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Isobaric Vapor−Liquid Equilibria of Trichloroethylene with 1-Propanol and 2-Propanol at 20 and 100 kPa

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Vapor−liquid equilibrium data were obtained for binary systems of trichloroethylene + 1-propanol and + 2-propanol at 20 and 100 kPa. The results are thermodynamically consistent according to the point-to-point consistency test. Both systems present a positive deviation from ideality.

Introduction

Distillation has been used as an effective means of separation in chemical processing. Vapor−liquid equilibrium data are essential for the development and design of separation processes. These data can be obtained experimentally or by using generalized methods that allow the calculation of the properties of the mixtures. Among these methods, the most noteworthy are those of group contribution, mainly the UNIFAC method (*1*). To obtain the interaction parameters for this model, a lot of experimental information is necessary.

The present work is part of a project for determining vapor−liquid equilibrium (VLE) data in mixtures in which one component, at least, is an alcohol. In this paper we report the equilibrium data at 20 and 100 kPa for the systems of trichloroethylene with 1-propanol and 2-propanol. 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): trichloroethylene, 99.86 mass %; 1-propanol, 99.97 mass %; and 2-propanol, 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*−*4*). The concordance between experimental data and those found in the literature is good.

Apparatus and Procedure. The equilibrium vessel used in this work was an all-glass, dynamic recirculating still described by Walas (*5*), 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 obtained at 20 and 100 kPa for both systems.

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(100 kPa)/K	
component	exptl	lit.	exptl	lit.	exptl	lit.
trichloroethylene	1.464 04	1.464 2[a]	1.4779	1.4773[a]	359.55	359.45[b]
1-propanol	0.803 66	0.803 75[c]	1.3853	1.38556[c]	369.75	369.95[c]
2-propanol	0.785 34	0.785 45[c]	1.3774	1.3772[c]	354.85	355.09[c]

[a] From ref 2. [b] Calculated using the Antoine coefficients from ref 3. [c] From ref 4.

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

		Antoine coefficients[a]			
component	temp range/K	A	B	C	$\delta(P_i^\circ)$[b]/kPa
trichloroethylene	297−360	14.2231	3030.47	−44.232	0.046
1-propanol	303−370	16.0353	3415.56	−70.733	0.036
2-propanol	300−355	16.4089	3439.60	−63.417	0.025

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

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 constant temperature and pressure were obtained for 15 min or longer. At this time, samples of the 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. Samples of the 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 a vapor or liquid sample 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 sample.

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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 Trichloroethylene (1) + 1-Propanol (2) at 20 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	332.75		
0.011	0.067	331.45	3.186	0.996
0.019	0.111	330.55	3.060	1.000
0.027	0.150	329.75	2.998	1.005
0.036	0.190	329.05	2.895	1.001
0.049	0.240	328.15	2.826	0.997
0.067	0.309	326.55	2.797	1.004
0.090	0.380	324.75	2.750	1.014
0.119	0.450	323.05	2.624	1.017
0.151	0.507	321.55	2.469	1.026
0.187	0.575	319.45	2.463	1.035
0.241	0.629	317.65	2.247	1.068
0.289	0.656	316.55	2.043	1.124
0.344	0.703	315.15	1.944	1.140
0.435	0.742	313.95	1.706	1.232
0.515	0.766	313.15	1.539	1.360
0.580	0.782	312.75	1.418	1.499
0.669	0.801	312.35	1.279	1.780
0.751	0.819	312.15	1.175	2.180
0.825	0.835	312.05	1.096	2.831
0.888	0.856	312.05	1.043	3.866
0.935	0.881	312.35	1.008	5.381
0.982	0.946	313.35	0.988	8.137
1.000	1.000	314.35		

