J. Chem. Eng. Data **1999,** *44,* 286−290

Vapor−Liquid Equilibrium of Binary Mixtures of Tetrachloroethylene with 1-Pentanol, 3-Methyl-1-butanol, and 2-Methyl-1-butanol

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Isobaric vapor−liquid equilibria have been obtained for the systems tetrachloroethylene + 1-pentanol, tetrachloroethylene + 3-methyl-1-butanol, and tetrachloroethylene + 2-methyl-1-butanol, using a dynamic still. The three systems have been studied at 20 kPa, and for the tetrachloroethylene + 2-methyl-1-butanol system equilibrium has been obtained also at 100 kPa. The experimental error in temperature is ±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 the liquid and vapor mole fraction ±0.001. The systems satisfy the point-to-point thermodynamic consistency test. All the systems show a positive deviation from ideality. The data have been well-correlated with the Wilson equation.

Introduction

Distillation processes are extensively used for the separation of liquid mixtures. The correct design of distillation columns requires the availability of accurate and thermodynamically consistent vapor−liquid equilibria (VLE) data. Although these data can be estimated from available predictive models as the UNIFAC method (Fredenslund et al., 1977; Hansen et al., 1991), experimental data are required to update and improve the data bank used to fit the model parameters. There is a lack of VLE data for some groups. Gmehling et al. (1993) propose different parameters for the different alcohols (primary, secondary, and tertiary) by introducing different contribution parameters. This involves a great increase in the number of required group interaction parameters. To obtain these parameters, a reliable and extensive database is necessary. The present work is part of a project to determine vapor−liquid equilibrium in mixtures in which one or more components is an alcohol. The ClC═C group is another functional group for which more experimental data are desirable.

In previous work, we have reported equilibrium data for tetrachloroethylene + 1-butanol and tetrachloroethylene + 2-butanol systems (Dejoz et al., 1995) and for tetrachloroethylene + 1-propanol and tetrachloroethylene + 2-propanol systems (Dejoz et al., 1996). These systems present a minimum boiling azeotrope, and the azeotropic point varies with pressure. Rao et al. (1980) and Raviprasad et al. (1981) studied the tetrachloroethylene + 1-pentanol and the tetrachloroethylene + 3-methyl-1-butanol systems at 101.32 kPa, and, for both systems, a minimum boiling azeotrope was observed. Experimental data for these systems at different pressures have not been found in the literature.

In this work we report equilibrium data at 20 kPa for binary mixtures of tetrachloroethylene with three C_5 branched alcohols with the alcohol group in a primary position (1-pentanol, 3-methyl-1-butanol, and 2-methyl-1-butanol). Experimental data for the tetrachloroethylene + 2-methyl-1-butanol system at atmospheric pressure have not been found in the literature, so in this work equilibrium values for this system at 100 kPa have been obtained also.

Table 1. 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-Pentanol (2) at 20 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	368.65		
0.016	0.100	366.75	2.855	0.997
0.042	0.234	363.95	2.786	0.988
0.088	0.395	359.85	2.571	0.990
0.135	0.509	356.55	2.417	0.990
0.185	0.593	353.75	2.265	0.997
0.239	0.656	351.65	2.089	1.001
0.288	0.700	349.65	1.988	1.031
0.343	0.735	348.15	1.852	1.064
0.401	0.767	346.95	1.728	1.091
0.459	0.790	345.95	1.613	1.147
0.509	0.809	345.25	1.529	1.192
0.565	0.822	344.65	1.432	1.294
0.617	0.834	344.15	1.356	1.407
0.670	0.844	343.75	1.283	1.567
0.726	0.854	343.45	1.212	1.794
0.778	0.865	343.25	1.154	2.069
0.825	0.873	343.15	1.102	2.483
0.871	0.885	343.05	1.063	3.066
0.910	0.897	342.95	1.035	3.957
0.956	0.924	343.25	1.003	5.878
0.982	0.959	343.65	0.998	7.590
1.000	1.000	344.35		

Experimental Section

Chemicals. All the components used were purchased from Aldrich Chemical Co. The purity of all chemicals was checked by gas chromatography (GC) and found to be as follows: tetrachloroethylene (99.60 mass %), 1-pentanol (99.30 mass %), 3-methyl-1-butanol (99.71 mass %), and 2-methyl-1-butanol (99.05 mass %). They were used without further purification. The water content was less than 0.05% in all chemicals, as determined by GC using a thermal conductivity detector.

