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Suitable Experimentation-Modeling Binomial to Design the Extraction of an Alkanol with Water in Aqueous Ternary Solutions of Ester-Akanol

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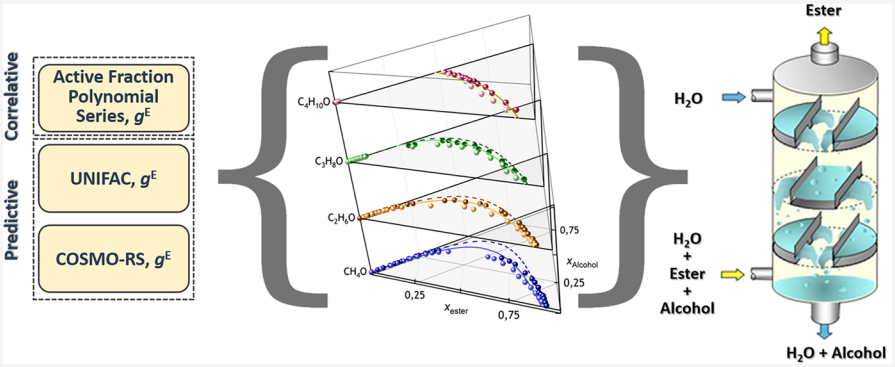

ABSTRACT: This work presents an investigation on phase equilibria in partially miscible systems comprised of water, esters, and alkanols. Experimental liquid−liquid equilibria (LLE) were determined for ternaries of water+$H_{2u-1}C_{u-1}CO_2C_vH_{2v+1}$+$C_wH_{2w+1}(OH)$ (u = 3,4; v = 2,3; w = 1−4) at 298.15 K and for the four corresponding water+ester binaries, in the temperature interval T = [283−328] K. The results reveal a complex behavior of the ternary LLE. The ester barely dissolves in the aqueous phase, even in the presence of alkanol ($x^{II}_{max,ester} \approx 0.15$). However, the organic phase contains high quantities of water when the compositions approach the plait point ($x^{I}_{max,water} \approx 0.75$). Data modeling was carried out with a multiparametric model, obtaining an acceptable correlation with a maximum deviation in the compositions of s_x = 0.031 for the system water(1)+propyl butanoate(2)+propan-1-ol(3). Estimations with COSMO-RS and UNIFAC differed from experimental values in all cases, especially in the systems containing propan-1-ol, since both models predict a nonreal immiscibility at 298.15 K in the binary water+propan-1-ol. Therefore, the simulation of the extractive process using UNIFAC was not adequate.

1. INTRODUCTION

Characterization of liquid−liquid equilibria (LLE) in heterogeneous systems is essential for the design of extraction/decantation operations in the chemical industry.[1,2] For specific conditions, the experimental information can reveal (a) the liquid phases formed, (b) the amount of material in each phase, and (c) the proportion of each component in each phase. These three factors influence the consideration of these items, because they determine the composition of the products generated and their influence in the design of above the aforementioned operations. LLE information is also required for certain esterification heterogeneous reactions, the object of our current investigations, where the immiscibility of the ester/water appears, although the addition of alcohol produces a higher conversion grade in the cited reaction. Esterification of a carboxylic acid with alkanol is a biphasic chemical reaction in liquid state, as the aforementioned immiscibility between the reaction products, ester and water, can split the system into two phases[3] (Figure 1). In this case, the reagents act as cosolvents, and the separation of the system into phases will depend on the alcohol, the acid used and its composition, in addition to other factors such as the temperature or the catalyst employed.

For the production of esters, especially in catalyzed reactions in liquid phase (*e.g.*, enzymatic catalysis), it is essential to have a complete information on the LLEs.[4] As the alkanol is often an excess reagent, it is reasonable to assume that the carboxylic acid reacts completely, and as a result, the outlet stream of the reactor is composed of alkanol, ester, and water (Figure 1).

This work is the first of a research project on LLE in systems formed by ester, alkanol, and water. Its purpose is to provide

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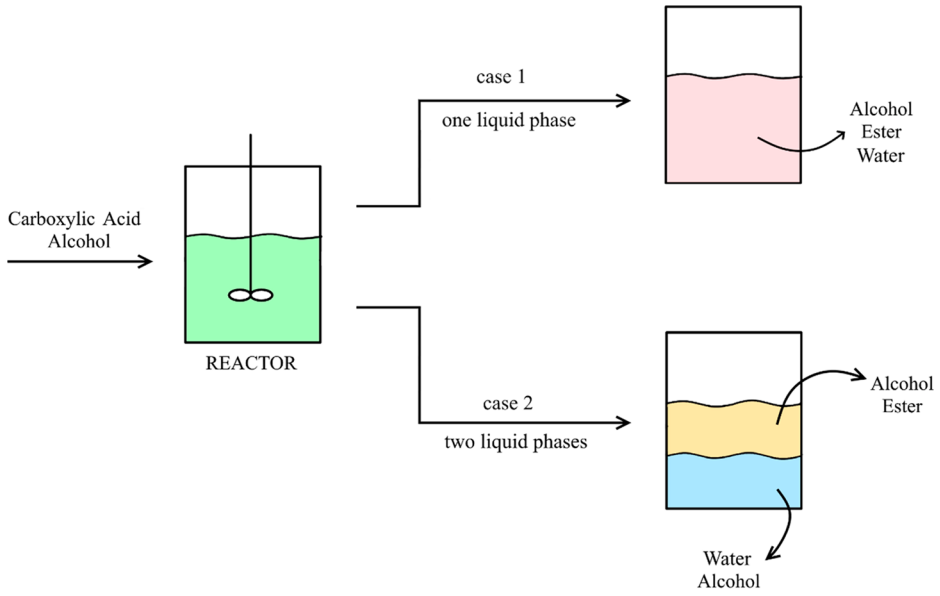

Figure 1. Esterification of a carboxylic acid with an alkanol and two possible outlet streams: 1, products forming a homogeneous phase; 2, products forming two phases.

useful information to optimize the esterification processes in the liquid phase. The research is based on dense experimentation, with the corresponding mathematical treatment, to evaluate the implications of the mentioned tasks in the practical of the studied systems. Hence, this work is undertaken with a global content that reflects the tasks constituting a set of actions of our research team prior to the design: experimentation ↔ modeling/checking ↔ simulation. In this work, the LLEs are determined for a set of 20 systems (binary and ternary): specifically, for 16 ternaries of water +ethyl propionate, ethyl butyrate, propyl propionate, or propyl butyrate, with methanol, ethanol, propan-1-ol, or butan-1-ol, and for the four corresponding binaries water+ester. The literature provides information on the four binaries[5,6] and six ternaries[7−11] (Table S1), which are used for purposes of comparison with our data, having previously observed that some systems showed inadequate values. For miscible binaries, a thermodynamic database of enthalpies, h^E, and isobaric vapor−liquid equilibria, iso-p VLE, was used. Nonetheless, in this work experimental VLE data were provided for the binaries of propyl alkanoate (2)+methanol(3) and h^E values for the 16 binaries of ester+alkanol not described in the literature. The experimental contribution of this work, the capacity of several models to represent the LLE is evaluated in the systems studied: one of a polynomial nature[11] and others already known such as UNIFAC[13] and COSMO-RS.[14]

The applied part of this research, based on a previous modeling of the LLEs, entails the simulation of an extraction process of alkanol with water in ternary systems of water-ester-alkanol, which is frequently carried out in the production of esters. This informs on the feasibility of the extraction of different alkanols with water, the effectiveness of the modeling, and the quality of the LLE data. The chemical engineer also obtains additional information on design errors associated depending on the different models employed. The computational process, carried out with Aspen Plus,[15] is highly dependent on the modeling of the experimental data; prior to the simulation, a diverse predictive and correlative modeling is carried out to achieve the best possible representation of the LLE.

