

## Measurement and modelling of phase equilibria for ethanol+water+1-pentanol at isobaric condition

José Manuel Goenaga, Rafael Gonzalez-Olmos\*, Miguel Iglesias\* and Jose María Resa†

Dpto. de Ingeniería Química, Universidad del País Vasco, Apto. 450, 01006 Vitoria, España

\*Departament d'Enginyeria Química, Escola Tècnica Superior d'Enginyeria Química, Universitat Rovira i Virgili, Avinguda Països Catalans 26, Campus Sescelades, 43007 Tarragona, España

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**Abstract**—In the same way as in other processes, the simulation of the distillation of wine and must is a challenging task due to the lack of thermodynamic information because of scarcity of accurate studies of phase equilibria. Simulation of these processes is rather complicated because of the presence of polar substances (called congeners) at very low concentration. These congeners are essential enological components of the organoleptic matrix, so the availability of accurate studies and quality data is of primary interest. This work studies the phase behaviour of the ternary system ethanol+water+1-pentanol at 101.3 kPa, being the third compound one of the most important legal congeners in common alcoholic distillation. Experimental results showed that this system is partially miscible and exhibits two binary minimum azeotropes. Prediction of activity coefficients and equilibrium compositions with different UNIFAC group contribution models showed poor accurate results. Consistency of experimental data was tested by the McDermott-Ellis method. In addition, available literature was compared and commented upon. The lack of experimental data in multicomponent alcoholic distillation mixtures and the low reliability of the group contribution methods suggest a prudent work into simulation of this kind of distillation processes.

Key words: Phase Equilibria, Prediction, Azeotrope, Ethanol, Water, 1-Pentanol, Thermodynamic Topological Analysis

### INTRODUCTION

In the last few decades, considerable effort has been devoted in the field of thermodynamics and phase equilibria of chemical systems closely related to industrial processes. The Evaluated Process Design Data Project developed by the Design Institute for Physical Properties was focused on making available a useful, critically-evaluated, consistent and complete data compilation of thermodynamic, physical and transport properties of compounds, which are important in design and optimization of unit operations. Despite this, the experimental data collections of phase equilibria for ternary or higher complexity are scarce because the experimental procedure to obtain a complete description of every mixture of industrial interest has a high economical and time cost. In the processing of alcoholic beverages, multicomponent vapor-liquid equilibrium (VLE) data is very important for distillation design and operation. This information is interesting to test and develop new models, correlate and/or predict thermodynamic properties of multicomponent mixtures although only a few attempts have been made oriented towards a better description of complex mixtures in alcoholic distilled beverages [Faundez et al., 2004a, b]. Must distillation results to be an operation with two main characteristics: the liquid is a mixture of substances where some of them are in low concentrations (so-called congeners) [Hikari and Kubo, 1975], different from ethanol and water. These congener compounds are an essential part of the aroma organoleptic matrix in terms of enological values [Lora et al., 1992]. These chemical substances are complex and they may not be forgotten in calcula-

tions. In the open literature, it can be observed that there exist a huge quantity of congeners in different distillation drinks [Fernandez-Garcia et al., 1998; Selli et al., 2003]; however, of all these compounds only few of them are controlled by legislation, meaning that their concentration cannot be higher than that established limit. The conditions in the industrial process are not severe. The operating pressure to produce alcoholic beverages is close to atmospheric and the temperature is approximately between 100-150 °C. Most of the substances involved in this process are highly polar, making theoretical studies and an adequate selection of the thermodynamic options during simulations difficult. These facts make it a challenging task to fit the operational parameters in terms of energy consumption during the distillation process and simultaneously, ensure high quality of final commercial product. For these reasons and as an extension of our earlier works concerning phase equilibria [Tourinho et al., 2003; Resa et al., 2004a], we present in this paper a new phase equilibria data of the ternary mixture ethanol + water+1-pentanol at 101.3 kPa.

The 1-pentanol is one of the legal congeners of the highest composition in alcoholic distillation. Because experimental data are often not available, group contribution methods can be used for the prediction of the required vapor-liquid equilibria. In the past, the group contribution method UNIFAC [Fredenslund et al., 1997] 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 behaviour of systems at other mixing or operation conditions. The application of the UNIFAC group contribution method leads to only qualitative predictions in terms of activity coefficients and compositions for this ternary system. Fitting parameters corre-

†To whom correspondence should be addressed.  
E-mail: iqpredij@vc.ehu.es

sponding to boiling temperatures (Tamir-Wisniak equation) [Tamir and Wisniak, 1978] and activity coefficients (UNIQUAC equation) [Abrams and Prausnitz, 1975], mole fraction dependence is gathered. The experimental results showed that this ternary mixture is partially miscible, exhibits two azeotropes and a slight complex topology in terms of phase equilibria. Consistency of the data was ensured by the McDermott-Ellis method [McDermott and Ellis, 1965]. Available literature was compared and commented upon.

