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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 Methanol + 2-Methyl-1-butanol and Ethanol + 2-Methyl-1-butanol

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Densities, refractive indices, and speeds of sound at 298.15 K and isobaric vapor−liquid equilibria (VLE) data at 101.3 kPa were reported for the binary mixtures methanol + 2-methyl-1-butanol and ethanol + 2-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

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.[1,2] 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. By this, 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 would be calculated, and results can be applied to study the distillation of wine.

Experimental Section

Materials. Methanol (99.8 mol %) was supplied by Fluka. Ethanol (99.5 %) was supplied by Panreac. Both were used without further purification. 2-Methyl-1-butanol (99 mol %) from Aldrich was 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 %. All products were degassed using ultrasound and dried on molecular sieves (pore diameter 3.10(E−10) m from Fluka) before use. Densities, refractive indexes, and normal boiling points of the pure substances are given in Table 1 and compared with literature values of Riddick et al.[3] and Tojo et al..[4]

Apparatus and Procedure. The still used to measure VLE data was a dynamic recirculating apparatus described by Resa et al.[5] 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·cm^{-3}, which 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 temperature was controlled like 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·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.

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 methanol + 2-methyl-1-butanol and ethanol + 2-methyl-1-butanol.

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

$$V^E = x_1 M_1 (1/\rho - 1/\rho_1) + x_2 M_2 (1/\rho - 1/\rho_2) \qquad (1)$$

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

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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.[b]	obs	lit.[a]
methanol	0.78714	0.78637	1.32667	1.32652	1102	1102	337.65	337.696
ethanol	0.78536	0.78493	1.35916	1.35941	1143	1142	351.50	351.44
2-methyl-1-butanol	0.81487	0.8150	1.40872	1.4086	1253	na[c]	401.86	401.9

[a] Ref 1. [b] Ref 4. [c] na, not available.

Table 2. Densities, Refractive Indices, and Speed of Sounds for Methanol (1) + 2-Methyl-1-butanol (2) and Ethanol (1) + 2-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)

	ρ	V^E			u	δu
x_1	g·cm^{-3}	cm^3·mol^{-1}	n_D	δn_D	m·s^{-1}	m·s^{-1}
Methanol (1) + 2-Methyl-1-butanol (2)						
0.0485	0.81430	0,007	1.40702	0.003	1250.7	4.8
0.1016	0.81363	0,016	1.40511	0.005	1246.7	8.8
0.1543	0.81290	0,029	1.40324	0.007	1242.6	12.5
0.1987	0.81222	0,038	1.40162	0.010	1238.7	15.6
0.2528	0.81135	0,051	1.39907	0.012	1233.9	18.9
0.3017	0.81050	0,062	1.39712	0.013	1229.0	21.4
0.3496	0.80949	0,086	1.39461	0.015	1223.0	22.6
0.4005	0.80836	0,106	1.39181	0.016	1217.0	24.5
0.4506	0.80725	0,117	1.38875	0.018	1210.7	25.7
0.4987	0.80612	0,125	1.38569	0.019	1204.2	26.5
0.5502	0.80484	0,133	1.38222	0.019	1197.2	27.1
0.6003	0.80340	0,143	1.37832	0.019	1188.8	26.4
0.6487	0.80191	0,147	1.37416	0.019	1180.7	25.7
0.7003	0.80027	0,147	1.36946	0.019	1171.5	24.1
0.7504	0.79844	0,147	1.36420	0.018	1162.7	23.0
0.8002	0.79650	0,140	1.35846	0.016	1151.4	19.2
0.8503	0.79435	0,132	1.35214	0.014	1142.2	17.6
0.9004	0.79196	0,118	1.34482	0.010	1131.5	14.4
0.9503	0.78939	0,094	1.33618	0.006	1120.5	11.0
Ethanol (1) + 2-Methyl-1-butanol (2)						
0.0486	0.81411	−0.005	1.40734	0.001	1247.7	1.6
0.1013	0.81323	−0.007	1.40583	0.002	1245.0	4.5
0.1523	0.81231	−0.007	1.40424	0.003	1241.4	6.4
0.1987	0.81139	−0.006	1.40277	0.004	1237.6	7.8
0.2503	0.81038	−0.005	1.40112	0.005	1233.6	9.2
0.3004	0.80933	−0.006	1.39926	0.005	1229.6	10.7
0.3486	0.80822	−0.003	1.39756	0.006	1225.3	11.7
0.4003	0.80702	−0.002	1.39549	0.007	1221.0	12.9
0.4502	0.80574	0.002	1.39341	0.007	1215.9	13.3
0.5004	0.80441	0.003	1.39120	0.007	1210.5	13.3
0.5502	0.80301	0.006	1.38899	0.007	1205.4	13.5
0.6004	0.80143	0.015	1.38636	0.007	1199.4	12.9
0.6503	0.79981	0.017	1.38373	0.007	1193.1	12.2
0.7000	0.79810	0.019	1.38109	0.007	1186.9	11.3
0.8009	0.79432	0.019	1.37475	0.006	1173.0	8.4
0.8503	0.79234	0.016	1.37134	0.005	1166.0	6.6
0.9002	0.79013	0.011	1.36758	0.003	1158.2	4.3
0.9503	0.78777	0.0059	1.36358	0.002	1150.2	1.7