2. EXPERIMENTAL SECTION

2.1. Materials. Organic compounds were supplied by Sigma-Aldrich with the highest commercial quality available. Before use, the quality of the compounds was checked by gas chromatography (GC) and several properties were determined, such as the water content, density, and refractive index. The compounds were degasified by ultrasound and stored in the dark for a few days over a Fluka 3 Å molecular sieve to improve the aforementioned properties before use. The water, bidistilled in our laboratory, presented a conductance <1 μS. After treatment, the quality of the compounds was checked again, showing in Table S2 the measurements and a comparison with values from literature.[16−21] Table S3 indicates the binary and ternary mixtures considered in this work.

2.2. Apparatus and Procedures. *2.2.1. Properties of the Pure Compounds.* The moisture was determined by a Karl Fischer (KF) coulometric titrator C-20 from Mettler. Densities were measured with an Anton-Paar DMA-60/602 densimeter ($\rho \pm 0.02$) kg m^{-3} and the refractive indices with an Abbe refractometer, model 320, from Zuzi ($n_D \pm 0.0003$). The temperature of both was controlled with water from a recirculating water bath at $T = (298.15 \pm 0.02)$ K. Chromatographic analysis of both the pure compounds and solutions was performed in a Varian-450 GC equipped with FID.

2.2.2. Properties of Solutions. Determination of h^E: the pair of values (x,h^E) were determined at 298.15 K with a quasi-isothermal calorimeter from Setaram, MS80, with a thermal control of ±1mK, electrically calibrated with a Joule effect that was used to calculate the impedance of the apparatus from the input/output ratio. The verification entailed determining the h^E of the binary 1-butanol+benzene[22] at the same temperature. The comparison gave rise to a mean error of the measurements of ($x \pm 0.0003$; (1% h^E)).

2.2.2.1. Determination of Liquid−Liquid Equilibria (LLE). The LLEs of the binaries were determined at atmospheric

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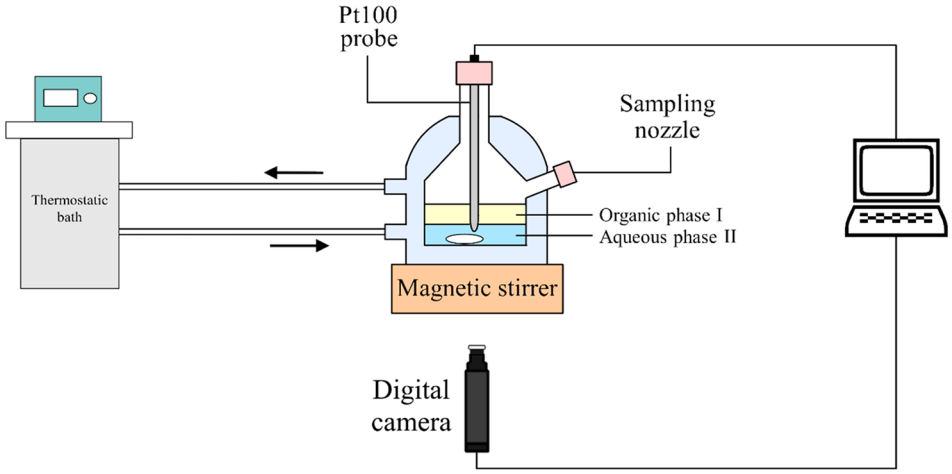

Figure 2. Set up for determination of LLE with optical detection of the cloud point.

pressure within an approximate temperature interval of $T \epsilon$ (283−330) K, using the installation described. A small glass double-cell (12 cm^3) with a stirrer was used (see Figure 2), circulating water from a Heto-PH808 thermostatic bath in the space between them. The temperature inside the cell was measured with a Pt100 probe ($T \pm 0.01$) K, previously calibrated according to ITS-90, connected to a PC. Turbidity change was visually detected and confirmed with the action of a 5 Mpixel digital camera, controlled by a software design by us using a procedure detailed in a previous work.[23] The experimental procedure for a generic binary A-B was carried out in four steps: (i) known quantities of both components, A and B, were placed inside the cell at a fixed working temperature, which was controlled during the entire procedure, (ii) the heterogeneous solution was stirred for approximately 1 h to favor the mass transfer between the phases until the compositions reached equilibrium, (iii) separation of the phases was facilitated by incorporating pauses between periods of stirring, and (iv) samples were taken of each phase and their compositions were determined by a combined method of GC/KF. This procedure was repeated successively, from step (i) until another temperature was reached, to cover the preset entire temperature range. This cycle generated a set of values for the variables (p,T,x_A^I,x_A^{II}) in the organic I and aqueous II phases. This practice was validated by comparing LLE data obtained for the system water+butan-1-ol with data from literature;[6,24−27] numerical values are shown in Table S4 and the graphical comparison in Figure S1. The series of tasks (i)−(iv) was used to define the LLEs of the binaries water (1)+ester(2). For these systems, the aforementioned measuring procedure was relatively short, with working temperatures < 330 K to prevent possible hydrolysis of the ester during the LLE experiments, which was verified by GC/KF in all cases. The LLEs of the ternaries were determined isothermally at (298.15 ± 0.01) K. The procedure followed is similar to the one described previously for binaries, although in this case, the composition of components in the global solution was modified by the successive addition of small amounts of cosolvent (alkanol), obtaining a set of values (p = 101.32 kPa, T = 298.15 K, x_1^I,x_1^{II},x_2^I,x_2^{II}) for the different ternaries water (1)-ester(2)-alkanol(3).

2.2.2.2. Analysis of LLE Samples. Analysis of samples of the phases at equilibrium was done by a combined procedure of GC/KF using the procedure indicated in Table S5, with an accuracy in the determination of compositions of $x \pm 0.002$. The aqueous phase (at the bottom of the cell) was analyzed by GC, using a column HP5, to determine the mass of each organic compound, and the quantity of water is obtained by difference, as this is the majority component in that phase. However, the reduced water content in the organic phase (on the aqueous phase) was analyzed by KF titration and the composition of each organic compound by GC. The GC analysis had a duration of 10 min and employed a constant carrier gas (helium) flow of 1.5 mL/min and injector, oven, and detector temperatures of 250, 45, and 300 °C, respectively. Calibration was done with an internal standard, selecting the most appropriate standard and solvent in each case to prevent overlapping in the chromatogram peaks, see Table S5.

2.2.2.3. Determination of the iso-p VLE. The iso-p VLEs were experimentally determined in a recirculation ebulliometer, whose design and auxiliary elements have been described previously.[16,28−31] After reaching the equilibrium state of the working solution, observing the constancy of pressure (101.32 ± 0.05) kPa and temperature ($T \pm 0.02$) K, samples were taken from both phases, liquid and vapor, whose respective compositions were determined by densimetry ($x \pm 2 \times 10^{-3}$, $y \pm 3 \times 10^{-3}$), using an analytical representation of the mixing data studied, obtained previously.