## EXPERIMENTAL SECTION

### 1. Materials

Ethanol (99.5 mol%) was supplied by Panreac and was used without further purification. 1-Pentanol (99.9 mol%) was supplied by Fluka. Water was Millipore quality with organic total mass <5 ppb and resistivity 18.2 MΩcm. The purity of the materials so obtained was checked by gas liquid chromatography and was found to be better than 99.6 mol%. All products were degassed by using ultrasound and dried on molecular sieves (pore diameter of  $3 \times 10^{-10}$  m from Fluka) before use. Densities, refractive indices and normal boiling points of the pure substances were checked and listed in Table 1 and compared with literature values, as well as other relevant information.

### 2. Apparatus and Procedure

The system used to measure VLE data was a dynamic recirculating apparatus described previously [Resa et al., 2004a]. The equilibrium temperature was measured with a digital platinum 100 resistance thermometer with an accuracy of  $\pm 0.1$  K. For the pressure measurement, a digital manometer regulator (Divatronic DT1 model), manufactured by Leybold with an accuracy of  $\pm 0.1$  kPa, was used. Both vapor and liquid phase compositions for the two systems were determined by measurement of physical properties. Densities were measured at 298.15 K by using an Anton Paar DMA 58 vibrating-tube densimeter with an accuracy of  $\pm 0.00001$  gcm<sup>-3</sup> 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  $\pm 0.01$  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  $\pm 0.00001$ , and temperature was controlled like the densimeter. Thermal isolation was ensured in the whole apparatus except for the part corresponding to vapor condenser. Each experiment was continued at least for 1 h after the boiling temperature had become stable. Samples of both liquid and vapor phases were taken at low temperature by a built-in refrigeration device and sealed in ice-cooled graduated test tubes to prevent evaporation leakage. Precautions were taken in order to minimize evap-

oration losses during storage and manipulation of the phase samples. The estimated uncertainty in the determination of both liquid and vapor phase mol fractions is better than 0.001. A more detailed description of the experimental procedure in our laboratory may be collected from earlier works [Resa et al., 2004a].

## RESULTS AND DISCUSSION

### 1. Equilibrium Equation and Activity Coefficients

The values of the experimental density ( $\rho$ ) and refractive index ( $n_D$ ) at 298.15 K for this ternary system as a function of  $x_i$ , have been published previously [Resa et al., 2004b] and were compared with values found in the literature. Such physical properties were applied in order to compute mixing composition by application of the corresponding fitting polynomials. The experimental VLE data are given in Table 2 with values of the activity coefficients ( $\gamma_i$ ) which were computed by Eq. (1):

$$\gamma_i = \phi_i \cdot y_i \cdot P / \{ \phi_i^S \cdot x_i \cdot P_i^S \cdot \exp[v_i^L \cdot (P - P_i^S) / R \cdot T] \} \quad (1)$$

where the liquid molar volume,  $v_i^L$ , was calculated by the Yen and Woods equation [Yen and Woods, 1966] and the fugacity coefficients,  $\phi_i$  and  $\phi_i^S$ , were obtained using a value of the second virial coefficient computed by the Hayden and O'Connell method [Hayden and O'Connell, 1975] to characterize the vapor phase deviation from ideal behaviour.  $P_i^S$  is the vapor pressure which was calculated from the Antoine equation:

$$\log P_i^S = A - \frac{B}{T + C} \quad (2)$$

where A, B and C are fitting parameters. The properties of the pure components required to calculate  $\gamma_i$  are listed in Table 3. Fig. 1 gives the corresponding liquid and vapor experimental compositions for the ternary mixture.

### 2. Temperature Correlation

In order to obtain general parameters of the experimental measured magnitudes, the Tamir-Wisniak [Tamir and Wisniak, 1978] equation was applied to correlate the boiling temperatures, which is expressed as follows:

$$T = \sum_{i=1}^N x_i T_i^0 + \sum_{j=1}^{N-1} \sum_{i=j+1}^N x_i x_j [A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2] + x_1 x_2 x_3 [D_1 + D_2(x_1 - x_2) + D_3(x_1 - x_3) + D_4(x_2 - x_3)] \quad (3)$$

where N is the number of components (N=3),  $T_i^0$  is the boiling temperature of every pure component and  $A_{ij}$ ,  $B_{ij}$ ,  $C_{ij}$  and  $D_{ij}$  are correlation parameters, which are gathered in Table 4. The root mean square deviation computed for temperature (as defined by Eq. (4)) is  $\sigma = 0.67$  K.

