Isobaric Vapor−Liquid Equilibria of the Water + 2-Propanol System at 30, 60, and 100 kPa

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Isobaric vapor−liquid equilibria were obtained for the water + 2-propanol system at 30, 60, and 100 kPa. The activity coefficients were found to be thermodynamically consistent by the methods of Van Ness−Byer−Gibbs, Kojima, and Wisniak. The data were correlated with five liquid phase activity coefficient models (Margules, Van Laar, Wilson, NRTL, and UNIQUAC).

Introduction

Distillation is perhaps the separation process most widely used in the chemical processing industry. The correct design of distillation columns requires the availability of accurate and, if possible, thermodynamically consistent vapor−liquid equilibria (VLE) data.

The present work is part of a project studying the effect of pressure on the behavior of the azeotropic point in mixtures in which at least one component is an alcohol. For this purpose, experimental VLE data of the azeotropic system water + 2-propanol at three pressures (30, 60, and 100 kPa) have been obtained and correlated.

In the literature, numerous papers reporting VLE data for the system water + 2-propanol have been found (Ramalho and Drolet, 1971; Gmehling and Onken, 1977, 1981; Scaramucci and Vangeli, 1984; Gmehling et al. 1988; Morrison et al. 1990). However, in the majority of these works, no thermodynamic consistency study has been performed and, in some of them, only $P-x$ data (at constant temperature) or $T-x$ data (at constant pressure) have been obtained and no experimental vapor phase composition data have been included.

The DECHEMA *Chemistry Data Series* (Gmehling and Onken, 1977, 1981; Gmehling et al. 1988) compilation of VLE data for the system water + 2-propanol includes 40 experimental data sets. Among these, 27 correspond to isobaric data (17 at atmospheric pressure), but only 12 achieve the positive evaluation of the point-to-point thermodynamic consistency test of Van Ness−Byer−Gibbs (1973), modified by Fredenslund (1977).

The contribution presented in this paper includes three VLE data sets at different pressures that fulfill the most rigorous thermodynamic consistency tests (Van Ness−Byer−Gibbs (1973), Kojima et al. (1990), and Wisniak (1993)).

Experimental Section

Chemicals. Milli-Q water and 2-propanol high purity grade purchased from Aldrich Chemical were used. The purity of these chemicals was checked by gas chromatography (GC): water (100.00 mass %) and 2-propanol (99.90 mass %). These chemicals were used without further purification. The experimental densities, refractive indexes, and boiling points of both compounds are listed in Table 1 along with 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	
compd	exptl	lit.	exptl	lit.	exptl	lit.
water	0.988 06	0.998 20[a]	1.3334	1.3330[a]	372.78	372.79[a]
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 apparatus 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) can handle pressures from 0.25 up to 400 kPa, and temperatures up to 523.15 K. In the boiler, with a volume of 80 cm^3, vapor bubbles are generated by external heating. The Cottrell pump ensures the intimate contact between the liquid and vapor phases and also with the temperature probe. The equilibrium temperature is measured with a digital Ditel thermometer with an accuracy of 0.01 K. For the pressure measuring, 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 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 with special syringes under partial vacuum.

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 with gravimetrically prepared standard solutions. The accuracy of the measured mole fraction was ±0.001. At least two analyses were made for each liquid and each vapor sample.

Results and Discussion

Vapor pressures P_i^0 were calculated with the Antoine equation

$$\ln(P_i^0/\text{kPa}) = A - \frac{B}{(C + T/\text{K})} \tag{1}$$

For water and 2-propanol Antoine constants given in the DECHEMA *Chemistry Data Series* (Gmehling and Onken,

