

Liquid–Liquid Equilibria for the Ternary System Water + 2-Methyl-2-butanol + Diethylene Glycol Monobutyl Ether

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Liquid–liquid equilibria of a ternary system water + 2-methyl-2-butanol + diethylene glycol monobutyl ether were measured at 293.15 K, 303.15 K, and 313.15 K under atmospheric pressure. The experimental equilibrium data were correlated with the UNIQUAC model, and a good agreement was obtained.

Introduction

Thermodynamic data of liquid–liquid equilibrium are important in liquid extraction and partition processes in the chemical industry. Recently, liquid–liquid equilibrium data have been measured for binary and ternary mixtures in our laboratory.^{1–4} In this study liquid–liquid equilibrium measurements were performed for a ternary system water + 2-methyl-2-butanol + diethylene glycol monobutyl ether at 293.15 K, 303.15 K, and 313.15 K under atmospheric pressure. The experimental data were correlated with the UNIQUAC model of Abrams and Prausnitz.⁵ The phase behavior of the system was successfully described by the UNIQUAC model.

Experimental Section

2-Methyl-2-butanol was obtained from Merck with a purity of 99%. The nonionic surfactant diethylene glycol monobutyl ether was an Aldrich Chemical product with a purity of 99%. These two chemicals were used without further purification. Water was purified by a Millipore Milli-RO PLUS 10 and Milli-Q system with a resistivity of >18.2 M Ω ·cm. For each tie line, the water + 2-methyl-2-butanol + diethylene glycol monobutyl ether mixtures were prepared in three test tubes with the same total composition. These samples were vigorously shaken and then put into a water thermostat, the temperature stability of which was controlled in uncertainty of T within ± 0.005 K, for at least 12 h to reach equilibrium. During the equilibration process, these samples were shaken several times to ensure thorough mixing. After equilibrium was reached, both liquid phases were analyzed by gas chromatography to determine the compositions. The compositions for each tie line were determined by averaging over three samples.

A gas chromatograph (China Chromatography 9800) equipped with a thermal conductivity detector was used to analyze the composition of the samples. A 1 m long by 3.175×10^{-3} m diameter stainless steel column (Poropak P 80/100 mesh) was used. The signal was transferred to an integrator (Shimadzu, Chromatopac C-R6A) to accomplish data recording. The temperatures of the injection port and the detector were held at 553.15 K and 573.15 K, respectively. The oven temperature was initially held at 398.15 K. Five minutes after injection, the oven temperature was raised to a final temperature of 508.15 K at a speed of 37 K·min⁻¹. Helium was the carrier gas with a

Table 1. Experimental Mass Fraction of Water of Equilibrium Liquid Phases for the Binary System Water (1) + 2-Methyl-2-butanol (2)

| T/K | w_1^u | w_1^l |
|--------|---------|---------|
| 293.15 | 0.8671 | 0.2488 |
| 303.15 | 0.8926 | 0.2307 |
| 313.15 | 0.9127 | 0.2166 |

Table 2. Experimental and Calculated Mass Fractions of Equilibrium Liquid Phases for the Ternary System Water (1) + 2-Methyl-2-butanol (2) + Diethylene glycol Monobutyl Ether (3) at 293.15 K

| exptl results | | | | calcd results | | | |
|----------------------------|---------|---------|---------|---------------|---------|---------|---------|
| w_1^u | w_3^u | w_1^l | w_3^l | w_1^u | w_3^u | w_1^l | w_3^l |
| 0.2597 | 0.0327 | 0.8700 | 0.0043 | 0.2622 | 0.0345 | 0.8677 | 0.0049 |
| 0.2750 | 0.0621 | 0.8675 | 0.0087 | 0.2767 | 0.0650 | 0.8676 | 0.0097 |
| 0.2811 | 0.0753 | 0.8655 | 0.0116 | 0.2835 | 0.0773 | 0.8673 | 0.0117 |
| 0.3034 | 0.1100 | 0.8605 | 0.0199 | 0.3092 | 0.1144 | 0.8650 | 0.0189 |
| 0.3279 | 0.1370 | 0.8549 | 0.0280 | 0.3362 | 0.1409 | 0.8609 | 0.0256 |
| 0.3569 | 0.1576 | 0.8477 | 0.0342 | 0.3638 | 0.1586 | 0.8551 | 0.0320 |
| 0.3699 | 0.1667 | 0.8350 | 0.0408 | 0.3768 | 0.1643 | 0.8519 | 0.0350 |
| 0.4146 | 0.1692 | 0.8265 | 0.0489 | 0.4181 | 0.1739 | 0.8392 | 0.0441 |
| 0.4512 | 0.1737 | 0.8229 | 0.0525 | 0.4606 | 0.1740 | 0.8217 | 0.0539 |
| 0.5164 | 0.1682 | 0.7637 | 0.0800 | 0.5771 | 0.1478 | 0.7166 | 0.0978 |
| average absolute deviation | | | | 0.0108 | 0.0044 | 0.0100 | 0.0037 |

