Isobaric Vapor−Liquid Equilibria of Tetrachloroethylene + 1-Propanol and +2-Propanol at 20 and 100 kPa

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Isobaric vapor−liquid equilibria were obtained for tetrachloroethylene + 1-propanol and +2-propanol systems at 20 and 100 kPa using a dynamic still. The experimental error in temperature was ±0.1 K, in pressure ±0.01 kPa and ±0.1 kPa for the experiments carried out at 20 and 100 kPa, respectively, and in liquid and vapor composition 0.001. The two systems satisfy the point-to-point thermodynamic consistency test. Both systems show a positive deviation from ideality. The data were well correlated with the Wilson equation.

Introduction

Vapor−liquid equilibrium (VLE) data are indispensable in the design of separation processes such as distillation and extractive distillation. Values can be obtained by either experimental or predictive methods. Among the estimation methods, the most noteworthy are those of group contribution, mainly the UNIFAC method (Fredenslund et al., 1977). This model requires a complete and updated experimental VLE data bank in order to fit the group interaction parameters. There is a lack of VLE measurements for some groups (Gmehling et al., 1993). These authors propose different parameters for the different alcohols (primary, secondary, and tertiary) by introducing different contribution parameters for different alcohol groups. This would, however, involve a great increase in the number of required group interaction parameters and the present data base does not allow a fit of these parameters. The present work is part of a project for determining vapor−liquid equilibrium in mixtures in which one component, at least, is an alcohol. On the other hand, another functional group for which more experimental data are desirable is the ClC=C group.

In this article we report the equilibrium data at 20 and 100 kPa for tetrachloroethylene + 1-propanol and +2-propanol. These alcohols form azeotropic mixtures with tetrachloroethylene (Horsley, 1952; Sagnes and Sanchez, 1971; Venkateswara Rao et al., 1980; Venkateswara Rao and Ravi Prasad, 1984). However, only the azeotropic data and the vapor−liquid equilibrium data at 760 mmHg for the tetrachloroethylene + 1-propanol system and at 101.08 kPa for the tetrachloroethylene + 2-propanol system are given in these works, so a study of the influence of the pressure on the azeotropic composition is of interest.

Experimental Section

Chemicals. All components used were purchased from Aldrich Chemie Co. The purity of all chemicals was checked by gas chromatography (GC) and found to be tetrachloroethylene (99.60 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 (<0.05 mass %, checked by GC). The densities of the pure liquids were measured at 298.15 K using an Anton Paar DMA 55 densimeter. The refractive indexes of the pure liquids were measured at 298.15 K in an Abbe refractometer, Atago 3T. The temperature was

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

component	d(298.15 K)/ kg·m^{-3} exptl	lit.[a]	n(D, 298.15 K) exptl	lit.[a]	T_b(100 kPa)/K exptl	lit.[a]
tetrachloro-ethylene	1614.26	1614.30	1.5036	1.5037	394.15	394.23[b]
1-propanol	799.63	799.75	1.3832	1.3837	369.75	369.95
2-propanol	781.21	781.26	1.3750	1.3752	354.85	355.09

[a] TRC, 1996. [b] At 101.325 kPa.

controlled to ±0.01 K with a thermostated bath. The accuracies in density and refractive index measurements are ±0.01 kg·m^{-3} and ±0.0002, respectively. The experimental values of these properties and the boiling points are given in Table 1 together with those of the literature (TRC, 1996).

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 *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.

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. The experimental error in temperature was ±0.1 K and in pressure was ±0.01 kPa and ±0.1 kPa for the experiments carried out at 20 and 100 kPa, respectively. At this time, samples of liquid and condensate were taken for analysis. The extractions were carried out with special syringes that allowed us to take small volume samples in a system under partial vacuum.

