

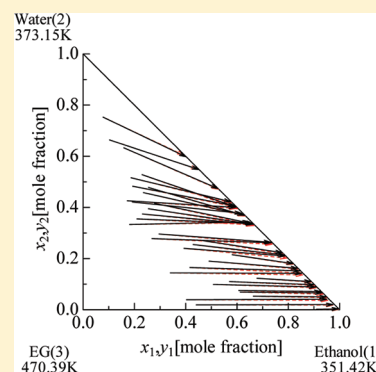
## Isobaric Vapor–Liquid Equilibria for Ethanol + Water + Ethylene Glycol and Its Constituent Three Binary Systems

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**ABSTRACT:** Isobaric vapor–liquid equilibria were measured for the ternary system ethanol + water + ethylene glycol and its three constituent binary mixtures at 101.3 kPa using a modified Rogalski–Malanoski equilibrium still. The thermodynamic consistency of experimental binary data was checked using the point and area tests. The experimental binary data were then correlated by the Wilson, nonrandom two-liquid (NRTL), and universal quasichemical activity coefficient (UNIQUAC) equations. The ternary vapor–liquid equilibria data were predicted using the binary parameters for the three equations with good accuracy. The selectivity of ethylene glycol as entrainer for the separation of the azeotropic system ethanol + water by extractive distillation was discussed using the NRTL parameters.



### INTRODUCTION

Since the 1970s, higher oil prices have driven the development of fermented ethanol as an alternative fuel, and concerns related to global warming have accelerated these efforts. The reduction of the energy requirements in the refining step of ethanol production is a major process development challenge in ensuring that ethanol becomes an effective alternative energy source. The widely used distillation technology is not ideal for ethanol dehydration owing to ethanol's azeotropic nature with water. Azeotropic distillation or extractive distillation with an additional solvent component (the entrainer) would therefore be required. Azeotropic distillations are widely used in ethanol dehydration for nonfuel applications. Extractive distillation has an inherent advantage in that it can reduce the energy requirement based on the nature of the entrainers that do not need to boil up to the top of the column. On the other hand, azeotropic distillation requires all entrainers to distill from the top of the column.

Ethylene glycol has been proposed by Washall<sup>1</sup> as a potential entrainer for alcohol dehydrations. Landisch and Dyck<sup>2</sup> proposed several entrainers including glycol for ethanol dehydration, while ethylene glycol was proposed by Lee and Pahl.<sup>3</sup> These entrainers seem to possess favorable characteristics for ethanol dehydration that breaks the ethanol–water azeotrope. However, the available vapor–liquid equilibrium data for the ethanol, water, and ethylene glycol system are not sufficient for the optimal design of the extractive distillation system with effective heat integration. This paper presents the measurement of vapor–liquid equilibria (VLE) for the ternary system ethanol + water + ethylene glycol and its constituent three binary mixtures at 101.3 kPa. Some already reported binary and ternary VLE data<sup>3–5</sup> were compared with the experimental data. The thermodynamic consistency of the

experimental binary data was checked using the point and area tests,<sup>6,7</sup> and then the data were correlated by the Wilson,<sup>8</sup> nonrandom two-liquid (NRTL),<sup>9</sup> and universal quasichemical activity coefficient (UNIQUAC)<sup>10</sup> equations. The ternary VLE data were predicted using the binary parameters for the three equations.

### EXPERIMENTAL SECTION

**Apparatus and Procedure.** Figure 1 shows the apparatus for measuring VLE data. A modified Rogalski–Malanoski equilibrium still with pressure control was used. The analysis was similar to that described in the literature.<sup>11</sup> In addition to the still, the apparatus consisted of a data logger (34970A, Agilent Technologies Co., Santa Clara, CA), an personal computer, pressure controller, two buffer tanks, a refrigerator, and a vacuum pump.

The equilibrium temperature was measured with a calibrated platinum resistance thermometer with an accuracy of  $\pm 0.01$  K. The pressure in the still was determined with a pressure controller (DOI3-20, Druck Co., UK), and the accuracy was estimated to be  $\pm 0.03$  kPa.

