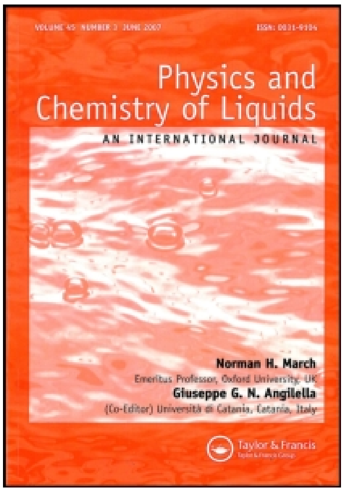

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Isobaric phase equilibrium of the ternary mixture ethanol + water + 2-propanol

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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. This work studies the phase behavior of the ternary system, ethanol + water + 2-propanol at 101.3 kPa being the third compound one of the most important legal congener in common alcoholic distillation. Experimental results showed that this system 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, disposable 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 alcoholic distillation.

Keywords: Prediction; Azeotrope; Ethanol; Water; 2-Propanol; Thermodynamic topological analysis

1. Introduction

In the last few decades, considerable efforts have been developed in the field of thermodynamics and phase equilibria of chemical systems closely related to industrial processes. 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

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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 the 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.* [1,2]. 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 [3]), different of ethanol and water.

These congener compounds are an essential part of the aroma organoleptic matrix in terms of enological values [4]. These chemical substances are complex and they may not be forgotten in calculations. In open literature, it can be observed that there exists a huge quantity of congeners in different distillation drinks [5,6], 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 the atmospheric and the temperature is between 100–150°C approximately. Most of the substances involved in this process are highly polar, making theoretical studies and an adequate selection of the thermodynamic options difficult during simulations. These facts make 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 [7–9], we present in this article a new phase equilibria data of the ternary mixture ethanol + water + 2-propanol at 101.3 kPa. The 2-propanol is one of the legal congener of the highest composition in alcoholic distillation. Because the experimental data are often not available, group contribution methods can be used for the prediction of the required VLE. In the past, the group contribution method UNIFAC [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. 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 corresponding to boiling temperatures (Tamir–Wisniak equation) Tamir and Wisniak, [11] and activity coefficients (UNIQUAC equation) [12], mole fraction dependence are gathered. The experimental results showed that this ternary mixture exhibits two azeotropes and a slight complex topology in terms of phase equilibria. Consistency of the data was ensured by the McDermott–Ellis method [13]. Disposable literature was compared and commented upon.

2. Materials and methods

Ethanol (99.5 mol%) was supplied by Merck and was used without further purification. 2-Propanol (99.9 mol%) was supplied by Merck. Water was Millipore quality with organic total mass <5 ppb and resistivity 18.2 MΩ cm. The purity of the materials

Table 1. Densities ρ, speed of sound u, and normal boiling temperatures T_b of the pure components.

		ρ (298.15 K) (g cm^{-3})		u (298.15 K) (m s^{-1})		T_b (K)	
Component	MW[a] (kg (kg^{-1} mol^{-1}))	Exptl.	Lit[b].	Exptl.	Lit.[c]	Exptl.	Lit.[a]
Ethanol	46.069	0.78589	0.78493	1143.12	1143.1	351.40	351.40
Water	18.015	0.99704	0.99705	1496.89	1196.9	373.15	373.15
2-Propanol	60.096	0.78093	0.78126	1139.96	1140.1[d]	355.38	355.39

[a]Poling *et al.* [23]; [b]Riddick *et al.* [24]; [c]Resa *et al.* [25]; [d]Savaroglu *et al.* [26].

so obtained was checked by gas–liquid chromatography and was found to be better than 99.6 mol%. All products were degassed using ultrasound and dried on molecular sieves (pore diameter of 3×10^{-10} m from Fluka) before use. Densities, speeds of sound, 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.

The system used to measure VLE data was a dynamic recirculating apparatus described previously [7]. The equilibrium temperature was measured with a digital platinum 100 resistance thermometer with an accuracy of ±0.1 K. For the pressure measurement, a digital manometer regulator (Divatronic DT1 model), manufactured by Leybold with an accuracy of ±0.1 kPa, was used. Both vapor and liquid phase compositions for the two systems were determined by measurement of physical properties. Densities and speeds of sound were measured simultaneously at 298.15 K by using an Anton Paar DSA 5000 vibrating tube densimeter with an accuracy of ±0.000001 g cm^{-3} for the density and with an accuracy of ±0.01 for the speed of sound. The DSA 5000 had been calibrated at atmospheric pressure with twice-distilled water and dry air. The temperature of the DSA 5000 was maintained at 298.15 K with a precision of ±0.001 K by means of a semiconductor Peltier element and measured by a calibrated platinum-resistance thermometer. 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 evaporation 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 [7].