**Table 1. Densities  $\rho$ , refractive indices  $n_D$ , and normal boiling temperatures  $T_b$  of the pure components**

Component	MW <sup>a</sup> /kg/kg mol	$\rho$ (298.15 K)/g·cm <sup>-3</sup>		$n_D$ (298.15 K)		$T_b$ /K	
		exptl. <sup>b</sup>	lit. <sup>d</sup>	exptl. <sup>d</sup>	lit. <sup>e</sup>	exptl.	lit. <sup>e</sup>
Ethanol	46.069	0.78589	0.78493	1.35941	1.35941	351.40	351.40
Water	18.015	0.99704	0.99705	1.33250	1.33250	373.15	373.15
1-Pentanol	88.149	0.81096 <sup>c</sup>	0.81080	1.40770 <sup>c</sup>	1.40800	410.59	411.13

<sup>a</sup>Poling et al., 2001. <sup>b</sup>Resa et al., 2004b. <sup>c</sup>Resa et al., 2004a. <sup>d</sup>Riddick et al., 1986

**Table 2. Experimental vapor-liquid equilibrium data: temperature T, liquid phase  $x_i$ , and vapor phase  $y_i$ , mole fraction, activity coefficient  $\gamma_i$  for ethanol (1)+water (2)+1-pentanol (3) at 101.3 kPa, and root mean square deviation from the UNIFAC prediction (into brackets in the last row)**

T/K	$x_1$	$x_2$	$y_1$	$y_2$	$\gamma_1$	$\gamma_2$	$\gamma_3$	T/K	$x_1$	$x_2$	$y_1$	$y_2$	$\gamma_1$	$\gamma_2$	$\gamma_3$
354.8	0.447	0.462	0.604	0.382	1.189	1.643	1.519	362.1	0.134	0.289	0.312	0.627	1.575	3.254	0.723
355.5	0.405	0.499	0.571	0.411	1.210	1.590	1.788	362.7	0.192	0.184	0.416	0.521	1.430	4.151	0.679
356.0	0.368	0.529	0.548	0.431	1.252	1.544	1.929	367.6	0.143	0.106	0.405	0.494	1.578	5.727	0.719
357.4	0.332	0.561	0.508	0.465	1.225	1.488	2.158	394.1	0.043	0.027	0.313	0.294	1.801	5.614	0.766
358.1	0.289	0.601	0.486	0.485	1.308	1.410	2.214	354.0	0.229	0.757	0.603	0.397	0.528	2.276	18.052
358.6	0.259	0.638	0.446	0.519	1.316	1.393	2.812	355.1	0.828	0.025	0.963	0.035	1.011	2.758	0.131
359.4	0.243	0.650	0.409	0.548	1.251	1.400	3.144	354.4	0.817	0.035	0.953	0.047	1.040	2.719	0.030
360.1	0.229	0.664	0.401	0.556	1.269	1.353	3.044	354.7	0.800	0.033	0.951	0.046	1.049	2.789	0.176
358.4	0.245	0.655	0.430	0.533	1.355	1.404	3.056	355.3	0.782	0.032	0.948	0.047	1.046	2.870	0.256
357.6	0.284	0.615	0.473	0.496	1.321	1.437	2.594	355.5	0.766	0.030	0.946	0.048	1.057	3.102	0.277
356.6	0.336	0.566	0.522	0.454	1.281	1.486	2.147	356.1	0.749	0.029	0.944	0.047	1.055	3.069	0.371
355.9	0.382	0.522	0.549	0.429	1.216	1.564	2.054	356.7	0.724	0.028	0.941	0.047	1.065	3.105	0.429
355.1	0.418	0.488	0.589	0.396	1.226	1.595	1.538	387.4	0.120	0.011	0.568	0.112	1.411	6.364	0.859
354.6	0.463	0.446	0.616	0.372	1.178	1.669	1.377	386.8	0.134	0.007	0.623	0.078	1.411	7.100	0.831
354.1	0.507	0.407	0.648	0.343	1.153	1.721	1.055	385.1	0.109	0.036	0.463	0.290	1.355	5.409	0.739
355.2	0.400	0.525	0.573	0.411	1.243	1.532	2.035	353.5	0.751	0.067	0.907	0.092	1.114	2.880	0.057
356.2	0.311	0.628	0.526	0.453	1.413	1.356	3.100	353.6	0.762	0.061	0.916	0.084	1.105	2.862	0.026
356.5	0.289	0.653	0.512	0.466	1.464	1.325	3.500	353.9	0.786	0.053	0.928	0.072	1.073	2.805	0.006
356.8	0.261	0.684	0.507	0.470	1.586	1.262	3.724	353.6	0.805	0.044	0.942	0.058	1.075	2.755	0.021
356.5	0.291	0.653	0.514	0.464	1.459	1.320	3.509	353.4	0.826	0.034	0.953	0.046	0.920	2.454	8.996
355.6	0.352	0.595	0.555	0.429	1.347	1.389	2.806	357.8	0.143	0.823	0.459	0.513	2.529	1.101	6.965
354.1	0.446	0.504	0.624	0.368	1.263	1.494	1.564	357.6	0.144	0.823	0.470	0.503	2.660	1.117	0.266
353.9	0.542	0.363	0.665	0.327	1.116	1.853	0.915	353.4	0.464	0.517	0.611	0.380	1.220	1.544	4.968
354.1	0.559	0.315	0.662	0.327	1.069	2.124	0.859	353.1	0.514	0.468	0.667	0.327	1.216	1.486	3.547
354.1	0.510	0.344	0.671	0.318	1.187	1.891	0.737	353.3	0.482	0.496	0.658	0.341	1.270	1.450	0.479
356.9	0.396	0.234	0.596	0.375	1.223	2.939	0.684	355.9	0.448	0.351	0.582	0.393	1.097	2.131	1.152
387.3	0.139	0.015	0.559	0.114	1.208	4.846	0.905	355.7	0.437	0.341	0.587	0.388	1.142	2.183	1.053
373.2	0.206	0.042	0.648	0.218	1.451	5.200	0.746	355.4	0.459	0.321	0.610	0.369	1.143	2.232	0.906
381.1	0.142	0.026	0.610	0.197	1.543	5.827	0.697	355.1	0.485	0.302	0.628	0.351	1.126	2.283	0.949
358.6	0.247	0.659	0.437	0.527	1.352	1.371	3.097	355.0	0.495	0.291	0.639	0.342	1.127	2.318	0.859
358.0	0.262	0.647	0.464	0.506	1.387	1.370	2.751	354.8	0.505	0.274	0.652	0.330	1.135	2.395	0.796
357.7	0.261	0.664	0.467	0.502	1.416	1.342	3.439	353.8	0.613	0.214	0.715	0.276	1.064	2.669	0.534
357.8	0.244	0.691	0.465	0.505	1.504	1.292	3.836	353.8	0.627	0.203	0.756	0.240	1.100	2.447	0.242
357.9	0.229	0.711	0.460	0.509	1.576	1.260	4.348	353.7	0.634	0.196	0.764	0.233	1.104	2.470	0.182
357.3	0.256	0.685	0.483	0.490	1.517	1.288	3.937	353.6	0.642	0.190	0.772	0.228	1.106	2.493	0.056
357.6	0.329	0.465	0.479	0.480	1.156	1.840	1.681	353.7	0.646	0.184	0.777	0.222	1.102	2.507	0.061
357.9	0.314	0.452	0.476	0.488	1.189	1.900	1.321	366.7	0.441	0.023	0.848	0.081	1.105	4.467	0.735
358.8	0.284	0.422	0.449	0.509	1.199	2.049	1.156	370.2	0.377	0.017	0.818	0.079	1.108	5.195	0.806
360.0	0.209	0.338	0.399	0.554	1.390	2.655	0.792								
360.9	0.167	0.272	0.368	0.578	1.557	3.339	0.692								
363.3	0.136	0.198	0.341	0.602	1.627	4.350	0.555								
363.7	0.085	0.263	0.239	0.701	1.790	3.754	0.593								
											$\sigma(T/K)$	$\sigma(y_1)$	$\sigma(y_2)$	$\sigma(y_3)$	
											UNIFAC	2.67	0.034	0.022	0.042
											UNIFAC-Lyngby	2.47	0.035	0.019	0.041

