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# Isobaric Vapor−Liquid Equilibrium for the Binary Mixtures (2-Butanol + *n*-Hexane) and (2-Butanol + 1-Butylamine) and for the Ternary System (2-Butanol + *n*-Hexane + 1-Butylamine) at 101.3 kPa

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Isobaric vapor−liquid equilibrium has been experimentally studied for the binary mixtures 2-butanol + *n*-hexane and 2-butanol + 1-butylamine and for the ternary mixture 2-butanol + *n*-hexane + 1-butylamine at 101.3 kPa. The activity coefficients were found to be thermodynamically consistent, and they were satisfactorily correlated with the Margules, van Laar, Wilson, NRTL, and UNIQUAC equations. The activity coefficients were also compared with the results obtained from the application of the ASOG and modified UNIFAC group contribution methods. The boiling points of the solutions were correlated with compositions by the Wisniak−Tamir equations. The results obtained indicate that the binary system 2-butanol + *n*-hexane deviates positively from ideality, whereas 2-butanol + 1-butylamine deviates negatively from ideality. The ternary system deviates positively or negatively depending on the composition. Only the binary systems present azeotropy. Azeotropic behavior was not found in the ternary mixture.

## Introduction

Distillation has been used as an effective method of separation in the chemical processing industry, and vapor−liquid equilibrium (VLE) data are essential for the development, design, and simulation of separation sequences of mixtures. This paper is a continuation of our work on the determination of isobaric VLE data for binary and ternary mixtures.[1−4] The present paper reports experimental isobaric vapor−liquid equilibrium data for the binary systems 2-butanol (1) + *n*-hexane (2) and 2-butanol (1) + 1-butylamine (2) and for the ternary mixture containing 2-butanol, *n*-hexane, and 1-butylamine at a pressure of 101.3 kPa. In previous work, we presented results on the densities and excess molar volumes,[5] viscosities,[6] and isentropic compressibilities[7] for the ternary mixture 2-butanol (1) + *n*-hexane (2) + 1-butylamine (3) and the related binary mixtures. No values for the isobaric VLE are available for this ternary system in the open literature, but several references can be found for the isothermal VLE of binary systems.[8−13]

The experimental results are compared with those calculated according to the equations of Margules,[14] van Laar,[15] Wilson,[16] NRTL,[17] and UNIQUAC[18] and with those predicted by the ASOG[19] and modified UNIFAC[20] group contribution methods.

## Experimental Section

**Chemicals.** 2-Butanol (>99.0 mol %), *n*-hexane (>99.5 mol %), and 1-butylamine (>99 mol %) were provided by Aldrich. The measured physical properties of the pure compounds (densities, refractive indices, and normal boiling points) are presented in Table 1, along with the corresponding values found in the literature. Liquids were used without further purification. 2-Butanol and 1-butylamine were dried over activated molecular sieve type 0.3 nm from Merck.

**Table 1. Physical Properties: Densities ($\rho$), Refractive Indices ($n_D$), and Normal Boiling Points ($T_b$) of the Pure Components**

| | $\rho$(298.15 K) ($kg \cdot m^{-3}$) | | $n_D$(298.15 K) | | $T_b$(101.3 kPa) (K) | |
|---|---|---|---|---|---|---|
| component | exptl | lit | exptl | lit | exptl | lit[a] |
| 2-butanol | 802.39 | 802.41[a] | 1.394 88 | 1.3950[b] | 372.75 | 372.66 |
| *n*-hexane | 654.93 | 654.84[a] | 1.375 44[c] | 1.3723[c,d] | 341.98 | 341.89 |
| 1-butylamine | 732.25 | 733.00[e] | 1.398 75 | 1.3984[b] | 350.33 | 350.22 |

[a] Riddick et al.[21] [b] TRC tables.[22] [c] At 293.15 K. [d] Lide.[23] [e] Davolio et al.[24]

**Apparatus and Procedure.** The vapor−liquid equilibrium experiments in this study were performed using an all-glass dynamic recirculating still, equipped with a Cottrell pump. It is a commercial unit (Labodest model) built by Fischer capable of handling pressures from 0.25 to 400 kPa and temperatures up to 523.15 K.

Temperatures were measured using a thermometer (model F25) from Automatic System Laboratories with an accuracy of ±0.01 K. Pressures were measured using a Druck PDCR 110/W pressure transducer and a PDI201 pressure indicator with an accuracy of ±0.1 kPa.

