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Phase Equilibria for Reactive Distillation of Propyl Propanoate. Pure Component Property Data, Vapor−Liquid Equilibria, and Liquid−Liquid Equilibria

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ABSTRACT: Isobaric vapor−liquid equilibrium (VLE) data were measured for the binary systems propan-1-ol + propanoic acid, propan-1-ol + propyl propanoate, propyl propanoate + propanoic acid, and water + propyl propanoate at 101.3 kPa. Isothermal liquid−liquid equilibrium (LLE) data were measured for the ternary system propan-1-ol + water + propyl propanoate at 288.15 K. VLE and LLE data were fitted using the UNIQUAC model to account for non idealities in the liquid phase while the Hayden O'Connell equation of state was used to account for nonidealities in the vapor phase. The models are in good agreement with the experimental data. The UNIQUAC parameters obtained from the data regression can be used to effectively describe the thermodynamic behavior of the quaternary mixture in a reactive distillation process.

1. INTRODUCTION

The advancement in chemical processing operations in terms of efficiency gain, waste reduction, and safety improvement is a challenge for both academia and industry. To meet this demand, engineers have been applying alternative process methodologies categorized in modern chemical engineering as process intensification (PI). This new progress area is often exemplified with innovative milestones based in four generic principles.[1,2] One of the most relevant applications of PI is the reactive distillation (RD) process used in esterification syntheses, where reaction, separation, and enthalpy exchange take place in a single unit.[3] In the present paper, we present thermodynamic equilibrium data needed for the synthesis of propyl propanoate (ProPro) in a RD process. This system, as other esterification reactions used in RD processes,[4−9] is characterized by strong liquid and vapor phase nonidealities with several azeotropes present. As ProPro is considered a nonhazardous air pollutant, it is broadly used as a solvent with different industrial applications including inks, cleaners, paints, and flavors. The ester is obtained from the acidic catalyzed esterification reaction of propanoic acid (ProAc) and propan-1-ol (ProOH) following eq 1. Since the reaction is reversible, the simultaneous withdrawal of the products (ProPro and water) shifts the equilibrium improving product formation. Albeit the reaction occurs under acidic conditions, it is not self-catalyzed and addition of a strong acid catalyst, either homogeneous or heterogeneous, is needed. At the present time acidic ion-exchange resins are the preferred catalysts in industry.

$$C_3H_8O + C_3H_6O_2 \overset{H^+}{\rightleftarrows} C_6H_{12}O_2 + H_2O \qquad (1)$$

Ion-exchange resins have proven to be very attractive in the range from 100 to 120 °C, suppressing important side reactions.[10] Besides, in esterification reactions performed in RD processes, one of the reactants is often fed in excess (in this case ProOH) to achieve the maximum conversion of the other. As a result, the distillate product is a mixture of the water produced, the excess of ProOH that does not react, and some ProPro. An easy way to separate this mixture (as compared to distillation or membrane processes) is to take advantage of the phase split by coupling the column with a liquid−liquid separator and reflux back, part of the organic phase rich in ProOH and ProPro. The rest can be mixed with the ProOH feed. The schematic representation of the process can be seen in Figure 1. ProPro is collected at the bottom of the column together with the acid that did not react.

For accurate process design, reliable kinetic and thermodynamic data are needed. The reaction kinetics for this system have been reported by Duarte et al.[11] and show the experimental conditions for the determination of the reaction rate and the equilibrium constant using the resin Amberlyst 46 from Rohm and Haas as catalyst. In the case of thermo-physical data, the behavior of the quaternary mixture can be built on the information of the six constituent binary systems. Buchaly et al.[12] presented the set of UNIQUAC binary interaction parameters for the quaternary VLE calculation based on data extracted from ASPEN Properties Plus and data predicted using the UNIFAC-Dortmund method.[13] Limited experimental data are available for some of the constituent binary pairs (Dortmund Data Bank (DDB2000)), these being predominantly not up to date. In addition, large differences in concentrations and temperatures are found among data sets of the same system. Consequently, more recent experimental data are needed for comparison. The experimental data found comprise one data set[14] for the binary system ProOH + ProAc, two data sets,[15,16] for the binary ProOH + ProPro, two data sets[16,17] for water + ProPro, 66 data sets[18,19]

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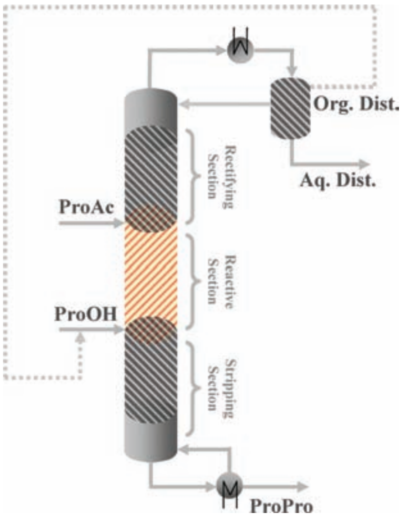

Figure 1. Schematic representation of the proposed reactive distillation process for the synthesis of propyl propanoate with a decanter separator on top for reactant and product recovery.

