

## Articles

# Vapor–Liquid Equilibrium of the Ethanol + 2-Methyl-1-butanol System

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Vapor–liquid equilibrium data were presented for the ethanol + 2-methyl-1-butanol system, obtained at three operating pressures. A modified Othmer still was used for data acquisition. When the Herington area test was applied to the experimental result, good thermodynamic consistency was found. Several equations based on both classic  $G^E$  models (Margules and Van Laar) and local composition based models (Wilson, NRTL, and UNIQUAC) were used for data correlation. The UNIFAC group contribution model was applied to predict the activity coefficients of the binary system under study. Results for the ethanol + 2-methyl-1-butanol binary system showed a positive deviation from ideality at all pressures investigated.

### Introduction

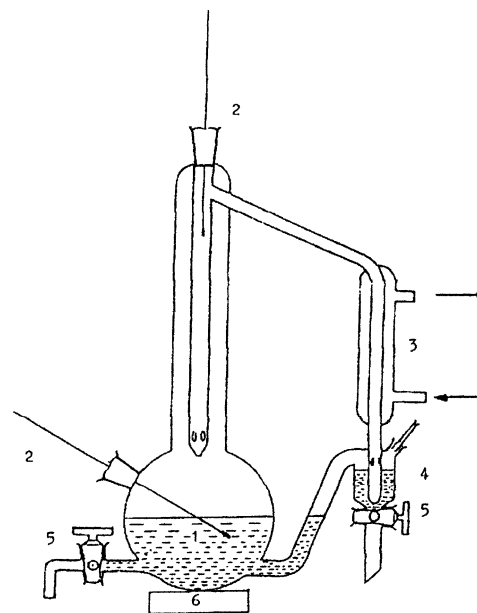
Presently, isoamyl alcohols (a mixture of 2-methyl-1-butanol and 3-methyl-1-butanol) are routinely obtained as a byproduct during ethyl alcohol production, after wine and similar raw material distillation.<sup>1</sup> Because of their low water solubility, they concentrate at the bottom of distillation towers and have to be removed to improve operation of the column. Due to an increasing demand for flavor compounds, especially from the food industry,<sup>2</sup> it is of primary interest to design distillation processes that focus on the recovery and use of these byproducts, as well as on optimization of the operating conditions and the overall yield.

To reach this goal, a knowledge is needed of the phase equilibria for the binary and ternary systems that are formed by the main components (water, ethanol, and isoamyl alcohols). The binary system ethanol–water has been widely studied<sup>3,4</sup> as well as the binary and ternary systems consisting of ethanol, water, and 3-methyl-1-butanol.<sup>5–8</sup> Nevertheless, published data on 2-methyl-1-butanol are scarce.<sup>9,10</sup>

Accordingly, it is worthwhile to study several equilibrium systems that involve 2-methyl-1-butanol. The present work describes data obtained for the binary system ethanol + 2-methyl-1-butanol, when operating under three pressures (33.3, 66.6, and 101.3 kPa).

### Experimental Section

**Apparatus, Procedures, and Chemicals.** A modified Othmer still (Figure 1) was used for the acquisition of vapor–liquid equilibrium data at atmospheric pressure. For a study at low pressure, a vacuum device was coupled to the previous still (Figure 2). The operating method was described in a previous paper.<sup>11</sup> Auxiliary equipment