In each experiment, the experimental pressure was fixed, and the heating and stirring system of the liquid mixture

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**Table 2. Experimental Vapor−Liquid Equilibrium Data for the Binary Systems 2-Butanol (1) + *n*-Hexane (2) and 2-Butanol (1) + 1-Butylamine (2) at 101.3 kPa**

| $T$ (K) | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|
| | | 2-butanol (1) + *n*-hexane (2) | | |
| 340.89 | 0.0413 | 0.0683 | 5.989 | 1.001 |
| 340.61 | 0.0930 | 0.1001 | 3.948 | 1.031 |
| 340.67 | 0.1490 | 0.1217 | 2.987 | 1.070 |
| 340.90 | 0.2115 | 0.1400 | 2.395 | 1.123 |
| 341.41 | 0.2917 | 0.1588 | 1.924 | 1.205 |
| 342.31 | 0.4038 | 0.1836 | 1.543 | 1.352 |
| 343.77 | 0.5259 | 0.2122 | 1.282 | 1.572 |
| 345.61 | 0.6240 | 0.2478 | 1.162 | 1.793 |
| 349.32 | 0.7514 | 0.3200 | 1.060 | 2.205 |
| 353.09 | 0.8272 | 0.3980 | 1.022 | 2.529 |
| 358.80 | 0.8959 | 0.5316 | 0.999 | 2.802 |
| 363.05 | 0.9348 | 0.6530 | 0.996 | 2.969 |
| 367.75 | 0.9769 | 0.8431 | 1.031 | 3.368 |
| 369.85 | 0.9853 | 0.9000 | 1.011 | 3.204 |
| 371.11 | 0.9907 | 0.9363 | 0.999 | 3.129 |
| | | 2-butanol (1) + 1-butylamine (2) | | |
| 351.26 | 0.0369 | 0.0100 | 0.621 | 0.995 |
| 352.36 | 0.0771 | 0.0206 | 0.585 | 0.993 |
| 353.67 | 0.1226 | 0.0349 | 0.590 | 0.989 |
| 356.41 | 0.2176 | 0.0742 | 0.632 | 0.979 |
| 359.67 | 0.3176 | 0.1357 | 0.695 | 0.952 |
| 363.51 | 0.4318 | 0.2369 | 0.769 | 0.904 |
| 367.69 | 0.5729 | 0.4105 | 0.858 | 0.827 |
| 370.51 | 0.6930 | 0.5910 | 0.921 | 0.740 |
| 371.66 | 0.7626 | 0.7020 | 0.954 | 0.676 |
| 372.27 | 0.8237 | 0.7954 | 0.979 | 0.615 |
| 372.60 | 0.8632 | 0.8506 | 0.988 | 0.574 |
| 372.77 | 0.9098 | 0.9101 | 0.997 | 0.521 |
| 372.79 | 0.9435 | 0.9468 | 0.999 | 0.492 |
| 372.77 | 0.9692 | 0.9745 | 1.002 | 0.433 |

**Table 3. Experimental Vapor−Liquid Equilibrium Data for the Ternary Mixture 2-Butanol (1) + *n*-Hexane (2) + 1-Butylamine (3) at 101.3 kPa**

