

Measurement and Modeling of Phase Equilibria for Ethanol + Water + Methanol at Isobaric Condition

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This work reports the phase behavior of the ternary system ethanol + water + methanol at 101.3 kPa. Prediction of activity coefficients and equilibrium compositions with different UNIFAC group contribution models showed poor agreement. Consistency of experimental data was tested by the McDermott–Ellis method. 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.

Introduction

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 disposability of accurate studies and quality data are of primary interest.

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. 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 that are important in the design and optimization of unit operations. Despite this, the experimental data collections of phase equilibria for ternary or higher complexity are scarce due to the fact that the experimental procedure to obtain a complete description of every mixture of industrial interest is very costly in both time and money. In the processing of alcoholic beverages, multicomponent vapor–liquid equilibrium (VLE) data are 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 toward a better description of complex mixtures in alcoholic distilled beverages.^{1,2} In must are substances with low concentrations (so-called congeners).³ 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 should not be forgotten in calculations. In open literature, it can be observed that a huge quantity of congeners exist in different distillation drinks;^{5,6} however, only few of them are controlled by legisla-

tion, meaning that their concentration cannot be higher than the established limit. In what is referred to the industrial process, the conditions are not severe. The operating pressure to produce alcoholic beverages is close to atmospheric, and the temperature is between (100 and 150)°C approximately. Most of the substances involved in this process are highly polar; this fact complicates the theoretical studies and the adequate selection of the thermodynamic options 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 the final commercial product. For these reasons and as an extension of our earlier works concerning phase equilibria,⁷ we present in this paper new phase equilibria data of the ternary mixture ethanol + water + methanol at 101.3 kPa. Because 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 UNIFAC⁸ 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 to 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 equation⁹) and activity coefficients (UNIQUAC equation¹⁰) mole fraction dependence are determined. The experimental results showed that this ternary mixture is miscible, exhibits one azeotrope, and has a simple topology in terms of phase equilibria. Consistency of the data was ensured by the McDermott–Ellis method.¹¹ Comparison with Kiyofumi et al.¹² was made and commented upon. Others authors have studied this system.^{13–21}

Experimental Section

Materials. Ethanol ($x = 99.5\%$) was supplied by Panreac and was used without further purification. Methanol ($x = 99.9\%$) was supplied by Panreac. Water was Millipore quality with

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Table 1. Densities ρ , Refractive Indices n_D , and Normal Boiling Temperatures T_b of the Pure Components

component	MW ^a	$\rho(298.15\text{ K})/\text{g}\cdot\text{m}^{-3}$		$n_D(298.15\text{ K})$		T_b/K	
		exptl	lit. ^b	exptl	lit. ^b	exptl	lit. ^a
ethanol	46.069	0.78589 ^c	0.78493	1.35941	1.35941	351.40	351.40
water	18.015	0.99704 ^c	0.99705	1.33250	1.33250	373.15	373.15
methanol	32.042	0.78646	0.78637	1.32667 ^d	1.32652	337.65 ^d	337.70 ^b

^a Ref 22. ^b Ref 25. ^c Ref 23. ^d Ref 24.**Table 2. Experimental Vapor–Liquid Equilibrium Data: Temperature T , Liquid-Phase x_i , and Vapor-Phase y_i Mole Fraction, and Activity Coefficient γ_i for Ethanol (1) + Water (2) + Methanol (3) at 101.3 kPa**

