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Density, Refractive Index, Speed of Sound at 298.15 K, and Vapor−Liquid Equilibria at 101.3 kPa for Binary Mixtures of Propanol + 2-Methyl-1-butanol and Propanol + 3-Methyl-1-butanol

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Densities, refractive indices, and speeds of sound at 298.15 K and isobaric vapor−liquid equilibria data at 101.3 kPa were reported for the binary mixtures propanol + 2-methyl-1-butanol and propanol + 3-methyl-1-butanol. Excess molar volumes, refractive index deviations, and changes of speed of sound on mixing were calculated from the measurement results that were fitted with Redlich−Kister polynomials. VLE experimental data were tested for thermodynamic consistency by means of a modified Dechema test and were demonstrated to be consistent. The activity coefficients were correlated with the Margules, van Laar, UNIQUAC, NRTL, and Wilson equations. The ASOG model also was used for prediction.

Introduction

Knowledge of thermodynamic properties and phase equilibria of ethanol, water, and the different flavor components in distilled alcoholic beverages is of practical interest to the food technology industry since industrial procedures that are applied are closely related to their temperature and pressure dependence. In accordance to that, in the past few years a considerable amount of effort has been devoted to the field of thermodynamic properties, although scarcity of data is observed in the open literature for mixtures added to alcoholic beverages. Because of the different origins of grapes, thermal conditions of fermentation in chemical reactions and the complexity of composition and molecular chains of components, a considerable lack of accuracy or thermodynamic consistency can be observed in the disposable open literature data. Simulation and optimization are not used in a proper way in this matter, an overestimation of equipment or high energy-consuming conditions usually being applied due to inaccurate calculations.[1] This work is part of a research project whose objective is to measure thermodynamic properties and concentration in equilibrium for binary systems involved in wine distillation processes for further simulation. In this process, multicomponent mixtures are seen. The main components are water and ethanol, and several minor compounds such as alcohols, aldehydes, and acetates are also present. These minor compounds are called congeners. For modeling and process simulation in which mixtures appear, binary data are needed. It is very important to have available vapor−liquid equilibrium (VLE) data of mixtures formed by water + congeners, ethanol + congeners, and congeners + congeners. From the measurements, parameters of some classic correlations such as Wilson, NRTL, and UNIQUAC could be calculated, and the results applied to study the distillation of wine.

Experimental Section

Materials. Propanol (99.5 mol %) was supplied by Panreac and was used without further purification. 2-Methyl-1-butanol (99 mol %) from Aldrich and 3-methyl-1-butanol (99 mol %) from Fluka were purified by distillation in a laboratory column of 100 plates. The purity of the material was checked by gas−liquid chromatography and was higher than 99.6 mol %. All products were degassed using ultrasound and dried on molecular sieves (pore diameter 0.3 nm from Fluka) before use. Densities, refractive indices, and normal boiling points of the pure substances are given in Table 1 and compare with the literature values of Riddick et al.[2]

Apparatus and Procedure. The still used to measure VLE data was a dynamic recirculating apparatus described by Resa et al.[3] The equilibrium temperature was measured with a digital platinum 100 Ω resistance thermometer with an accuracy of ± 0.01 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 densimetry, refractometry, and speed of sound. Densities were measured at 298.15 K by using an Anton Paar DMA 58 vibrating tube densimeter with an accuracy of ± 0.00001 $g \cdot cm^{-3}$ that had been calibrated at atmospheric pressure with twice distilled water and dry air. The temperature of the densimeter was maintained at 298.15 K with a precision of ± 0.01 K by means a semiconductor Peltier element and measured by a calibrated platinum resistance thermometer. Refractive indices were measured with a Mettler RE50 refractometer with an accuracy of ± 0.00001, and temperature was controlled the same way as the densimeter, with a temperature precision of ± 0.01 K. Speeds of sound were measured with an Anton Paar DSA 48 sound analyzer with an accuracy of ± 0.1 $m \cdot s^{-1}$, and temperature was controlled by a Peltier cooler to a precision of ± 0.1 K. Prior to measurements, density calibration, refractive index, and speed of sound curves for these systems were obtained to calculate the compositions of the vapor and liquid phases. The binary mixtures were prepared by directly weighing the constituent components with an electronic balance (Salter model ER-182A) that has an accuracy of ± 0.0001 g. Precautions were taken in order to minimize evaporation losses during storage and preparation of the solutions. The estimated uncertainty in the determination of both liquid and vapor phase mole fractions is ± 0.001.

