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Isobaric VLE data for the binary systems 1,4-dichlorobutane with isomeric butanols at 40.0 and 101.3 kPa

C. Lafuente, J. Pardo, M.C. López, F.M. Royo, J.S. Urieta*

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

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Abstract

Isobaric vapour–liquid equilibrium data at 40.0 and 101.3 kPa for the binary systems 1,4-dichlorobutane with 1-butanol, 2-butanol, 2-methyl-1-propanol and 2-methyl-2-propanol are reported. The systems 1,4-dichlorobutane + 1-butanol or 2-methyl-1-propanol at 40.0 kPa show azeotropes. The VLE data are thermodynamically consistent, and the activity coefficients were satisfactorily correlated with the Margules, Van Laar, Wilson, NRTL and UNIQUAC equations.

Keywords: Binary systems; Butanols; VLE

1. Introduction

Vapour–liquid equilibria of binary mixtures can be used to derive information about molecular interactions between the components of the mixtures. With this aim, we present here the vapour–liquid equilibrium data for the binary systems 1,4-dichlorobutane with isomeric butanols at pressures of 40.0 and 101.3 kPa. This work is part of our program for determining VLE data for systems in which one of the components is an haloalkane and the other is an isomer of butanol [1,2]. No isobaric VLE data were found in the literature for these mixtures.

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* Corresponding author.

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2. Experimental

2.1. Materials

All liquids were 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 1,4-dichlorobutane (better than 99 mol%). The purity of the materials was checked by GLC. The physical properties of the chemicals, the density and normal boiling point, appear together with published values [3] in Table 1.

2.2. Apparatus and procedure

The still used to measure VLE data was an all-glass, dynamic recirculating still, equipped with a Cottrell pump. It is a commercial unit (Labodest model) manufactured by Fischer (Germany), capable of handling pressures from 0.25 to 400 kPa, and temperatures up to 523.15 K. This still allows good mixing of the vapour 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 vapour 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 Druck PDCR 110/W pressure transducer (pressure indicator DPI201) with an accuracy of ±0.1 kPa.

In each experiment the working 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 of liquid and vapour was taken from the Cottrell pump. The composition of the liquid and vapour samples was 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, the density calibration curves for 1,4-dichlorobutane + isomeric butanols were determined; excess values calculated from these density measurements are reported in an earlier paper [4].

The apparatus and experimental technique was checked by measuring the standard mixture benzene–cyclohexane [5].

Table 1
Physical properties (densities at 298.15 K and normal boiling points) of the pure compounds

Compound	$\rho/\mathrm{kg\,m^{-3}}$		T_b/K	
	Exptl.	Lit.	Exptl.	Lit.
1,4-Dichlorobutane	1135.40	1135.3	427.01	427.05
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

Table 2
Experimental vapour–liquid equilibrium data for 1,4-dichlorobutane(1) with isomeric butanols(2) at the indicated pressures