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.

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, and 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.

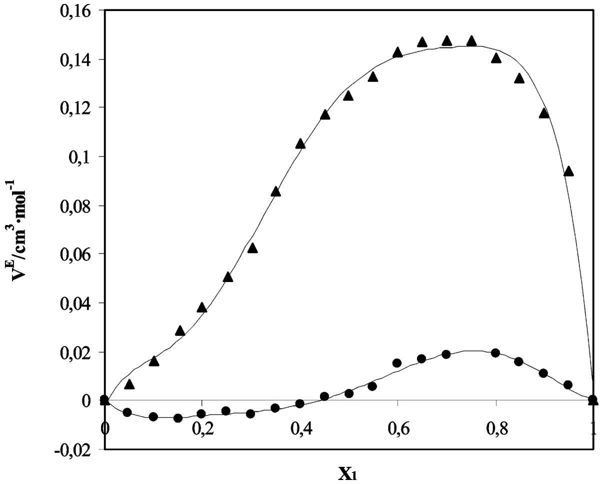

Figure 1. Excess molar volumes of mixtures of ▲, methanol (1) + 2-methyl-1-butanol (2); ●, ethanol (1) + 2-methyl-1-butanol (2). —, Redlich−Kister fit curves at 298.15 K.

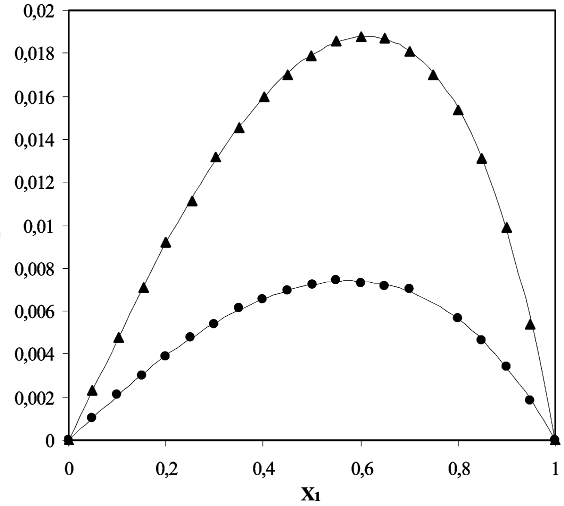

Figure 2. Change of refractive indices on ▲, methanol (1) + 2-methyl-1-butanol (2); ●, ethanol (1) + 2-methyl-1-butanol (2). —, Redlich−Kister fit curves at 298.15 K.

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

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

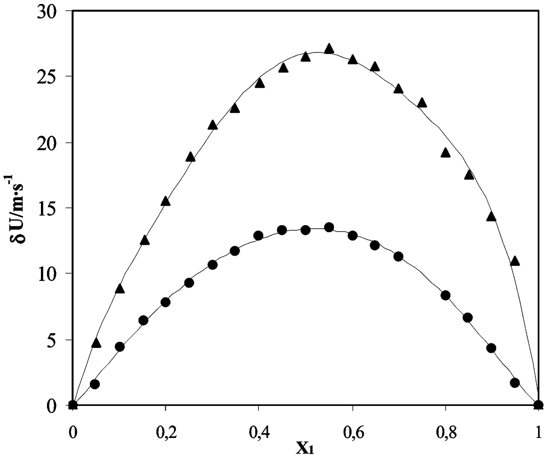

Figure 3. Change of speed of sounds on mixing ▲, methanol (1) + 2-methyl-1-butanol (2); ●, ethanol (1) + 2-methyl-1-butanol (2). —, Redlich−Kister fit curves at 298.15 K.