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Table 1. Physical Properties of Pure Compounds: Densities (ρ), Refractive Indices (n_D), Speeds of Sound (u) at 298.15 K and Normal Boiling Points (T_b)

	ρ/kg·m^{-3}		n_D		u/m·s^{-1}		T_b/K	
	obs	lit.[a]	obs	lit.[a]	obs	lit.[a]	obs	lit.[a]
propanol	799.75	799.99	1.38304	1.38370	1205.69	not avaliable	370.29	370.301
2-methyl-1-butanol	814.87	815.0	1.40872	1.4086	1253.29	not avaliable	401.93	401.9
3-methyl-1-butanol	806.78	807.1	1.40515	1.4052	1238.80	not avaliable	404.27	403.7

[a] Ref 2.

Table 2. Densities, Refractive Indices, Speed Sounds, for Propanol (1) + 2-Methyl-1-butanol (2) and Propanol (1) + 3-Methyl-1-butanol (2) at 298.15 K with Excess Molar Volume (V^E), Refractive Index Deviation (δn_D), and Speeds of Sound Deviation (δu)

	r	V^E			u	δu
x_1	g·cm^{-3}	cm^3·mol^{-1}	n_D	δn_D	m·s^{-1}	m·s^{-1}
Propanol (1) + 2-Methyl-1-butanol (2)						
0.051	0.81437	−0.029	1.40768	0.000	1252.4	1.1
0.100	0.81384	−0.030	1.40677	0.001	1250.6	1.6
0.151	0.81328	−0.030	1.40573	0.001	1248.7	2.2
0.200	0.81271	−0.030	1.40478	0.001	1246.8	2.6
0.251	0.81209	−0.028	1.40380	0.002	1244.7	3.0
0.300	0.81146	−0.025	1.40272	0.002	1242.8	3.5
0.351	0.81080	−0.024	1.40164	0.002	1240.5	3.7
0.408	0.81004	−0.022	1.40039	0.002	1238.0	3.9
0.450	0.80944	−0.020	1.39934	0.002	1236.1	4.0
0.501	0.80869	−0.016	1.39815	0.002	1233.7	4.0
0.550	0.80794	−0.012	1.39697	0.002	1231.3	4.0
0.600	0.80714	−0.009	1.39556	0.002	1228.8	3.9
0.650	0.80630	−0.004	1.39422	0.002	1226.2	3.7
0.700	0.80538	0.006	1.39279	0.002	1223.2	3.2
0.750	0.80450	0.009	1.39133	0.002	1220.7	3.0
0.801	0.80353	0.016	1.38982	0.002	1217.6	2.4
0.850	0.80260	0.017	1.38815	0.001	1214.8	1.9
0.899	0.80161	0.021	1.38658	0.001	1211.8	1.3
0.949	0.80064	0.017	1.38483	0.000	1208.7	0.6
Propanol (1) + 3-Methyl-1-butanol (2)						
0.050	0.80640	0.018	1.40447	0.000	1234.4	−2.7
0.100	0.80612	0.021	1.40366	0.001	1233.5	−2.0
0.150	0.80583	0.024	1.40281	0.001	1232.3	−1.5
0.201	0.80554	0.026	1.40200	0.001	1231.1	−1.0
0.251	0.80525	0.026	1.40115	0.002	1230.0	−0.5
0.300	0.80497	0.026	1.40020	0.002	1228.8	−0.1
0.351	0.80466	0.026	1.39919	0.002	1227.5	0.3
0.400	0.80437	0.024	1.39830	0.002	1226.2	0.7
0.450	0.80407	0.021	1.39734	0.002	1224.9	1.0
0.500	0.80375	0.019	1.39621	0.002	1223.4	1.2
0.551	0.80341	0.018	1.39507	0.002	1222.0	1.4
0.600	0.80308	0.015	1.39396	0.002	1220.0	1.1
0.650	0.80272	0.012	1.39278	0.002	1218.5	1.2
0.700	0.80234	0.012	1.39148	0.002	1217.0	1.4
0.749	0.80196	0.010	1.39035	0.002	1215.3	1.3
0.799	0.80155	0.008	1.38898	0.002	1213.6	1.3
0.850	0.80113	0.006	1.38757	0.001	1211.8	1.2
0.900	0.80069	0.004	1.38610	0.001	1210.0	1.0
0.950	0.80022	0.003	1.38458	0.000	1208.2	0.8

