J. Chem. Eng. Data **1994**, 39, 823−826

# Liquid−Liquid Equilibria for 2,3-Butanediol + Water + Organic Solvents at 303.15 K

**Sadhana Sharma, Girish Pandya, Tapan Chakrabarti,* and Purushottam Khanna**

National Environmental Engineering Research Institute, Nehru Marg, Nagpur, India

Liquid−liquid equilibria at 303.15 ± 0.5 K were measured for water + 2,3-butanediol + butan-1-ol, + 3-methyl-1-butanol, + 4-methyl-2-pentanone, + tributyl phosphate, and + butyl acetate. Complete phase diagrams were obtained by evaluating the solubility and tie-line results for each ternary mixture. The consistency of the tie-line results was ascertained using an Othmer−Tobias plot. The distribution coefficient and separation factors were evaluated over the immiscibility region. Among the solvents studied, butan-1-ol is the most effective one though tributyl phosphate and 3-methyl-1-butanol may be preferred because of their low solubility and high selectivity.

## Introduction

2,3-Butanediol, an important industrial chemical, is of interest because of its application as a solvent and liquid fuel additive. Its dehydration products, butadiene and methyl ethyl ketone, are used in rubber industries and as a solvent, respectively.

Production of 2,3-butanediol has been successful from a variety of substrates using different microorganisms. One of the limitations in 2,3-butanediol fermentation lies in the recovery of 2,3-butanediol from dilute fermentation broth due to its high boiling temperature (182−185 °C) and its affinity for water. These properties of 2,3-butanediol make its recovery extremely difficult by conventional distillation methods, thereby making the cost of the product far from economical.

Solvent extraction has been found to be an effective means of recovery of diols. Othmer *et al.* (1945) investigated the extraction of 2,3-butanediol from aqueous solutions. Ternary equilibrium data together with tie lines were presented in an effort to evaluate the efficacy of solvents used for extraction of 2,3-butanediol. Results on butan-1-ol, butyl acetate, butylene glycol diacetate, and methyl vinyl carbinol acetate indicated that methyl vinyl carbinol acetate was an effective extracting solvent for removing glycol from aqueous solution as compared to butyl acetate and butylene glycol diacetate. Butan-1-ol, though, has a high extracting efficiency but also has a high solubility in water.

The present investigation was undertaken to measure liquid−liquid equilibria for the following systems: water + 2,3-butanediol + butan-1-ol, water + 2,3-butanediol + 3-methyl-1-butanol, water + 2,3-butanediol + 4-methyl-2-pentanone, water + 2,3-butanediol + tributyl phosphate, and water + 2,3-butanediol + butyl acetate. The five solvents studied are fairly nonvolatile, and the density difference between water and the solvents is considerable which facilitates separation of aqueous and solvent phases effectively.

**Table 1**[a]

Mutual Solubility for Water (1) + 2,3-Butanediol (2) + Butan-1-ol (3)

| $w_1$ | $w_2$ | $w_3$ | $w_1$ | $w_2$ | $w_3$ |
|---|---|---|---|---|---|
| 0.919 | | 0.081 | 0.341 | 0.112 | 0.547 |
| 0.822 | 0.101 | 0.077 | 0.320 | 0.105 | 0.575 |
| 0.760 | 0.125 | 0.115 | 0.299 | 0.085 | 0.616 |
| 0.733 | 0.132 | 0.135 | 0.246 | 0.042 | 0.712 |
| 0.621 | 0.135 | 0.244 | 0.219 | | 0.781 |
| 0.480 | 0.130 | 0.390 | | | |

Tie Lines for Water (1) + 2,3-Butanediol (2) + Butan-1-ol (3)

| water-rich layer | | | solvent-rich layer | | |
|---|---|---|---|---|---|
| $w_{11}$ | $w_{21}$ | $w_{31}$ | $w_{13}$ | $w_{23}$ | $w_{33}$ |
| 0.885 | 0.040 | 0.075 | 0.284 | 0.034 | 0.682 |
| 0.865 | 0.070 | 0.065 | 0.263 | 0.057 | 0.680 |
| 0.840 | 0.091 | 0.069 | 0.278 | 0.072 | 0.650 |
| 0.810 | 0.105 | 0.085 | 0.306 | 0.094 | 0.600 |

[a] $w$ = mass fraction.