Table 1. Comparison of the Boiling Points T_B and Densitiy ρ at 298.15 K of the Pure Components with Literature Data

	T_B/K		ρ/g·cm^{-3}	
component	experimental	literature[a]	experimental	literature
propan-1-ol	370.29	370.93	0.804269	0.78102[b]
propanoic acid	414.53	414.31	0.993722	0.988797[b]
propyl propanoate	395.10	395.64	0.881619	0.8755[c]
water	373.26	373.15	0.998216	0.98803[d]

[a] Reference 27. [b] Reference 28. [c] Reference 29. [d] Reference 30.

for ProOH + water, and 31 data sets[20,21] for the system water + ProAc. No experimental data were found for the system ProAc + ProPro. Finally, only one data set[22] is available for the ternary system ProOH + water + ProPro. In this paper, we present experimental vapor–liquid equilibrium data for the constituent binary systems, where scarce or no data are available and liquid–liquid equilibrium data of the ternary system that condensates at the column top. The experimental data were regressed using the tool built in ASPEN Properties Plus to describe the phase behavior of the quaternary system inside the column and to predict the phase behavior of the ternary mixture after phase split in a decanter.

2. EXPERIMENTAL SECTION

2.1. Chemicals. ProOH, ProAc, and ProPro were purchased from Sigma-Aldrich. The purities of these components were reported to be more than $w = 0.995$ for ProOH and more than $w = 0.990$ for ProAc and ProPro. The reagents were degassed with an ultrasonic bath and dried over molecular sieve pellets from Sigma-Aldrich. Water used was bidistillated and deionized with an HPLC (Elgastat Maxima from Elga). The reagents were used without further treatment after being analyzed by gas chromatography. The densities were measured at 298.15 K using a density meter DMA 5000 (Anton Paar) with a reported uncertainty of ±0.000 005 g cm^{-3}. Boiling points of pure components were determined with the VLE apparatus. The pure component experimental values were compared with literature data showing good agreement and are presented in Table 1.

Table 2. Vapor–Liquid Equilibrium Data of the Binary System Propan-1-ol (1) + Propanoic Acid (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
414.53	0.0000	0.0000		1.0000
413.55	0.0025	0.0031	0.9618	1.0065
412.25	0.0171	0.0432	0.9557	1.0090
411.25	0.0385	0.0919	0.9045	1.0025
409.55	0.0635	0.1432	0.8745	1.0117
408.15	0.0854	0.1824	0.8463	1.0236
406.55	0.1055	0.2160	0.8374	1.0441
404.15	0.1474	0.3066	0.8740	1.0388
399.45	0.2114	0.4456	0.9591	1.0394
396.71	0.2559	0.5310	0.9907	1.0295
395.55	0.2757	0.5600	0.9936	1.0348
393.25	0.3229	0.6359	1.0044	1.0141
390.35	0.3699	0.7106	1.0446	0.9876
386.35	0.4547	0.7857	1.0421	1.0152
383.05	0.5375	0.8534	1.0444	0.9947
380.45	0.6093	0.8940	1.0407	1.0016
379.39	0.6452	0.9139	1.0356	0.9777
378.30	0.6796	0.9306	1.0346	0.9540
377.00	0.7250	0.9486	1.0294	0.9236
375.83	0.7714	0.9647	1.0211	0.8637
374.21	0.8477	0.9800	0.9964	0.8673
373.07	0.8872	0.9879	0.9983	0.7980
372.23	0.9232	0.9926	0.9929	0.7844
371.27	0.9643	0.9965	0.9870	0.8793
370.29	1.0000	1.0000	1.0000	

2.2. Apparatus and Procedure. A glass Fischer LABODEST vapor–liquid equilibrium apparatus model 602/D, (Fischer Labor) was used in the VLE determinations. The apparatus is a dynamic recirculating still equipped with a Cottrell circulation pump. The pure component boiling points as well as the equilibrium temperatures were measured with a digital thermometer (Yokogawa model 7563) with an accuracy of ±0.01 K. When the temperature remained constant for 30 min or longer, thermodynamic equilibrium was assumed and liquid and condensed vapor samples were taken for analysis.