3. Theory and calculation

3.1. *Equilibrium equation and activity coefficients*

The values of the experimental density (ρ) and refractive index (n_D) at 298.15 K for this ternary system as a function of x_i have been published previously [14] 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 (γ_i) which were computed by equation 1:

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

where the liquid molar volume, v_i^{L}, was calculated by the Yen and Woods equation [15] and the fugacity coefficients, ϕ_i and ϕ_i^{S}, were obtained using a value of the second virial coefficient computed by the Hayden and O'Connell method [16], to characterize the vapor phase deviation from ideal behavior. P_i^{S} is the vapor pressure which was calculated from the Antoine equation:

$$\log P_i^{\mathrm{S}} = A - \frac{B}{T + C} \tag{2}$$

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

3.2. *Temperature correlation*

In order to obtain general parameters of the experimental measured magnitudes, the Tamir–Wisniak, [11] equation was applied to correlate the boiling temperatures, which is expressed as follows:

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

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 equation 4) is $\sigma = 0.67\,\mathrm{K}$.

$$\sigma(M) = \left\{\frac{\sum \left(M_{\mathrm{exptl}} - M_{\mathrm{Calcd}}\right)^2}{\mathrm{ND}}\right\}^{1/2} \tag{4}$$

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

3.3. *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

Table 2. Experimental VLE data.

T (K)	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
351.1	0.827	0.031	0.847	0.029	1.012	2.163	1.013
351.2	0.786	0.062	0.799	0.061	1.001	2.265	1.064
351.2	0.752	0.077	0.771	0.075	1.009	2.242	1.040
351.3	0.765	0.074	0.777	0.076	0.996	2.354	1.050
351.4	0.759	0.074	0.768	0.073	0.988	2.252	1.091
351.5	0.748	0.074	0.750	0.072	0.975	2.212	1.141
351.8	0.751	0.034	0.763	0.032	0.977	2.115	1.074
352.0	0.676	0.033	0.705	0.031	0.994	2.093	1.014
351.8	0.748	0.019	0.771	0.018	0.991	2.129	1.020
351.9	0.714	0.028	0.751	0.025	1.007	1.998	0.974
352.0	0.623	0.032	0.724	0.026	1.108	1.810	0.810
351.8	0.657	0.079	0.682	0.071	0.998	2.019	1.054
351.7	0.665	0.115	0.709	0.107	1.029	2.098	0.946
351.3	0.449	0.217	0.513	0.206	1.120	2.175	0.968
351.7	0.440	0.200	0.484	0.196	1.062	2.209	1.006
352.6	0.038	0.213	0.057	0.207	1.397	2.113	1.071
352.8	0.031	0.157	0.047	0.207	1.401	2.844	0.994
352.8	0.019	0.174	0.365	0.180	17.752	2.230	0.610
353.0	0.181	0.628	0.309	0.383	1.565	1.302	1.731
353.1	0.153	0.659	0.306	0.388	1.826	1.252	1.740
353.6	0.035	0.734	0.224	0.413	5.732	1.172	1.647
353.6	0.029	0.730	0.231	0.401	7.134	1.145	1.600
354.0	0.043	0.717	0.228	0.396	4.674	1.132	1.615
353.9	0.037	0.722	0.230	0.396	5.501	1.129	1.606
353.9	0.046	0.709	0.214	0.396	4.117	1.150	1.647
353.8	0.118	0.667	0.276	0.386	2.079	1.196	1.634
353.7	0.145	0.656	0.292	0.384	1.797	1.215	1.699
353.1	0.283	0.562	0.404	0.351	1.304	1.328	1.690
352.9	0.315	0.538	0.421	0.351	1.230	1.399	1.672
353.0	0.337	0.521	0.429	0.347	1.167	1.422	1.693
352.8	0.369	0.505	0.454	0.340	1.137	1.450	1.770
352.8	0.407	0.462	0.468	0.327	1.063	1.524	1.694
352.7	0.438	0.448	0.501	0.321	1.061	1.549	1.697
352.6	0.456	0.428	0.530	0.311	1.083	1.577	1.496
352.5	0.439	0.423	0.520	0.308	1.108	1.587	1.366
352.2	0.648	0.334	0.709	0.261	1.035	1.724	1.849
352.4	0.449	0.391	0.521	0.294	1.089	1.646	1.272
352.8	0.335	0.304	0.378	0.274	1.043	1.942	1.043
352.8	0.340	0.279	0.340	0.268	0.924	2.070	1.113
352.8	0.358	0.239	0.401	0.239	1.035	2.155	0.967
352.7	0.334	0.224	0.368	0.233	1.022	2.251	0.981
352.7	0.309	0.268	0.317	0.264	0.952	2.131	1.076
353.0	0.693	0.164	0.723	0.182	0.956	2.371	0.713
353.3	0.005	0.168	0.007	0.209	1.268	2.628	1.004
353.6	0.003	0.147	0.006	0.193	1.791	2.741	0.986
353.3	0.040	0.122	0.042	0.159	0.951	2.755	1.010
352.9	0.079	0.112	0.083	0.146	0.967	2.801	1.027
352.6	0.057	0.136	0.063	0.170	1.029	2.719	1.036
352.4	0.348	0.088	0.430	0.101	1.160	2.516	0.914
352.4	0.452	0.077	0.515	0.089	1.069	2.534	0.924
352.3	0.380	0.081	0.495	0.096	1.227	2.608	0.838
352.4	0.248	0.113	0.550	0.108	2.082	2.094	0.588
352.4	0.486	0.091	0.588	0.099	1.136	2.384	0.813
352.3	0.231	0.124	0.655	0.111	2.672	1.969	0.400
352.3	0.527	0.095	0.588	0.108	1.051	2.501	0.888
352.1	0.208	0.142	0.740	0.113	0.460	1.762	1.342
353.5	0.073	0.457	0.101	0.366	1.245	1.678	1.194
353.3	0.073	0.325	0.093	0.315	1.155	2.048	1.044