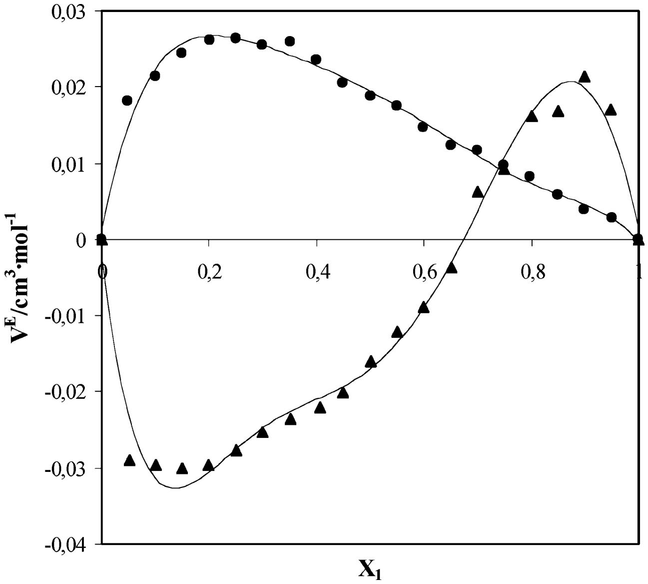

Figure 1. Excess molar volumes of mixtures: ▲, propanol (1) + 2-methyl-1-butanol (2); ●, propanol (1) + 3-methyl-1-butanol (2). Redlich−Kister fit curves (—) at 298.15 K.

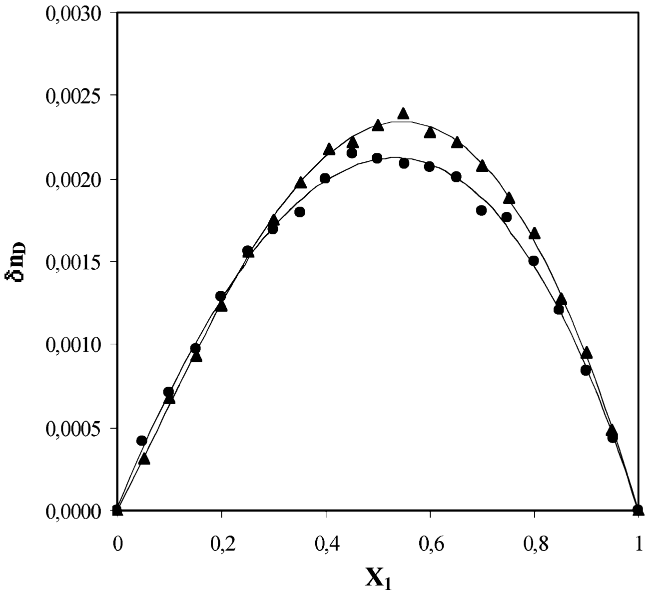

Figure 2. Change of refractive indices: ▲, propanol (1) + 2-methyl-1-butanol (2); ●, propanol (1) + 3-methyl-1-butanol (2). Redlich−Kister fit curves (—) at 298.15 K.

Results and Discussion

Density, Refractive Index, and Speed of Sound. Table 2 lists the measured density ρ, refractive index n_D, and speed of sound u data at 298.15 K with the corresponding excess molar volume V^E, refractive index deviation δn_D, and speed of sound deviation δu for the binary mixtures of propanol + 2-methyl-1-butanol and propanol + 3-methyl-1-butanol.

The excess molar volumes of binary mixtures were calculated from density measurements by applying

$$V^E = x_1M_1(1/\rho - 1/\rho_1) + x_2M_2(1/\rho - 1/\rho_2) \qquad (1)$$

where ρ is the density of the mixture, ρ_1 and ρ_2 are the densities of the pure substances, M_1 and M_2 are the molar masses, and x_1 and x_2 are the mole fractions. The uncertainty in the calculation of V^E from density measurements was estimated to be ± 0.001 cm^3·mol^{-1}. Figure 1 illustrates the excess molar volumes of the two binary systems at 298.15 K.

