JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

ARTICLE

pubs.acs.org/jced

Phase Equilibria Involved in the Extractive Distillation of Cyclohexane + Cyclohexene Using Diethyl Carbonate as an Entrainer

Beatriz Marrufo,[†] Sonia Loras,[*,‡] and Estela Lladosa[‡]

[†]Departamento de Ingeniería Química Básica, Universidad del Zulia, 4011, Maracaibo, Venezuela

[‡]Departamento de Ingeniería Química, Escuela Técnica Superior de Ingeniería, Universitat de València, 46100 Burjassot, Valencia, Spain

ABSTRACT: Isobaric vapor−liquid equilibrium (VLE) data at 100 kPa have been measured for the ternary system cyclohexane + cyclohexene + diethyl carbonate and two constituent binary systems: cyclohexane + diethyl carbonate and cyclohexene + diethyl carbonate. Both binary systems show moderate positive deviations from ideal behavior and do not present an azeotrope. The VLE data have been correlated by the Wilson, universal quasichemical activity coefficient (UNIQUAC), and nonrandom two-liquid (NRTL) equations. The ternary system does not present an azeotrope and is well-estimated from binary interaction parameters. A prediction with the universal functional activity coefficient (UNIFAC)-Dortmund method has been also obtained.

INTRODUCTION

The separation of paraffins and olefins is a specific problem in the area of hydrocarbon processing due to the close proximity of their boiling points. The separation of these mixtures by conventional distillation is very expensive because of the high reflux ratios and large number of stages required. Extractive distillation is commonly applied in industry to separate close boiling mixtures by the addition of a solvent, known as an entrainer, which alters the relative volatility of the components to be separated. The selection of a suitable solvent is very important to ensure an effective and economical design of extractive distillation. A good solvent selection for extractive distillation must be based on complete and accurate vapor−liquid equilibrium (VLE) data of the mixtures formed by the components to be separated and the selected solvent.

The present work was undertaken as a part of thermodynamic research on the separation of paraffins and olefins using different solvents. In this work, cyclohexane and cyclohexene are taken to represent olefin and paraffin mixtures, and the capability of diethyl carbonate as a possible entrainer is investigated and compared to other solvents previously chosen: 2-methoxyethanol,[1] morpholine,[2] and methyl isobutyl ketone.[3] To consider a good entrainer it should not only take into account its effect in VLE (a high alteration of the relative volatility is desired) and its high selectivity but also find entrainers within the so-called "eco-friendly" solvents. For this reason, in this paper diethyl carbonate has been selected as a possible entrainer for separating cyclohexane−cyclohexene, since it is an "ecofriendly" and green solvent.

In this work, we measured isobaric VLE data for the ternary system cyclohexane (1) + cyclohexene (2) + diethyl carbonate (3) and two constituent binary systems, cyclohexane (1) + diethyl carbonate (3) and cyclohexene (2) + diethyl carbonate (3), at 100 kPa. In a previous paper,[4] we reported VLE data for the binary system cyclohexane (1) + cyclohexene (2). For the system cyclohexane + diethyl carbonate, isobaric and isothermal VLE data have been reported in the literature.[5,6] However, for the binary system cyclohexene + diethyl carbonate and for the ternary system, no VLE data have been previously published.

EXPERIMENTAL SECTION

Chemicals. The chemicals cyclohexane ($100\,w \geq 99.8$, for residue analysis) and cyclohexene ($100\,w \geq 99.5$, puriss. p.a.) and diethyl carbonate ($100\,w \geq 99$, GC grade) were supplied by Fluka. Diethyl carbonate was purified to $w = 0.999$ by batch distillation in a Fischer SPALTROHR HMS 500 column, controlled by a Fischer system D301-C. The other reagents were used without further purification since their impurities are smaller than the detection limit of the analytical method used. The specifications of used chemicals are summarized in Table 1.

