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Vapor−Liquid Equilibrium of Binary Mixtures Containing Ethyl Acetate + 2-Methyl-1-propanol and Ethyl Acetate + 2-Methyl-1-butanol at 101.3 kPa

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Isobaric vapor−liquid equilibria (VLE) data at 101.3 kPa were reported for the binary mixtures ethyl acetate + 2-methyl-1-propanol and ethyl acetate + 2-methyl-1-butanol. 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 vapor−liquid equilibrium (VLE) data for binary systems involved in wine distillation processes for subsequent simulation.[1−5] In this process, multicomponent mixtures are present with the main components being water and ethanol, with several minor compounds such as alcohols, aldehydes, and acetates present. These minor compounds are called congeners. For modeling and process simulation in such mixtures, binary data are needed. By this, it is very important to have available vapor−liquid equilibrium data of mixtures formed by water + congeners, ethanol + congeners, and congeners + congeners. From measurements, parameters of the Wilson, NRTL, and UNIQUAC equations can be calculated, and the results can be applied to simulate the distillation of wine.

Experimental Section

Ethyl acetate mole fraction ($x > 0.998$) and 2-methyl-1-propanol ($x > 0.995$) were supplied by Fluka, and 2-methyl-1-butanol ($x > 0.99$) was supplied by Aldrich. 2-Methyl-1-butanol was purified by distillation in a laboratory column of 100 plates; the purity of the material was checked by gas−liquid chromatography (GLC $x > 0.997$). All products were degassed using ultrasound and dried over molecular sieves (type pore diameter, $3 \cdot 10^{-3}$ m from Fluka) before use. Densities, refractive indices, and boiling points of the pure substances are given in Table 1 and compared with literature values.[6] Instrumentation and apparatus specifications are defined in refs 1 and 2. Standard curves of density versus mole fraction were used to calculate the compositions of the vapor and liquid phases. All samples were prepared by weighing with a Salter electronic balance (model ER-182A, uncertainly ± 0.0001 g). The uncertainty of comparison measurements was estimed to be ± 0.001 mole fraction. Table 2 shows the density composition values.

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

	$\rho/(\mathrm{kg \cdot m^{-3}})$		n_D		$u/(\mathrm{m \cdot s^{-1}})$		T_b/K	
	obs	lit.[a]	obs	lit.[a]	obs	lit.	obs	lit.[a]
ethyl acetate	894.3	894.5	1.36978	1.36978	1139.6	1137.66[b]	350.15	350.261
2-methyl-1-propanol	797.8	797.8	1.39366	1.39389	1186.4	1185.63[b]	380.93	381.036
2-methyl-1-butanol	814.7	815.0	1.40866	1.40860	1251.8	1253.29[c]	401.93	401.850

[a] Riddick et al.[6] [b] Resa et al.[2] [c] Resa et al.[17]

Table 2. Densities ρ for Ethyl Acetate (1) + 2-Methyl-1-propanol (2) and Ethyl Acetate (1) + 2-Methyl-1-butanol (2) at 298.15 K

ethyl acetate (1) + 2-methyl-1-propanol (2)		ethyl acetate (1) + 2-methyl-1-butanol (2)	
x_1	$\rho/(\mathrm{kg \cdot m^{-3}})$	x_1	$\rho/(\mathrm{kg \cdot m^{-3}})$
0.049	802.3	0.050	817.8
0.101	806.8	0.099	820.9
0.153	811.5	0.150	824.2
0.202	816.0	0.200	827.5
0.251	820.6	0.250	830.9
0.300	825.2	0.300	834.4
0.350	829.9	0.349	838.0
0.401	834.7	0.399	841.7
0.451	839.5	0.451	845.6
0.501	844.3	0.499	849.4
0.550	849.0	0.549	853.3
0.600	853.8	0.598	857.3
0.650	858.8	0.650	861.6
0.700	863.7	0.699	865.8
0.751	868.9	0.750	870.2
0.801	873.8	0.793	874.2
0.850	878.7	0.846	879.1
0.900	883.8	0.900	884.2
0.950	888.9	0.950	889.1

Results and Discussion

The activity coefficients γ_i of the components were calculated from

$$\gamma_i = \frac{y_i \Phi_i P}{x_i P_i^0} \tag{1}$$

where x_i and y_i are the liquid and vapor mole fractions in equilibrium, ϕ_i is the fugacity cofficient, P is the total pressure, and P_i^0 is the vapor pressure of pure component i.