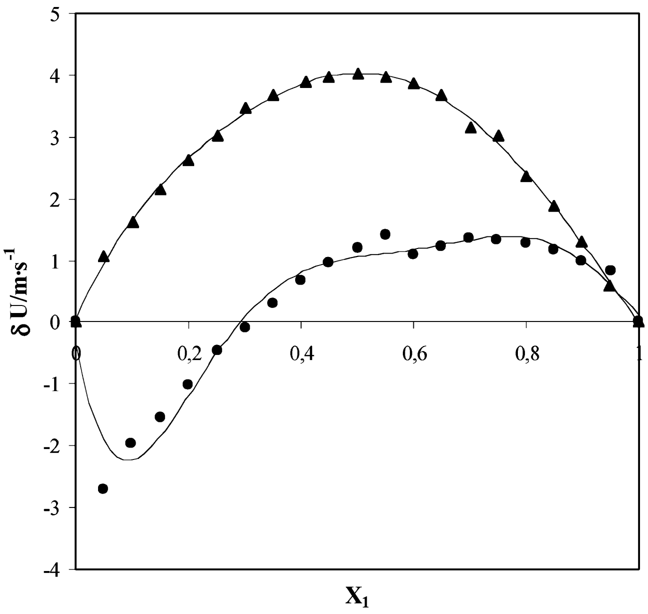

Figure 3. Change of speed sounds on mixing: ▲, propanol (1) + 2-methyl-1-butanol (2); ●, propanol (1) + 3-methyl-1-butanol (2). Redlich−Kister fit curves (—) at 298.15 K.

The changes of refractive index δn_D at 298.15 K from the linear additive value of the mole fraction is obtained by

$$\delta n_D = n_D - (x_1 n_{D1} + x_2 n_{D2}) \tag{2}$$

where n_D is the refractive index of the mixture; n_{D1} and n_{D2} are the refractive indices of the pure compounds. The plot of δn_D versus the mole fraction x_1 of the most volatile compound of each binary system is given in Figure 2.

In the same way, the changes of speed of sound on mixing were calculated by

$$\delta u = u - (x_1 u_1 + x_2 u_2) \tag{3}$$

where u is the speed of sound of the mixture; u_1 and u_2 are the speeds of sound of the pure compounds. The plot of δu versus the mole fraction x_1 of the more volatile compound of each binary system is given in Figure 3.

Excess molar volumes and changes of refractive index and speeds of sound on mixing of the binary systems were fitted to Redlich−Kister polynomials of the form:

$$(V^E \text{ or } \delta_D \text{ or } \delta u) = x_1 x_2 \sum_{k \geq 0} a_k (x_1 - x_2)^k \tag{4}$$

where a_k is the adjustable parameters obtained by a least-squares fit method; k is the degree of the polynomial expansion. Table 3 lists the parameters with their standard deviations σ. The coefficients a_k were used to calculate the solid curves (see Figures 1 to 3). The standard deviations σ are defined as follows:

$$\sigma = \sqrt{\frac{\sum (Z_{cal} - Z_{exp})_i^2}{N - m}} \tag{5}$$

where N is the number of experimental data, m is the number of equation parameters, and Z is the considered property (V^E or δn_D or δu).

Table 3. Adjustable Parameters (a_K) with the Standard Deviations (σ) for Excess Molar Volumes (V^E), Refractive Index Deviations (δn_D), and Speeds of Sound Deviations (δu)

	V^E/cm^3·mol^{-1}	δn_D	δu/m·s^{-1}
	Propanol (1) + 2-Methyl-1-butanol (2)		
a_0	−0,068	0.008	16.2
a_1	0,105	0.001	0.4
a_2	0,142	0.014	−2.2
a_3	0,394	0.001	−4.6
a_4	−0,216	−0.023	3.6
σ	0.004 (cm^3·mol^{-1})	0.000	0.1 (m·s^{-1})
	Propanol (1) + 2-Methyl-1-butanol (2)		
a_0	0,079	0.008	4,2
a_1	−0,075	0.001	2,2
a_2	0,028	0,014	−0,5
a_3	−0,070	0.001	31,7
a_4	0,127	−0,023	−26,6
σ	0.001 (cm^3·mol^{-1})	0.000	0.2 (m·s^{-1})

VLE Data. Vapor−liquid equilibrium data (T, x_1, y_1) for propanol (1) + 2-methyl-1-butanol (2) and propanol (1) + 3-methyl-1-butanol (2) binary systems at 101.3 kPa are presented in Table 4. The $T-x_1-y_1$ phase diagrams are shown in Figures 4 and 5.

The activity coefficients γ_i of the components were calculated from

$$\gamma_i = \frac{y_i \Phi_i P}{x_i P_i^0} \tag{6}$$

where x_i and y_i are the liquid and vapor mole fractions in equilibrium, Φ_i is a vapor phase correction factor, P is the total pressure, and P_i^0 is the vapor pressure of pure component i. These vapor pressures were calculated from the Antoine equation:

$$\log (P_i^0/\text{kPa}) = A_i - \frac{B_i}{(T/\text{K}) + C_i} \tag{7}$$

The constants A_i, B_i, and C_i are reported in Table 5, and their values were obtained from Riddick et al.[2]

The vapor phase correction factor is given by

$$\Phi_i = \frac{\phi_i}{\phi_i^{sat}} \exp\left[-\frac{V_i(P - P_i^0)}{RT}\right] \tag{8}$$

where ϕ_i is the fugacity coefficient of component i in the mixture, ϕ_i^{sat} is the fugacity coefficient at saturation, and V_i is the molar volume of component i in the liquid phase.