**Table 2**[a]

Mutual Solubility for Water (1) + 2,3-Butanediol (2) + 3-Methyl-1-butanol (3)

| $w_1$ | $w_2$ | $w_3$ | $w_1$ | $w_2$ | $w_3$ |
|---|---|---|---|---|---|
| 0.987 | | 0.013 | 0.456 | 0.292 | 0.252 |
| 0.838 | 0.140 | 0.022 | 0.339 | 0.282 | 0.379 |
| 0.753 | 0.212 | 0.035 | 0.244 | 0.221 | 0.535 |
| 0.691 | 0.252 | 0.056 | 0.188 | 0.162 | 0.650 |
| 0.600 | 0.292 | 0.108 | 0.133 | 0.066 | 0.801 |
| 0.548 | 0.294 | 0.158 | 0.094 | | 0.906 |

Tie Lines for Water (1) + 2,3-Butanediol (2) + 3-Methyl-1-butanol (3)

| water-rich layer | | | solvent-rich layer | | |
|---|---|---|---|---|---|
| $w_{11}$ | $w_{21}$ | $w_{31}$ | $w_{13}$ | $w_{23}$ | $w_{33}$ |
| 0.950 | 0.032 | 0.018 | 0.090 | 0.020 | 0.890 |
| 0.906 | 0.076 | 0.018 | 0.100 | 0.029 | 0.871 |
| 0.852 | 0.128 | 0.020 | 0.110 | 0.040 | 0.850 |
| 0.830 | 0.149 | 0.021 | 0.120 | 0.060 | 0.820 |
| 0.775 | 0.195 | 0.030 | 0.131 | 0.080 | 0.790 |

[a] $w$ = mass fraction.

## Experimental Section

***Chemicals.*** All chemicals used in this investigation were of analytical grade and were used directly without any further purification. Double-distilled water was used throughout the experimental work.

***Procedure.*** A cloud point titrator, which is a modification of Haddad & Edmister's cloud point titrator, was fabricated and used to determine the binodal/mutual solubility curves and the tie lines of the ternary systems. The apparatus was maintained within ±0.5 K of the experimental temperature by circulating water through a

0021-9568/94/1739-0823$04.50/0

**Table 3**[a]

Mutual Solubility for Water (1) + 2,3-Butanediol (2) + 4-Methyl-2-pentanone (3)

| $w_1$ | $w_2$ | $w_3$ | $w_1$ | $w_2$ | $w_3$ |
|---|---|---|---|---|---|
| 0.974 | | 0.026 | 0.303 | 0.455 | 0.242 |
| 0.829 | 0.138 | 0.033 | 0.258 | 0.441 | 0.301 |
| 0.633 | 0.317 | 0.050 | 0.217 | 0.400 | 0.383 |
| 0.556 | 0.370 | 0.074 | 0.157 | 0.325 | 0.518 |
| 0.489 | 0.407 | 0.104 | 0.106 | 0.264 | 0.630 |
| 0.431 | 0.431 | 0.138 | 0.020 | | 0.980 |

Tie Lines for Water (1) + 2,3-Butanediol (2) + 4-Methyl-2-pentanone (3)

| water-rich layer | | | solvent-rich layer | | |
|---|---|---|---|---|---|
| $w_{11}$ | $w_{21}$ | $w_{31}$ | $w_{13}$ | $w_{23}$ | $w_{33}$ |
| 0.880 | 0.095 | 0.025 | 0.020 | 0.010 | 0.970 |
| 0.760 | 0.200 | 0.040 | 0.023 | 0.027 | 0.950 |
| 0.655 | 0.298 | 0.047 | 0.025 | 0.051 | 0.925 |
| 0.540 | 0.380 | 0.080 | 0.042 | 0.107 | 0.851 |
| 0.380 | 0.448 | 0.172 | 0.056 | 0.142 | 0.802 |

[a] $w$ = mass fraction.

