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

Ana Dejoz, Vicenta González-Alfaro, Pablo J. Miguel, and M. Isabel Vázquez*

Departamento de Ingenieria Quimica, Facultad de Quimica, Universitat de Valencia, 46100 Burjassot, Valencia, Spain

Vapor−liquid equilibria for trichloroethylene + 1-butanol, and + 2-butanol are reported at 20 and 100 kPa. The two systems satisfy the point-to-point thermodynamic consistency test. Both systems show a positive deviation from ideality.

Introduction

Knowledge of vapor−liquid equilibria is of great importance to the development of chemical processing and the design of separation equipment. Such information can be obtained experimentally or estimated by using generalized methods that allow the calculation of the properties of the mixtures. For ideal systems, it is relatively easy to estimate vapor−liquid equilibria, but most systems of industrial interest show deviations from ideal behavior. Among the estimation methods, the most noteworthy are those of group contributions, mainly the UNIFAC method (Fredenslund et al., 1977). To obtain the interaction parameters for this model, experimental results are necessary.

The present work is part of a project for determining vapor−liquid equilibrium (VLE) data in mixtures in which at least one component is an alcohol. In this paper we report the equilibrium data at 20 and 100 kPa for the systems of trichloroethylene with 1-butanol and 2-butanol. These alcohols form azeotropic mixtures with trichloroethylene (Horsley, 1952; Ravi Prasad et al., 1977). However, only the azeotropic data and the vapor−liquid equilibrium data at 101.325 kPa are reported, so a study of the influence of the pressure on the azeotropic composition is required to expand and understand these systems.

Experimental Section

Chemicals. All components used in this study were purchased from Aldrich Chemical Co. The purities of all chemicals, by gas−liquid chromatography (GLC), were for trichloroethylene 99.86 mass %, for 1-butanol 99.94 mass %, and for 2-butanol 99.92 mass %. They were used without further purification. The water content was small in all chemicals (<0.1 mass %, checked by GLC). The densities of the pure liquids were measured at 298.15 K using an Anton Paar digital precision densimeter (model DMA 55) with a thermostated bath controlled to ±0.01 K. The refractive indexes of the pure liquids were measured at 298.15 K with an Abbe refractometer (type 3T). The experimental values of these properties and the boiling points are given in Table 1 together with those of the literature (TRC, 1994).

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

	d(293.15 K)/(kg m^{-3})		n(D, 293.15 K)		T_b (100 kPa)/K	
components	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.[a]
trichloroethylene	1464.04	1464.0	1.4779	1.4770	359.55	360.05[b]
1-butanol	809.50	809.7	1.3988	1.3993	390.25	390.51
2-butanol	807.20	806.9	1.3974	1.3972	371.85	372.34

[a] TRC (1994). [b] Obtained at 101.325 kPa.

Apparatus and Procedure. The equilibrium vessel used in this work was 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 (Germany) is capable of handling pressures from 0.25 to 400 kPa and temperatures 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.

In each experiment, the heating and shaking system of the liquid mixture was connected and the pressure was fixed and remained constant using a vacuum pump. The still was kept at constant temperature and pressure for 15 min or longer to ensure the stationary state. At this time, samples of liquid and condensate were taken for analysis. The equilibrium conditions were corroborated by the reproducibility of the results of GLC analysis of successive samples. 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 by using a Varian STAR 3400 CX gas−liquid chromatograph, 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 GLC response was treated with a Star Chromatography Station. 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.

Results and Discussion

The vapor pressures of the pure components $P_i°$ were measured with the same recirculating still. The experi-