10.1021/je980170f CCC: $18.00

Table 2. 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) + 3-Methyl-1-butanol (2) at 20 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	363.05		
0.019	0.098	361.35	2.811	0.994
0.046	0.218	358.85	2.809	0.993
0.093	0.373	355.25	2.690	0.991
0.140	0.483	352.45	2.553	0.985
0.191	0.561	350.15	2.360	0.995
0.243	0.621	348.25	2.200	1.010
0.296	0.664	346.75	2.041	1.038
0.350	0.699	345.55	1.901	1.071
0.405	0.726	344.65	1.765	1.115
0.460	0.749	343.95	1.646	1.167
0.513	0.768	343.35	1.548	1.235
0.566	0.781	342.85	1.454	1.342
0.616	0.791	342.55	1.369	1.471
0.669	0.804	342.25	1.296	1.626
0.721	0.816	342.05	1.230	1.830
0.774	0.826	341.85	1.169	2.159
0.825	0.837	341.75	1.115	2.626
0.885	0.854	341.75	1.061	3.579
0.926	0.871	342.05	1.022	4.837
0.964	0.907	342.65	0.999	6.946
0.987	0.959	343.45	1.001	8.134
1.000	1.000	344.35		

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) + 2-Methyl-1-butanol (2) at 20 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	360.95		
0.019	0.096	359.05	2.973	1.006
0.044	0.198	357.05	2.835	1.004
0.090	0.339	353.95	2.643	1.006
0.139	0.445	351.45	2.455	1.007
0.191	0.527	349.35	2.282	1.012
0.241	0.588	347.65	2.147	1.022
0.293	0.635	346.25	2.009	1.043
0.345	0.669	345.25	1.866	1.075
0.398	0.694	344.45	1.729	1.126
0.454	0.720	343.75	1.615	1.178
0.503	0.736	343.25	1.519	1.252
0.554	0.754	342.85	1.434	1.328
0.605	0.767	342.45	1.357	1.450
0.654	0.779	342.15	1.289	1.595
0.704	0.791	341.95	1.226	1.782
0.754	0.804	341.75	1.172	2.032
0.804	0.816	341.65	1.120	2.407
0.853	0.831	341.75	1.071	2.932
0.902	0.850	341.95	1.028	3.862
0.950	0.887	342.45	0.999	5.556
0.979	0.935	343.15	0.995	7.336
1.000	1.000	344.35		

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 apparatus (Labodest model) manufactured by Fischer Labor und Verfahrenstechnik is capable of handling pressures from 0.25 to 400 kPa and temperatures up to 523.15 K. This still ensures good mixing of the vapor and liquid phases and good separation of the phases once they reach equilibrium, and it prevents entrainment of liquid drops and partial condensation in the vapor phase. The equilibrium temperature was measured using a digital Fisher thermometer provided with a Pt-100 temperature sensor, and the pressure, with a digital manometer. The experimental error in temperature was ±0.1 K and in pressure ±0.01 kPa and ±0.1 kPa for the experiments carried out at 20 and 100 kPa, respectively.

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

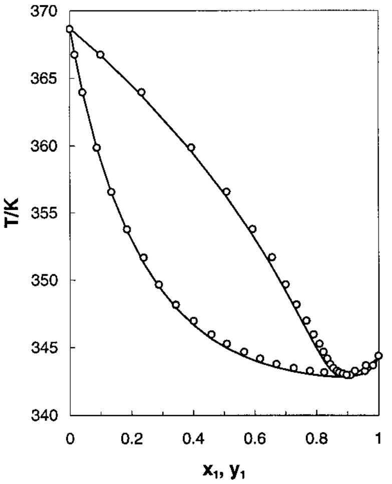

Figure 1. Vapor–liquid equilibrium of the system tetrachloroethylene (1) + 1-pentanol (2) at 20 kPa as a function of the mole fraction of component 1: (○) experimental points; (—) Wilson model.

