Isobaric Vapor–Liquid Equilibrium Measurements on 2-Chlorobutane + Isomeric Butanols at 60.0 and 101.3 kPa

Pilar Cea, Carlos Lafuente, M. Luisa Sanz, Félix M. Royo, and José S. Urieta*

Departamento de Química Orgánica-Química Física, Facultad de Ciencias, Universidad de Zaragoza, Ciudad Universitaria, Zaragoza 50009, Spain

Isobaric vapor–liquid equilibrium measurements are reported for 2-chlorobutane + 1-butanol, + 2-butanol, + 2-methyl-1-propanol, and + 2-methyl-2-propanol. The activity coeficients were found to be thermodynamically consistent. They were well correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations.

Introduction

The knowledge of vapor–liquid equilibrium (VLE) provides information about thermodynamic behavior of the liquid mixtures, and it is essential for designing separation processes of liquid mixtures through distillation. Following earlier works on isobaric VLE of binary mixtures containing a haloalkane as one component and an isomer of butanol as the other (Artigas et al., 1994; Lafuente et al., 1994; Rodríguez et al., 1994), we report here new isobaric vapor–liquid equilibrium measurements for the four systems containing 2-chlorobutane with isomeric butanols at two pressures, 60.0 and 101.3 kPa. These compounds have several uses in the chemical industry (Kirk and Othmer, 1984; Gerhartz, 1985). For each binary system the VLE results have been checked for thermodynamic consistency. The activity coefficients were evaluated and correlated with the following models: Margules (1895), Van Laar (1910), Wilson (1964), NRTL (Renon and Prausnitz, 1968), and UNIQUAC (Abrams and Prausnitz, 1975).

Experimental Section

Chemicals. All liquids were of the best quality available from Aldrich: 1-butanol (better than 99.8 mol %), 2-methyl-1-propanol and 2-methyl-2-propanol (better than 99.5 mol %), and 2-butanol and 2-chlorobutane (better than 99 mol %). The purity of the materials was checked by GLC. The purities obtained were better than 99.7 mol %. The comparison of measured physical properties of the chemicals, densities and normal boiling points, with literature values from the TRC tables (TRC, 1966) are shown in Table 1. Liquids were used without further purification. All isomeric butanols were dried over activated molecular sieves, type 0.3 nm, from Merck.

Apparatus and Procedure. The still used to measure VLE was an all-glass, dynamic recirculating one, equipped with a Cottrell pump. It is a commercial unit (Labodest model) built in Germany by Fischer, capable of handling pressures from 0.25 to 400 kPa, and temperatures up to 523.15 K. This still allows 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 temperatures were measured to an accuracy of ±0.01 K by means of a thermometer (model F25) from Automatic Systems Laboratories, and the pressure in the still was measured with a pressure transducer, Druck PDCR 110/W (pressure indicator DPI201), with an accuracy of ±0.1 kPa. In each experiment, the pressure was fixed and the heating and shaking system of the liquid mixture was connected. This was kept at the boiling point for 15 min to ensure the stationary state. Once it was reached, a sample, approximately 2 mL, of liquid and vapor from the Cottrell pump was taken. Both vapor and liquid phase compositions were determined by measuring their densities at 298.15 K with an Anton Paar DMA-58 vibrating tube densimeter that was previously calibrated at atmospheric pressure with doubly distilled water and dry air. Prior to this, density-calibration curves for these systems were obtained; excess volumes calculated from these density measurements are reported in a previous paper (Cea et al.,

