# Liquid−Liquid Equilibrium Diagrams of Ethanol + Water + (Ethyl Acetate or 1-Pentanol) at Several Temperatures

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There are a great amount of substances found in the must distillations and at very low concentrations (called congeners). Other than that, ethanol and water are the major compounds. These facts make it difficult to simulate and optimize this industrial process. To extend the scarce knowledge of mixing thermodynamics related to these compounds, this paper contains the results of a new experimental study of liquid−liquid equilibrium (LLE) at temperatures of (298.15, 308.15, and 318.15) K for the ternary mixtures ethanol + water + (ethyl acetate or 1-pentanol) under atmospheric conditions. Ethyl acetate and 1-pentanol are important natural and legal congeners in common alcoholic distillation. A comparative analysis was performed by application of different group contribution methods to predict experimental equilibria behavior of these mixtures. The experimental tie line data were correlated to test consistency with the Othmer−Tobias equation. Disposable literature was revised and commented upon.

## Introduction

Fluid phase equilibria and mixing properties are of primary interest for practical and theoretical purposes (equipment optimization, mathematical models, parameter estimation, etc). As in any other distillation industrial process, the knowledge of multicomponent phase equilibrium data is important for beverage technology. In the past few years, only a few attempts have been made oriented toward a better description of complex mixtures in distillation beverages. Must distillation production, irrespective of the origin of grapes or geographic place, results in the manufacture of a product with two main characteristics: a great amount of substances found in the mixture to be distilled and the low concentration of many components (so-called congeners)[1] different from ethanol and water. Several of the congener compounds are an essential part of the aroma organoleptic matrix in terms of enological values.[2] These chemical substances are complex and usually present in mixtures at very low concentration, but they may not be neglected in calculations for design. Most of the substances involved in this process are highly polar. From open literature, it can be observed that a huge quantity of congeners has been found in different distillation drinks.[3,4] However, of all these compounds, only a few of them are controlled by legislation, meaning that their concentration cannot be higher than that established limit. Despite technology advances, must distillation is still a traditional elaboration process, and it is far away from working under optimized cost conditions. These facts make it very difficult to fit the operational parameters in terms of energy consumption during the distillation process and then to ensure high quality of the final commercial product and low cost production. To extend the scarce knowledge of mixing thermodynamics related to these compounds, and as an extension of our earlier works concerning phase equilibria,[5−7] this paper contains the results of a new experimental study of liquid−liquid equilibrium (LLE) of the ternary mixtures ethanol + water + (ethyl acetate or 1-pentanol) at the temperatures (298.15, 308.15, and 318.15) K. The experimental tie lines were correlated with the UNIQUAC equation.[8] The corresponding fitting parameters were gathered. Because experimental data are often not available for process synthesis, group contribution methods can be used for the prediction of the required phase equilibria. In the past several decades, the group contribution method UNIFAC[9,10] has become very popular, and it has been integrated into most commercial simulators. This model requires complete and fully updated experimental data in order to compute group interaction parameters and reproduce the behavior of systems at other mixing or operation conditions. Due to the importance of theoretical data on industrial design, predictive group contribution methods were applied. The obtained results being analyzed and commented upon. The functional group contribution methods are a reliable path for, at least, a qualitative prediction of liquid-phase activity coefficients and availability of interaction parameters as a function of temperature being necessary. The present study of solubility shows a slight dependence on

**Table 1. Physical Properties of Pure Compounds: Densities ($\rho$) and Refractive Indices ($n_D$) at 298.15 K**

| | MW[a] | $\rho$/kg·m$^{-3}$ | | $n_D$ | |
|---|---|---|---|---|---|
| | kg·mol$^{-1}$·kg$^{-1}$ | obsd | lit.[d] | obsd | lit.[e] |
| ethanol | 46.069 | 785.89[b] | 787.30 | 1.35941 | 1.35941 |
| water | 18.015 | 997.04[b] | 997.05 | 1.33250 | 1.33250 |
| ethyl acetate | 88.107 | 894.44[b] | 894.55 | 1.36978 | 1.36978 |
| 1-pentanol | 88.149 | 810.91[c] | 810.80 | 1.40770 | 1.40800 |

[a] Ref 14. [b] Ref 12. [c] Ref 13. [d] Ref 15. [e] Ref 16.

