

Isothermal Vapor–Liquid Equilibria for the Ternary System 2-Propanol + Tetrahydrofuran + 1-Chlorobutane at 25°C

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Isothermal vapor–liquid equilibria (VLE) for mixtures containing 2-propanol + tetrahydrofuran + 1-chlorobutane have been measured using a modified version of a Boublik–Benson still at 25°C. A test of thermodynamic consistency, like the McDermott–Ellis method was applied to the activity coefficients. Excess molar Gibbs free energies were calculated over the entire range composition. Different expressions existing in the literature were used to predict activity coefficients.

KEY WORDS: Vapor–liquid equilibrium; binary and ternary systems; excess molar free energies; activity coefficients.

1. INTRODUCTION

Measurements of vapor–liquid (VLE) are necessary for the interpretation of distillation processes. This paper reports the results of measurements on VLE for the 2-propanol (2-PR) (1) + tetrahydrofuran (THF) (2) + 1-chlorobutane (CIBU) (3) system at 25°C.

Experimental data for this system have not been previously reported. Some thermodynamic properties of the corresponding binary mixtures have been published.^(1–3) This work is a continuation of our study on thermodynamic properties of mixtures.

In this system, the three components are polar and the first component presents association in its pure state. From the experimental VLE data activity coefficients can be calculated, as well the excess molar Gibbs free energies (G^E). In

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the literature there are different expressions for calculating G^E for a ternary system knowing the values for the corresponding binary systems.

Thermodynamic interactions of some chloroalkanes with THF have been studied by Birós *et al.*⁽⁴⁾ and by Sharma *et al.*⁽⁵⁾

For activity coefficients, we applied the semiempirical van Laar equation (modified by Carlson and Colburn), as well as the Wilson, NRTL, and UNIQUAC equations. Finally, we applied the predictive group-contribution method (UNIFAC).

2. EXPERIMENTAL

The substances have been purified as described Ref. 1. Densities were determined with a digital densimeter AP model 45. A thermostatically controlled bath (constant to ± 0.01 K) was used. Calibration was done with air and doubly distilled water. Temperatures were read from calibrated thermometers. The accuracy in density was $\pm 0.1 \text{ kg}\cdot\text{m}^{-3}$.

Equilibrium data were determined by using a modified version of the equilibrium still described by Boublik and Benson⁽⁶⁾ working at 25°C . The pressures were determined using a Barocel pressure transducer, type 590, and a digital pressure display and controller, model 1501. The estimated error in pressure was ± 0.15 kPa. The analysis of the liquid and condensed vapor were carried out using Perkin-Elmer Sigma 300 gas chromatograph, with a thermal conductivity detector. The current supplied to the detector was 150 mA. The copper column was 1.8 m long and was packed with 1.5% Carbowax 20 M over Carbopack B 60/80.

The column temperature was 150°C and hydrogen was used as the carrier gas. Calibration analyses were carried out with 15 samples of known composition. Three or more injections for each sample were made and an LCI-100 integrator was used to calculate areas. Mole fractions were obtained with a computation program. With this method, the sample concentrations were accurate to better than 0.001 mole fraction.

3. RESULTS AND DISCUSSION

The experimental results for the pure liquids are reported in Table I, together with literature values for comparison.

Values of the mole fractions in the liquid and the vapor phases, and values of pressures, activity coefficients, and Gibbs free energies of the mixtures are summarized in Table II.