T/K	x_1	y_1	γ_1	γ_2	G^E/J mol^{-1}
1,4-Dichlorobutane(1) + 1-butanol(2) at 40.0 kPa					
366.40	0.0292	0.0322	3.089	1.015	143.0
366.40	0.0798	0.0791	2.776	1.018	299.5
366.56	0.1601	0.1297	2.255	1.048	515.7
366.87	0.2436	0.1684	1.900	1.097	691.5
367.73	0.3829	0.2144	1.488	1.227	850.7
368.36	0.4451	0.2331	1.358	1.298	860.0
369.25	0.5512	0.2706	1.229	1.472	882.2
370.23	0.6289	0.2999	1.150	1.643	837.1
371.55	0.6838	0.3271	1.096	1.758	745.4
373.16	0.7409	0.3655	1.064	1.898	657.3
377.35	0.8413	0.4568	1.002	2.257	411.2
383.43	0.9250	0.6240	1.002	2.637	238.4
388.85	0.9682	0.7868	1.003	2.906	118.9
1,4-Dichlorobutane(1) + 1-butanol(2) at 101.3 kPa					
390.91	0.0272	0.0251	2.644	1.001	89.5
391.00	0.0541	0.0452	2.386	1.005	169.1
391.15	0.1131	0.0838	2.106	1.024	341.1
391.48	0.2115	0.1334	1.773	1.077	584.2
391.87	0.2729	0.1559	1.586	1.122	683.6
392.43	0.3283	0.1758	1.459	1.164	738.0
393.26	0.4262	0.2128	1.325	1.266	833.7
395.04	0.5174	0.2508	1.214	1.350	805.1
397.37	0.6242	0.2976	1.109	1.505	721.2
401.75	0.7438	0.3787	1.034	1.696	535.5
404.15	0.8092	0.4386	1.024	1.909	478.1
410.97	0.8882	0.5588	0.973	2.081	196.1
417.73	0.9408	0.7146	0.988	2.126	115.3
1,4-Dichlorobutane(1) + 2-butanol(2) at 40.0 kPa					
350.26	0.0434	0.0265	3.383	0.997	145.5
350.53	0.0724	0.0388	2.934	1.003	236.2
350.93	0.1243	0.0597	2.582	1.022	399.7
352.35	0.2618	0.0964	1.858	1.097	674.7
353.28	0.3363	0.1141	1.643	1.150	762.7
354.72	0.4523	0.1412	1.420	1.272	855.8
356.45	0.5484	0.1632	1.256	1.399	820.1
358.79	0.6486	0.1957	1.153	1.572	749.4
361.55	0.7436	0.2323	1.064	1.843	609.9
365.55	0.8001	0.2901	1.050	1.873	499.9
373.35	0.8916	0.4273	1.026	2.090	318.7
379.77	0.9365	0.5510	0.995	2.236	146.3
388.15	0.9760	0.7600	0.984	2.401	16.8
1,4-Dichlorobutane(1) + 2-butanol(2) at 101.3 kPa					
373.06	0.0383	0.0183	2.565	1.007	131.6
373.47	0.0710	0.0312	2.323	1.014	224.6
375.07	0.1708	0.0639	1.863	1.037	426.1

Table 2 *(continued)*

T/K	x_1	y_1	γ_1	γ_2	G^E/J mol^{-1}
376.51	0.2705	0.0888	1.551	1.092	571.9
377.53	0.3389	0.1052	1.413	1.142	643.5
383.03	0.5682	0.1753	1.154	1.340	662.7
388.52	0.7079	0.2387	1.046	1.533	505.5
393.37	0.7914	0.3066	1.024	1.684	416.8
400.25	0.8579	0.4119	1.021	1.711	313.3
408.60	0.9147	0.5540	1.003	1.712	164.6
414.57	0.9480	0.6772	0.997	1.736	90.6
421.75	0.9800	0.8500	0.996	1.751	23.8
1,4-Dichlorobutane(1) + 2-methyl-1-propanol(2) at 40.0 kPa					
357.67	0.0485	0.0413	3.412	1.008	198.8
357.76	0.1079	0.0774	2.863	1.030	417.2
358.48	0.1845	0.1110	2.329	1.054	592.0
359.36	0.2751	0.1368	1.855	1.109	732.6
359.87	0.3397	0.1544	1.660	1.168	821.6
360.68	0.4271	0.1758	1.453	1.269	887.6
361.99	0.5262	0.2010	1.278	1.409	877.2
363.96	0.6289	0.2406	1.181	1.578	829.2
367.15	0.7370	0.2912	1.074	1.831	645.9
371.95	0.8212	0.3707	1.019	1.986	426.9
376.61	0.8871	0.4716	1.008	2.221	304.7
385.05	0.9525	0.6800	1.003	2.371	139.4
390.23	0.9794	0.8313	1.000	2.421	60.3
1,4-Dichlorobutane(1) + 2-methyl-1-propanol(2) at 101.3 kPa					
381.28	0.0187	0.0128	2.724	0.998	52.2
381.70	0.0809	0.0474	2.297	1.013	251.0
382.60	0.1702	0.0844	1.884	1.045	459.5
383.42	0.2370	0.1102	1.716	1.074	581.4
383.99	0.2885	0.1242	1.558	1.111	648.4
384.66	0.3414	0.1407	1.457	1.151	708.2
386.25	0.4388	0.1707	1.303	1.236	754.0
388.37	0.5395	0.2030	1.173	1.348	721.9
390.74	0.6360	0.2375	1.076	1.509	637.5
394.08	0.7226	0.2911	1.041	1.654	551.5
398.95	0.8054	0.3726	1.024	1.792	440.4
404.15	0.8612	0.4667	1.023	1.825	347.8
413.25	0.9363	0.6460	1.000	2.035	154.8
420.44	0.9740	0.8185	0.999	2.105	64.1
1,4-Dichlorobutane(1) + 2-methyl-2-propanol(2) at 40.0 kPa					
334.56	0.0464	0.0136	3.458	1.004	170.4
334.93	0.0780	0.0213	3.161	1.013	283.2
335.56	0.1324	0.0314	2.658	1.036	445.8
336.37	0.1893	0.0419	2.381	1.057	585.3
337.38	0.2701	0.0487	1.843	1.115	685.5
338.15	0.3277	0.0567	1.702	1.160	770.2
339.53	0.4325	0.0705	1.497	1.275	881.6
340.76	0.4947	0.0801	1.400	1.343	894.4
343.15	0.6279	0.0992	1.217	1.614	860.1