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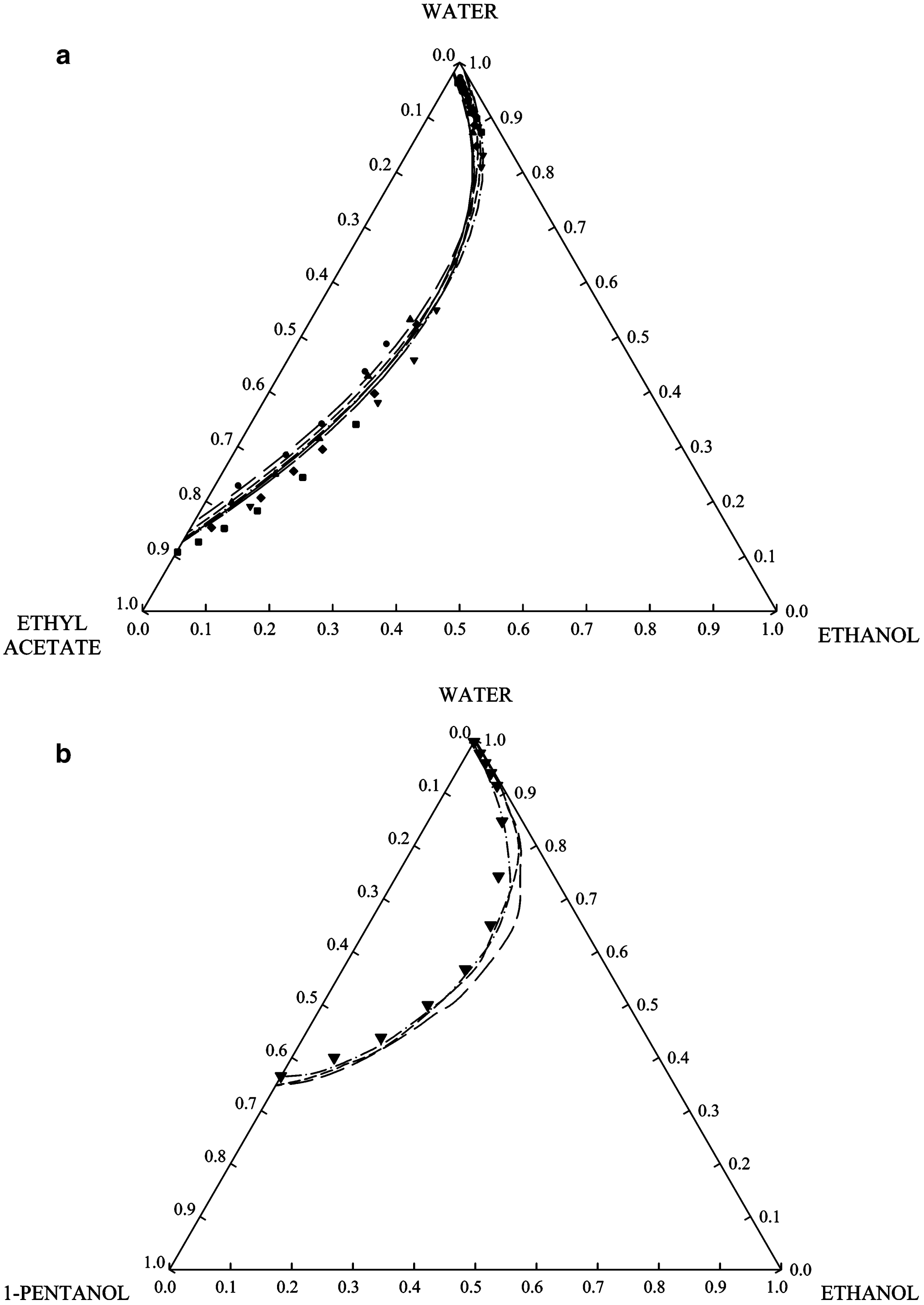