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
337.9	0.020	0.003	0.012	0.008	1.033	12.267	0.995	352.1	0.514	0.453	0.606	0.310	1.147	1.517	1.507
338.9	0.015	0.058	0.012	0.022	1.306	1.492	0.996	351.8	0.510	0.445	0.623	0.300	1.201	1.509	1.046
339.0	0.031	0.058	0.021	0.023	1.130	1.576	0.998	351.5	0.499	0.442	0.605	0.288	1.208	1.479	1.099
339.7	0.028	0.105	0.021	0.040	1.164	1.410	1.006	351.3	0.487	0.437	0.585	0.283	1.203	1.485	1.068
339.8	0.047	0.106	0.034	0.040	1.161	1.414	1.010	351.0	0.475	0.433	0.569	0.279	1.217	1.492	1.022
340.8	0.043	0.158	0.035	0.076	1.265	1.715	0.990	350.6	0.455	0.421	0.535	0.268	1.212	1.496	1.002
341.0	0.055	0.156	0.042	0.061	1.162	1.391	1.004	350.3	0.438	0.417	0.511	0.259	1.215	1.484	1.006
342.2	0.051	0.217	0.046	0.094	1.295	1.459	0.994	350.7	0.405	0.457	0.506	0.277	1.282	1.420	0.986
342.4	0.079	0.217	0.069	0.106	1.240	1.627	0.985	351.2	0.367	0.498	0.496	0.299	1.360	1.378	0.941
343.0	0.075	0.269	0.066	0.108	1.233	1.305	1.034	350.9	0.358	0.494	0.474	0.291	1.348	1.370	0.991
344.4	0.089	0.331	0.089	0.140	1.315	1.291	1.039	353.1	0.208	0.700	0.443	0.371	1.993	1.127	1.174
344.4	0.106	0.336	0.105	0.138	1.304	1.253	1.061	353.0	0.204	0.706	0.444	0.371	2.045	1.120	1.204
345.3	0.094	0.404	0.108	0.169	1.450	1.232	1.090	353.2	0.200	0.713	0.444	0.374	2.068	1.113	1.208
345.8	0.120	0.397	0.147	0.211	1.524	1.530	0.988	353.2	0.196	0.721	0.440	0.379	2.096	1.113	1.255
346.8	0.106	0.475	0.136	0.197	1.536	1.144	1.142	353.6	0.174	0.757	0.440	0.388	2.327	1.067	1.414
347.2	0.145	0.472	0.184	0.204	1.489	1.172	1.132	354.0	0.161	0.779	0.435	0.400	2.452	1.052	1.547
348.5	0.176	0.503	0.240	0.235	1.525	1.198	1.107	355.2	0.128	0.831	0.414	0.433	2.808	1.019	1.984
349.1	0.216	0.523	0.304	0.258	1.539	1.234	1.110	357.2	0.083	0.885	0.362	0.504	3.502	1.029	2.150
349.9	0.247	0.546	0.362	0.275	1.550	1.221	1.132	359.8	0.048	0.924	0.282	0.602	4.274	1.065	1.974
350.6	0.273	0.546	0.406	0.291	1.531	1.254	1.057	362.0	0.034	0.943	0.195	0.723	3.943	1.153	1.499
351.0	0.246	0.593	0.406	0.310	1.677	1.211	1.092	362.9	0.029	0.950	0.220	0.684	5.043	1.047	1.909
351.2	0.924	0.055	0.900	0.055	0.980	2.333	1.303	366.2	0.018	0.974	0.149	0.793	4.880	1.047	2.717
350.7	0.890	0.052	0.851	0.052	0.981	2.322	1.056	354.4	0.240	0.739	0.558	0.410	2.078	1.120	0.821
350.8	0.827	0.116	0.804	0.107	0.993	2.160	0.979	354.4	0.227	0.754	0.539	0.423	2.123	1.133	1.071
350.4	0.802	0.114	0.769	0.103	0.995	2.155	0.963	353.8	0.215	0.738	0.505	0.393	2.146	1.103	1.210
350.8	0.714	0.228	0.713	0.186	1.020	1.905	1.088	353.7	0.204	0.737	0.481	0.389	2.155	1.095	1.260
350.5	0.694	0.227	0.690	0.179	1.027	1.868	1.051	353.5	0.195	0.735	0.458	0.384	2.166	1.093	1.293
350.9	0.556	0.349	0.662	0.223	1.212	1.484	0.757	344.7	0.500	0.060	0.367	0.035	0.953	1.782	1.050