The fugacity coefficients for ϕ_1 and ϕ_2 were calculated by

$$\ln \phi_1 = \frac{P}{RT}(B_{11} + y_2^2 \delta_{12}) \tag{9}$$

$$\ln \phi_2 = \frac{P}{RT}(B_{22} + y_1^2 \delta_{12}) \tag{10}$$

where P is the total pressure; T is the experimental temperature; y_1 and y_2 are the vapor mole fractions of compounds 1 and 2; B_{11} and B_{22} are the second virial coefficients of pure compounds 1 and 2; and $\delta_{12} = 2B_{12} - B_{11} - B_{22}$, in which B_{12} is the second cross virial coefficient.

Pitzer's correlation for the second virial coefficient was extended to mixtures by Reid et al.[4] to calculate B_{12}

Table 4. Vapor−Liquid Equilibrium Data for Propanol (1) + 2-Methyl-1-butanol (2) and Propanol (1) + 3-Methyl-1-butanol (2) Systems: Liquid-Phase Mole Fraction (x_1), Vapor-Phase Mole Fraction (Y_1), Boiling Temperature (T), Activity Coefficients (γ_1 and γ_2), Fugacity Coefficients (ϕ_1 and ϕ_2), and Fugacity Coefficients at Saturation (ϕ_1^s and ϕ_2^s) at 101.3 kPa

x_1	y_1	T/K	γ_1	γ_2	ϕ_1	ϕ_2	ϕ_1^s	ϕ_2^s
Propanol (1) + 2-Methyl-1-butanol (2)								
0.000	0.000	401.93						
0.039	0.115	399.59	1.120	0.991	0.979	0.962	0.939	0.965
0.071	0.198	397.83	1.118	0.985	0.978	0.961	0.941	0.966
0.124	0.312	395.18	1.091	0.980	0.977	0.960	0.944	0.968
0.177	0.396	392.97	1.039	0.988	0.976	0.959	0.947	0.970
0.220	0.467	391.16	1.043	0.981	0.976	0.959	0.949	0.971
0.277	0.541	388.90	1.032	0.987	0.975	0.958	0.951	0.973
0.345	0.622	386.49	1.029	0.979	0.974	0.957	0.954	0.974
0.373	0.652	385.52	1.030	0.976	0.974	0.957	0.955	0.975
0.405	0.679	384.51	1.022	0.985	0.974	0.956	0.956	0.976
0.442	0.709	383.52	1.010	0.988	0.973	0.956	0.957	0.976
0.474	0.736	382.52	1.011	0.987	0.973	0.955	0.958	0.977
0.524	0.776	381.04	1.014	0.979	0.973	0.955	0.960	0.978
0.625	0.836	378.43	1.001	1.007	0.972	0.954	0.962	0.980
0.685	0.873	376.83	1.009	0.988	0.971	0.953	0.964	0.981
0.741	0.898	375.53	1.004	1.016	0.971	0.953	0.965	0.981
0.803	0.928	374.13	1.006	0.998	0.970	0.952	0.966	0.982
0.856	0.951	373.08	1.004	0.969	0.970	0.951	0.967	0.983
0.898	0.965	372.16	1.004	1.015	0.970	0.951	0.968	0.983
0.935	0.980	371.43	1.006	0.938	0.970	0.951	0.968	0.983
0.962	0.988	370.87	1.006	0.985	0.969	0.950	0.969	0.984
0.980	0.994	370.57	1.004	0.948	0.969	0.950	0.969	0.984
1.000	1.000	370.29						
Propanol (1) + 3-Methyl-1-butanol (2)								
0.000	0.000	404.27						
0.040	0.102	401.44	0.917	1.006	0.979	0.961	0.937	0.965
0.080	0.192	399.36	0.918	1.014	0.978	0.961	0.939	0.966
0.130	0.293	396.92	0.927	1.019	0.977	0.960	0.942	0.968
0.181	0.395	394.48	0.967	1.008	0.977	0.959	0.945	0.970
0.239	0.489	391.49	0.995	1.019	0.976	0.958	0.948	0.972
0.293	0.563	389.35	1.000	1.014	0.975	0.957	0.951	0.974
0.329	0.610	388.11	1.005	0.997	0.975	0.957	0.952	0.975
0.404	0.692	385.33	1.016	0.984	0.974	0.956	0.955	0.976
0.441	0.725	383.99	1.019	0.986	0.973	0.955	0.956	0.977
0.511	0.778	381.93	1.011	0.985	0.973	0.954	0.959	0.979
0.559	0.810	380.62	1.006	0.983	0.972	0.954	0.960	0.979
0.597	0.836	379.47	1.011	0.972	0.972	0.953	0.961	0.980
0.620	0.851	378.94	1.010	0.956	0.972	0.953	0.961	0.980
0.670	0.868	377.55	1.000	1.032	0.971	0.953	0.963	0.981
0.739	0.901	375.76	1.002	1.052	0.971	0.952	0.964	0.982
0.809	0.932	374.20	1.000	1.054	0.970	0.951	0.966	0.983
0.864	0.951	373.05	0.996	1.117	0.970	0.951	0.967	0.984
0.900	0.966	372.30	0.998	1.088	0.970	0.950	0.967	0.984
0.935	0.981	371.60	1.001	0.964	0.970	0.950	0.968	0.984
0.961	0.989	371.08	1.000	0.985	0.969	0.950	0.968	0.985
0.978	0.994	370.75	0.999	0.994	0.969	0.950	0.969	0.985
1.000	1.000	370.29						