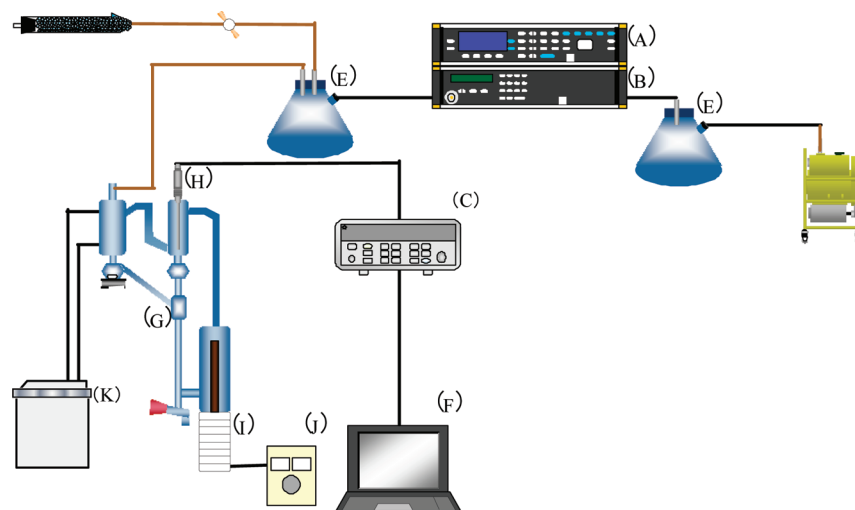
**Analysis.** Vapor and liquid samples were analyzed with a gas chromatograph (GC-4000, GL Sciences Co. Ltd., Tokyo, Japan) equipped with a thermal conductivity detector. Gaskuropack S4 60/80 was used as the column packing and helium as the carrier gas. The compositions were determined using the relative area method with an accuracy of  $\pm 0.1$  mol %.

**Materials.** Ethanol and ethylene glycol (special grade pure from Wako Pure Chemical Industry, Ltd.) were used after

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**Figure 1.** Apparatus for measuring VLE data (A). (B) Pressure controller; (C) data acquisition; (D) vacuum pump; (E) buffer tank; (F) personal computer; (G) modified Rogalski–Malanoski equilibrium still; (H) thermometer; (I) stick heater; (J) slidac; (K) refrigerant unit.

removing traces of water with 3A molecular sieves. The water was passed through an ion exchanger and distilled. The material purity was checked by gas chromatography and found to be greater than 99.6 mass % for ethanol and 99.9 mass % for ethylene glycol. The water contents of the purified chemicals were checked by Karl Fischer titration, and the values were to be 60 and 25 mass ppm for ethanol and ethylene glycol, respectively.

Tables 1 and 2 show the experimental vapor pressures and Antoine equation constants for ethanol, water, and ethylene glycol, respectively. The average deviations between the experimental and the calculated values using the literature Antoine constants from Riddick and Bunger<sup>12</sup> and Boublik et al.<sup>13</sup> are 1.58 % and 0.98 % for the ethanol and ethylene glycol, respectively.

## EXPERIMENTAL RESULTS

**Binary Systems.** The experimental VLE data at 101.3 kPa for ethanol + water, water + ethylene glycol, and ethanol + ethylene glycol are shown in Tables 3 to 5 and Figures 2 to 4. The activity coefficients,  $\gamma_i$ , in Tables 3 to 5 were evaluated by eq 1:

$$\gamma_i = P y_i / P_i^S x_i \quad (1)$$

where  $P_i^S$  is the vapor pressure of pure component  $i$ . Here the nonideality of the vapor phase has been neglected, because the binary coefficients in Tsionopoulos's procedure<sup>14</sup> have not been found for ethylene glycol.

The already published  $x$ – $y$  data for the binary systems including ethylene glycol were given in Figures 5 and 6. The agreement was good for ethanol (1) + ethylene glycol, but the deviation was large for the water (2) + ethylene glycol (3) system.

The experimental VLE data were examined for thermodynamic consistency using the point test of Fredenslund et al.<sup>6</sup> and the area test of Herington as described by Gmehling and Onken.<sup>15</sup> The results of these consistency tests are shown in Table 6. The experimental binary VLE data were found to be thermodynamically consistent according to the point and area tests.