**Figure 1.** (a) Experimental binodal curves (— • —, 298.15 K; - - -, 308.15 K; and —, 318.15 K from this work) and literature data (— • • —, at 298.15 K;[17] — —, at 308.15;[17] —, at 318.15 K;[17] ▼, at 273.15 K;[18] ■, at 273.15 K;[18] ◆, at 293.15 K;[19] ▲, at 313.15 K;[20] and ●, at 328.15[20]) for the system ethanol + water + ethyl acetate. (b) Experimental binodal curves (— • —, 298.15 K; - - -, 308.15 K; and —, 318.15 K from this work) and literature data[21] (▼, at 298.15 K) for the system ethanol + water + 1-pentanol.

temperature and the asymmetry of the coexistence curves with respect to equimolar water + congener (ethyl acetate or 1-pentanol) composition. This ternary mixture shows a LLE trend type 1, in accordance to the usual literature. The experimental tie line data were correlated to test consistency with the Othmer−Tobias[11] equation. Disposable literature was revised and commented upon.

## Experimental Section

***Materials.*** Ethanol (99.5 mol %) was supplied by Merck and was used without further purification. Ethyl acetate (99.9 mol %) and 1-pentanol (99.5 mol %) were supplied by Fluka and Merck, respectively. Water was Millipore quality with organic total mass < 5 ppb and resistivity 18.2 MΩ•cm. The purity of the materials so obtained was checked by gas−liquid chromatography (GLC) and was found to be better than 99.7 mol %. All products were ultrasonically degassed and dried over molecular sieves (pore diameter of $3 \cdot 10^{-10}$ m from Fluka) before use. Densities and refractive index of the pure substances are listed in Table 1 and compared with literature values as well as other relevant information. Precautions were taken in order to avoid evaporation losses during experimental manipulation by

**Table 2. Experimental Liquid−Liquid Equilibrium Data for the Ternary Systems**

| $x_1^{I}$ | $x_2^{I}$ | $x_1^{II}$ | $x_2^{II}$ |
|---|---|---|---|
| Ethanol (1) + Water (2) + Ethyl Acetate (3) | | | |
| 298.15 K | | | |
| 0.002 | 0.997 | 0.015 | 0.162 |
| 0.015 | 0.984 | 0.034 | 0.178 |
| 0.021 | 0.978 | 0.043 | 0.188 |
| 0.029 | 0.970 | 0.054 | 0.200 |
| 0.063 | 0.931 | 0.107 | 0.296 |
| 0.072 | 0.915 | 0.139 | 0.374 |
| 0.086 | 0.888 | 0.172 | 0.478 |
| 308.15 K | | | |
| 0.002 | 0.997 | 0.012 | 0.168 |
| 0.019 | 0.980 | 0.034 | 0.187 |
| 0.035 | 0.963 | 0.057 | 0.217 |
| 0.050 | 0.946 | 0.080 | 0.257 |
| 0.064 | 0.926 | 0.126 | 0.359 |
| 0.071 | 0.914 | 0.148 | 0.418 |
| 0.085 | 0.888 | 0.172 | 0.523 |
| 318.15 K | | | |
| 0.013 | 0.982 | 0.009 | 0.175 |
| 0.018 | 0.979 | 0.032 | 0.204 |
| 0.034 | 0.962 | 0.060 | 0.245 |
| 0.046 | 0.947 | 0.087 | 0.298 |
| 0.062 | 0.925 | 0.137 | 0.407 |
| 0.068 | 0.916 | 0.153 | 0.459 |
| 0.084 | 0.882 | 0.166 | 0.564 |
| Ethanol (1) + Water (2) + 1-Pentanol (3) | | | |
| 298.15 K | | | |
| 0.005 | 0.985 | 0.081 | 0.357 |
| 0.011 | 0.981 | 0.110 | 0.345 |
| 0.038 | 0.940 | 0.220 | 0.505 |
| 0.029 | 0.950 | 0.200 | 0.480 |
| 0.047 | 0.924 | 0.240 | 0.589 |
| 0.000 | 0.995 | 0.000 | 0.363 |
| 308.15 K | | | |
| 0.019 | 0.980 | 0.023 | 0.367 |
| 0.030 | 0.969 | 0.060 | 0.410 |
| 0.053 | 0.945 | 0.119 | 0.462 |
| 0.058 | 0.940 | 0.127 | 0.489 |
| 0.062 | 0.936 | 0.169 | 0.548 |
| 0.000 | 0.998 | 0.000 | 0.348 |
| 318.15 K | | | |
| 0.026 | 0.973 | 0.047 | 0.353 |
| 0.036 | 0.963 | 0.086 | 0.364 |
| 0.054 | 0.944 | 0.159 | 0.448 |
| 0.056 | 0.941 | 0.200 | 0.490 |
| 0.056 | 0.942 | 0.224 | 0.522 |
| 0.000 | 0.992 | 0.000 | 0.347 |

