JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

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pubs.acs.org/jced

# Liquid−Liquid Equilibria of Water + 3-Hydroxy-2-butanone + Butyl Ethanoate at Several Temperatures

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**ABSTRACT:** Liquid−liquid equilibrium (LLE) data of the solubility curves and tie-line compositions have been determined for mixtures of (water + 3-hydroxy-2-butanone + butyl ethanoate) at (298.15, 308.15, and 318.15) K and 101.3 kPa. Distribution coefficients and separation factors have been evaluated for the immiscibility region. The reliability of the experimental tie-lines has been confirmed by using the Othmer−Tobias correlation. The LLE data of the ternary systems have been predicted by UNIFAC methods.

## INTRODUCTION

3-Hydroxy-2-butanone (CAS number: 513-86-0), also known as acetoin or acetylmethylcarbinol, is a valuable flavor existing naturally in corn, kidney beans, peas, and broccoli[1−3] and also the common intermediate for 2,3-butanedione and 2,3-butanediol synthesis.[4] Meanwhile, it has become a platform chemical in recent years and been included in the top value chemicals from biomass by the Department of Energy, USA, in 2004.[5]

There are several chemical synthetic methods for 3-hydroxy-2-butanone preparation,[6,7] among which the microbial way has attracted much attention nowadays because it is more environmentally friendly and more cost-effective than petroleum-based chemical processes. Its microbial preparation has been observed in several yeasts and bacteria from various genera such as *Klebsiella*, *Bacillus*, and *Enterobacter aerogenes*.[8−13] The separation and purification of 3-hydroxy-2-butanone from fermentation broth is essential to realize the industrial production for 3-hydroxy-2-butanone.

Since the fermented liquors contain only a few percent of 3-hydroxy-2-butanone along with complicated impurities which cause difficulty in separation and since 3-hydroxy-2-butanone has a higher boiling point than that of water and can form an azeotrope (∼0.03 by weight of 3-hydroxy-2-butanone) with water and cannot be distilled out directly,[14] extraction from the fermentation liquors by a suitable solvent seems to be a feasible method. No organic solvent has been investigated and reported for 3-hydroxy-2-butanone extraction in the literature until now. Butyl ethanoate used in this study may be a suitable solvent for extraction of 3-hydroxy-2-butanone from water, being capable of forming azeotropic mixtures with water to take it from 3-hydroxy-2-butanone.

The aim of this work is to present the phase behavior of LLE for the (water + 3-hydroxy-2-butanone + butyl ethanoate) ternary system at (298.15, 308.15, and 318.15) K and 101.3 kPa. The tie-lines have also been predicted using the UNIFAC method (a group contribution method) developed by Fredenslund et al.[15] and compared with the experimental data.

## EXPERIMENTAL SECTION

**Chemicals.** All the chemicals used in this study were purchased from the commercial sources. Butyl ethanoate was provided by Shanghai Lingfeng Chemical Reagent Co., Ltd. and had a minimum mass fraction purity of 0.995. It was used directly without further treatment in this study. Water was distilled twice before utilization. 3-Hydroxy-2-butanone was supplied by Sigma-Aldrich with a minimum mass fraction purity of 0.98. It exists as its crystalline dimer. Liquor 3-hydroxy-2-butanone and its crystalline dimer transform each other through changing the temperature. The transformation between them has been studied in this research. We found that the crystalline dimer can be decomposed into liquor 3-hydroxy-2-butanone completely when being heated above 333.15 K for 8 h, which is in accordance with the literature.[16] Meanwhile, the liquor 3-hydroxy-2-butanone has not found any crystallization when being cooled at 293.15 K within 72 h. Therefore, all the experiments related to 3-hydroxy-2-butanone in this study have been carried out within 24 h after the liquor 3-hydroxy-2-butanone was obtained to make sure 3-hydroxy-2-butanone has not become its dimer during the experiments.

The purity of these materials was checked and assured by gas chromatography. The normal boiling point and refractive index values were measured in this study and reported in Table 1 in comparison with the literature data to demonstrate the purity of the compounds. The boiling points were determined by an Ebuillometer (DZBW model, made in Nanjing, China), with an accuracy of ± 0.01 K.