**Table 4**[a]

Mutual Solubility for Water (1) + 2,3-Butanediol (2) + Tributyl Phosphate (3)

| $w_1$ | $w_2$ | $w_3$ | $w_1$ | $w_2$ | $w_3$ |
|---|---|---|---|---|---|
| 0.996 | | 0.040 | 0.263 | 0.520 | 0.217 |
| 0.853 | 0.143 | 0.040 | 0.176 | 0.449 | 0.375 |
| 0.597 | 0.399 | 0.040 | 0.124 | 0.356 | 0.520 |
| 0.390 | 0.584 | 0.026 | 0.082 | 0.234 | 0.684 |
| 0.328 | 0.603 | 0.069 | 0.057 | 0.139 | 0.804 |
| 0.314 | 0.556 | 0.130 | 0.033 | | 0.967 |

Tie Lines for Water (1) + 2,3-Butanediol (2) + Tributyl Phosphate (3)

| water-rich layer | | | solvent-rich layer | | |
|---|---|---|---|---|---|
| $w_{11}$ | $w_{21}$ | $w_{31}$ | $w_{13}$ | $w_{23}$ | $w_{33}$ |
| 0.900 | 0.912 | 0.008 | 0.030 | 0.033 | 0.937 |
| 0.801 | 0.195 | 0.004 | 0.044 | 0.065 | 0.891 |
| 0.671 | 0.326 | 0.003 | 0.045 | 0.075 | 0.880 |
| 0.581 | 0.409 | 0.010 | 0.045 | 0.090 | 0.865 |
| 0.411 | 0.569 | 0.020 | 0.050 | 0.113 | 0.840 |

[a] $w$ = mass fraction.

**Table 5**[a]

Mutual Solubility for Water (1) + 2,3-Butanediol (2) + Butyl Acetate (3)

| $w_1$ | $w_2$ | $w_3$ | $w_1$ | $w_2$ | $w_3$ |
|---|---|---|---|---|---|
| 0.990 | | 0.010 | 0.187 | 0.569 | 0.244 |
| 0.648 | 0.324 | 0.028 | 0.122 | 0.439 | 0.439 |
| 0.580 | 0.387 | 0.033 | 0.083 | 0.275 | 0.644 |
| 0.524 | 0.437 | 0.039 | 0.048 | 0.190 | 0.762 |
| 0.474 | 0.474 | 0.052 | 0.029 | 0.097 | 0.874 |
| 0.361 | 0.544 | 0.095 | 0.010 | | 0.990 |

Tie Lines for Water (1) + 2,3-Butanediol (2) + Butyl Acetate (3)

| water-rich layer | | | solvent-rich layer | | |
|---|---|---|---|---|---|
| $w_{11}$ | $w_{21}$ | $w_{31}$ | $w_{13}$ | $w_{23}$ | $w_{33}$ |
| 0.896 | 0.086 | 0.018 | 0.010 | 0.008 | 0.982 |
| 0.810 | 0.171 | 0.019 | 0.010 | 0.010 | 0.980 |
| 0.730 | 0.248 | 0.022 | 0.015 | 0.050 | 0.935 |
| 0.630 | 0.345 | 0.025 | 0.040 | 0.150 | 0.810 |

[a] $w$ = mass fraction.

constant-temperature bath. A microburet calibrated to ±0.02 cm$^3$ was used for titrating the liquids.

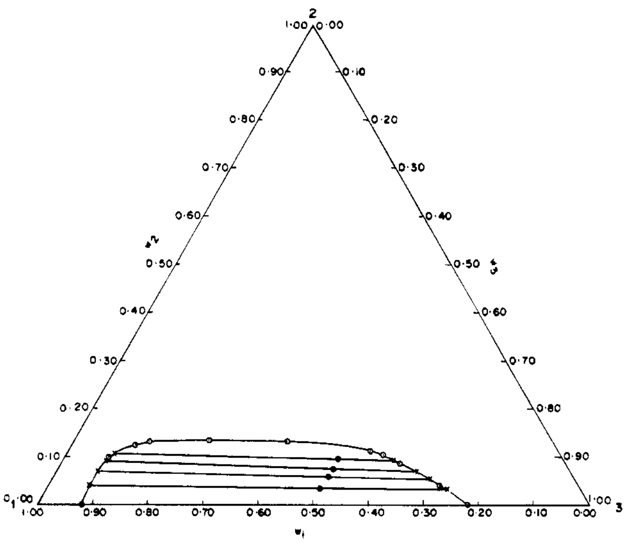

**Figure 1.** Ternary diagram for experimental liquid–liquid extraction of water (1) + 2,3-butanediol (2) + butan-1-ol (3) at 303.15 K: ⊙, solubility results; ×, tie-line values; ⊗, overall composition for the tie line.