cooling the materials and storing under an inert atmosphere of argon (less than $3 \cdot 10^{-6}$ by volume) before sample preparation. The purity of components was checked by GLC and was ascertained by comparing their physical properties with literature findings. Samples were prepared by mass, covering the whole composition ranges of the mixtures under immiscibility.

***Apparatus and Procedure.*** The apparatus for the LLE determination consists of a glass cell with a water jacket in order to maintain a constant temperature. Temperature was controlled within $\pm\, 5 \cdot 10^{-2}$ K inside the cell. The cell was connected to a controller bath, with a stability of $\pm\, 10^{-2}$ K. The temperature of the cell was controlled by a water jacket and maintained with an accuracy of within 0.1 K. A magnetic stirrer provided sufficient agitation within the apparatus. The prepared mixtures were introduced into the extraction cell and were stirred for 1 h and then left to settle for 24 h for phase separation. Samples of less than 1 mL were carefully taken from the upper layer with a syringe and from the lower layer through a sampling tap. Densities were measured at 298.15 K by using an Anton Paar DMA 58 vibrating-tube densimeter with an accuracy of $\pm\, 0.00001\ \mathrm{g \cdot cm^{-3}}$ that had been calibrated at atmospheric pressure with twice distilled water and dry air. The temperature of the densimeter was maintained at 298.15 K with a precision of ± 0.01 K by means of a semiconductor Peltier element and measured by a calibrated platinum-resistance thermometer. Refractive indices were measured with a Mettler RE50 refractometer with an accuracy of ± 0.00001, and temperature was controlled like the densimeter, with a temperature precision of ± 0.01 K. Previously published results on density and refractive index were used as calibration polynomials to compute the equilibrium compositions.[12,13] Analogous results may be obtained by GLC procedure (peak areas are converted to the mole fractions using weight factors determined by the GLC analysis of mixtures of known composition) or measurement of physical properties as we previously observed.[5] Estimated uncertainty for mole fractions was determined as $\pm\, 5 \cdot 10^{-4}$ and $\pm\, 7 \cdot 10^{-4}$ in hydroxylic-rich phase and alkane-rich phase, respectively.