The liquid-phase activity coefficients were calculated from experimental data, taking into account the nonideality of the vapor phase by employing the equation

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - V_i)(P - P_i^0)}{RT} + \frac{P}{2RT} \sum_{j=1}^n \sum_{k=1}^n y_j y_k (2\delta_{ji} - \delta_{ik}) \quad (1)$$

Table I. Properties Characterizing Pure Components at 25°C

| Substance | $\rho_i \times 10^{-3} \text{ (kg-m}^{-3}\text{)}$ | | $P_i^0 \text{ (kPa)}$ | |
|-----------------|--|----------------------|-----------------------|--------------------|
| | Exp. | Lit. | Exp. | Lit. |
| 2-Propanol | 0.7813 | 0.78126 ^a | 5.81 | 5.81 ^b |
| Tetrahydrofuran | 0.8819 | 0.8811 ^a | 21.60 | 21.60 ^b |
| 1-Chlorobutane | 0.8803 | 0.88095 ^a | 13.34 | 13.54 ^a |

^aRef. 7.^bRef. 8.

where

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

P_i^0 is the vapor pressure of pure liquid i and x_i, y_i are the respective mole fractions in the liquid and vapor phases of the mixture.

Table II. Experimental Values of 2-Propanol(1) + Tetrahydrofuran(2) + 1-Chlorobutane(3) System at 25°C

| x_1 | x_2 | y_1 | y_2 | $P \text{ (kPa)}$ | γ_1 | γ_2 | γ_3 | $G_{123}^E \text{ (J-mol}^{-1}\text{)}$ |
|-------|-------|-------|-------|-------------------|------------|------------|------------|---|
| 0.012 | 0.755 | 0.010 | 0.835 | 19.89 | 2.826 | 1.019 | 0.987 | 59.4 |
| 0.026 | 0.241 | 0.043 | 0.305 | 15.95 | 4.514 | 0.938 | 1.061 | 166.6 |
| 0.115 | 0.469 | 0.087 | 0.554 | 17.35 | 2.258 | 0.951 | 1.116 | 286.6 |
| 0.197 | 0.729 | 0.095 | 0.841 | 18.62 | 1.532 | 0.996 | 1.203 | 235.7 |
| 0.213 | 0.197 | 0.166 | 0.219 | 16.34 | 2.177 | 0.844 | 1.274 | 681.6 |
| 0.256 | 0.645 | 0.140 | 0.759 | 17.45 | 1.629 | 0.953 | 1.331 | 302.6 |
| 0.266 | 0.388 | 0.155 | 0.480 | 16.57 | 1.653 | 0.951 | 1.308 | 513.5 |
| 0.295 | 0.590 | 0.148 | 0.735 | 17.06 | 1.461 | 0.986 | 1.298 | 331.8 |
| 0.307 | 0.563 | 0.154 | 0.713 | 16.95 | 1.452 | 0.997 | 1.297 | 362.9 |
| 0.343 | 0.507 | 0.180 | 0.653 | 16.25 | 1.457 | 0.972 | 1.354 | 397.1 |
| 0.343 | 0.167 | 0.212 | 0.188 | 15.95 | 1.686 | 0.834 | 1.461 | 829.4 |
| 0.376 | 0.445 | 0.201 | 0.584 | 15.80 | 1.443 | 0.963 | 1.421 | 456.4 |
| 0.394 | 0.323 | 0.213 | 0.420 | 15.50 | 1.429 | 0.936 | 1.508 | 583.9 |
| 0.446 | 0.343 | 0.219 | 0.465 | 15.33 | 1.287 | 0.966 | 1.719 | 532.9 |
| 0.451 | 0.302 | 0.221 | 0.403 | 15.08 | 1.264 | 0.935 | 1.719 | 543.0 |
| 0.483 | 0.133 | 0.257 | 0.163 | 14.70 | 1.338 | 0.837 | 1.663 | 774.5 |
| 0.507 | 0.265 | 0.244 | 0.390 | 14.65 | 1.205 | 1.002 | 1.762 | 556.1 |
| 0.565 | 0.130 | 0.267 | 0.202 | 14.25 | 1.153 | 1.030 | 1.859 | 677.2 |
| 0.598 | 0.119 | 0.307 | 0.146 | 13.63 | 1.198 | 0.778 | 1.975 | 671.1 |
| 0.618 | 0.208 | 0.313 | 0.340 | 13.28 | 1.151 | 1.010 | 1.985 | 516.9 |
| 0.655 | 0.183 | 0.369 | 0.303 | 12.39 | 1.195 | 0.954 | 1.883 | 522.6 |
| 0.713 | 0.160 | 0.347 | 0.312 | 12.48 | 1.039 | 1.134 | 2.522 | 408.9 |
| 0.721 | 0.041 | 0.346 | 0.059 | 12.83 | 1.055 | 0.859 | 2.407 | 598.2 |
| 0.754 | 0.140 | 0.400 | 0.287 | 11.52 | 1.048 | 1.099 | 2.559 | 367.2 |
| 0.756 | 0.073 | 0.371 | 0.130 | 12.30 | 1.034 | 1.020 | 2.695 | 486.7 |
| 0.860 | 0.051 | 0.471 | 0.123 | 10.60 | 0.996 | 1.191 | 3.636 | 297.8 |