3. MODELING

3.1. Data Correlation. The data that characterize the LLEs (T,$x_1^I x_1^{II}$) of the binaries were correlated with a thermodynamic-mathematical model defined for the excess Gibbs energy g^E, used in previous works,[12,32] for the binaries,

$$g_{12}^E = z_1 z_2 \sum_{k=0}^{2} g_k(T) z_1^k \quad \text{where } g_k = \sum_{i=-1}^{1} g_{ki+1} T^i \tag{1}$$

where g_{ki+1} are parameters obtained by correlation of the binary LLE data. The so-called "active fraction" links g^E with the composition by the following functional, eq 2, obtained by considering each of the components (the first in this case) as a reference in all the calculations

$$z_i = \frac{k_{1i} x_i}{x_1 + \sum_{j=2}^{j=3} k_{1j} x_j} \quad \text{where } k_{1i} = 1 \text{ when } i = 1 \tag{2}$$

The coefficients g_{ki+1} of eq 1 and the parameters k_{1j} of eq 2 are determined by independently fitting the experimental data of

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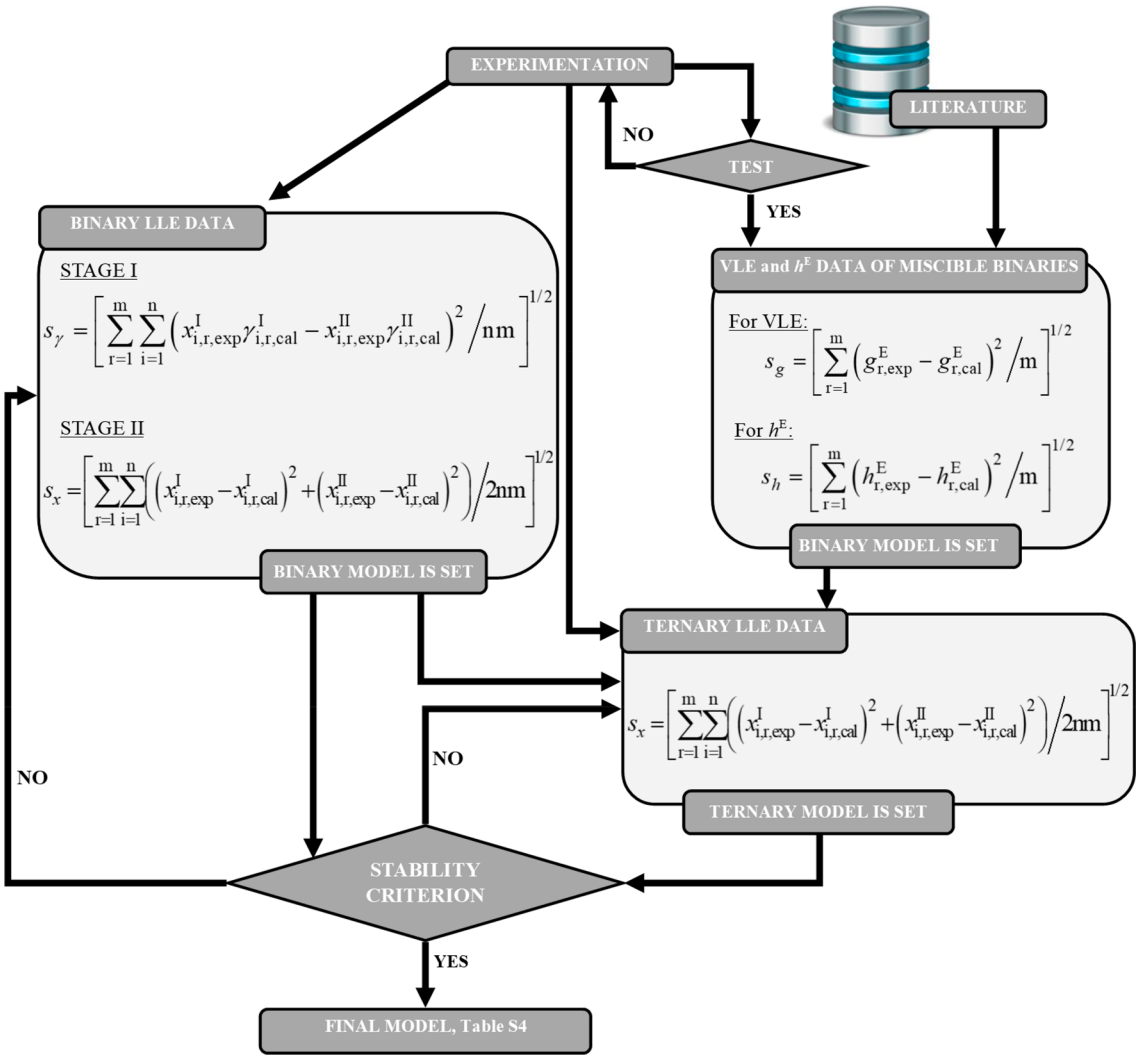

Figure 3. Scheme of the methodology indicating the modeling, including the application stages of phases stability criterion.

the binaries to the model defined by eq 1, minimizing the error between them. A two-step mathematical procedure is proposed, optimizing the correlative process with a particular objective function (OF) in each step, which were implemented in MATLAB with the corresponding algorithm.

First step: a first fitting is carried out using the isoactivity-criterion between the phases for each component in solution:

$$x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II} \tag{3}$$

where the subindex i refers to each of the n components of the system; namely, i = 1,2 in the binaries and i = 1,2,3 for the ternaries. The objective function that is minimized in this fitting-stage is the standard deviation s_γ.

$$s_\gamma = \left[\sum_{j=1}^{m} \sum_{i=1}^{n} (x_{i,j,\mathrm{exp}}^I \gamma_{i,j,\mathrm{cal}}^I - x_{i,j,\mathrm{exp}}^{II} \gamma_{i,j,\mathrm{cal}}^{II})^2 / \mathrm{nm} \right]^{1/2} \tag{4}$$

since n is already defined, m and x_{exp} are, respectively, the number of data and molar fractions determined experimentally, and γ_{cal} the activity coefficients calculated by the model expressed by eq 1.

Second step: the results obtained in the previous step are refined to minimize the error of the model used, eq 1, in order to calculate the compositions of the conjugate phases. In this case, the optimization is done by minimizing a standard deviation relative to the compositions of the components of each of the phases in equilibrium; the OF in this case is

$$s_x = \left[\sum_{j=1}^{m} \sum_{i=1}^{n} ((x_{i,j,\mathrm{exp}}^I - x_{i,j,\mathrm{cal}}^I)^2 + (x_{i,j,\mathrm{exp}}^{II} - x_{i,j,\mathrm{cal}}^{II})^2)/2 \ \mathrm{nm} \right]^{1/2} \tag{5}$$

where now $x_{\mathrm{i,j,exp}}^I$ and $x_{\mathrm{i,j,cal}}^I$ are the experimental and calculated compositions, respectively, of compound i in phase I and the corresponding one for phase II. The calculated compositions are obtained by solving the equations for the isoactivity criterion, eq 3, and using eq 1. The phases stability criterion was implemented in the correlation methodology,[32,33] being positively assessed for all the binaries studied. If the modeling achieved does not meet this criterion, this is discarded and the entire process is repeated to obtain a new parametrization. A diagram of the commented methodology is shown in Figure 3, including the possible rejection of experimental data/model when indicated by the stability criterion.