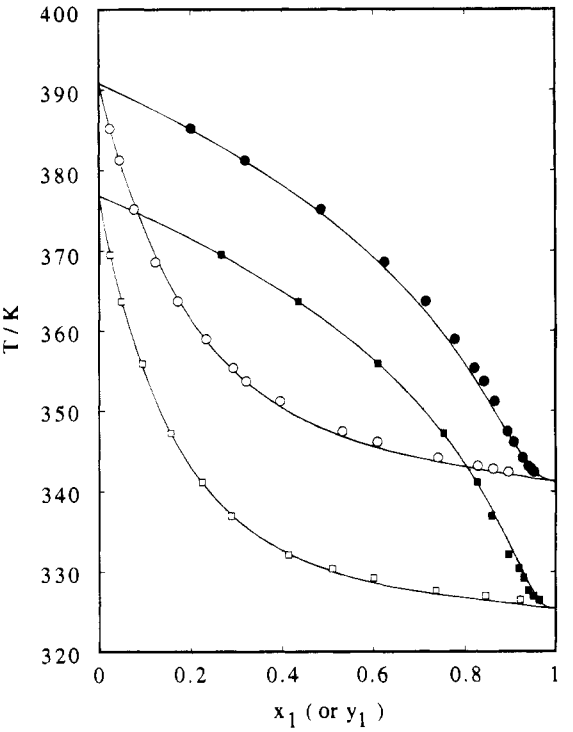

Figure 1. T–x_1–y_1 diagram for 2-chlorobutane (1) + 1-butanol (2): (□, ■) experimental data at 60.0 kPa; (○, ●) experimental data at 101.3 kPa; (—) Wilson equation.

Table 1. Physical Properties (Densities at 298.15 K and Normal Boiling Points) of the Pure Compounds

	ρ/(kg m^{-3})		T_b/K	
compound	exptl	lit.	exptl	lit.
2-chlorobutane	867.43	867.1	341.26	341.25
1-butanol	805.85	806.0	390.84	390.81
2-butanol	802.40	802.6	372.65	372.70
2-methyl-1-propanol	797.98	797.8	380.72	380.81
2-methyl-2-propanol	781.00	781.2	355.50	355.57

0021-9568/95/1740-0692$09.00/0

Table 2. Vapor–Liquid Equilibrium Data, Temperature T, Liquid Phase Mole Fraction x_1, Vapor Phase Mole Fraction y_1, and Activity Coeficients γ_i for 2-Chlorobutane (1) + Isomeric Butanols (2) at the Indicated Pressure