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

		Antoine coefficients		
component	temp range/K	*A*	*B*	*C*
water	274−373	16.5700	3984.92	−39.724
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 Water (1) + 2-Propanol (2) System at 30 kPa

x_1	y_1	*T*/K	γ_1	γ_2
0.000	0.000	327.85		
0.052	0.084	326.73	3.276	1.021
0.091	0.135	326.34	3.069	1.026
0.171	0.216	325.63	2.733	1.055
0.229	0.265	325.40	2.524	1.076
0.288	0.304	325.37	2.303	1.106
0.369	0.345	325.33	2.046	1.176
0.441	0.376	325.52	1.846	1.254
0.510	0.398	325.67	1.679	1.370
0.585	0.417	325.89	1.517	1.549
0.660	0.432	326.20	1.373	1.814
0.720	0.443	326.42	1.278	2.132
0.783	0.459	326.73	1.199	2.633
0.861	0.474	327.13	1.105	3.917
0.887	0.484	327.58	1.071	4.620
0.911	0.501	328.03	1.056	5.533
0.931	0.528	328.80	1.051	6.493
0.946	0.546	329.84	1.018	7.576
0.957	0.588	331.00	1.025	8.201
0.966	0.629	332.61	1.008	8.659
0.978	0.697	334.70	1.001	10.116
0.986	0.773	336.69	1.007	10.937
0.992	0.859	338.93	1.006	9.982
0.995	0.913	340.26	1.004	10.066
1.000	1.000	342.33		

Table 4. 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 Water (1) + 2-Propanol (2) System at 60 kPa

x_1	y_1	*T*/K	γ_1	γ_2
0.000	0.000	342.73		
0.026	0.041	342.12	3.219	1.011
0.073	0.106	341.59	2.987	1.015
0.140	0.182	340.90	2.774	1.031
0.214	0.249	340.60	2.510	1.050
0.274	0.290	340.53	2.291	1.078
0.353	0.336	340.52	2.060	1.132
0.421	0.368	340.64	1.882	1.198
0.488	0.390	340.81	1.706	1.299
0.560	0.410	341.07	1.548	1.442
0.629	0.428	341.42	1.415	1.633
0.683	0.440	341.68	1.325	1.851
0.743	0.451	342.03	1.229	2.207
0.793	0.460	342.36	1.159	2.646
0.834	0.467	342.71	1.102	3.210
0.869	0.482	343.11	1.071	3.899
0.894	0.491	343.63	1.038	4.606
0.921	0.511	344.19	1.023	5.804
0.936	0.533	345.13	1.009	6.591
0.951	0.567	346.48	0.998	7.434
0.970	0.635	348.62	1.001	9.451
0.975	0.695	350.52	1.008	8.731
0.987	0.776	353.14	0.998	11.441
0.990	0.830	354.61	1.003	10.184
0.995	0.913	356.98	0.999	9.364
1.000	1.000	359.14		

1977) and Aucejo et al. (1995), respectively, were used and are summarized in Table 2.

The experimental VLE data for the binary system at 30, 60, and 100 kPa are given in Tables 3−5. The *T*−*x*−*y* diagrams at the three pressures are shown in Figure 1. From this figure it can be observed that the system presents a minimum boiling azeotrope and the azeotropic point is scarcely shifted with pressure.

To calculate the liquid phase activity coefficients, γ_i, the Poynting factor was considered as unity at the experimental conditions. The fugacity coefficients were calculated on the basis of the virial equation of state, with the second

Table 5. 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 Water (1) + 2-Propanol (2) System at 100 kPa

