

# Isobaric Vapor–Liquid Equilibria for Binary Mixtures of 1-Chlorobutane with Isomeric Butanols at 40.0 and 101.3 kPa

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Isobaric vapor–liquid equilibrium (VLE) data at 40.0 and 101.3 kPa for binary mixtures 1-chlorobutane + 1-butanol, + 2-butanol, + 2-methyl-1-propanol, and + 2-methyl-2-propanol are reported. Mixtures containing 2-methyl-1-propanol at 101.3 kPa, 2-butanol and 2-methyl-2-propanol at 40.0 and 101.3 kPa show azeotropes. The VLE data are thermodynamically consistent and were correlated with Margules, Van Laar, Wilson, and NRTL equations.

## Introduction

Over the last few years we have been working on the thermodynamic properties of mixtures containing isomeric butanols (1–6). As an extension of this work we present here isobaric vapor–liquid equilibrium (VLE) data for the binary systems 1-chlorobutane with isomeric butanols at 40.0 and 101.3 kPa. These compounds, chloroalkanes and butanols, have several uses in the chemical industry. No isobaric VLE data are found in the literature for these mixtures.

## Experimental Section

**Materials.** The liquids used were 1-butanol (better than 99.8 mol %), 2-methyl-1-propanol and 2-methyl-2-propanol (better than 99.5 mol %), and 2-butanol (better than 99 mol %) obtained from Aldrich and 1-chlorobutane (better than 99.8 mol %) provided by Lab-Scan. The purity of the chemicals was checked by gas-liquid chromatography. Liquids were used without further purification. All isomeric butanols were dried over activated molecular sieves type 0.3 nm from Merck. The physical properties of the components, density and normal boiling point, appear together with published values (7) in Table 1.

**Apparatus and Procedure.** The vapor–liquid equilibrium measurements were carried out in a still (Labodest model) manufactured by Fischer und Verfahrenstechnik (Germany). Temperatures,  $T$ , were measured with an Automatic Systems Laboratories thermometer, model F25, with an accuracy of  $\pm 0.01$  K. The pressure in the apparatus was measured with a pressure transducer Druck PDCR 110/W (pressure indicator DPI 201) with an accuracy of  $\pm 0.1$  kPa. Liquid-phase and vapor-phase compositions,  $x_1$  and  $y_1$ , were determined by densimetric analysis using an Anton Paar DMA-58 vibrating tube densimeter. Prior to this, the calibration curves for 1-chlorobutane + isomeric butanols were determined; excess volumes calculated from these density measurements are reported in ref 4.

The experimental technique was checked by determining the isobaric vapor–liquid equilibria for the standard mixture benzene + cyclohexane at 101.3 kPa, and our results (8) are in good agreement with published values.

**Table 1.** Densities at 298.15 K,  $\rho$ , and Normal Boiling Points,  $T_b$ , of the Components and Comparison with Literature Data (7)

component	$\rho/(\text{kg}\cdot\text{m}^{-3})$		$T_b/\text{K}$	
	exptl	lit.	exptl	lit.
1-chlorobutane	880.47	880.4	351.52	351.58
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	764.75 <sup>a</sup>	764.9 <sup>a</sup>	355.50	355.57

<sup>a</sup> Density at 313.5 K.

## Results and Discussion

The vapor–liquid equilibrium data ( $T$ ,  $x_1$ , and  $y_1$ ), along with activity coefficients and excess Gibbs free energies at 40.0 and 101.3 kPa, are gathered in Table 2 and Figures 1–4. Mixtures containing 2-methyl-1-propanol at 101.3 kPa and 2-butanol and 2-methyl-2-propanol at 40.0 and 101.3 kPa show azeotropes. Furthermore, when the pressure increases, the azeotropic composition becomes richer in isomeric butanol, and the shift with mixtures containing 2-methyl-2-propanol becomes more noticeable. Information about the azeotropes is summarized in Table 3.