T/K	x_1	y_1	γ_1	γ_2	T/K	x_1	y_1	γ_1	γ_2
2-Chlorobutane (1) + 1-Butanol (2) at 60.0 kPa									
362.20	0.0250	0.1960	2.632	1.014	332.15	0.4411	0.8628	1.566	1.204
358.25	0.0486	0.3292	2.523	1.021	330.20	0.5471	0.8867	1.382	1.359
349.87	0.1103	0.5688	2.418	1.010	329.20	0.6350	0.9031	1.253	1.521
344.46	0.1618	0.6753	2.288	1.035	327.87	0.7402	0.9194	1.144	1.909
339.25	0.2434	0.7767	2.045	1.012	326.81	0.8598	0.9386	1.041	2.854
336.36	0.3107	0.8146	1.837	1.064	326.11	0.9282	0.9561	1.006	4.140
2-Chlorobutane (1) + 1-Butanol (2) at 101.3 kPa									
385.24	0.0240	0.2011	2.700	0.996	351.23	0.3958	0.8658	1.639	1.068
381.25	0.0455	0.3202	2.479	1.001	347.47	0.5322	0.8939	1.400	1.298
375.12	0.0769	0.4859	2.564	0.985	346.15	0.6088	0.9079	1.291	1.435
368.60	0.1230	0.6246	2.412	0.977	344.20	0.7417	0.9270	1.145	1.891
363.69	0.1717	0.7150	2.238	0.960	343.19	0.8287	0.9392	1.070	2.494
358.94	0.2339	0.7790	2.024	0.984	342.82	0.8622	0.9461	1.047	2.799
355.35	0.2936	0.8216	1.872	1.008	342.43	0.8956	0.9531	1.027	3.276
353.70	0.3218	0.8428	1.833	0.996					
2-Chlorobutane (1) + 2-Butanol (2) at 60.0 kPa									
338.10	0.0675	0.2461	2.421	0.991	325.71	0.5877	0.7466	1.257	1.337
335.10	0.1363	0.3891	2.081	0.991	324.93	0.6961	0.7886	1.151	1.572
331.85	0.2189	0.5058	1.868	1.028	324.15	0.7600	0.8000	1.098	1.957
329.72	0.3058	0.5912	1.675	1.057	324.44	0.8310	0.8363	1.040	2.242
328.43	0.3619	0.6370	1.591	1.085	324.15	0.8939	0.8795	1.027	2.668
327.21	0.4536	0.6655	1.381	1.238					
2-Chlorobutane (1) + 2-Butanol (2) at 101.3 kPa									
370.36	0.0175	0.0864	2.247	1.010	346.78	0.4770	0.7762	1.383	1.190
368.32	0.0367	0.1776	2.315	0.999	343.29	0.7048	0.8545	1.141	1.601
363.35	0.0925	0.3567	2.091	1.000	343.00	0.7438	0.8648	1.103	1.737
356.95	0.1838	0.5556	1.938	0.987	342.05	0.8412	0.8981	1.042	2.205
351.50	0.3008	0.6750	1.669	1.055	341.63	0.8967	0.9208	1.015	2.686
349.75	0.3519	0.7220	1.603	1.049	341.48	0.9459	0.9487	0.996	3.345
347.85	0.4192	0.7593	1.493	1.100					
2-Chlorobutane (1) + 2-Methyl-1-propanol (2) at 60.0 kPa									
369.50	0.0249	0.2670	2.993	1.001	332.15	0.4145	0.8971	1.733	1.334
363.65	0.0489	0.4364	2.886	1.003	330.40	0.5100	0.9190	1.527	1.380
355.90	0.0950	0.6099	2.547	1.021	329.20	0.6011	0.9297	1.363	1.571
347.25	0.1562	0.7544	2.441	1.027	327.66	0.7369	0.9387	1.181	2.263
341.15	0.2247	0.8276	2.228	1.057	327.00	0.8448	0.9505	1.066	3.214
336.95	0.2884	0.8589	2.048	1.168	326.50	0.9212	0.9628	1.007	4.894
2-Chlorobutane (1) + 2-Methyl-1-propanol (2) at 101.3 kPa									
379.00	0.0143	0.0865	2.243	0.996	350.88	0.3648	0.7948	1.649	1.059
377.27	0.0243	0.1494	2.373	0.997	345.10	0.6302	0.8747	1.239	1.442
374.46	0.0406	0.2458	2.496	0.996	343.46	0.7370	0.8971	1.140	1.797
369.89	0.0762	0.3822	2.308	1.005	342.63	0.8296	0.9179	1.062	2.302
359.19	0.2046	0.6744	1.991	0.941	342.12	0.8956	0.9370	1.019	2.953
354.24	0.2765	0.7309	1.823	1.053	341.63	0.9415	0.9561	1.004	3.759
2-Chlorobutane (1) + 2-Methyl-2-propanol (2) at 60.0 kPa									
353.62	0.0457	0.2363	2.184	1.008	330.79	0.4947	0.8277	1.400	1.229
349.70	0.0788	0.3807	2.277	1.000	329.00	0.6019	0.8589	1.266	1.400
343.75	0.1433	0.5500	2.149	1.017	327.77	0.7111	0.8837	1.148	1.695
339.50	0.2089	0.6560	1.997	1.024	326.60	0.8217	0.9109	1.065	2.238
335.36	0.3120	0.7485	1.734	1.050	325.65	0.9100	0.9490	1.034	2.669
332.76	0.4096	0.7930	1.520	1.145					
2-Chlorobutane (1) + 2-Methyl-2-propanol (2) at 101.3 kPa									
354.12	0.0267	0.0821	2.128	0.993	340.11	0.6005	0.7225	1.245	1.285
352.72	0.0513	0.1460	2.047	1.000	339.85	0.6380	0.7392	1.208	1.347
349.42	0.1154	0.3113	2.127	0.983	339.45	0.7314	0.7789	1.124	1.566
347.14	0.1941	0.4162	1.804	1.002	339.32	0.8061	0.8158	1.072	1.817
345.25	0.2668	0.5019	1.672	1.014	339.49	0.8760	0.8562	1.030	2.203
341.85	0.4406	0.6357	1.417	1.119	340.03	0.9137	0.8863	1.006	2.446
340.95	0.5169	0.6799	1.327	1.182	339.99	0.9365	0.9087	1.008	2.674
340.45	0.5650	0.7035	1.275	1.242	340.49	0.9673	0.9462	1.000	2.995

1994). The estimated error in the determination of both liquid and vapor phase mole fractions is 0.0001.

