexene (2) + 2-methoxyethanol (3) at 1.0 kPa simulated by Aspen split using the NRTL model with the parameters given in Table 7: —, residue curves; − −, liquid−liquid immiscibility region.

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.[13] In Figure 6, 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 five singular points (nodes and saddles): three pure component vertices and two binary azeotropes. Cyclohexene and 2-methoxyethanol are stables nodes (where residue curves terminate); the binary azeotrope cyclohexane−2-methoxyethanol is an unstable node (where residue curves begin); and cyclohexane and the binary azeotrope cyclohexene−2-methoxyethanol are saddles (where residue curves are deflected). Also, a distillation boundary (separatrix) can be observed which begins

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

		A_{ij}	A_{ij}		bubble point		
model	system $i + j$	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$	α_{ij}	ARDT[a]/%	$100 \cdot AADy_1$[b]	$100 \cdot AADy_2$[b]
Wilson[c]	1 + 2[d]	831.37	−598.78		0.036	0.075	
	1 + 3	2068.99	8047.42		0.519	0.932	
	2 + 3	1456.83	6535.05		0.244		0.561
	1 + 2 + 3[e]				0.219	0.374	0.355
NRTL	1 + 2[d]	−1195.08	1403.45	0.20	0.038	0.072	
	1 + 3	6199.59	3332.83	0.47	0.460	0.847	
	2 + 3	5208.64	2384.66	0.47	0.232		0.539
	1 + 2 + 3[e]				0.167	0.315	0.404
UNIQUAC[f]	1 + 2[d]	−365.51	422.30		0.038	0.070	
	1 + 3	2711.82	−222.70		0.477	0.777	
	2 + 3	2578.68	−396.27		0.340		0.638
	1 + 2 + 3[e]				0.365	0.385	0.442
UNIFAC[g]	1 + 2[d]				0.062	0.072	
	1 + 3				2.591	2.220	
	2 + 3				3.488		3.300
	1 + 2 + 3[e]				2.644	0.801	1.499

[a] Average relative deviation in temperature. [b] Average absolute in vapor phase composition. [c] Molar liquid volumes of pure components have been estimated with the Rackett equation.[15] [d] Ref 2. [e] Ternary estimation from binary parameters. [f] Volume and surface parameters from DECHEMA.[16] [g] Calculations based on original UNIFAC.[9,10]

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

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
359.00	0.048	0.244	0.159	0.643	2.840	2.394	1.061
355.43	0.049	0.431	0.104	0.740	2.002	1.724	1.311
354.19	0.052	0.664	0.074	0.793	1.393	1.244	2.148
354.00	0.050	0.904	0.054	0.877	1.058	1.016	6.900
353.62	0.100	0.806	0.111	0.790	1.093	1.038	4.996
353.70	0.102	0.711	0.123	0.753	1.196	1.119	3.106
353.99	0.102	0.605	0.141	0.720	1.363	1.246	2.196
354.56	0.098	0.486	0.165	0.686	1.625	1.454	1.626
355.10	0.101	0.388	0.201	0.642	1.882	1.677	1.366
356.06	0.095	0.284	0.238	0.588	2.327	2.040	1.193
357.22	0.098	0.204	0.305	0.502	2.786	2.346	1.126
360.37	0.104	0.123	0.415	0.357	3.255	2.530	1.057
355.98	0.177	0.107	0.559	0.255	2.931	2.357	1.109
354.56	0.197	0.196	0.459	0.368	2.245	1.941	1.287
353.88	0.210	0.302	0.385	0.460	1.806	1.600	1.482
353.68	0.209	0.403	0.323	0.528	1.527	1.384	1.812
353.42	0.206	0.504	0.276	0.584	1.334	1.233	2.298
353.16	0.201	0.651	0.229	0.652	1.143	1.075	3.857
353.39	0.197	0.748	0.210	0.711	1.061	1.013	6.894
352.66	0.301	0.598	0.319	0.572	1.080	1.041	5.292
352.77	0.299	0.504	0.348	0.521	1.184	1.122	3.239
352.92	0.299	0.393	0.401	0.455	1.356	1.251	2.268
353.12	0.299	0.294	0.453	0.383	1.522	1.400	1.936
353.35	0.303	0.199	0.540	0.304	1.779	1.627	1.499
353.73	0.289	0.056	0.727	0.111	2.484	2.083	1.163
352.55	0.405	0.109	0.697	0.153	1.756	1.542	1.519
352.49	0.406	0.206	0.597	0.256	1.506	1.360	1.870
352.44	0.403	0.306	0.517	0.343	1.315	1.228	2.382
352.37	0.397	0.405	0.456	0.409	1.180	1.108	3.386
352.83	0.392	0.548	0.400	0.514	1.033	1.016	7.041
352.10	0.494	0.407	0.504	0.385	1.055	1.045	5.698
351.95	0.499	0.309	0.557	0.309	1.161	1.112	3.517
352.09	0.493	0.205	0.629	0.228	1.321	1.228	2.389
352.21	0.500	0.055	0.777	0.077	1.605	1.553	1.631
351.70	0.600	0.105	0.748	0.115	1.305	1.229	2.375
351.67	0.579	0.193	0.659	0.205	1.192	1.190	3.057
352.27	0.590	0.348	0.588	0.322	1.027	1.018	7.242
351.52	0.697	0.202	0.698	0.188	1.054	1.051	5.797
351.39	0.701	0.057	0.806	0.059	1.216	1.178	2.873
351.30	0.780	0.100	0.793	0.094	1.077	1.063	4.928
351.35	0.897	0.051	0.866	0.046	1.022	1.017	8.799