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 Trichloroethylene (1) + 1-Propanol (2) at 100 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	369.75		
0.009	0.032	369.05	2.751	0.981
0.033	0.113	367.25	2.691	0.987
0.060	0.189	365.55	2.595	0.991
0.080	0.240	364.45	2.572	0.990
0.114	0.309	362.75	2.417	1.001
0.196	0.422	359.75	2.108	1.038
0.251	0.490	358.15	2.000	1.050
0.314	0.536	356.85	1.824	1.098
0.383	0.577	355.85	1.655	1.163
0.468	0.619	355.05	1.491	1.254
0.541	0.648	354.55	1.373	1.368
0.615	0.668	354.35	1.251	1.554
0.667	0.693	354.15	1.203	1.678
0.733	0.718	354.15	1.135	1.920
0.811	0.752	354.45	1.064	2.362
0.874	0.784	354.95	1.015	3.007
0.900	0.811	355.35	1.007	3.263
0.919	0.837	355.75	1.004	3.438
0.947	0.872	356.55	0.992	3.958
0.956	0.890	356.85	0.994	4.023
0.974	0.929	357.75	0.990	4.279
0.986	0.958	358.45	0.988	4.568
1.000	1.000	359.55		

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 Trichloroethylene (1) + 2-Propanol (2) at 20 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	319.85		
0.007	0.030	319.25	3.428	0.999
0.013	0.051	318.95	3.296	0.998
0.023	0.093	318.25	3.306	1.001
0.032	0.118	317.85	3.192	1.002
0.042	0.156	317.35	3.226	0.996
0.055	0.188	316.75	3.065	1.002
0.077	0.246	315.75	2.979	1.005
0.103	0.304	314.75	2.863	1.007
0.135	0.359	313.75	2.674	1.017
0.170	0.412	312.75	2.541	1.026
0.213	0.464	311.75	2.385	1.042
0.256	0.510	310.85	2.269	1.059
0.319	0.543	310.25	1.986	1.116
0.381	0.579	309.75	1.811	1.164
0.461	0.617	309.15	1.639	1.256
0.542	0.644	308.85	1.472	1.399
0.614	0.666	308.65	1.357	1.573
0.696	0.690	308.55	1.244	1.866
0.770	0.713	308.65	1.157	2.271
0.836	0.738	308.95	1.089	2.857
0.891	0.769	309.35	1.047	3.695
0.932	0.806	309.95	1.021	4.847
0.974	0.898	311.95	1.001	5.895
0.987	0.941	313.05	0.989	6.317
1.000	1.000	314.35		

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 Trichloroethylene (1) + 2-Propanol (2) at 100 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	354.85		
0.008	0.021	354.55	3.029	0.982
0.032	0.080	353.55	2.901	0.985
0.068	0.147	352.45	2.626	0.991
0.106	0.209	351.45	2.498	0.996
0.156	0.273	350.35	2.286	1.015
0.218	0.337	349.45	2.074	1.037
0.290	0.394	348.75	1.866	1.074
0.357	0.437	348.35	1.700	1.121
0.433	0.477	348.05	1.548	1.194
0.509	0.508	347.95	1.404	1.304
0.573	0.539	347.95	1.323	1.407
0.632	0.562	348.15	1.243	1.537
0.695	0.587	348.45	1.169	1.729
0.752	0.611	348.85	1.110	1.970
0.798	0.641	349.35	1.081	2.184
0.862	0.688	350.55	1.034	2.641
0.908	0.745	352.05	1.015	3.035
0.941	0.801	353.65	1.001	3.457
0.949	0.830	354.45	1.003	3.328
0.967	0.871	355.65	0.996	3.715
0.979	0.907	356.65	0.994	3.940
0.985	0.929	357.35	0.990	4.215
0.991	0.951	358.15	0.984	4.451
1.000	1.000	359.55		

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. Comparison with data from the literature (*6*) shows differences of about 1%.

The VLE measurements were made at 20 and 100 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 observed that both systems present a minimum boiling azeotrope and the azeotropic point changes slightly with pressure. VLE data obtained in this study are in good agreement with those found in the literature (*7–9*).

The liquid-phase activity coefficients of the components were calculated by the equation

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

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.