$$\sigma(M) = \left\{ \sum (M_{exp, i} - M_{cal, i})^2 / ND \right\}^{1/2} \quad (4)$$

In this equation M is a general magnitude (as temperature, vapor phase composition, etc) and ND is the number of experimental data. Fig. 2 shows the equilibrium isotherms on the liquid-phase composition diagram calculated from Eq. (3). The shape of the curves indicates that the system exhibits azeotropic behaviour at two binary compositions as literature suggests.

### 3. VLE Consistency Data

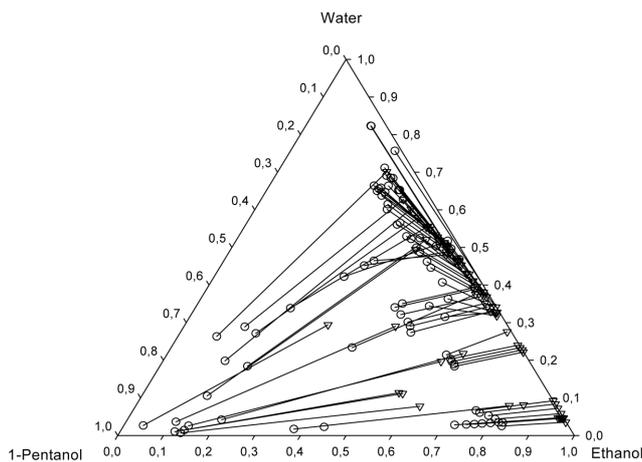
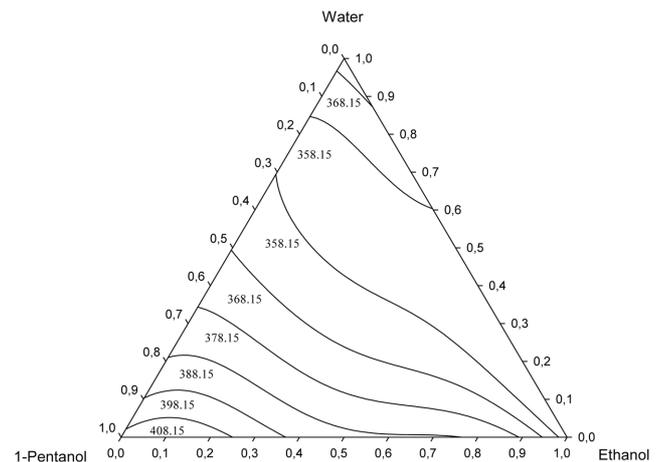
Vapor-liquid equilibrium data is the foundation for a variety of separation procedures, which are essential to the chemical processes. However, phase equilibrium data should be tested in order to assure and guarantee acceptable quality and reliability. Open literature offers different procedures to test the thermodynamic consistency of a set of data for isothermal or isobaric conditions. The thermodynamic consistency of the measured vapor-liquid equilibria data have been tested with the McDermott and Ellis method [McDermott and Ellis, 1965] to reject possible inconsistent equilibrium points

