# Liquid−Liquid Equilibria for the Ternary Systems Water + 3-Methyl-2-cyclopentenone with Ethyl Acetate or Methyl *tert*-Butyl Ether at 293.2 K

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The liquid−liquid equilibria for water + 3-methyl-2-cyclopentenone + ethyl acetate and water + 3-methyl-2-cyclopentenone + methyl *tert*-butyl ether system were determined at 293.2 K. The NRTL and UNIQUAC models were applied to both ternary systems. The interaction parameters obtained from both models successfully correlated the equilibrium compositions.

## Introduction

The cyclopentenone structural units are important building blocks for versatile ligands of organometallic complexes. Especially a ligand of *ansa*-zirconocene compound[1] is active toward copolymerization of ethylene and norbornene as a metallocene catalyst. 3-Methyl-2-cyclopentenone is a key starting material for metallocene catalysts for olefin polymerization. It can be found in a variety of therapeutically important compounds such as trichothecenes,[2] precapnelladiene,[3] cyclopentanoid antibiotics,[4] and cyclopentenone prostaglandin,[5,6] which have anti-inflammatory and antiviral activities. It is also useful synthetic intermediate for preparation of flavor and fragrance compounds.[7] When 3-methyl-2-cyclopentenone is synthesized, a liquid−liquid extraction step is essential because of the low chemical stability of 3-methyl-2-cyclopentenone. In this work, the ternary phase equilibrium data for water + 3-methyl-2-cyclopentenone + ethyl acetate and water + 3-methyl-2-cyclopentenone + methyl *tert*-butyl ether have been studied. Tie lines were measured, and the results of the measurement were correlated by means of the UNIQUAC model[8] and the NRTL model.[9]

## Experimental Section

Ethyl acetate (99.8 %), methyl *tert*-butyl ether (MTBE) (99.8 %), toluene (99.8 %), and 3-methyl-2-cyclopentenone (97 %) were obtained from Aldrich Company. The purity was confirmed by gas chromatography, and the materials were used without further purification. Water was purified by the Direct-Q Tap-Fed water purification system (Millipore) with a resistivity of 18.2 MΩ·cm. Karl Fischer reagents, hydranal-composite-5 and hydranal-methanol dry, were purchased from Riedel-de Haën Fine Chemicals. The solubility data for ternary systems were determined by the cloud-point method.[10] A binary mixture of known composition of 3-methyl-2-cyclopentenone and water was prepared by mass with a precision of 0.0001 g on a Mettler AG204 balance and was stirred in a cell (50 mL) equipped with a jacket for circulating water from a constant temperature water bath (293.2 ± 0.1) K. The other component, ethyl acetate or MTBE, was then added by mass until a transition point was reached. The ternary mixtures were prepared by mass with a precision of 0.0001 g. The estimated uncertainty in mole fraction was less than $10^{-4}$. The experimental apparatus used for extraction consists of a 50 mL glass cell equipped with a jacket circulated by a Julabo F33 water bath. The jacket temperature was controlled within ± 0.1 K. The mixtures were vigorously stirred with a magnetic stir bar for 1 h and then left to settle for 12 h. Samples were taken by syringes through both top and side PTFE/silicone septum caps.

Quantitative analysis of 3-methyl-2-cyclopentenone was performed by a 6890N gas chromatograph (Agilent Technologies) equipped with 7863 series automatic injector, a flame ionization detector, and the HP ChemStation data system. The components were separated using an AT-1000 capillary column (15 m × 0.53 mm i.d. × 1.2 $\mu$m film thickness, Alltech). GC peak areas were obtained using a cool on-column inlet with electronic pressure control since 3-methyl-2-cyclopentenone is a thermally labile compound and breaks down in a standard hot flash injection before reaching the column. The oven temperature was programmed to be maintained at 323.2 K for the first 4 min and then increased to 503.2 K at 10 K/min, and the cool on-column inlet tracked the oven temperature. Helium was used as a carrier gas at a flow rate of 4 $cm^3$/min. Toluene was used as an internal standard for quantitative analysis of 3-methyl-2-cyclopentenone, ethyl acetate, and MTBE. The response factors for these components were measured at the same conditions as that used in the gas chromatograph measurement for each phase equilibrium data. Water concentrations were calculated to make the mole fraction equal to 1 and also measured with a Mettler Toledo DL31 Karl Fisher titrator to validate the chromatographic results.

