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Isobaric Vapor−Liquid Equilibria of Tetrachloroethylene with 1-Butanol and 2-Butanol at 6 and 20 kPa

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Vapor−liquid equilibria were measured for binary systems of tetrachloroethylene + 1-butanol and + 2-butanol at 6 and 20 kPa. The results are thermodynamically consistent according to the point-to-point consistency test. Both systems show a positive deviation from ideality.

Introduction

Distillation has been used as an effective means of separation in chemical processing, and a knowledge of the vapor−liquid equilibrium on the mixture under consideration is necessary for the design of separation equipment. Vapor−liquid equilibrium can be obtained experimentally or by using generalized methods that permit the calculation of the properties of the mixtures. Among these methods, the most noteworthy are those of group contribution, mainly the UNIFAC method (*1*).

The present work is part of a program for determining vapor−liquid equilibrium (VLE) data in mixtures in which one component, at least, is an alcohol. In this paper we report results at 6 and 20 kPa for the systems of tetrachloroethylene with 1-butanol and 2-butanol. The results have been treated thermodynamically, considering the nonideality of both phases and verifying their thermodynamic consistency.

Experimental Section

Chemicals. All components used in this study were purchased from Aldrich Chemie Co. The purity of all chemicals was checked by gas chromatography (GC): tetrachloroethylene, 99.55 mass %; 1-butanol, 99.94 mass %; and 2-butanol, 99.92 mass %. They were used without further purification. The water content was small in all chemicals (<0.1 mass %, checked by GC). The experimental densities, refractive indexes, and boiling points given in Table 1 are compared with literature values (*2, 3*). There is good agreement between the experimental values and those in the literature.

Apparatus and Procedure. The equilibrium vessel used in this work was an all-glass, dynamic recirculating still described by Walas (*4*), equipped with a Cottrell pump. The still (Labodest model), manufactured by Fischer Labor und Verfahrenstechnik (Germany), is capable of handling pressures P from 0.25 to 400 kPa, and temperatures T up to 523.15 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact and also in contact with the temperature-sensing element. The equilibrium temperature was measured with a digital Fisher thermometer with an accuracy of ±0.1 K, and the pressure with a digital manometer with an accuracy of ±0.01 kPa. The temperature probe was calibrated against the ice and steam points of distilled water. The manometer was calibrated against high purity (>99.9 mass %) hexane vapor pressures. VLE measurements were made at 6 and 20 kPa for both systems.

In each experiment, the pressure was fixed and the heating and shaking system of the liquid mixture was connected. The still was operated until equilibrium was reached. Equilibrium conditions were assumed when

Table 1. Densities d, Refractive Indexes n, and Boiling Points T_b of the Chemicals

	d(293.15 K)/(g cm^{-3})		n(D, 293.15 K)		T_b(20 kPa)/K	
component	exptl	lit. (*2*)	exptl	lit. (*2*)	exptl	lit.[a]
tetrachloroethylene	1.622 99	1.6227	1.5059	1.5053	344.35	344.37
1-butanol	0.809 50	0.8098	1.3988	1.3993	350.95	351.45
2-butanol	0.807 20	0.8070	1.3974	1.3975	334.65	334.70

[a] Calculated using the Antoine coefficients from ref 3.

Table 2. Vapor Pressures $P_i°$, Antoine Coefficients A, B, and C, and Mean Average Deviations $\delta(P_i°)$ of the Pure Components

		Antoine coefficients[a]			
component	temp range/K	A	B	C	$\delta(P_i°)$[b]/kPa
tetrachloroethylene	307−393	14.4128	3416.70	−45.055	0.04
1-butanol	315−390	15.8219	3499.92	−78.111	0.04
2-butanol	306−373	15.4438	3110.70	−84.708	0.07

[a] $\ln(P_i°/\text{kPa}) = A - B/((T/\text{K}) + C)$. [b] $\delta(P_i°) = \sum|P°_{\text{exptl}} - P°_{\text{calcd}}|/N$ (N = number of data points).