**Table 3. Physical properties of the pure compounds: critical pressure Pc, mean gyration radius of RD, dipole moment  $\mu$ , association parameter ETA, critical temperature Tc, critical compressibility factor Zc and Antoine parameters A, B and C**

Compound	Pc/kPa <sup>a</sup>	RD <sup>a</sup> $\times 10^{10}$ /m	$\mu^a \times 10^{30}$ /(C·m)	ETA <sup>b</sup>	Tc/K <sup>a</sup>	Zc <sup>a</sup>	Antoine constants <sup>c</sup>		
							A	B	C
Ethanol	6383.5	2.259	5.6372	1.40	516.25	0.248	8.11220	1592.864	226.184
Water	2209.0	0.615	6.1709	1.70	647.29	0.233	8.07131	1730.630	233.426
1-Pentanol	4438.0	3.679	1.7 (dbye)	2.20 <sup>d</sup>	585.16	0.260	7.18246	1287.625	161.330

<sup>a</sup>Daubert and Danner, 1986. <sup>b</sup>Prausnitz et al., 1980. <sup>c</sup>Gmehling and Onken, 1999.

<sup>d</sup> is the value of butanol due to the value for the 1-pentanol is not available

**Fig. 1. Composition (mole fractions) diagram for ethanol+water+1-pentanol at 101.3 kPa: (○) liquid phase, (▽) vapor phase.****Fig. 2. Isotherms (temperature in K) for ethanol+water+1-pentanol at 101.3 kPa using Eq. (3) with coefficients from Table 4.****Table 4. Parameters of Tamir-Wisniak and UNIQUAC equations for ethanol+water+1-pentanol at 101.3 kPa**

Parameters of Tamir-Wisniak equation			
A <sub>12</sub> =-37.0826	B <sub>12</sub> =37.8960	C <sub>12</sub> =-97.6551	D <sub>1</sub> =-152.7295
A <sub>13</sub> =-56.6375	B <sub>13</sub> =53.4851	C <sub>13</sub> =-47.9231	D <sub>2</sub> =119.2692
A <sub>23</sub> =-46.0136	B <sub>23</sub> =206.5450	C <sub>23</sub> =-61.5829	D <sub>3</sub> =1.4222
			D <sub>4</sub> =-76.7770
$\sigma=0.67$			
Parameters of UNIQUAC equation $\Delta u_{ij}$ (cal/mol)			
$\Delta u_{12}$ =126.20	$\Delta u_{13}$ =350.73	$\Delta u_{23}$ =173.89	
$\Delta u_{21}$ =193.34	$\Delta u_{31}$ =-92.42	$\Delta u_{32}$ =737.98	
$\sigma$ (T/K)	$\sigma$ (y <sub>1</sub> )	$\sigma$ (y <sub>2</sub> )	$\sigma$ (y <sub>3</sub> )
0.91	0.025	0.013	0.037

from the experimental determined collection. According to this test, two experimental points (a) and (b) are thermodynamically consistent when:

$$D < D_{\max} \quad (5)$$

where D is the local deviation, which is expressed as:

$$D = \sum_{i=1}^{N_{\text{comp}}} [(x_{ia} + x_{ib}) \ln \gamma_{ib} - \ln \gamma_{ia}] \quad (6)$$

where  $x_{ia}$  and  $x_{ib}$  are molar fraction of pure compounds,  $\gamma_{ia}$  and  $\gamma_{ib}$  are activity coefficients of pure compounds.