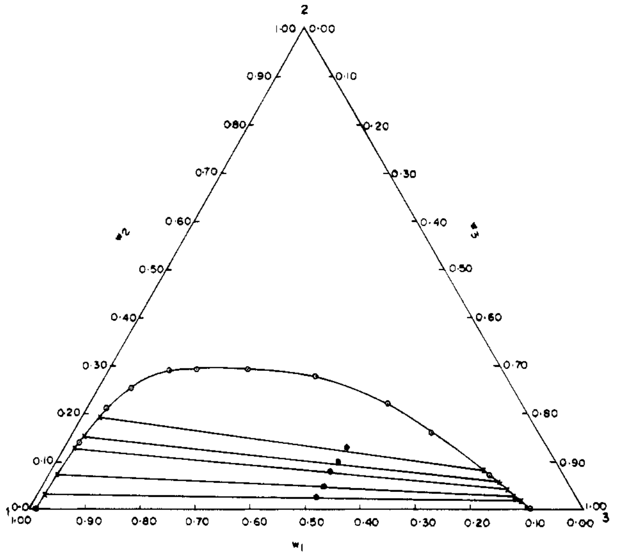

**Figure 2.** Ternary diagram for experimental liquid–liquid extraction of water (1) + 2,3-butanediol (2) + 3-methyl-1-butanol (3) at 303.15 K: ⊙, solubility results; ×, tie-line values; ⊗, overall composition for the tie line.

The binodal/mutual solubility curves of the ternary systems were determined by the method of Othmer *et al.* (1941) by titrating mixtures of known composition of two components with the third one until a permanent turbidity was observed at a constant temperature of 303.15 ± 0.5 K.

A volume of 3 cm$^3$ of the solvent was placed in the sample bottle inside the constant-temperature water jacket and titrated with water using a microburet while maintaining a constant agitation by means of a magnetic stirrer until the solution became cloudy. The solution should remain cloudy after it is allowed to stand for 5 min. This titration established the solubility of water in the solvent. A known quantity of 2,3-butanediol was then added to this mixture which resulted in a solution whose composition was well within the one-phase region. This mixture was then titrated with water again until it became cloudy. This procedure was repeated, and successive cloud points were determined to produce a binodal curve. For obtaining the water-rich side of the solubility curve, the procedure was repeated by titrating a mixture of 2,3-butanediol + water with the solvent to produce turbidity. The cloud points

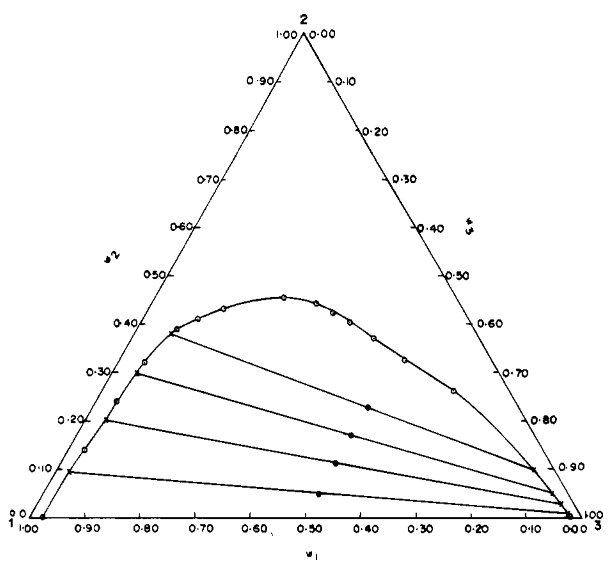

**Figure 3.** Ternary diagram for experimental liquid–liquid extraction of water (1) + 2,3-butanediol (2) + 4-methyl-2-pentanone (3) at 303.15 K: ⊙, solubility results; ×, tie-line values; ⊗, overall composition for the tie line.