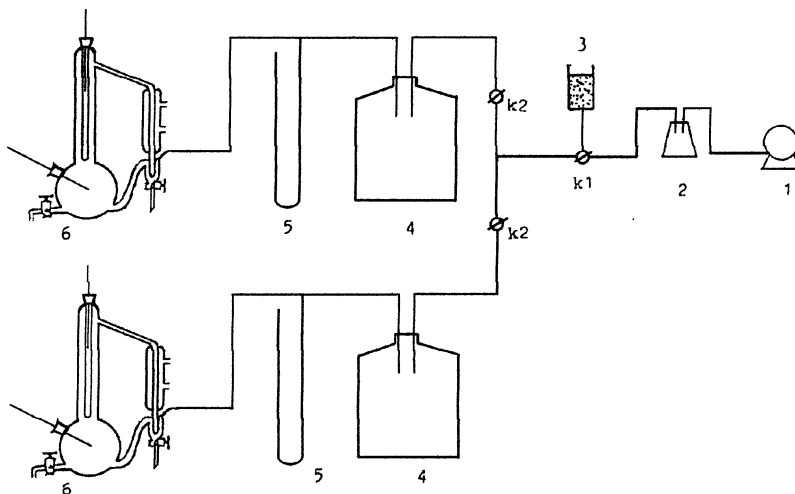


**Figure 1.** Modified Othmer still: (1) reboiler; (2) thermowell; (3) condenser; (4) condensate drum; (5) sample valve; (6) heater–stirrer.

includes a Crison 621 digital thermometer with six thermowells and an accuracy of  $\pm 0.1$  °C, two mercury manometers with an accuracy of  $\pm 1$  mmHg, two heaters with a magnetic stirrer system from Selecta Agimatic, and a cryothermostatic bath from Hetofrig. 2-Methyl-1-butanol (99 mass %) was purchased from Aldrich. Ethanol (99.8 mass %) and 1-butanol (95 mass %) were obtained from Merck. The water used was bidistilled.

**Analytical Methods.** The equilibrium compositions of the liquid and vapor phases were determined by gas chromatography (GC) by using 1-butanol as an internal

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**Figure 2.** System for the determination of low-pressure VLE: (1) vacuum pump; (2) trap; (3) drying vessel (CaCl<sub>2</sub>); (4) pressure controller vessel; (5) mercury manometer; (6) modified Othmer still.

**Table 1. Vapor-Liquid Equilibrium Data for the Ethanol + 2-Methyl-1-butanol System, at Three Different Operating Pressures (33.3, 66.6, and 101.3 kPa)**

33.3 kPa					66.6 kPa					101.3 kPa				
<i>x</i> <sub>1</sub>	<i>y</i> <sub>1</sub>	<i>t</i> <sup>o</sup> C	<i>γ</i> <sub>1</sub>	<i>γ</i> <sub>2</sub>	<i>x</i> <sub>1</sub>	<i>y</i> <sub>1</sub>	<i>t</i> <sup>o</sup> C	<i>γ</i> <sub>1</sub>	<i>γ</i> <sub>2</sub>	<i>x</i> <sub>1</sub>	<i>y</i> <sub>1</sub>	<i>t</i> <sup>o</sup> C	<i>γ</i> <sub>1</sub>	<i>γ</i> <sub>2</sub>
0.000	1.000	99.8			0.000	1.000	117.2			0.000	1.000	117.2		
0.076	0.393	90.4	1.107	0.991	0.063	0.312	109.0	1.120	0.997	0.063	0.312	109.0	1.120	0.997
0.125	0.541	85.7	1.096	0.988	0.076	0.359	107.6	1.117	0.995	0.076	0.359	107.6	1.117	0.995
0.246	0.748	76.7	1.086	0.991	0.182	0.617	98.1	1.097	0.989	0.182	0.617	98.1	1.097	0.989
0.294	0.798	74.0	1.079	0.981	0.224	0.679	95.1	1.088	0.995	0.224	0.679	95.1	1.088	0.995
0.336	0.828	72.1	1.056	0.986	0.279	0.743	91.7	1.077	0.997	0.279	0.743	91.7	1.077	0.997
0.384	0.858	70.0	1.044	0.987	0.394	0.835	85.7	1.064	1.008	0.394	0.835	85.7	1.064	1.008
0.422	0.878	68.3	1.042	0.996	0.438	0.860	83.7	1.062	1.015	0.438	0.860	83.7	1.062	1.015
0.488	0.907	65.7	1.039	0.997	0.477	0.878	82.2	1.053	1.024	0.477	0.878	82.2	1.053	1.024
0.562	0.931	63.2	1.030	1.006	0.541	0.904	79.8	1.048	1.035	0.541	0.904	79.8	1.048	1.035
0.643	0.951	60.7	1.025	1.022	0.628	0.933	76.9	1.042	1.035	0.628	0.933	76.9	1.042	1.035
0.774	0.974	57.4	1.009	1.059	0.733	0.958	73.9	1.032	1.060	0.733	0.958	73.9	1.032	1.060
0.887	0.988	54.9	1.000	1.156	0.885	0.985	70.2	1.020	1.077	0.885	0.985	70.2	1.020	1.077
0.907	0.990	54.5	0.999	1.198	0.910	0.989	69.7	1.016	1.085	0.910	0.989	69.7	1.016	1.085
1.000	0.000	52.6			1.000	0.000	68.0			1.000	0.000	68.0		