**Equilibrium Measurements.** Three different temperatures [(298.15, 308.15, and 318.15) K] at 101.3 kPa were selected to study the ternary equilibrium system to observe the evaluation of the binodal curves and tie-lines.

The binodal (solubility) curves were determined by the cloud point method in an equilibrium glass cell with a water jacket to maintain isothermal conditions. The temperature in the cell was kept constant by circulating water from a water bath (SUPER-CONSTANTTEP BATH, Shanghai precision science instrument Co., Ltd.), which is equipped with a temperature controller capable of maintaining the temperature within ± 0.1 K. The

**Special Issue:** John M. Prausnitz Festschrift

**Received:** August 20, 2010
**Accepted:** October 28, 2010
**Published:** November 17, 2010

dx.doi.org/10.1021/je100861u | *J. Chem. Eng. Data* 2011, 56, 910–914

**Table 1. Refractive Indexes ($n_D$) at $T$ = 293.15 K and Boiling Points ($T_b$) at 101.3 kPa, of the Compounds**

| component | $n_D$ |  | $T_b$/K |  |
|---|---|---|---|---|
|  | experimental | literature[a] | experimental | literature[a] |
| 3-hydroxy-2-butanone | 1.4198 | 1.4171 | 421.53 | 421.15 |
| butyl ethanoate | 1.3941 | 1.3942 | 399.11 | 399.15 |
| water | 1.3325 | 1.3325 | 373.30 | 373.26 |

[a] Taken from ref 17.

**Table 2. Experimental Binodal Curve Data (Mass Fraction $W_i$) of {Water (1) + 3-Hydroxy-2-butanone (2) + Butyl Ethanoate (3)} at Different Temperatures**