350.6	0.622	0.298	0.642	0.216	1.063	1.709	1.112	344.8	0.494	0.059	0.368	0.036	0.962	1.802	1.031
350.9	0.575	0.355	0.623	0.248	1.104	1.623	1.144	344.7	0.489	0.059	0.328	0.034	0.872	1.734	1.091
350.6	0.635	0.302	0.602	0.241	0.976	1.881	1.574	344.9	0.507	0.060	0.380	0.036	0.963	1.799	1.037
351.1	0.507	0.407	0.585	0.270	1.167	1.526	1.049	341.7	0.288	0.033	0.179	0.013	0.913	1.397	1.024
351.4	0.473	0.446	0.574	0.290	1.213	1.482	1.028	342.1	0.323	0.033	0.206	0.014	0.918	1.472	1.029
359.6	0.027	0.912	0.109	0.723	2.997	1.304	1.296	342.1	0.325	0.033	0.209	0.015	0.927	1.465	1.028
359.4	0.028	0.907	0.123	0.669	3.274	1.223	1.512	343.0	0.397	0.032	0.265	0.015	0.926	1.564	1.037
358.7	0.028	0.899	0.122	0.620	3.365	1.176	1.685	343.2	0.392	0.045	0.264	0.022	0.929	1.566	1.035
358.6	0.036	0.895	0.128	0.665	2.688	1.270	1.470	343.8	0.383	0.082	0.272	0.044	0.954	1.671	1.023
358.2	0.034	0.887	0.137	0.583	3.167	1.142	1.733	346.5	0.621	0.052	0.502	0.038	0.976	2.063	1.020
357.4	0.045	0.883	0.171	0.569	3.026	1.156	1.814	346.8	0.629	0.060	0.519	0.044	0.985	2.030	1.009
356.9	0.050	0.870	0.188	0.520	3.051	1.093	1.862	347.0	0.624	0.078	0.531	0.058	1.009	2.024	0.982
356.7	0.059	0.868	0.230	0.487	3.207	1.034	1.987	347.8	0.564	0.182	0.499	0.121	1.014	1.768	1.037
355.8	0.082	0.852	0.293	0.458	3.026	1.028	1.998	348.4	0.534	0.243	0.503	0.161	1.055	1.712	1.024
340.4	0.051	0.125	0.027	0.064	0.837	1.863	0.996	348.6	0.545	0.244	0.509	0.163	1.041	1.715	1.042
354.0	0.033	0.808	0.088	0.433	2.410	1.099	1.693	345.8	0.411	0.182	0.342	0.105	1.033	1.668	1.010
355.7	0.026	0.843	0.086	0.461	2.755	1.050	1.837	345.7	0.396	0.177	0.322	0.101	1.013	1.656	1.008
357.3	0.030	0.908	0.078	0.512	2.121	1.017	3.284	345.9	0.390	0.195	0.329	0.112	1.044	1.642	0.998
358.8	0.013	0.893	0.069	0.572	4.072	1.088	1.824	343.9	0.303	0.153	0.229	0.071	1.011	1.443	1.025
360.5	0.009	0.912	0.064	0.611	4.903	1.067	1.869	343.8	0.303	0.153	0.221	0.070	0.981	1.440	1.041
362.3	0.006	0.930	0.056	0.666	5.926	1.065	1.876	347.4	0.007	0.605	0.008	0.267	1.288	1.185	1.314
363.9	0.005	0.947	0.041	0.762	5.437	1.126	1.678	347.6	0.013	0.607	0.018	0.296	1.582	1.302	1.260
365.9	0.005	0.964	0.038	0.778	4.600	1.049	2.245	347.9	0.034	0.609	0.052	0.282	1.752	1.219	1.289
366.8	0.005	0.971	0.035	0.789	3.954	1.023	2.720	348.9	0.122	0.574	0.192	0.278	1.725	1.222	1.167
367.6	0.006	0.978	0.026	0.829	2.455	1.035	3.366	349.2	0.151	0.565	0.234	0.263	1.686	1.162	1.170
368.3	0.006	0.985	0.024	0.846	2.054	1.023	5.171	349.4	0.204	0.537	0.300	0.264	1.586	1.217	1.105
368.8	0.007	0.989	0.018	0.869	1.360	1.027	11.371	349.7	0.222	0.538	0.324	0.268	1.555	1.219	1.103
					$\sigma(T/\text{K})$				$\sigma(y_1)$		$\sigma(y_2)$		$\sigma(y_3)$		
	UNIFAC				1.63				0.030		0.038		0.039		
	UNIFAC-Lyngby				0.12				0.049		0.032		0.018		