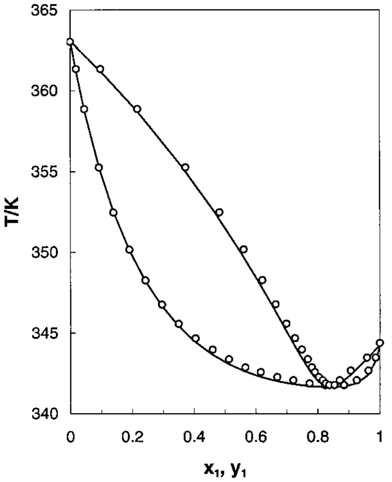

Figure 2. Vapor–liquid equilibrium of the system tetrachloroethylene (1) + 3-methyl-1-butanol (2) at 20 kPa as a function of the mole fraction of component 1: (○) experimental points; (—) Wilson model.

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) + 2-Methyl-1-butanol (2) at 100 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	401.75		
0.025	0.086	399.85	2.962	1.000
0.053	0.162	398.15	2.747	0.999
0.094	0.247	396.25	2.480	1.001
0.140	0.318	394.55	2.240	1.012
0.194	0.383	392.95	2.031	1.032
0.243	0.430	391.95	1.869	1.052
0.294	0.477	390.95	1.760	1.072
0.346	0.518	390.05	1.664	1.101
0.399	0.552	389.35	1.567	1.142
0.453	0.589	388.85	1.492	1.172
0.508	0.614	388.55	1.399	1.237
0.556	0.635	388.25	1.332	1.310
0.605	0.654	388.05	1.268	1.406
0.653	0.674	387.95	1.214	1.513
0.701	0.693	387.95	1.163	1.654
0.749	0.714	388.15	1.115	1.822
0.798	0.736	388.35	1.073	2.075
0.843	0.763	388.75	1.042	2.362
0.892	0.800	389.45	1.013	2.827
0.933	0.853	390.55	1.002	3.221
0.961	0.898	391.55	0.997	3.706
0.979	0.937	392.35	1.000	4.134
1.000	1.000	394.15		

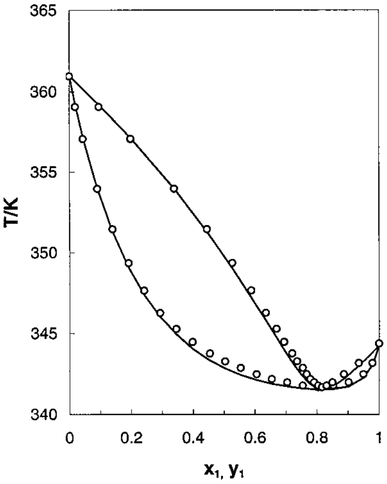

Figure 3. Vapor−liquid equilibrium of the system tetrachloroethylene (1) + 2-methyl-1-butanol (2) at 20 kPa as a function of the mole fraction of component 1: (○) experimental points; (—) Wilson model.

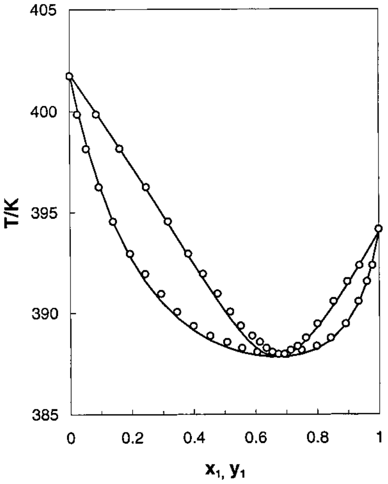

Figure 4. Vapor−liquid equilibrium of the system tetrachloroethylene (1) + 2-methyl-1-butanol (2) at 100 kPa as a function of the mole fraction of component 1: (○) experimental points; (—) Wilson model.

reached. Equilibrium conditions were assumed when constant temperature and pressure were obtained for 15 min or longer. At this time, samples of liquid and condensate were taken for analysis without disruption of the operation of the still.

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 of the measured mole fraction was ±0.001.