| $T$ (K) | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $\gamma_1$ | $\gamma_2$ | $\gamma_3$ |
|---|---|---|---|---|---|---|---|
| 348.18 | 0.038 | 0.081 | 0.007 | 0.168 | 0.482 | 1.729 | 0.999 |
| 349.82 | 0.107 | 0.072 | 0.025 | 0.168 | 0.570 | 1.858 | 0.995 |
| 352.20 | 0.189 | 0.063 | 0.053 | 0.167 | 0.618 | 1.976 | 0.981 |
| 356.18 | 0.317 | 0.047 | 0.122 | 0.164 | 0.720 | 2.334 | 0.936 |
| 361.35 | 0.461 | 0.032 | 0.246 | 0.144 | 0.813 | 2.628 | 0.862 |
| 365.52 | 0.609 | 0.018 | 0.419 | 0.121 | 0.894 | 3.530 | 0.785 |
| 368.33 | 0.707 | 0.010 | 0.577 | 0.078 | 0.955 | 3.819 | 0.718 |
| 371.10 | 0.808 | 0.004 | 0.760 | 0.036 | 0.995 | 4.117 | 0.593 |
| 343.80 | 0.033 | 0.271 | 0.005 | 0.409 | 0.481 | 1.427 | 1.034 |
| 344.70 | 0.068 | 0.255 | 0.017 | 0.413 | 0.762 | 1.492 | 1.004 |
| 347.53 | 0.196 | 0.213 | 0.056 | 0.434 | 0.769 | 1.730 | 0.939 |
| 351.25 | 0.336 | 0.166 | 0.120 | 0.438 | 0.819 | 2.018 | 0.859 |
| 355.20 | 0.485 | 0.114 | 0.214 | 0.419 | 0.859 | 2.523 | 0.786 |
| 360.04 | 0.614 | 0.082 | 0.356 | 0.361 | 0.930 | 2.658 | 0.693 |
| 364.19 | 0.729 | 0.054 | 0.507 | 0.282 | 0.950 | 2.833 | 0.642 |
| 368.22 | 0.831 | 0.023 | 0.704 | 0.150 | 0.995 | 3.199 | 0.591 |
| 369.81 | 0.902 | 0.013 | 0.824 | 0.094 | 1.012 | 3.410 | 0.546 |
| 341.81 | 0.044 | 0.466 | 0.019 | 0.572 | 1.499 | 1.231 | 1.095 |
| 343.17 | 0.106 | 0.431 | 0.033 | 0.594 | 1.016 | 1.328 | 1.010 |
| 345.40 | 0.258 | 0.374 | 0.077 | 0.613 | 0.882 | 1.479 | 0.982 |
| 349.21 | 0.417 | 0.259 | 0.158 | 0.602 | 0.948 | 1.881 | 0.765 |
| 354.40 | 0.614 | 0.158 | 0.299 | 0.537 | 0.980 | 2.383 | 0.632 |
| 359.93 | 0.765 | 0.091 | 0.470 | 0.423 | 0.989 | 2.812 | 0.555 |
| 366.21 | 0.881 | 0.038 | 0.705 | 0.230 | 1.013 | 3.119 | 0.501 |
| 369.40 | 0.906 | 0.018 | 0.808 | 0.130 | 1.003 | 3.440 | 0.467 |
| 340.74 | 0.038 | 0.670 | 0.022 | 0.715 | 2.111 | 1.105 | 1.225 |
| 341.93 | 0.116 | 0.606 | 0.052 | 0.728 | 1.548 | 1.200 | 1.034 |
| 343.64 | 0.252 | 0.504 | 0.100 | 0.731 | 1.268 | 1.378 | 0.855 |
| 345.80 | 0.422 | 0.383 | 0.162 | 0.715 | 1.114 | 1.665 | 0.726 |
| 349.22 | 0.591 | 0.267 | 0.246 | 0.670 | 1.041 | 2.030 | 0.610 |
| 354.50 | 0.742 | 0.156 | 0.374 | 0.571 | 1.010 | 2.558 | 0.473 |
| 361.03 | 0.871 | 0.073 | 0.577 | 0.391 | 1.022 | 3.148 | 0.413 |
| 366.56 | 0.928 | 0.036 | 0.750 | 0.225 | 1.009 | 3.192 | 0.430 |
| 369.33 | 0.969 | 0.015 | 0.870 | 0.111 | 1.012 | 3.530 | 0.681 |
| 340.85 | 0.047 | 0.852 | 0.040 | 0.860 | 3.088 | 1.041 | 1.341 |
| 341.19 | 0.123 | 0.773 | 0.085 | 0.841 | 2.468 | 1.111 | 0.953 |
| 341.99 | 0.257 | 0.653 | 0.128 | 0.818 | 1.715 | 1.249 | 0.782 |
| 343.65 | 0.428 | 0.507 | 0.177 | 0.786 | 1.321 | 1.472 | 0.703 |
| 345.43 | 0.564 | 0.386 | 0.221 | 0.752 | 1.156 | 1.756 | 0.629 |
| 348.67 | 0.695 | 0.266 | 0.288 | 0.693 | 1.061 | 2.140 | 0.511 |
| 352.63 | 0.788 | 0.181 | 0.371 | 0.617 | 1.019 | 2.506 | 0.359 |
| 358.86 | 0.881 | 0.094 | 0.531 | 0.458 | 1.012 | 3.030 | 0.339 |
| 365.04 | 0.943 | 0.041 | 0.728 | 0.264 | 1.021 | 3.416 | 0.323 |
| 369.10 | 0.976 | 0.015 | 0.876 | 0.116 | 1.021 | 3.709 | 0.513 |
| 371.14 | 0.990 | 0.004 | 0.952 | 0.038 | 1.016 | 4.337 | 0.910 |

was connected. The system was kept at the boiling point for 15 min to ensure an equilibrium state. Then electromagnetic valves permitted extraction of samples (approximately 2 mL) of liquid and vapor. The compositions of the liquid and vapor samples for the binary mixtures were determined by measuring their densities at 298.15 K with an Anton Paar DSA-58 vibrating tube densimeter. Excess volumes calculated from these density measurements were reported in a previous paper. [5] For the ternary mixture, the compositions of the liquid and vapor samples were determined by measuring their densities and speeds of sound at 298.15 K with an Anton Paar DMA-48 vibrating tube densimeter and sound analyzer. The composition dependence of the density and speed of sound has been previously reported.[7] These apparatuses were previously calibrated at atmospheric pressure with doubly distilled water and dry air. The maximum estimated uncertainties in the determination of the liquid- and vapor-phase mole fractions for the binary and ternary mixtures are ±0.0002 and ±0.002, respectively.