## Results and Discussion

***Correlation of Liquid−Liquid Equilibria Data.*** The equilibrium compositions are gathered in Table 2. The UNIQUAC equation was used to correlate the experimental data for the mixture discussed here. An acceptable accuracy has been achieved for all cases with temperature dependence parameters for the UNIQUAC equation, as follows:

$$\tau_{ij} = \exp\left(\frac{b_{ij}}{T}\right) \tag{1}$$

The fitting parameters $b_{ij}$ are given in Table 3 together with the root mean square deviations. The expression of the activity coefficients for a multicomponent mixture has the following form for the UNIQUAC model:

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{comb}} + \ln \gamma_i^{\mathrm{res}} \tag{2}$$

$$\ln \gamma_i^{\mathrm{comb}} = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_{j=1}^{C} x_j l_j \tag{3}$$

$$\ln \gamma_i^{\mathrm{res}} = -q_i \ln \sum_{j=1}^{C} \theta_j \tau_{ji} + q_i - q_i \sum_{j=1}^{C} \frac{\theta_j \tau_{ij}}{\sum_{k=1}^{C} \theta_k \tau_{kj}} x_j l_j \tag{4}$$

$$\theta_i = \frac{q_i x_i}{\sum_{j=1}^{C} q_j x_j} \tag{5}$$

$$\Phi_i = \frac{r_i x_i}{\sum_{j=1}^{C} r_j x_j} \tag{6}$$

with the $r_i$ and $q_i$ parameters being computed from the number of molecular groups and the individual values of the van der Waals area and volume, determined by the Bondi method. The detailed descriptions of the meaning of parameters and equations are widely defined in current literature. As can be seen from Table 3, the theoretical tie lines are relatively in good agreement with the experimental data in both cases. In other words, the UNIQUAC model describes adequately the experimental data for this ternary system at each temperature. The optimum interaction parameters between pairs of chemicals were deter-

**Table 3. Correlation Parameters of UNIQUAC Model and Root Mean Square Deviation ($\sigma$) for the Ternary Systems**

| | $b_{12}$ | $b_{21}$ | $b_{13}$ | $b_{31}$ | $b_{23}$ | $b_{32}$ | $\sigma(x_1^{\mathrm{I}})$ | $\sigma(x_2^{\mathrm{I}})$ | $\sigma(x_1^{\mathrm{II}})$ | $\sigma(x_2^{\mathrm{II}})$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Ethanol (1) + Water (2) + Ethyl Acetate (3) | | | | | | |
| $B_{ij}/(\mathrm{K}^{-1})$ | −137.836 | −109.102 | −355.791 | 390.218 | 176.158 | 320.830 | 0.011 | 0.010 | 0.001 | 0.019 |
| | | | | Ethanol (1) + Water (2) + 1-Pentanol (3) | | | | | | |
| $B_{ij}/(\mathrm{K}^{-1})$ | 99.751 | −425.373 | −297.257 | −211.986 | 242.413 | 90.395 | 0.022 | 0.021 | 0.021 | 0.035 |

**Table 4. Fitting Parameters of Othmer−Tobias Equation and Deviations for the Ternary Systems at the Range of Temperatures**

| | | | |
|---|---|---|---|
| | Ethanol (1) + Water (2) + Ethyl Acetate (3) | | |
| 298.15 K | $a = 0.7349$ | $b = -0.0165$ | $R^2 = 0.9507$ |
| 308.15 K | $a = 0.5972$ | $b = 0.3618$ | $R^2 = 0.9909$ |
| 318.15 K | $a = 0.9456$ | $b = -0.4915$ | $R^2 = 0.9487$ |
| | Ethanol (1) + Water (2) + 1-Pentanol (3) | | |
| 298.15 K | $a = 1.461$ | $b = -2.0384$ | $R^2 = 0.9346$ |
| 308.15 K | $a = 3.2841$ | $b = 13.025$ | $R^2 = 0.9438$ |
| 318.15 K | $a = 3.8988$ | $b = 16.523$ | $R^2 = 0.8117$ |

mined using the observed (liquid + liquid) data, which describe the interaction energy between molecules $i$ and $j$ or between each pair of compounds. In this work, a least-squares technique all points weighting equally was used for estimating the parameters in each model from tie line data. An objective function was stated in terms of concentration difference between experimental mole fraction and calculated mole fraction of tie lines. This function had the following form:

$$F = \sum_{i}^{n} \min \sum_{j}^{3} \sum_{k}^{2} [x_{jk}^{\mathrm{exp}}(i) - x_{jk}^{\mathrm{cal}}(i)]^2 \qquad (7)$$