x_1	y_1	*T*/K	γ_1	γ_2
0.000	0.000	354.85		
0.026	0.039	354.39	3.075	1.003
0.047	0.070	353.97	3.068	1.010
0.106	0.149	353.33	2.955	1.011
0.161	0.208	353.03	2.754	1.015
0.219	0.252	352.81	2.468	1.040
0.293	0.301	352.65	2.217	1.080
0.373	0.343	352.68	1.983	1.143
0.449	0.368	352.85	1.756	1.242
0.533	0.395	353.12	1.570	1.388
0.595	0.410	353.40	1.442	1.544
0.649	0.420	353.80	1.331	1.725
0.701	0.425	354.03	1.236	1.990
0.742	0.436	354.40	1.181	2.226
0.779	0.449	354.66	1.147	2.509
0.820	0.454	354.97	1.089	3.011
0.861	0.461	355.55	1.027	3.768
0.891	0.490	356.07	1.035	4.455
0.924	0.509	357.03	0.999	5.868
0.939	0.528	358.00	0.980	6.789
0.954	0.586	360.11	0.986	7.309
0.963	0.641	362.12	0.989	7.251
0.974	0.718	364.20	1.012	7.372
0.982	0.773	366.23	1.000	8.036
0.987	0.809	367.55	0.992	8.987
0.995	0.901	370.03	1.001	10.707
1.000	1.000	372.78		

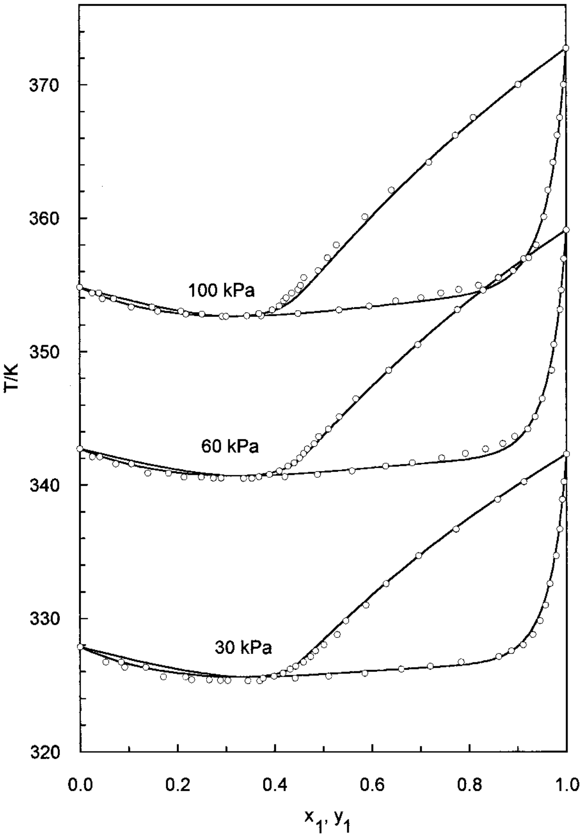

Figure 1. Temperature *T* vs composition (x_1, y_1) for the system water (1) + 2-propanol (2) at constant pressure, *P* = 30, 60, and 100 kPa: (○) experimental; (−) UNIQUAC model.

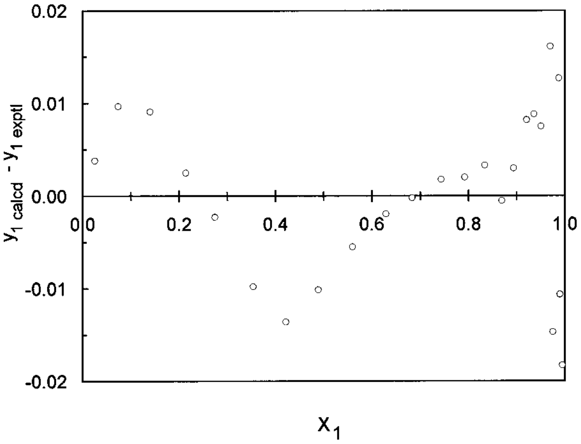

Figure 2. Deviation between calculated and measured vapor phase mole fraction (y_1) vs liquid phase mole fraction (x_1) for the water (1) + 2-propanol (2) system at constant pressure, P = 60 kPa.