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 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 manometer was calibrated using the vapor pressure of ultrapure water. The measured pressure in the still was (100.0 ± 0.1) kPa.

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 liquid and vapor phase was less than

Special Issue: Kenneth N. Marsh Festschrift

Received: July 25, 2011
Accepted: October 12, 2011
Published: October 27, 2011

Table 1. Specifications of Chemical Samples

chemical name	source	initial mass fraction purity	purification method	final mass fraction purity	analysis method
cyclohexane	Fluka	0.998	none		GC[a]
cyclohexene	Fluka	0.995	none		GC[a]
diethyl carbonate	Fluka	0.99	distillation	0.999	GC[a]

[a] Gas−liquid chromatography.

Table 2. Experimental Vapor Pressure (P_i^o) of Diethyl Carbonate[a]

T/K	P/kPa	T/K	P/kPa
354.68	22.56	384.81	64.97
357.44	25.03	385.98	67.44
359.95	27.54	387.13	70.02
362.26	29.99	388.28	72.51
364.46	32.51	389.32	74.96
366.57	35.05	390.35	77.43
368.45	37.52	391.39	79.97
370.28	40.03	392.45	82.52
372.04	42.49	393.34	84.84
373.73	45.05	394.36	87.52
375.26	47.47	395.23	89.81
376.81	50.04	396.21	92.53
378.22	52.46	397.03	94.89
379.67	55.03	397.96	97.54
381.03	57.56	398.81	100.03
382.32	59.95	399.27	101.38
383.60	62.52		

[a] $u(T)$= 0.02 K, and $u(p)$ = 0.05 kPa.

0.001. The sample extractions were carried out with special syringes that allowed withdrawal of small volume samples.

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 No. 1 for Windows. The column, injector, and detector temperatures were 353.15 K, 473.15 K, and 493.15 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 diethyl carbonate, P_i^o, 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:

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

Table 3. Antoine Coefficients, Equation 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
diethyl carbonate (3)	14.9327	3616.95	−48.60

[a] Parameters obtained in ref 4.

Table 4. Experimental VLE Data for the Binary System Cyclohexane (1) + Diethyl Carbonate (3) at 100.0 kPa[a]

T/K	x_1	y_1	γ_1	γ_3
396.14	0.014	0.077	1.854	1.011
392.79	0.036	0.184	1.855	1.007
390.27	0.054	0.263	1.871	0.999
386.59	0.082	0.358	1.826	1.003
380.74	0.143	0.500	1.681	1.005
376.41	0.186	0.581	1.671	1.020
372.83	0.239	0.655	1.605	1.011
369.80	0.300	0.709	1.497	1.028
366.91	0.366	0.749	1.399	1.082
364.92	0.420	0.779	1.337	1.117
363.59	0.456	0.802	1.315	1.118
362.22	0.508	0.820	1.253	1.181
360.85	0.555	0.839	1.218	1.227
359.61	0.617	0.857	1.159	1.325
358.68	0.659	0.875	1.137	1.346
357.74	0.704	0.887	1.108	1.452
356.74	0.764	0.902	1.068	1.639
356.16	0.805	0.916	1.047	1.738
355.27	0.864	0.936	1.022	1.963
354.67	0.902	0.951	1.012	2.134
353.94	0.954	0.973	1.000	2.577
353.64	0.981	0.989	0.997	2.572

[a] $u(T)$= 0.02 K, $u(p)$ = 0.1 kPa, and $u(x_1)$ = $u(y_1)$ = 0.001.

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[4] and were fitted by a nonlinear optimization method to minimize the average relative deviation in pressure (ARDP). The vapor pressures of diethyl carbonate were correlated with an ARDP of 0.05 %. Experimental data are in good agreement to the equation reported by Rodríguez et al.[5] since this equation gives a correlation of the experimental vapor pressures reported in this work with a ARDP = 1.28 %.