**Ternary Systems.** Table 7 and Figure 7 show the experimental VLE data for ethanol + water + ethylene glycol

**Table 1.** Experimental Vapor Pressures

| $P/\text{kPa}$ |                 | $T/\text{K}$ |
|----------------|-----------------|--------------|
|                | Ethanol         |              |
| 40.00          |                 | 329.67       |
| 53.33          |                 | 336.06       |
| 66.66          |                 | 341.23       |
| 79.99          |                 | 345.59       |
| 93.32          |                 | 349.38       |
| 99.74          |                 | 351.03       |
|                | Water           |              |
| 40.00          |                 | 349.09       |
| 53.33          |                 | 356.17       |
| 66.66          |                 | 361.87       |
| 79.99          |                 | 366.69       |
| 93.32          |                 | 370.88       |
| 100.0          |                 | 372.76       |
|                | Ethylene Glycol |              |
| 13.33          |                 | 412.81       |
| 20.00          |                 | 422.78       |
| 26.66          |                 | 430.26       |
| 33.33          |                 | 436.37       |
| 40.00          |                 | 441.50       |
| 46.66          |                 | 445.96       |
| 53.33          |                 | 449.93       |
| 60.00          |                 | 453.52       |
| 66.66          |                 | 456.78       |
| 73.33          |                 | 459.79       |
| 79.99          |                 | 462.58       |
| 86.66          |                 | 465.18       |
| 93.32          |                 | 467.62       |
| 98.66          |                 | 469.48       |
| 100.4          |                 | 470.02       |

**Table 2.** Antoine Equation Constants (kPa·K)<sup>a</sup>

| substance       | A       | B       | C       | $ \Delta P^b/P _{\text{av}}$ (%) |
|-----------------|---------|---------|---------|----------------------------------|
| ethanol         | 7.25298 | 1598.95 | −46.715 | 0.02                             |
| water           | 7.23605 | 1754.35 | −37.731 | 0.04                             |
| ethylene glycol | 6.69332 | 1706.33 | −106.38 | 0.06                             |

<sup>a</sup> $\log P/\text{kPa} = A - B/(T/\text{K}) + C$ . <sup>b</sup> $\Delta P = \sum_k |(P_{\text{expt}} - P_{\text{calc}})/P_{\text{expt}}|/N \cdot 100$ , where  $N$  is the number of data points.

**Table 3. Experimental Vapor–Liquid Equilibria and Activity Coefficients  $\gamma_i$  for Ethanol (1) + Water (2) at 101.3 kPa**

| T/K    | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ |
|--------|-------|-------|------------|------------|
| 373.15 | 0.000 | 0.000 |            | 1.000      |
| 368.18 | 0.018 | 0.180 | 5.328      | 1.001      |
| 360.50 | 0.079 | 0.418 | 3.731      | 1.013      |
| 359.70 | 0.090 | 0.441 | 3.561      | 1.016      |
| 357.27 | 0.147 | 0.510 | 2.764      | 1.045      |
| 355.38 | 0.244 | 0.567 | 1.991      | 1.123      |
| 354.55 | 0.311 | 0.589 | 1.676      | 1.209      |
| 354.11 | 0.353 | 0.604 | 1.540      | 1.263      |
| 353.45 | 0.425 | 0.627 | 1.362      | 1.375      |
| 352.96 | 0.488 | 0.652 | 1.258      | 1.470      |
| 352.39 | 0.570 | 0.688 | 1.162      | 1.606      |
| 352.11 | 0.616 | 0.713 | 1.127      | 1.673      |
| 351.82 | 0.670 | 0.736 | 1.082      | 1.812      |
| 351.64 | 0.711 | 0.760 | 1.060      | 1.895      |
| 351.37 | 0.802 | 0.819 | 1.024      | 2.109      |
| 351.30 | 0.835 | 0.844 | 1.016      | 2.188      |
| 351.27 | 0.869 | 0.873 | 1.011      | 2.246      |
| 351.26 | 0.901 | 0.900 | 1.006      | 2.341      |
| 351.26 | 0.914 | 0.912 | 1.004      | 2.372      |
| 351.27 | 0.922 | 0.920 | 1.004      | 2.376      |
| 351.29 | 0.940 | 0.937 | 1.002      | 2.431      |
| 351.35 | 0.972 | 0.969 | 1.000      | 2.557      |
| 351.44 | 1.000 | 1.000 | 1.000      |            |