The values of the virial coefficients of the pure components and the cross-virial coefficients for the binary systems are: $B_{11} = -2.047 \times 10^{-3} \text{ m}^3\text{-mol}^{-1}$; $B_{22} = -1.280 \times 10^{-3} \text{ m}^3\text{-mol}^{-1}$; $B_{33} = -2.112 \times 10^{-3} \text{ m}^3\text{-mol}^{-1}$; $B_{12} = -1.507 \times 10^{-3} \text{ m}^3\text{-mol}^{-1}$; $B_{13} = -1.780 \times 10^{-3} \text{ m}^3\text{-mol}^{-1}$; $B_{23} = -1.629 \times 10^{-3} \text{ m}^3\text{-mol}^{-1}$. These values were estimated by the method of Hayden and O'Connell.⁽⁹⁾

The ternary data reported in Table II were found to be thermodynamically consistent, as tested by the McDermott-Ellis⁽¹⁰⁾ method. Following Tamir and Wisniak,⁽¹¹⁾ two experimental points are considered thermodynamically consistent if the following condition is fulfilled:

$$D < D_{\max} \quad (3)$$

where:

$$D = \sum_{i=1}^n (x_{ia} + x_{ib})(\ln \gamma_{ib} - \ln \gamma_{ia}) \quad (4)$$

$$D_{\max} = \sum_{i=1}^n (x_{ia} + x_{ib}) \left[\frac{1}{x_{ib}} + \frac{1}{y_{ib}} + \frac{1}{x_{ia}} + \frac{1}{y_{ia}} \right] \Delta x + 2 \sum_{j=1}^n (\ln \gamma_{ib} - \ln \gamma_{ia}) \Delta x + \sum_{i=1}^n (x_{ia} + x_{ib}) \frac{\Delta P}{P} \quad (5)$$

The uncertainties in the measurements were $\Delta x = 0.001$ and $\Delta P = 0.15 \text{ kPa}$.

Knowing the activity coefficients, it is possible to calculate the excess molar Gibbs free energies by the expression

$$G_{123}^E = RT \sum_{i=1}^n x_i \ln \gamma_i \quad (6)$$

Figure 1 shows the lines of G^E of the three binary systems. The excess function of the binary system can be represented by the expression

$$G_{ij}^E = x_i x_j \sum_{k=0}^n a_k (x_i - x_j)^k \quad (7)$$

The least-squares method (using the Marquardt⁽¹²⁾) algorithm was used to determine the values of the coefficients. In each case, n was varied and the minimum number of coefficients needed to represent the results was found by examining the minor standard deviation of the estimate

$$\sigma = \left[\sum (G_{\text{exp}}^E - G_{\text{cal}}^E)^2 / (n_{\text{exp}} - n) \right]^{1/2} \quad (8)$$

The values adopted for the coefficients and standard deviations of the fit are indicated in Table III.