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) + diethyl carbonate (3) and cyclohexene (2) + diethyl carbonate (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[7] assuming nonideality of both liquid and vapor phases:

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

Table 5. Experimental VLE Data for the Binary System Cyclohexene (2) + Diethyl Carbonate (3) at 100.0 kPa[a]

T/K	x_2	y_2	γ_2	γ_3
396.36	0.017	0.075	1.601	1.010
393.68	0.040	0.165	1.585	1.009
391.13	0.065	0.251	1.569	1.002
388.57	0.093	0.336	1.554	0.989
385.76	0.127	0.412	1.488	0.991
382.24	0.171	0.504	1.467	0.983
379.00	0.219	0.575	1.413	0.991
375.62	0.274	0.641	1.367	1.006
372.90	0.332	0.698	1.316	1.007
370.60	0.381	0.736	1.282	1.027
368.65	0.436	0.770	1.233	1.050
366.87	0.480	0.796	1.213	1.074
365.27	0.532	0.821	1.178	1.108
363.89	0.580	0.842	1.151	1.145
362.58	0.641	0.866	1.110	1.190
361.62	0.681	0.878	1.087	1.263
360.65	0.728	0.898	1.069	1.283
359.66	0.781	0.916	1.044	1.360
358.65	0.827	0.931	1.031	1.468
357.72	0.883	0.950	1.012	1.629
356.56	0.944	0.974	1.003	1.848
355.95	0.983	0.990	0.996	2.396

[a] $u(T)$= 0.02 K, $u(p)$ = 0.1 kPa, and $u(x_2) = u(y_2)$ = 0.001.

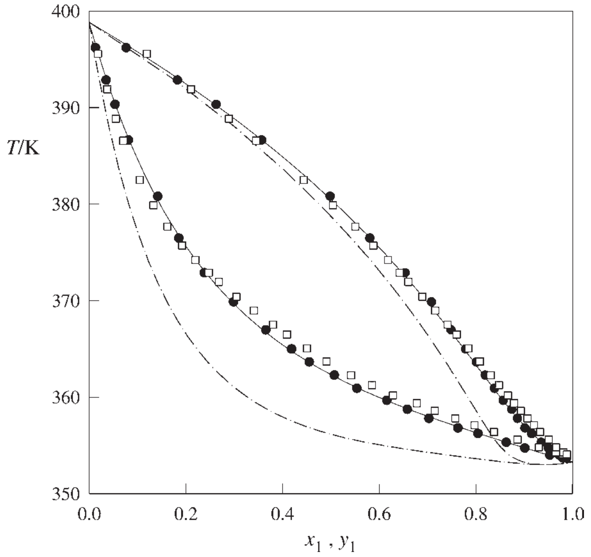

Figure 1. Experimental VLE data for the system cyclohexane (1) + diethyl carbonate (3) at 100.0 kPa: ●, experimental data; □, ref 5; solid line, smoothed data using the nonrandom two-liquid (NRTL) model with the parameters given in Table 7; dotted−dashed line, predicted by the universal functional activity coefficient (UNIFAC)-Dortmund method.

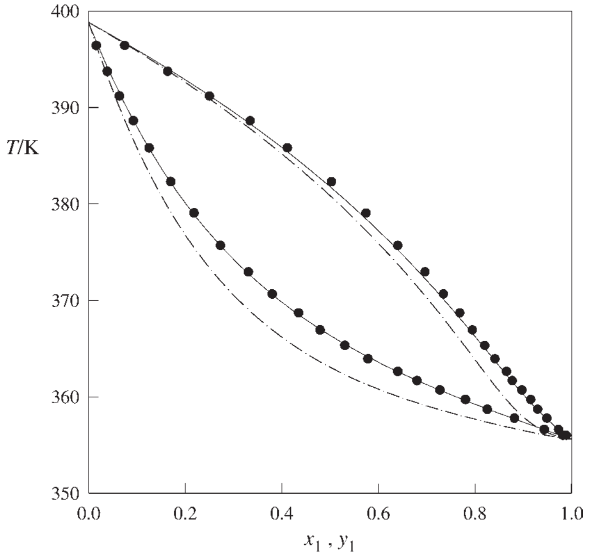

Figure 2. Experimental VLE data for the system cyclohexene (2) + diethyl carbonate (3) at 100.0 kPa: ●, experimental data; solid line, smoothed data using the NRTL model with the parameters given in Table 7; dotted−dashed line, predicted by the UNIFAC-Dortmund method.

