# Isobaric Vapor–Liquid Equilibrium for Ethanol + Water + Cobalt(II) Chloride

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Isobaric vapor–liquid equilibrium for ethanol (1) + water (2) + cobalt(II) chloride (3) at different mole fractions of cobalt(II) chloride has been measured at 100.0 kPa. The results in the range where the mole fraction of salt in the liquid phase was less than 0.23 times the mole fraction of water were correlated by assuming that the salt was in ionic form and was associated only with the water. Thermodynamic consistency was checked by Herington's method with satisfactory results.

## Introduction

Although the salt effect on the vapor–liquid equilibria (VLE) of volatile substances has been noted, well-established equations are not avalaible for the correlation and prediction of VLE data of salt-containing systems. The reviews by Ciparis (1, 2) are the only compilations on the salt effect on the vapor–liquid equilibria in organic mixtures.

Some proposed methods for the correlation of experimental results [Natarajan (3), Schmitt and Vogelpohl (4), and Vercher et al. (5, 6)] consider that solvent mixtures containing a salt can be treated as pseudobinary systems. Recently, some researchers [Chen et al. (7, 8), Sander et al. (9), Tan (10), and Kikic et al. (11)] have used modifications of VLE local composition model to take account of the electrolyte contribution.

The vapor–liquid equilibrium of the ethanol + water system saturated with cobalt(II) chloride has been studied by several researchers, such as Alvarez et al. (12), Martinez de la Ossa and Galán (13, 14) and Jacques and Galán (15), but we have not found any reported vapor–liquid equilibrium for ethanol + water with varying concentrations of cobalt(II) chloride below saturation.

## Experimental Section

The chemicals were absolute ethanol (Baker-analyzed reagent, >99.5 mass %), distilled water, and cobalt(II) chloride (Probus, >99.5 mass %). They were used without further purification.

The equilibrium apparatus was a recirculating still of the Labodest model, manufactured by Fischer. The vapor–liquid equilibrium data were obtained at 100.00 ± 0.04 kPa. The vapor pressure of water with a varying concentration of salt was also measured with the same apparatus.

Every experimental point was obtained from an initial sample prepared gravimetrically by using a Sartorius analytical balance with a precision of ±0.0001 g and, afterward, by adding different quantities of ethanol, water, ethanol–salt solution or water–salt solution. Each experiment was kept at the boiling point for 15 min or more to ensure the stationary state. The accuracy of the temperature measurement was ±0.1 K.

Compositions of the condensed vapor phase were analyzed by using a Hewlett-Packard 5700 A gas chromatograph with a thermal conductivity detector, connected to a Hewlett-Packard 3394 A integrator. The chromatographic column (2 m × 1/8 in.) was packed with Porapak P. The gas carrier was helium flowing at 50 cm³/min, and the column temperature was 383 K. The calibration was carried out with gravimetrically prepared standard solutions. The accuracy of the measured vapor-phase mole fraction was ±0.002.

The liquid phase was composed of ethanol, water, and cobalt(II) chloride. The salt composition in the liquid phase was gravimetrically determined after separating the volatile components by evaporation to dryness. Water and ethanol compositions in the liquid phase containing dissolved salt were obtained by density measurements with an Anton Paar DMA 55 densimeter matched to a Julabo circulator with proportional temperature control and an automatic drift correction system that kept the samples at 298.15 ± 0.01 K. The densimeter was calibrated by measuring a set of standard solutions with known mole fractions of ethanol, water, and salt in the ternary mixtures, and the correlation obtained was used to calculate the ethanol mole fraction with the known salt mole fraction. The accuracy in the measurement of the ethanol, water, and cobalt(II) chloride mole fractions in the liquid phase was ±0.003. This method of analyzing the composition of salt-containing mixtures was found to be reproducible and of consistent accuracy, as described in a previous work (6).

## Results and Discussion

In Tables 1 and 2, the vapor–liquid equilibrium for the ethanol (1) + water (2) + cobalt(II) chloride (3) system at a pressure of 100.0 kPa is reported. Included are the equilibrium temperature ($T$/K), the mole fractions of ethanol ($x_1$), water ($x_2$), and salt ($x_3$) in the ternary liquid phase, and the mole fraction of ethanol in the vapor phase ($y_1$). In Table 1, we give the results in the range of $x_3 < 0.23x_2$, and in Table 2, we show the results in the range of $x_3 > 0.23x_2$.