Results and Discussion

The vapor–liquid equilibrium data (T, x_1, and y_1) along with activity coefficients at 60.0 and 101.3 KPa are presented in Table 2. The $T - x_1 - y_1$ diagrams are shown in Figures 1–4. Some of the systems show minimun temperature azeotropes. Information about the composition and boiling temperature of the azeotropes is sumarized in Table 3.

The activity coefficients γ_i were calculated, taking into account the nonideality of the vapor phase, from following equation:

$$\gamma_1 = \frac{y_i P}{x_i p_i^\circ} \exp\left[\frac{(B_{ii} - V_i^\circ)(P - p_i^\circ) + (1 - y_i)^2 P \delta_{ij}}{RT}\right] \quad (1)$$

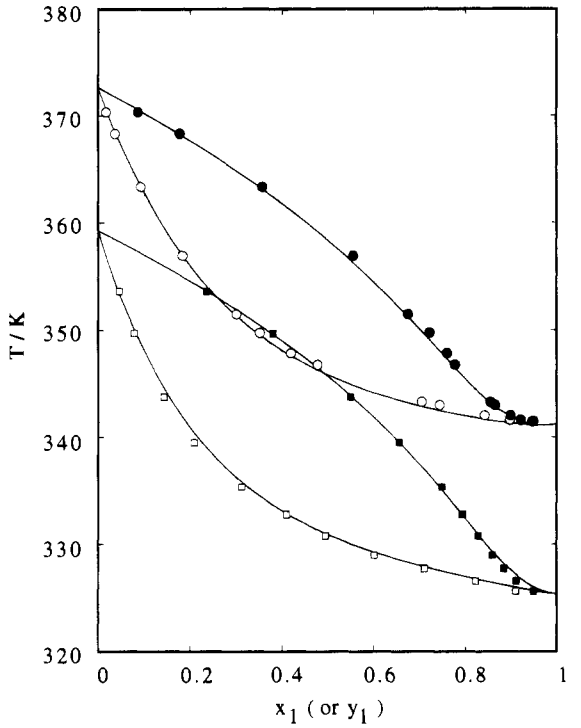

Figure 2. T–x_1–y_1 diagram for 2-chlorobutane (1) + 2-butanol (2): (□, ■) experimental data at 60.0 kPa; (○, ●) experimental data at 101.3 kPa; (—) Wilson equation.

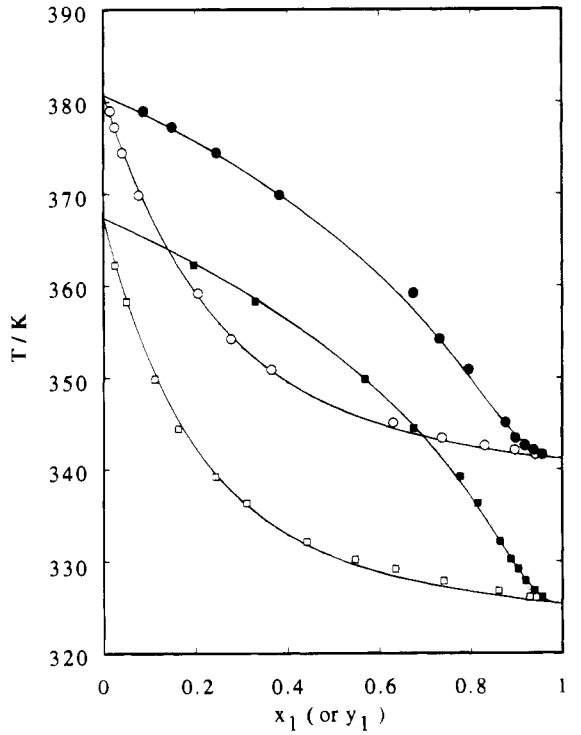

Figure 3. T–x_1–y_1 diagram for 2-chlorobutane (1) + 2-methyl-1-propanol (2): (□, ■) experimental data at 60.0 kPa; (○, ●) experimental data at 101.3 kPa; (—) Wilson equation.

where

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

x_1 and y_1 are the liquid and vapor phase compositions, P is the total pressure, and p_i^o are the vapor pressures of the pure compounds calculated with the Antoine equation using the coefficients which appear in Table 4, taken from Riddick et al. (1986). The second virial coefficients of the pure components, B_{ii}, were obtained from the TRC tables