**Table 2. Experimental Data for the Vapor Pressure of 2-Methyl-1-butanol**

<i>P</i> /kPa	16.7	23.3	30.0	36.7	43.3	50.0	56.6	63.3	70.0	76.6	83.3	90.0	96.6	101.3
<i>t</i> <sup>o</sup> C	84.7	91.7	97.3	102.0	105.9	109.6	112.5	115.8	118.5	121.0	123.5	125.7	127.9	129.3

**Table 3. Antoine Equation<sup>a</sup> Parameters for the Pure Components**

component	<i>A</i>	<i>B</i>	<i>C</i>
ethanol	8.112	1592.86	226.18
2-methyl-1-butanol	6.211	778.25	104.4

$$^a \log P/\text{mmHg} = A - B/((t/^\circ\text{C}) + C).$$

standard. The chromatograph equipment was from Perkin-Elmer (Sigma 3D Model) and had an FID detector, a stainless steel column (3 m by 2 mm i.d.), and the stationary phase 5% Carbowax-1500 on Carbowax 80-100 mesh. The analytical operating conditions were as follows: injector temperature, 200 °C; detector temperature, 200 °C; oven temperature, 110 °C; carrier gas (nitrogen) flow rate, 30 mL·min<sup>-1</sup>. The sample analyses were carried out twice. The accuracy of the measured mole fraction was ±0.002.

## Results and Discussion

Experimental data are presented in Table 1 for the vapor-liquid equilibrium of the ethanol + 2-methyl-1-butanol system at three different operating pressures, together with the liquid-phase activity coefficients of both

components. A positive deviation from ideality was observed for the activity coefficients at the three different pressures investigated. Application of the Herington<sup>12</sup> thermodynamic consistency test to these data showed them to be within the established limits.

The activity coefficients have been calculated according to the thermodynamic equilibrium criteria, using a Poynting<sup>13</sup> factor equal to unity, since the operating pressures were always lower or equal to atmospheric pressure. The virial equation used was truncated after the first two terms. The equations applied are as follows:

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

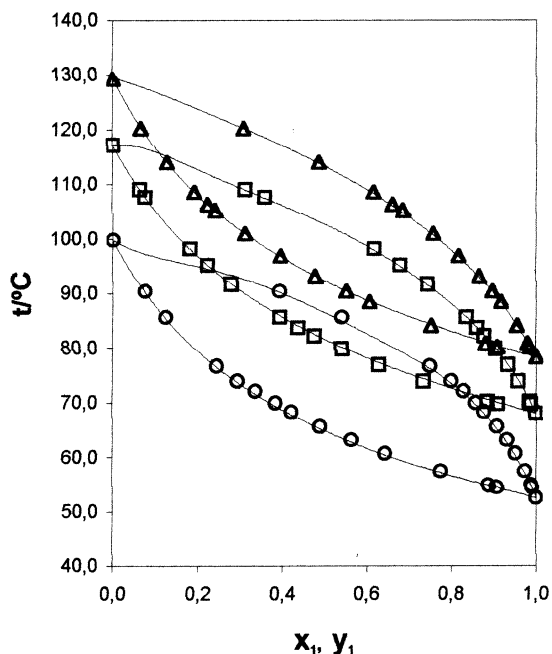
$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \quad (2)$$

where  $\gamma_i$  is the activity coefficient of component *i*,  $x_i$  and  $y_i$  are the mole fractions of component *i* in the liquid and vapor phases in equilibrium, *P* is the total pressure,  $P_i^s$  is the vapor pressure of component *i*, *R* is the gas constant, *T* is the temperature in kelvin,  $B_{ii}$  is the second virial coefficient of the pure gas, and  $B_{ij}$  is the cross second virial coefficient.