Table 2. Vapor Pressure P_i^o, Antoine Coefficients A, B, and C, and Standard Deviations (σ^a), of Pure Components

tetrachloroethylene		1-propanol		2-propanol	
T/K	P_i^o/kPa	*T*/K	P_i^o/kPa	*T*/K	P_i^o/kPa
307.75	4.00	303.35	3.82	300.35	6.59
311.25	4.73	306.85	4.82	303.85	8.17
314.45	5.56	310.05	5.82	306.75	9.71
318.45	6.70	312.75	6.86	306.85	9.75
321.75	7.89	316.15	8.31	309.45	11.34
324.45	8.88	319.25	9.91	311.45	12.71
327.05	9.94	322.45	11.85	313.55	14.30
329.35	10.94	325.95	14.21	315.25	15.68
331.35	11.91	329.25	16.83	317.35	17.56
333.25	12.89	332.15	19.46	319.45	19.62
336.95	14.97	334.15	21.51	321.45	21.76
338.35	15.88	335.95	23.51	322.85	23.30
339.95	16.91	338.05	25.99	324.35	25.17
341.45	17.92	340.85	29.67	326.15	27.56
344.15	19.90	343.35	33.33	327.55	29.57
345.55	20.98	346.05	37.59	329.55	32.62
347.35	22.47	348.85	42.64	331.85	36.45
349.15	24.06	351.75	48.41	334.55	41.41
355.35	30.15	354.15	53.72	336.95	46.28
360.05	35.47	356.35	58.97	339.55	52.09
364.55	41.21	358.55	64.62	341.55	56.93
368.05	46.30	360.45	69.85	343.25	61.39
371.15	51.07	362.15	74.80	345.05	66.40
374.45	56.58	363.65	79.42	346.75	71.44
377.55	62.34	365.35	84.97	348.35	76.52
381.05	69.20	366.45	88.69	349.85	81.57
383.95	75.34	367.65	92.93	351.35	86.75
386.35	80.71	368.55	96.20	352.65	91.52
388.55	85.92	369.95	101.37	353.85	96.08
390.55	90.86			354.95	100.46
392.35	95.63				
393.85	99.53				
394.55	101.41				

component	A	B	C	σ/kPa
tetrachloroethylene	13.2979	2770.06	−75.348	0.040
1-propanol	16.0353	3415.56	−70.733	0.045
2-propanol	16.4089	3439.60	−63.417	0.036

^{a} $\sigma = \sqrt{\sum(P^o - P^o(\text{calc}))^2/(N-p)}$; N = no. of data points; p = no. of parameters.

Analysis. Samples of the liquid and condensed vapor phases were analyzed by using 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. At least two analyses were made of each liquid and each vapor sample. The experimental error in these variables was less than 0.001 mole fraction.

Results and Discussion

The vapor pressures of the pure components P_i^o were measured with the same recirculating still. The experimental values, in the range of work temperature, together with the parameters of the Antoine equation

$$\ln(P_i^o/\text{kPa}) = A_i - \frac{B_i}{(T/\text{K}) + C_i} \qquad (1)$$

and the standard deviation (σ) are given in Table 2. Figure 1 presents a comparison between the experimental values obtained in this work for the three components and those of the literature (TRC, 1996).
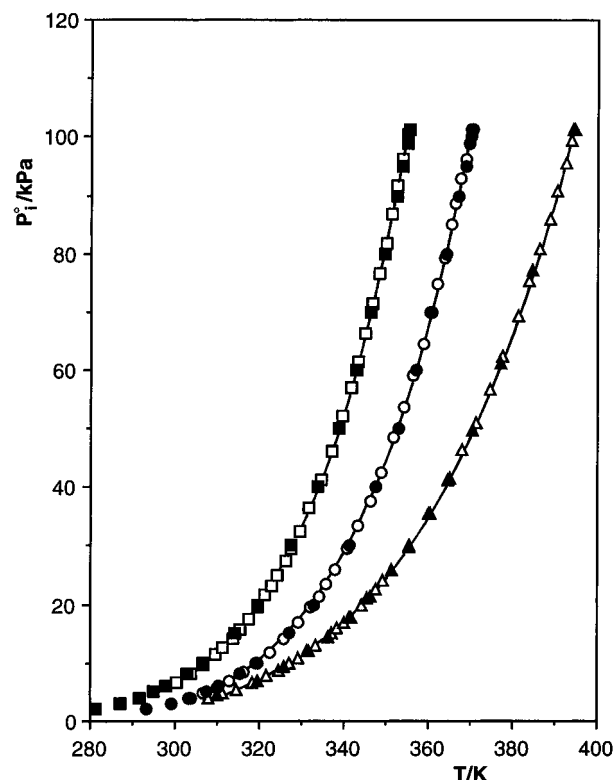