| $T$/K | $W_1$ | $W_2$ | $W_3$ | $W_1$ | $W_2$ | $W_3$ | $W_1$ | $W_2$ | $W_3$ |
|---|---|---|---|---|---|---|---|---|---|
| 298.15 | 0.0158 | 0.0000 | 0.9842 | 0.0827 | 0.5138 | 0.4036 | 0.4675 | 0.4957 | 0.0369 |
|  | 0.0150 | 0.2780 | 0.7070 | 0.0983 | 0.5274 | 0.3743 | 0.4875 | 0.4833 | 0.0292 |
|  | 0.0180 | 0.2773 | 0.7047 | 0.1293 | 0.5544 | 0.3164 | 0.5585 | 0.4175 | 0.0240 |
|  | 0.0160 | 0.3594 | 0.6246 | 0.1511 | 0.5699 | 0.2791 | 0.6118 | 0.3687 | 0.0196 |
|  | 0.0316 | 0.4164 | 0.5521 | 0.1710 | 0.5839 | 0.2451 | 0.6864 | 0.2971 | 0.0166 |
|  | 0.0429 | 0.4702 | 0.4869 | 0.1806 | 0.5903 | 0.2291 | 0.7373 | 0.2449 | 0.0178 |
|  | 0.0669 | 0.4936 | 0.4396 | 0.4334 | 0.5269 | 0.0397 | 0.9853 | 0.0000 | 0.0147 |
| 308.15 | 0.9868 | 0.0000 | 0.0132 | 0.3751 | 0.5253 | 0.0996 | 0.1302 | 0.4753 | 0.3945 |
|  | 0.7456 | 0.2364 | 0.0180 | 0.3615 | 0.5274 | 0.1111 | 0.1114 | 0.4606 | 0.4281 |
|  | 0.6413 | 0.3333 | 0.0254 | 0.3423 | 0.5307 | 0.1270 | 0.0851 | 0.4306 | 0.4844 |
|  | 0.5810 | 0.3879 | 0.0311 | 0.3178 | 0.5341 | 0.1481 | 0.0692 | 0.3948 | 0.5360 |
|  | 0.5183 | 0.4389 | 0.0429 | 0.2650 | 0.5350 | 0.2000 | 0.0493 | 0.3551 | 0.5955 |
|  | 0.4679 | 0.4754 | 0.0567 | 0.2450 | 0.5550 | 0.2500 | 0.0289 | 0.2728 | 0.6983 |
|  | 0.4293 | 0.5061 | 0.0646 | 0.1850 | 0.5150 | 0.3100 | 0.0194 | 0.0912 | 0.8894 |
|  | 0.4048 | 0.5141 | 0.0811 | 0.1479 | 0.4937 | 0.3584 | 0.0160 | 0.0000 | 0.9841 |
| 318.15 | 0.9846 | 0.0000 | 0.0154 | 0.5358 | 0.4158 | 0.0484 | 0.1378 | 0.4337 | 0.4286 |
|  | 0.9504 | 0.0317 | 0.0179 | 0.5086 | 0.4366 | 0.0549 | 0.1161 | 0.3932 | 0.4907 |
|  | 0.9128 | 0.0682 | 0.0190 | 0.4640 | 0.4676 | 0.0683 | 0.1085 | 0.3694 | 0.5221 |
|  | 0.8793 | 0.1020 | 0.0187 | 0.4491 | 0.4774 | 0.0735 | 0.0991 | 0.3512 | 0.5497 |
|  | 0.8246 | 0.1499 | 0.0256 | 0.4169 | 0.4921 | 0.0910 | 0.0912 | 0.3248 | 0.5841 |
|  | 0.7946 | 0.1808 | 0.0247 | 0.3960 | 0.4989 | 0.1051 | 0.0741 | 0.2808 | 0.6452 |
|  | 0.7309 | 0.2403 | 0.0289 | 0.3675 | 0.5058 | 0.1267 | 0.0637 | 0.2577 | 0.6786 |
|  | 0.7065 | 0.2632 | 0.0304 | 0.3391 | 0.5148 | 0.1462 | 0.0461 | 0.2202 | 0.7337 |
|  | 0.6591 | 0.3075 | 0.0335 | 0.3094 | 0.5091 | 0.1815 | 0.0341 | 0.1605 | 0.8054 |
|  | 0.6203 | 0.3454 | 0.0342 | 0.2150 | 0.4850 | 0.3000 | 0.0205 | 0.0652 | 0.9143 |
|  | 0.5621 | 0.3935 | 0.0444 | 0.1650 | 0.4550 | 0.3800 | 0.0275 | 0.0000 | 0.9726 |

major central part of the solubility curves was obtained by titrating heterogeneous mixtures of water + butyl ethanoate with 3-hydroxy-2-butanone until the turbidity had disappeared. For the water-side and solvent side, regions in which the curve and the sides of the triangle are close and exhibit similar slopes, binary mixtures of either (water + 3-hydroxy-2-butanone) or (butyl ethanoate + 3-hydroxy-2-butanone) were titrated against the third component until the transition from homogeneity to heterogeneity was observed.

All mixtures were prepared by weighing with a Sartorius scale accurate to within ± $10^{-4}$ g. Mutual solubility values of the (water + butyl ethanoate) binary were measured using the method based on the detection of the cloud point.[18−20] The transition point between the homogeneous and heterogeneous zones was determined visually. The reliability of the method depends on the precision of the microburet with an accuracy of ± 0.01 $cm^3$ and is limited by the visual inspection of the transition across the apparatus. The accuracy of the visual inspection of the transition is achieved by waiting approximately 5 min in the transition point and observing the heterogeneity. All visual experiments were repeated at least three times to acquire high accuracy.