flow rate of 55 mL·min⁻¹. Each analysis took ~ 15 min. Single-phase binary mixtures with known compositions were used to calibrate the instrument in the composition range of interest. The measurements in the composition analysis have <1% deviation.

Results and Discussion

The experimental results of liquid–liquid equilibrium of the binary system water + 2-methyl-2-butanol at 293.15 K, 303.15 K, and 313.15 K are listed in Table 1. The data are expressed in units of mass fraction, and the superscripts u and l stand for upper and lower phases, respectively. The experimental compositions of tie lines for the ternary system water + 2-methyl-2-butanol + diethylene glycol monobutyl ether at 293.15 K, 303.15 K, and 313.15 K are given in Tables 2–4.

The UNIQUAC model of Abrams and Prausnitz⁵ was used to correlate the experimental data. The excess Gibbs free energy G^E of the UNIQUAC model is divided into a combinatorial contribution term, G_c^E , and residual contribution term, G_r^E . In this work, r_i and q_i were adopted from the UNIQUAC group contribution of Hansen et al.,⁶ listed in Table 5.

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Table 3. Experimental and Calculated Mass Fractions of Equilibrium Liquid Phases for the Ternary System Water (1) + 2-Methyl-2-butanol (2) + Diethylene Glycol Monobutyl Ether (3) at 303.15 K

| exptl results | | | | calcd results | | | |
|----------------------------|---------|---------|---------|---------------|---------|---------|---------|
| w_1^u | w_3^u | w_1^l | w_3^l | w_1^u | w_3^u | w_1^l | w_3^l |
| 0.2389 | 0.0271 | 0.8948 | 0.0026 | 0.2375 | 0.0280 | 0.8930 | 0.0032 |
| 0.2454 | 0.0453 | 0.8924 | 0.0044 | 0.2424 | 0.0462 | 0.8930 | 0.0054 |
| 0.2536 | 0.0668 | 0.8904 | 0.0076 | 0.2487 | 0.0669 | 0.8929 | 0.0080 |
| 0.2600 | 0.0881 | 0.8896 | 0.0108 | 0.2561 | 0.0887 | 0.8925 | 0.0109 |
| 0.2772 | 0.1274 | 0.8866 | 0.0174 | 0.2733 | 0.1293 | 0.8907 | 0.0170 |
| 0.2944 | 0.1570 | 0.8840 | 0.0234 | 0.2895 | 0.1583 | 0.8879 | 0.0223 |
| 0.3273 | 0.1904 | 0.8786 | 0.0330 | 0.3184 | 0.1936 | 0.8810 | 0.0312 |
| 0.3640 | 0.2151 | 0.8690 | 0.0426 | 0.3570 | 0.2189 | 0.8671 | 0.0430 |
| 0.4060 | 0.2274 | 0.8473 | 0.0569 | 0.3999 | 0.2286 | 0.8424 | 0.0588 |
| 0.4871 | 0.2194 | 0.8022 | 0.0835 | 0.4839 | 0.2185 | 0.7111 | 0.1248 |
| average absolute deviation | | | | 0.0047 | 0.0015 | 0.0116 | 0.0049 |

Table 4. Experimental and Calculated Mass Fractions of Equilibrium Liquid Phases for the Ternary System Water (1) + 2-Methyl-2-butanol (2) + Diethylene Glycol Monobutyl Ether (3) at 313.15 K