## Results and Discussion

The liquid−liquid phase diagram for water + 3-methyl-2-cyclopentenone + ethyl acetate and water + 3-methyl-2-cyclopentenone + MTBE systems are presented in Figures 1 and 2, respectively. Both liquid−liquid phase

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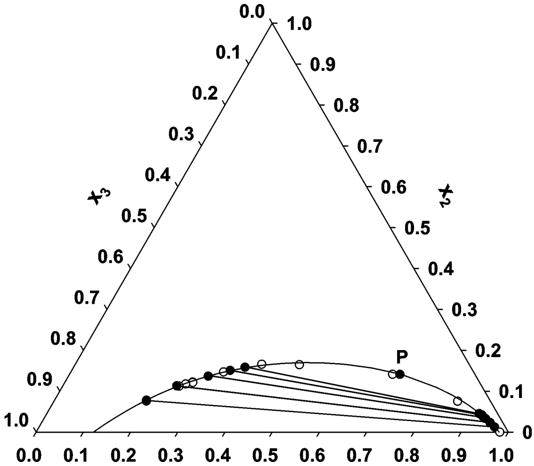

**Figure 1.** LLE of water (1) + 3-methyl-2-cyclopentenone (2) + ethyl acetate (3) at 293.2 K: ●, experimental tie-line data; ○, experimental solubility data; —, NRTL and UNIQUAC; P represents the plait point.

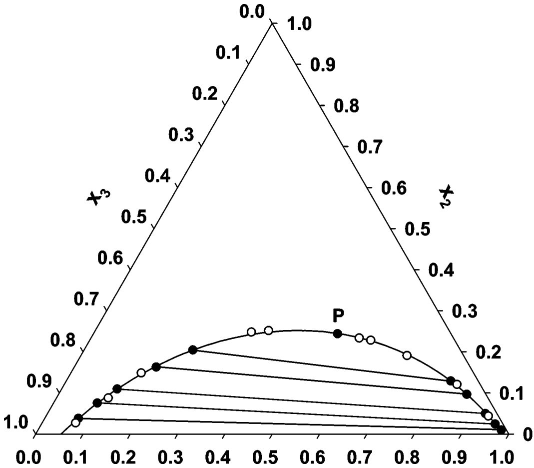

**Figure 2.** LLE of water (1) + 3-methyl-2-cyclopentenone (2) + MTBE (3) at 293.2 K: ●, experimental tie-line data; ○, experimental solubility data; —, NRTL and UNIQUAC; P represents the plait point.

**Table 1. Mole Fractions of the Experimental Solubility Curve**

| water (1) + 3-methyl-2-cyclopentenone (2) + ethyl acetate (3) | | water (1) + 3-methyl-2-cyclopentenone (2) + MTBE (3) | |
|---|---|---|---|
| $x_1$ | $x_2$ | $x_1$ | $x_2$ |
| 0.1948 | 0.0779 | 0.0709 | 0.0273 |
| 0.2467 | 0.1123 | 0.1095 | 0.0880 |
| 0.2579 | 0.1174 | 0.1487 | 0.1489 |
| 0.2704 | 0.1222 | 0.2002 | 0.1862 |
| 0.2711 | 0.1213 | 0.3317 | 0.2484 |
| 0.3236 | 0.1469 | 0.3663 | 0.2519 |
| 0.3949 | 0.1659 | 0.5670 | 0.2337 |
| 0.4753 | 0.1646 | 0.5939 | 0.2284 |
| 0.6843 | 0.1411 | 0.6893 | 0.1911 |
| 0.8551 | 0.0753 | 0.7480 | 0.1655 |
| 0.9232 | 0.0418 | 0.8301 | 0.1209 |
| 0.9819 | 0.0000 | 0.9349 | 0.0438 |

diagrams are type 1,[11] where only one liquid pair has very low partially miscibility and two liquid pairs are miscible, and each triangular phase diagram shows a plait point. The solubility curves for both systems are also presented in Figure 1, Figure 2, and Table 1. The water + 3-methyl-2-cyclopentenone + ethyl acetate system has a smaller immiscibility region comparing with the water + 3-methyl-2-cyclopentenone + MTBE system.

**Table 2. Parameters of the UNIQUAC and NRTL Models for the Water (1) + 3-Methyl-2-cyclopentenone (2) + Ethyl Acetate (3) System at 293.2 K and Their RMSD Values**

| $b_{ij}$/K and $\alpha_{ij}$ | | | RMSD |
|---|---|---|---|
| | UNIQUAC | | |
| $b_{12} = 319.471$ | $b_{13} = -52.318$ | $b_{23} = 162.931$ | 0.0020 |
| $b_{21} = -1276.566$ | $b_{31} = -451.691$ | $b_{32} = -162.415$ | |
| | NRTL | | |
| $b_{12} = 676.972$ | $b_{13} = -1803.981$ | $b_{23} = -874.189$ | 0.0025 |
| $b_{21} = -473.963$ | $b_{31} = 1365.778$ | $b_{32} = 1026.065$ | |
| $\alpha_{12} = 0.3$ | $\alpha_{13} = 0.2$ | $\alpha_{23} = 0.3$ | |