$D_{\max}$  is the maximum deviation. McDermott and Ellis proposed a value of 0.01 for  $D_{\max}$  if the uncertainty in the mole fraction of the liquid and vapor compositions is between  $\pm 0.001$ , as in this case but the maximum local deviation is not a constant, and Wisniak and Tamir [1977] propose the following expression for this magnitude:

$$D_{\max} = \sum_{i=1}^{N_{\text{comp}}} (x_{ia} + x_{ib}) \left( \frac{1}{x_{ia}} + \frac{1}{x_{ib}} + \frac{1}{y_{ia}} + \frac{1}{y_{ib}} \right) \Delta x + 2 \sum_{i=1}^{N_{\text{comp}}} |\ln \gamma_{ib} - \ln \gamma_{ia}| \Delta x + \sum_{i=1}^{N_{\text{comp}}} (x_{ia} + x_{ib}) \frac{\Delta P}{P} + \sum_{i=1}^{N_{\text{comp}}} (x_{ia} + x_{ib}) B_i \left( \frac{1}{(t_a + C_i)^2} + \frac{1}{(t_b + C_i)^2} \right) \Delta t \quad (7)$$

In Eq. (7),  $B_i$  and  $C_i$  are the Antoine constants and  $\Delta x$ ,  $\Delta P$ , and  $\Delta t$  are the experimental uncertainties of mole fraction, pressure and temperature ( $7.0 \times 10^{-3}$ , 0.098 kPa and  $10^{-2}$  °C of the used devices), respectively, and  $x_{ia}$  and  $x_{ib}$  are molar fraction of pure compounds,  $\gamma_{ia}$  and  $\gamma_{ib}$  are activity coefficients of pure compounds. The experimental data gathered in this work show thermodynamic consistency attending to the McDermott-Ellis test with the  $D_{\max}$  Wisniak-Tamir criteria.

#### 4. Activity Coefficients Correlation

The activity coefficients play a key role, overall in non-ideal mixtures, in vapor-liquid equilibria calculations. For strongly non-ideal mixtures, as solutions of alcohols, water, etc, the UNIQUAC equation is suitable to represent the data successfully. This equation offers three advantages: it has only two fitting parameters for each pair of compounds, a weaker dependence on temperature for such param-

eters, and surface fraction as a primary concentration variable. This equation is applicable to a wide range of mixtures with small or large molecules and to both vapor-liquid or liquid-liquid equilibria. The description of this model is widely presented in the open literature [Abrams and Prausnitz, 1975; Poiling et al., 2001] and hence it is not discussed here. The fitting parameters of this model and deviations are gathered in Table 4.

### 5. VLE Prediction Model

Prediction of vapor-liquid equilibria for the ternary system ethanol+water+1-pentanol at 101.3 kPa has been carried out by the UNIFAC group contribution method [Fredenslund et al., 1977; Larsen et al., 1987]. The group interaction parameters applied were those available in open literature. The results are compared with the experimental values, and the root mean square deviations for the temperature  $\sigma(T)$  and the composition of the vapor phase  $\sigma(y_i)$  are shown in the last rows of the Table 2. A qualitative description was obtained with the UNIFAC method due to the partially heterogeneous character of the mixture (around water+1-pentanol mixture) and the dislike structure of the molecules enclosed.

### 6. Thermodynamic Topological Analysis

Many chemical processes involve one or more distillation processes and food technology is not an exception. These distillation operations can be quite complex, involving immiscible phases, multicomponent systems, azeotropes and many other complicated features. During the past decade, a powerful tool for understanding such distillation systems or, as in this case, the description of complex mixtures related to alcoholic distillation industries, the *Thermodynamic Topological Analysis* (TTA) has been increasingly applied to solving industrial problems. It provides an efficient way for a preliminary analysis and ensures consistency of VLE data in terms of distillation regions and thermodynamic boundaries [Matsuyama and Nishimura, 1977; Foucher et al., 1991]. The TTA is based on the classical works of Schreinemakers and Ostwald [Widagdo and Seider, 1996], where the relationship between the phase equilibrium of a mixture and the trend in open evaporation residue curves for mixtures was established. Although open evaporation with no reflux itself is not of industrial interest, it nevertheless conceptually forms an important tool for understanding distillation operation (a continuum of steps of partial vaporization with reflux). The reason for this renewed interest was the realization that, in spite of the advances in phase equilibrium calculations and simulations, until now, there has been a need for simpler tools to understand the limitations and possibilities in complex distillation, graphical VLE consistency and a previous characterization of natural liquid mixtures to be distilled. The classification of ternary vapor-liquid equilibrium (VLE) diagrams is a key to simple distillation processes and analysis of complex mixtures. All ternary mixtures reported so far to be occurring in nature can be qualitatively represented by a combination of topology characteristics. This greatly reduces the number of VLE diagram structures that need to be analyzed in order to reveal the qualitative characteristics of any mixture. From a practical point of view, the TTA tool is a graphical representation of phase equilibrium information, which helps for understanding similarities and differences among mixtures. Two types of figures are used, residual curve maps and relative volatility maps. A residual curve map is a diagram showing all of the azeotropic information of the constituent pairs and the residual curves of the mixture. A residual curve