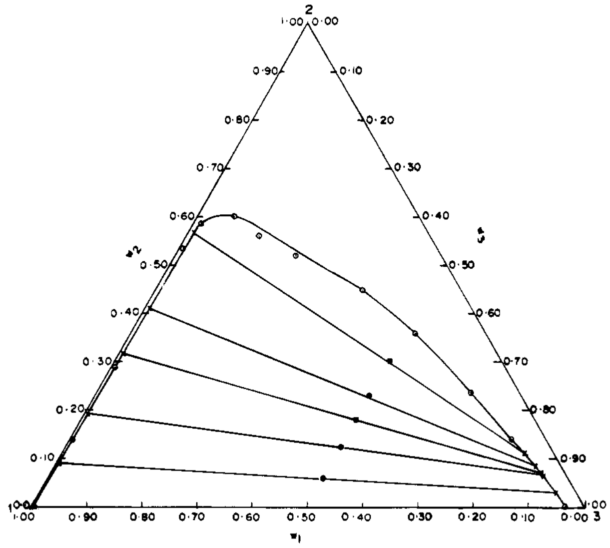

**Figure 4.** Ternary diagram for experimental liquid–liquid extraction of water (1) + 2,3-butanediol (2) + tributyl phosphate (3) at 303.15 K: ⊙, solubility results; ×, tie-line values; ⊗, overall composition for the tie line.

were determined in triplicate, and the average value was considered. The composition determination was accurate to ±0.0026 mass fraction. Tie-line values were determined by making mixtures of the three components whose compositions fell within the two-phase region of the curve. The mixtures of a 3 $cm^3$ solution of 2,3-butanediol in water and 3 $cm^3$ of solvent were taken in sample bottles and stirred for 1 h to reach equilibrium at 303.15 ± 0.5 K. The mixtures were transferred to conical bottom graduated centrifuge tubes, and the two layers were separated by centrifuging at 500 rpm. An aliquot of sample was removed from both the layers, and analyzed for 2,3-butanediol concentration by a GLC PE GC Model Sigma 3B equipped with an FID, using a stainless steel column (2.5 m × 1/8 in. o.d.) packed with chromosorb 101 (80/100 mesh) coated with 3% FFAP. The complete compositions of the conjugated layers were obtained from the binodal curve. Three samples were examined for each tie line, the average of which was considered.

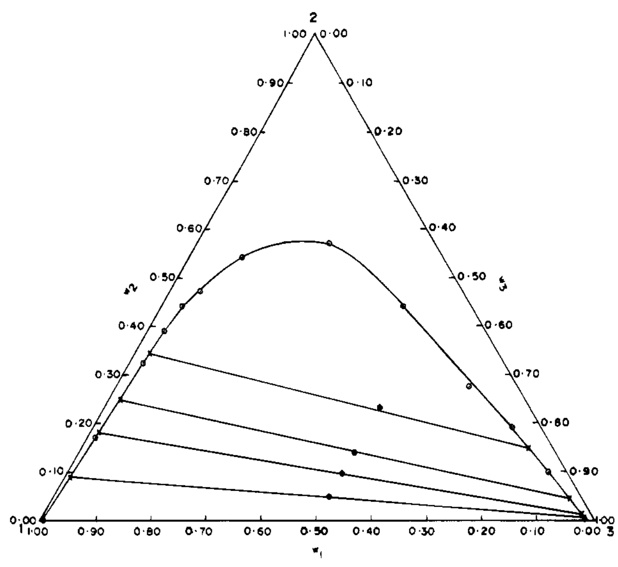

**Figure 5.** Ternary diagram for experimental liquid–liquid extraction of water (1) + 2,3-butanediol (2) + butyl acetate (3) at 303.15 K: ⊙, solubility results; ×, tie-line values; ⊗, overall composition for the tie line.