Liquid–liquid equilibrium measurements for the ternary mixture were performed at constant temperature. Mixtures of a known composition in the immiscibility region were prepared, poured inside glass vials with a magnetic stirrer and then placed in an isothermal bath with built in temperature control. The bath temperature was kept at 288.15 ± 0.02 K. The samples were stirred for 1 h and then set for 24 h. At this point, thermodynamic equilibrium was assumed and samples from both phases were taken with a syringe for analysis. Preliminary experiments were performed to establish the time to achieve equilibrium (no variation of composition in time).

2.3. Analysis. Vapor and liquid phases obtained in the experimental determination of binary VLE and ternary LLE were measured by gas chromatography with a Varian 3900GC instrument equipped with a flame ionization detector. The column used was a CP-Wax 58 FFAP CB (50 m, 0.25 mm, 0.2 μm/CP7727) and helium was used as carrier gas. Injector, detectors, and oven

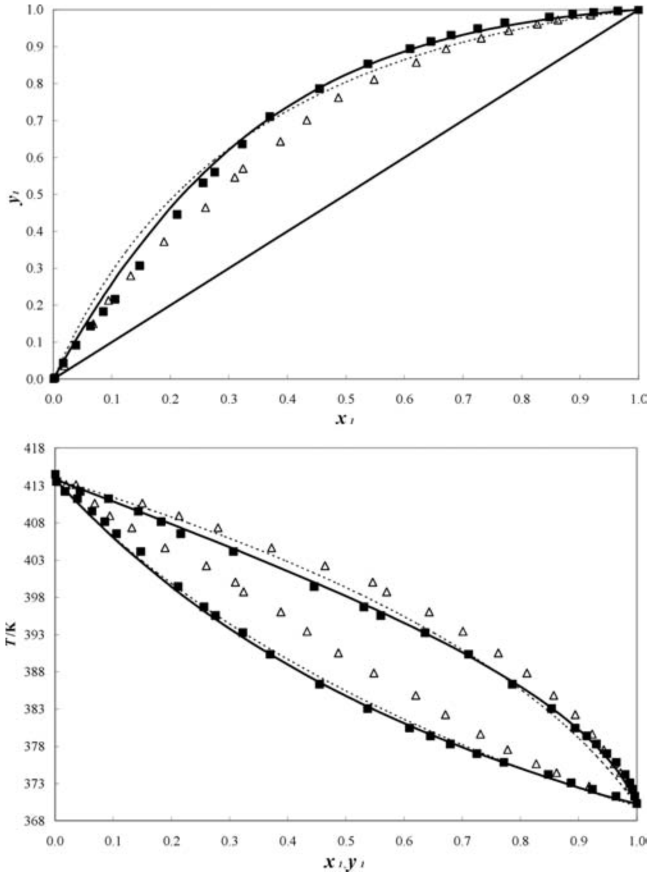

Figure 2. Binary system propan-1-ol (1) + propanoic acid (2) at 101.3 kPa: ■ experimental data from this work; Δ, experimental data from ref 14; ---, data predicted using UNIFAC-Dortmund; —, data calculated using the regressed parameters with the UNIQUAC-HOC model.

temperature were set at 473.15, 503.15, and 423.15 K, respectively. The column temperature profile started at 80 °C, kept constant for 5 min, followed by a 60 °C/min ramp to 130 °C, where it remained constant for an additional 15 min. A good peak separation was achieved under these conditions for all components. Samples were analyzed in triplicate. The reproducibility of the measurements was determined by doing repetitive analyses of the same sample using the calibrated GC. The standard deviation of the measurements (mole fraction) in the GC was ±0.0015. The quality of the calibration was evaluated by measuring several samples of known compositions three times and calculating the standard deviations between the known compositions and the GC measurements. The estimated uncertainty in the mole fraction of liquid and vapor compositions was 0.0045. For the systems containing water, data from the GC measurements (calculated by subtraction) was compared with results obtained from Karl Fischer (KF) titration using a 756 KF Coulometer from Metrohm. The difference between KF and GC results was not greater than 0.0005 (mole fraction).