Table 2 *(continued)*

T/K	x_1	y_1	γ_1	γ_2	G^E/J mol^{-1}
345.15	0.7048	0.1158	1.151	1.836	800.0
353.32	0.8347	0.1865	1.080	2.176	566.1
362.50	0.9000	0.2771	1.008	2.271	270.0
373.65	0.9508	0.4460	0.993	2.415	113.4
382.23	0.9775	0.6244	0.990	2.729	39.9
1,4-Dichlorobutane(1)+2-methyl-2-propanol(2) at 101.3 kPa					
356.35	0.0477	0.0122	2.682	1.005	153.1
356.95	0.0854	0.0189	2.262	1.016	250.8
358.35	0.1641	0.0318	1.867	1.042	408.3
360.15	0.2750	0.0477	1.550	1.107	581.7
362.45	0.3991	0.0589	1.200	1.216	572.8
365.25	0.5090	0.0886	1.264	1.306	760.5
368.75	0.6165	0.1051	1.079	1.457	585.8
372.65	0.6919	0.1333	1.050	1.544	519.1
379.75	0.7799	0.1895	1.021	1.613	382.4
392.65	0.8830	0.3304	1.012	1.716	241.8
400.75	0.9222	0.4367	0.992	1.744	118.4
410.62	0.9565	0.6053	0.988	1.703	40.8

3. Results and discussion

The vapour–liquid equilibrium data (T, x_1, and y_1), along with activity coefficients and excess free energies at 40.0 and 101.3 kPa, are gathered in Table 2 and Figs. 1–4. Mixtures containing 1-butanol or 2-methyl-1-propanol at 40.0 kPa show minimum temperature azeotropes. Information on the composition and boiling temperature of the azeotropes is summarized in Table 3.

The activity coefficients γ_i were calculated, taking into account the non-ideality of the vapour phase, from the following equations

$$\gamma_i = \frac{y_i P}{x_i p_i^0} \exp\left[\frac{(B_{ii} - V_i^0)(P - p_i^0) + (1 - y_i)^2 P \delta_{ij}}{RT}\right] \tag{1}$$

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \tag{2}$$

Table 3

Composition ($x_{1(\mathrm{az})}$) and boiling temperature ($T_{(\mathrm{az})}$) of the azeotropic mixtures

System	P/kPa	$x_{1(\mathrm{az})}$	$T_{(\mathrm{az})}$/K
1,4-Dichlorobutane +			
1-butanol	40.0	0.0788	366.59
2-methyl-1-propanol	40.0	0.0170	357.60