The activity coefficients  $\gamma_i$  of the components in the liquid phase were calculated from

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

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

The vapor pressures,  $p_i^\circ$ , of the pure components were calculated by use of the Antoine equation with the constants from Riddick et al. (9). The second virial coefficients of the pure components,  $B_{ii}$ , were obtained from TRC tables (7), and the cross second virial coefficients,  $B_{ij}$ , were calculated using the Amdur–Mason equation (10). The molar volumes,  $V_i^\circ$ , of the saturated liquids were estimated by the Yen and Woods method (11).

The thermodynamic consistency of the data was tested by using the Herington integral method (12). The  $D$  and

**Table 2. Isobaric VLE Data, Temperature  $T$ , Liquid-Phase  $x_1$  and Vapor-Phase  $y_1$  Mole Fractions, Activity Coefficients  $\gamma_i$ , and Excess Gibbs Free Energies  $G^E$ , for 1-Chlorobutane (1) + Isomeric Butanols (2) at the Indicated Pressure**

$T/K$	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$	$G^E/(J\cdot mol^{-1})$	$T/K$	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$	$G^E/(J\cdot mol^{-1})$
1-Chlorobutane (1) + 1-Butanol (2) at 40.0 kPa											
361.80	0.0250	0.1935	2.334	1.021	125.7	327.42	0.5847	0.8991	1.374	1.628	1056.4
357.19	0.0500	0.3455	2.374	1.040	238.6	326.51	0.6567	0.9132	1.283	1.785	984.4
350.15	0.0875	0.5214	2.519	1.091	467.1	326.01	0.6885	0.9210	1.257	1.842	942.5
341.26	0.1672	0.7041	2.350	1.138	711.6	325.46	0.7725	0.9310	1.155	2.273	807.3
334.60	0.2797	0.8103	2.015	1.191	895.4	325.16	0.8275	0.9353	1.095	2.860	693.8
331.25	0.3728	0.8548	1.789	1.254	988.6	324.62	0.9009	0.9549	1.048	3.581	454.3
329.03	0.4832	0.8826	1.541	1.391	1038.1	324.47	0.9327	0.9614	1.024	4.552	335.9
1-Chlorobutane (1) + 1-Butanol (2) at 101.3 kPa											
384.02	0.0369	0.2301	2.637	1.016	163.9	356.54	0.5037	0.8263	1.420	1.326	938.0
378.70	0.0757	0.3858	2.450	1.026	288.7	354.75	0.6135	0.8546	1.269	1.543	925.6
373.25	0.1304	0.5050	2.133	1.081	517.9	354.40	0.6847	0.8764	1.178	1.633	786.4
368.15	0.1852	0.6077	2.063	1.119	690.9	353.05	0.7820	0.8966	1.098	2.099	688.8
364.86	0.2445	0.6785	1.905	1.131	760.2	352.07	0.8741	0.9245	1.042	2.775	482.4
362.71	0.2955	0.7263	1.789	1.129	776.5	351.47	0.9337	0.9513	1.022	3.494	302.2
359.05	0.4062	0.7877	1.565	1.208	878.4						
1-Chlorobutane (1) + 2-Butanol (2) at 40.0 kPa											
345.00	0.0392	0.2210	2.794	1.002	120.0	325.49	0.6053	0.8123	1.285	1.533	867.0
339.67	0.0962	0.4094	2.501	1.032	330.4	324.67	0.6974	0.8373	1.185	1.811	804.0
333.13	0.2019	0.5893	2.135	1.117	668.7	324.10	0.8013	0.8681	1.091	2.306	636.2