Table 3 shows the calculated values of the equations binary interaction parameters. The goodness of the fitting results between the observed and calculated mole fractions was calculated in terms of the root mean square deviation ($\sigma$). The UNIQUAC structural parameters $r$ and $q$ (group volume and surface area parameters) were calculated from the group contribution data that has been previously reported. The compositions of the mixtures at equilibrium on the binodal curve at (298.15, 308.15, and 318.15) K are plotted in Figure 3.

As could be observed in Figure 1, the aqueous layer compositions from different authors[17−20] and experimental data are not exactly coincident. Otherwise congener layer compositions are dispersed and of poor quality for both mixtures. Due to the slight influence of temperature on the mutual solubility of the ternary mixtures, the author's results show an adequate agreement with those in previous literature, attending to the disposable data. The solubility of the congeners in water is almost nonexistent as reflected in open literature. The negligible differences may be questionable due to impurity of the used chemicals. This fact is more notorious in ethyl acetate mixture. The solubility curves of the binary system congener + water emerge for congener in the hydroxylic-rich layer from the ethanol + water side of the triangle. In both cases, the binodal curves are very close to the axis water corner of the composition diagram. The hydroxylic-rich phase contains little quantities of congener while the organic phase contains little water for initial compositions lower than 0.05 in molar fraction of ethanol. The influence of temperature on LLE is slight, diminishing at lower ethanol compositions.

***Consistency of Experimental Tie Line Data.*** The experimental tie line data at each temperature were correlated to test consistency by the method of Othmer and Tobias,[11] and the results are represented in Table 4. In this table, nearly linear correlations for every case are shown, which point out the consistency of the experimental data. The correlation coefficients ($a$ and $b$) and the correlation factor ($R^2$) values were determined by the least-squares method by a Marquardt algorithm. A correlation factor close to one suggests a high degree of consistency of the related data. The equation proposed by Othmer−Tobias was expressed for ternary mixtures as