**Table 4. Parameter Values Used for Each Model and Average Absolute Deviations between Experimental and Calculated Data, for the Mole Fraction and the Temperature**

model	$A_{12}$	$A_{21}$	$\alpha$	$\Delta y^c$	$\Delta T^d/K$
$P = 33.3 \text{ kPa}$					
Margules	0.069 <sup>a</sup>	0.190 <sup>a</sup>		0.0022	0.210
Van Laar	0.083 <sup>a</sup>	0.105 <sup>a</sup>		0.0020	0.213
Wilson	1336.72 <sup>b</sup>	-1007.59 <sup>b</sup>		0.0025	0.222
NRTL	2998.96 <sup>b</sup>	-1809.99 <sup>b</sup>	0.39 <sup>a</sup>	0.0024	0.221
UNIQUAC	-597.54 <sup>b</sup>	1019.11 <sup>b</sup>		0.0026	0.224
$P = 66.6 \text{ kPa}$					
Margules	0.118	0.136		0.0027	0.241
Van Laar	0.118	0.137		0.0027	0.241
Wilson	2422.86	-2018.41		0.0031	0.292
NRTL	810.94	-377.86	0.39	0.0030	0.237
UNIQUAC	-804.79	1358.57		0.0037	0.283
$P = 101.3 \text{ kPa}$					
Margules	0.133	0.159		0.0031	0.097
Van Laar	0.134	0.161		0.0031	0.094
Wilson	2367.59	-1901.43		0.0034	0.104
NRTL	1024.55	-744.20	0.38	0.0035	0.082
UNIQUAC	-804.03	1392.45		0.0037	0.101

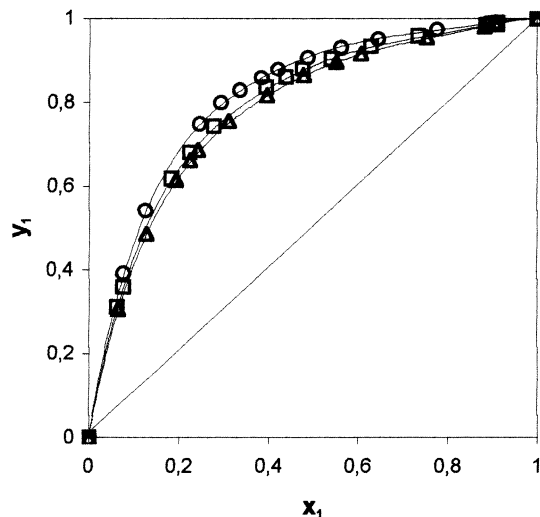
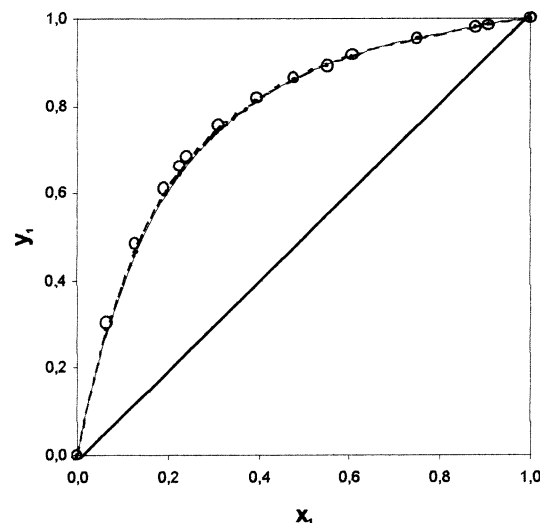
<sup>a</sup> Dimensionless. <sup>b</sup> J·mol<sup>-1</sup>. <sup>c</sup>  $\Delta y = \sum\{|y - y_{(cal)}|\}/\{N\}$ . <sup>d</sup>  $\Delta T = \sum\{|T - T_{(cal)}|\}/\{N\}$ .  $N$  = number of data points.

**Figure 3.** VLE ( $T$ - $x$ ) of the system ethanol (1) + 2-methyl-1-butanol (2) at three different working pressures: (○) 33.3, (□) 66.6, and (△) 101.3 kPa for experimental values and (—) for the NRTL model.