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Table 3. Antoine Coefficients (Equation 2)[a]

compound	A_i	B_i	C_i
ethyl acetate	6.18799	1224.673	−57.44
2-methyl-1-propanol	6.50091	1275.197	−97.36
2-methyl-1-butanol	6.19220	1195.26	−116.32

[a] Riddick et al.[6]

Table 4. Vapor−Liquid Equilibrium Data at 101.3 kPa for Ethyl Acetate (1) + 2-Methyl-1-propanol (2) and Ethyl Acetate (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
Ethyl Acetate (1) + 2-Methyl-1-propanol (2)								
0.016	0.053	379.96	1.467	0.994	0.971	0.931	0.965	0.971
0.048	0.148	377.93	1.390	0.995	0.971	0.933	0.964	0.972
0.083	0.237	375.96	1.361	0.994	0.970	0.936	0.963	0.974
0.110	0.306	374.37	1.378	0.988	0.970	0.937	0.962	0.975
0.159	0.397	371.87	1.330	0.997	0.969	0.940	0.961	0.977
0.213	0.484	369.40	1.295	1.002	0.968	0.943	0.961	0.978
0.281	0.565	366.75	1.233	1.025	0.967	0.946	0.959	0.980
0.357	0.641	364.08	1.186	1.052	0.966	0.948	0.958	0.982
0.403	0.681	362.67	1.162	1.068	0.966	0.950	0.958	0.982
0.446	0.712	361.47	1.136	1.092	0.965	0.951	0.957	0.983
0.489	0.745	360.19	1.127	1.102	0.965	0.952	0.957	0.984
0.528	0.771	359.24	1.109	1.117	0.965	0.953	0.956	0.984
0.571	0.794	358.30	1.085	1.153	0.964	0.954	0.956	0.985
0.614	0.817	357.26	1.073	1.183	0.964	0.955	0.955	0.985
0.652	0.836	356.99	1.058	1.216	0.964	0.956	0.955	0.985
0.695	0.858	355.59	1.046	1.253	0.963	0.956	0.954	0.986
0.741	0.880	354.72	1.034	1.294	0.963	0.957	0.954	0.986
0.781	0.899	353.95	1.027	1.321	0.963	0.958	0.954	0.987
0.818	0.916	353.29	1.019	1.364	0.962	0.959	0.953	0.987
0.849	0.930	352.73	1.015	1.401	0.962	0.959	0.953	0.987
0.879	0.945	352.20	1.011	1.430	0.962	0.959	0.953	0.987
Ethyl Acetate (1) + 2-Methyl-1-butanol (2)								
0.022	0.129	398.48	1.617	0.994	0.977	0.961	0.908	0.965
0.040	0.197	396.72	1.414	0.991	0.976	0.961	0.910	0.967
0.057	0.257	395.04	1.345	0.988	0.976	0.960	0.912	0.968
0.073	0.310	393.35	1.317	0.989	0.975	0.959	0.915	0.970
0.101	0.391	390.75	1.276	0.986	0.975	0.958	0.918	0.971
0.143	0.489	386.95	1.235	0.995	0.973	0.957	0.923	0.974
0.173	0.548	384.53	1.214	0.997	0.973	0.956	0.926	0.976
0.215	0.623	380.95	1.215	1.003	0.972	0.955	0.930	0.978
0.274	0.698	376.93	1.184	1.015	0.970	0.953	0.935	0.980
0.349	0.760	373.00	1.123	1.053	0.969	0.951	0.939	0.983
0.430	0.823	368.19	1.126	1.084	0.968	0.949	0.944	0.985
0.507	0.862	364.92	1.096	1.124	0.967	0.947	0.947	0.987
0.566	0.886	362.72	1.075	1.162	0.966	0.946	0.950	0.988
0.635	0.909	360.39	1.052	1.224	0.965	0.945	0.952	0.988
0.711	0.931	357.99	1.033	1.308	0.964	0.943	0.954	0.989
0.743	0.941	356.86	1.033	1.325	0.964	0.943	0.955	0.990
0.819	0.959	354.79	1.017	1.441	0.963	0.941	0.957	0.991
0.894	0.976	352.60	1.015	1.600	0.962	0.940	0.959	0.991
0.937	0.984	351.59	1.007	1.884	0.962	0.939	0.960	0.992

