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Isobaric Vapor−Liquid Equilibria for Binary and Ternary Systems Composed of Water, 1-Propanol, and 2-Propanol at 100 kPa

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Isobaric vapor−liquid equilibria data were obtained for the 2-propanol + 1-propanol binary system and the water + 1-propanol + 2-propanol ternary system at 100 kPa. The data were found to be thermodynamically consistent according to the Van Ness−Byer−Gibbs method for the binary system and according to the McDermott−Ellis method for the ternary one. The binary system is well represented by assuming ideal behavior. The binary interaction parameters obtained from this and our previous work are used to predict the vapor−liquid equilibrium for the ternary system using the UNIQUAC, NRTL, and Wilson models. The ternary system is well predicted from binary data.

Introduction

Distillation is the most common operation for the separation of binary and multicomponent liquid mixtures. The correct design of distillation columns requires the availability of accurate and, if possible, thermodynamically consistent vapor−liquid equilibria (VLE) data and the use of generalized methods to predict the properties of the mixtures. Experimental measurements of vapor−liquid equilibria for ternary or higher mixtures are quite scarce due to the experimental effort necessary to obtain a complete description of the system. VLE data for multicomponent mixtures can usually be predicted using the related binary and pure component data, with fewer experimental measurements.

The binary mixtures of water + 2-propanol and water + 1-propanol at 100 kPa have been investigated previously (Marzal et al., 1996; Gabaldón et al., 1996). In this work, VLE data of the 2-propanol + 1-propanol binary system and the water + 1-propanol + 2-propanol ternary system at 100 kPa are reported.

For the binary system 2-propanol + 1-propanol seven VLE sets of data have been found in the literature (Ballard and Van Winkle, 1952; Polak et al., 1970; Ocon et al., 1973; Gültekin, 1985, 1989; Oracz, 1989; Hongo et al., 1992), as reported in the *TRC Data Bases Floppy Book on Vapor-Liquid Equilibrium Data* (1996). Among these, three sets of data were obtained under isothermal conditions. The three others correspond to isobaric at 101.3 kPa, but differences in measured temperature up to 1.5 K have been observed. No VLE data have been previously reported for the ternary system.

Experimental Section

Chemicals. Milli-Q water and high-purity grade 1-propanol and 2-propanol purchased from Aldrich Chemical were used without further purification. The purities of all chemicals, checked by gas chromatography (GC), were as follows: water, 100.00 mass %; 1-propanol, 99.80 mass %; and 2-propanol, 99.90 mass %. Experimental densities of the pure liquids at 293.15 K were measured in a digital precision densimeter, Anton Paar DMA55, with a thermostated bath controlled to ±0.01 K. The refractive indexes at 293.15 K were measured using an Abbe refractometer (ATAGO 3T). The accuracies in density and refractive index measurements were ±0.000 01 g·cm^{-3} and ±0.0002, respectively. The boiling points were determined using the apparatus described below. The experimental values of these properties are listed in Table 1 together with the literature values (CRC, 1990; TRC, 1994).

Table 1. Physical Properties of Chemicals: Densities *d*, Refractive Indexes *n*, and Boiling Points T_b

	d(293.15 K)/ g·cm^{-3}		n(293.15 K)		T_b(100.0 kPa)/ K	
compound	exptl	lit.	exptl	lit.	exptl	lit.
water	0.998 06	0.998 20^a	1.3334	1.3330^a	372.78	372.79^a
1-propanol	0.803 66	0.803 75^b	1.3853	1.3855^b	369.75	369.95^b
2-propanol	0.785 34	0.785 45^b	1.3774	1.3772^b	354.85	355.09^b

[a] *CRC Handbook of Chemistry and Physics*, 1990. [b] *TRC Thermodynamic Tables Hydrocarbons*, 1994.