End-point determinations of the tie-lines were based upon the independent analysis of the conjugate phases that were regarded as being in equilibrium.[17−19] For this purpose, mixtures of known masses of water, 3-hydroxy-2-butanone, and butyl ethanoate lying within the heterogeneous zone were introduced into the equilibrium cell and were agitated for 3 h with a magnetic stirrer vigorously and then left for 4 h to settle down into raffinate (aqueous) and extract (solvent) layers. The compositions of liquid samples withdrawn from conjugate phases were analyzed by a gas chromatograph (GC112A) with a thermal conductivity detector (TCD), after calibration with gravimetrically prepared standard solutions. A GDX-102 packed column (3 m × Φ 3 mm × 0.5 mm) was used to separate components. They were all produced by Shanghai Hengping Scientific Instrument Co., Ltd. The oven, injector, and detector temperatures were (433.15, 453.15, and 453.15) K, respectively. High-purity hydrogen (0.999999 purity) was used as the carrier gas at a constant flow rate of 30 mL·$min^{-1}$. The detector was connected to a FJ-2003B integrator. Each sample was analyzed at least three times to ensure accuracy. The uncertainty in mass fractions was within ± 0.001.

## RESULTS AND DISCUSSION

The LLE measurements were made for the ternary system of (water + 3-hydroxy-2-butanone + butyl ethanoate) at (298.15, 308.15, and 318.15) K and 101.3 kPa. The experimental binodal

**Table 3. Experimental Tie-Line Data in Mass Fractions for Water (1) + 3-Hydroxy-2-butanone (2) + Butyl Ethanoate (3) Ternary System**

|  | organic phase |  |  | aqueous phase |  |  |
|---|---|---|---|---|---|---|
| $T$/K | $W_{13}$ | $W_{23}$ | $W_{33}$ | $W_{11}$ | $W_{21}$ | $W_{31}$ |
| 298.15 | 0.0252 | 0.3035 | 0.6713 | 0.4723 | 0.4969 | 0.0308 |
|  | 0.0224 | 0.2677 | 0.7099 | 0.5164 | 0.4502 | 0.0335 |
|  | 0.0216 | 0.1730 | 0.8054 | 0.6023 | 0.3787 | 0.0190 |
|  | 0.0169 | 0.0694 | 0.9137 | 0.7362 | 0.2431 | 0.0207 |
|  | 0.0225 | 0.1140 | 0.8635 | 0.6721 | 0.3080 | 0.0199 |
|  | 0.0238 | 0.2224 | 0.7538 | 0.5611 | 0.4184 | 0.0205 |
| 308.15 | 0.0244 | 0.1789 | 0.7966 | 0.5845 | 0.3781 | 0.0374 |
|  | 0.0212 | 0.1021 | 0.8767 | 0.6884 | 0.2917 | 0.0199 |
|  | 0.0222 | 0.1190 | 0.8588 | 0.6413 | 0.3314 | 0.0274 |
|  | 0.0128 | 0.0785 | 0.9088 | 0.7234 | 0.2583 | 0.0183 |
|  | 0.0132 | 0.0418 | 0.9450 | 0.7952 | 0.1897 | 0.0152 |
|  | 0.0190 | 0.0526 | 0.9284 | 0.7688 | 0.2076 | 0.0236 |
| 318.15 | 0.0230 | 0.0873 | 0.8897 | 0.6750 | 0.2914 | 0.0335 |
|  | 0.0403 | 0.2163 | 0.7435 | 0.4777 | 0.4607 | 0.0616 |
|  | 0.0220 | 0.0706 | 0.9073 | 0.7028 | 0.2636 | 0.0336 |
|  | 0.0213 | 0.0516 | 0.9271 | 0.7259 | 0.2400 | 0.0341 |
|  | 0.0243 | 0.1057 | 0.8700 | 0.6359 | 0.3304 | 0.0337 |
|  | 0.0229 | 0.0387 | 0.9384 | 0.7454 | 0.2255 | 0.0291 |
|  | 0.0359 | 0.1716 | 0.7924 | 0.5428 | 0.4063 | 0.0509 |

curves for this ternary system at each temperature are listed in Table 2, for which $W_i$ refers to the mass fraction of the *i*th component. The experimental tie-line compositions of the equilibrium phases are shown in Table 3, for which $W_{i1}$ and $W_{i3}$ refer to the mass fractions of the *i*th component in the aqueous and solvent phases, respectively.