329.78	0.3178	0.6926	1.790	1.159	784.1	323.82	0.8710	0.9055	1.058	2.584	462.3
327.72	0.4049	0.7411	1.618	1.246	887.0	323.86	0.9405	0.9443	1.020	3.296	242.3
326.76	0.4909	0.7757	1.445	1.327	882.7						
1-Chlorobutane (1) + 2-Butanol (2) at 101.3 kPa											
369.55	0.0346	0.1290	2.260	1.009	114.2	352.68	0.5368	0.7122	1.284	1.343	794.0
366.47	0.0772	0.2518	2.145	1.016	224.6	351.57	0.6272	0.7579	1.209	1.470	767.6
361.33	0.1742	0.4409	1.914	1.032	418.4	350.46	0.7750	0.8214	1.096	1.884	621.8
357.45	0.2876	0.5575	1.635	1.104	629.4	350.31	0.8883	0.8945	1.046	2.256	380.7
354.95	0.3846	0.6370	1.501	1.160	730.6	350.55	0.9391	0.9358	1.028	2.493	236.5
353.97	0.4478	0.6715	1.398	1.218	762.3						
1-Chlorobutane (1) + 2-Methyl-1-propanol (2) at 40.0 kPa											
353.37	0.0261	0.1921	2.827	0.999	75.7	326.99	0.5099	0.8403	1.495	1.428	1031.9
346.62	0.0659	0.3914	2.798	1.063	360.1	325.89	0.5954	0.8600	1.363	1.611	1022.4
341.13	0.1250	0.5586	2.505	1.068	487.9	325.06	0.6954	0.8790	1.229	1.936	932.2
337.15	0.1790	0.6407	2.286	1.127	689.6	324.54	0.7786	0.8967	1.142	2.341	786.5
331.38	0.3003	0.7555	1.954	1.210	921.9	324.18	0.8860	0.9267	1.051	3.292	484.0
328.63	0.4043	0.8131	1.721	1.258	972.8	324.06	0.9481	0.9625	1.024	3.725	245.0
1-Chlorobutane (1) + 2-Methyl-1-propanol (2) at 101.3 kPa											
374.25	0.0474	0.2343	2.655	1.026	220.0	352.89	0.5799	0.7951	1.319	1.464	941.2
368.63	0.1040	0.4088	2.441	1.041	393.8	351.83	0.6861	0.8295	1.200	1.708	857.5
361.73	0.2008	0.5643	2.102	1.129	740.4	351.73	0.7747	0.8562	1.100	2.016	678.4
357.67	0.3158	0.6717	1.782	1.175	870.3	350.89	0.8603	0.9013	1.069	2.316	510.6
356.18	0.3881	0.7184	1.618	1.200	883.2	350.87	0.9348	0.9452	1.033	2.758	280.7
354.49	0.4663	0.7535	1.484	1.294	947.4						
1-Chlorobutane (1) + 2-Methyl-2-propanol (2) at 40.0 kPa											
331.06	0.0483	0.1578	2.568	1.009	149.3	321.04	0.6001	0.6630	1.247	1.570	835.4
328.35	0.1111	0.2982	2.320	1.024	312.1	320.78	0.6998	0.7011	1.142	1.880	753.4
325.86	0.1958	0.4253	2.053	1.046	478.6	320.99	0.8077	0.7795	1.091	2.143	579.6
322.31	0.3918	0.5851	1.608	1.191	783.9	321.37	0.8807	0.8196	1.050	2.551	437.2
321.64	0.4889	0.6379	1.440	1.280	814.5	321.97	0.9346	0.8778	1.024	3.322	269.0
1-Chlorobutane (1) + 2-Methyl-2-propanol (2) at 101.3 kPa											
353.50	0.0392	0.0941	2.269	1.017	141.5	345.74	0.6250	0.6238	1.192	1.468	728.7
351.86	0.0849	0.1818	2.124	1.027	257.9	346.05	0.7249	0.6785	1.107	1.689	626.3
349.56	0.1740	0.3124	1.908	1.046	433.6	346.67	0.8005	0.7372	1.068	1.857	508.2
347.81	0.2832	0.4205	1.664	1.088	592.3	347.86	0.8966	0.8176	1.020	2.371	309.3
346.61	0.4113	0.5128	1.449	1.169	704.7	348.95	0.9423	0.8745	1.004	2.800	183.7
345.84	0.5001	0.5665	1.348	1.264	766.1						

$J$  values were calculated by means of the following equations:

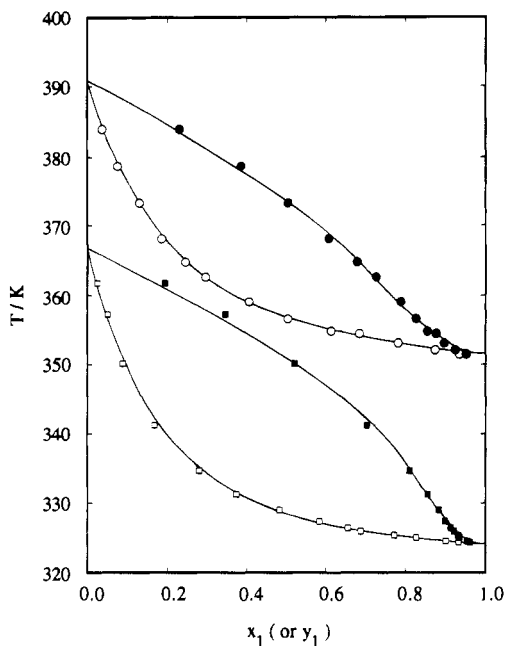
$$D = 100 \left| \int_{x_1=0}^{x_1=1} \ln(\gamma_1/\gamma_2) dx_1 \right| / \left| \int_{x_1=0}^{x_1=1} \ln|\gamma_1/\gamma_2| dx_1 \right| \quad (3)$$

$$J = 150|\theta|/T_{\min} \quad (4)$$

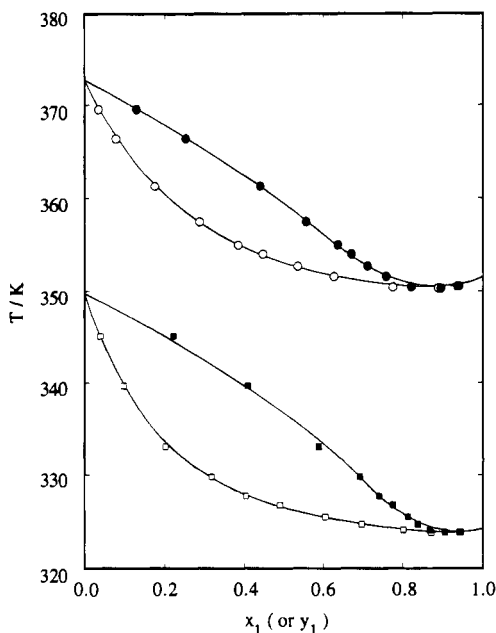
$\theta$  is the difference between the maximum and minimum boiling points, and  $T_{\min}$  is the lowest boiling point measured in the whole range of composition. With Herington's test the results are considered to be consistent when  $D - J <$

10. The eight binary systems studied here proved to be consistent, presenting deviations  $D - J < 3$ .

Calculated activity coefficients present positive deviations from ideality and decrease with increasing pressure. This behavior can be explained by taking into account that the breaking of the dipole interactions in the chlorobutane and the self-association of butanols contribute to positive deviations from ideality and, on the other hand, that the OH group of the butanols interacts with the Cl group of the chlorobutane, which leads to negative deviations from ideality.



**Figure 1.**  $T$ - $x_1$ - $y_1$  diagram for 1-chlorobutane (1) + 1-butanol (2): (□, ■) experimental data at 40.0 kPa; (○, ●) experimental data at 101.3 kPa; (—) data from the Wilson equation.

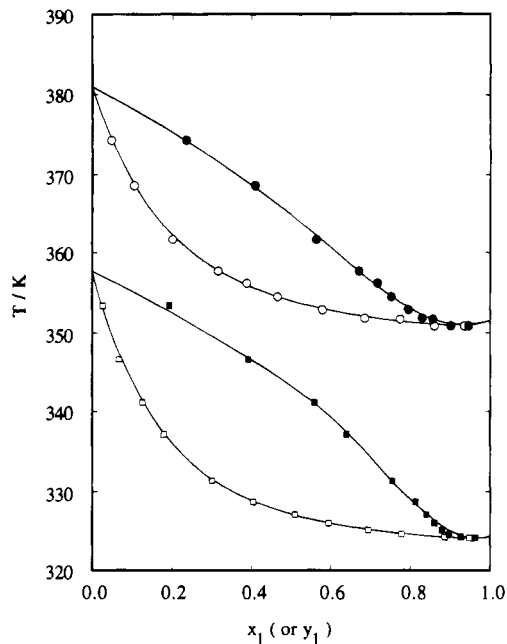


**Figure 2.**  $T$ - $x_1$ - $y_1$  diagram for 1-chlorobutane (1) + 2-butanol (2): (□, ■) experimental data at 40.0 kPa; (○, ●) experimental data at 101.3 kPa; (—) data from the Wilson equation.