Apparatus and Procedure. The equilibrium vessel used in this work is an all-glass, dynamic recirculating still described by Walas (1985), equipped with a Cottrell pump. The still (Labodest model), manufactured by Fischer Labor und Verfahrenstechnik (Bonn, Germany), is capable of handling pressures from 0.25 to 400 kPa and temperatures up to 523.15 K. In the boiler, vapor is generated by external heating. The Cottrell pump ensures the intimate contact between the liquid and vapor phases and also with the temperature sensing element The equilibrium temperature is measured with a digital Ditel thermometer with an accuracy of ±0.01 K. For the pressure measurement, a digital manometer with an accuracy of ±0.01 kPa is used. The temperature probe was calibrated against the ice and steam points of distilled water. High-purity (>99.9 mass %) hexane vapor pressures were used for the manometer calibration.

In each VLE experiment, the pressure was fixed and remained constant using a vacuum pump, and the heating and shaking system of the liquid mixture were turned on. The system was kept at the boiling point at least for 30 min to ensure that the steady state was reached. At this moment, 0.2 cm^3 samples of liquid and condensed vapor of the Cottrell pump were taken for analysis.

Analysis. All the samples were analyzed by using a Varian Star 3400 CX gas chromatograph with a thermal conductivity detector. The GC response was treated with a Star Chromatography Station. The chromatographic column (2 m × $^1/_8$ in.) was packed with Porapak P. The gas carrier was helium flowing at 50 cm^3·min^{-1}, and the column temperature was 383.15 K. The GC was calibrated

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Table 2. Antoine Coefficients *A*, *B*, and *C*

component	temp range/K	Antoine coefficients *A*	*B*	*C*
water	274−373	16.5700	3984.92	−39.724
1-propanol	303−370	16.0353	3415.56	−70.733
2-propanol	300−355	16.4089	3439.60	−63.417

Table 3. Vapor−Liquid Equilibrium Data, Liquid Phase Mole Fraction x_1, Vapor Phase Mole Fraction y_1, Temperature *T*, and Activity Coefficients γ_i for the 2-Propanol (1) + 1-Propanol (2) System at 100 kPa

x_1	y_1	*T*/K	γ_1	γ_2
0.000	0.000	369.75		
0.032	0.054	368.83	0.998	1.004
0.054	0.087	368.45	0.966	1.006
0.097	0.150	367.70	0.952	1.009
0.136	0.224	366.84	1.046	0.995
0.185	0.285	366.06	1.006	1.001
0.251	0.362	365.10	0.976	1.009
0.314	0.445	363.96	1.000	1.001
0.381	0.519	362.94	0.998	1.001
0.469	0.611	361.60	1.003	0.995
0.558	0.697	360.28	1.011	0.981
0.652	0.772	359.02	1.006	0.986
0.729	0.829	357.99	1.005	0.990
0.808	0.883	356.93	1.006	0.998
0.868	0.922	356.19	1.006	0.998
0.914	0.952	355.63	1.009	0.964
0.946	0.970	355.22	1.009	0.976
0.978	0.987	354.95	1.004	1.052
1.000	1.000	354.85		

with gravimetrically prepared standard solutions. Forty samples running all over the composition range were prepared to calibrate the GC for the ternary system. The uncertainty of composition measurements was estimated to be ±0.001 mole fraction for the binary system and ±0.002 mole fraction for the ternary one. At least two analyses were made for each liquid and each condensed vapor sample.

Results and Discussion

Vapor pressures P_i° were calculated with the Antoine equation

$$\ln(P_i^\circ/\mathrm{kPa}) = A - \frac{B}{(C + T/\mathrm{K})} \tag{1}$$

The Antoine constants for water were those given in the DECHEMA Chemistry Data Series (Gmehling and Onken, 1977). For 1-propanol and 2-propanol, the values given in Aucejo et al. (1995) were used. Antoine constants for the three compounds are summarized in Table 2.