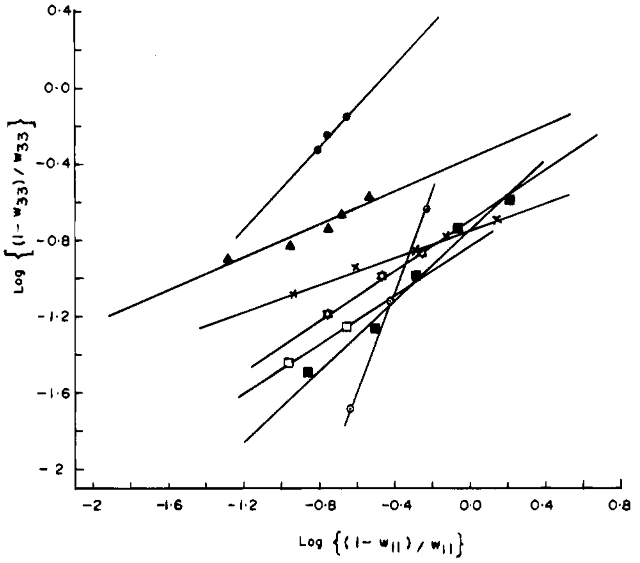

**Figure 6.** Othmer–Tobias correlation for water (1) + 2,3-butanediol (2) + solvent (3) at 303.15 K: ●, butan-1-ol, ▲, 3-methyl-1-butanol, ×, tributyl phosphate, ■, 4-methyl-2-pentanone, ☆, butylene glycol diacetate, □, methyl vinyl carbinol acetate, ⊙, butyl acetate.

**Table 6. Experimental Distribution Coefficients $D_i$ of Water ($i$ = 1) and 2,3-Butanediol ($i$ = 2) and Separation Factors**

| solvent | $D_2$ | $D_1$ | $S = D_2/D_1$ |
|---|---|---|---|
| butan-1-ol | 0.88 | 0.370 | 2.38 |
| 3-methyl-1-butanol | 0.60 | 0.094 | 6.38 |
| tributyl phosphate | 0.36 | 0.030 | 12.00 |
| butyl acetate | 0.10 | 0.017 | 5.88 |
| 4-methyl-2-pentanone | 0.10 | 0.020 | 5.00 |
| methyl vinyl carbinol acetate[a] | 0.24 | 0.016 | 15.00 |
| butylene glycol diacetate[a] | 0.132 | 0.050 | 2.64 |

[a] Data from Othmer (1945) at 299.15 K.

## Results and Discussion

The experimental results for the mutual solubility and equilibrium distribution of aqueous solution of 2,3-butanediol with solvents butan-1-ol, 3-methyl-1-butanol, 4-methyl-2-pentanone, tributyl phosphate, and butyl acetate are

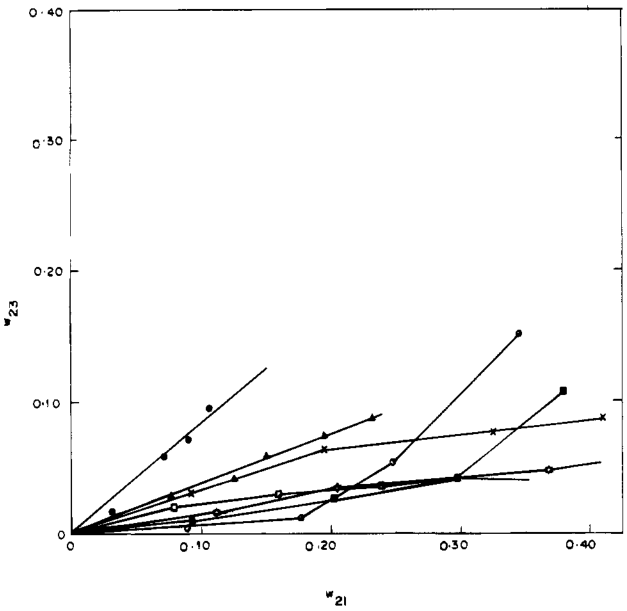

**Figure 7.** Distribution of 2,3-butanediol (2) between water (1) and solvent (3): ●, butan-1-ol, ▲, 3-methyl-1-butanol, ×, tributyl phosphate, ■, 4-methyl-2-pentanone, ☆, butylene glycol diacetate, □, methyl vinyl carbinol acetate, ⊙, butyl acetate.

given in Tables 1–5, respectively. Binodal curves along with tie lines and mixture compositions have been plotted on a ternary diagram and are shown in Figures 1–5.