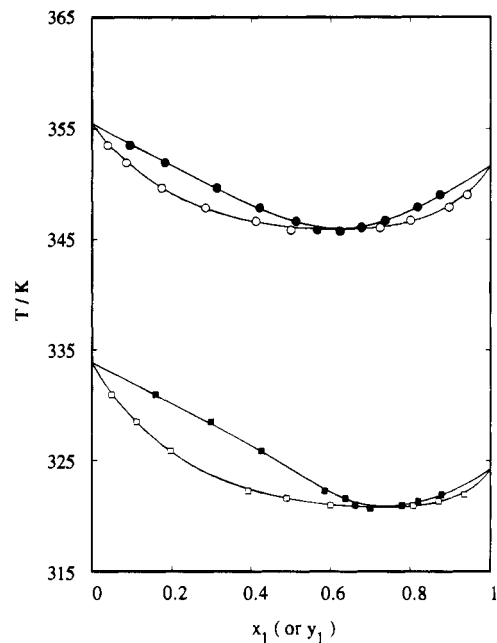
The activity coefficients were correlated with the Margules (13), Van Laar (14), Wilson (15), and NRTL (16) equations. The parameters  $A_{12}$ ,  $A_{21}$  and  $\alpha_{12}$  of the equations (see definitions in ref 17), average deviations between experimental and calculated temperatures  $\Delta T$  and vapor-phase compositions  $\Delta y_1$ , and activity coefficients at infinite dilution are listed in Table 4. The results indicate that the Wilson equation is the most suitable to correlate the activity coefficients.

From activity coefficients the excess Gibbs free energies are calculated by means of the following equation:

$$G^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \quad (5)$$



**Figure 3.**  $T$ - $x_1$ - $y_1$  diagram for 1-chlorobutane (1) + 2-methyl-1-propanol (2): (□, ■) experimental data at 40.0 kPa; (○, ●) experimental data at 101.3 kPa; (—) data from the Wilson equation.



**Figure 4.**  $T$ - $x_1$ - $y_1$  diagram for 1-chlorobutane (1) + 2-methyl-2-propanol (2): (□, ■) experimental data at 40.0 kPa; (○, ●) experimental data at 101.3 kPa; (—) data from the Wilson equation.

**Table 3.** Azeotropic Compositions in Mole Fraction  $x_{1(\text{az})}$  at Temperature  $T_{(\text{az})}$

system	$P/\text{kPa}$	$x_{1(\text{az})}$	$T_{(\text{az})}/\text{K}$
1-chlorobutane + 2-butanol	40.0	0.9450	324.03
	101.3	0.9120	350.30
2-methyl-1-propanol + 2-methyl-2-propanol	101.3	0.9600	351.37
	40.0	0.7200	320.74
	101.3	0.6165	345.74

The excess Gibbs free energies are positive over the entire range of composition and decrease with increasing

**Table 4. Correlation Parameters  $A_{12}$ ,  $A_{21}$ , and  $\alpha_{12}$ , Average Deviations between Calculated and Experimental Temperatures  $\Delta T$  and Vapor-Phase Compositions  $\Delta y_1$ , and Activity Coefficients at Infinite Dilution  $\gamma_1^\infty$  for 1-Chlorobutane (1) + Isomeric Butanols (2) at the Indicated Pressure**