To correlate the LLE data (T = 298.15,x_1^I,x_1^{II},x_2^I,x_2^{II}) of the ternaries water(1)+ester(2)+alcohol(3), an extended version of eq 1 was used in which an additional term, Δg_{123}^E,

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corresponding to the synergic effect caused by the simultaneous presence of the three compounds studied, was added to the partial contributions of the binaries, g^{E}_{ij}. Hence, the global property is expressed as

$$g^{E}_{123} = g^{E}_{12} + g^{E}_{13} + g^{E}_{23} + \Delta g^{E}_{123} \quad (6)$$

The last term can be calculated by considering all possible interactions of different order between the molecules present, although for this work the final expression of this summand was considered as

$$\Delta g^{E}_{123} = z_1 z_2 z_3(\Delta g_0 + \Delta g_1 z_1 + \Delta g_2 z_2), \text{ verifying that} \sum_{i=1}^{i=3} z_i = 1 \quad (7)$$

Δg_k are the specific parameters for each ternary that are obtained using the same modeling procedure above indicated for the binaries. The sequence of correlation tasks for the ternaries is divided in two parts, one for the miscible or immiscible binaries, and another for achieving the parameters of ternaries. A detailed description is as follows: (i) modeling for miscible binaries water (1)+alcohol(3) and the immiscible binary water(1)+butan-1-ol(3), on the one hand, and then, the miscible of ester(2)+alcohol(3), obtaining the corresponding particular contributions g^{E}_{13} and g^{E}_{23} in each case for eq 6. The particular submodels were obtained for all the miscible binaries using an extensive database of VLE and h^{E} data, including data from the literature[16,27−31,34−38] and values obtained in our laboratory for this work. A combined-correlation of both properties was applied, as recommended in previous works,[12,39,40] with a multiobjective optimization procedure (MOO) with two additional OFs (see Figure 3), one for the VLE data and another for the h^{E}s. Modeling of the immiscible binaries of water (1)+ester(2) was carried out as described at the beginning of this section.

In the next step, (ii), the parameters of the ternary contribution, Δg_k, were determined, minimizing the OF of eq 5 for $n = 3$. The initial resolution of the objective function, proposed by eq 4, is expendable since the starting-point, $\Delta g_k = 0$, is adequate for the optimization algorithm. As with the binaries, each set of parameters obtained in the modeling is verified using the phase stability criterion, rejecting those that do not satisfy that condition. The methodology applied to the ternaries is depicted on the right of Figure 3, indicating a possible rejection of the model established in the case of noncompliance with the mentioned rule.

3.2. Predictive Modeling. The theoretical estimation of the LLE studied in this work was done using two known theoretical models, UNIFAC and COSMO-RS, to determine their capacity to represent the binary and ternary systems studied here. Both methods are already introduced in the field of chemical engineering to estimate thermodynamic properties and even to design equipment and process. The first version of the UNIFAC[13] has undergone several modifications, not only consisting in updating parametrizations by Hansen et al.[41] and others but also in its formalism, as Larsen et al.,[42] Gmehling et al.,[43] and Magnussen et al.[44] even established a particular version to estimate LLE data at 25 °C which is, evidently, very limited. The most recent reparametrization of UNIFAC was presented by Kang et al.[45] Estimations with COSMO-RS[14] were made with the COSMOthermX software of COSMOlogic. The ideal screening charges on the molecular surfaces of each component was made at the level of theory of BVP86/TZVP/DGA1 (implementation BP_TZVP_C30_1201). The molecular geometry of each compound was optimized at the DFT B3-LYP level of theory with the tool TmolX17 from COSMOlogic. Vibrational frequencies were calculated to confirm that electronic energy is at an actual minimum.

4. DISCUSSION OF RESULTS

4.1. Experimental Data and Correlative Modeling. VLE, h^{E}, and modeling of miscible binaries: iso-p VLE data for the binary systems ester(2)+alcohol(3) were compiled from previous publications by our research group[16,28−31] with the exception of data for the binaries propyl propanoate(2) or propyl butanoate(2)+methanol(3), which are recorded in Table S6. The database used for the modeling was completed by including a series published by other authors for the binaries water (1)+alcohol(3).[36−38] The values for (x_1,h^{E}) obtained at T = 298.15K for the 16 systems of ester(2)+alcohol(3) considered in this work are recorded in Table S7, showing $h^{E} > 0$ in all cases. For the water(1)+alcohol(3) systems, the values were taken from the literature.[27,34,35]

For the set of miscible systems, the same modeling procedure as described in section 3 was employed. Table 1 presents the values that define the eq 1 for each of the binaries. The corresponding individual representations of VLE and h^{E} are depicted in Figures S2 and S3, respectively, reflecting an adequate experimental behavior. A combined-modeling was used to validate the experimental data, applying the consistency test proposed previously,[46] with a positive assessment. In addition, all binaries also were validated according to the methodology suggested by us in another papers.[46,47] This checking guarantees the use of data in subsequent operations.

LLE of Binary Systems. Experimental LLE data for the binaries of water(1)+ester(2) are recorded in Table S8 and graphically represented in Figure 4. The ester shows a low solubility in the aqueous phase, being $x_2^{II} < 0.004$ for the binary with ethyl propanoate, which decreases as the organic compound chain length increases. Owing to this low composition, Figure 4a−d shows the uncertainty interval for the compositions for all the data obtained in the aqueous phase. The solubility of the lightest ester (ethyl propanoate) in water decreases with increasing temperature more clearly than that shown by the other esters (Figures 4b−d). On the other hand, the solubility of water in the organic phase is somewhat greater, $x_2^{I} \in (0.05,0.10)$ and rises with temperature. The data in this work are similar to those reported by Stephenson et al.,[6] whereas those of Bomshtein et al.[5] present a different behavior, describing a higher solubility in both phases with $|x_{exp} - x_{lit}| \approx 0.1$.

The parameters g_{ki} and k_{1i} of eq 1 used to correlate the systems are presented in Table 1 for each of the LLE binary systems, together with the errors in the representation of LLE data, s_x. The model provides an acceptable representation of the composition of both phases. The qualitative differences observed in Figure 4 for the aqueous phase are not significant, taking into consideration the magnitude of the axes.

LLE of Ternary Systems. Table S9 compiles the set of LLE data obtained for 16 ternary systems of water (1)+ester(2)+alcohol(3) at T = 298.15 K and atmospheric pressure. These data are represented in ternary diagrams in Figure 5.

The behavior of the LLE is not regular with increasing alcohol chain length and is especially different in the case of systems with methanol. In systems with ethanol, propan-1-ol,

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Table 1. Parameters of Eqs 1−7 Obtained for Ternaries Water(1)+Ester(2)+Alcohol(3) and Their Corresponding Binaries