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

trichloroethylene		1-butanol		2-butanol	
T/K	P_i°/kPa	T/K	P_i°/kPa	T/K	P_i°/kPa
296.85	9.27	315.35	2.86	305.65	3.92
299.55	10.42	319.55	3.76	309.65	5.04
302.85	12.25	323.85	4.85	313.25	6.25
304.55	13.19	326.45	5.62	316.25	7.43
307.85	15.26	329.45	6.65	318.55	8.51
310.65	17.26	332.25	7.77	320.85	9.72
313.25	19.27	334.65	8.83	323.15	11.00
315.65	21.31	336.75	9.86	324.95	12.11
317.75	23.24	338.85	11.01	326.75	13.37
319.75	25.19	340.65	12.08	328.35	14.50
322.35	27.68	342.25	13.10	329.75	15.61
325.25	31.03	343.85	14.18	331.25	16.85
327.85	34.28	345.25	15.20	332.55	18.03
329.75	36.83	346.95	16.52	333.85	19.25
331.25	38.97	348.35	17.68	335.45	20.82
333.55	42.45	349.75	18.89	336.65	22.08
336.75	47.62	350.75	19.82	337.75	23.35
339.75	52.91	352.45	21.43	340.65	26.88
341.65	56.51	356.25	25.48	344.05	31.56
343.75	60.67	359.05	28.88	347.25	36.50
345.55	64.44	363.55	35.15	350.55	42.22
347.75	69.31	366.65	40.12	353.25	47.62
349.95	74.46	369.35	44.91	355.55	52.47
351.45	78.11	372.85	51.75	358.05	58.27
353.05	82.19	374.95	56.35	360.05	63.30
354.65	86.43	377.25	61.68	361.95	68.46
355.55	88.91	380.25	69.27	363.95	74.13
357.15	93.42	382.35	74.81	365.95	80.07
358.05	96.23	384.15	80.01	367.45	84.85
359.55	100.40	385.85	85.42	368.95	89.84
359.85	101.64	387.25	90.09	370.35	94.64
		388.55	94.27	371.65	99.52
		390.25	100.04	372.95	104.61

components	*A*	*B*	*C*	$\delta(P_i^\circ)^a$/kPa
trichloroethylene	14.2231	3030.47	−44.232	0.05
1-butanol	15.8219	3499.92	−78.111	0.04
2-butanol	15.4438	3110.70	−84.708	0.07

[a] $\delta(P_i^\circ) = \sum|P^\circ_{\mathrm{exptl}} - P^\circ_{\mathrm{calcd}}|/N$ (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 Trichloroethylene (1) + 1- Butanol (2) at 20 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	350.95		
0.016	0.137	348.15	2.457	0.995
0.031	0.243	345.75	2.402	0.996
0.051	0.345	343.15	2.296	0.998
0.077	0.449	339.85	2.196	1.019
0.116	0.586	336.05	2.175	0.972
0.153	0.659	332.45	2.108	1.012
0.199	0.733	329.05	2.042	1.007
0.253	0.790	325.75	1.959	1.022
0.306	0.829	323.25	1.870	1.034
0.364	0.858	321.25	1.757	1.053
0.423	0.874	319.65	1.641	1.132
0.474	0.890	318.25	1.576	1.176
0.542	0.902	317.25	1.454	1.283
0.604	0.912	316.45	1.362	1.401
0.658	0.919	315.85	1.292	1.539
0.704	0.925	315.45	1.236	1.684
0.752	0.931	315.05	1.184	1.904
0.807	0.939	314.75	1.127	2.186
0.843	0.944	314.55	1.092	2.540
0.870	0.947	314.35	1.071	2.911
0.881	0.947	314.35	1.057	3.167
0.915	0.955	314.15	1.036	3.821
0.934	0.960	314.15	1.019	4.430
0.946	0.964	314.05	1.015	4.869
0.959	0.968	314.05	1.006	5.589
0.971	0.975	313.95	1.004	6.380
0.981	0.982	313.95	1.001	7.138
0.993	0.993	313.95	0.999	8.107
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-Butanol (2) at 100 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	390.25		
0.011	0.052	389.15	2.023	0.983
0.023	0.100	388.05	1.976	0.983
0.044	0.194	385.55	2.109	0.985
0.076	0.288	383.15	1.925	0.983
0.117	0.403	379.65	1.932	0.982
0.172	0.499	376.15	1.779	1.005
0.227	0.576	372.75	1.708	1.040
0.295	0.648	369.85	1.603	1.063
0.351	0.692	367.55	1.539	1.108
0.412	0.740	365.55	1.480	1.124
0.478	0.772	363.95	1.396	1.184
0.546	0.802	362.65	1.318	1.250
0.608	0.821	361.65	1.248	1.366
0.668	0.840	360.85	1.189	1.498
0.727	0.858	360.35	1.134	1.646
0.781	0.871	359.85	1.087	1.909
0.831	0.885	359.55	1.047	2.243
0.871	0.902	359.25	1.028	2.512
0.905	0.919	359.05	1.014	2.842
0.930	0.934	359.05	1.002	3.164
0.950	0.948	359.05	0.996	3.493
0.966	0.963	359.05	0.995	3.690
0.980	0.976	359.15	0.992	3.916
0.989	0.986	359.25	0.990	4.049
0.996	0.995	359.25	0.991	4.164
1.000	1.000	359.55		