**Table 3. Parameters of the UNIQUAC and NRTL Models for the Water (1) + 3-Methyl-2-cyclopentenone (2) + MTBE (3) System at 293.2 K and Their RMSD Values**

| $b_{ij}$/K and $\alpha_{ij}$ | | | RMSD |
|---|---|---|---|
| | UNIQUAC | | |
| $b_{12} = 2381.083$ | $b_{13} = -28.570$ | $b_{23} = 15.041$ | 0.0043 |
| $b_{21} = -108.753$ | $b_{31} = -658.889$ | $b_{32} = 2249.063$ | |
| | NRTL | | |
| $b_{12} = -708.318$ | $b_{13} = 1054.179$ | $b_{23} = -516.411$ | 0.0041 |
| $b_{21} = -317.787$ | $b_{31} = 440.5$ | $b_{32} = -749.124$ | |
| $\alpha_{12} = 0.3$ | $\alpha_{13} = 0.2$ | $\alpha_{23} = 0.3$ | |

**Table 4. Structure Parameters for the UNIQUAC Equation**

| compound | van der Waals volume, $r$ | van der Waals area, $q$ |
|---|---|---|
| Water | 0.92 | 1.4 |
| 3-methyl-2-cyclopentenone | 3.8642 | 3.244 |
| ethyl acetate | 3.4786 | 3.116 |
| MTBE | 4.0679 | 3.632 |

The NRTL model was fitted to each experimental tie line data as well as the non-randomness parameter $\alpha_{ij}$ for the NRTL model.[12] The NRTL binary parameters of both ternary systems correlated at 293.2 K are listed in Tables 2 and 3 with the root-mean-square deviation (RMSD) values of 0.0025 and 0.0041, respectively. The RMSD value is a measure of the agreement between the experimental data and the calculated values defined as follows:[13]

$$\mathrm{RMSD} = \left(\sum_{k}^{M}\sum_{j}^{2}\sum_{i}^{3}(x_{ijk}^{\mathrm{exp}} - x_{ijk}^{\mathrm{calc}})^2/6M\right)^{1/2} \qquad (1)$$

where $M$ is the number of tie lines, $x^{\mathrm{exp}}$ is the experimental mole fraction, $x^{\mathrm{calc}}$ indicates the calculated mole fraction, and the subscript $i$ indexes the components, $j$ indexes the phases, and $k$ indexes the tie lines.

The UNIQUAC model was also used to correlate the experimental results. The interaction parameters, $b_{ij}$ are shown in Table 2 for the water + 3-methyl-2-cyclopentenone + ethyl acetate and in Table 3 for water + 3-methyl-2-cyclopentenone + MTBE with RMSD values of 0.0020 and 0.0043, respectively. The results of both the NRTL and UNIQUAC models are shown in Tables 5 and 6 with the experimental data. The interaction parameters between water (1) and ethyl acetate (3) or MTBE (3) ($b_{13}$ and $b_{31}$) were retrieved from Aspen Plus (Aspen Technology Inc., MA) system databanks; other parameters of the UNIQUAC and NRTL models in Tables 2, 3, and 4 were determined by the data regression system within Aspen Plus using the Britt−Luecke maximum likelihood estimation method.[14] Once all parameters were determined, the liquid−liquid flash calculations were performed using Aspen Plus process simulator. The compositions of both liquid phases along each tie line in the liquid−liquid-phase envelopes were predicted as shown in Figures 1 and 2. The predicted

**Table 5. Experimental and Predicted LLE Data for the Water (1) + 3-Methyl-2-cyclopentone (2) + Ethyl Acetate (3) System**

| ethyl acetate-rich phase (mole fraction) | | | | | | water-rich phase (mole fraction) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $x_1^{\mathrm{exp}}$ | $x_1^{\mathrm{UNIQ}}$ | $x_1^{\mathrm{NRTL}}$ | $x_2^{\mathrm{exp}}$ | $x_2^{\mathrm{UNIQ}}$ | $x_2^{\mathrm{NRTL}}$ | $x_1^{\mathrm{exp}}$ | $x_1^{\mathrm{UNIQ}}$ | $x_1^{\mathrm{NRTL}}$ | $x_2^{\mathrm{exp}}$ | $x_2^{\mathrm{UNIQ}}$ | $x_2^{\mathrm{NRTL}}$ |
| 0.1955 | 0.1918 | 0.1887 | 0.0758 | 0.0757 | 0.0766 | 0.9645 | 0.9640 | 0.9636 | 0.0126 | 0.0127 | 0.0126 |
| 0.2413 | 0.2465 | 0.2483 | 0.1129 | 0.1134 | 0.1125 | 0.9498 | 0.9499 | 0.9497 | 0.0234 | 0.0230 | 0.0229 |
| 0.2963 | 0.2981 | 0.3008 | 0.1366 | 0.1375 | 0.1359 | 0.9354 | 0.9357 | 0.9357 | 0.0330 | 0.0328 | 0.0329 |
| 0.3355 | 0.3305 | 0.3322 | 0.1509 | 0.1485 | 0.1469 | 0.9268 | 0.9263 | 0.9265 | 0.0384 | 0.0391 | 0.0394 |
| 0.3634 | 0.3651 | 0.3649 | 0.1584 | 0.1572 | 0.1563 | 0.9157 | 0.9159 | 0.9160 | 0.0451 | 0.0458 | 0.0464 |