could be determined experimentally or mathematically simulating the experiment procedure by means an adequate thermodynamic model. For the azeotropic or extractive distillation, the azeotropic temperature and composition are the information needed for the process design. In a specific residual curve map, the azeotropic information is used to draw the distillation boundaries dividing the map into several distillation regions that any distillation operation cannot cross at usual conditions [Widagdo and Seider, 1996]. Relative volatility maps are a tool of actual relevance due to provide key information for distillation in terms of equivocality. The study of volatility in mixtures leads to analysis of the influence of a new solvent into mixture in what is referred to the phase transference and the interactions among compounds. Its use was studied earlier for different applications as breaking azeotropes and design of distillation units [Laroche et al., 1991]. These tools (residue curve/relative volatility maps) are included in the main recent publications in chemical engineering, as important elements for distillation design and mixing understanding. It allows one to determine the thermodynamic limits and boundaries of the separation attending to the nature and behaviour of the mixture, as well as a rapid screening of thermodynamic nature in terms of phase equilibrium. Figs. 3 and 4 are the relative volatility and residual curve map of this ternary mixture, respectively. As can be observed, the equivocality line is shown by a collection of points attaching the binary azeotrope in ethanol+water mixture and a locus into the binary water+1-pentanol. From this line, two regions are defined, one where the water pure compound is enclosed in which low volatility values are observed and other region enclosing ethanol and 1-pentanol pure corners with high values of volatility. Attending to the residual curve map, it is clear the strong tendency under distillation, to lose light compounds and raise the water composition of the residual liquid into boiler, as well as the special trend of must and alcoholic mixtures during this process due to the distillation oriented lines (Fig. 4) and partial heterogeneous behaviour at low concentrations of 1-pentanol and ethanol.

### 7. Previously Published Data of the Ternary Mixture

In the open literature only one publication [Fernandez et al., 2001] can be found related to the ternary mixture that was experimentally studied. In Fig. 5, a comparison of the boiling temperature devia-

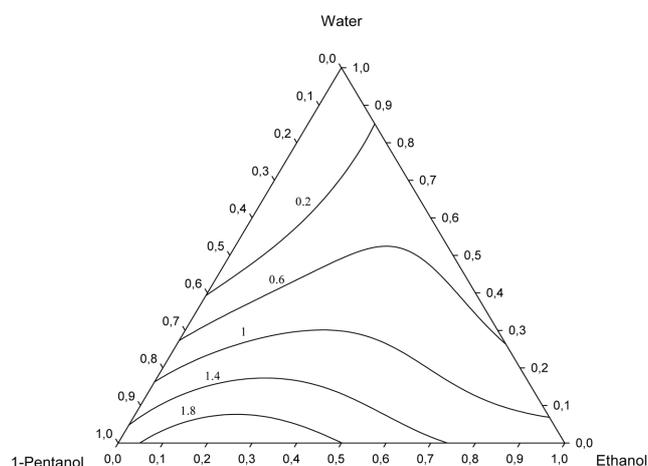


Fig. 3. Isolines of relative volatility (adimensional) for ethanol+water+1-pentanol at 101.3 kPa derived from the experimental data.

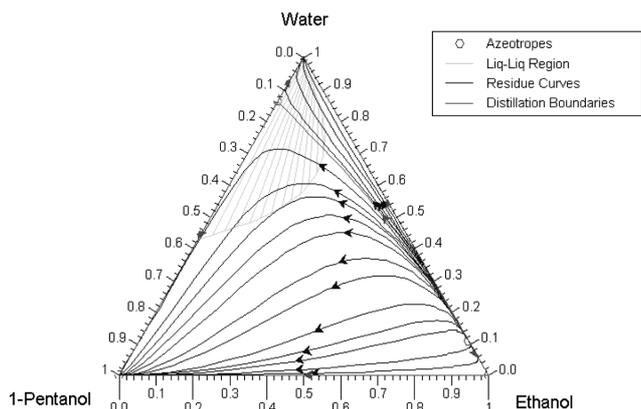


Fig. 4. Residual curve map for ethanol+water+1-pentanol at 101.3 kPa by UNIFAC method.

tions corresponding to literature data points from the experimental data correlation obtained in this paper are shown. In the figure, the experimental data of Fernandez et al., 2001 are indicated using as abscise an arbitrary parameter ( $z$ ) which expresses the product of total molar fractions in mixture. In a simple way, we could describe this figure as an easy and clear procedure to locate trends or zones in the composition diagram where high or low deviations exist from a set of experimental data. Low values of  $z$  refer to those compositions in the Gibbs triangle which are close to binary axis, while high values in this parameter are related to approximately multicomponent equimolar compositions. In general terms, a high difference is observed among our experimental data and those reported in that work in those compositions of rich 1-pentanol (an average deviation

of 2%, but for rich 1-pentanol compositions, the deviation is greater, around 6-8 K, where the experimental points are of the highest boiling temperatures) (see Fig. 5). The composition coverage of this work is adequate but an important quantity of the experimental data shows important deviations in terms of temperature. Attending to the literature until now, it is clear that poor results in simulation or calculation could be obtained from the data indicated above.