with Tsonopoulos[5] modification for polar molecules to calculate B_{12} by

$$B_{12} = \frac{RT_{c12}}{P_{c12}}(B_{11} + \omega_{12}B_{22} + aT_r^{-6} - bT_r^{-8}) \tag{11}$$

where a is the polarity parameter, b is the association parameter, T_r is the reduced temperature, and B_{11} and B_{12} are functions that depend exclusively on reduced temperature that can be represented satisfactorily by

$$B_{11} = 0.083 - 0.422/T_r^{1.6} \tag{12}$$

$$B_{22} = 0.139 - 0.172/T_r^{4.2} \tag{13}$$

The mixing rules proposed by Prausnitz[6] for the calculation of ω_{12}, T_{c12}, and P_{c12} are

$$\omega_{12} = \frac{\omega_1 + \omega_2}{2} \tag{14}$$

where ω_1 and ω_2 are the acentric factors of compounds 1 and 2, and

$$T_{c12} = (1 - k_{ij})(T_{c1}T_{c2})^{0.5} \tag{15}$$

where T_{c1} and T_{c2} are the critical temperatures of compounds 1 and 2, and k_{ij} is the binary interaction constant proposed by Lee and Chen.[7] For the alcohol + acetate mixtures, $k_{ij} = 0.08$.

Also

$$P_{c12} = \frac{Z_{c12}RT_{c12}}{V_{c12}} \tag{16}$$

where Z_{c12} is calculated by

$$Z_{c12} = \frac{Z_{c1} + Z_{c2}}{2} \tag{17}$$

Z_{c1} and Z_{c2} are the critical compressibility factors, and V_{c12} is defined by the expression:

$$V_{c12} = \left(\frac{V_{c1}^{\ 1/3} + V_{c2}^{\ 1/3}}{2}\right)^3 \tag{18}$$

where V_{c1} and V_{c2} are the critical volumes of compounds 1 and 2. Values of P_c, V_c, T_c, Z_c, and ω have been obtained from the literature[8] and are presented in Table 6.

The fugacity coefficients at saturation ϕ_1^{sat} and ϕ_2^{sat} were calculated by the expressions:

$$\phi_1^{sat} = \exp\frac{B_{11}P_1^{sat}}{RT} \tag{19}$$

$$\phi_2^{sat} = \exp\frac{B_{22}P_2^{sat}}{RT} \tag{20}$$

The activity coefficients were correlated with the Margules, van Laar, Wilson, NRTL, and UNIQUAC equations. To determine the constants of each model, we have used the method