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 Tetrachloroethylene (1) + 1-Butanol (2) at 6 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	327.65		
0.016	0.095	325.85	3.771	1.009
0.026	0.151	324.85	3.852	1.012
0.036	0.199	323.95	3.813	1.016
0.061	0.298	322.45	3.600	0.997
0.096	0.395	320.05	3.376	1.029
0.137	0.483	318.15	3.153	1.032
0.189	0.554	316.65	2.808	1.038
0.256	0.619	314.85	2.519	1.080
0.330	0.662	313.85	2.190	1.133
0.400	0.692	313.25	1.943	1.197
0.466	0.711	312.75	1.755	1.303
0.558	0.731	312.35	1.536	1.503
0.647	0.747	312.05	1.373	1.804
0.733	0.761	311.95	1.241	2.267
0.793	0.776	312.05	1.164	2.723
0.857	0.783	312.15	1.081	3.795
0.909	0.809	312.45	1.038	5.149
0.937	0.826	312.85	1.009	6.607
0.948	0.832	312.95	1.000	7.680
0.961	0.858	313.15	1.008	8.547
0.970	0.872	313.55	0.995	9.766
0.987	0.922	314.55	0.987	12.898
1.000	1.000	315.95		

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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 Tetrachloroethylene (1) + 1-Butanol (2) at 20 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	350.95		
0.023	0.109	348.75	4.004	1.006
0.048	0.197	347.25	3.665	0.999
0.089	0.306	345.15	3.322	0.999
0.126	0.380	343.65	3.085	1.001
0.180	0.460	341.95	2.790	1.011
0.255	0.530	340.25	2.424	1.055
0.318	0.571	339.35	2.169	1.101
0.373	0.594	338.75	1.970	1.169
0.446	0.623	338.35	1.755	1.254
0.527	0.649	338.05	1.566	1.389
0.587	0.665	337.95	1.446	1.526
0.641	0.677	337.95	1.348	1.692
0.705	0.694	337.85	1.262	1.961
0.758	0.705	337.95	1.187	2.293
0.804	0.718	338.15	1.131	2.679
0.870	0.742	338.45	1.067	3.638
0.902	0.760	338.75	1.042	4.421
0.935	0.783	339.35	1.011	5.845
0.952	0.808	340.05	0.997	6.759
0.973	0.860	341.05	0.999	8.330
0.990	0.935	342.75	1.000	9.591
1.000	1.000	344.35		

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 Tetrachloroethylene (1) + 2-Butanol (2) at 6 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	312.65		
0.018	0.062	311.75	4.156	1.002
0.047	0.140	310.75	3.771	1.006
0.074	0.207	309.95	3.681	1.002
0.114	0.280	308.85	3.410	1.017
0.163	0.341	308.05	3.021	1.036
0.220	0.391	307.35	2.657	1.073
0.285	0.435	306.85	2.339	1.121
0.353	0.467	306.55	2.058	1.191
0.425	0.487	306.45	1.791	1.298
0.516	0.508	306.35	1.547	1.488
0.570	0.534	306.45	1.465	1.576
0.635	0.551	306.55	1.350	1.778
0.692	0.566	306.75	1.260	2.011
0.796	0.593	307.15	1.125	2.777
0.839	0.610	307.45	1.081	3.309
0.883	0.629	307.75	1.044	4.251
0.904	0.648	308.05	1.035	4.825
0.934	0.676	308.65	1.015	6.223
0.950	0.701	309.15	1.009	7.350
0.964	0.735	309.95	1.003	8.614
0.980	0.815	311.75	1.003	9.704
1.000	1.000	315.95		

constant temperature and pressure were obtained for 15 min or longer. At this time, samples of liquid and condensate were taken for analysis. The extractions were carried out with special syringes which allowed us to take small volume samples in a system under partial vacuum.

Analysis. Compositions of the sampled liquid and condensed vapor phases were analyzed with a Hewlett-Packard 5890 S-II gas chromatograph (GC), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 60-m, 0.2-mm-i.d. fused silica capillary column, SUPELCOWAX 10. The GC response peaks were integrated by using a Hewlett-Packard 3396 integrator. A single analysis of the vapor or liquid composition by gas chromatography is frequently imprecise. However, with repeated measurements, the standard deviation of a composition analysis was usually less than 0.001 mole fraction. At least two analyses were made of each liquid and each vapor composition.