Figure 1. Comparison among the experimental vapor pressure values obtained in this work and those of the literature for tetrachloroethylene (($\triangle$) experimental, ($\blacktriangle$) literature), 1-propanol (($\bigcirc$) experimental, ($\bullet$) literature), and 2-propanol (($\square$) experimental, ($\blacksquare$) literature).

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-Propanol (2) at 20 kPa

x_1	y_1	*T*/K	γ_1	γ_2
0.000	0.000	332.75		
0.007	0.024	332.45	5.117	0.989
0.014	0.044	332.15	4.954	0.989
0.028	0.080	331.65	4.710	0.990
0.053	0.134	330.85	4.351	0.995
0.080	0.191	330.05	4.184	0.998
0.117	0.242	329.35	3.773	1.008
0.154	0.280	328.75	3.399	1.030
0.199	0.326	328.35	3.102	1.040
0.247	0.353	328.05	2.752	1.078
0.295	0.377	327.85	2.473	1.122
0.344	0.395	327.75	2.233	1.176
0.397	0.412	327.65	2.029	1.250
0.448	0.425	327.75	1.847	1.328
0.499	0.442	327.75	1.722	1.421
0.553	0.446	327.85	1.566	1.569
0.602	0.450	327.95	1.442	1.745
0.650	0.459	328.05	1.357	1.941
0.697	0.471	328.25	1.286	2.173
0.739	0.480	328.45	1.228	2.447
0.775	0.490	328.65	1.184	2.759
0.812	0.500	328.95	1.138	3.186
0.845	0.511	329.35	1.100	3.700
0.878	0.526	329.85	1.066	4.437
0.905	0.542	330.55	1.033	5.352
0.932	0.566	331.65	1.001	6.670
0.953	0.602	332.95	0.987	8.233
0.969	0.671	335.15	0.987	9.443
0.982	0.763	338.05	0.986	10.296
0.991	0.858	340.65	0.990	10.821
0.996	0.932	342.85	0.983	11.499
1.000	1.000	344.35		

The VLE measurements were made at 20 and 100 kPa and are presented in Tables 3−6. The *T*−*x*−*y* diagrams

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-Propanol (2) at 100 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	369.75		
0.007	0.015	369.55	4.287	0.982
0.014	0.029	369.35	4.180	0.982
0.029	0.055	368.95	3.989	0.985
0.049	0.088	368.35	3.787	0.993
0.082	0.131	367.85	3.415	1.000
0.115	0.172	367.45	3.253	1.003
0.154	0.207	367.05	2.961	1.020
0.203	0.242	366.85	2.646	1.042
0.248	0.268	366.75	2.399	1.072
0.300	0.293	366.75	2.172	1.112
0.350	0.309	366.75	1.961	1.170
0.401	0.328	366.85	1.812	1.230
0.445	0.340	367.05	1.681	1.295
0.498	0.353	367.25	1.549	1.392
0.544	0.362	367.45	1.448	1.497
0.598	0.373	367.85	1.339	1.644
0.634	0.382	368.15	1.279	1.764
0.684	0.394	368.65	1.204	1.964
0.725	0.406	369.15	1.153	2.168
0.761	0.418	369.75	1.109	2.391
0.790	0.434	370.35	1.088	2.584
0.826	0.448	371.05	1.052	2.959
0.880	0.494	373.35	1.013	3.619
0.910	0.549	375.55	1.017	3.983
0.925	0.582	377.65	0.997	4.088
0.940	0.627	379.35	1.004	4.300
0.956	0.690	381.85	1.010	4.464
0.972	0.770	385.05	1.010	4.665
0.984	0.845	388.25	1.001	4.943
0.993	0.921	390.65	1.012	5.316
1.000	1.000	394.15		