The virial coefficients  $B_{ij}$  and  $B_{ji}$  have been calculated using the Pitzer and Curl equations with the corrections for alcohols proposed by Tsonopoulos.<sup>14</sup> The parameters used for the calculation of the latter coefficients were obtained from the literature.<sup>15</sup>

The Antoine equation was used to calculate the vapor pressures of the pure compounds. The Antoine parameters for 2-methyl-1-butanol were obtained experimentally using the modified Othmer still, as shown in Table 2, whereas those corresponding to ethanol were obtained from the literature.<sup>16</sup> The Antoine equation parameters for both components are included in Table 3.

**Activity Coefficients Correlation.** After obtaining the activity coefficients from the experimental VLE data (eqs 1 and 2), several models were used for correlation.

**Figure 4.** VLE ( $y$ - $x$ ) of the system ethanol (1) + 2-methyl-1-butanol (2) at three different working pressures: (○) 33.3, (□) 66.6, and (△) 101.3 kPa for experimental values and (—) for the NRTL model.**Figure 5.** VLE ( $y$ - $x$ ) of the system ethanol (1) + 2-methyl-1-butanol (2) at 101.3 kPa working pressure vs mole fraction of component 1: (○) experimental values; (---) UNIFAC model; and (—) UNIFAC-Dortmund model.**Table 5. Ethanol (1) + 2-Methyl-1-butanol (2) System at Three Different Operating Pressures: Average Absolute Deviations between Experimental Equilibrium Data ( $x$ ,  $T$ ) and Data Obtained by Using the UNIFAC and UNIFAC-Dortmund Models**

$P/kPa$	UNIFAC		UNIFAC-D	
	$\Delta y$	$\Delta T/K$	$\Delta y$	$\Delta T/K$
33.3	0.0050	0.229	0.0070	0.362
66.6	0.0061	0.547	0.0088	0.733
101.3	0.0083	0.557	0.0120	0.877

Equations based on classic models (Margules and Van Laar) and three models based on the local composition concept (Wilson, NRTL, and UNIQUAC<sup>17</sup>) were applied.

To obtain the binary interaction parameters characteristic of the different equations, the following objective function was used:

$$F = \sum (y_1 - \gamma_{1(cal)})^2 + \sum (\gamma_2 - \gamma_{2(cal)})^2 \quad (3)$$

This multiparametric regression has been carried out by

using the SOLVER macro function from the Excel Microsoft Office 97 data calculation sheet. The values of the adjustable parameters ( $A_{12}$ ,  $A_{21}$ , and  $\alpha$ ), together with the average deviations obtained by comparing the experimental equilibrium data to the calculated values obtained through the different theoretical models, are shown in Table 4. It can be observed that, regardless of the model used, average deviations fall within the same range, which is in fact the range expected for the systems studied.

From the data of Table 4 it can be concluded that all of the theoretical models agree well with the VLE data obtained in this work. As an example, Figures 3 and 4 illustrate the good agreement between the experimental and calculated data using the NRTL equation.

It is worthwhile to note that the lower the pressure, the higher the relative volatility of the system. In addition, a lower pressure implies a lower equilibrium temperature, with the consequential energy savings. A lower distillation temperature implies smaller utilities costs, for example, a reduction in reboiler duty and feed preheating.

Finally, the activity coefficients for the ethanol (1) + 2-methyl-1-butanol (2) system have been calculated using the UNIFAC<sup>18,19</sup> and UNIFAC–Dortmund<sup>20</sup> models. Figure 5 shows the agreement between the calculated values and the experimental data. However, the UNIFAC–Dortmund model does not improve the results obtained by the original UNIFAC model, as can be seen in Table 5.

### Summary

Experimental VLE data for the binary system ethanol + 2-methyl-1-butanol were measured at three different pressures (33.3, 66.6, and 101.3 kPa). Results fit very well with the Margules, Van Laar, Wilson, NRTL, UNIQUAC, and UNIFAC prediction models. A reduction of the operating pressure produces a higher separation yield and a decrease in equilibrium temperature as well.

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