To make possible the thermodynamic treatment of vapor–liquid equilibrium, we postulate that, in the range of liquid-phase salt compositions studied, the salt is in ionic form and is associated only with the water (5). Therefore, the ternary system can be treated as a pseudobinary system composed of pure ethanol (I) and water + salt (II) components. This assumption is only acceptable when there is enough water to dissolve all the salt present in

**Table 1. Vapor–Liquid Equilibrium for Ethanol + Water + Cobalt(II) Chloride at 100.0 kPa in the Range of $x_3 < 0.23x_2$**

| T/K | $x_1$ | $x_2$ | $x_3$ | $y_1$ | $\gamma_I$ | $\gamma_{II}$ | T/K | $x_1$ | $x_2$ | $x_3$ | $y_1$ | $\gamma_I$ | $\gamma_{II}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 364.2 | 0.035 | 0.936 | 0.029 | 0.374 | 6.341 | 0.954 | 353.7 | 0.365 | 0.593 | 0.042 | 0.702 | 1.690 | 1.239 |
| 364.3 | 0.038 | 0.919 | 0.043 | 0.424 | 6.635 | 0.933 | 353.2 | 0.390 | 0.572 | 0.038 | 0.705 | 1.615 | 1.279 |
| 363.9 | 0.040 | 0.908 | 0.052 | 0.459 | 6.925 | 0.934 | 353.7 | 0.397 | 0.554 | 0.049 | 0.721 | 1.595 | 1.329 |
| 362.3 | 0.051 | 0.934 | 0.015 | 0.397 | 5.022 | 0.956 | 353.9 | 0.398 | 0.549 | 0.053 | 0.723 | 1.580 | 1.360 |
| 360.2 | 0.061 | 0.889 | 0.050 | 0.539 | 6.130 | 0.936 | 353.4 | 0.405 | 0.556 | 0.039 | 0.711 | 1.558 | 1.292 |
| 361.4 | 0.061 | 0.930 | 0.009 | 0.415 | 4.485 | 0.952 | 353.3 | 0.406 | 0.586 | 0.009 | 0.653 | 1.436 | 1.249 |
| 360.1 | 0.067 | 0.919 | 0.014 | 0.455 | 4.692 | 0.954 | 353.2 | 0.413 | 0.569 | 0.019 | 0.681 | 1.477 | 1.239 |
| 358.7 | 0.076 | 0.896 | 0.028 | 0.527 | 5.021 | 0.930 | 353.2 | 0.416 | 0.554 | 0.030 | 0.703 | 1.512 | 1.272 |
| 358.0 | 0.086 | 0.874 | 0.040 | 0.565 | 4.910 | 0.944 | 353.5 | 0.428 | 0.525 | 0.048 | 0.730 | 1.508 | 1.384 |
| 358.3 | 0.089 | 0.854 | 0.057 | 0.601 | 4.987 | 0.942 | 353.1 | 0.435 | 0.533 | 0.031 | 0.711 | 1.465 | 1.313 |
| 358.0 | 0.096 | 0.891 | 0.013 | 0.516 | 3.999 | 0.949 | 353.6 | 0.474 | 0.468 | 0.058 | 0.758 | 1.405 | 1.538 |
| 357.3 | 0.107 | 0.846 | 0.047 | 0.601 | 4.286 | 0.951 | 352.8 | 0.475 | 0.509 | 0.016 | 0.698 | 1.336 | 1.332 |
| 357.5 | 0.117 | 0.876 | 0.007 | 0.515 | 3.364 | 0.974 | 353.1 | 0.478 | 0.477 | 0.045 | 0.744 | 1.396 | 1.474 |
| 356.8 | 0.121 | 0.863 | 0.016 | 0.551 | 3.558 | 0.959 | 353.8 | 0.488 | 0.447 | 0.065 | 0.765 | 1.369 | 1.601 |
| 356.9 | 0.124 | 0.821 | 0.055 | 0.630 | 3.946 | 0.966 | 353.4 | 0.492 | 0.454 | 0.055 | 0.759 | 1.369 | 1.575 |
| 356.3 | 0.127 | 0.838 | 0.035 | 0.605 | 3.790 | 0.943 | 352.7 | 0.498 | 0.471 | 0.031 | 0.732 | 1.339 | 1.441 |
| 355.8 | 0.148 | 0.827 | 0.025 | 0.591 | 3.242 | 0.979 | 352.7 | 0.505 | 0.469 | 0.026 | 0.728 | 1.315 | 1.403 |
| 355.9 | 0.153 | 0.828 | 0.019 | 0.586 | 3.104 | 0.966 | 352.8 | 0.506 | 0.457 | 0.036 | 0.744 | 1.333 | 1.482 |