The experimental and predicted equilibrium data through the UNIFAC model of the ternary system at $T = 298.15$ K are plotted in Figure 1. As can be seen from Figure 1, the system exhibited type 1 phase behavior,[21,22] having only one liquid pair that was partially miscible (butyl ethanoate + water) and two pairs that were completely miscible (water + 3-hydroxy-2-butanone) and (3-hydroxy-2-butanone + butyl ethanoate). Also, similar results are observed at $T = 308.15$ K and $T = 318.15$ K in Figures 2 and 3.

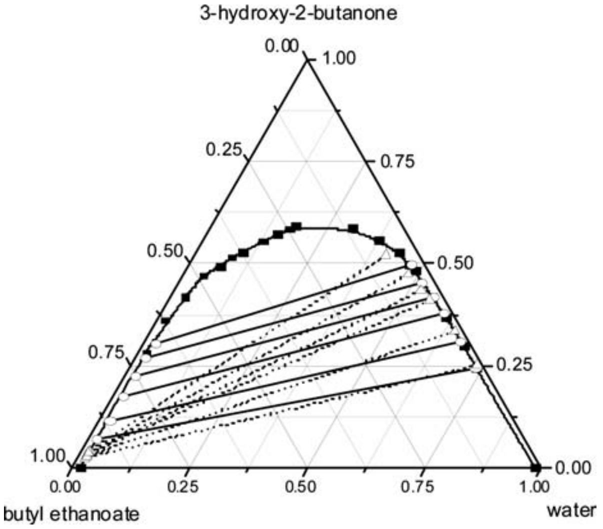

**Figure 1.** Ternary diagram for LLE (mass fraction) of (water + 3-hydroxy-2-butanone + butyl ethanoate) at 298.15 K: ■, experimental solubility; —, experimental solubility curve; ○, experimental tie-line data; Δ, calculated (UNIFAC) tie-line data; · · ·, calculated tie-lines.

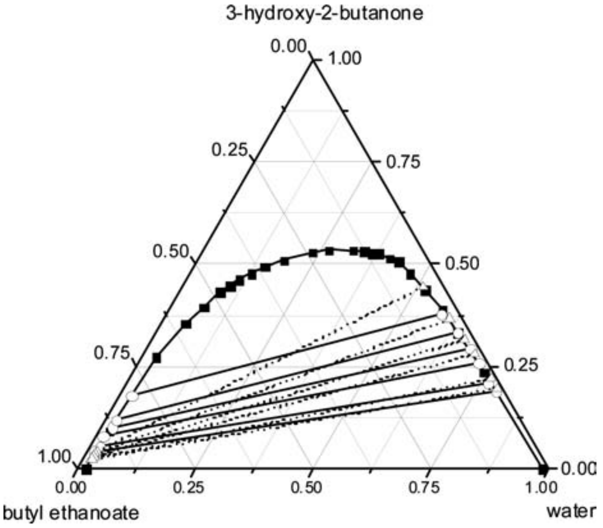

**Figure 2.** Ternary diagram for LLE (mass fraction) of (water + 3-hydroxy-2-butanone + butyl ethanoate) at 308.15 K: ■, experimental solubility; —, experimental solubility curve; ○, experimental tie-line data; Δ, calculated (UNIFAC) tie-line data; · · ·, calculated tie-lines.

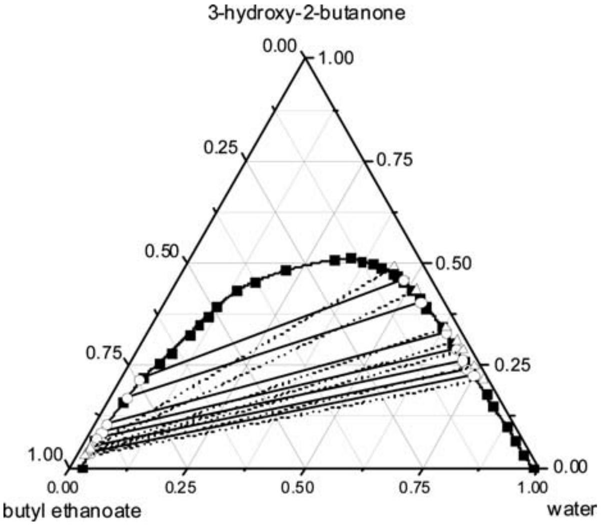

**Figure 3.** Ternary diagram for LLE (mass fraction) of (water + 3-hydroxy-2-butanone + butyl ethanoate) at 318.15 K: ■, experimental solubility; —, experimental solubility curve; ○, experimental tie-line data; Δ, calculated (UNIFAC) tie-line data; · · ·, calculated tie-lines.