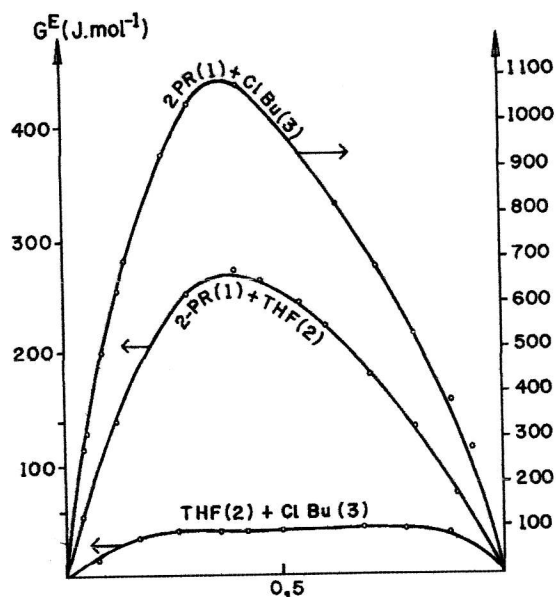


Fig. 1. Excess molar Gibbs free energies for the binary systems at 25°C.

If interactions in a ternary system $1 + j + k$ are assumed to be dependent on the pairwise interactions of the constituents $i + j$, $j + k$, and $i + k$, it should be possible to evaluate excess properties of ternary mixture of nonelectrolytes from the corresponding functions of the binary systems. All three binary systems shows positive values of G^E with large values for the 2-PR(1) + ClBU(3) system and small values for the THF(2) + ClBU(3) system.

From the different expressions existing in the literature to predict Gibbs free energies of a ternary system from the binary systems,⁽¹³⁻¹⁵⁾ we applied those introducing fitting parameters, like that of Cibulka,⁽¹⁶⁾ who proposes the following expression

$$G_{123}^E = G_{12}^E + G_{23}^E + G_{13}^E + x_1 x_2 x_3 (A + B x_1 + C x_2) \quad (9)$$

Table III. Coefficients a_k for Eq. (7) and Standard Deviations for Binary Systems at 25°C

| Systems | a_0 | a_1 | a_2 | a_3 | a_4 | σ (J·mol ⁻¹) |
|-------------------|--------|---------|-------|--------|--------|---------------------------------|
| 2-PR(1) + THF(2) | 1020.6 | -497.1 | 376.9 | 183.3 | -657.6 | 0.025 |
| 2-PR(1) + ClBU(3) | 4059.8 | -2220.6 | 459.5 | 1024.9 | 1357.8 | 0.22 |
| THF(2) + ClBU(3) | 156.8 | -15.6 | 282.8 | 102.1 | -91.8 | 0.67 |