	Binaries							
	water+				water+			
	ethyl propanoate	ethyl butanoate	propyl propanoate	propyl butanoate	methanol	ethanol	propan-1-ol	butan-1-ol
g_{00}	2604341.94	2616364.51	0	0	0	−359347.60	−890798.93	0
g_{01}	−5817.04	−9423.18	7211.64	6659.38	−2249.11	2431.20	8720.45	−13489.99
g_{02}	0	27.00	0	0	12.24	3.35	−4.78	0.20
g_{10}	0	0	0	14689527.92	0	−1150476.08	−527329.45	143545.96
g_{11}	19104.96	0	0	0	−3180.60	8159.86	−2758.98	11231.32
g_{12}	0	28.57	35.57	0	8.70	−9.80	12.15	0
g_{20}	0	0	0	0	0	−2307691.87	0	7142034.48
g_{21}	0	0	0	0	0	7982.05	1258.95	−12551.32
g_{22}	0	0	0	0	0	−2.52	0	0
k	0.800	1.049	1.054	1.250	1.170	1.059	1.250	0.959
s_x	0.004	0.003	0.002	0.002	−	−	−	0.007
$s_T/s_g/s_\gamma$	−	−	−	−	0.153/0.011/0.043	0.118/0.013/0.089	1.198/0.009/2.992	−
s_h	−	−	−	−	70	100	100	−
	ethyl propanoate+				ethyl butanoate+			
	methanol	ethanol	propan-1-ol	butan-1-ol	methanol	ethanol	propan-1-ol	butan-1-ol
g_{00}	0	0	0	0	0	1383885.6	0	0
g_{01}	5177.53	5544.33	8800.99	8321.76	3863.52	−4374.57	3738.32	6802.15
g_{02}	−1.59	−3.87	−13.55	−14.18	1.36	10.19	−1.11	−12.38
g_{10}	0	−670283.50	0	0	0	0	0	0
g_{11}	−2732.61	−286.40	−7494.27	−7587.94	−209.9	−254.24	3582.52	−4640.36
g_{12}	−1.65	−6.90	4.13	10.65	−6.38	−2.25	−19.43	7.51
g_{20}	0	939141.52	0	0	0	0	−657159.13	0
g_{21}	0	0	4777.87	6034.04	0	0	4168.09	5457.08
g_{22}	0	0	0	−8.91	0	0	0	−8.48
k	1.462	1.323	1.562	1.199	1.115	1.009	1.191	0.914
$s_T/s_g/s_\gamma$	0.808/0.020/0.063	0.152/0.014/0.078	0.112/0.005/0.065	0.097/0.006/0.051	0.566/0.020/0.096	0.474/0.055/0.233	0.075/0.014/0.051	0.112/0.003/0.063
s_h	80	100	85	50	45	80	150	60
	propyl propanoate+				propyl butanoate+			
	methanol	ethanol	propan-1-ol	butan-1-ol	methanol	ethanol	propan-1-ol	butan-1-ol
g_{00}	0	0	0	966857.34	0	0	0	0
g_{01}	3289.91	5195.28	5617.79	−387.87	2720.05	3728.44	6439.91	5001.53
g_{02}	3.30	−5.96	−5.93	−1.09	3.88	−1.24	−9.05	−8.27
g_{10}	0	0	−1326597.09	0	0	0	0	0
g_{11}	1808.55	1373.51	6051.61	−1438.67	3404.20	3861.17	−5071.90	624.83
g_{12}	−15.02	−6.45	−19.79	0.47	−16.52	−14.70	4.72	−5.28
g_{20}	−261885.79	0	0	0	0	0	0	0
g_{21}	0	0	3605.86	1327.66	0	0	4846.68	1588.37
g_{22}	7.26	0	0	0	5.94	0	−7.30	0
k	1.110	1.004	1.186	0.910	0.936	0.847	1.000	0.767

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Table 1. continued

	propyl propanoate+				propyl butanoate+			
	methanol	ethanol	propan-1-ol	butan-1-ol	methanol	ethanol	propan-1-ol	butan-1-ol
$s_T/s_g/s_\gamma$	0.168/0.009/0.065	0.258/0.016/0.113	0.259/0.010/0.086	0.184/0.005/0.028	0.535/0.007/0.177	1.122/0.033/0.245	0.335/0.014/0.108	0.294/0.008/0.053
s_h	60	105	105	90	60	105	105	80
Ternaries								
water+ethyl propanoate+					water+ethyl butanoate+			
	methanol	ethanol	propan-1-ol	butan-1-ol	methanol	ethanol	propan-1-ol	butan-1-ol
Δg_0	−1118.80	25334.08	23204.38	−23306.57	−9504.62	−132.43	292.17	15381.41
Δg_1	−17360.99	−73046.63	−67140.68	24311.48	3379.51	−22888.05	−22420.74	13817.43
Δg_2	−5248.51	−32196.10	−38522.62	5425.38	3053.93	−8322.05	−10550.65	−24596.97
s_x	0.014	0.015	0.014	0.009	0.013	0.012	0.012	0.005
water+propyl propanoate+					water+propyl butanoate+			
	methanol	ethanol	propan-1-ol	butan-1-ol	methanol	ethanol	propan-1-ol	butan-1-ol
Δg_0	−9850.40	4765.20	5005.79	−9211.55	−9909.32	4882.94	−5834.33	−33.08
Δg_1	3385.50	−28350.86	−32170.76	42221.39	10163.46	−30548.38	−11461.15	42851.26
Δg_2	3972.13	−18455.89	−16834.93	9777.95	6551.30	−22408.57	725.40	−5079.33
s_x	0.011	0.009	0.022	0.007	0.018	0.017	0.031	0.009

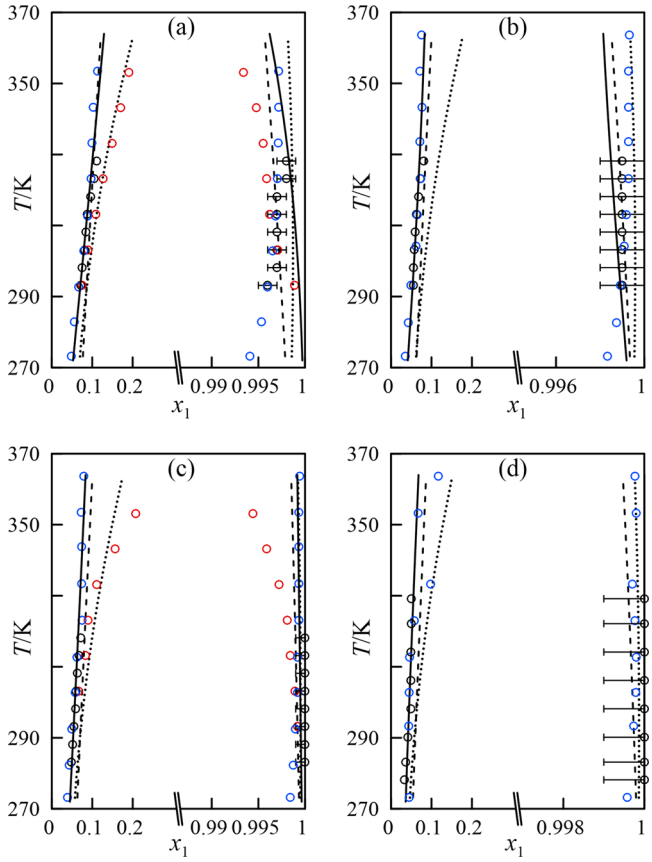

Figure 4. Comparison of LLE data obtained in this work (○), and those from literature: (red ○) values extracted from ref 5 and (blue ○) values extracted from ref 6 for (a) water(1)+ethyl propanoate(2), (b) water(1)+ethyl butanoate(2), (c) water(1)+propyl propanoate(2), and (d) water(1)+propyl butanoate(2). Lines correspond to models: solid-lines (black) eqs 1−2; dashed-lines, UNIFAC;[41] and dotted-lines, COSMO-RS.[14]

and butan-1-ol, the alkanol is more soluble in the organic phase than in the aqueous, and in cases with propan-1-ol and butan-1-ol, the highest amount of alcohol admitted by the aqueous phase is $x^{II}_{alcohol} < 0.1$. This preference of the organic phase is interesting from a practical perspective, as this means that the organic phase of an esterification reactor contains an important proportion of the surplus alkanol. By contrast, the miscibility of the systems with methanol is approximately equal in both phases, even in cases where the ester is ethyl butanoate or propyl butanoate, in which the quantity of alcohol is higher in the aqueous phase. This behavior indicates that the methanol establishes H-bonds with water, interaction that diminishes with increasing length of the alkyl chain of the alkanol, since the latter impedes the heteroassociation water-alkanol. On the other hand, for a given alkanol, the ternary systems with propyl esters present a greater immiscibility than those with ethyl esters, and this difference is even more pronounced in the case of methanol. For these ternaries, the literature does not include LLE data at T = 298.15 K, although data for other temperatures are presented. Hence, Figure S7 illustrates a comparison with data from similar studies.[7−11] It can be observed that temperature has an insignificant effect on the LLE, which is coherent with the behavior of the LLE of the binaries water+ester. The data of Rao et al.[7] for water(1)+ethyl butanoate(2)+methanol(3) show a smaller alkanol composi-

