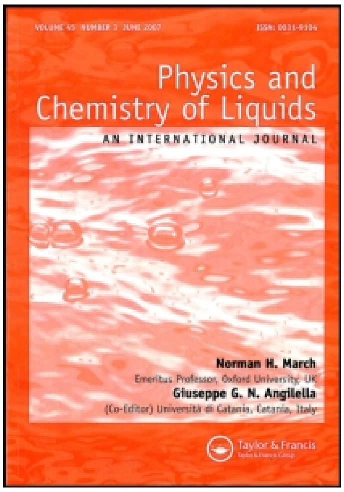
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Phase behaviour of ethanol + water + ethyl acetate at 101.3 kPa

Miguel Iglesias[a]; Rafael Gonzalez-Olmos[a]; Jose Manuel Goenaga[b]; Jose Maria Resa[b]
[a] PF&PT Research Team, Department of Chemical Engineering, School of Engineering, University of Santiago de Compostela, E-15782 Santiago de Compostela, España [b] Departamento de Ingeniería Química, Universidad del País Vasco, 01006 Vitoria, España

Online publication date: 14 July 2010

To cite this Article Iglesias, Miguel , Gonzalez-Olmos, Rafael , Manuel Goenaga, Jose and Resa, Jose Maria(2010) 'Phase behaviour of ethanol + water + ethyl acetate at 101.3 kPa', Physics and Chemistry of Liquids, 48: 4, 461 — 476
To link to this Article: DOI: 10.1080/00319100903096539
URL: http://dx.doi.org/10.1080/00319100903096539

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Physics and Chemistry of Liquids
Vol. 48, No. 4, August 2010, 461–476

Phase behaviour of ethanol + water + ethyl acetate at 101.3 kPa

Miguel Iglesias[a]*, Rafael Gonzalez-Olmos[a], Jose Manuel Goenaga[b]
and Jose Maria Resa[b]

[a]*PF&PT Research Team, Department of Chemical Engineering, School of Engineering, University of Santiago de Compostela, Rúa Lope Gómez de Marzoa, E-15782 Santiago de Compostela, España;* [b]*Departamento de Ingeniería Química, Universidad del País Vasco, Apartado 450, 01006 Vitoria, España*

(*Received 9 May 2009; final version received 7 June 2009*)

Must distillation processes simulation is a challenging task, due to the lack of thermodynamic interaction parameters and accurate studies of phase equilibria. The presence of polar substances, those different from ethanol and water, and their low concentrations make it very difficult to model industrial distillation. Several of the congeners are essential enological components of the organoleptic matrix. In this work, we are concerned with the study of phase behaviour of ethanol + water + ethyl acetate at 101.3 kPa, this being the third compound, the legal congener of the highest composition in common alcoholic distillation. The experimental results showed partial miscibility and four azeotropes into a complex medium. Group contribution models yield poor results. 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 application to process simulation.

Keywords: azeotrope; ethanol; water; ethyl acetate; phase equilibria; prediction; thermodynamic topological analysis

1. Introduction

In the last few years, a considerable effort has been developed in the field of phase equilibria and thermodynamic properties of mixtures closely related to chemical processes. The Evaluated Process Design Data Project developed by the Design Institute for Physical Properties under the umbrella of American Institute of Chemical Engineers (AIChE) 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 optimisation of unit operations. Despite this effort, the experimental data collections of phase equilibria for ternary or higher order complexity are scarce, due to the time consuming and high cost experimental procedure to obtain a complete description of each mixture of industrial interest. As in any other industrial process, the knowledge of multicomponent vapour–liquid equilibrium (VLE) data is important for the beverage distillation technology. This information may be used to test and develop

---

*Corresponding author. Email: miguel.iglesias@usc.es

ISSN 0031–9104 print/ISSN 1029–0451 online

DOI: 10.1080/00319100903096539
http://www.informaworld.com

new models for correlation and/or prediction of thermodynamic properties of multicomponent mixtures. Only a few attempts have been oriented towards a better description of complex mixtures in alcoholic distilled beverages [1,2]. 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 collection of substances found in the mixture to be distilled and the low concentration of many components (the so-called congeners) [3] which are different from ethanol and water. Several of the 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 neglected in calculations. From the literature it can be observed that a huge quantity of congeners have been found in different distillation drinks [5,6]; however, only few of them are controlled by legislation, meaning that their concentration cannot be higher than an established limit. The industrial work conditions are not severe, the operating pressure to produce alcoholic beverages being of the order of the atmospheric pressure and the temperature of distillation around 100–150°C. Most of the substances involved in this process are highly polar, difficult to study theoretically and to make an adequate selection of the thermodynamic options during theoretical studies and simulations. Despite technology advances, these distillation processes maintain a little bit of tradition, is far away from working under optimised 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. With these facts in mind and as an extension of our earlier works concerning VLE or liquid–liquid equilibria (LLE) [7,8] we present new phase equilibria data of the ternary mixture ethanol + water + ethyl acetate at 101.3 kPa. Because experimental data are often not available, at least for process synthesis, group contribution methods can be used for the prediction of the required VLE. In the past several decades, the group contribution method The Universal Functional Activity Coefficient (UNIFAC) [9] 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 the group interaction parameters and reproduce the behaviour of systems in other mixing or operation conditions. The application of the UNIFAC group contribution method leads to qualitative predictions in terms of activity coefficients and compositions for this ternary system due to the molecular characteristics of the chemicals. Fitting parameters corresponding to boiling temperatures (Tamir–Wisniak equation) [10] and activity coefficients Universal QuasiChemical equation (UNIQUAC) equation [11] mole fraction dependence are gathered. The experimental results showed that this ternary mixture is partially miscible, exhibits four azeotropes and a complex topology in terms of phase equilibria. Consistency of the data was ensured by the McDermott–Ellis method [12]. Disposable literature was compared and commented upon.