## Experimental Results and Discussion

The vapor−liquid equilibrium data and the activity coefficients for the binary mixtures 2-butanol (1) + *n*-hexane (2) and 2-butanol (1) + 1-butylamine (2) and for the ternary system 2-butanol (1) + *n*-hexane (2) + 1-butylamine (3) at 101.3 kPa are shown in Tables 2 and 3, respectively. The results for the binary mixture *n*-hexane (1) + 1-butylamine (2) are given in a previous work. [3]

The activity coefficients, $\gamma_i$,were calculated, taking into account the nonideality of the vapor phase, from the equations

binary system

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

ternary system

$$\gamma_i = \frac{y_i P}{x_i P_i^o} \exp\left[\frac{(B_{ii} - V_i^o)(P - P_i^o)}{RT} + \frac{P}{2RT}\sum_l^n\sum_l^n y_j y_k(2\delta_{ji} - \delta_{jk})\right] \tag{2}$$

where

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \tag{3}$$

and $x_i$ and $y_i$ are the mole fractions of component $i$ in the liquid phase and in the vapor phase, respectively; $P$ is the total pressure; $P_i^o$ is the vapor pressure of pure component $i$ calculated from the Antoine equation taking the coefficients $A$, $B$, and $C$ from Riddick et al.; [21] $B_{ii}$ represents the second virial coefficients of component $i$ obtained from

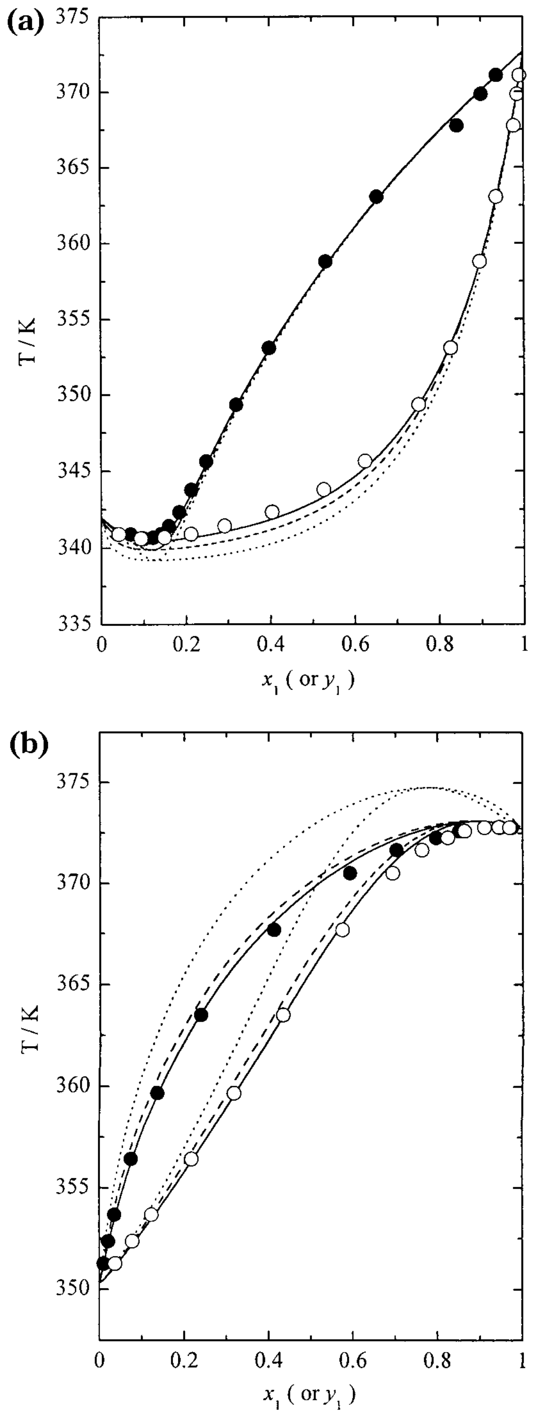

**Figure 1.** $T-x_1-y_1$ diagram at a pressure of 101.3 kPa for the binary mixtures (a) 2-butanol (1) + *n*-hexane (2) and (b) 2-butanol (1) + 1-butylamine (2). (○, ●) Experimental data; (—) correlated with the Wilson equation; (– – –) predicted by the UNIFAC model; (- - -) predicted by the ASOG model.

the expressions included in the TRC tables,[22] and $B_{ij}$ represents the cross second virial coefficients estimated by means of the Amdur−Mason equation.[25] The molar volumes of the saturated liquids, $V_i^{o}$, were determined using the Yen and Woods method.[26]