The effectiveness of 3-hydroxy-2-butanone extraction by butyl ethanoate is given by its separation factor, which is a measure of the ability of butyl ethanoate to separate the 3-hydroxy-2-butanone from water. To show the selectivity and extraction strength of the solvent to extract 3-hydroxy-2-butanone, the distribution coefficients, $D_i$, for water ($i = 1$) and 3-hydroxy-2-butanone ($i = 2$) and the separation factors, $S$, are calculated according to the following equations

$$D_i = \frac{W_{i3}}{W_{i1}} \tag{1}$$

$$S = \frac{\text{distribution coefficient of 3-hydroxy-2-butanone}}{\text{distribution coefficient of water}} = \frac{D_2}{D_1} \tag{2}$$

where $W_{i3}$ and $W_{i1}$ are the mass concentrations of component *i* in solvent-rich and water-rich phases, and $D_1$ and $D_2$ are the distribution coefficients of water and 3-hydroxy-2-butanone, respectively.

The distribution coefficients and separation factors for each temperature are given in Table 4. Separation factors were found to be much greater than 1, for the systems reported here, which means that the extraction of 3-hydroxy-2-butanone by butyl ethanoate is really possible. The separation factor is not constant over the whole two-phase region. The extracting power of the solvent at each temperature, plots of $D_2$ versus $W_{21}$ and $S$ versus $W_{21}$, is shown in Figures 4 and 5, respectively.

The reliability of experimentally measured tie-line data can be ascertained by applying the Othmer–Tobias correlation[23] at each temperature as below

$$\ln\left(\frac{1 - W_{11}}{W_{11}}\right) = a + b \ln\left(\frac{1 - W_{33}}{W_{33}}\right) \tag{3}$$

where $W_{11}$ is the mass fraction of water in the water-rich phase; $W_{33}$ is the mass fraction of butyl ethanoate in the solvent-rich phase; and $a$ and $b$ are the constants.

**Table 4. Distribution Coefficients ($D_i$) of Water ($i$ = 1) and 3-Hydroxy-2-butanone ($i$ = 2) and Separation Factors ($S$)**

| $T$/K | $D_1$ | $D_2$ | $S$ |
|---|---|---|---|
| 298.15 | 0.0534 | 0.6107 | 11.4424 |
| | 0.0434 | 0.5947 | 13.6899 |
| | 0.0359 | 0.4569 | 12.7292 |
| | 0.0229 | 0.2856 | 12.4487 |
| | 0.0335 | 0.3702 | 11.0578 |
| | 0.0425 | 0.5317 | 12.5237 |
| 308.15 | 0.0418 | 0.4732 | 11.3216 |
| | 0.0309 | 0.3499 | 11.3415 |
| | 0.0346 | 0.3592 | 10.3760 |
| | 0.0314 | 0.3037 | 9.6687 |
| | 0.0256 | 0.2201 | 8.5954 |
| | 0.0248 | 0.2534 | 10.2378 |
| 318.15 | 0.0341 | 0.2997 | 8.7943 |
| | 0.0843 | 0.4694 | 5.5698 |
| | 0.0314 | 0.2679 | 8.5431 |
| | 0.0293 | 0.2150 | 7.3335 |
| | 0.0382 | 0.3198 | 8.3694 |
| | 0.0307 | 0.1715 | 5.5831 |
| | 0.0662 | 0.4224 | 6.3798 |