(*Continued*)

Table 2. Continued.

T (K)	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
353.0	0.160	0.293	0.182	0.286	1.044	2.088	1.045
353.0	0.118	0.294	0.142	0.293	1.104	2.132	1.032
352.9	0.117	0.291	0.152	0.285	1.197	2.104	1.026
351.9	0.840	0.025	0.843	0.031	1.050	2.778	1.026
351.9	0.845	0.020	0.855	0.021	1.145	2.352	0.960
351.9	0.857	0.018	0.863	0.023	1.132	2.862	0.965
352.0	0.352	0.277	0.406	0.248	1.101	1.994	1.043
351.9	0.405	0.304	0.425	0.269	1.005	1.979	1.181
352.4	0.431	0.409	0.479	0.319	1.601	1.708	0.717
353.3	0.382	0.553	0.531	0.369	2.722	1.409	0.393
352.6	0.413	0.545	0.623	0.355	2.767	1.415	0.638
355.2	0.191	0.808	0.508	0.442	2.243	1.070	49.234
356.1	0.159	0.816	0.472	0.470	2.418	1.087	2.205
	σ (T (K))	σ (y_1)		σ (y_2)		σ (y_3)	
UNIFAC	0.69	0.107		0.024		0.093	
UNIFAC-Lyngby	0.62	0.107		0.023		0.092	

Notes: Temperature, T; liquid phase, x_i; and vapor phase, y_i; mole fraction; activity coefficient, γ_i; for ethanol (1) + water (2) + 2-propanol (3) at 101.3 kPa, and root mean square deviation from the UNIFAC prediction (into brackets in the last row).

Table 3. Physical properties of the pure compounds.

							Antoine constants[c]		
Compound	P_c (kPa^{-1})[a]	RD[a] $\times 10^{10}$ (m)	μ[a] $\times 10^{30}$ (C m)	ETA[b]	T_c (K^{-1})[a]	Z_c[a]	A	B	C
Ethanol	6383.5	2.250	5.6372	1.40	516.26	0.248	8.11220	1592.864	226.184
Water	2209.0	0.615	6.1709	1.70	647.37	0.229	8.07131	1730.630	233.426
2-Propanol	4764.3	2.807	5.5372	1.32	508.31	0.248	7.74128[d]	1360.131[d]	197.592[d]

Notes: [a]Daubert *et al.* [27]; [b]Prausnitz *et al.* [28]; [c]Gmehling and Onken [29]; [d]Riddick *et al.* [24]; Critical pressure P_c Mean gyration radius of RD; dipole moment, μ; association parameter, ETA; critical temperature, T_c; critical compressibility factor, Z_c; and antoine parameters, A, B and C.