Table 6. Vapor–Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature T, and Activity Coefficients γ_i for Tetrachloroethylene (1) + 2-Butanol (2) at 20 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	334.65		
0.012	0.030	334.15	3.721	1.005
0.042	0.098	333.25	3.603	1.008
0.074	0.156	332.55	3.349	1.011
0.119	0.219	331.85	3.009	1.018
0.169	0.277	331.15	2.759	1.036
0.230	0.325	330.65	2.428	1.071
0.296	0.362	330.35	2.128	1.124
0.362	0.399	330.25	1.925	1.174
0.435	0.425	330.25	1.707	1.269
0.510	0.449	330.35	1.531	1.395
0.577	0.469	330.55	1.402	1.541
0.629	0.484	330.75	1.316	1.690
0.692	0.501	330.95	1.228	1.949
0.748	0.520	331.55	1.150	2.222
0.795	0.542	332.05	1.105	2.541
0.841	0.562	332.65	1.057	3.040
0.885	0.592	333.55	1.019	3.742
0.917	0.633	334.75	1.002	4.393
0.936	0.665	335.55	0.998	4.999
0.956	0.711	337.15	0.980	5.801
0.966	0.756	338.15	0.991	6.039
0.983	0.850	340.65	0.992	6.589
1.000	1.000	344.35		

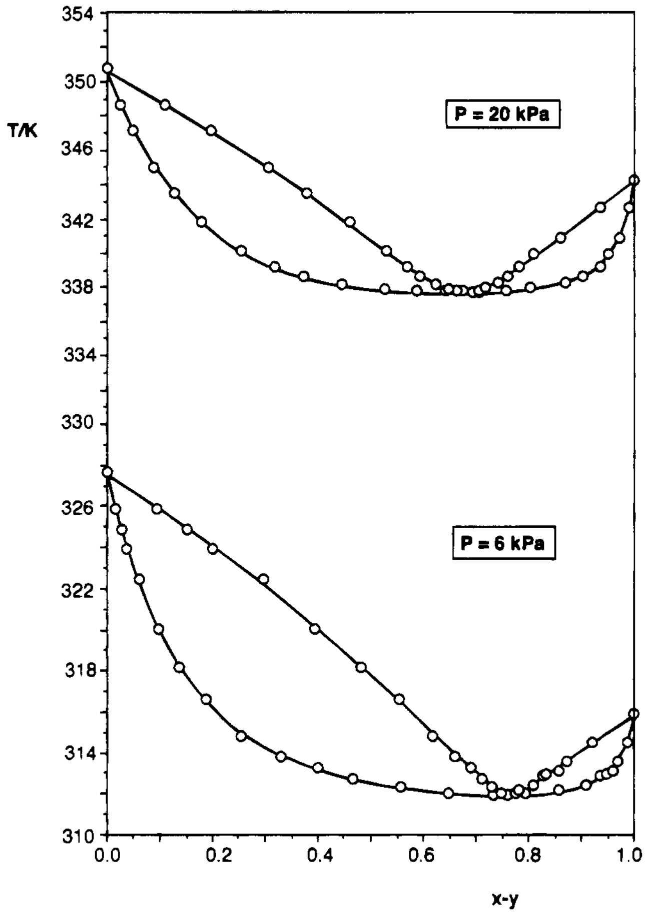

Figure 1. Vapor–liquid equilibrium of the system tetrachloroethylene (1) + 1-butanol (2) at 6 and 20 kPa as a function of the mole fraction of component 1.

Results and Discussion

The vapor pressures of the pure components P_i° were measured with the same recirculating still. These values were fitted to the Antoine equation. The parameters of this equation, together with the mean absolute deviation between experimental and calculated vapor pressures, $\delta(P_i^\circ)$, are given in Table 2.

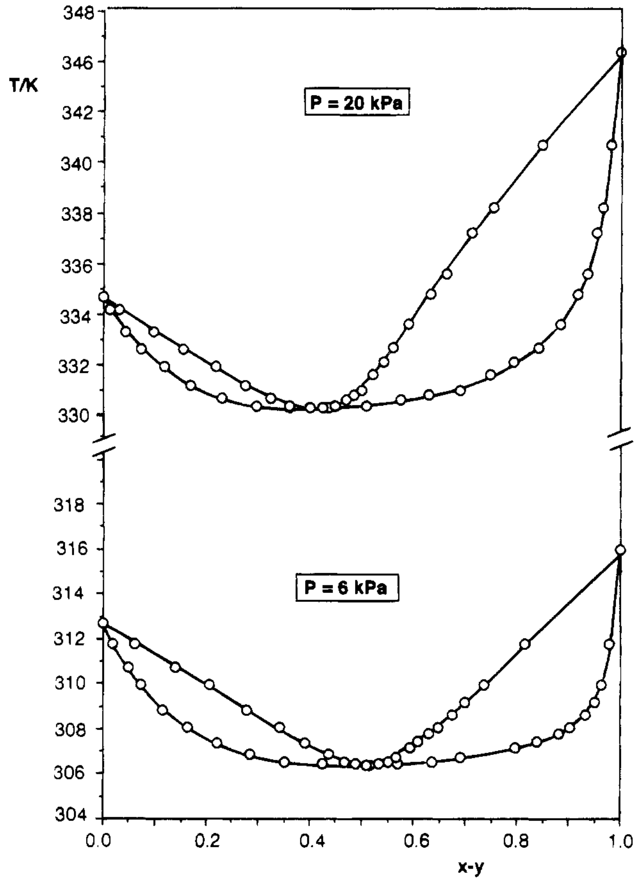

Figure 2. Vapor–liquid equilibrium of the system Tetrachloroethylene (1) + 2-butanol (2) at 6 and 20 kPa as a function of the mole fraction of component 1.