Binary System. The experimental VLE data for the binary system are given in Table 3. The experimental liquid phase activity coefficients, γ_i, were calculated from

$$\ln \gamma_i = \ln\left(\frac{P y_i}{x_i P_i^\circ}\right) + (B_{ii} - v_i^{\mathrm{L}})(P - P_i^\circ)/RT + (P/2RT)\sum_1^n\sum_1^n y_j y_k (2\delta_{ji} - \delta_{jk}) \tag{2}$$

$$\delta_{ji} = 2B_{ji} - B_{jj} - B_{ii} \tag{3}$$

where v_i^{L} is the molar liquid volume of component *i*, B_{ii} and B_{jj} are the second virial coefficients of the pure gases, and B_{ij} is the cross second virial coefficient. The second virial coefficients were estimated by the method of O'Connell and Prausnitz (1967). The last two terms in eq 2 contributed less than 2% to the activity coefficient.

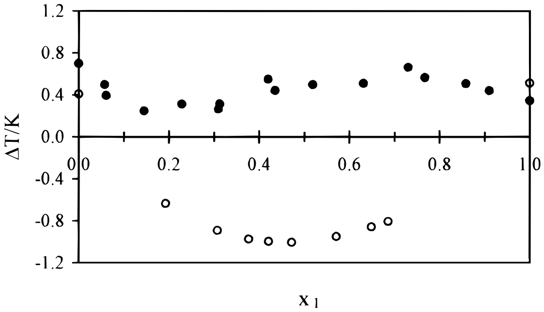

Figure 1. Deviation between *T* literature data and calculated values using the Wilson equation obtained by fitting experimental data of this work for the 2-propanol + 1-propanol system at 101.3 kPa.: (○) Gültekin (1985); (●) Ballard and Van Winkle (1952).

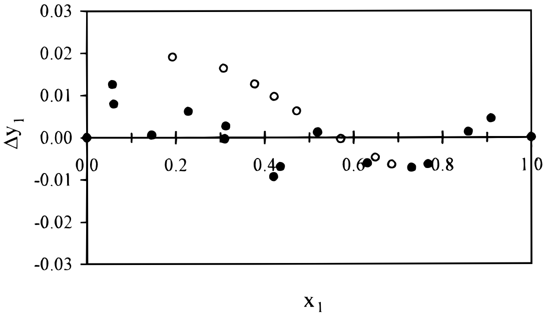

Figure 2. Deviation between y_1 literature data and calculated values using Wilson equation obtained by fitting experimental data of this work for the 2-propanol + 1-propanol system at 101.3 kPa.: (○) Gültekin (1985); (●) Ballard and Van Winkle (1952).

The thermodynamic consistency of the VLE experimental data was checked by the point-to-point test of Van Ness−Byer−Gibbs (1973) using a four parameter Legendre polynomial for the excess Gibbs free energy. The selected objective function to minimize was the sum of the squared relative deviations in the total pressure. The consistency criterion in this test is that the mean absolute deviation between calculated and measured mole fractions of component 1 in the vapor phase, MAD(*y*), is less than 0.01. Experimental VLE data were found thermodynamically consistent according to this test, with a value of MAD(*y*) of 0.0030.

As can be observed, the activity coefficients were close to unity, as could be expected from the small values of the heats of mixing and excess entropy of mixing for the isomer mixture. Thus ideal behavior was assumed to represent the system. Mean absolute deviations between experimental and calculated vapor phase mole fraction and temperatures were MAD(*y*) = 0.0030 and MAD(*T*) = 0.09 K. In order to predict the ternary data using the activity coefficient models, the binary interaction parameters for the 2-propanol + 1-propanol system are zero.

Comparison with literature values can be observed in Figures 1 and 2, where deviations between literature *T* and y_1 data and calculated values using the Wilson equation, obtained by fitting the experimental data presented in this work, as a function of x_1 are plotted.

Ternary System. The VLE data for the ternary system are shown in Table 4 and Figure 3. The activity coefficients γ_i were calculated from eq 2. The last two terms in eq 2 contributed less than 1.5% to the activity coefficient. As can be observed, the system shows positive deviations from ideality. The ternary data were found to be thermodynamically consistent, as tested by the McDermott−Ellis method (1965) modified by Wisniak and Tamir (1977). The test requires that $D < D_{\max}$ for every experimental point.