2. Experimental section

2.1. *Materials*

Ethanol (99.5 mol%) was supplied by Merck and was used without further purification. Ethyl acetate (99.9 mol%) was supplied by Fluka. Water was of millipore quality with organic total mass <5 ppb and resistivity of 18.2 MΩcm. The purity of the materials was checked by gas liquid chromatography and was found to be better than 99.7 mol%. All products were ultrasonically degassed and dried over molecular sieves (pore diameter of 3×10^{-10} m from Fluka) before use. Densities, refractive indices and normal boiling points of the pure substances are listed in Table 1 and compared with literature values, as well as other relevant information.

2.2. *Apparatus and procedure*

The still used to measure VLE data was a dynamic recirculating apparatus described earlier [8]. The equilibrium temperature was measured with a digital platinum 100 Ω 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 vapour-phase and liquid-phase compositions for the two systems were determined by the 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 ±0.00001 gcm^{-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 the temperature was controlled with a densimeter. Thermal isolation was ensured in the whole apparatus except for the part corresponding to vapour condenser. Each experiment was continued for at least 1 h after the boiling temperature had become stable. Samples of both liquid and vapour 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 minimise the evaporation losses during storage and manipulation of the phase samples. The estimated uncertainty in the determination of both liquid and vapour phase mol fractions is

Table 1. Densities ρ, refractive indices n_D, and normal boiling temperatures T_b of the pure components.

		ρ (298.15 K)(g cm^{-3})		n_D (298.15 K)		T_b (K)	
Component	MW[a](kg kmol^{-1})	Exptl.[b]	Lit.[c]	Exptl.[d]	Lit.[e]	Exptl.	Lit.[a]
Ethanol	46.069	0.78589	0.78730	1.35941	1.35941	351.40	351.40
Water	18.015	0.99704	0.99705	1.33250	1.33250	373.15	373.15
Ethyl acetate	88.107	0.89444	0.89455	1.36978	1.36978	350.30	350.30

Notes: [a]Poling *et al.* [13].
[b]Resa *et al.* [14].
[c]Thermodynamics Research Center (TRC) Thermodynamic Tables [15].
[d]Resa *et al.* [16].
[e]Riddick *et al.* [17]

better than 0.001. A more detailed description of the experimental procedure in our laboratory may be obtained from earlier works.

3. Results and discussion

3.1. *Equilibrium equation and activity coefficients*

Experimental density (ρ) and refractive index (n_D) values at 298.15 K for this ternary system as a function of x_i have been published previously [14,16]. Such physical properties were applied in order to compute the 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):

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

where the liquid molar volume, v_i^L, was calculated by the Yen and Woods equation [18] 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 [19] to characterise the vapour phase deviation from ideal behaviour. P_i^S is the vapour pressure which was calculated from the Antoine equation:

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

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 vapour experimental compositions for the ternary mixture.

3.2. *Boiling temperature correlation*

In order to obtain the general parameters of the experimental measured magnitudes, the Tamir–Wisniak [10] equation was applied to correlate the boiling temperatures, which is expressed as follows:

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

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 $\sigma = 0.698$ K.

$$\sigma(M) = \left\{ \sum (M_{\text{exptl}} - M_{\text{calcd}})^2 / \text{ND} \right\}^{1/2}. \tag{4}$$

In this equation M is a general magnitude (as temperature, vapour phase composition, etc.) and ND is the number of experimental data. Figure 2 shows the

Table 2. Experimental VLE data: temperature T, liquid phase and vapour phase mole fraction x_i y_i, activity coefficient γ_i for ethanol (1) + water (2) + ethyl acetate (3) at 101.3 kPa, and root mean square deviation from the UNIFAC Prediction σ (into brackets in the last row).