^a Root mean square deviation from the UNIFAC prediction (in parentheses).

organic total mass fraction < 5 ppb and resistivity 18.2 M Ω . The purity of the materials so obtained was checked by gas–liquid chromatography and was found to be better than $x =$

99.6 %. All products were degassed using ultrasound and dried on molecular sieves (pore diameter of 3×10^{-10} m from Fluka) before use. Densities, refractive indices, and normal boiling

Table 3. Physical Properties of the Pure Compounds: 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

compound	P_c/kPa^a	$\text{RD}^a \times 10^{10}/\text{m}$	$\mu^a \times 10^{30}/(\text{C}\cdot\text{m})$	ETA ^b	T_c/K^a	Z_c^a	Antoine constants ^c		
							A	B	C
ethanol	6383.5	2.259	5.6372	1.40	516.25	0.248	8.11220	1592.864	226.184
water	22055	0.615	6.1709	1.70	647.29	0.233	8.07131	1730.630	233.426
methanol	8095.9	1.552	5.670	1.63	512.58	0.224	8.08029 ^d	1581.993 ^d	239.711 ^d

^a Ref 28. ^b Ref 8. ^c Ref 12. ^d Ref 15.

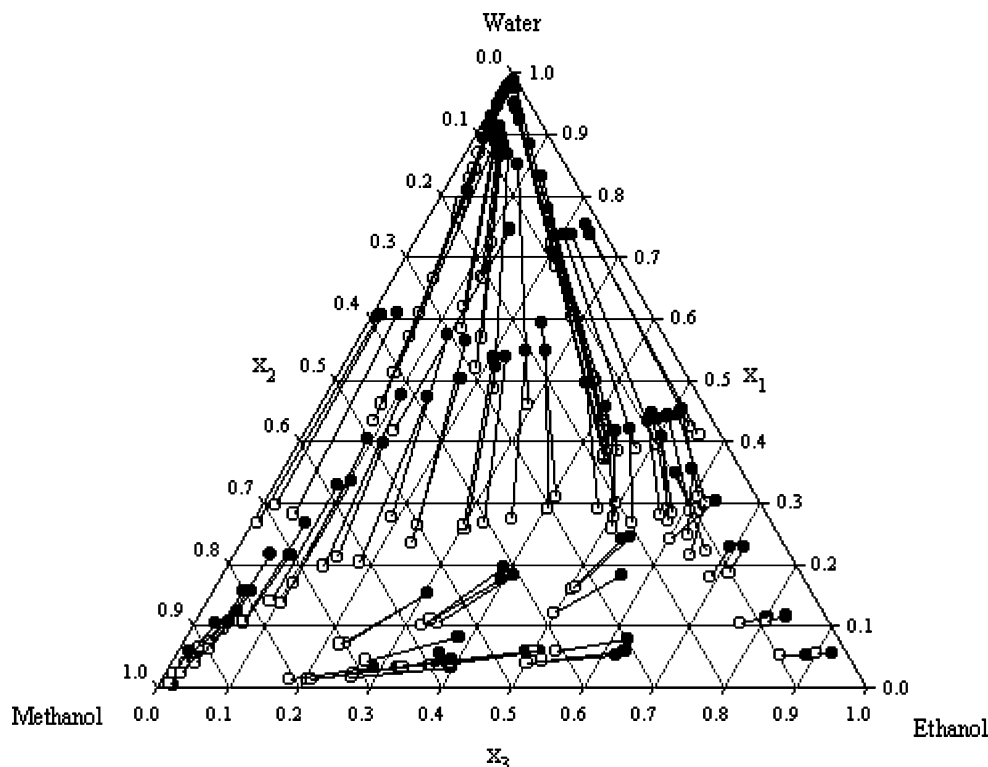


Figure 1. Mole fraction diagram for ethanol + water + methanol at 101.3 kPa: ●, liquid phase; ○, vapor phase.

points of the pure substances were checked and are listed in Table 1 and compared with literature values as well as other relevant information.

Apparatus and Procedure. 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 uncertainty of ± 0.01 K. For the pressure measurement, a digital manometer regulator (Divatronic DT1 model), manufactured by Leybold with an uncertainty of ± 0.01 kPa, was used. Both vapor- and liquid-phase compositions for determined from measurement of physical properties. Densities were measured at 298.15 K by using an Anton Paar DMA 58 vibrating-tube densimeter with an uncertainty of ± 0.00002 g·cm⁻³ that had been calibrated at atmospheric pressure with twice distilled water and dry air. The temperature of the densimeter was maintained at 298.15 K with a precision of ± 0.01 K by means of a semiconductor Peltier element and measured by a calibrated platinum resistance thermometer. Refractive indices were measured with a Mettler RE50 refractometer with an uncertainty of ± 0.00005 , and temperature was controlled as described for 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 evaporation losses during storage and manipulation of the phase samples. The estimated uncertainty in the determination of both liquid- and vapor-phase mole fractions is better than 0.001. A more detailed description of the experimental procedure in our laboratory was given previously.⁷