3. RESULTS AND DISCUSSION

3.1. Binary VLE Measurements. Vapor−liquid equilibrium data for the binary systems were obtained under isobaric conditions at 101.3 kPa. When possible, experimental data from this work was compared to experimental data presented in literature to prove the correct operation of the equilibrium apparatus and the methods employed. For comparison, the UNIFAC-Dortmund group contribution method[23] was used to generate data. All concentrations are expressed in mole fractions. Experimental data for the system ProOH (1) + ProAc (2) is quoted in Table 2. The experimental results from this binary pair, presented in this work, exhibit the largest deviation from data found in literature,[14] as can be seen in Figure 2 where the x_1, y_1 and T, x_1, y_1 plots are shown. Since there was only one data set available for comparison, the UNIFAC−Dortmund group contribution method was used to predict the VLE behavior of the system. It can be seen that the experimental data from this work agree with the predicted values in both diagrams. Experimental data for the system ProOH (1) + ProPro (2) is presented in Table 3 and in Figure 3 in terms of x_1, y_1 and T, x_1, y_1 diagrams. The x_1, y_1 diagram shows that our experimental data coincide very well with the data from Ortega et al.[15] and the data from the UNIFAC−Dortmund model. Experimental data for the system ProPro (1) + ProAc (2) are presented in Table 4 and in Figure 4. For this system, no literature data were available for comparison. The experimental data coincide well with the predicted UNIFAC-Dortmund model values in both x_1, y_1 and T, x_1, y_1 diagrams. Finally, the experimental data for the system water (1) + ProPro (2) are presented in Table 5 and in Figure 5. This system shows an azeotrope determined in our experiments to be at $x_{\text{water}} = 0.6480$ and $T = 363.15$ K, which is in good agreement with previously reported data.[12,24] The data from Mozzhukhin et al.[16] deviate considerably at low water concentrations. Data predicted with the UNIFAC-Dortmund model follow well the experimental points in the x_1, y_1 diagram but fails in predicting the azeotrope temperature and composition.

Table 3. Vapor−Liquid Equilibrium Data of the Binary System Propan-1-ol (1) + Propyl Propanoate (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
395.10	0.0000	0.0000		1.0000
390.85	0.0298	0.1000	1.6829	1.0474
388.35	0.0573	0.2038	1.9244	1.0264
386.25	0.0945	0.2809	1.7171	1.0278
383.85	0.1409	0.3492	1.5459	1.0547
382.50	0.1685	0.3917	1.5149	1.0621
381.85	0.1904	0.4238	1.4811	1.0547
380.15	0.2352	0.4747	1.4206	1.0739
379.65	0.2569	0.5002	1.3931	1.0687
379.05	0.2758	0.5383	1.4242	1.0332
378.45	0.2934	0.5608	1.4231	1.0271
377.80	0.3221	0.5843	1.3805	1.0350
377.15	0.3495	0.6056	1.3481	1.0453
374.70	0.4519	0.6596	1.2362	1.1601
373.23	0.5383	0.7126	1.1803	1.2220
372.21	0.6365	0.7685	1.1157	1.2957
371.72	0.6954	0.8020	1.0843	1.3460
371.35	0.7560	0.8364	1.0538	1.4077
370.93	0.8330	0.8805	1.0219	1.5267
370.55	0.9084	0.9310	1.0044	1.6318
370.33	0.9832	0.9886	0.9932	1.5855
370.29	1.0000	1.0000	1.0000	

3.2. Ternary LLE Measurements. Liquid−liquid equilibrium data for the ternary system ProOH (1) + water (2) + ProPro (3) was obtained under isobaric conditions at 101.3 kPa and at a

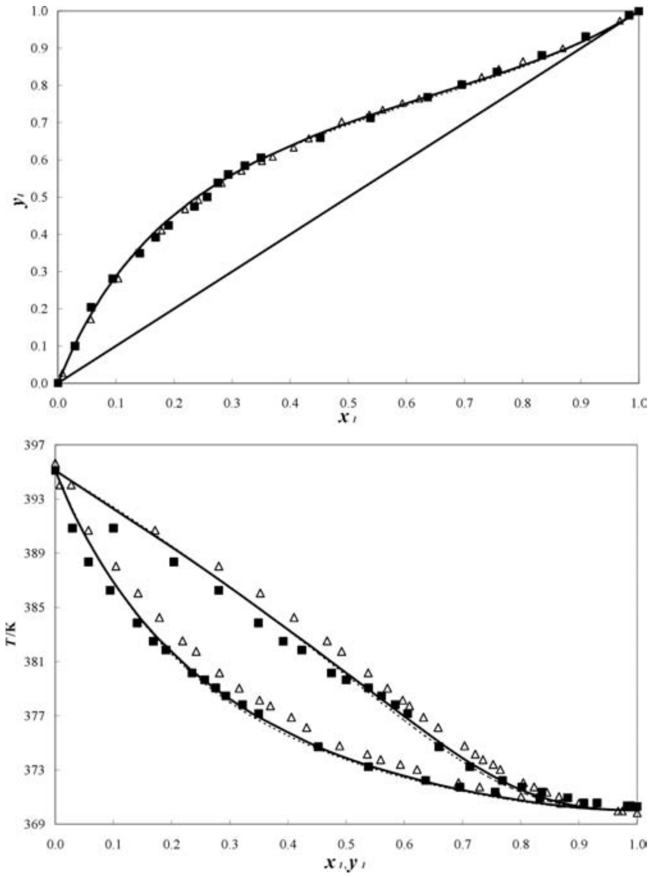

Figure 3. Binary system propan-1-ol (1) + propyl propanoate (2) at 101.3 kPa: ■ experimental data from this work; Δ, experimental data from ref 15; ---, data predicted using UNIFAC-Dortmund; —, data calculated using the regressed parameters with the UNIQUAC-HOC model.