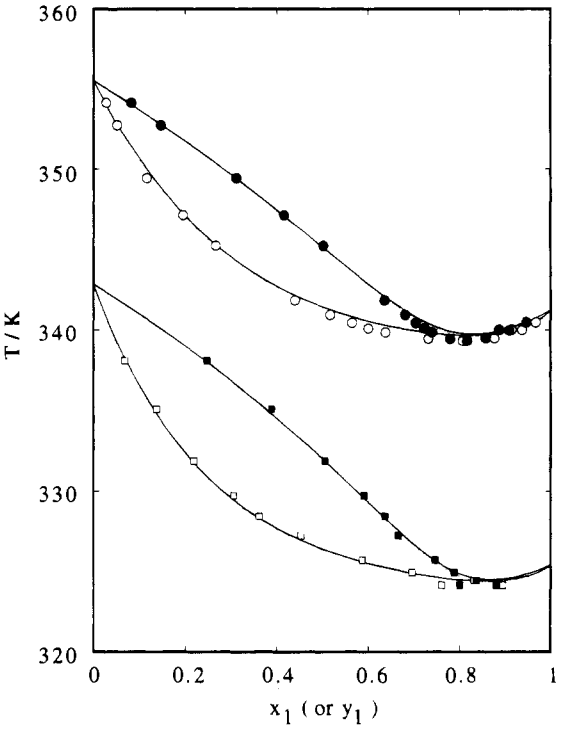

Figure 4. T–x_1–y_1 diagram for 2-chlorobutane (1) + 2-methyl-2-propanol (2): (□, ■) experimental data at 60.0 kPa; (○, ●) experimental data at 101.3 kPa; (—) Wilson equation.

Table 3. Composition ($x_{1(az)}$) and Boiling Temperature ($T_{(az)}$) of the Azeotropic Mixtures

system	P/kPa	$x_{1(az)}$	$T_{(az)}$/K
2-chlorobutane +			
2-butanol	101.3	0.962	341.1
2-methyl-1-propanol	101.3	0.987	341.2
2-methyl-2-propanol	60.0	0.863	324.4
	101.3	0.825	339.6

Table 4. Constants of Antoine's Equation, $\log(P/\text{kPa}) = A - B/(C + t/°\text{C})$ for Vapor Pressures of the Pure Compounds

compound	A	B	C
2-chlorobutane	6.122 2	1245.2	234.4
1-butanol	6.547 43	1338.769	177.042
2-butanol	6.354 57	1171.981	169.955
2-methyl-1-propanol	6.500 91	1275.197	175.187
2-methyl-2-propanol	6.356 48	1107.060	172.102

Table 5. Results of the Thermodynamic Consistency Test, Average Deviations ΔP and Δy

system	P/kPa	ΔP/kPa	Δy
2-chlorobutane +			
1-butanol	60.0	0.8	0.0064
	101.3	1.2	0.0061
2-butanol	60.0	0.6	0.0030
	101.3	1.1	0.0035
2-methyl-1-propanol	60.0	1.0	0.0030
	101.3	1.3	0.0040
2-methyl-2-propanol	60.0	0.7	0.0063
	101.3	0.5	0.0069

(TRC, 1966), and the cross second virial coefficients B_{ij} were calculated using a suitable mixing rule. The molar volumes of the saturated liquids, V_i^o were estimated by the Yen and Woods method (Yen and Woods, 1968). The correction for the nonideality of the vapor phase, represented by the exponential term in eq 1, was important only at very dilute concentrations.

The thermodynamic consistency of the experimental data was checked by means of the point-to-point test of Van Ness

Table 6. Correlation Parameters for Activity Coefficient Models, Average Deviations ΔT and Δy, and Activity Coefficients at Infinite Dilution