Results and Discussion

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 . The experimental VLE data are given in Table 2 with values of the activity coefficients (γ_i), which were computed by eq 1:

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

where the liquid molar volume (v_i^L) was calculated by the correlation of Yen and Woods,²⁶ 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 method²⁷ to characterize the vapor-phase deviation from ideal behavior. P_i^S is the vapor pressure that was calculated from the Antoine equation:

$$\log P^S/\text{kPa} = A + \frac{B}{(t/^\circ\text{C}) + C} \quad (2)$$

Table 4. Parameters of Tamir–Wisniak and UNIQUAC Equations for Ethanol + Water + Methanol at 101.3 kPa

Parameters of Tamir–Wisniak Equation			
$A_{12} = -39.9879$	$B_{12} = 38.8075$	$C_{12} = -57.5445$	$D_1 = 48.7248$
$A_{13} = 3.4711$	$B_{13} = 7.0495$	$C_{13} = -21.6887$	$D_2 = -165.0492$
$A_{23} = -36.4704$	$B_{23} = -61.0848$	$C_{23} = -64.8182$	$D_3 = 27.2532$
			$D_4 = 172.2532$
$\sigma = 0.95$			
Parameters of UNIQUAC Equation Δu_{ij} (J·mol ⁻¹)			
$\Delta u_{12} = 1372.26$	$\Delta u_{13} = 529.86$	$\Delta u_{23} = 70.03$	
$\Delta u_{21} = -43.20$	$\Delta u_{31} = -275.15$	$\Delta u_{32} = 299.63$	
σ (T/K)	σ (y ₁)	σ (y ₂)	σ (y ₃)
1.35	0.019	0.024	0.028

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.

Temperature Correlation. In order to obtain general parameters of the experimental measured variables, the Tamir–Wisniak equation⁹ was applied to correlate the boiling temperatures, which is expressed as follows:

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

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 $\sigma = 0.95$ K:

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

In this equation, M is a general magnitude (such 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 eq 3. The shape of the curves indicates that the system exhibits azeotropic behavior at the binary ethanol + water as literature suggests.