Results and Discussion

Vapor−liquid equilibrium data (x_1, y_1, T) are presented in Tables 1−4 and Figures 1−4. Figures 5−7 show the experimental values obtained in this work and those obtained by Rao et al. (1980) and Raviprasad et al. (1981) at 101.32 kPa for the tetrachloroethylene + 1-pentanol and tetrachloroethylene + 3-methyl-1-butanol systems, respectively. In these figures the values predicted by the UNIFAC method have been also included, and from these results it can be said that this method gives acceptable results for these systems. On the other hand, the three systems present a minimum boiling azeotrope and the results presented in these figures show that the azeotropic point changes with pressure. The composition and boiling temperature of the azeotropes obtained in this work are summarized in Table 5 together with literature values extracted from the azeotropic data collection by Gmehling et al. (1994) and those predicted by UNIFAC. The azeotropic compositions have been obtained in this work from experimental data by determining the x_1 values that make zero the function $(y_1 - x_1) = f(x_1)$.

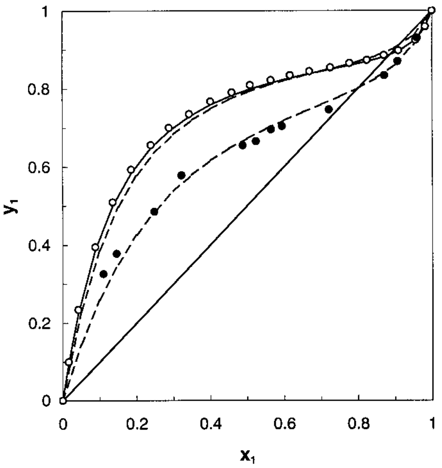

Figure 5. Comparison between the experimental values obtained in this work for the tetrachloroethylene (1) + 1-pentanol (2) system (○) and those calculated using the Wilson equation (—), predicted by the UNIFAC method (- -), and obtained by Rao et al. (1980) at 101.32 kPa (●).

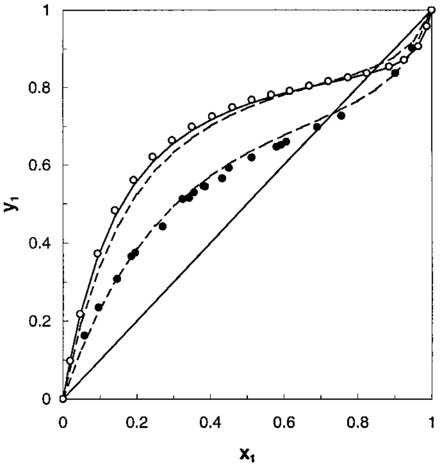

Figure 6. Comparison between the experimental values obtained in this work for the tetrachloroethylene (1) + 3-methyl-1-butanol (2) system (○) and those calculated using the Wilson equation (—), predicted by the UNIFAC method (- -), and obtained by Raviprasad et al. (1981) at 101.32 kPa (●).

The liquid-phase activity coefficients of the components have been calculated by the following equations:

$$\gamma_i = \frac{y_i P}{x_i P_i^\circ} \exp\left[\frac{(B_{ii} - v_i)(P - P_i^\circ) + (1 - y_i)^2 P \delta_{ij}}{RT}\right] \quad (1)$$

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \quad (2)$$

where γ_i is the activity coefficient, x_i and y_i are the liquid

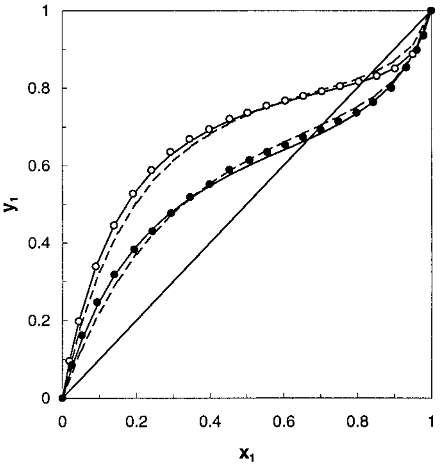

Figure 7. Comparison between the experimental values obtained in this work for the tetrachloroethylene (1) + 2-methyl-1-butanol (2) system at 20 kPa (○) and at 100 kPa (●) and those calculated using the Wilson equation (—) and predicted by the UNIFAC method (- -).