T(K)	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
351.4	1.000	0.000	1.000	0.000	1.000	1.503	1.055
373.2	0.000	1.000	0.000	1.000	1.392	1.000	1.569
350.3	0.000	0.000	0.000	0.000	1.031	1.437	1.000
345.2	0.114	0.117	0.121	0.148	1.336	3.730	1.120
343.9	0.228	0.181	0.213	0.201	1.248	3.464	1.217
343.9	0.275	0.199	0.250	0.207	1.213	3.251	1.268
344.1	0.320	0.229	0.272	0.211	1.127	2.845	1.399
344.9	0.397	0.309	0.331	0.216	1.070	2.093	1.832
345.3	0.414	0.340	0.313	0.112	0.956	0.971	2.736
345.5	0.388	0.129	0.369	0.219	1.195	4.945	0.993
346.0	0.401	0.127	0.390	0.215	1.196	4.845	0.959
346.7	0.447	0.414	0.401	0.192	1.075	1.290	3.255
347.2	0.458	0.431	0.431	0.235	1.105	1.479	3.324
347.8	0.468	0.434	0.454	0.231	1.113	1.411	3.455
347.9	0.628	0.193	0.560	0.178	1.020	2.438	1.570
348.3	0.630	0.234	0.572	0.184	1.021	2.045	1.906
348.8	0.627	0.255	0.590	0.191	1.039	1.903	1.939
349.3	0.622	0.274	0.606	0.194	1.054	1.765	1.981
350.3	0.606	0.318	0.637	0.091	1.095	0.683	3.569
351.2	0.564	0.399	0.646	0.237	1.153	1.365	3.034
351.5	0.564	0.394	0.657	0.240	1.161	1.383	2.310
351.7	0.557	0.414	0.663	0.250	1.174	1.361	2.925
352.1	0.558	0.415	0.687	0.240	1.198	1.282	2.510
352.6	0.486	0.511	0.672	0.138	1.320	0.587	59.313
354.6	0.214	0.780	0.585	0.384	2.419	0.986	4.634
355.5	0.183	0.804	0.560	0.418	2.620	1.004	1.485
355.4	0.158	0.827	0.571	0.404	3.107	0.948	1.425
356.0	0.130	0.852	0.547	0.444	3.551	0.987	0.399
356.9	0.105	0.885	0.524	0.469	4.051	0.969	0.603
357.6	0.098	0.896	0.497	0.501	4.042	0.996	0.160
347.5	0.223	0.721	0.329	0.287	1.714	1.068	7.407
348.8	0.132	0.812	0.335	0.329	2.811	1.028	6.275
350.3	0.094	0.852	0.361	0.367	3.988	1.027	5.097
352.7	0.077	0.886	0.389	0.408	4.803	0.996	5.161
355.8	0.089	0.890	0.460	0.459	4.382	0.986	3.323
354.1	0.107	0.868	0.486	0.424	4.096	0.998	3.187
354.1	0.131	0.842	0.493	0.407	3.382	0.989	3.309
352.7	0.181	0.796	0.484	0.429	2.551	1.165	3.421
350.9	0.203	0.773	0.450	0.339	2.252	1.020	8.840
349.5	0.249	0.724	0.418	0.317	1.806	1.078	10.074
349.1	0.274	0.701	0.415	0.296	1.652	1.058	12.206
349.3	0.299	0.677	0.425	0.300	1.539	1.100	11.814
348.5	0.314	0.650	0.404	0.289	1.437	1.142	8.945
348.4	0.338	0.626	0.411	0.274	1.363	1.131	9.082
351.5	0.297	0.694	0.495	0.315	1.660	1.031	18.582
350.5	0.420	0.562	0.533	0.278	1.309	1.171	10.738
349.5	0.581	0.332	0.583	0.214	1.078	1.591	2.380
348.9	0.639	0.255	0.603	0.193	1.038	1.918	2.004

(*continued*)

Table 2. Continued.