at the binary azeotrope cyclohexane−2-methoxyethanol and terminates at the binary azeotrope cyclohexene−2-methoxyethanol. It divides the triangle into two distillation regions. For the separation of homogeneous mixtures by simple distillation, this separatrix cannot be crossed. In both distillation regions, the azeotrope cyclohexane−2-methoxyethanol would be obtained as overhead product (unstable node), and as bottom product (stable nodes), it could be obtained or 2-methoxyethanol in the left-hand region, or cyclohexene in the right-hand region. The actual compositions of the final products obviously will depend on the number of plates, feed, reflux, and reboil ratios, etc.

On the other hand, a useful alternative is the study of the solvent influence on the phase behavior of the ternary mixture, on a solvent-free basis. In Figure 7, the VLE of ternary mixture on a solvent-free basis were plotted for different compositions of 2-methoxyethanol (x_3): 0.00, 0.10, and 0.70. As can be seen in this figure, the solvent enhances the relative volatility of the binary mixture ($\alpha_{12} = 1.070$)[2], and this enhancement is major for major compositions of the solvent: $\alpha_{12}^{S} = 1.165$ for $x_3 = 0.10$ and $\alpha_{12}^{S} = 1.355$ for $x_3 = 0.70$ (α_{12}^{S} is relative volatility in the presence of the solvent). There is an economic rule of thumb[1] that gives some orientations to determine if the extractive distillation with a specific solvent can be economically viable on the basis of the variation of the relative volatility. Figure 8 shows different regions according to the economic probability of the extractive distillation for the separation of our binary mixture, and it can be seen that the economic probability is high from a value of $\alpha_{12}^{S} = 1.33$. So, the extractive distillation with 2-methoxyethanol used as an entrainer would be carried out in the left-hand region of the residue curve map mentioned before. However, in this region, the azeotrope cyclohexane−2-methoxyethanol would be obtained as overhead product. In that respect, the effect of pressure in the behavior of the two binary azeotropes has been studied using the NRTL model with experimental parameters (Table 7). The results of this estimation indicate that the azeotropes cyclohexane−2-methoxyethanol and cyclohexene−2-methoxyethanol disappear at (1 and 2) kPa, respectively. In Figure 9, the residue curve map at 1 kPa is shown, and only one distillation region exists at this low pressure. So, it could be considered to carry out an extractive distillation using 2-methoxyethanol as an entrainer at 1 kPa. Nevertheless, working at 1 kPa could not be economically competitive with other separation techniques.

Conclusions

In this study, the vapor−liquid equilibria behavior of the binary systems cyclohexane + 2-methoxyethanol and cyclohexene + 2-methoxyethanol and the ternary system cyclohexane + cyclohexene + 2-methoxyethanol was experimentally investigated with the aim of testing the feasibility of using 2-methoxyethanol as an entrainer to the extractive distillation.

According to the results, 2-methoxyethanol enhances the relative volatility of cyclohexane to cyclohexene until economic recommended values. However, the two binary systems present a minimum boiling temperature azeotrope. This fact makes difficult the separation cyclohexane/cyclohexane by extractive distillation using 2-methoxyethanol as an entrainer since there is a separatrix which links both binary azeotropes and delimits two distillation regions. It would be necessary to work at very low pressure (1 kPa) to make these binary azeotropes disappear.

So, it can be concluded that 2-methoxyethanol is not a good entrainer for the separation of cyclohexane/cyclohexene, since neither pure cyclohexane nor pure cyclohexene can be obtained easily.

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