[a] x_1, liquid-phase mole fraction; y_1, vapor-phase mole fraction; T, boiling temperature; γ_1 and γ_2, activity coefficients; ϕ_1 and ϕ_2, fugacity coefficients; and ϕ_1^s and ϕ_2^s, fugacity coefficients at saturation at 101.3 kPa.

These vapor pressures were calculated from the Antoine equation:

$$\log (P/\text{kPa}) = A_i - \frac{B_i}{(T/\text{K}) + C_i} \tag{2}$$

and the constants A_i. B_i, and C_i are reported in Table 3. The value constants for ethyl acetate, 2-methyl-1-butanol, and 2-methyl-1-butanol were obtained in the literature from Riddick et al.[6]

The vapor phase correction factor is given by

$$\Phi_i = \frac{\phi_i}{\phi_i^{\text{sat}}} \exp\left[-\frac{V_i(P - P_i^0)}{RT}\right] \tag{3}$$

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.

Vapor−liquid equilibrium data for the two systems have been obtained at 101.3 kPa and are presented in Table 4. The $T-x_1-y_1$ diagrams are shown in Figures 1 and 2.

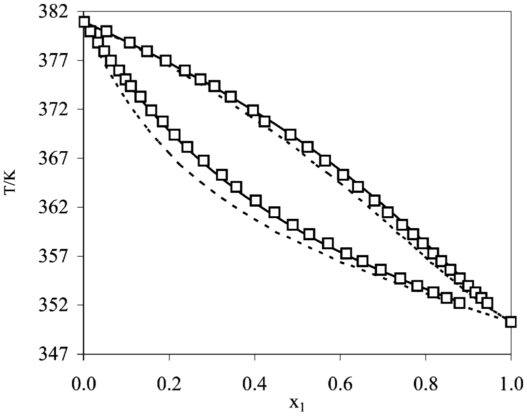

Figure 1. $T-x_1-y_1$ diagram for ethyl acetate (1) + 2-methyl-1-propanol (2) at 101.3 kPa: □, experimental data; —, Wilson correlation; - - -, ASOG prediction.

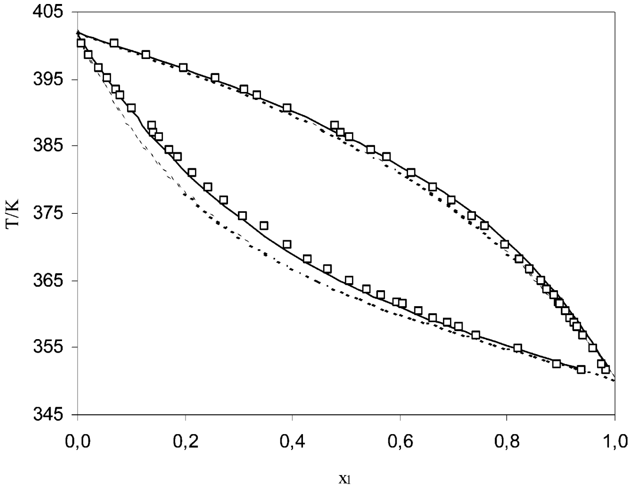

Figure 2. $T-x_1-y_1$ diagram for ethyl acetate (1) + 2-methyl-1-butanol (2) at 101.3 kPa: □, experimental data; —, Wilson correlation; - - -, ASOG prediction.