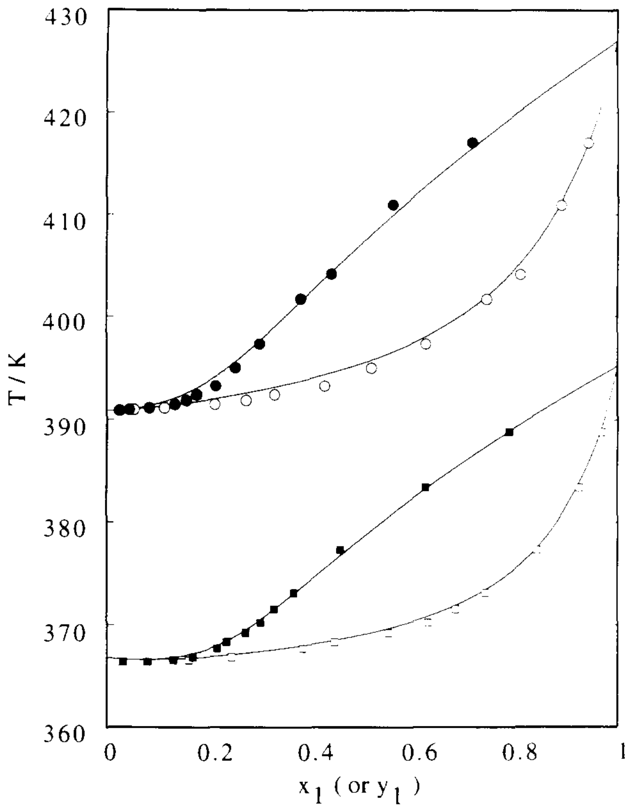

Fig. 1. T–x_1–y_1 diagrams for 1,4-dichlorobutane(1) + 1-butanol(2): (□, ■), experimental data at 40.0 kPa; (○, ●), experimental data at 101.3 kPa; (———), Wilson equation.

Table 4
Constants of Antoine's equation for vapour pressures of the pure compounds (pressure in kPa)

Compound	A	B	C
1,4-Dichlorobutane[a]	5.73340	1211.426	171.120
1-Butanol	6.54743	1338.769	177.042
2-Butanol	6.35457	1171.981	169.955
2-Methyl-1-propanol	6.50091	1275.197	175.187
2-Methyl-2-propanol	6.35648	1107.060	172.102

[a] Our own vapour pressure measurements.

where x_i and y_i are the liquid and vapour phase compositions, P is the total pressure, p_i^0 are the vapour pressures of the pure compounds calculated using the Antoine equation, where the constants are given in Table 4, B_{ii} are the second virial coefficients and B_{ij} are the cross second virial coefficients calculated using the Amdur–Mason equation [6],