VLE Consistency Data. VLE data are the foundation for a variety of separation procedures that are essential to the chemical processes. However, phase equilibrium data should be tested in order to ensure 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 have been tested with the McDermott–Ellis method¹¹ to reject possible inconsistent equilibrium points from the experimental determined collection. According with this test, two experimental points (a) and (b) are thermodynamically consistent when

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

where D is the local deviation, which is expressed as

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

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 ± 0.001 , as in this case, but the maximum local deviation is not a constant. Wisniak and Tamir²⁹ propose the following expression for this magnitude:

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

In eq 7, B_i and C_i are the Antoine constants and Δx , ΔP , and Δt are the experimental uncertainties ($\Delta x \pm 0.001$, $\Delta P \pm 0.1$ kPa, $\Delta t \pm 0.01$ K) of mole fraction, pressure, and temperature ($7.0 \cdot 10^{-3}$, 0.098 kPa, and 10^{-2} °C for the devices applied), respectively. The experimental data gathered in this work show thermodynamic consistency according to the McDermott–Ellis test with the D_{max} Wisniak–Tamir criteria.

Activity Coefficients Correlation. The UNIQUAC equation offers three advantages: it has only two fitting parameters for each pair of compounds, a weaker dependence on temperature for such parameter, 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 UNIQUAC model is widely presented in the open literature;¹⁰ hence, it is not discussed here. The fitting parameters of this model and deviations are gathered in Table 4.

VLE Prediction Model. The UNIQUAC model of VLE for the ternary system ethanol + water + methanol at 101.3 kPa has been carried out by the UNIFAC group contribution method.^{8,30} The group interaction parameters applied were those available 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 at the end of Table 2. A qualitative description was obtained with the original UNIFAC method. A UNIFAC modification³⁰ shows a better estimation in terms of boiling temperature of the ternary mixture.

Thermodynamic Topological Analysis. 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. A residual curve could be determined experimentally or mathematically simulating the experimental procedure by means an adequate thermodynamic model. It allows us to determine the thermodynamic limits and boundaries of the separation attending to the nature and behavior 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 could be observed, the equivolatility line is shown by a collection of points attaching the binary azeotrope in the ethanol + water mixture and a locus into the binary water + methanol. 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 methanol pure corners with high values of volatility. Attending to the residual curve map, it is clear the strong tendency under