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-Propanol (2) at 20 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	319.85		
0.007	0.016	319.75	6.036	0.988
0.014	0.030	319.65	5.795	0.986
0.030	0.056	319.45	5.307	0.984
0.054	0.091	319.05	4.873	0.993
0.082	0.125	318.75	4.428	1.001
0.122	0.159	318.55	3.817	1.017
0.163	0.189	318.45	3.430	1.033
0.206	0.212	318.35	3.048	1.065
0.254	0.232	318.35	2.704	1.105
0.307	0.248	318.45	2.392	1.156
0.355	0.259	318.55	2.145	1.219
0.408	0.267	318.65	1.914	1.307
0.456	0.284	318.75	1.813	1.383
0.509	0.291	318.95	1.650	1.500
0.562	0.295	319.25	1.498	1.643
0.618	0.298	319.45	1.362	1.858
0.663	0.310	319.65	1.307	2.049
0.705	0.317	319.95	1.240	2.281
0.746	0.327	320.35	1.187	2.560
0.785	0.330	320.65	1.121	2.958
0.821	0.345	321.15	1.096	3.399
0.847	0.353	321.75	1.059	3.796
0.873	0.381	322.65	1.064	4.168
0.909	0.392	323.65	1.006	5.431
0.935	0.430	325.15	1.002	6.620
0.956	0.486	327.45	1.003	7.873
0.974	0.582	331.75	0.980	8.937
0.985	0.687	335.65	0.975	9.578
0.994	0.830	339.85	0.986	10.295
0.997	0.910	342.15	0.985	10.544
1.000	1.000	344.35		

for the two systems are shown in Figures 2 and 3. From these figures it can be observed that both systems present