**Table 4. Experimental Vapor–Liquid Equilibria and Activity Coefficients  $\gamma_i$  for Water (2) + Ethylene Glycol (3) at 101.3 kPa**

| T/K    | $x_2$ | $y_2$ | $\gamma_2$ | $\gamma_3$ |
|--------|-------|-------|------------|------------|
| 470.39 | 0.000 | 0.000 |            | 1.000      |
| 462.57 | 0.020 | 0.227 | 0.900      | 1.000      |
| 448.77 | 0.063 | 0.527 | 0.912      | 0.998      |
| 438.69 | 0.104 | 0.681 | 0.914      | 0.997      |
| 433.60 | 0.128 | 0.742 | 0.921      | 0.996      |
| 426.70 | 0.167 | 0.810 | 0.924      | 0.994      |
| 422.03 | 0.197 | 0.848 | 0.930      | 0.989      |
| 415.27 | 0.250 | 0.892 | 0.931      | 0.988      |
| 411.98 | 0.279 | 0.910 | 0.935      | 0.982      |
| 408.00 | 0.317 | 0.928 | 0.942      | 0.983      |
| 405.33 | 0.346 | 0.939 | 0.945      | 0.977      |
| 400.18 | 0.409 | 0.956 | 0.952      | 0.982      |
| 397.27 | 0.444 | 0.964 | 0.968      | 0.976      |
| 393.53 | 0.501 | 0.973 | 0.974      | 0.972      |
| 390.22 | 0.557 | 0.980 | 0.982      | 0.952      |
| 384.51 | 0.674 | 0.989 | 0.989      | 0.945      |
| 381.51 | 0.747 | 0.993 | 0.992      | 0.904      |
| 379.47 | 0.797 | 0.995 | 0.999      | 0.895      |
| 377.30 | 0.861 | 0.997 | 0.999      | 0.880      |
| 376.05 | 0.900 | 0.998 | 1.000      | 0.873      |
| 373.15 | 1.000 | 1.000 | 1.000      |            |

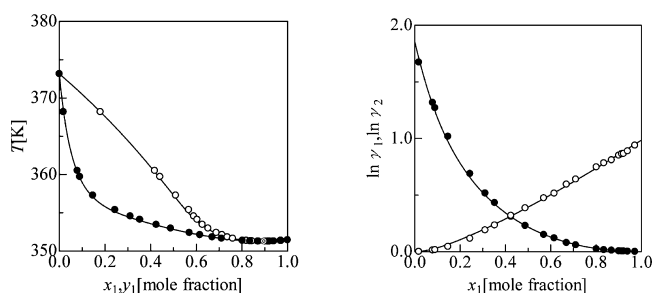
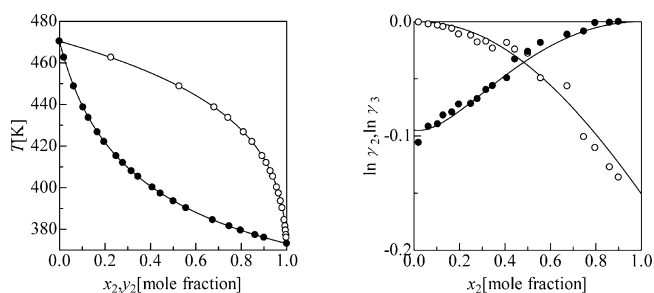
at 101.3 kPa. The tails and heads of solid arrows in Figure 7 represent the experimental liquid and vapor compositions on the same tie line, respectively.

## DISCUSSION

The activity coefficients of the three binary systems were correlated by the Wilson, NRTL, and UNIQUAC equations.