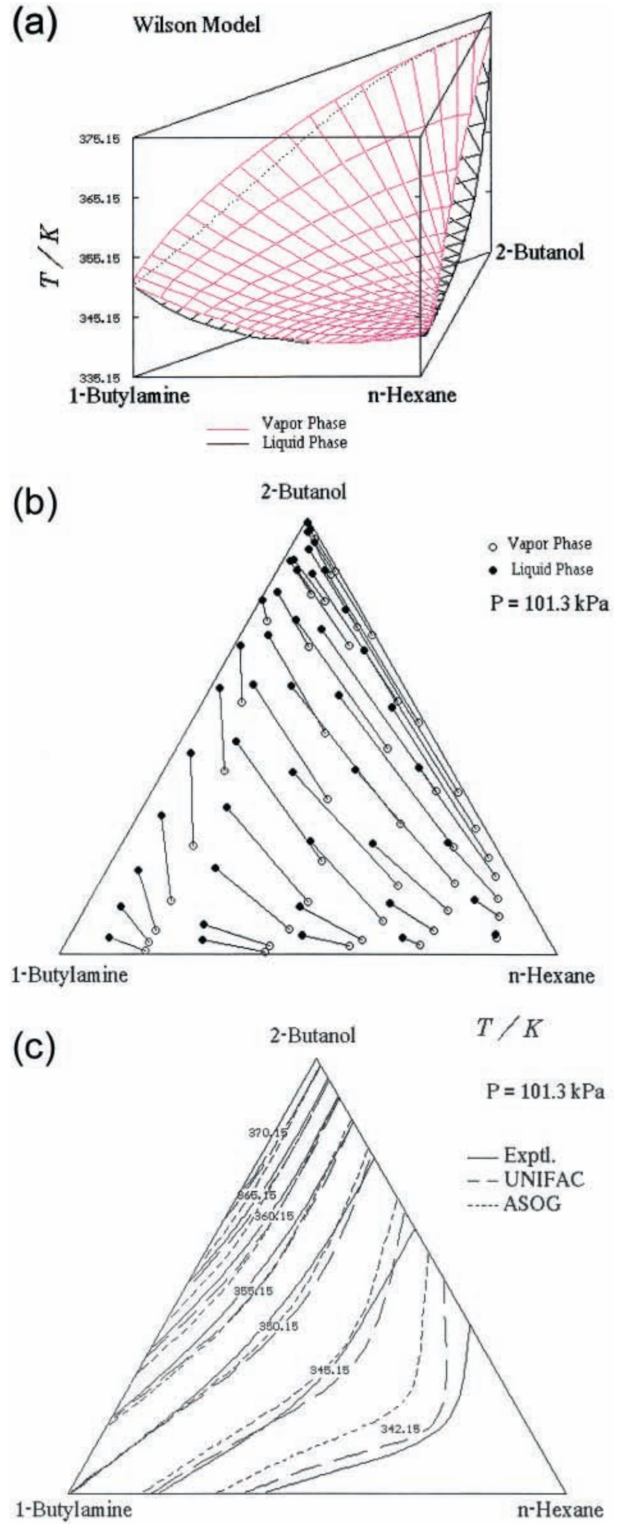

**Figure 2.** Isobaric VLE of the ternary system 2-butanol (1) + *n*-hexane (2) + 1-butylamine (3) at 101.3 kPa. (a) Three-dimensional surfaces of the vapor and liquid phases. (b) Tie lines: ●, liquid-phase mole fraction; ○, vapor-phase mole fraction. (c) Boiling isotherms in the liquid phase: (—) calculated from eq 5 and the parameters reported in Table 4, (– – –) predicted by the UNIFAC model, (- - -) predicted by the ASOG model.

The $T-x_1-y_1$ diagrams for the binary mixtures 2-butanol (1) + *n*-hexane (2) and 2-butanol (1) + 1-butylamine (2) are shown in Figure 1a and b, respectively. Calculations with the Wilson equation were employed to obtain this diagram. The precise locations of the binary azeotropes ($x_{1\text{az min}} = 0.111$, $T_{\text{az}} = 340.44$ K for the first mixture; $x_{1\text{az max}} = 0.907$, $T_{\text{az}} = 372.99$ K for the second mixture) were determined by establishing the following conditions at the azeotropic point

$$x_1 = y_1 \quad \left(\frac{\partial T}{\partial x_1}\right)_p = 0 \quad \left(\frac{\partial T}{\partial y_1}\right)_p = 0$$

**Table 4. Coefficients in the Correlation of Boiling Points with Liquid-Phase Composition, Standard Deviations ($\sigma$), and Root-Mean-Square Deviations (RMSDs) in Temperature**

| binary system | $C_0$ | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $\sigma$[a] | RMSD[b] |
|---|---|---|---|---|---|---|---|
| 2-butanol (1) + *n*-hexane (2) | −56.03 | −34.84 | −25.92 | −13.62 | −30.38 | 0.34 | 0.072 |
| 2-butanol (1) + 1-butylamine (2) | 16.40 | 16.19 | −2.15 | −6.38 | – | 0.04 | 0.008 |
| *n*-hexane (1) + 1-butylamine (2)[c] | −19.33 | 4.12 | −7.00 | – | – | 0.07 | 0.018 |

| ternary system | $A$ | $B$ | $C$ | $\sigma$[a] | RMSD[b] |
|---|---|---|---|---|---|
| 2-butanol (1) + *n*-hexane (2) + 1-butylamine (3) | −62.49 | −169.84 | – | 0.52 | 0.075 |

[a] $\sigma = [\sum(T_{\mathrm{exptl}} - T_{\mathrm{calc}})^2/(m - p)]^{1/2}$, where $p$ is the number of parameters. [b] $\mathrm{RMSD} = 1/m[\sum_i^m(T_{\mathrm{exptl}} - T_{\mathrm{calc}})^2]^{1/2}$. [c] Domínguez et al.[3]