temperature of 288.15 K. Experimental data are presented in Table 6 (tie lines). The experimental data agree with the trend of data presented by Mozzhukhin et al.[22] with experiments performed at 293.15 K. In Figure 6, the ternary diagram with the experimental tie line concentrations and the binodal curve is depicted. In this case, as the temperature is decreased, the immiscibility gap is reduced. To check the data consistency, the method of Othmer−Tobias[25] was used. A linear relation from tie line concentrations was obtained with a squared regression value of 0.9797.

3.3. Model Parameters. VLE experimental data were correlated using the UNIQUAC activity coefficient model in combination with the Hayden−O'Connell (HOC) equation of state.[26] In this way liquid and vapor phase nonidealities are taken into account, incorporating the chemical theory of dimerization necessary due to the presence of ProAc. The starting relationship for calculating equilibrium at low or moderate pressures P, and temperatures T, of a given mixture is shown in eq 2, where γ_i is the activity coefficient of component i, φ_i is the fugacity coefficient, and x_i and y_i are the compositions of component i in the liquid and vapor phases, respectively.

$$y_i \cdot \varphi_i(T,P,y) \cdot P = x_i \cdot \gamma_i(T,P,x) \cdot P_i^{\text{sat}}(T) \tag{2}$$

The vapor pressures of pure components at the given temperatures $P_i^{\text{sat}}(T)$ were calculated using the extended Antoine equation. Values of the surface area q and the molecular volume r were used in the UNIQUAC model. The pure component parameters used are available in the ASPEN Properties Plus library and are listed in Table 7. The thermodynamic behavior of the quaternary mixture can be built on the information of the six constituent binary systems by regressing separately each experimental data set finding the corresponding binary interaction parameters a_{ij} and $b_{ij}(T)$.

Table 4. Vapor−Liquid Equilibrium Data of the Binary System Propyl Propanoate (1) + Propanoic Acid (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
414.53	0.0000	0.0000		1.0000
412.81	0.0345	0.0594	1.5513	1.0072
411.54	0.0693	0.1182	1.5385	1.0105
410.42	0.1089	0.1733	1.4361	1.0194
408.83	0.1692	0.2735	1.4459	1.0108
408.12	0.2035	0.3002	1.3285	1.0373
407.44	0.2277	0.3325	1.3193	1.0438
406.76	0.2574	0.3727	1.3079	1.0469
405.54	0.3115	0.4400	1.2801	1.0586
404.69	0.3528	0.4754	1.2315	1.0899
404.14	0.3816	0.5051	1.2130	1.1034
403.41	0.4171	0.5455	1.2029	1.1141
402.65	0.4444	0.5758	1.2027	1.1280
401.88	0.4848	0.6162	1.1867	1.1476
401.05	0.5253	0.6617	1.1834	1.1547
400.10	0.5722	0.7029	1.1679	1.1890
399.36	0.6208	0.7475	1.1511	1.2094
398.49	0.6869	0.7921	1.1136	1.2943
397.49	0.7529	0.8515	1.1038	1.3052
396.43	0.8529	0.9238	1.0699	1.3393
395.10	1.0000	1.0000	1.0000	

The regression algorithm was calculated by minimizing the differences between estimated and experimental values considering the errors in the determination of all variables using the following objective function F_{VLE}:

$$F_{\text{VLE}} = \sum_{i=1}^{NP} \left[\left(\frac{T_{\text{est},i} - T_{\exp,i}}{\sigma_{T,i}} \right)^2 + \left(\frac{P_{\text{est},i} - P_{\exp,i}}{\sigma_{P,i}} \right)^2 + \sum_{j=1}^{NC-1} \left(\frac{x_{\text{est},i,j} - x_{\exp,i,j}}{\sigma_{x,i,j}} \right)^2 + \sum_{j=1}^{NC-1} \left(\frac{y_{\text{est},i,j} - y_{\exp,i,j}}{\sigma_{y,i,j}} \right)^2 \right] \tag{3}$$

As seen in Figures 2−5, the UNIQUAC-HOC model is able to effectively describe the experimental data. The list of regressed binary interaction parameters along with the average mean deviations of temperature (ΔT) and vapor molar fractions (Δy) for the VLE data can be seen in Table 8. Binary parameters from the remaining two binary pairs ProOH + water and water + ProAc that were not measured experimentally in this work were extracted from ref 12 and have been included in Table 8 as well. From the deviation values it is clear that the best fitted binary pair is the system ProOH (1) + ProAc (2) followed by ProPro (1) + ProAc (2). The nonideal system of water (1) + ProPro (2) show minor deviations in temperature, clearly denoted in Figure 5.