**Table 5. Experimental Vapor–Liquid Equilibria and Activity Coefficients  $\gamma_i$  for Ethanol (1) + Ethylene Glycol (3) at 101.3 kPa**

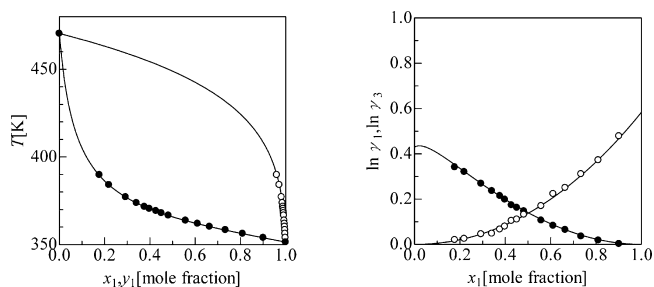
| T/K    | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_3$ |
|--------|-------|-------|------------|------------|
| 470.39 | 0.000 | 0.000 |            | 1.000      |
| 389.79 | 0.177 | 0.961 | 1.406      | 1.020      |
| 384.10 | 0.219 | 0.972 | 1.378      | 1.025      |
| 377.16 | 0.293 | 0.982 | 1.308      | 1.046      |
| 373.78 | 0.341 | 0.986 | 1.266      | 1.049      |
| 371.65 | 0.376 | 0.988 | 1.239      | 1.068      |
| 370.51 | 0.398 | 0.989 | 1.219      | 1.082      |
| 369.25 | 0.427 | 0.990 | 1.189      | 1.110      |
| 368.05 | 0.451 | 0.991 | 1.176      | 1.117      |
| 366.65 | 0.482 | 0.992 | 1.158      | 1.140      |
| 363.80 | 0.558 | 0.994 | 1.112      | 1.185      |
| 361.99 | 0.611 | 0.995 | 1.086      | 1.250      |
| 360.28 | 0.664 | 0.996 | 1.066      | 1.284      |
| 358.41 | 0.734 | 0.997 | 1.036      | 1.364      |
| 356.32 | 0.810 | 0.998 | 1.018      | 1.451      |
| 354.00 | 0.901 | 0.999 | 1.002      | 1.613      |
| 351.44 | 1.000 | 1.000 | 1.000      |            |

**Figure 2. Temperature–composition diagram and activity coefficient–liquid composition for the binary system ethanol (1) + water (2) at 101.3 kPa: (●,○) experimental values. Curves are calculated using the NRTL equation.****Figure 3. Temperature–composition diagram and activity coefficient–liquid composition for the binary system water (2) + ethylene glycol (3) at 101.3 kPa: (●,○) experimental values. Curves are calculated using the NRTL equation.**

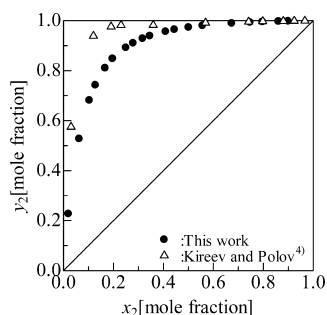
The objective function in eq 2 was minimized during optimization of the parameters in the equations.

$$F_{\text{obj}} = \sum_{k=1}^N \left[ \left( \frac{\gamma_{1,\text{calcd}} - \gamma_{1,\text{exptl}}}{\gamma_{1,\text{exptl}}} \right)_k^2 + \left( \frac{\gamma_{2,\text{calcd}} - \gamma_{2,\text{exptl}}}{\gamma_{2,\text{exptl}}} \right)_k^2 \right] \quad (2)$$

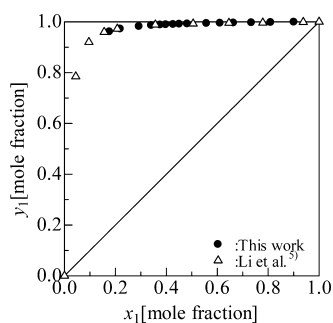
where  $N$  is the number of data points. Table 8 lists the estimated parameters of the binary systems and deviations



**Figure 4.** Temperature–composition diagram and activity coefficient–liquid composition for the binary system ethanol (1) + ethylene glycol (3) at 101.3 kPa: (●,○) experimental values. Curves are calculated using the NRTL equation.