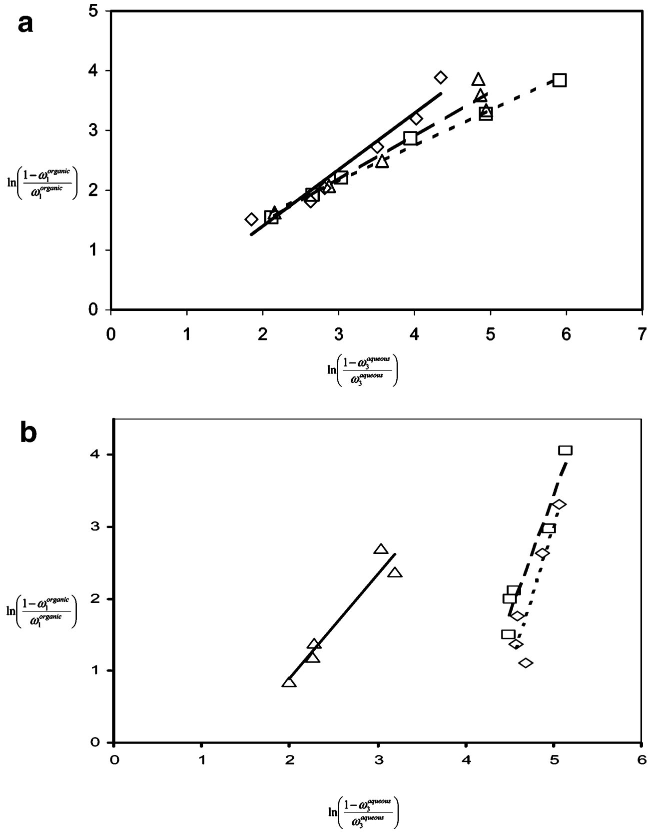

**Figure 2.** Othmer−Tobias test for (a) ethanol + water + ethyl acetate and (b) ethanol + water + 1-pentanol (△, 298.15 K; □, 308.15 K; and ●, 318.15 K).

$$\ln\left(\frac{1-\omega_1^{\mathrm{organic}}}{\omega_1^{\mathrm{organic}}}\right) = b \ln\left(\frac{1-\omega_3^{\mathrm{aqueous}}}{\omega_3^{\mathrm{aqueous}}}\right) + a \qquad (8)$$

where $\omega$ is mass fraction, the subscript means the compound in mixture (1 for ethanol, 2 for water, and 3 for ethyl acetate or 1-pentanol), the superscript means the equilibrium phase, and $a$ and $b$ are fitting coefficients as shown in Table 4. Figure 2 shows the Othmer−Tobias equation for both mixtures.

***Group Contribution Prediction.*** The group contribution methods with widespread application into any physical property are not very accurate in predicting the LLE due to several limitations. The main factors are the higher interactions among components in mixture than in vapor−liquid equilibria, the scarcity of experimental heterogeneous data of components with different functional groups at wide operational conditions, and a non-rigorous thermodynamic consistency test for quality evaluation of experimental equilibrium data. The UNIFAC group contribution method was applied to test their prediction capability, with only a qualitative description being obtained. Figure 3 shows the experimental tie lines of the systems at the