The activity coefficients were correlated with the Margules,[7] van Laar,[8] Wilson,[9] NRTL,[10] and UNIQUAC[11] equations. To determine the constants of each model, we have used the method "VLE calc" suggested by Gess et al.[12] Estimation of the parameters for the equation was based on the iterative solution, using the maximum likelihood regression of the objective function, Q_i,[13] with the activity coefficients obtained from the consistency test as experimental values:

$$Q_i = \sum_{i=1}^{n} \left(\frac{\gamma_{\text{exptl}} - \gamma_{\text{calcd}}}{\gamma_{\text{exptl}}}\right)^2 \tag{4}$$

where γ_{exptl} are the activity coefficients calculated from experimental data and γ_{calcd} are the coefficients calculated with the y and T of correlations. The parameters along with the average deviation in T (ΔT) and the average deviation in y (Δy) are listed in Table 5. Also the ASOG[14] method was also used for obtaining the predictions (see Figures 1 and 2).

The thermodynamic consistency of the experimental data was checked by means of modified Dechema test,[15] where the fugacity coefficients are calculated by the method of Hayden and O'Connell,[16] and activity coefficients were calculated using the following form of the four-suffix Margules equation:

$$g^E/RT = x_1x_2[Ax_2 + Bx_1 - Dx_1x_2] \tag{5}$$

Table 5. Correlation Parameters for Activity Coefficients and Average Deviation for the Studied Systems

equation	A_{12}	A_{21}	ΔT/K	Δy_1
Ethyl Acetate (1) + 2-Methyl-1-propanol (2)				
Margules[a]	0.3251	0.5055	0.06	0.004
van Laar[a]	0.3417	0.5241	0.05	0.004
Wilson[b]	−545.0541	2117.5819	0.05	0.004
NRTL[c] ($\alpha_{12} = 0.30$)	2547.0629	−927.5590	0.05	0.004
UNIQUAC[d]	1411.8241	−791.4319	0.05	0.004
Ethyl Acetate (1) + 2-Methyl-1-butanol (2)				
Margules[a]	0.2299	0.4494	0.26	0.011
van Laar[a]	0.2512	0.4990	0.24	0.011
Wilson[b]	−680.9558	2338.9882	0.24	0.011
NRTL[c] ($\alpha_{12} = 0.08$)	3417.6828	−1673.7832	0.25	0.011
UNIQUAC[d]	1580.2933	−979.8921	0.24	0.011

[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 6. Results of the Thermodynamic Consistency Test[a]

system	average deviation Δy_1	*A*	*B*	*D*
ethyl acetate (1) + 2-methyl-1-propanol (2)	0.004	0.3681	0.5314	0.1433
ethyl acetate (1) + 2-methyl-1-butanol (2)	0.009	0.3296	0.5165	0.3467

[a] *A*, *B*, and *D* are constants of the Dechema test.

with the corresponding activity coefficients:

$$\ln \gamma_1 = x_2^2[A + 2(B - A - D)x_1 + 3Dx_1^2] \tag{6}$$

$$\ln \gamma_2 = x_1^2[B + 2(A - B - D)x_2 + 3Dx_2^2] \tag{7}$$

Estimated parameters *A*, *B*, and *D* were obtained using the error-in-variables regression maximum likelihood tehnique. The constraint equation for the regression was

$$F = P - \left(\frac{x_1\gamma_1^* f_1^0}{\phi_1} + \frac{x_2\gamma_2^* f_2^0}{\phi_2}\right) \tag{8}$$

Here the asterisk (*) denotes a calculated or predicted value. The experimental value has no asterik; 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

$$y_1^* = \frac{x_1\gamma_1^* f_1^0}{\phi_1 P^*} \tag{9}$$

An average deviation were calculated as

$$\text{average deviation} = \frac{\sum_{i=1}^{n} |\Delta y|}{n} \tag{10}$$

Here $\Delta y = y_1 - y_1^*$ and n = the number of experimental data points. A system must have an average deviation less than 0.01 to satisfy the consistency test. The two systems included in this work have passed the consistency test. Table 6 lists the obtained values for *A*, *B*, and *D* of eqs 6 and 7.

We also carried out the Margules constant test using the program of Gess et al.[12] The Margules constant test 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 grater than 0.60 can be considered nonideal. This criterion for classification, however, is not rigorous. Table 7 shows the values of this constant.