equation	A_{12}	A_{21}	ΔT/K	Δy	γ_1^∞	γ_2^∞
2-Chlorobutane (1) + 1-Butanol (2) at 60.0 kPa						
Margules	1.0760	1.8609	0.62	0.0095	2.93	6.43
Van Laar	1.1205	2.0440	0.45	0.0079	3.07	7.73
Wilson[a]	0.7540	0.1184	0.45	0.0086	3.20	10.80
NRTL[b] (α_{12} = 0.3)	2.0292	0.0176	0.45	0.0079	3.07	7.74
UNIQUAC[b]	0.3676	1.3247	0.45	0.0079	3.08	7.90
2-Chlorobutane (1) + 1-Butanol (2) at 101.3 kPa						
Margules	0.9567	1.5526	0.44	0.0057	2.60	4.72
Van Laar	0.9857	1.6901	0.33	0.0064	2.68	5.42
Wilson	0.8332	0.1733	0.39	0.0071	2.74	6.82
NRTL	1.7276	−0.0438	0.33	0.0063	2.68	5.38
UNIQUAC	0.4184	1.3141	0.33	0.0064	2.68	5.50
2-Chlorobutane (1) + 2-Butanol (2) at 60.0 kPa						
Margules	0.8660	1.3140	0.29	0.0052	2.38	3.72
Van Laar	0.8979	1.3558	0.30	0.0057	2.45	3.88
Wilson	0.8155	0.2889	0.30	0.0065	2.50	4.16
NRTL	1.3720	−0.0132	0.29	0.0057	2.45	3.89
UNIQUAC	0.5032	1.2409	0.29	0.0057	2.46	3.91
2-Chlorobutane (1) + 2-Butanol (2) at 101.3 kPa						
Margules	0.8090	1.3229	0.37	0.0036	2.25	3.75
Van Laar	0.8300	1.4203	0.34	0.0033	2.29	4.14
Wilson	0.9128	0.2440	0.32	0.0039	2.33	4.47
NRTL	1.5899	−0.1550	0.40	0.0031	2.30	4.17
UNIQUAC	0.4450	1.3438	0.34	0.0033	2.30	4.15
2-Chlorobutane (1) + 2-Methyl-1-propanol (2) at 60.0 kPa						
Margules	0.9540	1.6306	0.42	0.0036	2.60	5.11
Van Laar	0.9909	1.7805	0.44	0.0036	2.69	5.93
Wilson	0.8326	0.1630	0.41	0.0046	2.77	7.25
NRTL	1.8404	−0.0696	0.43	0.0035	2.69	5.87
UNIQUAC	0.3944	1.3435	0.43	0.0036	2.70	6.00
2-Chlorobutane (1) + 2-Methyl-1-propanol (2) at 101.3 kPa						
Margules	0.8545	1.4870	0.37	0.0054	2.35	4.42
Van Laar	0.8813	1.6174	0.32	0.0047	2.41	5.04
Wilson	0.9148	0.1902	0.34	0.0057	2.46	5.73
NRTL	1.7834	−0.1617	0.36	0.0045	2.42	5.02
UNIQUAC	0.4013	1.3815	0.32	0.0047	2.42	5.07
2-Chlorobutane (1) + 2-Methyl-2-propanol (2) at 60.0 kPa						
Margules	0.9059	1.2649	0.28	0.0084	2.47	3.54
Van Laar	0.9202	1.3201	0.24	0.0077	2.51	3.74
Wilson	0.7719	0.3128	0.22	0.0070	2.58	4.02
NRTL	1.2615	0.0594	0.24	0.0076	2.52	3.74
UNIQUAC	0.5473	1.1850	0.24	0.0076	2.52	3.77
2-Chlorobutane (1) + 2-Methyl-2-propanol (2) at 101.3 kPa						
Margules	0.7365	1.1637	0.20	0.0048	2.09	3.20
Van Laar	0.7596	1.2110	0.21	0.0039	2.14	3.36
Wilson	0.9146	0.3143	0.22	0.0042	2.17	3.46
NRTL	1.3054	−0.1057	0.20	0.00043	2.17	3.31
UNIQUAC	0.5066	1.2985	0.21	0.0040	2.14	3.36

[a] Λ_{12}, Λ_{21}. [b] τ_{12}, τ_{21}.

(Van Ness et al., 1973), modified by Fredenslund (Fredenslund et al., 1977), using a third-order Legendre polynomial for the excess Gibbs free energy. According to this test, experimental data are considered consistent if the average deviation in y, Δy, is less than 0.01. In our systems, for all the cases Δy values obtained satisfactorily fulfill that condition as can be seen in Table 5.