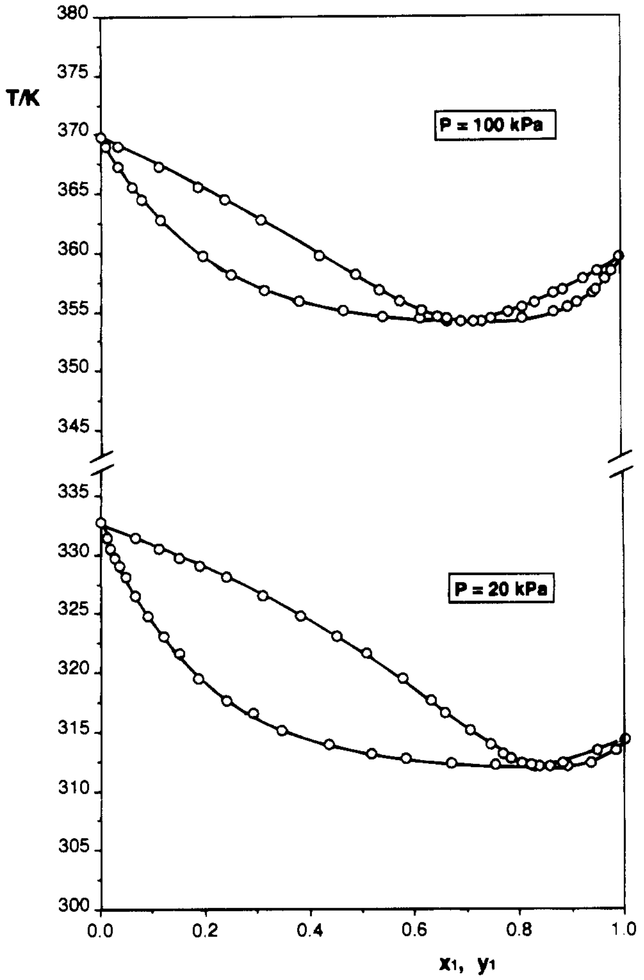

Figure 1. Vapor–liquid equilibrium of the system trichloroethylene (1) + 1-propanol (2) at 20 and 100 kPa as a function of the mole fraction of component 1: ○, experimental points; –, splined curves.

Table 7. Results of the Thermodynamic Consistency Test for the Binary Systems Used in This Study at 20 and 100 kPa

system	$\delta(y)^a$ $P = 20$ kPa	$\delta(y)^a$ $P = 100$ kPa
trichloroethylene + 1-propanol	0.0068	0.0056
trichloroethylene + 2-propanol	0.0059	0.0062

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

The exponential term (Poynting factor) is very nearly 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 literature (*10*). 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. Figure 3 shows experimental activity coefficients for the system trichloroethylene + 2-propanol at 100 kPa, as an illustration.

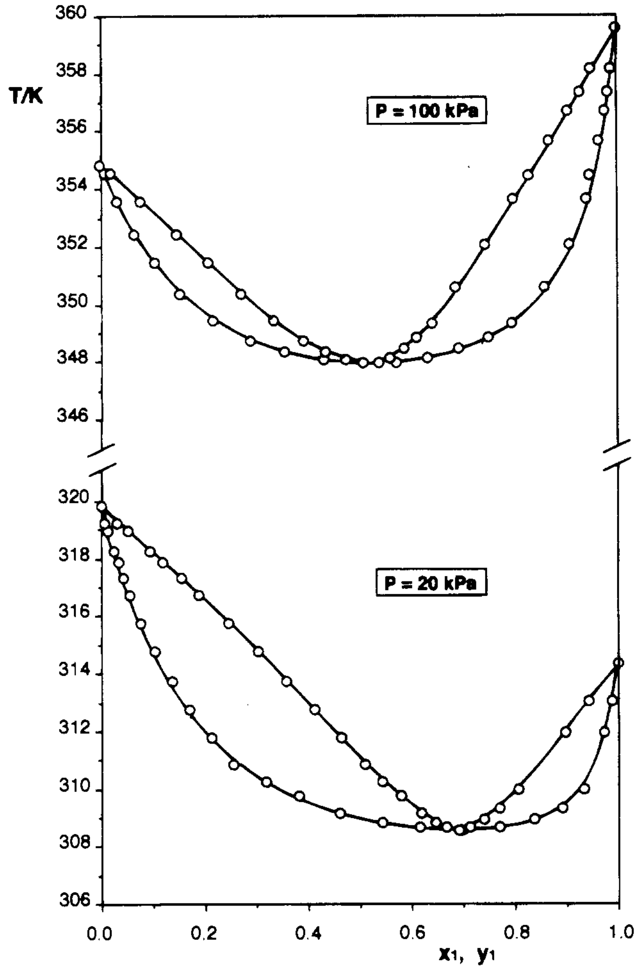

Figure 2. Vapor–liquid equilibrium of the system trichloroethylene (1) + 2-propanol (2) at 20 and 100 kPa as a function of the mole fraction of component 1: ○, experimental points; –, splined curves.