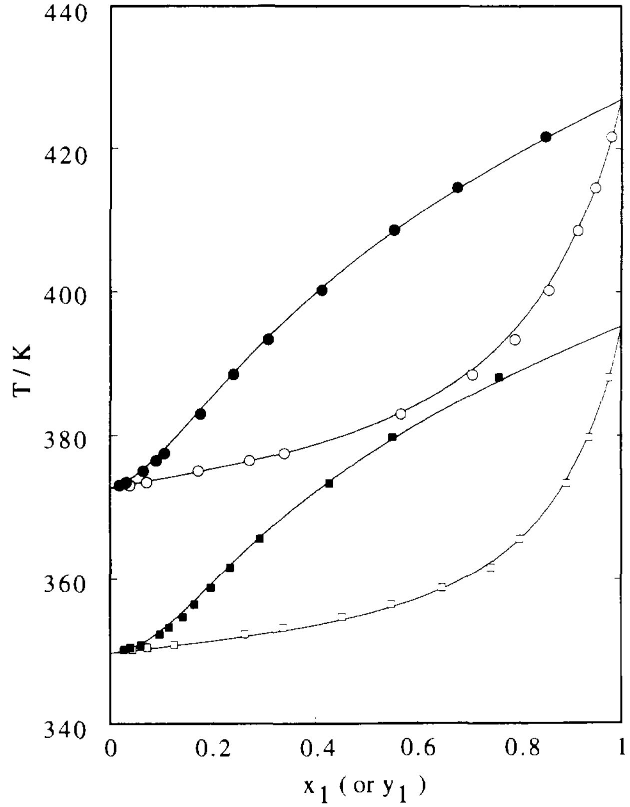

Fig. 2. T–x_1–y_1 diagrams for 1,4-dichlorobutane(1) + 2-butanol(2): (□, ■), experimental data at 40.0 kPa; (○, ●), experimental data at 101.3 kPa; (———), Wilson equation.

and V_i^0 are the molar volumes of the saturated liquids estimated by the Yen and Woods method [7]. Antoine's constants for 1,4-dichlorobutane were obtained from our own vapour pressure measurements over the pressure range 2–101.3 kPa; these measurements were carried out using the same still as for the binary systems. Those for the isomeric butanols were taken from Riddick et al. [8]. The second virial coefficients for the 1,4-dichlorobutane were estimated by the Redlich–Kwong equation [9], while they were obtained from TRC tables [3] for the isomeric butanols.

The thermodynamic consistency of the VLE data was tested using the Van Ness method [10], described by Fredenslund et al. [11], using a third-order Legendre polynomial. According to this test, experimental data are considered consistent if the average deviation in y (Δy) is smaller than 0.01; all the systems studied here satisfy this condition.

The activity coefficients were correlated with the Margules [12], Van Laar [13], Wilson [14], NRTL [15] and UNIQUAC [16] equations. Estimation of the parameters for

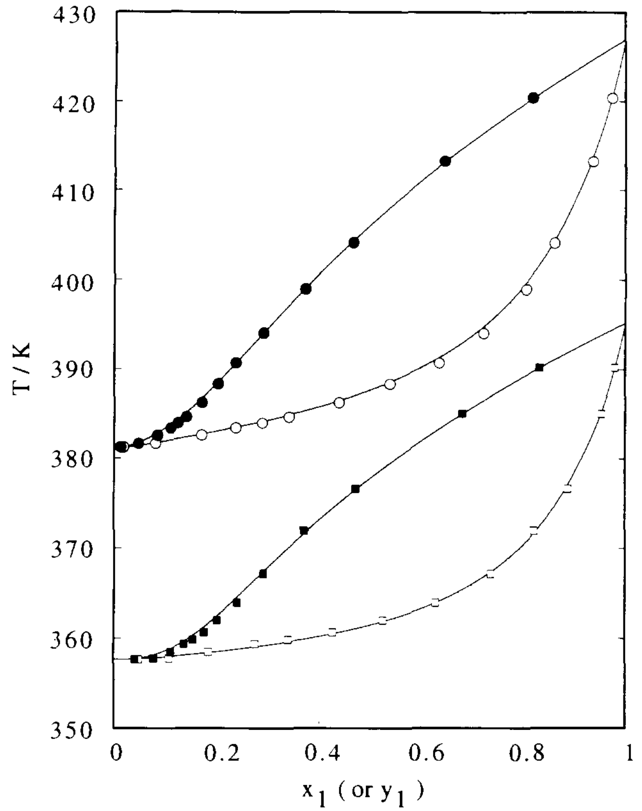

Fig. 3. T–x_1–y_1 diagrams for 1,4-dichlorobutane(1) + 2-methyl-1-propanol(2): (□, ■), experimental data at 40.0 kPa; (○, ●), experimental data at 101.3 kPa; (———), Wilson equation.

all the equations studied was based on minimization, using the Simplex method, of the objective function F [17] in terms of the experimental and calculated γ_i values. The function F for a binary system can be defined as

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

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 5. All the equations correlated the activity coefficients quite well.