Table 5. Variation of the Azeotropic Point with Pressure

P/kPa	y_1	T/K	ref
	Tetrachloroethylene (1) + 1-Pentanol (2)		
20	0.891	342.95	this work
20	0.912	343.60	UNIFAC
101.32	0.802	391.70	UNIFAC
101.32	0.750	390.95	Rao et al., 1980
101.32	0.7508	390.15	Lecat, 1949
	Tetrachloroethylene (1) + 3-Methyl-1-butanol (2)		
20	0.842	341.75	this work
20	0.860	342.80	UNIFAC
101.32	0.734	389.95	UNIFAC
101.32	0.705	389.85	Raviprasad et al., 1981
101.32	0.6938	389.35	Lecat, 1947
	Tetrachloroethylene (1) + 2-Methyl-1-butanol (2)		
20	0.821	341.65	this work
20	0.837	342.40	UNIFAC
100	0.688	387.95	this work
100	0.707	388.70	UNIFAC

Table 6. Antoine Coefficients[a] of the Pure Components

component	A	B	C
tetrachloroethylene	13.2979	2770.06	−75.348
1-pentanol	15.8163	3708.62	−79.441
3-methyl-1-butanol	14.9010	3141.77	−99.193
2-methyl-1-butanol	14.8958	3107.20	−99.883

[a] $\ln(P°/\text{kPa}) = A - B/((T/\text{K}) + C)$.

and vapor mole fractions in equilibrium, P is the total pressure, $P_i°$ is the pure component vapor pressure, v_i is the liquid molar volume, R is the universal gas constant, T is the absolute temperature, B_{ii} is the second virial coefficient of the pure gas, and B_{ij} is the cross second virial coefficient.

Table 7. Parameters of the Wilson Model and Deviations between Experimental and Calculated Vapor Phase Mole Fractions and Temperatures

system	A_{12}[a]	A_{21}[a]	Δy[b]	ΔT[c]
tetrachloroethylene (1) + 1-pentanol (2)	678.159	5943.518	0.0061	0.209
tetrachloroethylene (1) + 3-methyl-1-butanol (2)	799.057	6284.477	0.0060	0.173
tetrachloroethylene (1) + 2-methyl-1-butanol (2)	911.510	5448.560	0.0029	0.248
tetrachloroethylene (1) + 2-methyl-1-butanol (2) (100 kPa)	1357.281	3446.210	0.0071	0.183

[a] Units: J·mol^{-1}. [b] $\Delta y = \sum|y_{\text{expt}} - y_{\text{calc}}|/N$. [c] $\Delta T = \sum|T_{\text{expt}} - T_{\text{calc}})|/N$; N = number of data points.