Table 6. Consistency Test Statistics for the Binary Systems

system $i + j$	A_1[a]	A_2[a]	100·AAD y_i[b]	AAD P[c]/kPa
1 + 3	0.6958	0.2032	0.253	0.516
2 + 3	0.5676	0.1048	0.520	0.463

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

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} the cross second virial coefficient and

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \tag{3}$$

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[8] using the molecular parameters suggested by Prausnitz et al.[9] The critical properties of all components were taken from DIPPR.[10]

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.[11] Pertinent consistency details and statistics are presented in Table 6, and it can be seen that the consistency criteria (AADy < 0.01) was achieved using a two-parameter Legendre polynomial.

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,[12] and for the UNIQUAC model, volume and surface parameters were taken

Table 7. Parameters and Correlation Statistics for Different G^{E} Models for the System Cyclohexane (1) + Cyclohexene (2) + Diethyl Carbonate (3)

		A_{ij}	A_{ij}		bubble point		
model	system i +j	$\text{J}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$	α_{ij}	ARDT[a]/%	$100\cdot\text{AAD}\ y_1$[b]	$100\cdot\text{AAD}\ y_2$[b]
Wilson[c]	1 + 2[d]	831.37	−598.78		0.036	0.075	
	1 + 3	625.49	2323.56		0.121	0.274	
	2 + 3	310.35	1839.14		0.117		0.595
	1 + 2 + 3[e]				0.328	0.460	0.699
NRTL	1 + 2[d]	−1195.08	1403.45	0.20	0.038	0.072	
	1 + 3	2937.34	−74.83	0.30	0.139	0.274	
	2 + 3	2846.94	−682.42	0.30	0.119		0.585
	1 + 2 + 3[e]				0.177	0.376	0.424
UNIQUAC[f]	1 + 2[d]	−365.51	422.30		0.038	0.070	
	1 + 3	1424.53	−589.94		0.127	0.267	
	2 + 3	1442.37	−791.98		0.114		0.538
	1 + 2 + 3[e]				0.167	0.361	0.418
UNIFAC-D[g]	1 + 2				0.089	0.381	
	1 + 3				1.127	4.598	
	2 + 3				0.524		1.663
	1 + 2 +3				0.870	1.816	4.696

[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.[12] [d] Reference 4. [e] Ternary estimation from binary parameters. [f] Volume and surface parameters from DECHEMA.[13] [g] Calculations based on UNIFAC-Dortmund.[14,15]

from DECHEMA.[13] The parameters of these models have been determined minimizing the following objective function (OF):

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

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-Dortmund contribution method,[14,15] 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) + diethyl carbonate (3), since a minimum boiling azeotrope at $x_1 \approx 0.94$ and $T = 353.0$ K is predicted, and this point has not been found experimentally. Also, in those figures the calculated data using NRTL model and the VLE bibliographic data[5] are presented.

Ternary System. VLE data for the ternary system cyclohexane (1) + cyclohexene (2) + diethyl carbonate (3) are reported in Table 8 and Figure 3. 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[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:

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

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

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

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

VLE data for the ternary system 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-Dortmund method. Table 7 lists the average 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. Again, the absence of experimental azeotropy in the system cyclohexane + diethyl carbonate is also confirmed by the trend of the boiling isotherms of the ternary system shown in Figure 4.