| 355.8 | 0.154 | 0.801 | 0.045 | 0.632 | 3.321 | 0.985 | 353.5 | 0.539 | 0.396 | 0.066 | 0.790 | 1.294 | 1.644 |
| 355.2 | 0.181 | 0.786 | 0.033 | 0.628 | 2.883 | 0.992 | 352.4 | 0.547 | 0.439 | 0.014 | 0.721 | 1.216 | 1.450 |
| 355.2 | 0.186 | 0.791 | 0.023 | 0.608 | 2.712 | 1.000 | 353.3 | 0.548 | 0.392 | 0.061 | 0.787 | 1.279 | 1.700 |
| 355.5 | 0.187 | 0.762 | 0.051 | 0.652 | 2.865 | 1.033 | 352.9 | 0.548 | 0.401 | 0.051 | 0.779 | 1.284 | 1.689 |
| 355.4 | 0.189 | 0.800 | 0.012 | 0.579 | 2.530 | 1.019 | 353.7 | 0.548 | 0.380 | 0.072 | 0.797 | 1.274 | 1.564 |
| 354.7 | 0.221 | 0.752 | 0.027 | 0.629 | 2.404 | 1.033 | 352.5 | 0.556 | 0.414 | 0.030 | 0.754 | 1.245 | 1.550 |
| 354.6 | 0.233 | 0.745 | 0.022 | 0.624 | 2.274 | 1.045 | 352.6 | 0.576 | 0.383 | 0.041 | 0.779 | 1.236 | 1.704 |
| 354.7 | 0.239 | 0.722 | 0.040 | 0.656 | 2.323 | 1.065 | 352.2 | 0.593 | 0.382 | 0.025 | 0.761 | 1.192 | 1.608 |
| 354.7 | 0.250 | 0.741 | 0.009 | 0.601 | 2.033 | 1.067 | 352.0 | 0.597 | 0.382 | 0.021 | 0.759 | 1.190 | 1.569 |
| 354.2 | 0.251 | 0.718 | 0.031 | 0.652 | 2.234 | 1.059 | 352.8 | 0.613 | 0.331 | 0.056 | 0.814 | 1.204 | 1.785 |
| 354.4 | 0.257 | 0.713 | 0.030 | 0.650 | 2.161 | 1.062 | 353.2 | 0.617 | 0.316 | 0.067 | 0.826 | 1.197 | 1.494 |
| 354.4 | 0.262 | 0.702 | 0.036 | 0.659 | 2.149 | 1.084 | 352.2 | 0.621 | 0.345 | 0.033 | 0.788 | 1.177 | 1.774 |
| 354.3 | 0.271 | 0.711 | 0.018 | 0.631 | 1.998 | 1.075 | 352.0 | 0.625 | 0.363 | 0.012 | 0.753 | 1.127 | 1.586 |
| 354.5 | 0.272 | 0.722 | 0.007 | 0.602 | 1.890 | 1.095 | 352.1 | 0.634 | 0.342 | 0.024 | 0.782 | 1.149 | 1.686 |
| 354.2 | 0.283 | 0.682 | 0.036 | 0.666 | 2.031 | 1.104 | 351.7 | 0.654 | 0.339 | 0.007 | 0.780 | 1.129 | 1.485 |
| 354.0 | 0.298 | 0.659 | 0.044 | 0.685 | 1.996 | 1.148 | 351.8 | 0.688 | 0.293 | 0.019 | 0.795 | 1.090 | 1.819 |
| 354.0 | 0.301 | 0.684 | 0.015 | 0.632 | 1.822 | 1.116 | 351.8 | 0.690 | 0.295 | 0.016 | 0.796 | 1.088 | 1.738 |
| 354.2 | 0.302 | 0.657 | 0.041 | 0.679 | 1.938 | 1.145 | 352.3 | 0.708 | 0.242 | 0.050 | 0.856 | 1.117 | 1.731 |
| 353.9 | 0.315 | 0.657 | 0.028 | 0.666 | 1.841 | 1.123 | 351.8 | 0.717 | 0.255 | 0.027 | 0.831 | 1.092 | 2.014 |
| 354.0 | 0.320 | 0.644 | 0.036 | 0.677 | 1.832 | 1.156 | 352.0 | 0.724 | 0.237 | 0.039 | 0.849 | 1.097 | 2.103 |
| 353.9 | 0.336 | 0.622 | 0.041 | 0.692 | 1.791 | 1.192 | 351.4 | 0.777 | 0.210 | 0.013 | 0.837 | 1.030 | 2.042 |
| 353.7 | 0.346 | 0.643 | 0.011 | 0.641 | 1.627 | 1.165 | 351.4 | 0.778 | 0.211 | 0.011 | 0.838 | 1.031 | 1.967 |
| 354.0 | 0.348 | 0.605 | 0.047 | 0.701 | 1.748 | 1.234 | 351.8 | 0.788 | 0.182 | 0.030 | 0.878 | 1.050 | 2.230 |
| 353.5 | 0.361 | 0.615 | 0.024 | 0.674 | 1.649 | 1.178 | 351.5 | 0.795 | 0.188 | 0.017 | 0.872 | 1.046 | 1.983 |