The systems present positive deviation from ideality and the activity coefficients decrease with increasing pressure. This behaviour can be explained by considering that there is breaking of both the dipole–dipole interactions in the 1,4-dichlorobutane and

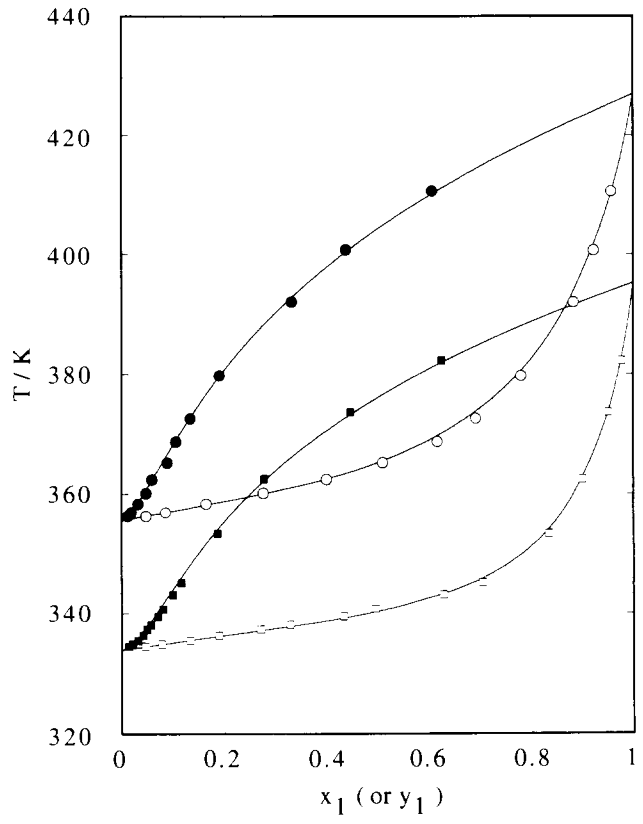

Fig. 4. T–x_1–y_1 diagrams for 1,4-dichlorobutane(1) + 2-methyl-2-propanol(2): (□, ■), experimental data at 40.0 kPa; (○, ●), experimental data at 101.3 kPa ; (———), Wilson equation.

the self-associations of the butanols, which contribute to positive deviations from ideality, and, conversely, there is a Cl–OH interaction which leads to negative deviations from ideality.

From the activity coefficients, the excess free energies G^E are calculated by means of the equation

$$G^E = RT(x_1 \ln\gamma_1 + x_2 \ln\gamma_2) \tag{4}$$

The excess free energies are positive over the entire range of composition and also decrease with increasing pressure. At 40.0 kPa, the maximum G^E values fall in the order 2-methyl-2-propanol > 2-methyl-1-propanol > 1-butanol > 2-butanol, while at 101.3 kPa the order is 1-butanol > 2-methyl-2-propanol > 2-methyl-1-propanol > 2-butanol. Furthermore, the G^E values for the studied mixtures are greater than those for the mixtures of 1-chlorobutane with isomeric butanols [1].

Table 5
Correlation parameters, average deviation in $T(\Delta T)$, average deviation in $y(\Delta y)$, and activity coefficients at infinite dilution, γ_i^∞