Since the regressed UNIQUAC-HOC parameters were not able to satisfactorily represent the LLE behavior of the ternary system, a separate model was calculated with the experimental data obtained

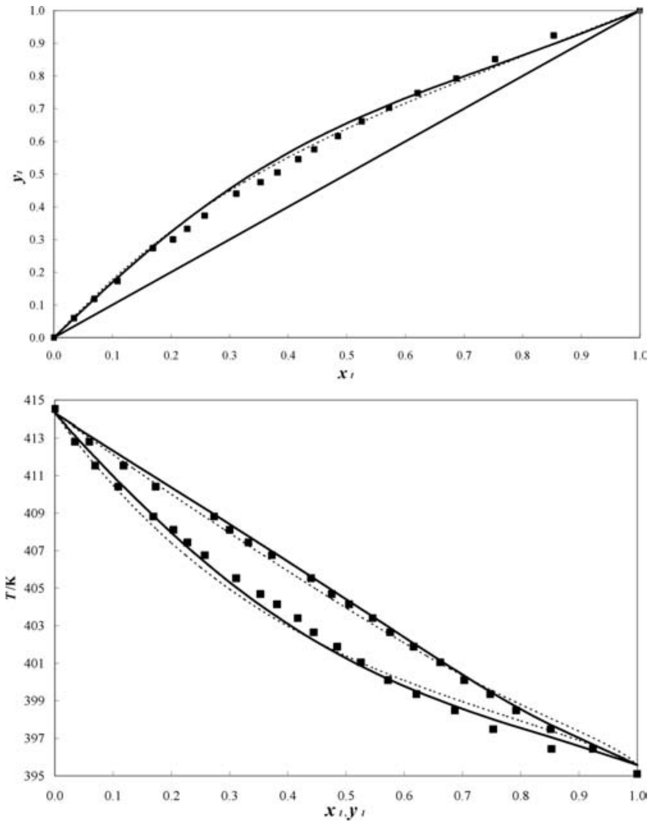

Figure 4. Binary system propyl propanoate (1) + propanoic acid (2) at 101.3 kPa: ■ experimental data from this work; ---, data predicted using UNIFAC-Dortmund; —, data calculated using the regressed parameters with the UNIQUAC-HOC model.

Table 5. Vapor−Liquid Equilibrium Data of the Binary System Water (1) + Propyl Propanoate (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
395.10	0.0000	0.0000		1.0000
385.00	0.0179	0.1850	10.5267	1.0006
375.00	0.0281	0.3550	11.5129	1.0018
370.00	0.0722	0.5926	9.8850	1.0130
364.07	0.1050	0.6474	8.6546	1.0308
363.15	0.6480	0.6480	1.6532	2.8295
363.36	0.9934	0.7500	1.0005	6.6142
367.00	0.9944	0.8300	1.0004	7.7989
370.00	0.9980	0.9300	1.0001	9.5817
373.26	1.0000	1.0000	1.0000	