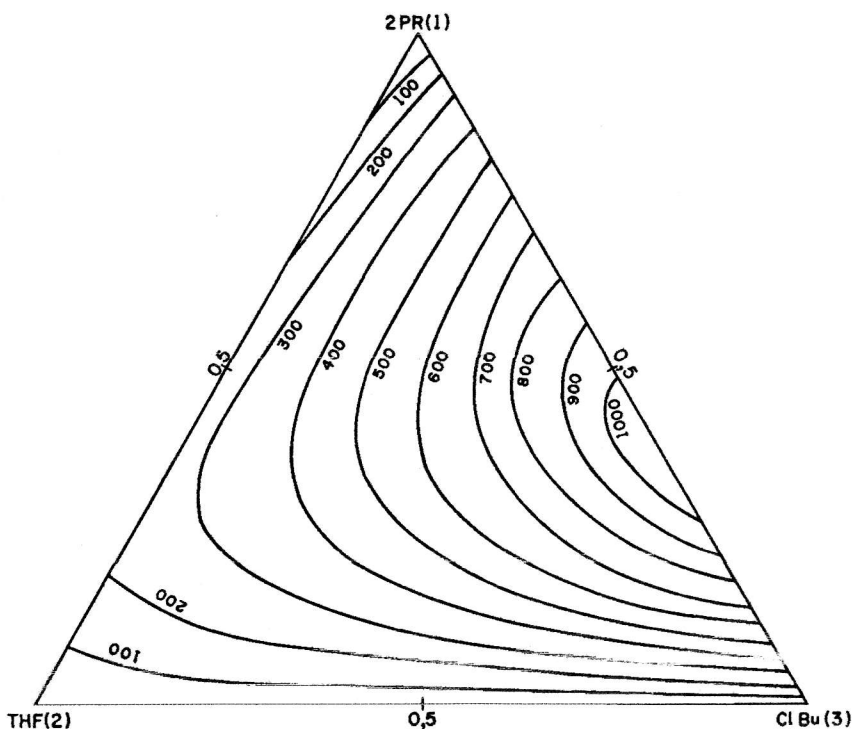


Fig. 2. Lines of constant excess molar Gibbs free energies ($\text{J}\cdot\text{mol}^{-1}$) for 2-propanol (1) + tetrahydrofuran (2) + 1-chlorobutane (3) system at 25°C .

where A , B , and C are fitting parameters calculated from experimental data. The parameters obtained for the excess Gibbs free energy are $A = -1234.7$, $B = 4255.4$, and $C = -505.1$ with the root-mean-square deviation defined as

$$SD = \left[\frac{\sum (G_{\text{obs}}^E - G_{\text{exp}}^E)^2}{n_{\text{exp}}} \right]^{1/2} \quad (10)$$

Figure 2 shows the lines of constant G_{123}^E .

Different equations exist in the literature to represent activity coefficients for ternary systems, as indicated by Prausnitz *et al.*⁽¹⁷⁾ The van Laar equation for a ternary system is

$$\ln \gamma_1 = x_2^2 \Lambda_{12} (\Lambda_{21} / \Lambda_{12})^2 + x_3^2 \Lambda_{13} (\Lambda_{31} / \Lambda_{13})^2 + x_2 x_3 \Lambda_{21} \Lambda_{31} / \Lambda_{12} \Lambda_{13} \\ + \Lambda_{12} + \Lambda_{13} - \Lambda_{12} (\Lambda_{13} / \Lambda_{31}) / (x_1 + x_2 \Lambda_{21} / \Lambda_{12} + x_3 \Lambda_{31} / \Lambda_{13})^2 \quad (11)$$

The expressions for γ_2 and γ_3 are of exactly the same form as that for γ_1 . To obtain γ_2 , the subscripts in Eq. (11) are changed by replacing 1 with 2, 2 with

Table IV. Constants of van Laar, Wilson, NRTL, and UNIQUAC Equations

| Equations | Systems | | |
|-----------|---|---|---|
| | 2-PR(1) + THF(2) | 2-PR(1) + CIBU(3) | THF(2) + CIBU(3) |
| van Laar | $\Lambda_{12} = 0.6792$ $\Lambda_{21} = 0.2952$ | $\Lambda_{13} = 2.8634$ $\Lambda_{31} = 1.1604$ | $\Lambda_{23} = 0.7861$ $\Lambda_{32} = 0.0791$ |
| Wilson | $\Lambda_{12} = 0.3116$ $\Lambda_{21} = 1.4825$ | $\Lambda_{13} = 0.0333$ $\Lambda_{31} = 0.7232$ | $\Lambda_{23} = 0.9666$ $\Lambda_{32} = 0.9566$ |
| NRTL | $\tau_{12} = -0.6569$ $\tau_{21} = 1.4438$ $\alpha_{12} = 0.424$ | $\tau_{13} = -0.0592$ $\tau_{31} = 2.9069$ $\alpha_{13} = 0.396$ | $\tau_{23} = 0.0940$ $\tau_{32} = -0.0151$ $\alpha_{23} = 12.63$ |
| UNIQUAC | $r_1 = 3.2491$ $q_1 = 3.124$ $\tau_{12} = 1.5007$ $\tau_{21} = 0.4907$ | $r_2 = 2.9415$ $q_2 = 2.720$ $\tau_{13} = 1.5262$ $\tau_{31} = 0.2390$ | $r_3 = 3.7153$ $q_3 = 3.192$ $\tau_{23} = 0.9895$ $\tau_{32} = 0.9884$ |

3, and 3 with 1. To obtain γ_3 , replace 1 with 3, 2 with 1, and 3 with 2. All the parameters in Eq. (11) may be obtained from binary data. Table IV shows these constants.