The area of the two-phase region increases in the following order of solvents: butan-1-ol < 3-methyl-1-butanol < 4-methyl-2-pentanone < butyl acetate and < tributyl phosphate. The mutual solubility of butan-1-ol in water is in agreement with the liquid–liquid equilibrium results reported by Othmer *et al.* (1945) for systems of water + 2,3-butanediol + butan-1-ol. For butyl acetate, however, a slightly expanded curve was obtained. The solubility of other solvents could not be compared as the same was not available in the literature. The reliability of measured tie-line compositions was ascertained by the Othmer–Tobias correlation method by plotting $\log\{(1 - w_{33})/w_{33}\}$ against $\log\{(1 - w_{11})/w_{11}\}$. The Othmer–Tobias correlation equation is

$$(1 - w_{33}/w_{33}) = K(1 - w_{11}/w_{11})^n \qquad (1)$$

where, $w$ = mass fraction, $w_{11}$ = mass fraction of water (1) in the aqueous phase, $w_{33}$ = mass fraction of solvent (3) in the solvent phase, and $K$, $n$ = Othmer–Tobias constants.

Figure 6 shows, for all the systems, a linear dependency of the plot $\log\{(1 - w_{33})/w_{33}\}$ against $\log\{(1 - w_{11})/w_{11}\}$, indicating the consistency of the results.

The effectiveness of the solvents for 2,3-butanediol extraction can be expressed in terms of the distribution coefficient of 2,3-butanediol and the separation factor of the solvent.

The distribution coefficient $D_i$ for 2,3-butanediol ($i$ = 2) and water ($i$ = 1) and the separation factor $S$ are determined by

$$D_i = w_{i,3}/w_{i,1} \qquad (2)$$

$$S = D_2/D_1 \qquad (3)$$

where $w_{i,3}$, $w_{i,1}$ = mass fraction of the $i$th component in the solvent phase and aqueous phase, respectively.

The distribution coefficients and separation factors have been analyzed for 5–10% aqueous 2,3-butanediol concentration using the solvents under investigation. The results are listed in Table 6. Assuming the selection criteria for the extraction distribution coefficient to be greater than 0.2 and the separation factor greater than 5, 3-methyl-1-butanol, tributyl phosphate, and methyl vinyl carbinol acetate can be used as solvents for extraction. Though butan-1-ol has the highest distribution coefficient for 2,3-butanediol, its solubility in water, as indicated by its distribution coefficient for water, detracts from its usefulness.

The distribution of 2,3-butanediol between water and solvent is shown in Figure 7. The curves are obtained by plotting the mass fraction of 2,3-butanediol in the aqueous phase ($w_{21}$) against the mass fraction of 2,3-butanediol in the solvent phase ($w_{23}$). The curves reflect a comparison of the ability of the solvents to extract 2,3-butanediol from water. The results of Othmer (1945) for methyl vinyl carbinol acetate and butylene glycol diacetate have been referenced. As found by Othmer (1945), butan-1-ol demonstrates excellent extracting power. 3-Methyl-1-butanol and tributyl phosphate are also good extractants and are shown to be better solvents than methyl vinyl carbinol acetate. Butylene glycol diacetate and butyl acetate have poor extracting power.

## Literature Cited

Haddad, P. O.; Edmister, W. C. Phase Equilibria in Acetic Acid-Diethyl Ketone-Water System. *J. Chem. Eng. Data* **1972**, *17*, 275–278.

Othmer, D. F.; Bergen, W. S.; Shlechter, M.; Bruins, P. F. Liquid-Liquid Extraction Data. *Ind. Eng. Chem.* **1945**, *37*, 890–894.

Othmer, D. F.; White, R. E.; Trueger, E. Liquid–Liquid Extraction Data. *Ind. Eng. Chem.* **1941**, *33*, 10, 1240–1248.

Received for review March 1, 1994. Accepted May 30, 1994.[⊗]

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1994.