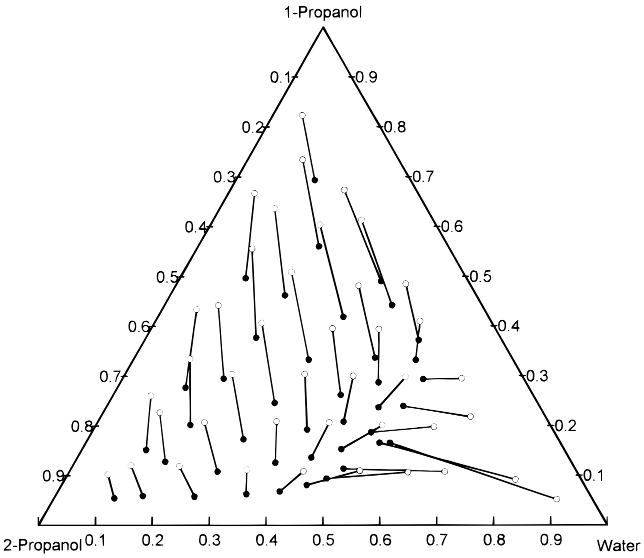

Figure 3. Vapor−liquid equilibrium tie lines for the water + 1-propanol + 2-propanol system at 100 kPa.: (○) liquid phase mole fractions; (●) vapor phase mole fractions.

Table 4. Vapor−Liquid Equilibrium data, Liquid Phase Mole Fraction x_i, Vapor Phase Mole Fraction y_i, Temperature T, and Activity Coefficients γ_i for the Water (1) + 1-Propanol (2) + 2-Propanol (3) System at 100 kPa

x_1	x_2	y_1	y_2	T/K	γ_1	γ_2	γ_3
0.071	0.102	0.106	0.055	354.89	2.920	0.961	1.012
0.067	0.261	0.113	0.152	356.90	3.048	0.955	1.008
0.061	0.434	0.120	0.277	359.20	3.253	0.954	1.007
0.046	0.667	0.115	0.497	362.59	3.635	0.973	1.003
0.052	0.823	0.139	0.693	365.03	3.548	1.000	0.912
0.097	0.734	0.213	0.560	362.73	3.173	0.991	0.992
0.097	0.636	0.202	0.462	361.40	3.164	0.994	0.977
0.097	0.556	0.194	0.377	360.31	3.167	0.969	1.000
0.095	0.442	0.178	0.295	358.92	3.130	1.009	0.971
0.099	0.335	0.166	0.202	357.46	2.964	0.967	1.007
0.100	0.227	0.159	0.128	356.02	2.973	0.959	1.011
0.102	0.121	0.154	0.059	354.57	2.989	0.880	1.023
0.188	0.119	0.245	0.058	354.03	2.633	0.900	1.038
0.188	0.207	0.261	0.108	355.06	2.693	0.923	1.033
0.188	0.304	0.274	0.173	356.28	2.695	0.958	1.028
0.189	0.407	0.292	0.246	357.54	2.719	0.966	1.029
0.190	0.509	0.308	0.333	358.86	2.711	0.991	1.020
0.193	0.603	0.326	0.419	360.07	2.697	1.003	1.021
0.201	0.673	0.357	0.490	361.09	2.727	1.009	0.954
0.261	0.613	0.400	0.442	360.00	2.452	1.044	1.027
0.322	0.481	0.423	0.337	358.34	2.239	1.085	1.063
0.319	0.395	0.400	0.262	357.29	2.227	1.072	1.074
0.316	0.304	0.376	0.192	356.17	2.208	1.068	1.079
0.314	0.209	0.353	0.126	355.06	2.179	1.067	1.083
0.310	0.112	0.334	0.063	353.93	2.184	1.044	1.081
0.411	0.109	0.390	0.068	354.13	1.908	1.148	1.161
0.408	0.206	0.411	0.136	355.31	1.933	1.157	1.152
0.403	0.300	0.432	0.208	356.54	1.959	1.155	1.134
0.401	0.394	0.454	0.287	357.72	1.976	1.157	1.129
0.403	0.485	0.482	0.372	358.94	1.992	1.159	1.112
0.465	0.410	0.497	0.332	358.44	1.814	1.249	1.190
0.496	0.298	0.479	0.237	357.13	1.725	1.294	1.261
0.504	0.201	0.456	0.153	355.85	1.699	1.305	1.274
0.510	0.110	0.431	0.081	354.63	1.665	1.328	1.295
0.596	0.107	0.459	0.094	355.20	1.483	1.547	1.484
0.596	0.198	0.491	0.187	356.75	1.493	1.561	1.451
0.596	0.295	0.529	0.294	358.32	1.513	1.545	1.419
0.650	0.218	0.521	0.240	357.46	1.413	1.767	1.635
0.660	0.108	0.479	0.114	355.64	1.374	1.826	1.701
0.792	0.092	0.516	0.166	357.11	1.164	2.938	2.510
0.885	0.052	0.535	0.166	357.73	1.054	5.069	4.243