**Figure 5.** Comparison of  $x$ – $y$  of published data with the experimental data for the water (2) + ethylene glycol (3) system at 101.3 kPa.



**Figure 6.** Comparison of  $x$ – $y$  of published data with the experimental data for the ethanol (1) + ethylene glycol (3) system at 101.3 kPa.

**Table 6. Results<sup>a</sup> of Thermodynamic Consistency Tests of VLE for Three Binary Systems at 101.3 kPa**

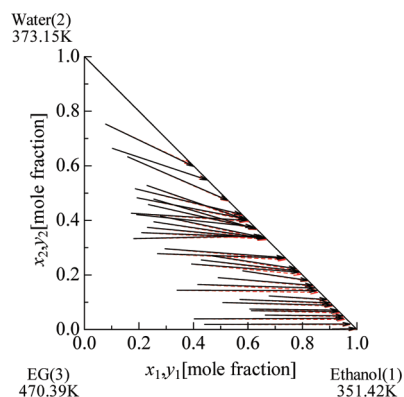
| system                            | point test <sup>b</sup>           | area test <sup>c</sup> |
|-----------------------------------|-----------------------------------|------------------------|
|                                   | $ \Delta y_{1,av}  \leq 0.01$ [+] | $D-J \leq 10$ [+]      |
| ethanol (1) + water (2)           | 0.003[+]                          | –28.82[+]              |
| water (2) + ethylene glycol (3)   | <0.001[+]                         | –27.98[+]              |
| ethanol (1) + ethylene glycol (3) | <0.001[+]                         | –12.80[+]              |

<sup>a</sup>Results of the tests are characterized by the signs “+” (pass) and “–” (fail). <sup>b</sup>The criterion for passing the test is  $|\Delta y_{1,av}| \leq -0.010$ . <sup>c</sup>The criterion for passing the tests is  $D-J \leq -10$  %.

between the calculated and the experimental vapor-phase compositions and bubble points using the activity coefficient equations. Table 9 shows the structural parameters  $r_i$  and  $q_i$  for UNIQUAC and liquid molar volume  $V_i^L$  for the Wilson equation. Calculated results using the NRTL equation are shown by solid lines in Figures 2 to 4.

**Table 7. Experimental Vapor–Liquid Equilibria and Activity Coefficients  $\gamma_i$  for Ethanol (1) + Water (2) + Ethylene Glycol (3) at 101.3 kPa**