T(K)	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
348.7	0.697	0.075	0.626	0.172	0.995	5.840	0.931
349.2	0.721	0.187	0.665	0.155	1.002	2.069	2.031
350.1	0.825	0.175	0.771	0.193	0.981	2.654	101.341
350.0	0.693	0.178	0.718	0.212	1.092	2.876	0.548
349.7	0.625	0.284	0.650	0.171	1.108	1.478	1.991
349.1	0.440	0.511	0.489	0.265	1.214	1.300	5.176
348.3	0.400	0.545	0.446	0.253	1.255	1.204	5.792
348.2	0.306	0.659	0.397	0.278	1.464	1.096	9.882
348.1	0.263	0.698	0.375	0.284	1.613	1.064	9.486
347.3	0.234	0.715	0.337	0.273	1.680	1.032	8.464
347.0	0.199	0.748	0.314	0.270	1.870	0.989	8.665
346.6	0.176	0.758	0.291	0.290	1.990	1.064	7.140
346.5	0.145	0.783	0.272	0.290	2.257	1.035	6.851
346.0	0.122	0.794	0.247	0.290	2.499	1.041	6.267
345.9	0.094	0.817	0.238	0.306	3.126	1.073	5.908
345.4	0.075	0.828	0.208	0.271	3.486	0.958	6.277
345.1	0.056	0.848	0.195	0.273	4.391	0.953	6.606
349.8	0.898	0.039	0.835	0.031	0.987	1.927	2.162
349.4	0.875	0.079	0.773	0.211	0.953	6.572	0.363
349.2	0.879	0.032	0.765	0.203	0.947	15.613	0.375
349.3	0.847	0.102	0.768	0.209	0.982	5.105	0.457
348.2	0.837	0.023	0.710	0.178	0.959	20.536	0.844
345.2	0.556	0.001	0.519	0.082	1.187	171.262	1.059
344.8	0.495	0.004	0.449	0.124	1.172	87.822	1.014
347.1	0.040	0.073	0.030	0.055	0.890	2.072	1.139
347.0	0.051	0.077	0.052	0.111	1.181	3.976	1.065
346.9	0.080	0.075	0.091	0.203	1.352	7.447	0.930
346.4	0.061	0.062	0.095	0.128	1.862	5.838	1.002
345.8	0.210	0.083	0.276	0.113	1.629	3.914	0.996
345.6	0.242	0.089	0.308	0.119	1.589	3.911	0.993
345.4	0.304	0.109	0.347	0.092	1.436	2.468	1.117
345.2	0.331	0.099	0.378	0.100	1.449	3.009	1.075
345.1	0.367	0.027	0.424	0.134	1.473	14.941	0.860
345.4	0.476	0.056	0.203	0.140	0.541	7.377	1.651
345.3	0.189	0.122	0.202	0.093	1.356	2.263	1.202
344.1	0.192	0.153	0.194	0.182	1.393	3.813	1.196
343.9	0.215	0.182	0.202	0.198	1.290	3.492	1.251
343.8	0.231	0.197	0.214	0.208	1.273	3.396	1.269
343.8	0.243	0.214	0.218	0.209	1.237	3.155	1.322
343.9	0.256	0.230	0.226	0.213	1.214	2.984	1.369
344.0	0.272	0.255	0.233	0.214	1.178	2.700	1.467
344.1	0.297	0.267	0.254	0.216	1.173	2.609	1.527
344.3	0.300	0.296	0.259	0.233	1.138	2.427	1.530
344.7	0.299	0.125	0.304	0.227	1.342	5.614	0.989
347.0	0.559	0.024	0.481	0.197	1.052	23.027	0.878
347.5	0.513	0.196	0.480	0.222	1.098	3.064	1.133
347.8	0.495	0.083	0.487	0.217	1.153	7.108	0.775

	σ (T) (K)	σ (y_1)	σ (y_2)	σ (y_3)
UNIFAC	2.293	0.079	0.069	0.114
UNIFAC-Lyngby	1.894	0.078	0.066	0.108

Table 3. Physical properties of the pure components: 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*.

							Antoine constants[c]			
Compound	P_c(kPa)[a]	RD[a] × 10^{10} (m)	μ[a] × 10^{30} (Cm)	ETA[b]	T_c(K)[b]	Z_c^a	*A*	*B*	*C*	Range *T*(K)
Ethanol	6383.5	2.2590	5.6372	1.40	516.25	0.248	8.11220	1592.864	226.184	293.15 – 366.15
Water	2209.0	0.615	6.1709	1.70	647.29	0.233	8.07131	1730.630	233.426	274.15 – 373.15
Ethyl acetate	3830.1	3.4680	5.9374	0.53	523.25	0.252	7.10179	1244.951	217.881	289.15 – 349.15

Notes: [a] Daubert and Danner [20].

[b] Prausnitz *et al*. [21].

[c] Gmehling and Onken [22].

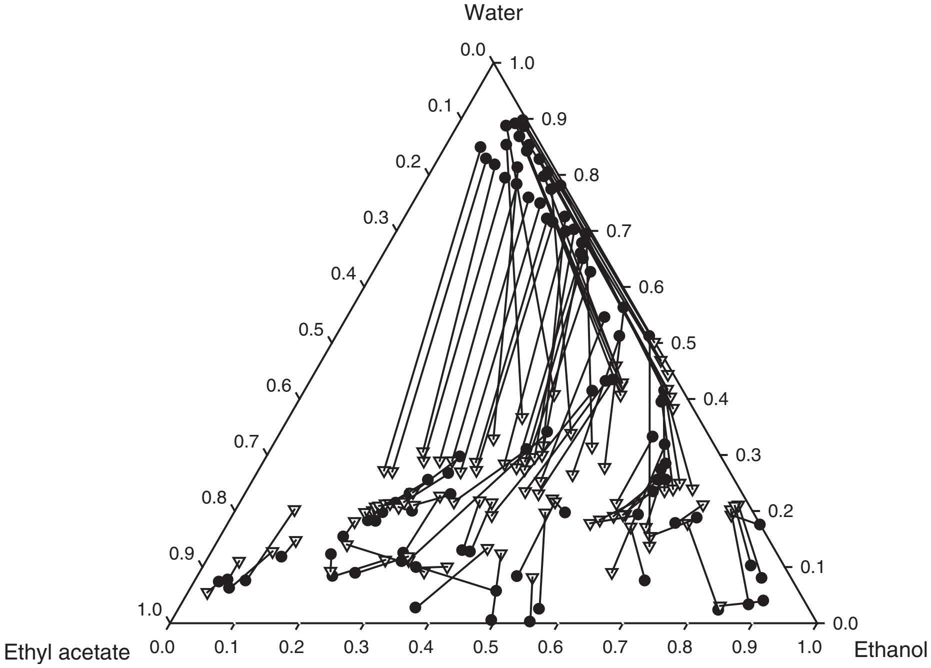


Figure 1. Composition (mole fractions) diagram for ethanol + water + ethyl acetate at 101.3 kPa: (●) liquid phase, (▽) vapour phase.