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-Propanol (2) at 100 kPa

| x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	354.85		
0.008	0.012	354.75	4.845	0.983
0.016	0.023	354.65	4.767	0.984
0.030	0.041	354.55	4.546	0.983
0.054	0.067	354.45	4.152	0.985
0.084	0.094	354.35	3.769	0.991
0.120	0.121	354.25	3.401	1.005
0.164	0.145	354.25	2.988	1.029
0.219	0.171	354.45	2.607	1.061
0.278	0.190	354.65	2.274	1.111
0.339	0.203	354.95	1.980	1.179
0.394	0.215	355.35	1.775	1.247
0.440	0.226	355.75	1.648	1.310
0.506	0.231	356.15	1.446	1.451
0.552	0.242	356.55	1.365	1.554
0.600	0.247	356.95	1.268	1.701
0.650	0.253	357.55	1.174	1.883
0.691	0.262	358.15	1.119	2.059
0.755	0.277	358.75	1.059	2.493
0.798	0.296	359.95	1.029	2.804
0.879	0.353	363.25	0.999	3.778
0.923	0.427	368.25	0.978	4.360
0.941	0.482	371.15	0.988	4.681
0.955	0.540	374.75	0.977	4.775
0.970	0.626	379.05	0.980	4.972
0.981	0.721	383.35	0.983	5.240
0.992	0.850	387.85	1.011	5.497
0.996	0.921	390.75	1.006	5.599
1.000	1.000	394.15		
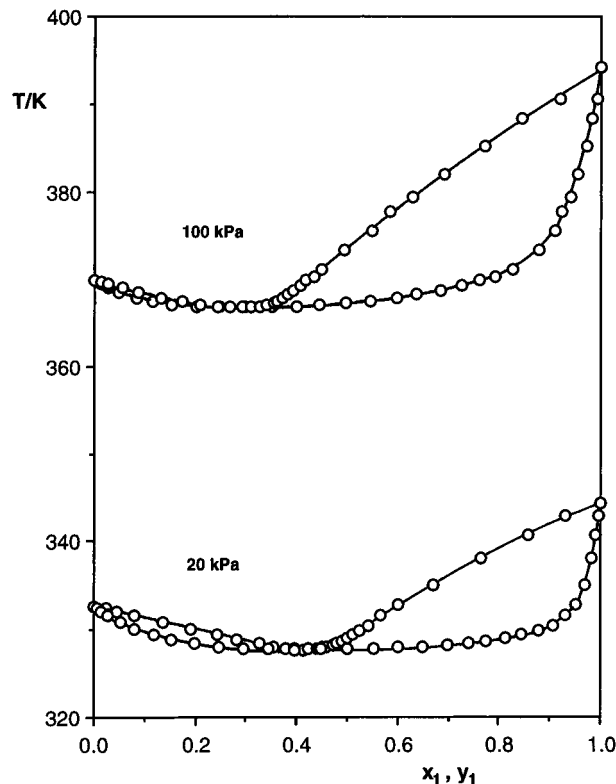
Figure 2. Vapor−liquid equilibrium of the system tetrachloroethylene (1) + 1-propanol (2) at 20 and 100 kPa as a function of the mole fraction of component 1: (○) experimental points; (—) splined curves.

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.
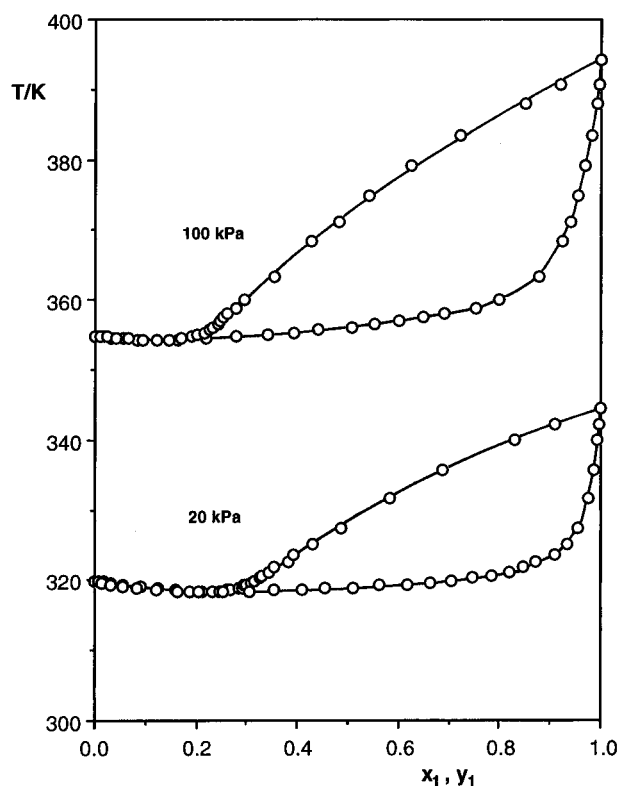
Figure 3. Vapor−liquid equilibrium of the system tetrachloro-ethylene (1) + 2-propanol (2) at 20 and 100 kPa as a function of the mole fraction of component 1: (○) experimental points, (−) splined curves.

Table 7. Azeotropic Data of Tetrachloroethylene (1) + 1-Propanol (2) and + 2-Propanol (2) Systems

system	T/K	x_1
tetrachloroethylene + 1-propanol	366.75[a]	0.287[a]
	367.15[b]	0.295[b]
	367.15[c]	0.300[c]
	367.20[d]	0.282[d]
tetrachloroethylene + 2-propanol	354.25[a]	0.122[a]
	354.85[d]	0.135[d]
	354.15[e]	0.144[e]

[a] This work. [b] Sagnes and Sanchez, 1971. [c] Venkateswara Rao et al., 1980. [d] Horsley, 1952. [e] Venkateswara Rao and Ravi Prasad, 1984.