The values calculated of $D_{\max}$ were at least 0.048, while the values of D for any given point never exceeded 0.025.

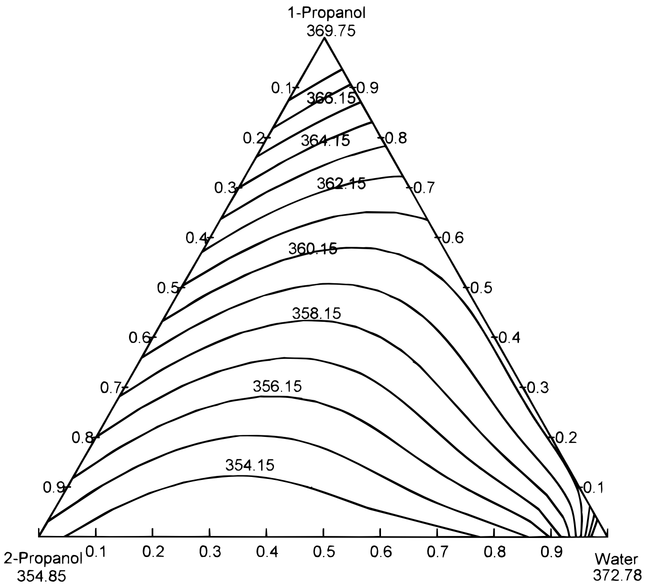

Figure 4. Vapor−liquid isotherms for the ternary system water + 1-propanol + 2-propanol at 100 kPa calculated with the UNIQUAC equation, as a function of the liquid mole fraction.

Table 5. Correlation Parameters for Activity Coefficients for the Binary Systems Water (1) + 1-Propanol (2), Water (1) + 2-Propanol (2) and 2-Propanol (1) + 1-Propanol (2) at 100 kPa

system	model	A_{12}/ J·mol^{-1}	A_{21}/ J·mol^{-1}	α_{12}
water + 1-propanol[a]	Wilson	5457.66	4505.32	
	NRTL	9218.80	−414.77	0.30
	UNIQUAC	2132.80	37.71	
water + 2-propanol[b]	Wilson	5447.63	2121.57	
	NRTL	6900.81	77.49	0.30
	UNIQUAC	286.62	1469.86	
2-propanol + 1-propanol	ideal			

[a] Gabaldón et al. (1996). [b] Marzal et al. (1996).

Table 6. Correlation of Experimental Ternary Data with Wilson, NRTL, and UNIQUAC Equations Using Binary Interaction Parameters

model	MAD(y_1)	MAD(y_2)	MAD(y_3)	max dev in y	MAD(T)
Wilson	0.0121	0.0079	0.0073	0.030	0.19
NRTL	0.0093	0.0064	0.0051	0.025	0.16
UNIQUAC	0.0112	0.0064	0.0064	0.027	0.29

Vapor−liquid equilibrium for the ternary system has been predicted by using Wilson, NRTL, and UNIQUAC models for the activity coefficients of the components with the binary interaction parameters obtained from the regression of binary data. The values of the binary interaction parameters have been taken from this study and our previous works (Marzal et al., 1996; Gabaldón et al., 1996) and are summarized in Table 5 for the reader's convenience. Table 6 lists the mean absolute deviations between experimental and calculated temperatures and vapor phase mole fractions of the components, and the maximum deviations in vapor phase mole fractions. The three models yield similar deviations, representing the data successfully. Thus, the models can be used to predict the vapor phase compositions and boiling points from the liquid phase composition at the system pressure. As an example, boiling isotherms calculated with the UNIQUAC model are presented in Figure 4.