The activity coefficients were correlated with the Margules, Van Laar , Wilson, NRTL, and UNIQUAC equations. Estimation of the parameters for all the equations studied was based on minimization, using the Simplex method, of the objective function F (Silverman and Tassios, 1984) in terms of experimental and calculated γ_i values. The function F for a binary system can be stated as

$$F = \sum_{i=1}^{i=N}\left[\left(\frac{\gamma_1^{\text{exptl}} - \gamma_1^{\text{calcd}}}{\gamma_1^{\text{exptl}}}\right)^2 + \left(\frac{\gamma_2^{\text{exptl}} - \gamma_2^{\text{calcd}}}{\gamma_2^{\text{exptl}}}\right)^2\right]_i \quad (3)$$

where N is the number of experimental data.

These parameters along with the average deviation in T, ΔT, the average deviation in y, Δy, and the activity coefficients at infinite dilution are listed in Table 6. All the equations correlated the activity coefficients quite well.

Calculated activity coefficients present positive deviation from ideality. The main effects that govern this behavior are on the one hand the breaking of both the dipole−dipole interactions in the 2-chlorobutane and the self-associations of butanols and on the other hand the Cl−OH interaction.

Literature Cited

Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures. New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE. J.* **1975**, *21*, 116−128.

Artigas, H.; Lafuente, C.; López, M. C.; Royo, F. M.; Urieta, J. S. Isobaric Vapor−Liquid Equilibria for Binary Mixtures of 1-Chlorobutane with Isomeric Butanols at 40.0 and 101.3 kPa. *J. Chem. Eng. Data* **1994**, *39*, 729−732.

Cea, P.; Lafuente, C. ; Artigas, H.; Royo, F. M. ; Urieta, J. S. Excess Volumes and Excess Viscosities of Binary Mixtures of 2-Chloro-2-methylpropane with Isomeric Butanols at 298.15 K. *Can. J. Chem.* **1994**, *72*, 1921−1925.

Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977.

Gerhartz, W., Ed. *Ullmann's Encyclopedia of Industrial Chemistry*; VCH Verlagsgesellschaf: Weinheim, 1985.

Kirk, K.; Othmer, D. F. *Encyclopedia of Chemical Tecnology*, 3rd ed.; Wiley-Interscience: New York, 1984.

Lafuente, C.; Domínguez, M.; López, M. C.; Royo, F. M.; Urieta, J. S. Isobaric VLE Data for the Binary Systems 1,3-Dichloropropane with Isomeric Butanols. *Phys. Chem. Liq.*, in press.

Margules, M. *S.-B. Akad. Wiss. Wien, math.-naturwiss. Kl. II.* **1895**, *104*, 1234.

Renon, H.; Prausnitz, J. M. Local Composition in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE. J.* **1968**, *14* , 135−44.

Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents. Physical Properties and Methods of Purification (Techniques of Chemistry)*, 4th ed.; Wiley-Interscience: New York, 1986.

Rodriguez, V.; Lafuente, C.; Santafé, J.; Royo, F. M.; Urieta, J. S. Isobaric VLE Data for the Binary Systems Dibromomethane Isomeric Butanols at 40.0 and 101.3 kPa. *Fuid Phase Equilib.*, in press.

Silverman, N.; Tassios, D. Prediction of Multicomponent VLE with the Wilson Equation. Effect of the Minimisation Function and of the Quality of Binary Data. *Ind. Eng. Chem. Process Des. Dev.* **1984**, *23*, 586−89.

TRC-Thermodynamic Tables Non-Hydrocarbons; Thermodynamic Research Center, Texas A&M University: College Station, TX, 1966.

Van Laar, J. J. Vapour Pressure of Binary Mixtures. *Z. Phys. Chem.* **1910**, *72*, 723−51.

Van Ness, H. C; Byer, S. M.; Gibbs, R. E. Vapor-Liquid Equilibria. I. Appraisal of Data Reduction Methods. *AIChE J.* **1973**, *19*, 238−44

Wilson, G. M. A New Expression for the Excess Free Energy of Mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127−30.

Yen, L. C.; Woods, S. S. A Generalized Equation for Computer Calculation of Liquid Densities. *AIChE J.* **1968**, *12*, 95−99.

Received for review December 6, 1994. Accepted January 30, 1995.[⊗] We are grateful for financial assistance from the Dirección General de Investigación Científica y Téchnica (DGICYT). P.C. gratefully acknowledges support by the Gobierno de La Rioja.

JE940264Z

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1995.