be tested in order to assure and guarantee an acceptable quality and reliability. Open literature offers different procedures to test the thermodynamic consistency of a set of data for isothermal or isobaric condition. The thermodynamic consistency of the measured vapor–liquid equilibria data have been tested with the McDermott and Ellis method [13] to reject possible inconsistent equilibrium points from the experimental determined collection. According to this test, two experimental points (a) and (b) are thermodynamically consistent when:

$$D < D_{\max} \tag{5}$$

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

$$D = \sum_{i=1}^{N\mathrm{comp}} \left[(x_{ia} + x_{ib}) \cdot (\ln \gamma_{ib} - \ln \gamma_{ia}) \right] \tag{6}$$

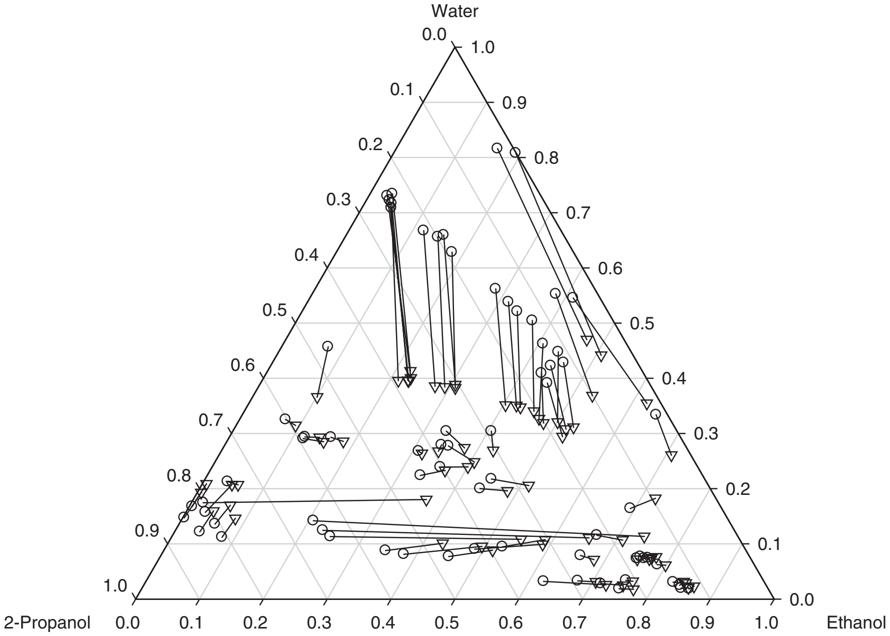

Figure 1. Composition (mole fractions) diagram for ethanol + water + 2-propanol at 101.3 kPa: (○) liquid phase, (∇) vapor phase.

Table 4. Parameters of Tamir–Wisniak and UNIQUAC equations for ethanol + water + 2-propanol at 101.3 kPa.

Parameters of Tamir–Wisniak equation			
$A_{12}=-41.6096$	$B_{12}=47.6424$	$C_{12}=-41.7206$	$D_1=55.8141$
$A_{13}=0.7363$	$B_{13}=-1.8661$	$C_{13}=-3.9514$	$D_2=-139.2902$
$A_{23}=-43.4186$	$B_{23}=-41.9683$	$C_{23}=-49.3854$	$D_3=28.7309$
			$D_4=130.9042$
$\sigma=0.33$			
Parameters of UNIQUAC equation Δu_{ij} ($J\,\mathrm{mol}^{-1}$)			
$\Delta u_{12}=84.255$	$\Delta u_{13}=76.476$	$\Delta u_{23}=232.351$	
$\Delta u_{21}=551.448$	$\Delta u_{31}=229.717$	$\Delta u_{32}=276.032$	
σ (T (K))	σ (y_1)	σ (y_2)	σ (y_3)
1.34	0.097	0.029	0.090

and $D_{\max}$ 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 are between ±0.001, as in this case, but the maximum local deviation is not a constant, and Wisniak and Tamir [17] proposed the following expression for this magnitude:

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

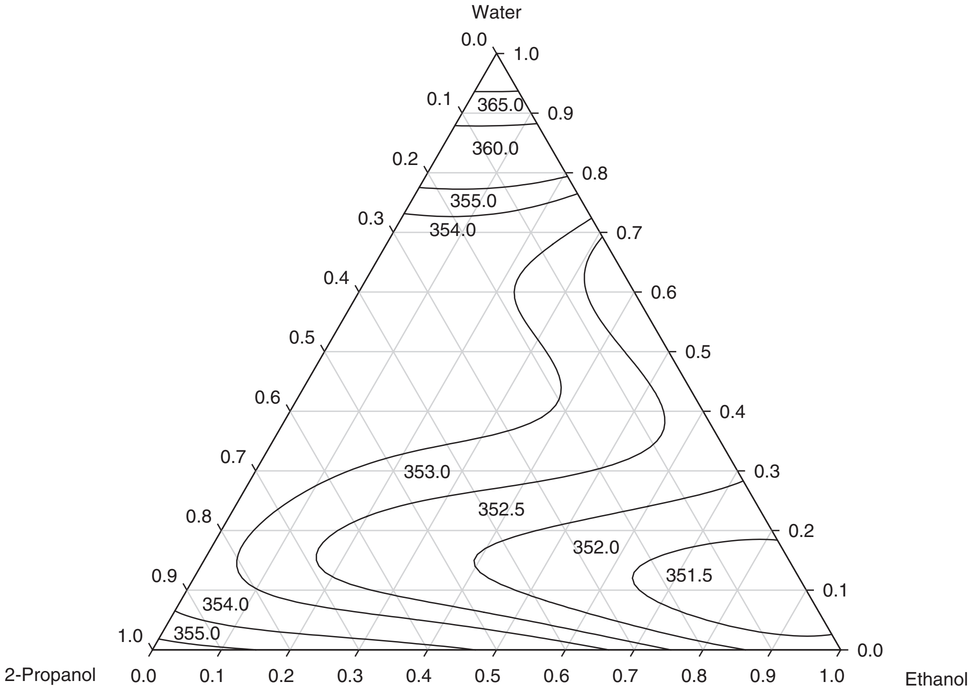

Figure 2. Isotherms (temperature in K) for ethanol + water + 2-propanol at 101.3 kPa using equation 3 with coefficients from table 4.

In the equation 7, B_i and C_i are the Antoine constants and Δx, ΔP, and Δt are the experimental uncertainties of mole fraction, pressure and temperature (7.0×10^{-3}, 0.098 kPa and 10^{-2}°C of the used devices), respectively. The experimental data gathered in this work show thermodynamic consistency attending to the McDermott–Ellis test with the $D_{\max}$ Wisniak–Tamir criteria.

3.4. *Activity coefficients correlation*

The activity coefficients play a key role, overall in nonideal mixtures, in VLE calculations. For strongly nonideal 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 parameters, 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 [12], and hence it is not discussed here. The fitting parameters of this model and deviations are gathered into table 4.

3.5. *VLE prediction model*

Prediction of VLE for the ternary system ethanol + water + 2-propanol at 101.3 kPa has been carried out by the UNIFAC group contribution method [10,18]. The group interaction parameters applied, were those disposable into 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 high polarity and dislike structure of the molecules enclosed.

3.6. *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 complicating 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 [19,20]. The TTA is based on the classical works of Schreinemakers and Ostwald, [21], 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 was 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 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. 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. 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, [21]. Figure 3 is the residual curve map of this ternary mixture. It is clear the strong tendence under distillation, to loose light compounds and rise the water