Table 6. Thermodynamic Consistency Tests

	Van Ness–Byer–Gibbs		Kojima		Wisniak		
			error for dilute component	error for dilute component			
P/kPa	MAD(y)	BIAS	1 (%)	2 (%)	L	W	D
30	0.0072	−0.0032	27.7	2.9	8.34	8.45	0.6
60	0.0073	0.0008	18.4	1.1	8.83	8.97	0.8
100	0.0099	0.0047	14.5	8.6	9.59	9.87	1.4

virial coefficient being estimated by means of the Pitzer and Curl equations (1957) with the correction proposed by Tsonopoulos (1974). For every experimental pressure–temperature–composition condition, the calculated fugacity coefficients were close to unity (0.9985 maximum, 0.9601 minimum) and were not considered in the analysis of the VLE data. So, the experimental liquid phase activity coefficients γ_i were calculated from

$$\gamma_i = \frac{Py_i}{x_i P_i^0} \tag{2}$$

The thermodynamic consistency of the VLE experimental data was checked by means of several tests: the point-to-point test of Van Ness–Byer–Gibbs (1973), the infinite dilution test proposed by Kojima et al. (1990), modified by Jackson and Wilsak (1995), and the L–W method of Wisniak (1993).

For the point-to-point test of Van Ness–Byer–Gibbs a four-parameter Legendre polynomial was used for the excess Gibbs free energy, and the selected objective function to minimize was the sum of the squared relative deviations in the total pressure. According to this test the experimental data are consistent if the mean absolute deviation between calculated and measured mole fractions of component 1 in the vapor phase, MAD(y), is less than 0.01, and if the absolute deviations are scattered randomly about zero. To check the absence of bias in the data, a graphical inspection of the error in y_1 must be carried out, y_1 residuals being plotted vs x_1. This plot for the 60 kPa data is shown, as an example, in Figure 2. Similar results were obtained at 30 and at 100 kPa. Experimental VLE data were found thermodynamically consistent according to this test, with the values of MAD(y) and the sum of y_1 residuals (BIAS) as listed in Table 6.

The application of the infinite dilution test of Kojima (1990) includes the calculation of the excess Gibbs free energy from the experimental data and the extrapolation to infinite dilution using smoothing functions. The extrapolated values are then compared with those extrapolated of ln γ_1 and ln γ_2 at infinite dilution, and thermodynamic consistency is achieved if the values agree to within 30%. The results at 60 kPa are shown in Figure 3 where G^E/RTx_1x_2, ln γ_1, and ln γ_2 have been plotted vs x_1. Deviations of the extrapolated values at the three pressures (Table 6) were within the method tolerance.

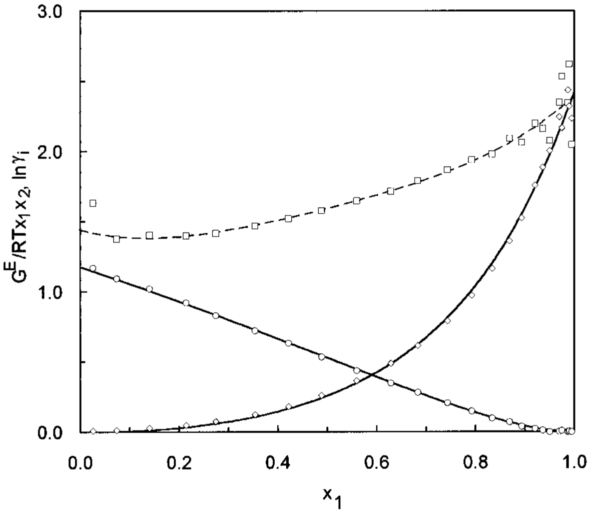

Figure 3. Infinite dilution test for the water (1) + 2-propanol (2) binary system at constant pressure, P = 60 kPa: (○) ln γ_1; (◇) ln γ_2; (□) G^E/RTx_1x_2; (—) UNIQUAC model; (– –) polynomial regression.

The L–W method of Wisniak requires the evaluation of the integrals L and W as described in the paper by Wisniak (1993) and values of the deviation D defined as

$$D = 100\frac{|L - W|}{L + W} \tag{3}$$

less than 3–5 indicate thermodynamic consistency. As can be observed in Table 6, experimental VLE data were also found consistent according to the Wisniak test.