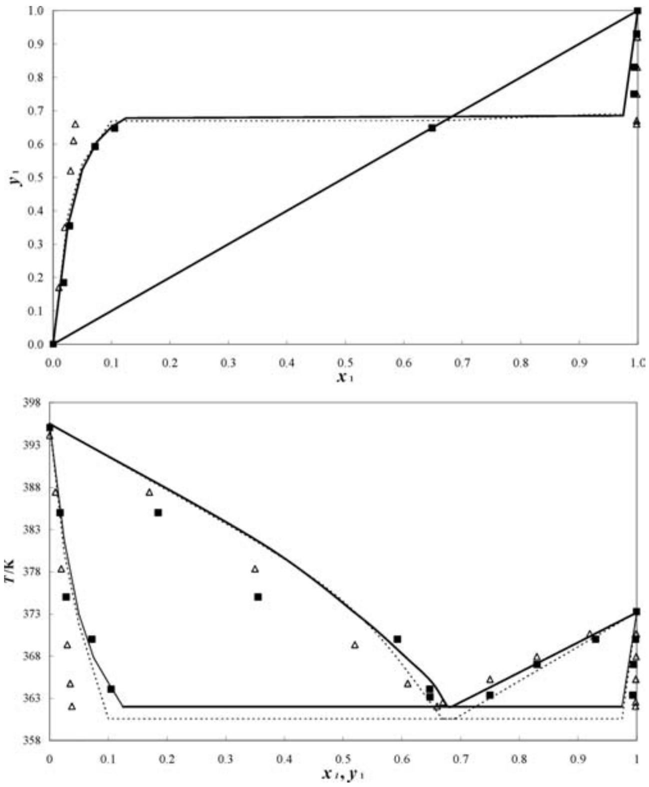

Figure 5. Binary system water (1) + propyl propanoate (2) at 101.3 kPa: ■ experimental data from this work; Δ, experimental data from ref 16; ---, data predicted using UNIFAC-Dortmund; —, data calculated using the regressed parameters with the UNIQUAC-HOC model.

Table 6. Ternary Liquid−Liquid Equilibrium Data for the System Propan-1-ol (1) + Water (2) + Propyl Propanoate (3) at 101.3 kPa

	aqueous phase (aq)		organic phase (org)	
T/K	x_1	x_2	x_1	x_2
288.15	0.0000	0.9998	0.1766	0.1343
	0.0200	0.9795	0.2600	0.1900
	0.0446	0.9544	0.3435	0.2585
	0.0465	0.9521	0.3489	0.2745
	0.0865	0.9097	0.3745	0.3890
	0.1650	0.8186	0.3573	0.4695
	0.2463	0.7182	0.3610	0.5168
	0.3053	0.6307	0.3409	0.5662

for the ternary mixture. The starting relationship for calculating LLE is shown in eq 4, where $x_i^{(\mathrm{org})}$ is the composition of component *i*, $\gamma_i^{(\mathrm{org})}$ is the activity coefficient of component *i* in the organic phase and $x_i^{(\mathrm{aq})}$ and $\gamma_i^{(\mathrm{aq})}$ are the composition and activity coefficient of component *i*, respectively, in the aqueous phase.

$$x_i^{(\mathrm{org})} \cdot \gamma_i^{(\mathrm{org})} = x_i^{(\mathrm{aq})} \cdot \gamma_i^{(\mathrm{aq})} \qquad (4)$$

The experimental data for the ternary mixture available in Table 7 was correlated using the UNIQUAC activity coefficient model to estimate the corresponding binary interaction parameters a_{ij} and $b_{ij}(T)$. The regression algorithm was calculated by minimizing the differences between estimated and experimental values considering the errors in the determination of all variables using the following objective function F_{LLE}:

$$F_{\mathrm{LLE}} = \sum_{i=1}^{NP} \left[\left(\frac{T_{\mathrm{est},i} - T_{\mathrm{exp}\ ,i}}{\sigma_{T,i}} \right)^2 + \sum_{j=1}^{NC-1} \left(\frac{x^{\mathrm{aq}}{}_{\mathrm{est},i,j} - x^{\mathrm{aq}}{}_{\mathrm{exp}\ ,i,j}}{\sigma_{x,i,j}} \right)^2 + \sum_{j=1}^{NC-1} \left(\frac{x^{\mathrm{org}}{}_{\mathrm{est},i,j} - x^{\mathrm{org}}{}_{\mathrm{exp}\ ,i,j}}{\sigma_{x,i,j}} \right)^2 \right] \qquad (5)$$

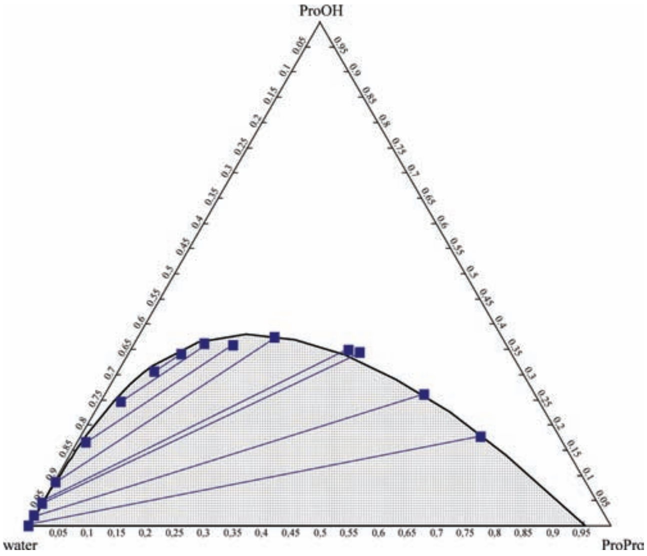

Figure 6. Ternary diagram for the system propan-1-ol + water + propyl propanoate at 101.3 kPa and 288.15 K with the binodal curve and experimental tie lines used for the prediction of phase split: ■, experimental data from this work; —, data calculated using the regressed parameters with the UNIQUAC model.