Solvent Effects. The solvent effects in the ELV of the mixture cyclohexane−cyclohexene will be discussed taking into account two aspects: the analysis of the residue curve map,[18] and changes in relative volatility. Furthermore, the analysis in this work for

Table 8. Experimental VLE Data for the System Cyclohexane (1) + Cyclohexene (2) + Diethyl Carbonate (3) at 100.0 kPa[a]

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
388.10	0.048	0.054	0.188	0.161	1.579	1.315	0.991
374.83	0.043	0.236	0.128	0.538	1.646	1.362	0.966
366.35	0.045	0.440	0.092	0.709	1.413	1.199	1.076
360.82	0.049	0.652	0.074	0.815	1.214	1.078	1.257
356.26	0.050	0.897	0.056	0.917	1.042	1.002	2.020
357.02	0.101	0.792	0.119	0.832	1.054	1.009	1.779
358.91	0.100	0.692	0.131	0.784	1.118	1.030	1.488
360.98	0.100	0.578	0.148	0.732	1.185	1.089	1.254
363.47	0.099	0.471	0.167	0.672	1.266	1.144	1.155
366.49	0.097	0.360	0.194	0.598	1.382	1.229	1.058
369.42	0.102	0.277	0.228	0.515	1.429	1.277	1.033
372.98	0.101	0.199	0.256	0.415	1.484	1.309	1.040
378.38	0.101	0.109	0.305	0.261	1.538	1.318	1.020
371.68	0.197	0.106	0.478	0.208	1.470	1.275	1.042
367.55	0.200	0.200	0.419	0.347	1.412	1.246	1.041
364.52	0.198	0.297	0.357	0.458	1.316	1.203	1.087
361.85	0.207	0.406	0.319	0.537	1.211	1.111	1.210
359.87	0.205	0.500	0.290	0.602	1.172	1.066	1.284
357.32	0.204	0.651	0.240	0.689	1.051	1.007	1.872
355.83	0.198	0.746	0.232	0.729	1.090	0.971	2.777
356.23	0.299	0.600	0.345	0.600	1.060	0.981	2.192
357.77	0.299	0.501	0.377	0.545	1.108	1.022	1.471
359.72	0.302	0.396	0.414	0.472	1.142	1.060	1.331
361.53	0.299	0.296	0.462	0.393	1.222	1.122	1.185
363.65	0.295	0.205	0.518	0.303	1.312	1.181	1.095
368.47	0.292	0.052	0.637	0.097	1.436	1.300	1.047
363.06	0.399	0.099	0.679	0.142	1.293	1.163	1.109
360.86	0.406	0.190	0.609	0.246	1.210	1.114	1.212
358.94	0.401	0.301	0.536	0.353	1.137	1.065	1.355
357.31	0.405	0.402	0.486	0.433	1.069	1.025	1.623
355.25	0.399	0.542	0.430	0.538	1.018	1.001	2.262
355.64	0.496	0.399	0.547	0.402	1.028	1.006	2.005
357.18	0.496	0.302	0.593	0.323	1.068	1.022	1.620
358.72	0.498	0.196	0.659	0.227	1.134	1.059	1.356
361.14	0.503	0.053	0.775	0.071	1.234	1.157	1.155
358.17	0.604	0.108	0.771	0.122	1.111	1.051	1.380
356.76	0.596	0.205	0.700	0.217	1.062	1.025	1.636
354.77	0.591	0.346	0.624	0.342	1.011	1.010	2.316
355.17	0.700	0.196	0.754	0.195	1.018	1.005	2.078
357.16	0.699	0.055	0.847	0.060	1.083	1.036	1.467
354.94	0.796	0.105	0.847	0.104	1.014	1.009	2.086
354.15	0.897	0.051	0.923	0.050	1.002	1.004	2.352

[a] $u(T) = 0.02$ K, $u(p) = 0.1$ kPa, and $u(x_1) = u(x_2) = u(y_1) = u(y_2) = 0.001$.