Equation	A_{12}	A_{21}	ΔT/K	Δy	γ_1^∞	γ_2^∞
1,4-Dichlorobutane(1) + 1-butanol(2) at 40.0 kPa						
Margules	1.2206	1.1006	0.20	0.0052	3.39	3.01
Van Laar	1.2233	1.1022	0.20	0.0052	3.40	3.01
Wilson[a]	0.4412	0.5647	0.23	0.0056	3.50	3.10
NRTL ($\alpha_{12}=0.3$)[b]	0.4642	0.8266	0.20	0.0053	3.42	3.03
UNIQUAC[b]	0.7773	0.8884	0.20	0.0053	3.41	3.02
1,4-Dichlorobutane(1) + 1-butanol(2) at 101.3 kPa						
Margules	1.0270	0.8394	0.44	0.0066	2.79	2.31
Van Laar	1.0318	0.8480	0.45	0.0066	2.81	2.33
Wilson	0.4659	0.7178	0.49	0.0068	2.85	2.38
NRTL ($\alpha_{12}=0.3$)	0.1893	0.8553	0.45	0.0066	2.81	2.34
UNIQUAC	0.8876	0.8393	0.45	0.0066	2.81	2.34
1,4-Dichlorobutane(1) + 2-butanol(2) at 40.0 kPa						
Margules	1.3100	0.8910	0.37	0.0074	3.71	2.44
Van Laar	1.3447	0.9126	0.37	0.0069	3.84	2.49
Wilson	0.3077	0.7876	0.36	0.0069	4.02	2.54
NRTL ($\alpha_{12}=0.3$)	0.0237	1.3222	0.37	0.0069	3.84	2.49
UNIQUAC	1.0359	0.6630	0.37	0.0069	3.85	2.49
1,4-Dichlorobutane(1) + 2-butanol(2) at 101.3 kPa						
Margules	1.0532	0.5817	0.24	0.0028	2.87	1.79
Van Laar	1.0908	0.6231	0.33	0.0044	2.98	1.86
Wilson	0.3096	1.0619	0.36	0.0048	3.04	1.88
NRTL ($\alpha_{12}=0.3$)	−0.3191	1.4362	0.32	0.0040	2.96	1.85
UNIQUAC	1.2329	0.5844	0.34	0.0044	2.98	1.86
1,4-Dichlorobutane(1) + 2-methyl-1-propanol(2) at 40.0 kPa						
Margules	1.3817	0.9226	0.28	0.0068	3.98	2.52
Van Laar	1.4191	0.9500	0.24	0.0070	4.13	2.59
Wilson	0.2870	0.7729	0.21	0.0072	4.37	2.64
NRTL ($\alpha_{12}=0.3$)	0.0335	1.3896	0.24	0.0070	4.24	2.55
UNIQUAC	1.0403	0.6465	0.24	0.0070	4.15	2.59
1,4-Dichlorobutane(1) + 2-methyl-1-propanol(2) at 101.3 kPa						
Margules	1.0473	0.7670	0.17	0.0025	2.85	2.15
Van Laar	1.0595	0.7834	0.20	0.0028	2.88	2.19
Wilson	0.4122	0.8117	0.25	0.0032	2.93	2.22
NRTL ($\alpha_{12}=0.3$)	0.0229	1.0378	0.20	0.0028	2.89	2.19
UNIQUAC	0.9870	0.7539	0.21	0.0028	2.89	2.19
1,4-Dichlorobutane(1) + 2-methyl-2-propanol(2) at 40.0 kPa						
Margules	1.3866	1.0033	0.34	0.0058	4.00	2.73
Van Laar	1.4110	1.0216	0.35	0.0055	4.10	2.78
Wilson	0.3116	0.7000	0.38	0.0053	4.33	2.84
NRTL ($\alpha_{12}=0.3$)	0.1577	1.2669	0.36	0.0055	4.13	2.78
UNIQUAC	0.9956	0.6830	0.35	0.0055	4.11	2.78

Table 5 *(continued)*

Equation	A_{12}	A_{21}	ΔT/K	Δy	γ_1^∞	γ_2^∞
1,4-Dichlorobutane(1) + 2-methyl-2-propanol(2) at 101.3 kPa						
Margules	1.0980	0.5581	0.15	0.0022	3.00	1.75
Van Laar	1.1736	0.6116	0.32	0.0028	3.23	1.84
Wilson	0.2643	1.1220	0.37	0.0031	3.35	1.86
NRTL ($\alpha_{12}=0.3$)	−0.3871	1.5906	0.37	0.0026	3.18	1.82
UNIQUAC	1.3421	0.5162	0.32	0.0028	3.24	1.84

[a] $\Lambda_{12}, \Lambda_{21}$. [b] τ_{12}, τ_{21}.

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