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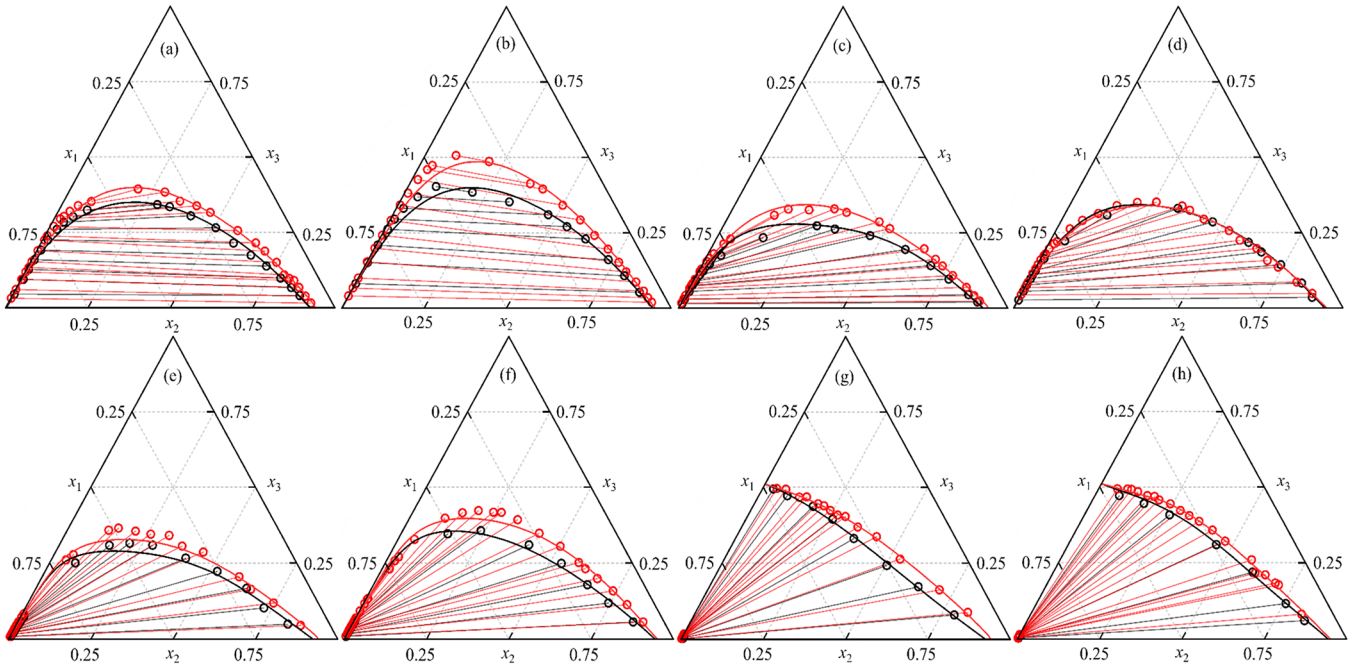

Figure 5. Ternary LLE data obtained in this work: experimental points and tie-lines, and modeling curves using eqs 1−7. Labels indicate the system: water(1)+alkyl propanoate(2)+: (a) methanol, (c) ethanol, (e) propan-1-ol, (g) butan-1-ol; water(1)+alkyl butanoate(2)+: (b) methanol, (d) ethanol, (f) propan-1-ol, (h) butan-1-ol. (○) Ethyl esters, and (red ○) propyl esters.

tion in the aqueous phase than that reported here, with $x^{II}_{3,exp} - x^{II}_{3,lit[7]} \approx 0.1$. Altman et al.[11] present LLE data for water+propyl propanoate + propan-1-ol that differ from those determined in this work. They describe much higher compositions of ester and alkanol in the aqueous phase, $x^{II}_{3,exp} - x^{II}_{3,lit[11]} \approx -0.25$. However, the data reported by Samarov et al.[10] are coherent with our data.

The quality of the LLE data determined for the ternaries was evaluated by the procedure developed by Othmer-Tobias[48] and Hand,[49] both expressed in eq 8. These equations show the existence of a linear relationship between the components of each phase and are written as

$$\log_{10}\left(\frac{1 - x_1^{II}}{x_1^{II}}\right) = a\cdot\log_{10}\left(\frac{1 - x_2^{I}}{x_2^{I}}\right) + b$$
$$\log_{10}\left(\frac{x_3^{II}}{x_1^{II}}\right) = a\cdot\log_{10}\left(\frac{x_3^{I}}{x_2^{I}}\right) + b \quad (8)$$

The application of these equations to experimental LLE data produced very similar results. In both cases, acceptable correlations were obtained (see Figure S5), with values of $R^2 > 0.858$, considering the point closest to the critical point of each series, as this presents the greatest experimental error. Otherwise, values of $R^2 > 0.929$ are obtained.

Figure 5 shows the experimental LLE data of the ternaries and the modeling results. The tie-lines generated by eqs 6 and 7 were obtained with the previously described series and also the parameters of Table 1. The model reproduces well the experimental behavior observed. Moreover, the quality of the fit was evaluated in terms of the modeling error when calculating the tie-lines according to eq 5, and in the definition of the limits of the immiscibility zone, evaluated from the calculation error for x_2 and x_3 for each value of x_1 in the solubility curve:

$$s'_x = \left[\sum_{j=1}^{m}\sum_{i=2}^{n}(x_{i,j,exp} - x_{i,j,cal})^2/nm\right]^{1/2} \quad (9)$$

The parameter that evaluates the deviation in the calculation of the tie-lines is recorded for each system in Table 1, where $s_x = 0.014$ is the mean value for the set of 16 systems, while the mean error made in defining the immiscible region (Table S10) is $s'_x = 0.009$. Figure S6 shows a matrix comparing the distribution coefficients of the 16 systems studied where the separation capacity of the alcohols in the corresponding system is clearly reflected.

The function corresponding to mixing Gibbs energy, $g/RT = (g^{ideal}/RT) + (g^{E}/RT) = \Sigma x_i \ln(x_i\gamma_i)$, using the model defined by eqs 1−7, with the different sets of parameters of Table 1 was checked to ensure that the modeling carried out verifies the phases stability-criterion. Figure 6 shows the function g/RT

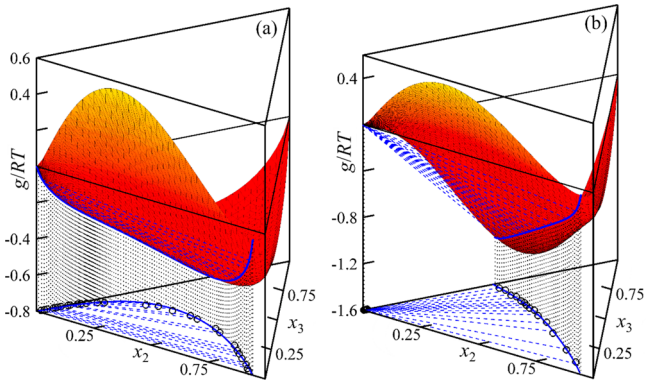

Figure 6. Plot of mixing Gibbs energy, g/RT, for water(1)+propyl propanoate(2)+: (a) ethanol(3) and (b) butan-1-ol(3). Lines were calculated with eqs 1−7: solid-lines delimit phases and dashed-lines are tie-lines. Symbols correspond to experimental data.