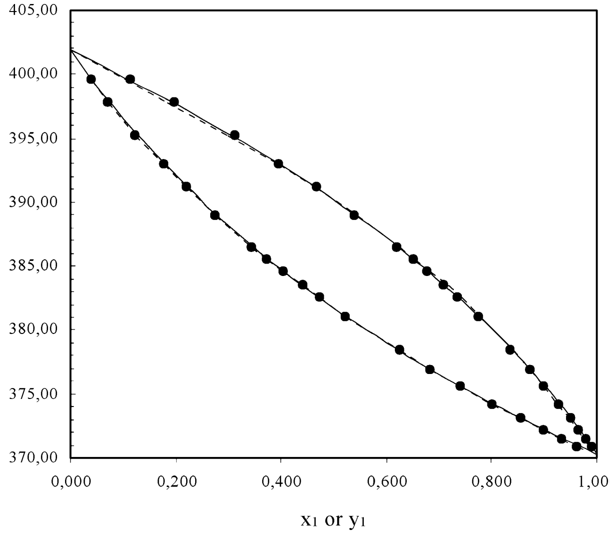

Figure 4. $T-x_1-y_1$ diagram for propanol (1) + 2-methyl-1-butanol (2) at 101.3 kPa: ●, experimental data; - -, Wilson correlation; —, ASOG prediction.

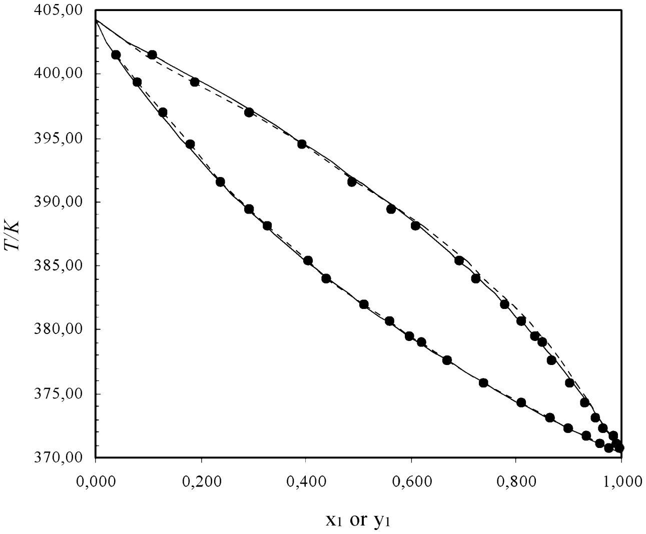

Figure 5. $T-x_1-y_1$ diagram for propanol (1) + 3-methyl-1-butanol (2) at 101.3 kPa: ●, experimental data; - -, Wilson correlation; —, ASOG prediction.

Table 5. Antoine Coefficients[a] (Equation 7)

compound	A_i	B_i	C_i
propanol	6.87613	1441.705	−74.291
2-methyl-1-butanol	6.19220	1195.26	−116.32
3-methyl-1-butanol	6.07851	1128.19	−126.68

[a] Ref 5.

"VLE calc" suggested by Gess et al.[9] Estimation of the parameters for the equation was based on the iterative solution, using the maximum likelihood regression of the objective function Q_i,[10] with the activity coefficients obtained from the consistency test as experimental values:

$$Q_i = \sum\left(\frac{\gamma_{\text{exptl}} - \gamma_{\text{calcd}}}{\gamma_{\text{exptl}}}\right)^2 \tag{21}$$

where γ_{exptl} is the activity coefficients calculated from experimental data; γ_{calcd} is the coefficients calculated with the correlations. The parameters, the average deviation in T (ΔT), and the average deviation in y (Δy) are listed in Table 7. Also, the ASOG[11] method was used to obtain predictions in Figures 4 and 5.

The thermodynamic consistency of the experimental data was checked by means of a modified Dechema test[12] where the fugacity coefficients are calculated by the method of Hayden and O'Connel.[13] Activity coefficients are calculated by using the four-suffix Margules equation:

$$\bar{g}^{E}/RT = x_1x_2[Ax_2 + Bx_1 - Dx_1x_2] \tag{22}$$

with the corresponding activity coefficients:

$$\ln \gamma_1 = x_2^{\,2}[A + 2(B - A - D)x_1 + 3Dx_1^{\,2}] \tag{23}$$

$$\ln \gamma_2 = x_1^{\,2}[B + 2(A - B - D)x_2 + 3Dx_2^{\,2}] \tag{24}$$

Table 6. Published Parameters[7] Used for the Calculation of Fugacity Coefficients: Critical Temperature (T_c), Critical Pressure (P_c), Critical Volume (V_c), Critical Compression Factor (Z_c), and Acentric Factor (ω) of Pure Compounds

	T_c	P_c	V_c		
	K	Pa	$m^3·kmol^{-1}$	Z_c	ω
propanol	536.71	5.17·E+6	0.2185	0.253	0.6279
2-methyl-1-butanol	565.00	3.88·E+6	0.3270	0.270	0.6784
3-methyl-1-butanol	579.45	3.88·E+6	0.3270	0.263	0.5558