mental values, in the range of work temperature, together with the parameters of the Antoine equation

$$\ln(P_i^\circ/\mathrm{kPa}) = A_i - \frac{B_i}{(T/K) + C_i} \tag{1}$$

and the mean absolute deviation between experimental and calculated vapor pressures, $\delta(P_i^\circ)$, are given in Table 2.

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. Table 7 shows a comparison between the azeotropic data reported in the literature for these systems and those obtained in this work at 100 kPa.

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

$$y_i\phi_i P = x_i\gamma_i\phi_i^{\mathrm{s}}p_i^\circ \exp[v_i(P - P_i^\circ)/RT] \tag{2}$$

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^{o} 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.

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 (Daubert and Danner, 1985). The values of the activity

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-Butanol (2) at 20 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	334.65		
0.009	0.047	333.85	2.390	0.999
0.025	0.102	332.85	1.934	1.006
0.046	0.192	331.15	2.134	1.008
0.072	0.286	329.55	2.157	0.995
0.101	0.375	327.55	2.176	0.996
0.131	0.448	325.55	2.157	1.013
0.171	0.528	323.55	2.101	1.012
0.215	0.597	321.55	2.043	1.017
0.270	0.651	319.85	1.898	1.042
0.322	0.687	318.45	1.777	1.089
0.399	0.732	317.05	1.618	1.139
0.470	0.763	315.95	1.498	1.213
0.511	0.777	315.25	1.444	1.289
0.567	0.798	314.55	1.374	1.374
0.637	0.817	314.15	1.272	1.526
0.689	0.833	313.85	1.214	1.653
0.744	0.840	313.55	1.149	1.950
0.778	0.853	313.35	1.124	2.099
0.814	0.867	313.25	1.097	2.280
0.839	0.871	313.25	1.070	2.541
0.872	0.883	313.25	1.043	2.912
0.899	0.896	313.15	1.031	3.293
0.921	0.906	313.15	1.017	3.804
0.939	0.922	313.25	1.011	4.054
0.951	0.929	313.35	1.002	4.528
0.957	0.943	313.45	1.006	4.214
0.970	0.954	313.55	0.999	4.871
0.982	0.967	313.75	0.994	5.548
0.992	0.985	313.85	0.998	5.568
0.999	0.998	314.05	0.995	6.078
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-Butanol (2) at 100 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	371.85		
0.012	0.038	371.25	2.292	0.998
0.021	0.060	370.75	2.027	1.003
0.043	0.120	369.75	2.032	0.998
0.086	0.193	368.25	1.724	1.014
0.136	0.288	366.45	1.706	1.015
0.205	0.391	364.55	1.623	1.017
0.261	0.461	362.95	1.573	1.031
0.303	0.515	361.55	1.578	1.041
0.363	0.564	360.25	1.499	1.079
0.415	0.608	359.25	1.455	1.101
0.467	0.659	358.45	1.435	1.087
0.525	0.688	357.95	1.354	1.138
0.570	0.703	357.55	1.290	1.217
0.642	0.726	357.15	1.197	1.371
0.693	0.745	356.95	1.143	1.505
0.734	0.757	356.85	1.101	1.657
0.774	0.779	356.75	1.079	1.777
0.810	0.797	356.75	1.054	1.945
0.838	0.821	356.85	1.046	2.008
0.865	0.839	357.05	1.028	2.158
0.892	0.860	357.25	1.017	2.301
0.910	0.877	357.45	1.011	2.406
0.932	0.895	357.65	0.999	2.722
0.948	0.916	357.95	0.997	2.801
0.963	0.936	358.25	0.994	3.003
0.980	0.961	358.75	0.989	3.194
0.988	0.978	358.95	0.991	3.009
0.994	0.988	359.15	0.990	3.418
0.998	0.995	359.35	0.988	3.150
1.000	1.000	359.55		