| exptl results | | | | calcd results | | | |
|----------------------------|---------|---------|---------|---------------|---------|---------|---------|
| w_1^u | w_3^u | w_1^l | w_3^l | w_1^u | w_3^u | w_1^l | w_3^l |
| 0.2269 | 0.0292 | 0.9129 | 0.0020 | 0.2222 | 0.0291 | 0.9118 | 0.0029 |
| 0.2351 | 0.0647 | 0.9093 | 0.0056 | 0.2294 | 0.0626 | 0.9107 | 0.0065 |
| 0.2424 | 0.1012 | 0.9087 | 0.0098 | 0.2388 | 0.1005 | 0.9092 | 0.0107 |
| 0.2588 | 0.1510 | 0.9069 | 0.0161 | 0.2539 | 0.1502 | 0.9067 | 0.0169 |
| 0.2799 | 0.2029 | 0.9020 | 0.0252 | 0.2749 | 0.2012 | 0.9028 | 0.0244 |
| 0.3008 | 0.2279 | 0.8999 | 0.0306 | 0.2909 | 0.2295 | 0.8996 | 0.0296 |
| 0.3171 | 0.2479 | 0.8938 | 0.0362 | 0.3054 | 0.2490 | 0.8963 | 0.0341 |
| 0.3413 | 0.2630 | 0.8849 | 0.0442 | 0.3253 | 0.2682 | 0.8915 | 0.0399 |
| 0.3910 | 0.2798 | 0.8669 | 0.0603 | 0.3709 | 0.2885 | 0.8774 | 0.0530 |
| 0.4558 | 0.2844 | 0.8336 | 0.0847 | 0.4394 | 0.2825 | 0.7666 | 0.1184 |
| average absolute deviation | | | | 0.0098 | 0.0024 | 0.0091 | 0.0053 |

Table 5. Relative van der Waals Volume r and van der Waals Surface Area q^b

| compound | r | q |
|-----------------------------------|--------|--------|
| water | 0.9200 | 1.4000 |
| 2-methyl-2-butanol | 4.5972 | 4.2840 |
| diethylene glycol monobutyl ether | 6.1695 | 5.0760 |

Table 6. UNIQUAC Group Interaction Parameters for the System Water (1) + 2-Methyl-2-butanol (2) + Diethylene Glycol Monobutyl Ether (3)

| ij | 293.15 K | | 303.15 K | | 313.15 K | |
|----|------------|------------|------------|------------|------------|------------|
| | a_{ij}/K | a_{ij}/K | a_{ij}/K | a_{ij}/K | a_{ij}/K | a_{ij}/K |
| 12 | -81.915 | 639.392 | -79.623 | 656.361 | -76.140 | 670.294 |
| 13 | -164.402 | 642.576 | -173.803 | 675.324 | -169.754 | 746.774 |
| 23 | -177.175 | 216.997 | -89.803 | 78.601 | -87.024 | 103.224 |

The relationship between the group interaction parameter, a_{ij} ,⁷ and the UNIQUAC interaction parameter, u_{ij} , between molecules i and j , is defined by

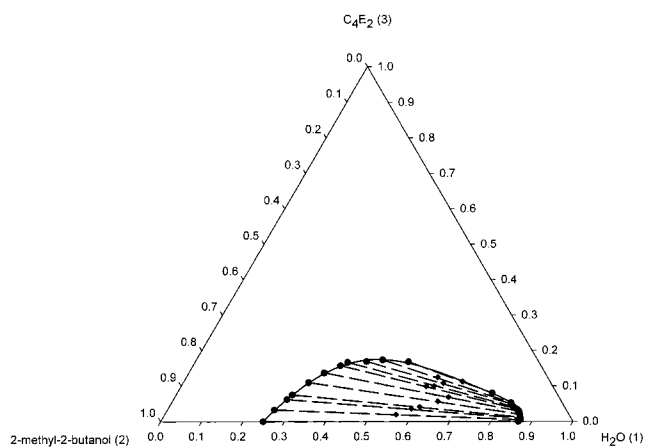
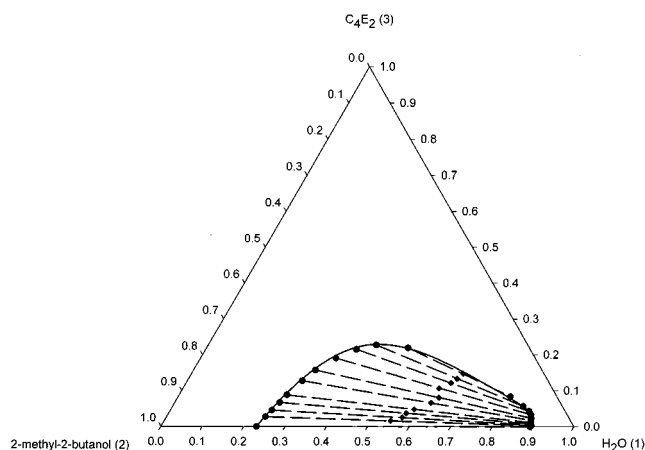
$$(u_{ij} - u_{ji}) = a_{ij}R \quad (1)$$

where R is the gas constant.