**Table 5. Results of the Thermodynamic Consistency Test: Average Deviations $\Delta P$ and $\Delta y$**

| binary system | $\Delta P$ (kPa) | $\Delta y$ |
|---|---|---|
| 2-butanol (1) + *n*-hexane (2) | 0.9 | 0.0021 |
| 2-butanol (1) + 1-butylamine (2) | 0.9 | 0.0019 |
| *n*-hexane (1) + 1-butylamine (2)[a] | 0.6 | 0.0019 |

| ternary system | $\Delta P$ (kPa) | $\Delta y$ | $\Delta y_1$ | $\Delta y_2$ | $\Delta y_3$ |
|---|---|---|---|---|---|
| 2-butanol (1) + *n*-hexane (2) + 1-butylamine (3) | 2.2 | 0.008 | 0.006 | 0.010 | 0.007 |

[a] Domínguez et al.[3]

In the system *n*-hexane (1) + 1-butylamine (2), the azeotrope was located at $x_{1\mathrm{az\,min}} = 0.725$, $T_{\mathrm{az}} = 340.35$ K.[3]

The boiling temperatures of the binary and ternary systems were correlated with the equations proposed by Tamir and Wisniak[27]

$$T_{ij} = \sum_{i=1}^{2} x_i T_i^{\mathrm{o}} + x_i x_j \sum_{k=0}^{m} C_k (x_i - x_j)^k \tag{4}$$

$$T = \sum_{i=1}^{2}\sum_{j>i}^{3} T_{ij} + x_1 x_2 x_3 [A + B(x_1 - x_2) + C(x_1 - x_3)] \tag{5}$$

where $T_i^{\mathrm{o}}$ is the boiling temperature of pure component $i$ in Kelvin and $m$ is the number of terms in the series expansion of $(x_i - x_j)$. The binary systems were correlated by eq 4 and the ternary system by eq 5 using the values of $T_{ij}$ from eq 4. $C_k$ represents the binary constants; and $A$, $B$, and $C$, are the ternary constants. The various constants, along with the standard deviations and root-mean-square deviations, are reported in Table 4. Figure 2a shows the three-dimensional surfaces of the vapor and liquid phases for the ternary system correlated with the Wilson model. The equilibrium composition diagram of the ternary system is shown in Figure 2b. The isotherms of the liquid phase calculated from eq 5 and the parameters reported in Table 4 are shown in Figure 2c.

To calculate the azeotropic temperature and compositions of the ternary mixture at a given total pressure, we used the method of Wang et al.[28] that employs a dual iterative technique. With this method, we verified that the ternary system 2-butanol (1) + *n*-hexane (2) + 1-butylamine (3) does not exhibit azeotropic behavior, according to Figure 2b.

The thermodynamic consistency of the experimental binary data was verified by means of the point-to-point test of Van Ness.[29] For the ternary mixture, we used the test of Van Ness modified by Fredenslund[30] and extended to multicomponent mixtures employing the following equation proposed by Prausnitz[31] to determine the activity coefficient, $\gamma_i$, of component $i$

$$\ln \gamma_i = Q + \left(\frac{\partial Q}{\partial x_i}\right)_{T,P,x_{j\neq i}} - \sum_{j=1}^{k-1} x_j \left(\frac{\partial Q}{\partial x_j}\right)_{T,P,x_{i\neq j}} \tag{6}$$

where $k$ is the number of components in the mixture, $x_i$ is the mole fraction of component $i$, and $Q$ is the reduced excess Gibbs free energy, $Q = G^{\mathrm{E}}/RT$. We used an equation of the Redlich−Kister type extended to a multicomponent mixture to establish the relationship between $Q$ and the liquid-phase composition

$$Q = \sum_{i=1}^{k}\sum_{j=i+1}^{k} x_i x_j \sum_{p=0}^{p} A_p (x_i - x_j)^p + x_1 x_2 (1 - x_1 - x_2)(B_1 + B_2 x_1 + B_3 x_2) \tag{7}$$

According to these consistency tests, the experimental data are considered thermodynamically consistent when the average deviation for the vapor-phase composition ($\Delta y$) is less than 0.01. The values of $\Delta y$ calculated for our systems (binary and ternary) satisfy that condition, as shown in Table 5.

The activity coefficients, $\gamma_i$, determined by means of the eqs 1−3 were fitted to the Margules, van Laar, Wilson, NRTL, and UNIQUAC equations. [32] The adjustable parameters for these equations were obtained through a least-squares approach using the Simplex method[33] to minimize an objective function OF expressed in terms of the experimental and calculated $\gamma_i$ values as

$$\mathrm{OF} = \sum_{i=1}^{m}\left[\sum_{j=1}^{n}\left(\frac{\gamma_j^{\mathrm{exptl}} - \gamma_j^{\mathrm{calc}}}{\gamma_j^{\mathrm{exptl}}}\right)^2\right]_i \tag{8}$$

where $m$ is the number of experimental data points and $n$ is the number of components in the mixture.