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

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

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, 1995). The values of the activity 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),

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}/ J·mol^{-1}	A_{21}/ J·mol^{-1}	$\delta(y)^a$	$\delta(T)^b$/ K
tetrachloroethylene +	20	1280.780	6562.508	0.0055	0.129
1-propanol	100	1392.659	4873.130	0.0059	0.209
tetrachloroethylene +	20	1666.041	5916.928	0.0034	0.258
2-propanol	100	1770.614	4708.387	0.0060	0.412

[a] $\delta(y) = \Sigma|y - y(\text{calc})|/N$. [b] $\delta(T) = \Sigma|T - T(\text{calc})|/N$, N = no. data points.
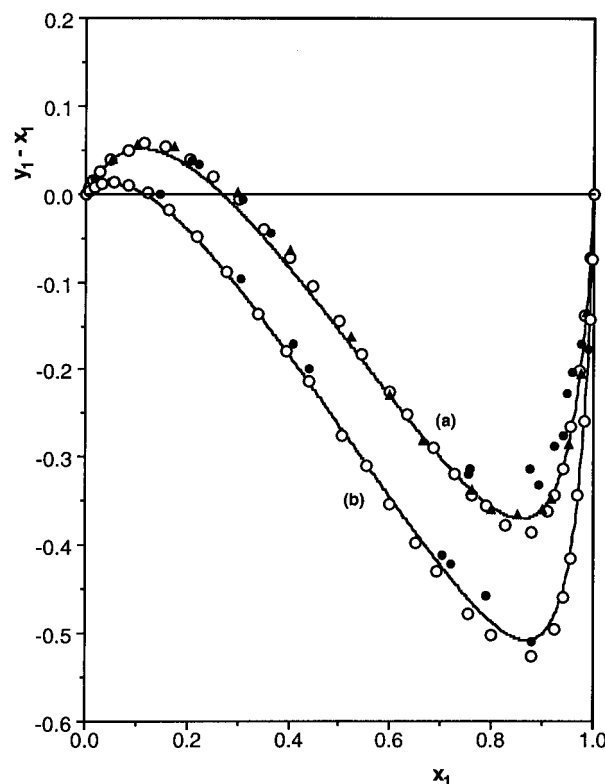

Figure 4. Comparison among the experimental values obtained in this work (○), those calculated using the Wilson equation (−), and those from the literature: (a) tetrachloroethylene + 1-propanol ((●) Venkateswara Rao et al., 1980; (▲) Sagnes and Sanchez, 1971); (b) tetrachloroethylene + 2-propanol ((●) Venkateswara Rao and Ravi Prasad, 1984).

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 values 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 $\delta(y) = 0.0058$ and $\delta(y) = 0.0059$ for the tetrachloroethylene + 1-propanol system at 20 and 100 kPa, respectively, and $\delta(y) = 0.0039$ and $\delta(y) = 0.0055$ for the tetrachloroethylene + 2-propanol system at 20 and 100 kPa, respectively. These results 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 (Gmehling and Onken, 1977). For fitting the binary parameters the following objective function was used:

$$F = \sum \left(\frac{\gamma_1 - \gamma_{1(\text{calc})}}{\gamma_1} \right)^2 + \sum \left(\frac{\gamma_2 - \gamma_{2(\text{calc})}}{\gamma_2} \right)^2 \tag{3}$$

For both systems, at the two pressures studied, the Wilson equation gives a good correlation between the experimental and calculated vapor compositions and temperatures. The parameters and average deviations obtained for this equation are reported in Table 8. Figure 4 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 those of the literature.

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