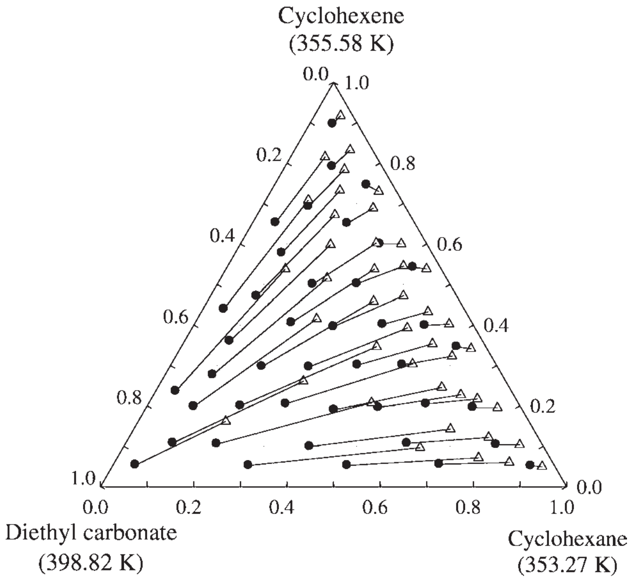

Figure 3. Diagram of VLE for the ternary system cyclohexane (1) + cyclohexene (2) + diethyl carbonate (3) at 100.0 kPa: ●, liquid-phase mole fractions; △, vapor-phase mole fractions.

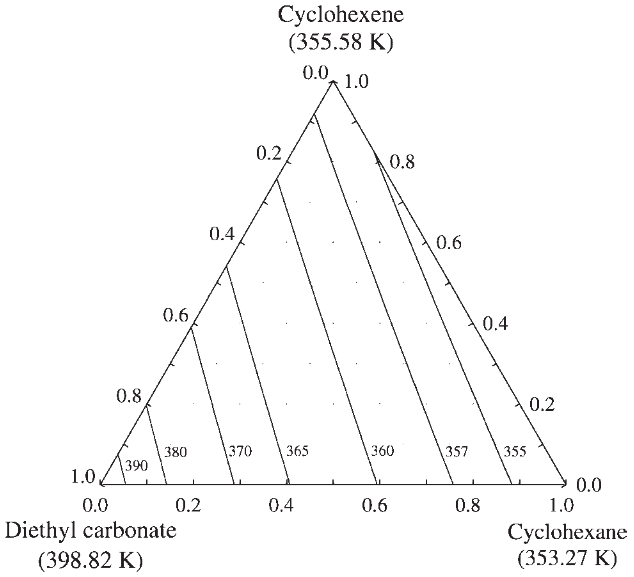

Figure 4. Boiling isotherms (K) for the ternary system cyclohexane (1) + cyclohexene (2) + diethyl carbonate (3) at 100.0 kPa calculated with the NRTL model with the parameters given in Table 7.

diethyl carbonate will be compared to the previously made for other solvents studied, to recommend the most suitable entrainer for the separation of the mixture cyclohexane—cyclohexene by extractive distillation.

In Figure 5, residue curves simulated by Aspen properties v7.2 using the NRTL model with the experimental parameters reported in Table 7 are shown. As can be seen in this figure, there is one unique distillation region with three singular points (nodes and saddles): three pure component vertices. Cyclohexane is an unstable node; cyclohexane is a saddle and diethyl carbonate is a stable node. This residue curve map is very similar to those obtained for morpholine and methyl isobutyl ketone, respectively.[2,3] So, in this case it is not possible to know which solvent is the best entrainer by observing only the residual curve maps. However, in ref 1 it was concluded that 2-methoxyethanol was not a good entrainer by analyzing the residual curve map, since it presented a separatrix which links two binary azeotropes and delimits two distillation regions.