The VLE measurements were made at 6 and 20 kPa and are presented in Tables 3–6. The T–x–y diagrams for the two systems are shown in Figures 1 and 2. From these figures it can be concluded that the composition of the azeotrope does not change significantly with pressure. In fact, for the system of tetrachloroethylene with 1-butanol, at 101.320 kPa (*5*) the azeotrope composition is only slightly different from those obtained at 6 and 20 kPa.

The liquid-phase activity coefficients of the components in a nonideal mixture are given by the equation

$$y_i\phi_iP = x_i\gamma_i\phi_i^{s}\,P_i^{\circ}\,\exp[v_i(P - P_i^{\circ})/RT] \qquad (1)$$

where x_i and y_i are the liquid and vapor mole fractions in equilibrium, ϕ_i is the fugacity coefficient, P is the total pressure, γ_i is the activity coefficient, ϕ_i^s is the pure component fugacity coefficient at saturation, P_i° is the pure component vapor pressure, v_i is the liquid molar volume, R is the universal gas constant, and T is the absolute temperature.

The exponential term (Poynting factor) was taken as unity for the experimental conditions of this work. Fugacity coefficients ϕ_i and ϕ_i^s were calculated by means of the virial equation of state. The liquid molar volumes as well as the equation and the parameters to calculate the second virial coefficients were taken from the literature (*6*). The γ_i values calculated with eq 1 are listed in Tables 3–6. It can be observed that both systems present a positive deviation from ideality.

The results were tested for thermodynamic consistency using the point-to-point method of Van Ness et al. (*7*), modified by Fredenslund et al. (*1*). A four-parameter Legendre polynomial was used for the excess Gibbs free energy. According to Fredenslund et al., the P–T–x–y data are consistent if the mean absolute deviation between calculated and measured mole fractions of component 1 in the vapor phase, $\delta(y)$, is less than 0.01. The results of this test for the binary systems in consideration given in Table 7 indicate that the experimental data for the two systems are thermodynamically consistent.

Table 7. Results of the Thermodynamic Consistency Test for the Binary Systems Used in This Study at 6 and 20 kPa

system	$\delta(y)^a$	
	P = 6 kPa	P = 20 kPa
tetrachloroethylene + 1-butanol	0.0062	0.0061
tetrachloroethylene + 2-butanol	0.0059	0.0059

[a] $\delta(y) = \sum|y_{\text{exptl}} - y_{\text{calcd}}|/N$ (N = number of data points).

Table 8. Parameters and Deviations between Calculated and Experimental Vapor-Phase Mole Fractions and Temperatures Obtained Using the Wilson Equation

system	P/kPa	A_{12}	A_{21}	$\delta(y)^a$	$\delta(T)^b$/K
tetrachloroethylene + 1-butanol	6	257.0527	1544.585	0.0026	0.159
	20	281.2185	1435.473	0.0064	0.157
tetrachloroethylene + 2-butanol	6	298.2106	1371.541	0.0053	0.150
	20	295.5987	1173.549	0.0030	0.170

[a] $\delta(y) = \sum|y_{\text{exptl}} - y_{\text{calcd}}|/N$. [b] $\delta(T) = \sum|T_{\text{exptl}} - T_{\text{calcd}}|/N$ (N = number of data points).

The activity coefficients were correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations (*8*). For fitting the binary parameters the following objective function was used:

$$F = \sum\left(\frac{y_{\text{exptl}} - y_{\text{calcd}}}{y_{\text{exptl}}}\right)^2 + \sum\left(\frac{T_{\text{exptl}} - T_{\text{calcd}}}{T_{\text{exptl}}}\right)^2 \qquad (2)$$

For both systems, at the two pressures studied, the Wilson equation yields the lowest mean deviation between the experimental and calculated vapor compositions and temperatures. The parameters and average deviations obtained for this equation are reported in Table 8.

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