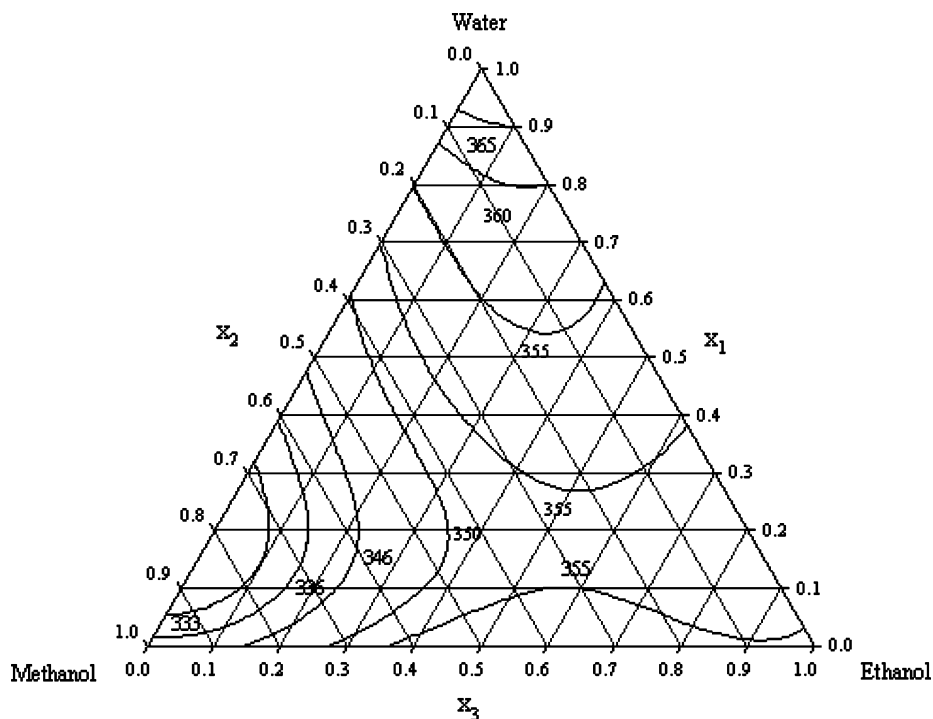


Figure 2. Isotherms (temperature in K) for ethanol + water + methanol at 101.3 kPa using eq 3 with coefficients from Table 4.

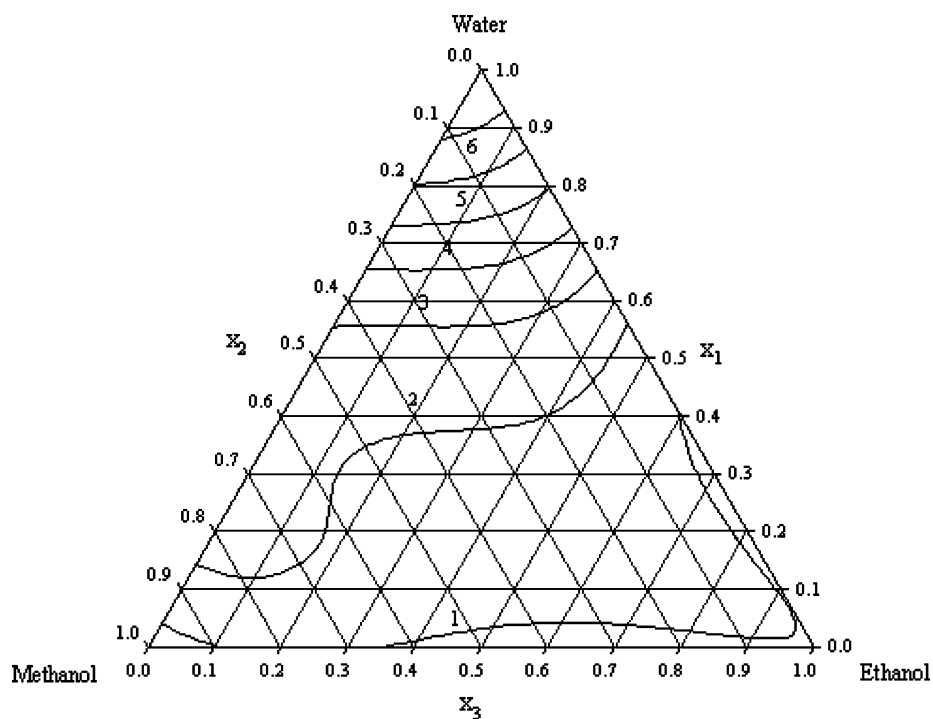


Figure 3. Isolines of relative volatility (adimensional) for ethanol + water + methanol at 101.3 kPa derived from the experimental data.

distillation to lose light compounds and raise the water composition of the residual liquid into boiler, when composition is into the greater region, as well as the special trend of must and alcoholic mixtures during this process due to the distillation oriented lines (Figure 4).

Previously Published Data of the Ternary Mixture. In open literature are a number of publications^{12–21} related to experimental data for this ternary mixture. In Figure 5, a comparison of the boiling temperature deviations corresponding to literature data points from the experimental data correlation obtained in this paper are shown. In Figure 5, the experimental data of Kiyofumi et al.¹² are indicated using an arbitrary parameter (z),

which expresses the product of total mole fractions in the mixture:

$$z = \prod_1^n X_n \quad (8)$$

with n being the number of system compounds and x being the mole fraction.