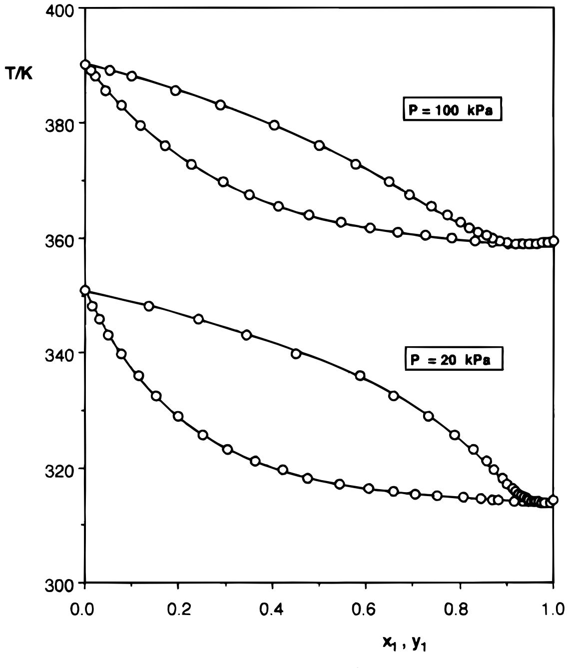

Figure 1. Vapor−liquid equilibrium of the system trichloroethylene (1) + 1-butanol (2) at 20 and 100 kPa as a function of the mole fraction of component 1: (○) experimental points, (—) splined curves.

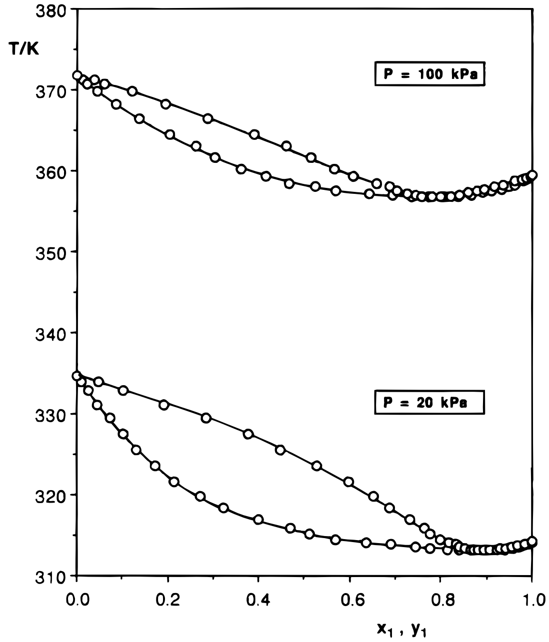

Figure 2. Vapor−liquid equilibrium of the system trichloroethylene (1) + 2-butanol (2) at 20 and 100 kPa as a function of the mole fraction of component 1: (○) experimental points, (—) splined curves.

coefficients calculated using eq 2 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. (1973), modified by Fredenslund et al. (1977). 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 are $\delta(y) = 0.0031$ and $\delta(y) = 0.0073$ for the tricloroethylene + 1-butanol system at 20 and 100 kPa, respectively, and $\delta(y) = 0.0048$ and $\delta(y) = 0.0045$ for the tricloroethylene + 2-butanol system at 20 and 100 kPa, respectively. These results

Table 7. Azeotropic Data of Trichloroethylene (1) + 1-Butanol (2) and + 2-Butanol (2) Systems

system	T/K	x_1
trichloroethylene + 1-butanol	359.80[a]	0.944[a]
	360.25[b]	0.980[b]
	359.05[c]	0.932[c]
trichloroethylene + 2-butanol	357.35[a]	0.762[a]
	356.95[b]	0.800[b]
	356.75[c]	0.775[c]

[a] Horsley (1952). [b] Ravi Prasad et al. (1977). [c] This work.