| T/K    | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $\gamma_1$ | $\gamma_2$ | $\gamma_3$ |
|--------|-------|-------|-------|-------|------------|------------|------------|
| 365.94 | 0.078 | 0.753 | 0.401 | 0.598 | 2.965      | 1.035      | 0.461      |
| 366.41 | 0.103 | 0.664 | 0.451 | 0.548 | 2.484      | 1.056      | 0.427      |
| 362.64 | 0.159 | 0.633 | 0.525 | 0.474 | 2.150      | 1.105      | 0.555      |
| 368.94 | 0.172 | 0.426 | 0.594 | 0.400 | 1.791      | 1.094      | 0.920      |
| 371.77 | 0.181 | 0.333 | 0.648 | 0.344 | 1.681      | 1.086      | 0.839      |
| 364.51 | 0.187 | 0.516 | 0.576 | 0.422 | 1.873      | 1.124      | 0.616      |
| 367.63 | 0.192 | 0.421 | 0.618 | 0.377 | 1.750      | 1.095      | 0.799      |
| 365.43 | 0.193 | 0.483 | 0.591 | 0.406 | 1.800      | 1.117      | 0.728      |
| 368.76 | 0.210 | 0.355 | 0.657 | 0.338 | 1.632      | 1.118      | 0.682      |
| 361.77 | 0.230 | 0.528 | 0.598 | 0.401 | 1.748      | 1.159      | 0.562      |
| 366.50 | 0.231 | 0.374 | 0.661 | 0.334 | 1.618      | 1.141      | 0.881      |
| 363.60 | 0.235 | 0.458 | 0.627 | 0.370 | 1.678      | 1.150      | 0.727      |
| 361.83 | 0.255 | 0.478 | 0.629 | 0.369 | 1.655      | 1.176      | 0.726      |
| 364.40 | 0.255 | 0.395 | 0.663 | 0.334 | 1.588      | 1.166      | 0.686      |
| 367.79 | 0.268 | 0.278 | 0.734 | 0.262 | 1.479      | 1.144      | 0.659      |
| 362.54 | 0.279 | 0.416 | 0.662 | 0.336 | 1.550      | 1.197      | 0.625      |
| 365.48 | 0.296 | 0.296 | 0.731 | 0.264 | 1.450      | 1.184      | 0.763      |
| 368.45 | 0.340 | 0.144 | 0.852 | 0.142 | 1.322      | 1.167      | 0.802      |
| 362.39 | 0.393 | 0.240 | 0.787 | 0.210 | 1.317      | 1.302      | 0.754      |
| 368.91 | 0.403 | 0.039 | 0.950 | 0.041 | 1.223      | 1.239      | 0.988      |
| 363.98 | 0.416 | 0.165 | 0.844 | 0.152 | 1.258      | 1.290      | 0.778      |
| 360.58 | 0.429 | 0.255 | 0.784 | 0.214 | 1.285      | 1.343      | 0.544      |
| 367.81 | 0.441 | 0.019 | 0.974 | 0.020 | 1.192      | 1.257      | 0.762      |
| 358.86 | 0.467 | 0.270 | 0.776 | 0.223 | 1.246      | 1.411      | 0.652      |
| 360.55 | 0.491 | 0.190 | 0.836 | 0.162 | 1.198      | 1.366      | 0.688      |
| 362.39 | 0.508 | 0.099 | 0.907 | 0.089 | 1.174      | 1.346      | 0.798      |
| 359.93 | 0.571 | 0.110 | 0.899 | 0.098 | 1.134      | 1.463      | 0.834      |
| 357.14 | 0.581 | 0.215 | 0.819 | 0.180 | 1.128      | 1.534      | 0.412      |
| 359.74 | 0.607 | 0.075 | 0.927 | 0.071 | 1.108      | 1.562      | 0.735      |
| 359.79 | 0.613 | 0.069 | 0.931 | 0.066 | 1.100      | 1.564      | 0.995      |
| 358.43 | 0.664 | 0.053 | 0.948 | 0.050 | 1.088      | 1.633      | 0.874      |
| 356.24 | 0.678 | 0.123 | 0.889 | 0.110 | 1.087      | 1.697      | 0.459      |
| 353.77 | 0.910 | 0.002 | 0.996 | 0.003 | 0.998      | 3.235      | 1.080      |



**Figure 7.** Vapor–liquid equilibria for ethanol (1) + water (2) + ethylene glycol (3) at 101.3 kPa: (solid arrows) experimental; (dashed arrows) NRTL equation.

The VLE for the ternary ethanol + water + ethylene glycol was predicted using the binary parameters listed in Table 8, and the average deviations between the experimental and predicted vapor-phase composition and bubble point using the three equations are given in Table 10. Predicted results using the NRTL equation are shown by dotted lines in Figure 7. The

Table 8. Activity Coefficient Model Parameters and Deviations between Experimental and Calculated Values

| model   | system | $A_{ij}$            | $A_{ji}$            | $\alpha_{ij}$ | $ \Delta T_{av} ^a$ | $ \Delta y_{1av} ^b$ | $ \Delta y_{2av} ^b$ |
|---------|--------|---------------------|---------------------|---------------|---------------------|----------------------|----------------------|
|         |        | J·mol <sup>-1</sup> | J·mol <sup>-1</sup> |               | K                   | mole fraction        | mole fraction        |
| NRTL    | 1 + 2  | 227.56              | 5196.9              | 0.40          | 0.07                | 0.002                |                      |
|         | 1 + 3  | 1035.6              | 708.38              | 0.23          | 0.10                | <0.001               |                      |
|         | 2 + 3  | -2510.0             | 2731.3              | 0.33          | 0.09                |                      | 0.001                |
| Wilson  | 1 + 2  | 1883.5              | 3871.3              |               | 0.08                | 0.004                |                      |
|         | 1 + 3  | 714.08              | 1111.4              |               | 0.10                | <0.001               |                      |
|         | 2 + 3  | 4155.6              | -4548.9             |               | 0.09                |                      | 0.001                |
| UNIQUAC | 1 + 2  | 1359.8              | -24.504             |               | 0.06                | 0.002                |                      |
|         | 1 + 3  | 770.69              | 92.746              |               | 0.11                | <0.001               |                      |
|         | 2 + 3  | -1026.9             | -213.82             |               | 0.12                |                      | 0.001                |