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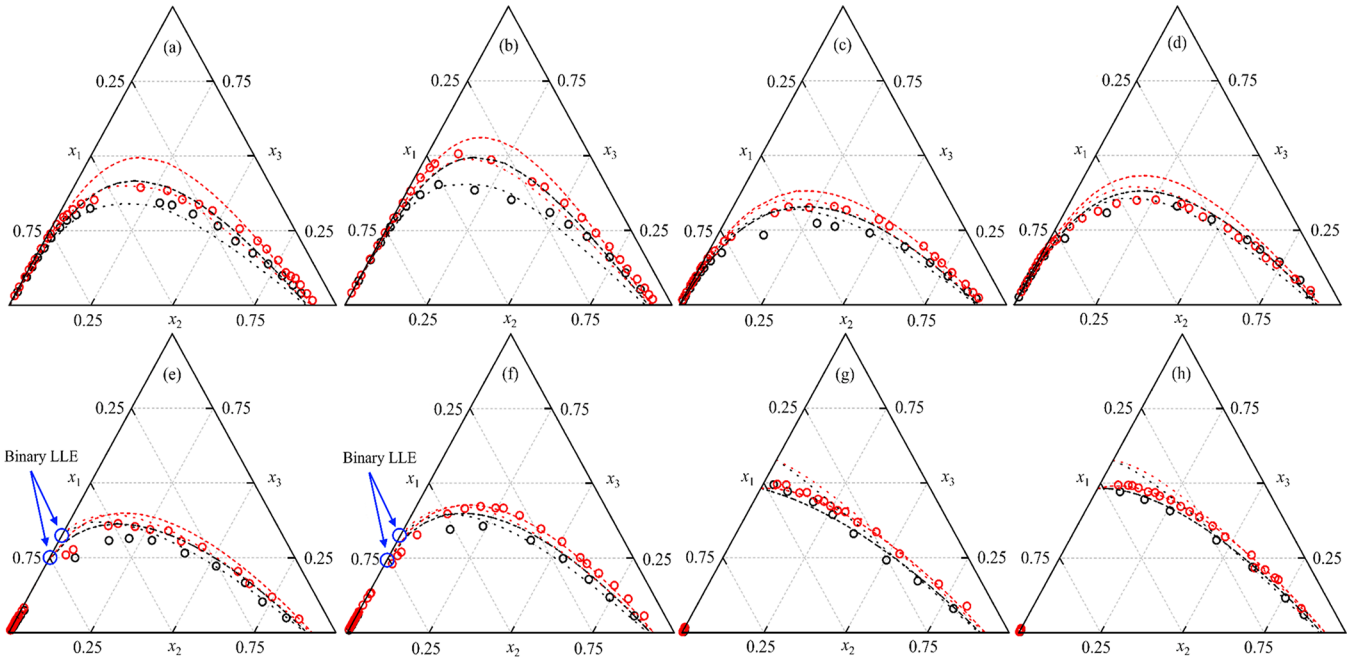

Figure 7. Comparison of ternary LLE data estimated for the systems: water(1)+alkyl propanoate(2)+: (a) methanol, (c) ethanol, (e) propan-1-ol, (g) butan-1-ol and water(1)+alkyl butanoate(2)+: (b) methanol, (d) ethanol, (f) propan-1-ol, (h) butan-1-ol. (Black) ethyl ester and (red) propyl ester. Symbols indicate data measured in this work. Dashed lines (- - -) UNIFAC[41] and dotted lines (·····) COSMO-RS.[14] Blue arrows indicate the erroneous LLE data estimated by both models for water+propan-1-ol.

for the ternaries water(1)+propyl propanoate(2)+, ethanol(3), and water(1)+propyl propanoate(2)+butan-1-ol(3), corresponding to ELL of type 1 and type 2, respectively. In both cases, the tie-lines produce straight lines tangential to the surface, only intersecting this surface at the equilibrium compositions. This corresponds to a suitable verification of the criteria that have been described in a previous article.[32,33]

4.2. Estimative Modeling with UNIFAC and COSMO-RS. Figure 4 and Figure S1 show the estimations made for the binaries water(1)+ester(2) and water(1)+butan-1-ol(3) by the UNIFAC[41] and COSMO-RS[14] models. Applying the updated version of the group contribution model resulted in estimates similar to Gmehling's version. However, the original version of UNIFAC, with the parameters of Hansen et al.,[41] gives a reasonable prediction of the LLE compositions in both phases for water(1)+ester(2) and for water(1)+butan-1-ol(3). Therefore, this latter was implemented in the Aspen-Plus software to simulate the alkanol extraction process.

By contrast, COSMO-RS presents significant deviations in experimental behavior in the organic phase, estimating a greater solubility of water in ester than the real value, $x^{I}_{1,exp} - x^{I}_{1,cal} \approx -0.1$ but less solubility in the case of the butan-1-ol, $x^{I}_{1,exp} - x^{I}_{1,cal} \approx 0.1$.

Figure 7 shows the results of the models employed and the experimental LLE data for the ternaries and Table S10 shows the errors in the estimation of the immiscibility zones, s'_x. For the systems with methanol and ethanol, Figure 7a−d, COSMO-RS underestimates the immiscibility zone and UNIFAC overestimates it, with approximately equal deviations. The choice of the most suitable predictive model for these systems will depend upon the working compositions, given that the qualitative analysis carried out in Figure 7a−d indicates that for $x_{alcohol} < 0.25$, UNIFAC presents a smaller deviation and for $x_{alcohol} > 0.25$ COSMO-RS is closer to the real behavior. In the case of systems with butan-1-ol, the LLE predictions with UNIFAC are acceptable, with $s'_x = 0.010$, whereas COSMO-RS presents a significantly higher standard deviation, $s'_x = 0.040$, as the LLE estimation for the binary water+butan-1-ol differs from the experimental values.

For the systems with propan-1-ol, Figure 7e,f, although the ternary immiscibility zone is well described for both models, these show the appearance of two immiscible liquid phases in the binary system of water+propan-1-ol. This is a serious error, as this binary is completely miscible at the working temperature, 298.15 K. This situation particularly affects the prediction of the behavior of systems of water+ester+propan-1-ol at low ester concentrations, $x_{ester} < 0.15$, in which COSMO-RS and UNIFAC estimate the formation of two liquid phases in compositions which experimentally behave as a homogeneous system, see Figure 7e,f.

The errors s'_x of the model, eq 9, are generally significantly lower than the errors of COSMO-RS and UNIFAC. However, for the system with butan-1-ol, estimations made with the latter model approximate the calculated LLE.