equation	$A_{12}$	$A_{21}$	$\Delta T/K$	$\Delta y_1$	$\gamma_1^\infty$	$\gamma_2^\infty$
1-Chlorobutane (1) + 1-Butanol (2) at 40.0 kPa						
Margules	1.0052 <sup>a</sup>	1.7821 <sup>a</sup>	0.47	0.0144	2.73	5.94
Van Laar	1.0614 <sup>a</sup>	1.9634 <sup>a</sup>	0.34	0.0149	2.89	7.12
Wilson	236.7469 <sup>b</sup>	5425.8272 <sup>b</sup>	0.29	0.0161	3.01	9.58
NRTL	4938.3034 <sup>b</sup>	-87.2544 <sup>b</sup>	0.34	0.0149	2.89	7.08
$(\alpha_{12} = 0.3)^b$						
1-Chlorobutane (1) + 1-Butanol (2) at 101.3 kPa						
Margules	0.9970	1.4191	0.33	0.0112	2.71	4.13
Van Laar	1.0155	1.4852	0.27	0.0107	2.76	4.42
Wilson	439.8882	3614.5197	0.20	0.0104	2.84	4.91
NRTL	3441.5924	258.2930	0.26	0.0107	2.77	4.43
$(\alpha_{12} = 0.3)$						
1-Chlorobutane (1) + 2-Butanol (2) at 40.0 kPa						
Margules	1.0764	1.5066	0.19	0.0106	2.93	4.51
Van Laar	1.0943	1.5640	0.15	0.0103	2.99	4.78
Wilson	631.1477	3717.1312	0.12	0.0100	3.10	5.41
NRTL	3482.7408	442.9650	0.15	0.0102	3.00	4.83
$(\alpha_{12} = 0.3)$						
1-Chlorobutane (1) + 2-Butanol (2) at 101.3 kPa						
Margules	0.8381	1.2402	0.24	0.0099	2.31	3.46
Van Laar	0.8527	1.3143	0.18	0.0102	2.35	3.72
Wilson	86.5436	3374.0834	0.13	0.0102	2.39	3.99
NRTL	3358.7999	-118.9833	0.19	0.0101	2.35	3.69
$(\alpha_{12} = 0.3)$						
1-Chlorobutane (1) + 2-Methyl-1-propanol (2) at 40.0 kPa						
Margules	1.1005	1.7358	0.36	0.0140	3.01	5.67
Van Laar	1.1339	1.8683	0.23	0.0142	3.11	6.48
Wilson	530.9677	4850.8579	0.14	0.0148	3.25	8.33
NRTL	4420.9739	234.7442	0.23	0.0143	3.12	6.52
$(\alpha_{12} = 0.3)$						
1-Chlorobutane (1) + 2-Methyl-1-propanol (2) at 101.3 kPa						
Margules	1.0956	1.4554	0.24	0.0153	2.99	4.29
Van Laar	1.1071	1.4975	0.22	0.0147	3.03	4.47
Wilson	750.1605	3425.4100	0.16	0.0137	3.13	4.98
NRTL	3189.7444	593.6772	0.21	0.0146	3.05	4.52
$(\alpha_{12} = 0.3)$						
1-Chlorobutane (1) + 2-Methyl-2-propanol (2) at 40.0 kPa						
Margules	0.9868	1.4686	0.09	0.0119	2.68	4.34
Van Laar	1.0150	1.5272	0.08	0.0121	2.76	4.61
Wilson	499.3121	3629.7257	0.06	0.0118	2.85	5.07
NRTL	3606.9297	192.1085	0.08	0.0121	2.77	4.62
$(\alpha_{12} = 0.3)$						
1-Chlorobutane (1) + 2-Methyl-2-propanol (2) at 101.3 kPa						
Margules	0.9515	1.1357	0.11	0.0082	2.59	3.11
Van Laar	0.9560	1.1458	0.11	0.0078	2.60	3.14
Wilson	760.7803	2344.5825	0.10	0.0070	2.66	3.25
NRTL	2226.4753	681.6753	0.10	0.0077	2.61	3.16
$(\alpha_{12} = 0.3)$						

<sup>a</sup> Dimensionless. <sup>b</sup> Joules per mole.

pressure. At 40.0 kPa  $G^E$  values increase in the sequence 2-methyl-2-propanol < 2-butanol < 2-methyl-1-propanol < 1-butanol, while at 101.3 kPa this arrangement changes little because it can be observed that the mixtures containing 2-methyl-1-propanol and 1-butanol present similar  $G^E$  values.

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