The parameters resulting from the fitting, along with the average deviations of both the temperature ($\Delta T$) and the composition of the vapor phase ($\Delta y$), and the activity coefficients at infinite dilution for the binary mixtures studied are given in Table 6 for the Margules, van Laar, Wilson, NRTL, and UNIQUAC equations. According to this table, the average deviation in $T$ is less than 0.41, and the average deviation in the vapor composition is less than 0.006; thus, all of the equations correlated the activity coefficients quite well.

The VLE study of the ternary system was carried out in two different ways. First, we fitted the experimental activity coefficients with the Wilson, NRTL, and UNIQUAC equations extended to multicomponent mixtures.[32] The

**Table 6. Correlation Parameters for the Margules, van Laar, Wilson, NRTL, and UNIQUAC Equations, Average Deviations between Calculated and Experimental Temperatures ($\Delta T$), Vapor-Phase Compositions ($\Delta y$), and Activity Coefficients at Infinite Dilution, $\gamma_i^\infty$, for the Binary Systems at 101.3 kPa**

| equation | $A_{12}$ | $A_{21}$ | $\Delta T$ (K) | $\Delta y$ | $\gamma_1^\infty$ | $\gamma_2^\infty$ |
|---|---|---|---|---|---|---|
| 2-butanol (1) + *n*-hexane (2) | | | | | | |
| Margules[a] | 1.79 | 1.16 | 0.41 | 0.0064 | 6.00 | 3.18 |
| van Laar[a] | 1.92 | 1.17 | 0.31 | 0.0056 | 6.83 | 3.22 |
| Wilson[b] | 6110.06 | 122.25 | 0.27 | 0.0035 | 8.33 | 3.41 |
| NRTL[c] ($\alpha_{12} = \alpha_{21} = 0.3$) | 549.40 | 4889.62 | 0.31 | 0.0055 | 5.81 | 3.24 |
| UNIQUAC[d] | −928.45 | 2914.50 | 0.31 | 0.0057 | 5.28 | 2.89 |
| 2-butanol (1) + 1-butylamine (2) | | | | | | |
| Margules[a] | −0.55 | −0.86 | 0.24 | 0.0016 | 0.58 | 0.42 |
| van Laar[a] | −0.57 | −0.88 | 0.21 | 0.0011 | 0.56 | 0.41 |
| Wilson[b] | −2188.30 | 504.02 | 0.26 | 0.0017 | 0.54 | 0.35 |
| NRTL[c] ($\alpha_{12} = \alpha_{21} = 0.4$) | 1643.42 | −2991.62 | 0.21 | 0.0016 | 0.60 | 0.42 |
| UNIQUAC[d] | 1763.34 | −1901.49 | 0.17 | 0.0016 | 0.62 | 0.47 |
| *n*-hexane (1) + 1-butylamine (2)[e] | | | | | | |
| Margules[a] | 0.61 | 0.61 | 0.18 | 0.0020 | 1.83 | 1.83 |
| van Laar[a] | 0.61 | 0.61 | 0.18 | 0.0020 | 1.83 | 1.83 |
| Wilson[b] | 194.96 | 1685.79 | 0.19 | 0.0022 | 1.85 | 1.83 |
| NRTL[c] ($\alpha_{12} = \alpha_{21} = 0.3$) | 822.67 | 994.40 | 0.19 | 0.0022 | 1.84 | 1.82 |
| UNIQUAC[d] | 794.10 | −224.98 | 0.19 | 0.0022 | 1.84 | 1.79 |

[a] Dimensionless. [b] $A_{ij} = (\lambda_{ij} - \lambda_{ii})/(\mathrm{J \cdot mol^{-1}})$. [c] $A_{ij} = (g_{ij} - g_{jj})/(\mathrm{J \cdot mol^{-1}})$. [d] $A_{ij} = (u_{ij} - u_{jj})/(\mathrm{J \cdot mol^{-1}})$. [e] Domínguez et al.[3]

**Table 7. Correlation Parameters for the Ternary System: Average Deviations in $T$ ($\Delta T$) and Average Deviations in $y$ ($\Delta y$) at 101.3 kPa (A) Correlated from the Ternary Coefficients and (B) Predicted from the Binary Coefficients**

| equation | *i*, *j* | $A_{ij}$ | $A_{ji}$ | | $\Delta T$ (K) | $\Delta y$ | $\Delta y_1$ | $\Delta y_2$ | $\Delta y_3$ |
|---|---|---|---|---|---|---|---|---|---|
| Wilson[a] | 1, 2 | 4734.93 | 840.06 | | | | | | |
| | 1, 3 | −1044.54 | −1266.69 | A | 0.39 | 0.006 | 0.005 | 0.007 | 0.007 |
| | 2, 3 | 999.30 | 942.46 | B | 0.69 | 0.010 | 0.009 | 0.013 | 0.009 |
| NRTL[b] | 1, 2 | 1021.14 | 4525.17 | | | | | | |
| | 1, 3 | −754.70 | −1486.99 | A | 0.54 | 0.006 | 0.005 | 0.007 | 0.006 |
| | 2, 3 | 804.15 | 1006.84 | B | 0.70 | 0.011 | 0.009 | 0.016 | 0.010 |
| UNIQUAC[c] | 1, 2 | −345.58 | 1881.37 | | | | | | |
| | 1, 3 | −227.10 | −554.92 | A | 0.46 | 0.007 | 0.005 | 0.008 | 0.008 |
| | 2, 3 | −458.26 | 1062.45 | B | 1.14 | 0.017 | 0.015 | 0.024 | 0.013 |