Another useful method is to study the changes in the relative volatility of cyclohexane to cyclohexene ($\alpha_{12} = 1.070$)[4] adding the solvent. For that, in Figure 6 the ternary VLE data have been

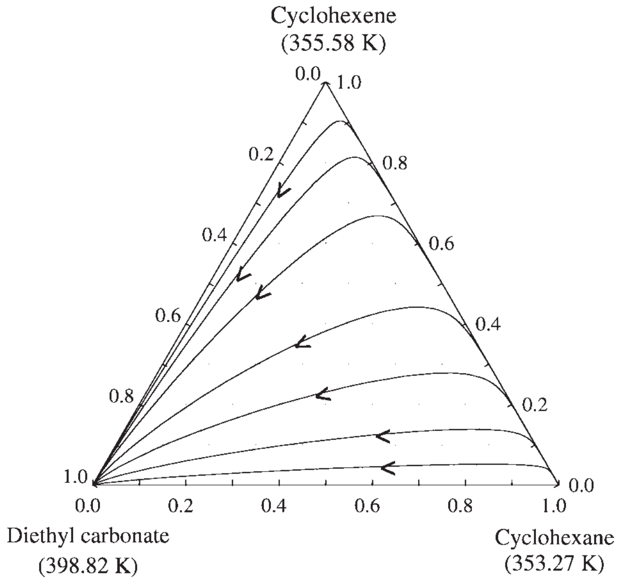

Figure 5. Residue curve map for the ternary system cyclohexane (1) + cyclohexene (2) + diethyl carbonate (3) at 100.0 kPa simulated by Aspen split using the NRTL model with the parameters given in Table 7.

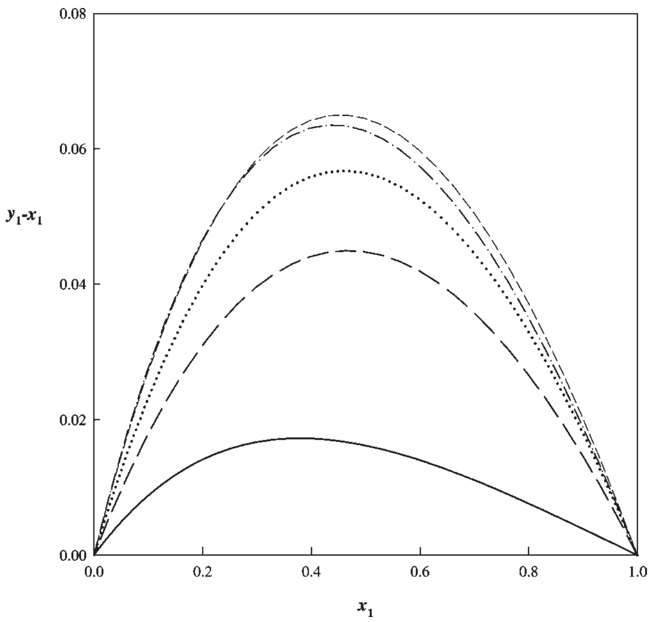

Figure 6. VLE data plotted on a solvent-free basis for the system cyclohexane (1) + cyclohexene (2) + solvent (3) at 100.0 kPa. Continuous line[4] for $x_3 = 0.00$; dashed line for $x_3 = 0.70$, calculated using the NRTL model with the parameters given in Table 7: — —, methyl isobutyl ketone;[3] · · ·, diethyl carbonate (in this work); — · —, with 2-methoxyethanol;[1] and - - -, with morpholine.[2].