The group interaction parameters a_{12} and a_{21} of the binary system water (1) + 2-methyl-2-butanol (2) can be numerically solved for each temperature by using experimental binary compositions as input data according to the isoactivity criterion

$$x_i^l \gamma_i^l = x_i^u \gamma_i^u, \quad i = 1 \text{ and } 2 \quad (2)$$

where x_i is the mole fraction of component i , γ_i is the activity coefficient of component i , and superscripts l and u stand for the lower and upper liquid phases, respectively.

**Figure 1.** Ternary liquid–liquid equilibria (mass fraction) for the system water (1) + 2-methyl-2-butanol (2) + diethylene glycol monobutyl ether (3) at 293.15 K: experimental tie lines (●, dashed line); calculated binodal curve (solid curve); experimental total compositions (◆).**Figure 2.** Ternary liquid–liquid equilibria (mass fraction) for the system water (1) + 2-methyl-2-butanol (2) + diethylene glycol monobutyl ether (3) at 303.15 K: experimental tie lines (●, dashed line); calculated binodal curve (solid curve); experimental total compositions (◆).

For a ternary system, there are six group interaction parameters, a_{ij} . In this work, two group interaction parameters, a_{12} and a_{21} , can be directly determined from the experimental data of the binary system water (1) + 2-methyl-2-butanol (2). Therefore, there are four group interaction parameters left to be determined by a numerical method.

First, we defined an objective function⁸

$$F_a = \sum_{j=1}^m \sum_{i=1}^3 (x_{ij}^l \gamma_{ij}^l - x_{ij}^u \gamma_{ij}^u)^2 \quad (3)$$

where x_{ij}^l and x_{ij}^u stand for the experimental mole fraction of component i of the lower and upper phases, respectively, along a tie line j , γ_{ij}^l and γ_{ij}^u are the corresponding activity coefficient calculated from the UNIQUAC model, and m is the total number of tie lines. Then the other four group interaction parameters of the UNIQUAC model were determined numerically by using the subroutine DUMPOL of the IMSL library to minimize the objective function F_a of eq 3.

The regression results of the UNIQUAC group interaction parameters are shown in Table 6. Note that these parameters are temperature-dependent. The liquid–liquid

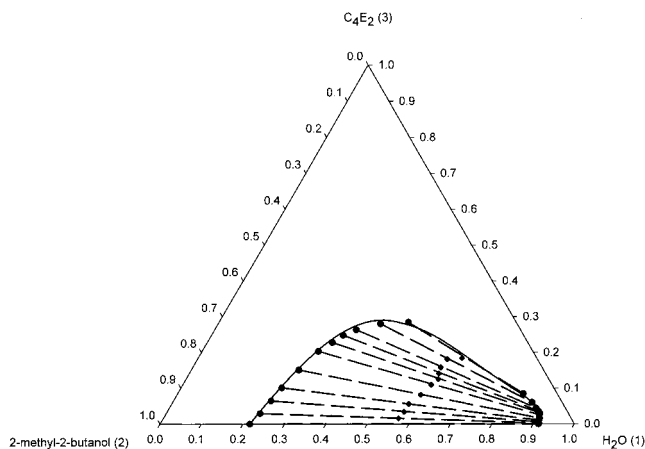


Figure 3. Ternary liquid-liquid equilibria (mass fraction) for the system water (1) + 2-methyl-2-butanol (2) + diethylene glycol monobutyl ether (3) at 313.15 K: experimental tie lines (●, dashed line); calculated binodal curve (solid curve); experimental total compositions (◆).

equilibrium flash calculation⁹ was applied to evaluate the compositions of the tie line by using the experimental total compositions as input data. The calculated results for each tie line are given in Tables 2–4 to make a comparison with experimental data. The average absolute deviation between experimental data and calculated results are also listed at the bottoms of Tables 2–4. Figures 1–3 show the corresponding triangular phase diagrams of the system water + 2-methyl-2-butanol + diethylene glycol monobutyl ether at 293.15 K, 303.15 K, and 313.15 K. Note that in Figures 1–3, diethylene glycol monobutyl ether is abbreviated as C₄E₂. Total compositions of samples prepared for tie-line measurements are given in Figures 1–3 by solid diamonds. The fit of a linear expression to each tie line and its corresponding total composition data point is always better

than 0.999. The calculated binodal curves are also presented by solid curves in Figures 1–3. As one can see, the phase behavior of the system water + 2-methyl-2-butanol + diethylene glycol monobutyl ether is successfully described by the UNIQUAC model.

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