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) + 1-Butanol (2)					
20	Margules	0.734[c]	1.866[c]		0.0078	0.454
	Van Laar	0.849[c]	2.106[c]		0.0034	0.104
	Wilson	46.096[d]	1338.751[d]		0.0026	0.135
	NRTL	1225.045[d]	121.986[d]	0.529[c]	0.0031	0.098
	UNIQUAC	735.242[d]	−247.297[d]		0.0034	0.105
100	Margules	0.673	1.416		0.0071	0.484
	Van Laar	0.745	1.482		0.0052	0.323
	Wilson	32.255	1035.868		0.0042	0.278
	NRTL	930.859	146.383	0.618	0.0043	0.290
	UNIQUAC	596.291	−215.304		0.0047	0.315
	Trichloroethylene (1) + 2-Butanol (2)					
20	Margules	0.737	1.726		0.0066	0.210
	Van Laar	0.846	1.835		0.0060	0.142
	Wilson	93.328	1064.713		0.0053	0.138
	NRTL	1054.045	102.395	0.510	0.0058	0.143
	UNIQUAC	608.898	−200.168		0.0055	0.137
100	Margules	0.665	1.184		0.0065	0.207
	Van Laar	0.711	1.217		0.0063	0.227
	Wilson	48.057	826.611		0.0070	0.244
	NRTL	788.489	83.176	0.544	0.0065	0.229
	UNIQUAC	541.402	−214.495		0.0062	0.246

[a] $\delta(y) = \sum|y_{\text{exptl}} - y_{\text{calcd}}|/N$ (N = number of data points). [b] $\delta(T) = \sum|T_{\text{exptl}} - T_{\text{calcd}}|/N$ (N = no. of data points). [c] Dimensionless. [d] Calories per mole.

indicate that the experimental data are thermodynamically consistent.

The activity coefficients were correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations (Gmehling and Onken, 1977). For fitting the binary parameters, the following objective function was used:

$$F = \sum\left(\frac{y_{\text{exptl}} - y_{\text{calcd}}}{y_{\text{exptl}}}\right)^2 + \sum\left(\frac{T_{\text{exptl}} - T_{\text{calcd}}}{T_{\text{exptl}}}\right)^2 \qquad (3)$$

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. Figure 3 presents a comparison between the experimental values obtained in this work at 100 kPa and those calculated using the Wilson equation. In this figure the experimental values found in the literature have also been included. It can be observed that the Wilson equation fits the VLE data obtained in this work well, and the data are in good agreement with the data obtained by Ravi Prasad et al. (1977).

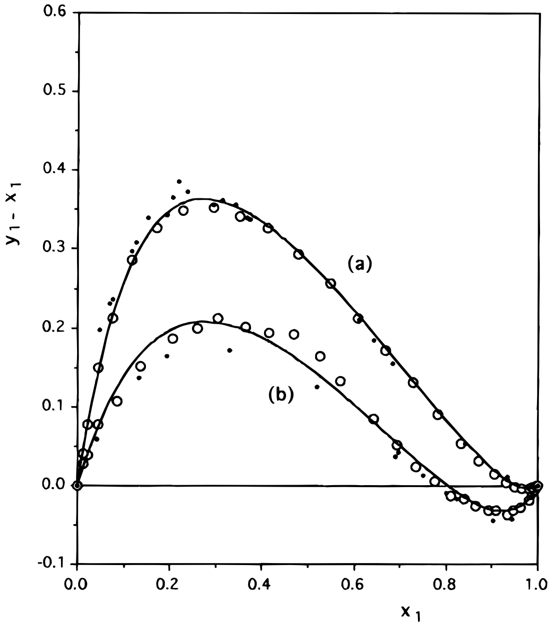

Figure 3. Comparison among the experimental values obtained in this work (○), those from the literature (●) (Ravi Prasad et al., 1977), and those calculated using the Wilson equation (—): (a) tricloroethylene + 1-butanol, (b) tricloroethylene + 2-butanol.

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