equilibrium isotherms on the liquid-phase composition diagram calculated from Equation (3). The shape of the curves indicates that the system exhibits azeotropic behaviour at each binary composition (instable nodes, minimum azeotropes, two homogeneous and one heterogeneous). Moreover, a ternary minimum azeotrope is also observed, which shows heterogeneous character (stable node), as previous literature indicates [23].

3.3. *VLE consistency data*

VLE 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 an 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 VLE data has been tested with the McDermott and Ellis method [12] to reject the possible inconsistent equilibrium points from the experimental determined collection. According to this test, two experimental points (a) and (b) are thermodynamically consistent when:

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

Table 4. Parameters of Tamir–Wisniak and UNIQUAC equations for ethanol + water + ethyl acetate at 101.3 kPa.

Parameters of Tamir–Wisniak equation			
$A_{12} = -38.5906$	$B_{12} = 46.7120$	$C_{12} = -56.6636$	$D_1 = 77.2329$
$A_{13} = -22.7609$	$B_{13} = 9.8672$	$C_{13} = -12.2098$	$D_2 = 43.7383$
$A_{23} = -97.7499$	$B_{23} = -116.0909$	$C_{23} = -75.0177$	$D_3 = 28.5286$
			$D_4 = 3.3488$
	$\sigma = 0.698$		
Parameters of UNIQUAC equation Δu_{ij} (cal mol^{-1})			
$\Delta u_{12} = 100.64$	$\Delta u_{13} = 122.47$		$\Delta u_{23} = 389.88$
$\Delta u_{21} = 89.00$	$\Delta u_{31} = -101.82$		$\Delta u_{32} = -521.80$
σ (T) (K)	σ (y_1)	σ (y_2)	σ (y_3)
8.05	0.162	0.118	0.207

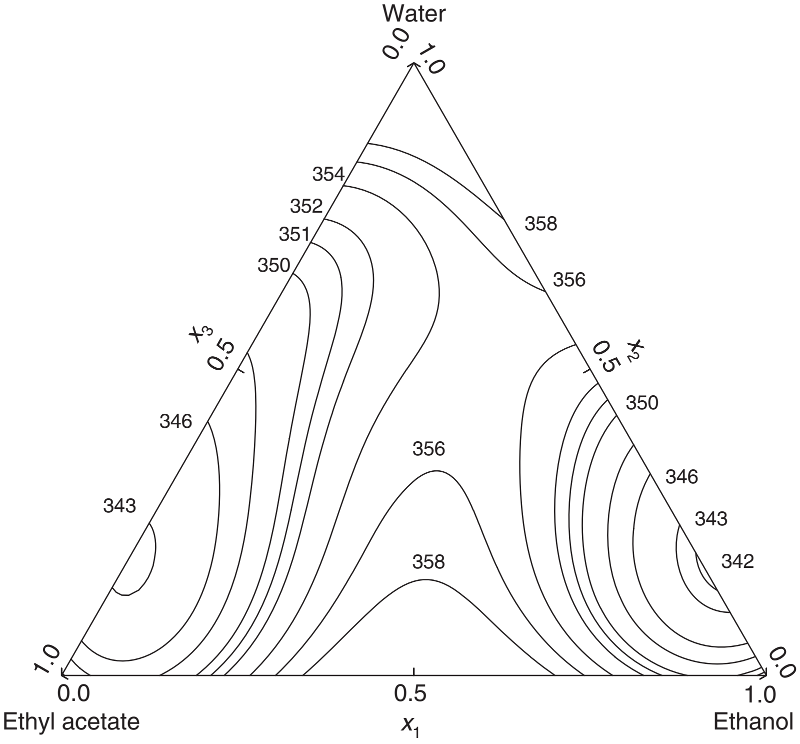


Figure 2. Isotherms (temperature in K) for ethanol + water + ethyl acetate at 101.3 kPa using Equation (3) with coefficients from Table 4.