Table 3. Adjustable Parameters (a_k) with 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})
	Methanol (1) + 2-Methyl-1-butanol (2)		
a_0	0.514	0.072	−22.2
a_1	0.375	0.029	5.8
a_2	−0.227	0.014	−0.6
a_3	0.541	0.010	0.0
a_4	0.984	−0.001	0.0
σ	0.004	0.000	8.7
	Ethanol (1) + 2-Methyl-1-butanol (2)		
a_0	0,133	0,029	53,6
a_1	0,204	0,009	4,4
a_2	0,115	0,003	−3,4
a_3	0,354	0,001	−5,9
a_4	0,411	−0,002	−11,8
σ	0.004	0.000	0.2

Table 4. Vapor−Liquid Equilibrium Data for for Methanol (1) + 2-Methyl-1-butanol (2) and Ethanol (1) + 2-Methyl-1-butanol (2) Systems[a]

x_1	y_1	T/K	γ_1	γ_2	ϕ_1	ϕ_2	ϕ_1^s	ϕ_2^s
		Methanol (1) + 2-Methyl-1-butanol (2)						
0.000	0.000	401.58						
0.012	0.098	398.75	1.105	1.011	1.018	0.962	0.989	0.965
0.038	0.273	393.59	1.138	0.998	1.008	0.962	0.991	0.969
0.064	0.393	389.25	1.090	1.002	1.002	0.963	0.992	0.973
0.090	0.474	385.55	1.044	1.024	0.998	0.965	0.993	0.975
0.122	0.572	381.02	1.054	1.028	0.994	0.967	0.994	0.978
0.155	0.634	377.68	1.013	1.045	0.991	0.969	0.995	0.980
0.167	0.663	376.22	1.027	1.034	0.990	0.971	0.995	0.981
0.212	0.737	371.44	1.043	1.041	0.988	0.974	0.996	0.983
0.247	0.777	368.67	1.031	1.043	0.986	0.976	0.996	0.985
0.307	0.827	364.51	1.010	1.057	0.985	0.979	0.997	0.987
0.351	0.856	361.64	1.006	1.065	0.984	0.981	0.997	0.988
0.389	0.883	358.71	1.031	1.061	0.983	0.983	0.998	0.989
0.446	0.900	356.29	0.996	1.120	0.982	0.984	0.998	0.990
0.474	0.915	354.56	1.012	1.092	0.982	0.985	0.998	0.991
0.638	0.965	347.70	1.013	0.915	0.980	0.990	0.999	0.993
0.698	0.967	345.73	0.999	1.142	0.979	0.999	0.999	0.993
0.787	0.980	343.04	0.992	1.126	0.979	0.991	0.999	0.994
0.833	0.985	341.81	0.988	1.129	0.978	0.992	0.999	0.994
0.905	0.993	339.90	0.985	1.090	0.978	0.993	0.999	0.995
0.956	0.997	338.64	0.983	0.905	0.977	0.993	0.999	0.995
0.975	0.999	338.23	0.981	0.813	0.977	0.993	0.999	0.995
0.000	0.000	337.65						
		Ethanol (1) + 2-Methyl-1-butanol (2)						
0.000	0.000	401.86						
0.021	0.118	398.77	1.194	1.106	0.987	0.962	0.922	0.965
0.062	0.286	393.79	1.127	1.111	0.985	0.960	0.929	0.969
0.102	0.405	389.90	1.089	1.112	0.984	0.959	0.934	0.972
0.141	0.488	386.61	1.047	1.130	0.983	0.957	0.938	0.974
0.175	0.559	383.66	1.053	1.132	0.982	0.956	0.942	0.976
0.216	0.624	380.78	1.041	1.138	0.981	0.955	0.945	0.978
0.274	0.692	377.18	1.022	1.160	0.980	0.954	0.950	0.980
0.328	0.755	373.73	1.041	1.148	0.980	0.953	0.953	0.982
0.385	0.795	371.02	1.024	1.174	0.979	0.952	0.956	0.984
0.416	0.817	369.67	1.017	1.174	0.978	0.951	0.958	0.984
0.446	0.837	368.20	1.021	1.176	0.978	0.951	0.959	0.985
0.476	0.852	366.72	1.024	1.205	0.978	0.950	0.960	0.986
0.516	0.871	365.22	1.018	1.213	0.977	0.949	0.962	0.986
0.550	0.887	363.97	1.019	1.209	0.979	0.949	0.963	0.987
0.580	0.898	362.95	1.012	1.227	0.977	0.948	0.964	0.987
0.695	0.937	359.39	1.002	1.222	0.976	0.947	0.967	0.989
0.817	0.967	355.97	0.998	1.251	0.975	0.945	0.970	0.990
0.922	0.987	353.32	0.996	1.358	0.974	0.944	0.972	0.991
0.972	0.997	352.08	1.000	1.046	0.974	0.943	0.973	0.991
0.993	0.999	351.61	1.000	1.171	0.973	0.943	0.973	0.992
1.000	1.000	351.50						