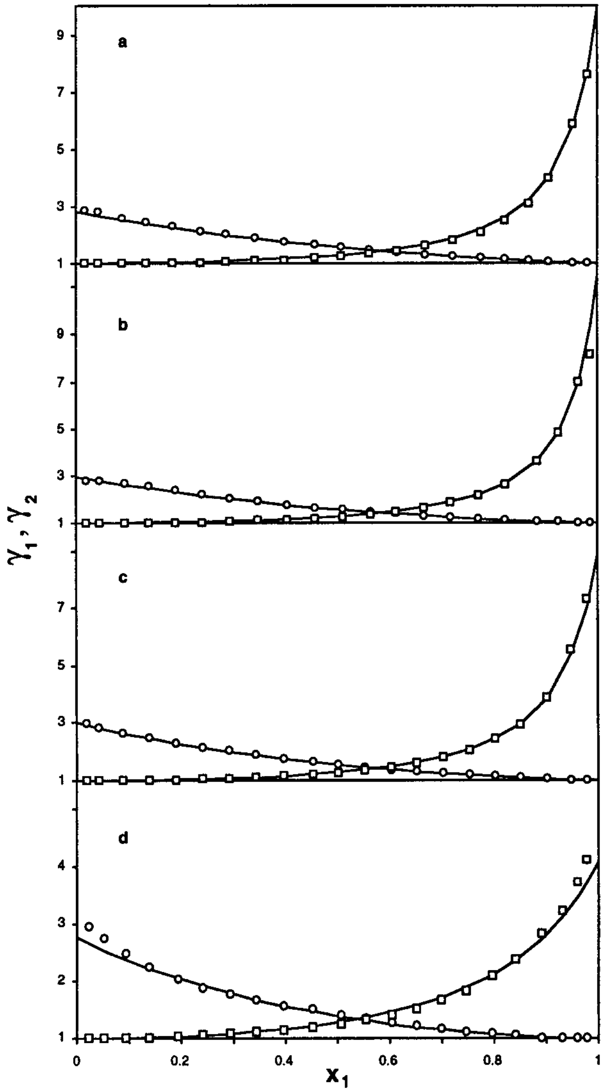

Figure 8. Comparison between the experimental activity coefficients ((○) γ_1, (□) γ_2) and those calculated using the Wilson equation: (a) tetrachloroethylene (1) + 1-pentanol (2) system, (b) tetrachloroethylene (1) + 3-methyl-1-butanol (2), (c) tetrachloroethylene (1) + 2-methyl-1-butanol (2) system at 20 kPa, and (d) tetrachloroethylene (1) + 2-methyl-1-butanol (2) system at 100 kPa.

The Antoine equation has been used to calculate the vapor pressure of the pure components. The Antoine constants used for this calculation were determined from experimental vapor pressure values obtained using the same chemicals and the same still used in this work (Aucejo et al., 1994a, 1994b; Dejoz et al., 1996) and are given in Table 6. The molar virial coefficients B_{ii} and B_{ij} have been estimated by means of the Pitzer and Curl equations (1957) with the correction proposed by Tsonopoulos (1974). Critical properties of the components and molar volumes of the saturated liquids have been taken from DIPPR (Daubert and Danner, 1995). The values of the calculated activity coefficients are listed in Tables 1−4. It can be observed that all the systems present a positive deviation from ideality.

The results have been tested for thermodynamic consistency using the point-to-point method of Van Ness et al. (1973), described by Fredenslund et al. (1977). A four-parameter Legendre polynomial has been used for the excess Gibbs energy. 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, Δy, is less than 0.01. The results of this test for the binary systems in consideration are $\Delta y = 0.0058$ for the tetrachloroethylene + 1-pentanol system, $\Delta y = 0.0048$ for the tetrachloroethylene + 3-methyl-1-butanol system, $\Delta y = 0.0045$ for the tetrachloroethylene + 2-methyl-1-butanol system at 20 kPa, and $\Delta y = 0.0032$ for the tetrachloroethylene + 2-methyl-1-butanol system at 100 kPa. These results indicate that the experimental data for all the systems are thermodynamically consistent.

The activity coefficients have been correlated with the Wilson equation, using for fitting the binary parameters, the following objective function:

$$F = \sum_{j=1}^{N}\left[\mathrm{ABS}\left(\frac{T_{\mathrm{expt}} - T_{\mathrm{calc}}}{T_{\mathrm{expt}}}\right) + \mathrm{ABS}(y_{1,\mathrm{expt}} - y_{1,\mathrm{calc}})\right]_j \qquad (3)$$

where N is the number of experimental data. The adjustable parameters and average deviations obtained for this model are reported in Table 7. The molar volumes used for fitting the Wilson parameters are 0.102 806 $\mathrm{m^3 \cdot kmol^{-1}}$ for the tetrachloroethylene, 0.108 534 $\mathrm{m^3 \cdot kmol^{-1}}$ for the 1-pentanol, 0.108 528 $\mathrm{m^3 \cdot kmol^{-1}}$ for the 3-methyl-1-butanol, and 0.108 266 $\mathrm{m^3 \cdot kmol^{-1}}$ for the 2-methyl-1-butanol (Daubert and Danner, 1995).

The temperature and vapor composition values calculated from the Wilson equation are shown in Figures 1−7 together with the experimental data. On the other hand, Figure 8 shows a comparison between the experimental values of the activity coefficients and those calculated from the Wilson model. From these figures, it can be observed that the Wilson equation fits well the VLE data obtained in this work.

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Received for review July 28, 1998. Accepted December 7, 1998. This work has been supported by the Generalitat Valenciana (Grant GV-3174/95).

JE980170F