Table 7. Results of the Margules Constant Test

system	Margules constant
ethyl acetate (1) + 2-methyl-1-propanol (2)	0.4573
ethyl acetate (1) + 2-methyl-1-butanol (2)	0.4250

Conclusions

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

Binary systems formed by ester and alcohol groups are considered ideals, based on Margulles constants, activity coefficients, and equilibrium plots. The ASOG method prediction does not have a perfect agreement with experimental data in both cases. As shown in Table 5, deviation of temperature with composition is very similar for all correlations in both systems.

Literature Cited

(1) Resa, J. M.; González, C.; Juez, M.; Ortiz de Landaluce, S. Density, refractive index, speed of sound, for mixtures of ethyl acetate with 2-butanol and 3-methyl-1-butanol. Vapor−liquid equilibrium of ethyl acetate + 3-methyl-1-butanol system. *Fluid Phase Equilib.* **2004**, *217*, 175−180.

(2) Resa, J. M.; González, C.; Goenaga, J. M.; Iglesias, M. Density, refractive index, speed of sound at 298.15 K and vapor−liquid equilibria at 101.3 kPa for binary mixtures of ethyl acetate + 1-pentanol and ethanol + 2-methyl-1-propanol. *J. Chem. Eng. Data* **2004**, *49*, 804−808.

(3) Resa, J. M.; Gonzalez, C.; Goenaga, J. M.; Iglesias, M. Temperature dependence of excess molar volumes of ethanol + water + ethyl acetate. *J. Solution Chem.* **2004**, *33*, 169−198.

(4) Resa, J. M.; Gonzalez, C.; Goenaga, J. M.; Iglesias, M. Influence of temperature on ultrasonic velocity measurements of ethanol + water + ethyl acetate mixtures. *Phys. Chem. Liq.* **2005**, *43*, 65−89.

(5) Resa, J. M.; Gonzalez, C.; Goenaga, J. M.; Iglesias, M. Influence of temperature on the volumetric properties of ethanol + water + 1-pentanol. *J. Serb. Chem. Soc.* **2004**, *69*, 1073−1097.

(6) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*; Wiley-Interscience: New York, 1986.

(7) Margules, M. S. *Akad. B. Wien. Math-Naturwiss. KI. II* **1895**, *104*, 1234−1239.

(8) van Laar, J. J. The vapor pressure of binary mixtures. *Z. Phys. Chem.* **1910**, *72*, 723−751.

(9) Wilson, G. M. Vapor−liquid equilibrium. XI. A new expression for the excess free energy of mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127−130.

(10) Renon, H.; Prausnitz, J. M. Estimation of parameters for the NRTL equation for excess Gibbs energies of strongly non-ideal liquid mixtures. *Ind. Eng. Chem. Process. Des. Dev.* **1969**, *8*, 413−419.

(11) Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partially or completely miscible systems. *AIChE J.* **1975**, *21*, 116−128.

(12) Gess. M. A.; Danner, R. P.; Nagvekar, M. *Thermodynamic Analysis of Vapor-Liquid Equilibria: Recommended Models and a Standard Data Base*; DIPPR/AIChE: New York, 1991.

(13) Patino-Leal, H; Reilly, P. Statistical estimation of parameters in vapor−liquid equilibrium. *AIChE J.* **1982**, *28*, 580−584.

(14) Kojima, K.; Tochigi, K. Prediction of vapor−liquid equilibria by the ASOG Method. Kodansha Ltd: Tokyo, 1979.

(15) Gmehling, J.; Onken, U. *Vapor Liquid Equilibrium Data Collection*; DECHEMA Chemistry Data Series, Vols. 1−8; DECHEMA: Frankfurt, 1977.
(16) Hayden, G.; O'Connell, J. P. A generalized method for predicting second virial coefficients. *Ind. Eng. Chem. Process. Des. Dev.* **1975**, *14*, 209−214.
(17) Resa, J. M.; Gonzalez, C.; Goenaga, J. M. 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. *J. Chem. Eng. Data* **2006**, *51*, 73−78.

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