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

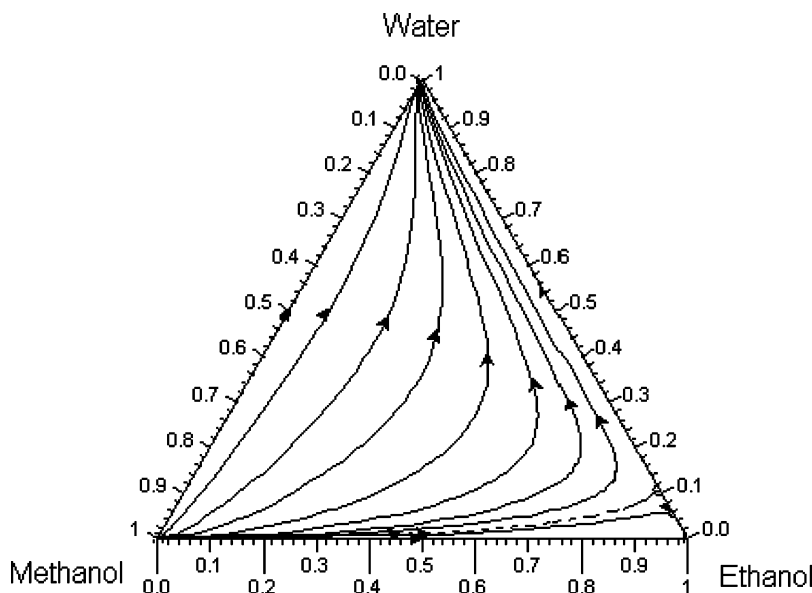


Figure 4. Residual curve map for ethanol + water + methanol at 101.3 kPa by UNIFAC method: ○, azeotrope; ---, distillation boundaries; —, residue curves.

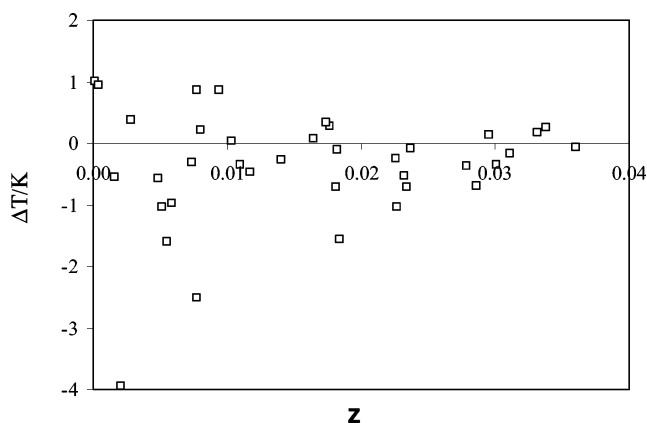


Figure 5. Comparison of the experimental and literature data (□, ref 12) for ethanol + water + methanol at 101.3 kPa.

experimental data. Low values of z refer to those compositions in the Gibbs triangle that are close to the binary axis while the high values in this parameter are related to approximately multicomponent equimolar compositions. In general terms, a big difference is observed among our experimental data and those reported to work in pseudobinary compositions (the greater deviation around 4 K) (see Figure 5). The composition range of this work is adequate, but an important quantity of the experimental data show important deviations in terms of temperature.

Conclusions

In this study, the VLE of the ethanol + water + methanol ternary mixture was studied in order to characterize the interactions of one of the most important congeners (methanol) in distilled alcoholic mixtures. The experimental results showed that this ternary mixture is miscible at any composition and exhibits a binary minimum azeotrope (homogeneous ethanol + water). In terms of TTA, this azeotrope shows a trend of instable node. The ternary VLE has been modeled using a correlating equation (UNIQUAC) and a predictive procedure (UNIFAC). The UNIQUAC model represents an adequate way for fitting VLE. The group contribution model modified UNIFAC³⁰ can be used for modeling work and for studies of mixtures containing this ternary system. The study done here

represents a new experimental contribution to complete the thermodynamic database for characterize alcoholic mixtures containing distilled beverages.

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