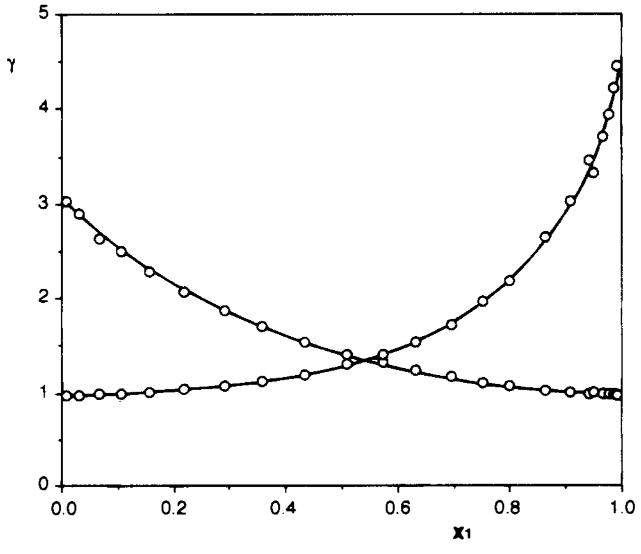

Figure 3. Experimental activity coefficients for the system trichloroethylene (1) + 2-propanol (2) at 100 kPa as a function of the mole fraction of component 1: ○, experimental points; –, splined curves.

The results were tested for thermodynamic consistency using the point-to-point method of Van Ness et al. (*11*), 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.

The activity coefficients were correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations

Table 8. Parameters and Deviations between Calculated and Experimental Vapor-Phase Mole Fractions and Temperatures

P/kPa	model	A_{12}	A_{21}	α_{12}	$\delta(y)$[a]	$\delta(T)$[b]
		Trichloroethylene + 1-Propanol				
20	Margules	1.123[c]	1.722[c]		0.0069	0.255
	Van Laar	1.130[c]	1.965[c]		0.0049	0.111
	Wilson	70.400[d]	1380.072[d]		0.0043	0.149
	NRTL	1216.430[d]	383.824[d]	0.627[c]	0.0059	0.251
	UNIQUAC	724.089[d]	−179.833[d]		0.0051	0.100
100	Margules	1.040	1.455		0.0051	0.151
	Van Laar	1.049	1.529		0.0043	0.143
	Wilson	115.116	1067.797		0.0043	0.190
	NRTL	842.458	337.598	0.557	0.0047	0.175
	UNIQUAC	605.496	−144.513		0.0038	0.234
		Trichloroethylene + 2-Propanol				
20	Margules	1.213	1.726		0.0075	0.160
	Van Laar	1.219	1.862		0.0052	0.107
	Wilson	122.494	1372.462		0.0054	0.202
	NRTL	1060.638	327.687	0.509	0.0041	0.142
	UNIQUAC	619.726	−125.860		0.0048	0.137
100	Margules	1.114	1.376		0.0060	0.217
	Van Laar	1.110	1.428		0.0046	0.241
	Wilson	192.377	936.035		0.0029	0.302
	NRTL	792.491	415.305	0.638	0.0029	0.261
	UNIQUAC	521.348	−97.448		0.0045	0.357

[a] $\delta(y) = \sum|y_{\mathrm{exptl}} - y_{\mathrm{calcd}}|/N$. [b] $\delta(T) = \sum|T_{\mathrm{exptl}} - T_{\mathrm{calcd}}|/N$ (N = number of data points). [c] Dimensionless. [d] Calories per mole.

(*12*). For fitting the binary parameters the following objective function was used:

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

For both systems, at the two pressures studied, all the models yield similar deviations between experimental and calculated vapor compositions and temperatures. The parameters and average deviations obtained for these equations are reported in Table 8.

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