**Table 6. Experimental and Predicted LLE Data for the Water (1) + 3-Methyl-2-cyclopentone (2) + MTBE (3) System**

| MTBE-rich phase (mole fraction) | | | | | | water-rich phase (mole fraction) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $x_1^{\mathrm{exp}}$ | $x_1^{\mathrm{UNIQ}}$ | $x_1^{\mathrm{NRTL}}$ | $x_2^{\mathrm{exp}}$ | $x_2^{\mathrm{UNIQ}}$ | $x_2^{\mathrm{NRTL}}$ | $x_1^{\mathrm{exp}}$ | $x_1^{\mathrm{UNIQ}}$ | $x_1^{\mathrm{NRTL}}$ | $x_2^{\mathrm{exp}}$ | $x_2^{\mathrm{UNIQ}}$ | $x_2^{\mathrm{NRTL}}$ |
| 0.2298 | 0.2221 | 0.2283 | 0.2049 | 0.1923 | 0.1897 | 0.8128 | 0.8103 | 0.8137 | 0.1291 | 0.1290 | 0.1255 |
| 0.1734 | 0.1766 | 0.1791 | 0.1630 | 0.1630 | 0.1630 | 0.8628 | 0.8642 | 0.8654 | 0.0969 | 0.0954 | 0.0942 |
| 0.1175 | 0.1236 | 0.1215 | 0.1097 | 0.1149 | 0.1151 | 0.9255 | 0.9267 | 0.9264 | 0.0498 | 0.0509 | 0.0513 |
| 0.0926 | 0.0919 | 0.0894 | 0.0755 | 0.0754 | 0.0751 | 0.9589 | 0.9593 | 0.9590 | 0.0245 | 0.0255 | 0.0258 |
| 0.0712 | 0.0683 | 0.0675 | 0.0382 | 0.0375 | 0.0380 | 0.9794 | 0.9784 | 0.9786 | 0.0096 | 0.0098 | 0.0097 |

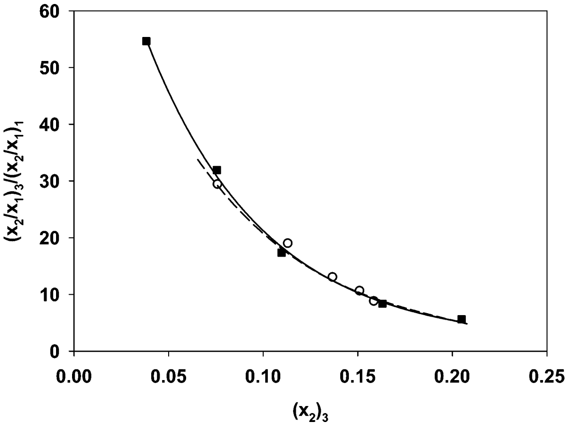

**Figure 3.** Relative separation for the systems at 293.2 K: ●, water (1) + 3-methyl-2-cyclopentenone (2) + ethyl acetate (3); ○, water (1) + 3-methyl-2-cyclopentenone (2) + MTBE (3).

binodal curves using the binary interaction parameters of UNIQUAC or NRTL were consistent with the experimental results.

The relative separation factor (or selectivity, $S$) between two components, water and solvent, can be described by the ratio of the two partition ratios as follows:

$$S = (x_2/x_1)_3/(x_2/x_1)_1 \tag{2}$$

where $x$ is the mole fraction. In Figure 3, the water (1) + 3-methyl-2-cyclopentenone (2) + ethyl acetate (3) and water (1) + 3-methyl-2-cyclopentenone (2) + MTBE (3) systems show a similar relative separation because MTBE system has larger two-phase region than ethyl acetate system while the slopes of tie lines in ethyl acetate system are steeper than those in MTBE system.

## Conclusion

The extraction data for the water + 3-methyl-2-cyclopentenone + ethyl acetate and water + 3-methyl-2-cyclopentenone + MTBE systems were obtained at 293.2 K with their solubility curves. The separation of 3-methyl-2-cyclopentenone from water can be achieved by using ethyl acetate or MTBE as a solvent. The tie-line correlation was fitted using the UNIQUAC and NRTL models, and the parameters for both models were calculated.

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