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

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

and $D_{\max}$ is the maximum deviation (subscripts a and b for two experimental points). McDermott and Ellis proposed a value of 0.01 for $D_{\max}$ if the uncertainty in the mole fraction of the liquid and vapour compositions are between ±0.001, as in this case but the maximum local deviation is not a constant, and Wisniak and Tamir [24] propose the following expression for this magnitude:

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

In 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 in VLE calculations since Raoult's law provides no more than a rough approximation in common non-ideal mixtures. For strongly non-ideal mixtures, as solutions of alcohols, water, etc., the UNIQUAC equation is likely 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 VLE or LLE. The description of this model is widely presented in the open literature [11,13] 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 + ethyl acetate at 101.3 kPa has been carried out by the UNIFAC group contribution method [9,25]. The group interaction parameters applied were those disposable from the 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 vapour 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 and the 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 [26,27]. The TTA is based on the classical works of Schreinemakers and Ostwald (see the review in [28]), 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 the distillation operation (a continuum of steps of partial vaporisation with reflux). The reason for this renewed interest was the realisation 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 characterisation of natural liquid mixtures to be distilled. The classification of ternary VLE diagrams is a key to the 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 analysed 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 in understanding the 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 by experimentally or mathematically simulating the experiment procedure by means of 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 [28]. Relative volatility maps are tools of actual relevance because they provide key information for distillation in terms of equivolatility. The study of volatility in mixtures leads to the analysis of the influence of a new solvent into a mixture in what is referred to as the phase transference and the interactions among compounds. Its use has been studied earlier for different applications as breaking azeotropes and design of distillation units [29]. These tools (residue curve/relative volatility maps) are included in the main recent publications in chemical engineering, as important elements for understanding the distillation design and mixing. It allows us 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. Figures 3 and 4 are the relative volatility and residual curve map of this ternary mixture, respectively. As it could be observed, equivolatility line is showed by a collection of points attaching the binary azeotrope in ethanol + water mixture and a locus into the binary water + ethyl acetate. From this line, two regions are defined, one where the water pure compound is enclosed in which high volatility values are observed and other region enclosing ethanol and

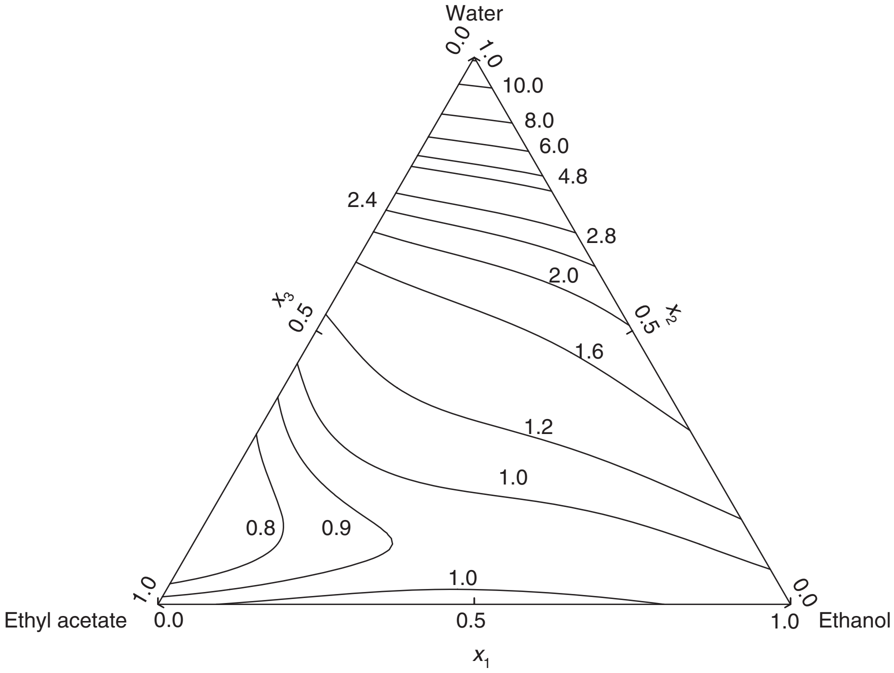


Figure 3. Isolines of relative volatility (a dimensional) for ethanol + water + ethyl acetate at 101.3 kPa derived from the experimental data.

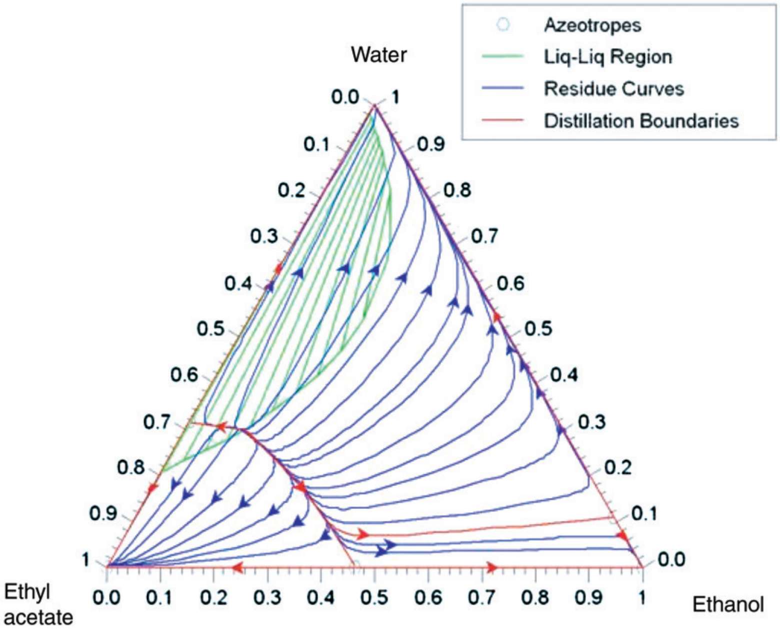


Figure 4. Residual curve map for ethanol + water + ethyl acetate at 101.3 kPa by UNIFAC method.

ethyl acetate pure corners with low values of volatility. Attending to the residual curve map, it is clear that during distillation there is a strong tendency to lose light compounds and then increase the water composition into the boiler. The alcoholic mixtures show this behaviour when they are distilled, due to the fact that they contain only traces of other compounds that deform only slightly the residual map.