## CONCLUSIONS

In this study, the phase equilibrium behaviour of the ethanol+water +1-pentanol ternary mixture was experimentally investigated in order to characterize the interactions of one of the most important congener (1-pentanol) into distilled alcoholic mixtures. The experimental results showed that this ternary mixture is partially miscible at low ethanol composition and exhibits two binary azeotropes (homogeneous ethanol+water, homogeneous 1-pentanol+water). All of them show minimum temperature trend, in accordance with literature. In terms of the Thermodynamic Topological Analysis, each binary azeotrope shows a saddle trend, which reveals the complex molecular interactions in this mixture (120 topological characters [Matsuyama and Nishimura, 1977]). The ternary vapor-liquid equilibrium has been modelled by using a correlating equation (UNIQUAC) and a predictive procedure (UNIFAC). Based on the results, the following conclusions can be drawn: (i) the UNIQUAC model represents an adequate way for fitting vapor-liquid equilibrium data of this kind of ternary mixtures, despite nonideality and partial miscibility; (ii) group contribution model UNIFAC model can be used for modelling work and for studies of mixtures containing this ternary system in which no-experimental data are available, but taking

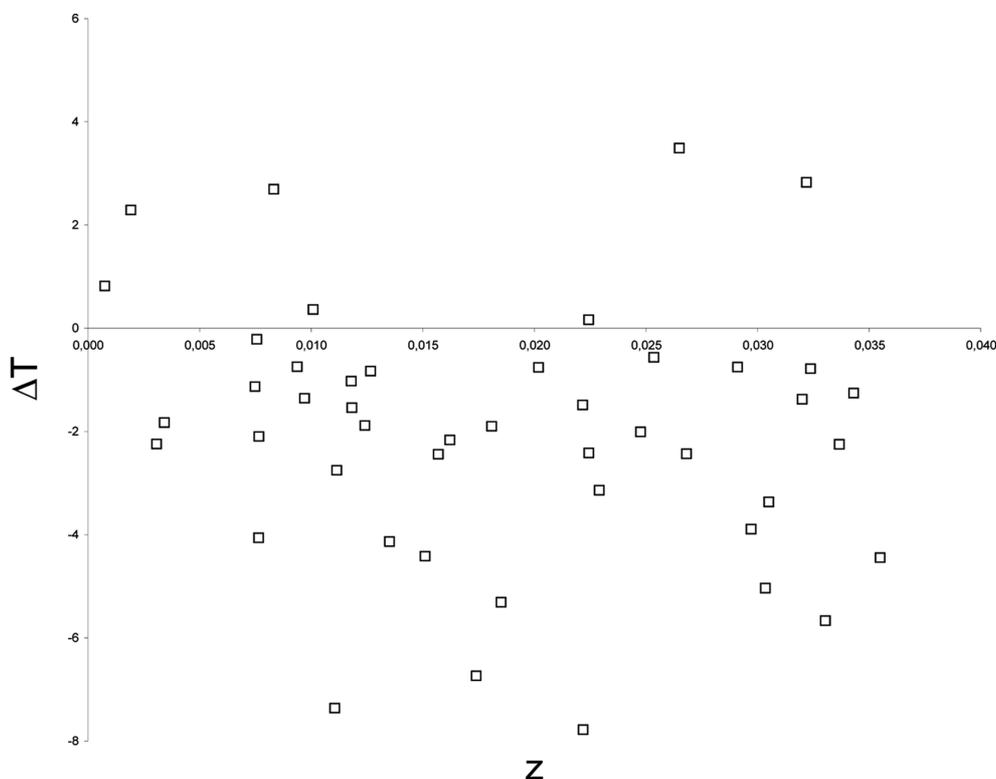


Fig. 5. Comparison of the experimental and literature data (□ [Fernandez et al., 2001]) for ethanol+water+1-pentanol at 101.3 kPa.

into account that an inaccurate thermodynamic description may be done if simulation of distillation processes is made and trace compounds are concerned; (iii) the study done here represents a new experimental contribution to complete the thermodynamic data base for characterizing alcoholic mixtures contained in distilled beverages, which means an improvement of the existing open literature for the ternary ethanol+water+1-pentanol, (iv) Thermodynamic Topological Analysis means a powerful tool for understanding distillation systems and analyzing the distillation path, boundaries and dynamic in beverage distillation processes and (v) the lack of experimental data in multicomponent alcoholic distillation mixtures and the qualitative reliability of the group contribution methods suggest a wider study of mixtures and a prudent utilization of the prediction results into simulations.

### NOMENCLATURE

$\phi_i$  : fugacity coefficients  
 $T_i^0$  : boiling temperature of every pure component  
 $\phi_i^s$  : saturation fugacity coefficients  
 $\sigma$  : root mean square deviation  
 $\Delta x$ ,  $\Delta P$ , and  $\Delta t$  : experimental uncertainties of mole fraction, pressure and temperature, respectively  
 $A_{ij}$ ,  $B_{ij}$ ,  $C_{ij}$  and  $D_{ij}$  : correlation parameters  
 $B_i$  and  $C_i$  : Antoine constants  
 $D$  : local deviation  
 $D_{\max}$  : maximum deviation  
 $N$  : number of components  
 $\gamma_i$  : activity coefficients  
 $P_i^s$  : vapor pressure  
 $v_i^L$  : liquid molar volume

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