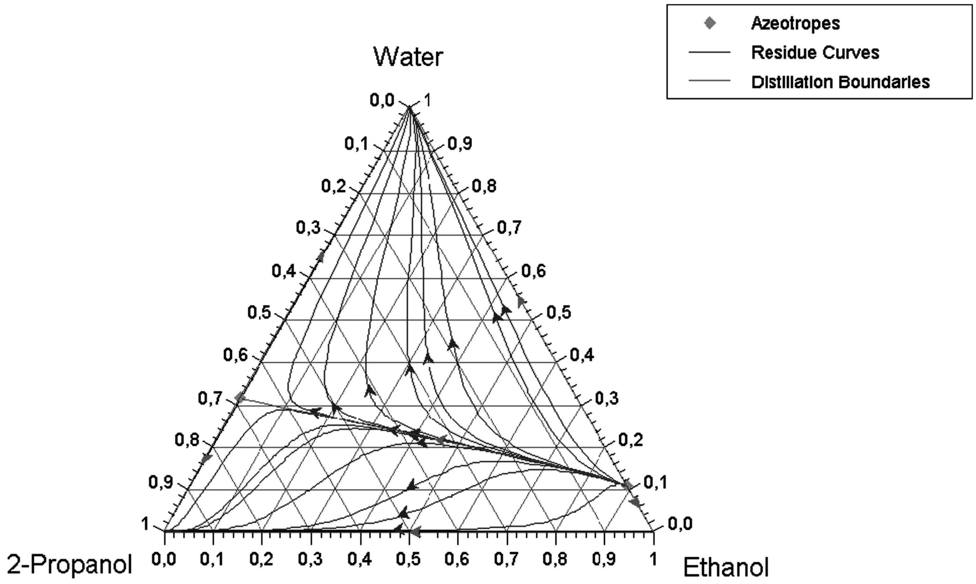

Figure 3. Residual curve map for ethanol + water + 2-propanol at 101.3 kPa by UNIFAC method.

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.

3.7. *Previously published data of the ternary mixture*

In open literature it may be found only one publication that [22] relates to the ternary mixture was experimentally studied. In figure 4, a comparison of the boiling temperature deviations corresponding to literature data points from the experimental data correlation obtained in this article are shown. In the figure, the experimental data of these authors 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 the work in those compositions of rich 2-propanol (an average deviation of 2%, but for rich 2-propanol compositions, the deviation is greater, around 6–8 K, where the experimental points are of the highest boiling temperatures) (figure 4). The composition coverage of this work is adequated, but an important quantity of the experimental data show important deviations in terms of temperature. Attending to the disposable literature until now, it is clear that poor results in simulation or calculation could be obtained from the data indicated above.

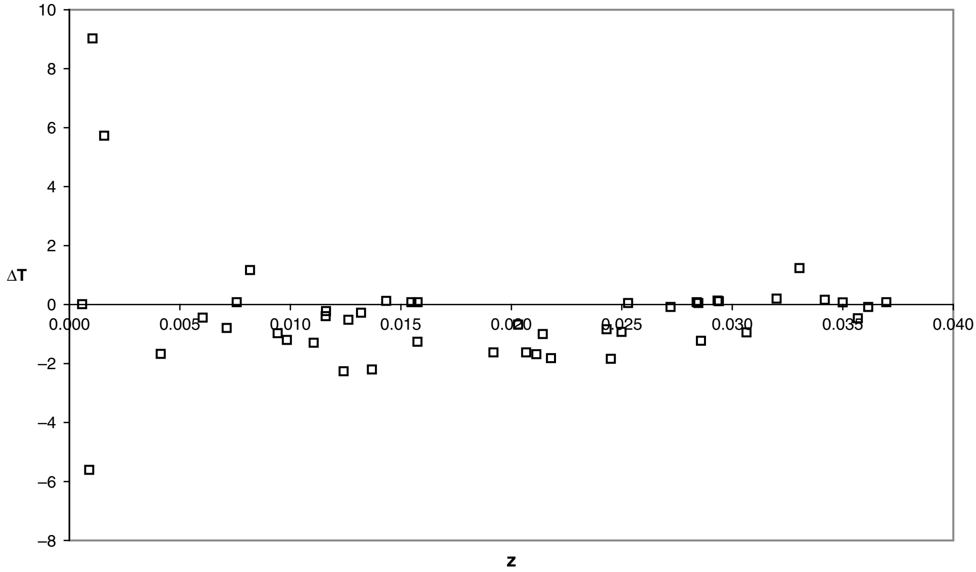

Figure 4. Comparison of the experimental and literature data (□ [Fernandez-Garcia *et al.* 1998]) for ethanol + water + 2-propanol at 101.3 kPa.

4. Conclusions

In this study, the phase equilibrium behavior of the ethanol + water + 2-propanol ternary mixture was experimentally investigated in order to characterize the interactions of one of the most important congener (2-propanol) into distillated alcoholic mixtures. The experimental results showed that this ternary mixture exhibits two binary azeotropes (homogeneous ethanol + water, homogeneous 2-propanol + water). All of them show minimum temperature trend, in accordance with literature. In terms of the TTA, each binary azeotrope shows a trend of saddle, which reveals the complex molecular interactions in this mixture (120 topological character [20]). The ternary VLE has been modeled 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 parcial miscibility; (ii) group contribution UNIFAC model can be used for modeling work and for studies of mixtures containing this ternary system in which no experimental data are available, but taking into account that 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 database for characterizng alcoholic mixtures contained in distillated beverages, which means an improvement of the existing open literature for the ternary ethanol + water + 2-propanol, (iv) TTA means a powerful tool for understanding distillation systems and analyze 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.

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