[a] 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; fugacity coefficients at saturation. ϕ_1^s and ϕ_2^s at 101.3 kPa.

where a_k are the adjustable parameters obtained by a least-squares fit method, and 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:

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

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

VLE Data. Vapor−liquid equilibrium data (T, x_1, y_1) for methanol (1) + 2-methyl-1-butanol (2) and ethanol (1) + 2-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.[3]

The vapor-phase correction factor is given by

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

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.

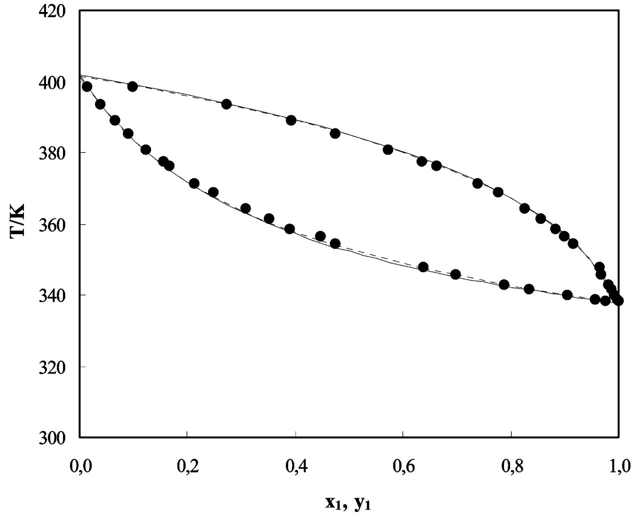

Figure 4. $T-x_1-y_1$ diagram for methanol (1) + 2-methyl-1-butanol (2) at 101.3 kPa: ●, experimental data; - -, Wilson correlation; —, ASOG prediction.

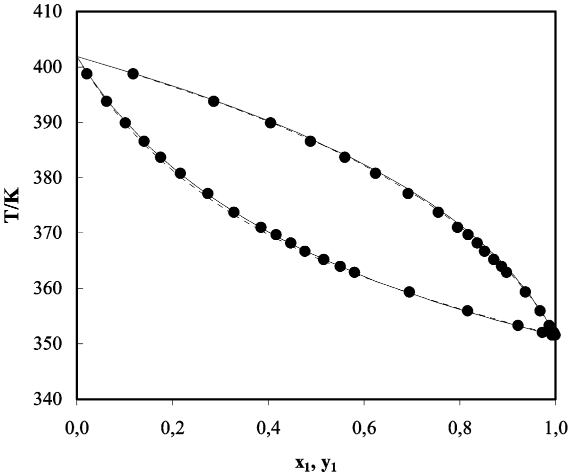

Figure 5. $T-x_1-y_1$ diagram for ethanol (1) + 2-methyl-1-butanol (2) at 101.3 kPa: ●, experimental data; - -, Wilson correlation; —, ASOG prediction.

Table 5. Antoine Coefficients (eq 7)

compound	A_i	B_i	C_i
methanol	7.20519	1581.993	−33.439
ethanol	7.16879	1552.601	−50.731
2-methyl-1-butanol	6.19220	1195.26	−116.32

The fugacity coefficients for ϕ_1 and ϕ_2 were calculated by the expressions:

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

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

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.[6] to calculate B_{12} with Tsonopoulos[7] modification for polar molecules to calculate B_{12} by

Table 6. Published Parameters[10] Used for Calculation of Fugacity Coefficients[a]

	T_c	P_c	V_c		
	K	Pa	$m^3 \cdot kmol^{-1}$	Z_c	ω
methanol	512.58	8.10·E+6	0.1178	0.224	0.5656
ethanol	513.92	6.38·E+6	0.1669	0.248	0.6371
2-methyl-1-butanol	565.00	3.88·E+6	0.3270	0.270	0.6784