[a] $A_{ij} = (\lambda_{ij} - \lambda_{ii})/(\mathrm{J \cdot mol^{-1}})$. [b] $A_{ij} = (g_{ij} - g_{jj})/(\mathrm{J \cdot mol^{-1}})$; $\alpha_{12} = \alpha_{21} = \alpha_{23} = \alpha_{32} = 0.3$; $\alpha_{13} = \alpha_{31} = 0.4$. [c] $A_{ij} = (u_{ij} - u_{jj})/(\mathrm{J \cdot mol^{-1}})$.

**Table 8. ASOG and UNIFAC Predictions, Average Deviations in $T$ ($\Delta T$), and Average Deviations in $y$ ($\Delta y$)**

| | ASOG | | | | | UNIFAC | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| binary system | $\Delta T$ (K) | $\Delta y$ | | | | $\Delta T$ (K) | $\Delta y$ | | | |
| 2-butanol (1) + *n*-hexane (2) | 1.18 | 0.0109 | | | | 0.61 | 0.0061 | | | |
| 2-butanol (1) + 1-butylamine (2) | 1.77 | 0.0228 | | | | 0.45 | 0.0042 | | | |
| *n*-hexane (1) + 1-butylamine (2)[a] | 0.91 | 0.0091 | | | | 0.28 | 0.020 | | | |
| ternary system | $\Delta T$ (K) | $\Delta y$ | $\Delta y_1$ | $\Delta y_2$ | $\Delta y_3$ | $\Delta T$ (K) | $\Delta y$ | $\Delta y_1$ | $\Delta y_2$ | $\Delta y_3$ |
| 2-butanol (1) + *n*-hexane (2) + 1-butylamine (3) | 1.16 | 0.014 | 0.012 | 0.015 | 0.015 | 0.75 | 0.009 | 0.009 | 0.012 | 0.007 |

[a] Domínguez et al.[3]

correlation parameters are considered "ternary parameters". These parameters, along with the deviations $\Delta T$ and $\Delta y$, are given in Table 7 marked by the letter A. Second, the VLE values for the ternary mixture were predicted by the same equations but with the "binary parameters" obtained from the fitting of the respective binary mixtures. The deviations from these predictions are also listed in Table 7 marked with the letter B. The deviations obtained through the direct correlation of the experimental values are smaller than the corresponding values predicted from the binary coefficients.

The binary mixture 2-butanol (1) + *n*-hexane (2) deviates positively from ideality, whereas 2-butanol (1) + 1-butylamine (2) deviates negatively from ideality. The molecular interactions that govern the thermodynamic behavior have been described in previous papers.[5−7] The most important effects in the mixing process are the breaking of the self-association in the alkanol + alkane mixture and the formation of OH−NH$_2$ crossed hydrogen bonds in the alcohol + amine system.

## Predictions

The ASOG and modified UNIFAC group contribution methods were also employed to predict the vapor−liquid equilibrium of the binary and ternary systems under study. The average deviations of both the temperature ($\Delta T$) and the composition of the vapor phase ($\Delta y$) are given in Table 8. In this table, we can see that, for both the binary and ternary mixtures, the UNIFAC model gives smaller deviations. Figures 1 and 2c show the predictions by the UNIFAC (− − −) and ASOG (- - -) models and compares them with the experimental values.

## Conclusions

Isobaric vapor−liquid equilibrium data for the binary mixtures 2-butanol (1) + *n*-hexane (2) and 2-butanol (1) +

1-butylamine and for the ternary system 2-butanol (1) + *n*-hexane (2) + 1-butylamine (3) were measured at a pressure of 101.3 kPa in a Labodest dynamic recirculating still. The results were found to be thermodynamically consistent, and the activity coefficients were evaluated with the Margules, van Laar, Wilson, NRTL, and UNIQUAC equations, showing that the correlation of the activity coefficients is satisfactory for all of these equations. The binary system 2-butanol (1) + *n*-hexane (2) presents a minimum-temperature azeotrope and deviates positively from ideality, whereas the *n*-hexane (1) + 1-butylamine (2) mixture presents a maximum azeotrope and deviates negatively from Raoult's law. The azeotropic behavior of the ternary mixture 2-butanol (1) + *n*-hexane (2) + 1-butylamine (3) was checked using the Wang's method. According to the results, the ternary system does not show an azeotrope. The ASOG and modified UNIFAC group contribution methods were used to predict the isobaric VLE. For the binary and ternary mixtures, the UNIFAC model gives smaller deviations.

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