3.7. *Previously published data of the ternary mixture*

In open literature it may be found that different publications [30-33] were related to the ternary mixture which was experimentally studied. All of them are of scarce utility due to the lack of thermodynamic consistency or inadequate coverage of the composition diagram (see points distribution in Figure 5). In Figure 5, a comparison of the boiling temperature deviations corresponding to literature data points from the experimental data correlation obtained in this article is showed. The symbols □, ◇, △, and × are used to indicate the experimental data of Griswold *et al.* [30], Bersatonis and Venskevicius [31], Van Zandijcke and Verhoeye [32] and Lee *et al.* [33], respectively, 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 slight concordance is observed among our experimental data and those reported by Van Zandijcke and Verhoeye (better than ±1% and a few points around 5% in error). The data from Bersatonis and Venskevicius's work show only compositions at diluted ethyl acetate

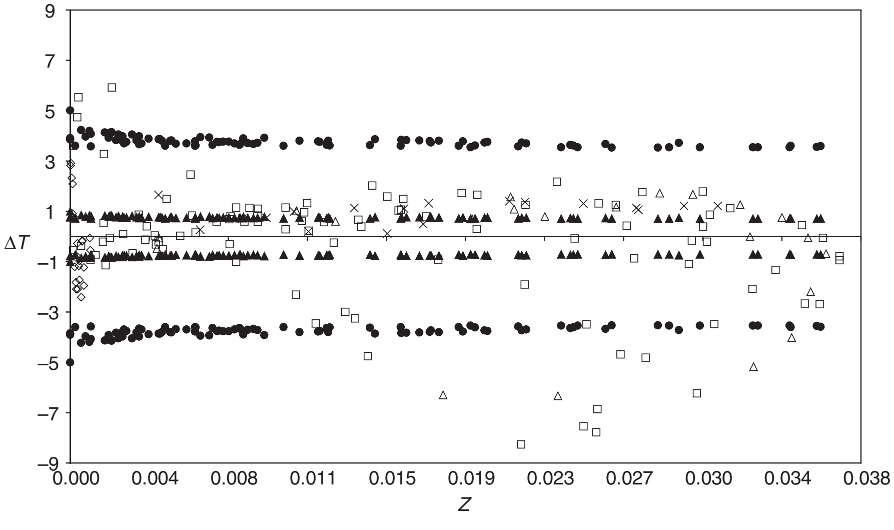


Figure 5. Comparison of the experimental and literature data (□ [30], ◇ [31], △ [32] and × [33]) for ethanol + water + ethyl acetate at 101.3 kPa (▲ show deviations of ±1% and ● show deviations of ±5% from the experimental data enclosed in this article).

and are of low utility for describing the whole mixture trend. This collection of data shows deviations around 3% in temperature. In what is referred to Griswold *et al.*'s work, it shows an adequate coverage of composition but higher deviations, with the poorest results at diluted and low concentrated compositions (low and medium values of the z parameter in Figure 5). Lee *et al.*'s work gathers a few data for this mixture, which shows the lowest deviations from our data. 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.

4. Conclusions

In this study, the phase equilibrium behaviour of the ethanol + water + ethyl acetate ternary mixture was experimentally investigated in order to characterise the interactions of the most important congener (ethyl acetate) into distilled alcoholic mixtures. The experimental results showed that this ternary mixture is partially miscible at low ethanol compositions and exhibits a heterogeneous ternary and three binary azeotropes (homogeneous ethanol + water, homogeneous ethanol + ethyl acetate and heterogeneous water + ethyl acetate mixtures). All of them show minimum temperature trend, in accordance with literature [23]. In terms of TTA, each binary azeotrope shows a trend of saddle, the ternary one as an instable node and the pure components as stable nodes [28,29], which reveals the complex molecular interactions in this mixture (123 m topological character [27]). The ternary VLE has been modelled 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 the VLE data of this kind of ternary mixtures, despite non-ideality and partial miscibility; (ii) the group contribution model (UNIFAC model) can be used for the modelling 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 obtained 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 characterising the alcoholic mixtures contained in distilled beverages, which means an improvement of the existing open literature for the ternary ethanol + water + ethyl acetate; (iv) TTA means a powerful tool for understanding the distillation systems and analysing the distillation path, boundaries and is 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 use of the prediction results into simulations.