[a] Critical temperature, T_c; critical pressure, P_c; critical volume, V_c; critical compression factor, Z_c; and acentric factor, ω, of pure compounds.

$$B_{12} = \frac{RT_{c12}}{P_{c12}}(B^0 + \omega_{12}B^1 + aT_r^{\,-6} - bT_r^{\,-8}) \tag{11}$$

where a is the polarity parameter, b is the association parameter, T_r is the reduced temperature, and B^0 and B^1 are functions that depend exclusively on reduced temperature that can be represented satisfactorily by

$$B^0 = 0.083 - 0.422/T_r^{\,1.6} \tag{12}$$

$$B^1 = 0.139 - 0.172/T_r^{\,4.2} \tag{13}$$

The mixing rules proposed by Prausnitz[8] 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.[9] For the alcohol + alcohol 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

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

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[10] and are presented in Table 6.

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

equation	A_{12}	A_{21}	ΔT/K	Δy_1
	Methanol (1) + 2-Methyl-1-butanol (2)			
Margules[a]	0.1190	0.2341	0.28	0.005
van Laar[a]	0.1213	0.2963	0.27	0.005
Wilson[b]	2009.02	−1116.49	0.31	0.005
NRTL[c] ($\alpha_{12} = 0.30$)	3262.01	−2014.23	0.27	0.005
UNIQUAC[d]	2592.50	−247.02	0.29	0.003
	Ethanol (1) + 2-Methyl-1-butanol (2)			
Margules[a]	0.0837	0.1316	0.12	0.004
van Laar[a]	0.0866	0.1403	0.12	0.004
Wilson[b]	1303.95	−843.85	0.12	0.004
NRTL[c] ($\alpha_{12} = 0.30$)	1997.92	−1380.45	0.12	0.004
UNIQUAC[d]	−404.12	821.13	0.13	0.004

[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}).

The fugacity coefficients at saturation ϕ_1^{s} and ϕ_2^{s} were calculated by

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

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

The activity coefficients were correlated with the Margules,[11] van Laar,[12] Wilson,[13] NRTL,[14] and UNIQUAC[15] equations. To determine the constants of each model, we have used the method "VLE calc" suggested by Gess et al.[16] Estimation of the parameters for the equation was based on the iterative solution, using the maximum likelihood regression of the objective function (Q_i),[17] with the activity coefficients obtained from the consistency test as experimental values:

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

where γ_{exptl} are the activity coefficients calculated from experimental data and γ_{calcd} are 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[18] method was used to obtain predictions (see Figures 4 and 5).

The thermodynamic consistency of the experimental data was checked by means of a modified Dechema test,[19] where the fugacity coefficients are calculated by the method of Hayden and O'Connell[20] and activity coefficients are calculated by using the four-suffix Margules equation:

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

with the corresponding activity coefficients

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

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

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

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

Table 8. Results of the Thermodynamic Consistency Test

system	avg dev Δy_1	A	B	D
methanol (1) + 2-methyl-1-butanol (2)	0.003	0.2221	0.3204	0.3649
ethanol (1) + 2-methyl-1-butanol (2)	0.003	0.1167	0.1593	0.1173

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

$$y_1^* = \frac{x_1y_1^*f_1^{\,0}}{\phi_1P^*} \tag{26}$$

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.

Conclusions

New vapor−liquid equilibria data not previously reported in the literature have been measured for the systems methanol + 2-methyl-1-butanol and ethanol + 2-methyl-1-butanol; as well as binary parameters, values of different correlations and necessary physical properties for modeling and simulation of wine distillation.

The ethanol + 2-methyl-1-butanol system presents a near ideal behavior, and the methanol + 2-methyl-1-butanol system presents a less ideal behavior. Correlations for both systems are very similar. The ASOG method prediction has a perfectly agreement with experimental data in both cases.

Values of excess molar volumes of the methanol + 2-methyl-1-butanol system are positive and clearly bigger than the ethanol + 2-methyl-1-butanol system due to expansive trend and bigger polarity of methanol. On the contrary, corresponding values for ethanol + 2-methyl-1-butanol are very close to zero, due to less polarity of ethanol and that the intermolecular interaction energy of the molecules is small.

In case of change of refractive indices appear positive values. The methanol + 2-methyl-1-butanol system is bigger than the ethanol + 2-methyl-1-butanol system. Finally, changes of speed of sound values are completely analogous as the change of refractive indices.

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