<sup>a</sup> $|\Delta T_{av}| = \sum_k |T_{\text{expt}} - T_{\text{calc}}|_k / N$ . <sup>b</sup> $|\Delta y_{iav}| = \sum_k |y_{i,\text{expt}} - y_{i,\text{calc}}|_k / N$ , where  $N$  is the number of data points.

Table 9. Structural Parameters  $r_i$  and  $q_i$  for UNIQUAC and Liquid Molar Volume  $V_i^L$  for the Wilson Equation

| compound        | $r_i$  | $q_i$  | $V_i^L \cdot 10^6$                |
|-----------------|--------|--------|-----------------------------------|
|                 |        |        | m <sup>3</sup> ·mol <sup>-1</sup> |
| ethanol         | 2.1055 | 1.9720 | 58.675                            |
| water           | 0.9200 | 1.4000 | 18.069                            |
| ethylene glycol | 2.4088 | 2.2480 | 55.918                            |

Table 10. Predicted Results of Vapor–Liquid Equilibrium for Ethanol (1) + Water (2) + Ethylene Glycol (3) at 101.3 kPa

| model   | $ \Delta T_{av} ^a$ | $ \Delta y_{1av} ^b$ | $ \Delta y_{2av} ^b$ |
|---------|---------------------|----------------------|----------------------|
|         | K                   | mole fraction        | mole fraction        |
| NRTL    | 0.14                | 0.004                | 0.005                |
| Wilson  | 0.15                | 0.004                | 0.005                |
| UNIQUAC | 0.40                | 0.011                | 0.011                |

<sup>a</sup> $|\Delta T_{av}| = \sum_k |T_{\text{expt}} - T_{\text{calc}}|_k / N$ . <sup>b</sup> $|\Delta y_{iav}| = \sum_k |y_{i,\text{expt}} - y_{i,\text{calc}}|_k / N$ , where  $N$  is the number of data points.

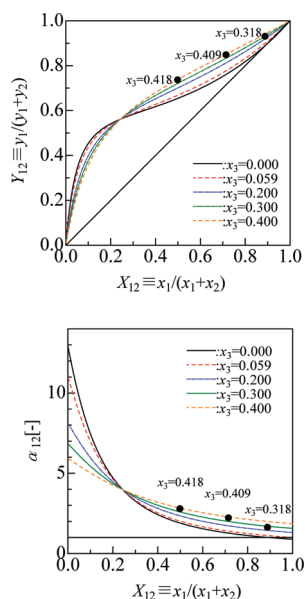


Figure 8. Effect of ethylene glycol for separating the ethanol + water mixture.

VLE data of Lee and Pahl were calculated using the NRTL equation. The absolute deviations of ethanol vapor composi-

tions and bubble points were 0.013 mole fraction and 0.59 K, respectively.

Figure 8 shows the effect of ethylene glycol for separating the ethanol + water mixture evaluated using the NRTL equation. The azeotropic behavior will disappear at the 0.059 mole fraction of ethylene glycol. Therefore, ethylene glycol can be used as an entrainer for the extractive distillation of the binary azeotropic mixture ethanol + water.

## CONCLUSION

The vapor–liquid equilibria for ethanol + water + ethylene glycol at 101.3 kPa were measured, and the binary parameters of three activity coefficient equations, for example, Wilson, NRTL, and UNIQUAC, were determined. The ternary vapor–liquid equilibria were predicted using the binary parameters. The determined parameters of these activity coefficient equations will be useful for the discussion of separation of ethanol aqueous mixtures using extractive distillation.

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