Conclusions

Vapor−liquid equilibrium data of the 2-propanol + 1-propanol system at 100 kPa showed minimum deviations from ideality, and ideal behavior can be assumed. For the ternary system water + 1-propanol + 2-propanol, positive deviations from ideality have been reported. The Wilson, NRTL, and UNIQUAC activity coefficient models using the binary interaction parameters previously obtained predict satisfactory ternary vapor−liquid equilibrium curves.

Literature Cited

Aucejo, A.; González-Alfaro, V.; Montón J. B.; Vázquez, M. I. Isobaric Vapor-Liquid Equilibria of Trichloroethylene with 1-Propanol and 2-Propanol at 20 and 100 kPa. *J. Chem. Eng. Data* **1995**, *40*, 332.

CRC Handbook of Chemistry and Physics, 71st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1990.

Gabaldón, C.; Marzal, P.; Montón, J. B.; Rodrigo, M. A. Isobaric Vapor-Liquid Equilibria of Water + 1-Propanol System at 30, 60 and 100 kPa. *J. Chem. Eng. Data* **1996**.

Gmehling, J., Onken, U., Eds. *Vapor-Liquid Equilibrium Data Collection;* Chemistry Data Series; DECHEMA: Frankfurt/Main, 1977; Vol. 1, Part 1.

Marzal, P.; Montón, J. B.; Rodrigo, M. A. Isobaric Vapor-Liquid Equilibria of Water + 2-Propanol System at 30, 60 and 100 kPa. *J. Chem. Eng. Data* **1996**, *41*, 608.

McDermott, C.; Ellis, S. R. M. A Multicomponent Consistency Test. *Chem. Eng. Sci.* **1965**, *20*, 293.

O'Connell, J. P.; Prausnitz, J. M. Empirical Correlation of Second Virial Coefficients for Vapor-Liquid Equilibrium Calculations. *Ind. Eng. Chem. Process Des. Dev.* **1967**, *6*, 245.

TRC Thermodynamic Tables Hydrocarbons; Thermodynamic Research Center, The Texas A&M University System: College Station, TX, 1994.

TRC Data Bases for Chemistry and Engineering Floppy Book on Vapor-Liquid Equilibrium Data; Thermodynamic Research Center, The Texas A&M University System: College Station, TX, 1996: Ballard, L. H.; Van Winkle, M. *Ind. Eng. Chem.* **1952**, *44*, 2450. Polak, J.; Murakami, S.; Benson, G. C.; Plug, H. D. *Can. J. Chem.* **1970**, *48*, 3782. Ocon, J.; Tojo, G.; Bao, M.; Arce, A. *An. Quim.* **1973**, *69*, 673. Gültekin, N. *Chim. Acta Turc.* **1985**, *13*, 369. Gültekin, N. *J. Chem. Eng. Data.* **1989**, *34*, 168. Oracz, P. *Int. Data Ser., Sel. Data Mixtures* **1989**, 274. Hongo, M.; Kusunoki, M.; Kumagae, Y.; Arai, Y. *J. Chem. Thermodyn.* **1992**, *24*, 649.

Van Ness, H. C.; Byer, S. M.; Gibbs, R. E. Vapor-Liquid Equilibrium: Part I. An Appraisal of Data Reduction Methods. *AIChE J.* **1973**, *19*, 238.

Walas, S. M. *Phase Equilibria in Chemical Engineering*; Butterworth: London, **1985**.

Wisniak, J.; Tamir, A. Vapor-Liquid Equilibria in the Ternary Systems Water-Formic Acid-Acetic Acid and Water-Acetic Acid-Propionic Acid. *J. Chem. Eng. Data* **1977**, *22*, 253.

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