Table 7. Physical Properties and Parameters Used in the Calculations for the Constituent Components[b,a]

	water	propan-1-ol	propanoic acid	propyl propanoate
T_c/K	647.10	536.80	600.81	568.60
P_c/kPa	22064	5169	4617	3060
ω	0.345	0.620	0.574	0.449
$\mu \cdot 10^{-30}$/C·m	6.163	5.596	5.836	5.963
r	0.92	2.78	2.86	4.83
q	1.40	2.51	2.61	4.20
C_1[c]	73.65	94.13	54.55	78.32
C_2[c]	−7258.2	−8604.8	−7149.4	−7256.9
C_3[c]	0	0	0	0
C_4[c]	0	0	0	0
C_5[c]	−7.3037	−10.1100	−4.2769	−8.2280
C_6[c]	4.17×10^{-6}	3.13×10^{-6}	1.18×10^{-18}	4.86×10^{-6}
C_7[c]	2	2	6	2
C_8[c]	273.16	146.95	252.45	197.25
C_9[c]	647.1	536.8	600.8	568.6

[a] Critical temperature T_c, critical pressure P_c, acentric factor ω, dipole moment μ, surface area r, and volume parameter q used in the UNIQUAC model and parameters C_i for the extended Antoine equation. [b] Taken from Aspen Properties 2006 data bank. [c] Extended Antoine equation with $\ln(P^S) = C_1 + (C_2)/(T + C_3) + C_4 \cdot T + C_5 \cdot \ln(T) + C_6 \cdot T^{C_7}$ for $C_8 < T < C_9$ where P^S is in kPa and T in K.

As seen in Figure 6, the UNIQUAC model with the regressed parameters is able to predict with good agreement the phase behavior of the ternary mixture at 288.15 K. The experimental tie lines agree with the calculated binodal curve; thus, the model can be used to predict phase split in a decanter and calculate the concentrations of the organic phase that will be recycled back to the column. The regressed parameters to model the phase behavior of the ternary mixture can be seen in Table 9.

Table 8. UNIQUAC Binary Interaction Parameters a_{ij} and b_{ij} Obtained from Vapor−Liquid Equilibrium Data and Average Mean Deviation of Temperature (ΔT) and Vapor Molar Fraction (Δy) Measured

component 1	component 2	i	j	a_{ij}	b_{ij}/K	ΔT	Δy
propan-1-ol	propanoic acid	1	2	0.00	−281.0260	0.0067	0.0043
		2	1	0.00	195.6222		
propan-1-ol	propyl propanoate	1	2	0.00	17.3160	0.2232	0.0032
		2	1	0.00	−122.7789		
propyl propanoate	propanoic acid	1	2	0.00	−413.3753	0.0928	0.0042
		2	1	0.00	204.9204		
water	propyl propanoate	1	2	−4.47	1688.5940	1.2610	0.0194
		2	1	6.75	−3212.2200		
water	propanoic acid	1	2	0.00	−244.8000		
		2	1	0.00	73.80000		
propan-1-ol	water	1	2	1.84	−669.0000		
		2	1	−2.41	620.8000		

Table 9. UNIQUAC Binary Interaction Parameters a_{ij} and b_{ij} Obtained from Liquid−Liquid Equilibrium Data

component 1	component 2	i	j	a_{ij}	b_{ij}/K
propan-1-ol	water	1	2	0.0000	124.380
		2	1	0.0000	−310.440
water	propyl propanoate	1	2	1.4741	−587.796
		2	1	1.3415	−928.157
propan-1-ol	propyl propanoate	1	2	0.0000	131.270
		2	1	0.0000	−212.480

4. CONCLUSIONS

Isobaric experimental VLE data for the binary systems ProOH + ProAc, ProOH + ProPro, ProPro + ProAc, water + ProPro, and LLE data for the system ProOH + water + ProPro have been measured. Binary parameters for a UNIQUAC-HOC model were regressed. Based on these results, the model obtained is able to accurately fit the VLE experimental data and therefore predict the phase behavior of the mixture inside a reactive distillation column. For optimal process design, the excess of alcohol used, together with some ester distilled should be separated from the water/alcohol mixture using a decanter and be recycled back to the column. This is possible due to the phase split that occurs under certain distillate concentrations at the column top. To predict the phase split, experimental LLE data were regressed and the binary parameters for a UNIQUAC model were found. The set of parameters obtained in this work can be used to design the proposed reactive distillation process.

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