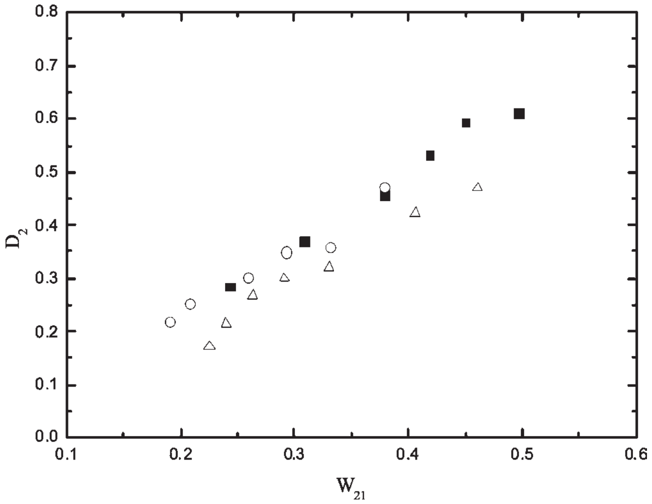

**Figure 4.** Distribution coefficient $D_2$ of 3-hydroxy-2-butanone as a function of the mass fraction $W_{21}$ of 3-hydroxy-2-butanone in the aqueous phase: ■, 298.15 K; ○, 308.15 K; Δ, 318.15 K.

The parameters of this correlation are listed in Table 5, and the correlation is shown in Figure 6 for the temperatures studied. The correlation factor ($R^2$) being approximately unity indicates the degree of consistency of the related data.

The experimental equilibrium data have been compared with predicted values by UNIFAC using the interaction parameters between $CH_3$, $CH_2$, CH, OH, $CH_3CO$, $CH_3COO$, and $H_2O$ functional groups obtained by Magnussen et al.[24] As shown in Figure 1, LLE data predicted by the UNIFAC method cannot be adequately fitted with the experimental LLE data at $T$ = 298.15 K. A similar lack of fits is observed at $T$ = 308.15 K and $T$ = 318.15 K.

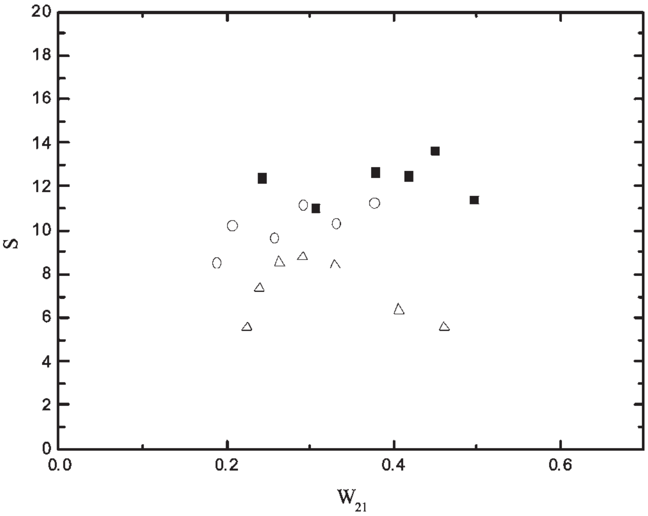

**Figure 5.** Separation factor, $S$, as a function of the mass fraction of 3-hydroxy-2-butanone in the aqueous phase, $W_{21}$: ■, 298.15 K; ○, 308.15 K; Δ, 318.15 K.

**Table 5. Constants of the Othmer−Tobias Equation for the Water + 3-Hydroxy-2-butanone + Butyl Ethanoate Ternary System[a]**

| $T$/K | $a$ | $b$ | $R^2$ |
|---|---|---|---|
| 298.15 | 0.5515 | 0.6787 | 0.9951 |
| 308.15 | 0.7050 | 0.6359 | 0.9902 |
| 318.15 | 0.7022 | 0.7872 | 0.9901 |

[a] $R^2$: regression coefficient.