For a solution of m components, the activity coefficients of any component k in Wilson's equation is:

$$\ln \gamma_k = -\ln \sum_{j=1}^m x_j \Lambda_{kj} + 1 - \sum_{i=1}^m \left(x_i \Lambda_{ik} / \sum_{j=1}^m x_j \Lambda_{ij} \right) \quad (12)$$

For each possible binary pair in the multicomponent system, two parameters are needed and the constants are listed in Table IV.

For a solution of m components, the NRTL equation is:

$$\ln \gamma_i = \left[\sum_{j=1}^m \tau_{ji} G_{ji} x_j / \sum_{l=1}^m G_{li} x_l \right] + \sum_{j=1}^m \left[x_j G_{ij} / \sum_{l=1}^m G_{lj} x_l \right] \times \left[\tau_{ij} - \left(\sum_{r=1}^m x_r \tau_{rj} G_{rj} / \sum_{i=1}^m G_{ij} x_i \right) \right] \quad (13)$$

where

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (14)$$

The constants used are listed in Table IV.

The UNIQUAC model for a ternary system gives:

Table V. Average Deviations for the 2-Propanol(1) + Tetrahydrofuran (2) + 1-Chlorobutane (3) at 25°C

| Equations | σ_P (kPa) | $\sigma_{\gamma 1}$ | $\sigma_{\gamma 2}$ | $\sigma_{\gamma 3}$ |
|-----------|------------------|---------------------|---------------------|---------------------|
| van Laar | 0.817 | 0.031 | 0.017 | 0.027 |
| Wilson | 0.065 | 0.026 | 0.017 | 0.021 |
| NRTL | 0.067 | 0.036 | 0.026 | 0.031 |
| UNIQUAC | 1.022 | 0.032 | 0.017 | 0.029 |
| UNIFAC | 2.218 | 0.032 | 0.017 | 0.029 |

$$\ln \gamma_i = \ln(\phi_i/x_i) + (z/2)q_i \ln(\theta_i/\phi_i) + l_i - (\phi_i/x_i) \sum_{j=1}^m x_j l_j - q \ln \sum_{j=1}^m \theta_j \tau_{ji} + q_i - q_i \sum_{j=1}^m \left[\frac{\theta_j \tau_{ji}}{\sum_{k=1}^m \theta_k \tau_{kj}} \right] \quad (15)$$

This equation requires only pure component and binary parameters and the constants are summarized in Table IV, where, for convenience only, z is taken as 10.

These equations are semiempirical and not predictive. We applied the UNIFAC method, which is a predictive group-contribution method used by Fredenslund *et al.*⁽¹⁸⁾ and Gmehling *et al.*⁽¹⁹⁾ and gives:

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^R \quad (16)$$

where γ_i^c is the combinatorial term and γ_i^R is the residual term. The constants used are in the references mentioned above.

The values P and y were computed with the following equation:

$$P_{\text{col}} = x_1 \gamma_1 P_1^s + x_2 \gamma_2 P_2^s + x_3 \gamma_3 P_3^s \quad (17)$$

$$y_{i \text{ col}} = x_i \gamma_i P_i^s / P_{\text{col}} \quad (18)$$

over the complete concentration range, where P_i^s are the corrected vapor pressures of the components following Eq. (1).

Table V gives the average deviation by applying all these equations.

Equation (12) gives smaller deviations compared with the average deviations from the other equations.

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