Table 9. Mean Relative Volatility in the Presence of the Solvent (α_{12}^{S}) Calculated Using the NRTL Model for the System Cyclohexane (1) + Cyclohexene (2) + Solvent (3) at 100.0 kPa

	α_{12}^{S}	
solvent	$x_3 = 0.7$	$x_3 = 0.8$
2-methoxyethanol[a]	1.286	1.338
morpholine[b]	1.296	1.333
methyl isobutyl ketone[c]	1.197	1.212
diethyl carbonate	1.254	1.279

[a] Reference 1. [b] Reference 2. [c] Reference 3.

represented on a solvent-free basis, and Table 9 shows the values of mean relative volatilities in the presence of the solvent (α_{12}^{S}), calculated using the NRTL model with the parameters given in Table 7, for two different solvent compositions (for $x_3 = 0.7$ and 0.8). As can be observed in Figure 6 and Table 9, all studied solvents enhance the relative volatility of cyclohexane to cyclohexene. To know whether these values of α_{12}^{S} are enough to consider extractive distillation as an economic separation process, 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 with 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 $\alpha_{12}^{S} = 1.20$, and the economic probability is high from a value of $\alpha_{12}^{S} = 1.33$. Attending to the achieved values of α_{12}^{S}, all studied solvents could be consider as a suitable entrainer, except for 2-methoxyethanol for the previously commented reason. Also, it could be concluded that morpholine is a better solvent than methyl isobutyl ketone and diethyl carbonate, since morpholine requires less quantity for the same separation. On the other hand, methyl isobutyl ketone and diethyl carbonate are considered ecofriendly solvents, and morpholine is not. In this sense, and taking into account the values of α_{12}^{S}, diethyl carbonate could be the most advisible entrainer.

■ CONCLUSIONS

Consistent VLE data at 100.0 kPa have been determined for the binary systems cyclohexane (1) + diethyl carbonate (3) and cyclohexane (2) + diethyl carbonate (3) and the ternary system cyclohexane (1) + cyclohexane (2) + diethyl carbonate (3). 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, diethyl carbonate enhances the relative volatility of cyclohexane to cyclohexene until reaching economic recommended values. So, it can be concluded that diethyl carbonate could be a good entrainer for the separation cyclohexane/cyclohexene by extractive distillation. This separation process is especially attractive since diethyl carbonate is a ecofriendly solvent.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +34 963544317; fax: +34 963544898. E-mail address: sonia.loras@uv.es.

Funding Sources

Financial support from Ministerio de Ciencia e Innovación of Spain, through Project No. CTQ2010-18848, is gratefully acknowledged. B.M. has been funded by a grant from La Universidad del Zulia, Venezuela.

■ REFERENCES

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

(3) Marrufo, B.; Loras, S.; Sanchotello, M. Isobaric Vapor—Liquid Equilibria for Binary and Ternary Mixtures of Cyclohexane, Cyclohexene, and Methyl Isobutyl Ketone at 100 kPa. *J. Chem. Eng. Data* **2010**, *55*, 5812–5817.

(4) 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.

(5) Rodríguez, A.; Canosa, J.; Domínguez, A.; Tojo, J. Isobaric Vapor—Liquid Equilibria: of Diethyl Carbonate with Four Alkanes at 101.3 kPa. *J. Chem. Eng. Data* **2002**, *47*, 1098–1102.

(6) Cocero, M. J.; Mato, F.; García, I.; Cobos, J. Thermodynamics of Binary Mixtures Containing Organic Carbonates. 3. Isothermal Vapor—Liquid Equilibria for Diethyl Carbonate + Cyclohexane, + Benzene, or + Tetrachloromethane. *J. Chem. Eng. Data* **1989**, *34*, 443–445.

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

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

(9) 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.

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

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

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

(13) Gmehling, J.; Onken, U. *Vapor—Liquid Equilibrium Data Collection*; DECHEMA: Frankfurt, 1977.

(14) Weidlich, U.; Gmehling, J. A Modified UNIFAC Model. 1. Prediction of VLE, h^E, and γ^∞. *Ind. Eng. Chem. Res.* **1987**, *26*, 1372–1381.

(15) Lohmann, J.; Gmehling, J. Modified UNIFAC (Dortmund): Reliable Model for the Development of Thermal Separation Processes. *J. Chem. Eng. Jpn.* **2001**, *34*, 43–54.

(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/ruleofthumbgraph.htm (accessed July 12, 2011).