5. PURIFICATION OF ESTERS BY LIQUID−LIQUID EXTRACTION: EFFECT OF ALKANOL IN SOLUTION ON THE EFFICACY OF THE PROCESS

As a practical application of the results obtained from the binomial experimentation-modeling, a simulation of the extraction of alkanols dissolved in ester was carried out, using water as entrainer. The simulation was conducted in Aspen Plus V11, implementing the model defined by eq 1 in the software to calculate the LLEs. This was done in the block EXTRACT in order to define the most suitable extractor. This procedure is illustrated in Figure 8 that shows the initial conditions of the different cases studied. The numerical values were obtained for an input flow of 100 kg h^{-1} and an equimolar composition of the ternary water:ester:alcohol (0.33:0.33:0.33). Two ratios were proposed for the entrainer:-

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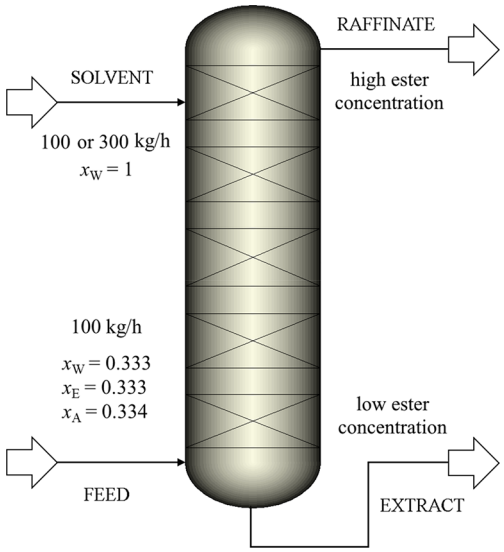

Figure 8. Process diagram for extraction of alkanol from a equimolar mixtures of water+ester+alcohol using water as an entrainer.

feed flow of 3:1 and 1:1. The simulation was performed with the correlation model presented in section 3 and the UNIFAC[41] model, which provided the best estimation for the systems as commented.

The results obtained are presented in Table 2, and some observations are discussed below. When an identical ratio is used for entrainer:feed, recovery of the ester is high (>90%) with a purity of 99% (w/w) in all the systems of water+ester +alcohol (methanol, ethanol). However, when propan-1-ol or butan-1-ol are used, although the recovery is still high, and similar to that of the lower alkanols, the purity of the product diminishes with increasing chain length of the alkanol and increases with the length of the ester chain. In the systems of water+ester+butan-1-ol, water has a very limited capacity to extract the alkanol, as shown by the tie-lines in Figure 5, so the ester obtained in the extraction process has a low purity (54−62%). In summary, the simulations of water+ester+propan-1-ol and water+ester+butan-1-ol systems do not reach an adequate separation efficacy when using the same ratios for entrainer:-feed as those used in the previous cases.

Therefore, a ratio of 3:1 was employed, see Table 2, and the ester was purified (>97%) in the mixtures of water+ester +propan-1-ol. When the same ratio was used for the ternary with butan-1-ol, the purity of the ester only increased by 6−8%, giving place to an ester of insufficient quality (61−72%). These results confirm the observations in the LLE diagrams, where the form of the tie-lines of the mixtures of water+ester +butan-1-ol indicate *a priori* a very limited capacity of the water to extract the butan-1-ol.

For the systems of water+ester+methanol, water+ester +ethanol, and water+ester+butan-1-ol, the results obtained with UNIFAC are similar to those obtained with the proposed model. However, extraction in the systems of water+ester +propan-1-ol differ significantly when evaluating the purity of the ester obtained, with differences of 7−17% w/w. This is due to the error of the UNIFAC model that predicts a nonexistent LLE in the binary water+propan-1-ol (Figure 7), resulting in an underestimation of the capacity of water to extract the alkanol. This error in the estimation of results of the process makes it unfeasible to use UNIFAC predictions for subsequent practices.

Table 2. Simulation Results for the Extraction Process Depicted in Figure 8

	ester purity in the refined (% *w*/*w*)							
	proposed model, eqs 1, 7				UNIFAC[41]			
	methanol	ethanol	propan-1-ol	butan-1-ol	methanol	ethanol	propan-1-ol	butan-1-ol
	Solvent:feed ratio, kg/h:kg/h 100:100							
ethyl propanoate	99	99	77	54	98	98	66	55
ethyl butanoate	99	99	80	58	99	99	73	60
propyl propanoate	99	99	83	58	99	99	73	60
propyl butanoate	99	99	96	62	99	99	79	64
	Solvent:feed ratio, kg/h:kg/h 300:100							
ethyl propanoate	–	–	98	54	–	–	97	61
ethyl butanoate	–	–	99	61	–	–	99	67
propyl propanoate	–	–	99	59	–	–	99	67
propyl butanoate	–	–	99	65	–	–	99	72
	ester recovery in the refined (%)							
	proposed model, eq 1				UNIFAC[41]			
	methanol	ethanol	propan-1-ol	butan-1-ol	methanol	ethanol	propan-1-ol	butan-1-ol
	Solvent:feed ratio, kg/h: kg/h 100:100							
ethyl propanoate	94	90	97	99	93	89	96	97
ethyl butanoate	98	94	96	99	97	95	98	99
propyl propanoate	98	97	96	99	97	95	98	99
propyl butanoate	97	95	96	99	99	98	99	99
	Solvent:feed ratio, kg/h:kg/h 300:100							
ethyl propanoate	–	–	95	98	–	–	87	92
ethyl butanoate	–	–	93	96	–	–	95	97
propyl propanoate	–	–	93	96	–	–	95	97
propyl butanoate	–	–	95	97	–	–	98	99

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6. CONCLUSIONS

This work focuses on the experimentation and analysis of these systems using four esters (ethyl or propyl propanoate or butanoate) and four alkan-1-ol (methanol to butan-1-ol), whose practical utility is discussed with a new modeling procedure. Dilution of the ester in the aqueous phase is low, even in the presence of high concentrations of alkanol ($x^{II}_{2,max} \approx 0.15$). On the other hand, the water is dissolved in significant proportions in the organic phase, reaching up to $x^{I}_{1} \approx 0.75$ in some cases. The methanol is distributed almost equally between the aqueous phase and the organic phase, with a mean distribution coefficient of $\overline{k}_{aq/org} = 1.15$, whereas the others alkanols tend to concentrate in the organic phase, $\overline{k}_{aq/org} = [0.01; 0.53]$. This implies that the organic phase of an esterification reactor will contain an important proportion of the surplus alkanol.

The modeling carried out with eq 1, showed a good representation of the LLEs, both in the immiscibility zones and in the tie-lines in all cases, with mean deviations in compositions for the 16 systems of 0.009 and 0.014, respectively. The behavior of phases simulated with the COSMO-RS and UNIFAC models present important errors, especially in systems with propan-1-ol, given that both models predict a nonexistent immiscibility in the binary water+propan-1-ol at 298.15 K. This affects the simulation/design process of the system that contains the binary, as it underestimates the capacity of water to extract that alkanol from the organic stream that contains the ester.

Simulation of the extraction process of the alkanol with water, emphasizes the need to use models based on the correlation of experimental data in the design of processes involving the systems of water+ester+methanol/ethanol/propan-1-ol in the immiscibility zone. This is demonstrated in the case of propan-1-ol, since the mistaken estimation of a limited solubility in the binary water+propan-1-ol, led to an underestimation of the capacity of water to extract alcohol from the organic phase containing the ester. This error affects the calculation of the amount of water required for the process, which is estimated to be much higher than the real amount required.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.1c01959.

(Table S1) Background on the solutions studied in this work; (Table S2) properties of pure component used and the corresponding binary and ternary solutions in (Table S3); (Tables S4 and S5 and Figure S1) the experimental LLE for water-butan-1-ol, the internal standard used in GC, and the corresponding representation, respectively; (Tables S6 and S7) the experimental VLE and h^E for binary ester+alkanol, respectively, where the graphics are (Figures S2 and S3); (Tables S8 and S9) LLE data of binary water+ester and ternary water +ester+alkanol, respectively; (Table S10) the deviation of estimations with different models; (Figure S4) ternary diagrams of the mixtures water+ester+alkanol; (Figure S5) tie-line correlations; and (Figure S6) the distribution coefficients obtained for ternary systems water(1)+-ester(2)+alcohol(3) (PDF)

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Notes

The authors declare no competing financial interest.

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