Table 7. Correlation Parameters for Activity Coefficients and Average Deviation for the Studied Systems

equation	A_{12}	A_{21}	ΔT/K	Δy_1
Propanol (1) + 2-Methyl-1-butanol (2)				
Margules[a]	−0.0085	0.1305	0.22	0.008
van Laar[a]	0.0292	0.5293	0.14	0.008
Wilson[b]	−1088.44	2837.92	0.19	0.008
NRTL[c] (α_{12} = 0.46)	2948.60	−1698.72	0.20	0.008
UNIQUAC[d]	3786.38	−2029.87	0.20	0.008
Propanol (1) + 3-Methyl-1-butanol (2)				
Margules[a]	−0.2512	0.1147	0.27	0.009
van Laar[a]	0.2007	−0.0113	2.10	0.047
Wilson[b]	−1921.09	5338.87	0.31	0.011
NRTL[c] (α_{12} = 11.05)	−165.89	62.98	0.47	0.011
UNIQUAC[d]	4362.53	−2337.46	0.31	0.010

[a] Margules and van Laar constants (dimensionless). [b] Wilson's interaction parameters ($J·mol^{-1}$). [c] NRTL's interaction parameters ($J·mol^{-1}$). [d] UNIQUAC's interaction parameters ($J·mol^{-1}$).

Table 8. Results of the Thermodynamic Consistency Test

system	average deviation Δy_1	A	B	D
propanol (1) + 2-methyl-1-butanol (2)	0.009	0.1229	0.2120	0.4183
propanol (1) + 3-methyl-1-butanol (2)	0.008	−0.2773	0.0725	−0.1848

Parameters A, B, and D were estimated using the error-in-variables regression maximum likelihood technique. The constraint equation for the regression was

$$F = P - \left(\frac{x_1\gamma_1^{*}f_1^{0}}{\phi_1} + \frac{x_2\gamma_2^{*}f_2^{0}}{\phi_2}\right) \tag{25}$$

Here the asterisk (*) denotes a calculated or predicted value. An experimental value has no asterisk; f_1^0 and f_2^0 are the standard state fugacities. The errors in the prediction of y_1 were calculated. Predicted y_1^* values were obtained using

$$y_1^{*} = \frac{x_1\gamma_1^{*}f_1^{0}}{\phi_1 P^{*}} \tag{26}$$

An average deviation was calculated from

$$\text{average deviation} = \frac{\sum_{i=1}^{n}|\Delta y|}{n} \tag{27}$$

Here $\Delta y = y_1 - y_1^*$ and n = number of experimental data points. To pass the consistency test, a system must have an average deviation less than 0.01. The two systems included in this work have passed this consistency test. In Table 8, we show these results and the values the A, B, and D of eqs 22 to 24.

We also carried out the Margules constant test using the program of Gess et al.[9] The Margules constant can be used to indicate the ideality of a system. Systems that yield a Margules constant whose absolute value is less than 0.60 can be considered ideal, while those that yield an absolute value greater than 0.60 can be considered nonideal. This criterion for

Table 9. Results of the Margules Constant Test

system	Margules constant
propanol (1) + 2-methyl-1-butanol (2)	0.0416
propanol (1) + 3-methyl-1-butanol (2)	−0.0932

classification however is not rigorous. Table 9 shows the values of this constant.

Conclusions

New VLE data not previously reported in the literature have been measured for the systems propanol + 2-methyl-1-butanol and propanol + 3-methyl-1-butanol as well as binary parameters, values of different correlations, and necessary physical properties for modeling and simulation of wine distillation. Both systems present ideal behavior. The ASOG method prediction has a perfect agreement with experimental data in both cases. Correlations for the propanol + 2-methyl-1-butanol system are very similar, with Van Laar correlation slightly better than the others. A better correlation for the propanol + 3-methyl-1-butanol system is the Margulles one, with the Van Laar correlation the one that has higher deviation from experimental data (shown in Table 7). The excess molar volume trend is very different between both systems. Values of propanol + 3-methyl-1-butanol system are positive and present asimetric curve, while values of propanol + 2-methyl-1-butanol system show a sigmoid trend. The change of refractive indices appear positive values, a bit bigger in case of propanol + 2-methyl-1-butanol. Finally, changes of the speed of sound values are positive in the propanol + 2-methyl-1-butanol system, otherwise in the propanol + 3-methyl-1-butanol system there is a sigmoid behavior.

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