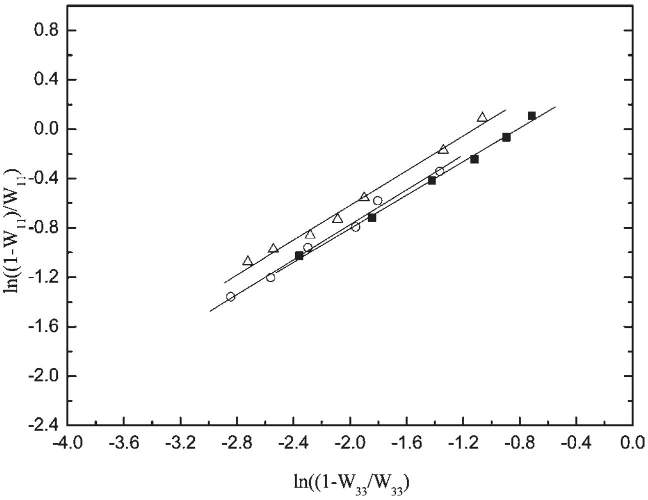

**Figure 6.** Othmer−Tobias plots of the (water + 3-hydroxy-2-butanone + butyl ethanoate) ternary systems: ■, 298.15 K; ○, 308.15 K; Δ, 318.15 K; —, eq 3.

The root-mean-square deviations (rsmd's) are calculated from the difference between the experimental data and the predictions of the UNIFAC model at each temperature according to the following formula

$$\text{rsmd} = \left[\frac{\sum_{k}^{N}\sum_{j}\sum_{i}(W_{ijk}^{\text{exp}} - W_{ijk}^{\text{cal}})^2}{6N}\right]^{1/2} \tag{4}$$

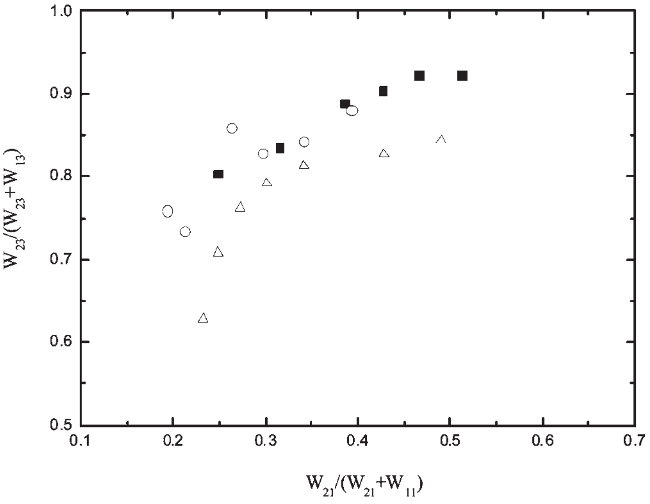

**Figure 7.** Selectivity diagram at investigated temperature values (solvent-free basis): ■, 298.15 K; ○, 308.15 K; Δ, 318.15 K.

where $W_{ijk}$ is the composition of component $i$ in phase $j$ on tie-line $k$. $N$ is the number of tie-lines. The UNIFAC model predicts the LLE data for (298.15, 308.15, and 318.15) K with a root-mean-square deviation of 0.0567, 0.0464, and 0.0435, respectively, between the observed and calculated mass concentrations. This value indicates that the LLE data of this ternary system were not predicted well with this equilibrium model. As can be seen from Figures 1 to 3, the predicted tie-lines (dashed lines) are in relatively poor agreement with the experimental data (solid lines). However, in the lack of experimental data, this model can be used for correlation.

Selectivity diagrams on a solvent-free basis are obtained by plotting $W_{23}/(W_{23} + W_{13})$ versus $W_{21}/(W_{21} + W_{11})$ for each temperature in Figure 7. The selectivity diagram indicated that the performance of the solvent decreases with increasing temperature.

## ■ CONCLUSION

The LLE data of the ternary mixtures water + 3-hydroxy-2-butanone + butyl ethanoate have been presented at (298.15, 308.15, and 318.15) K. The UNIFAC model has been used to predict the LLE data. It has been observed that the UNIFAC predictions do not fit the experimental results quantitatively, but it agrees qualitatively. The separation factor is found to be much greater than 1, and it is not constant over the whole two-phase region. It is concluded that butyl ethanoate may serve as a feasible solvent to extract 3-hydroxy-2-butanone from its aqueous solutions.

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