Acknowledgements

Miguel Iglesias wishes to thank the Basque Country Government, Departamento de Educación, Universidades e Investigación, Dirección de Política Científica (Eusko

Jaurlaritza, Herkuntza, Unibersitate eta Ikerketa Saila) for its support in the development of his research

References

[1] C.A. Faundez, V.H. Alvarez, and J.O. Valderrama, Ingenieria Química **25**, 40 (2004).
[2] C.A. Faundez, V.H. Alvarez, and J.O. Valderrama, J. Phase Equilib. **25**, 203 (2004).
[3] A. Hikari and R. Kubo, J. Chem. Eng. Japan **8**, 294 (1975).
[4] J. Lora, M.I. Iborra, R. Perez, and I. Carbonell, I. Revista Española de Ciencia y Tecnología de Alimentos **32**, 621 (1992).
[5] T. Fernández-García, M.E. Martín, and A. Casp, Z. Lebensm. Unters. Forsch. A. **206**, 414 (1998).
[6] S. Selli, T. Cabaroglu, and A. Canbas, Int. J. Food Sci. Technol. **38**, 587 (2003).
[7] A. Touriño, L.M. Casas, G. Marino, M. Iglesias, B. Orge, and J. Tojo, Fluid Phase Equilib. **206**, 61 (2003).
[8] J.M. Resa, C. Gonzalez, J.M. Goenaga, and M. Iglesias, J. Chem. Eng. Data **33**, 1765 (2004).
[9] A. Fredenslund, J. Gmehling, and P. Rasmussen, *Vapor–Liquid Equilibria Using UNIFAC*, *A Group Contribution Method* (Elsevier, Amsterdam, 1977).
[10] A. Tamir and J. Wisniak, Chem. Eng. Sci. **33**, 657 (1978).
[11] D.S. Abrams and J.M. Prausnitz, AIChE J. **21**, 116 (1975).
[12] C. McDermott and S.R.M. Ellis, Chem. Eng. Sci. **20**, 293 (1965).
[13] B.E. Poling, J.M. Prausnitz, and J.P. O'Connell, *The Properties of Gases and Liquids* (McGraw-Hill, New York, 2001).
[14] J.M. Resa, C.González, J.M. Goneaga, and M. Iglesias, J. Sol. Chem. **33**, 169 (2004).
[15] Thermodynamic Research Center, *TRC Thermodynamic Tables* (A&M University, College Station, TX, 1994).
[16] J.M. Resa, C. González, J.M. Goneaga, and M. Iglesias, Phys. Chem. Liq. **43**, 65 (2005).
[17] J.A. Riddick, W.B. Bunger, and T.K. Sakano, *Organic Solvents, Physical Properties and Methods of Purification*, 4th ed. (Wiley-Interscience, New York, 1986).
[18] L.C. Yen and S.S. Woods, AIChE J. **12**, 95 (1966).
[19] J.G. Hayden and J.P. O'Connell, Ind. Eng. Chem. Process Des. Dev. **14**, 209 (1975).
[20] T.E. Daubert and R.P. Danner, *Physical and Thermodynamic Properties of Pure Chemicals. Data Compilation* (Hemisphere Publishing Corporation, New York, 1986).
[21] J. Prausnitz, T. Anderson, E. Greens, C. Eckert, R. Hsieh, and J. O'Connell, *Computer Calculations for Multicomponent Vapor–Liquid and Liquid–Liquid Equilibria* (Prentice-Hall, INC., NJ, 1980).
[22] J. Gmehling, U. Onken, *Vapor–Liquid Equilibrium Data Collection. Chemistry Data*, Series (DECHEMA, Frankfurt/Main, 1977–1999).
[23] L.H. Horsley, *Azeotropic Data III, Advances in Chemistry Series 116, ACS* (Washington, DC, USA, 1973).
[24] J. Wisniak and A. Tamir, J. Chem. Eng. Data **22**, 253 (1977).
[25] B.L. Larsen, P. Rasmussen, and A. Fredenslund, Ind. Eng. Chem. Res. **26**, 2274 (1987).
[26] H. Matsuyama and H. Nishimura, J. Chem. Eng. Japan **10**, 181 (1977).
[27] E.R. Foucher, M.F. Doherty, and M.F. Malone, Ind. Eng. Chem. Res. **30**, 760 (1991).
[28] S. Widagdo and W.D. Seider, AIChE J. **42**, 96 (1996).
[29] L. Laroche, N. Bekiaris, H.W. Andersen, and M. Morari, Can. J. Chem. Eng. **69**, 1302 (1993).

[30] J. Griswold, P.L. Chu, and W.O. Winsauer, Ind. Eng. Chem. **41**, 2352 (1949).

[31] B. Bersatonis and J. Venskevicius, Liet. Tsr. Aukst. Mokyklu. Mokslo. Darb. Chem. Chem. Technol. **11**, 243 (1970).

[32] F. Van Zandijcke and L. Verhoeye, J. Appl. Chem. Biotech. **24**, 709 (1974).

[33] L.S. Lee, W.C. Chen, and J.F. Huang, J. Chem. Eng. Japan **29**, 427 (1996).