The activity coefficients were correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations (Gmehling and Onken, 1977). The molar volumes used in generating the Wilson equation energy parameters are 0.018 069 $m^3 \times mol^{-1}$ for water and 0.076 784 $m^3 \times mol^{-1}$ for 2-propanol (Daubert and Danner, 1994). The r and q used in generating the UNIQUAC parameters are r = 0.9200 and q = 1.4000 for water and r = 2.7791 and q = 2.5080 for 2-propanol (Gmehling and Onken, 1977). To fit the binary parameters, a nonlinear optimization method was used to minimize the following objective function

$$F = \sum_n \sum_i \left(\frac{\gamma_{\text{exptl}} - \gamma_{\text{calcd}}}{\gamma_{\text{exptl}}} \right)^2_{i,n} \tag{4}$$

where n is the number of data points. The adjustable parameters A_{12}, A_{21}, and α_{12} for the correlation equations, mean absolute deviations, and activity coefficients at infinite dilution γ_i^∞ are given in Table 7. At the three pressures, Van Laar, Wilson, NRTL, and UNIQUAC models yield similar deviations between experimental and calculated vapor compositions and temperatures, while Margules shows greater deviations in both variables.

The azeotropic point at the three pressures was estimated using the UNIQUAC correlation. The values obtained for the azeotrope temperature were 325.62, 340.71, and 352.06 K at 30, 60, and 100 kPa, respectively. The water mole fractions were 0.342, 0.327, and 0.315 at 30,

Table 7. Correlation Parameters for Activity Coefficients, Activity Coefficients at Infinite Dilution γ_i^∞ and Mean Absolute Deviations MAD(y) and MAD(T)

P/kPa	model	A_{12}	A_{21}	α_{12}	γ_1^∞	γ_2^∞	MAD-(y)	MAD-(T)
30.00	Margules	1.0432[a]	2.3481[a]		2.84	10.47	0.0177	0.48
	Van Laar	1.2298[a]	2.4454[a]		3.42	11.54	0.0083	0.30
	Wilson	5300.58[b]	2095.82[b]		3.69	12.88	0.0113	0.41
	NRTL	6726.08[b]	111.46[b]	0.30[a]	3.33	11.06	0.0085	0.28
	UNIQUAC	426.02[b]	1319.93[b]		3.47	11.89	0.0073	0.27
60.00	Margules	0.9870[a]	2.2959[a]		2.68	9.93	0.0180	0.60
	Van Laar	1.1645[a]	2.4207[a]		3.20	11.25	0.0073	0.30
	Wilson	5294.22[b]	2302.15[b]		3.39	12.59	0.0120	0.30
	NRTL	6899.21[b]	106.99[b]	0.30[a]	3.30	10.46	0.0095	0.36
	UNIQUAC	609.21[b]	1087.85[b]		3.21	11.54	0.0067	0.27
100.00	Margules	1.0443[a]	2.2101[a]		2.84	9.12	0.0129	0.53
	Van Laar	1.1810[a]	2.3108[a]		3.26	10.08	0.0076	0.29
	Wilson	5447.63[b]	2121.57[b]		3.31	11.39	0.0134	0.31
	NRTL	6900.81[b]	77.49[b]	0.30[a]	3.22	9.51	0.0081	0.31
	UNIQUAC	286.62[b]	1469.86[b]		3.30	10.53	0.0079	0.25

[a] Dimensionless. [b] J·mol^{-1}.

60, and 100 kPa, respectively. As can be observed, the azeotrope water composition is slightly shifted to lower values as the pressure increases. Wilson and Simons (1952) reported the same sequence of variation of the azeotropic composition with pressure, with values of 0.3295, 0.3250, and 0.3130 at 25.3, 50.7, and 101.3 kPa, respectively.

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