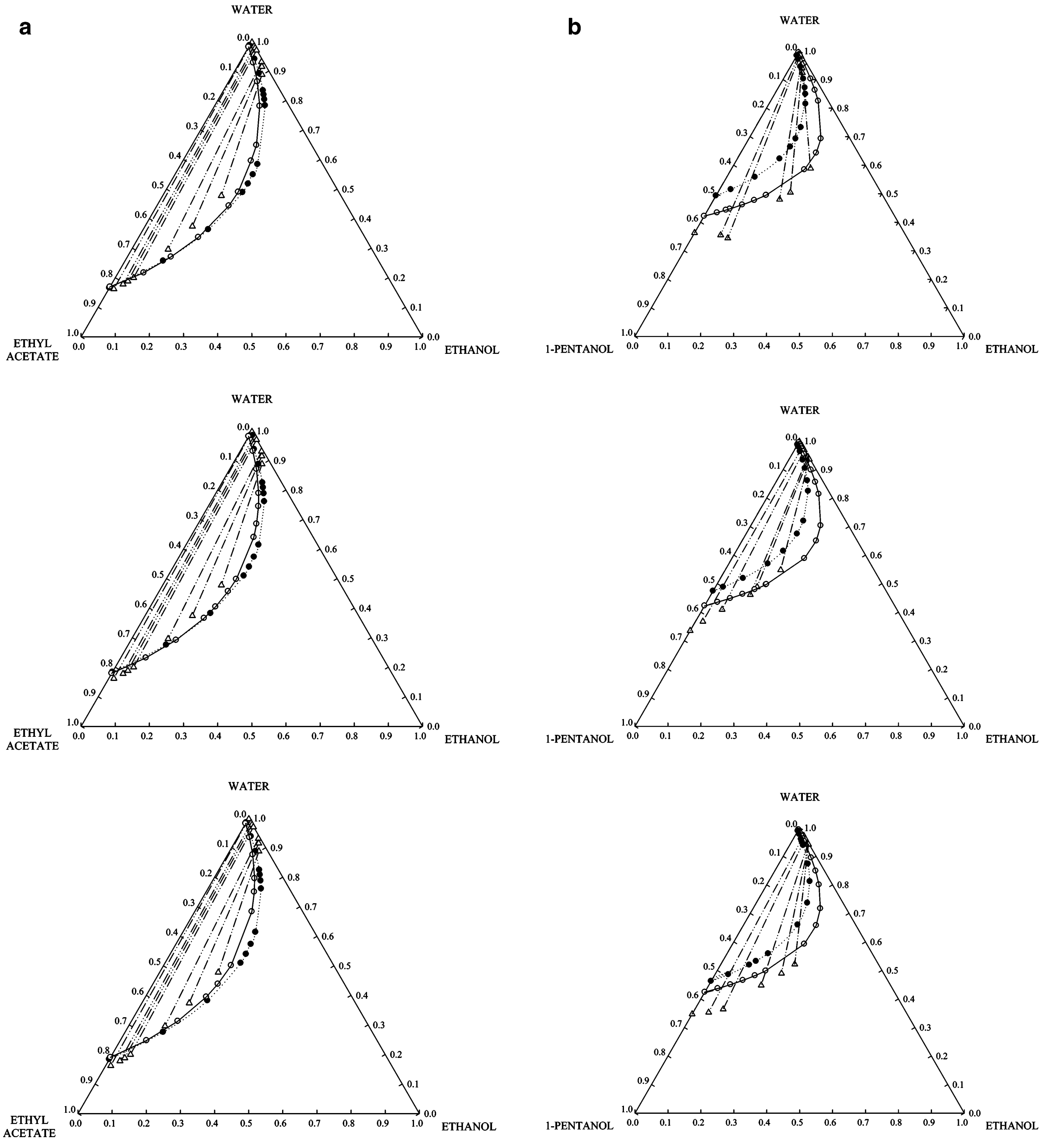

**Figure 3.** Inmiscibility region: - - -, experimental; ○, UNIFAC; ●, UNIFAC-Lyngby at the temperatures (1) 298.15 K, (2) 308.15 K, and (3) 318.15 K for (a) ethanol + water + ethyl acetate and (b) ethanol + water + 1-pentanol.

range of temperatures. The immiscibility region for the systems measured is increased with decreasing temperature, but only a slight influence was appreciated. The UNIFAC group contribution method was applied to predict the immiscibility region, describing the interactions parameters among the functional groups $CH_3$, $CH_2$, $CH_3COO$, OH, and $H_2O$. In Figure 3, the experimental and predicted borderlines of LLE are plotted. A qualitative description was obtained by means of this group contribution method, with only vapor−liquid equilibria database UNIFAC showing qualitative accuracy. UNIFAC underestimates the splitted region at each temperature by assigning a low role to the polar behavior of water for liquid phase splitting, perhaps due to insufficient water group information into the group contribution method database. Such an effect reveals the importance of a wider disposable thermodynamic liquid split data for an adequate description of multicomponent heterogeneous systems by means of contribution methods.

## Conclusions

In this work, the experimental LLE data of ethanol + water + congener (ethyl acetate or 1-pentanol) and the enclosed binary (water + congener) were studied at the range (298.15 to 318.15) K, the corresponding fitting of data being collected. The temperature had a slight effect on the size of the immiscibility region at the temperatures studied. Only a relative reduction of immiscibility takes place for rising temperatures. The UNIFAC method predictions fitted only qualitatively to the experimental data for the ternary system. The experimental data were correlated to test consistency with the Othmer−Tobias equation, with an almost linear tendency being obtained at each temperature.

In open literature, different publications[17−20] related to the ternary mixtures that were experimentally studied may be determined. All of them are of low utility due to the lack of thermodynamic consistency (see points distribution into Figure 1, panels a and b). Attending to the disposable literature until now, it is clear that poor results in simulation or calculation could be obtained from the collections of data indicated above.

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