**Table 2. Vapor–Liquid Equilibrium for Ethanol + Water + Cobalt(II) Chloride at 100.0 kPa in the Range of $x_3 > 0.23x_2$**

| T/K | $x_1$ | $x_2$ | $x_3$ | $y_1$ |
|---|---|---|---|---|
| 353.6 | 0.625 | 0.299 | 0.076 | 0.843 |
| 353.8 | 0.631 | 0.287 | 0.082 | 0.845 |
| 352.8 | 0.678 | 0.260 | 0.062 | 0.854 |
| 353.8 | 0.683 | 0.229 | 0.089 | 0.883 |
| 353.1 | 0.707 | 0.218 | 0.075 | 0.880 |
| 352.8 | 0.730 | 0.204 | 0.067 | 0.889 |
| 353.7 | 0.740 | 0.170 | 0.090 | 0.921 |
| 353.0 | 0.760 | 0.160 | 0.081 | 0.917 |
| 354.0 | 0.760 | 0.142 | 0.098 | 0.935 |
| 352.3 | 0.776 | 0.171 | 0.054 | 0.899 |
| 352.0 | 0.792 | 0.166 | 0.042 | 0.894 |
| 354.0 | 0.804 | 0.097 | 0.099 | 0.965 |
| 352.9 | 0.807 | 0.119 | 0.074 | 0.938 |
| 353.2 | 0.827 | 0.085 | 0.089 | 0.962 |
| 354.4 | 0.840 | 0.051 | 0.109 | 0.983 |
| 352.4 | 0.856 | 0.084 | 0.060 | 0.953 |
| 352.1 | 0.869 | 0.085 | 0.046 | 0.947 |
| 351.8 | 0.874 | 0.093 | 0.033 | 0.938 |
| 351.5 | 0.892 | 0.088 | 0.020 | 0.931 |

**Table 3. Boiling Points of Water + Cobalt(II) Chloride Mixtures at 100.0 kPa**

| $x_3^*$ | T/K | $x_3^*$ | T/K |
|---|---|---|---|
| 0.113 | 387.7 | 0.055 | 378.6 |
| 0.109 | 386.9 | 0.053 | 378.4 |
| 0.106 | 386.5 | 0.051 | 378.1 |
| 0.102 | 385.6 | 0.049 | 377.8 |
| 0.097 | 384.9 | 0.048 | 377.6 |
| 0.094 | 384.4 | 0.046 | 377.3 |
| 0.091 | 383.9 | 0.044 | 377.1 |
| 0.089 | 383.6 | 0.041 | 376.7 |
| 0.085 | 383.1 | 0.039 | 376.4 |
| 0.082 | 382.5 | 0.034 | 375.8 |
| 0.077 | 382.0 | 0.031 | 375.4 |
| 0.074 | 381.5 | 0.028 | 375.0 |
| 0.071 | 380.9 | 0.025 | 374.7 |
| 0.069 | 380.6 | 0.023 | 374.4 |
| 0.066 | 380.3 | 0.020 | 374.2 |
| 0.065 | 380.0 | 0.018 | 373.9 |
| 0.062 | 379.6 | 0.015 | 373.7 |
| 0.060 | 379.3 | 0.012 | 373.4 |
| 0.057 | 378.9 | | |

the liquid phase, which happens when $x_3 < 0.23x_2$. When equilibrium is established between vapor and liquid phases, the activity coefficients of both pseudocomponents will be given by these expressions:

$$\gamma_I = y_I\phi_I P/x_I P_I^\circ \qquad \gamma_{II} = y_{II}\phi_{II} P/x_{II} P_{II}^\circ \qquad (1)$$

where $x_I$ is the mole fraction of pseudocomponent I in the

liquid phase ($=x_1$), $x_{II}$ is the mole fraction of pseudocomponent II in the liquid phase ($=x_2 + x_3$), $y_I$ is the mole fraction of ethanol in the vapor phase ($=y_1$), $y_{II}$ is the mole fraction of water in the vapor phase ($=1 - y_1$), $\phi_I$ is the fugacity coefficient of pseudocomponent I in the vapor phase, $\phi_{II}$ is the fugacity coefficient of pseudocomponent II in the vapor phase, $P$ is the system pressure (kPa), $P_I^\circ$ is the vapor pressure of pure ethanol ($=P_1^\circ$), and $P_{II}^\circ$ is the vapor pressure of pseudocomponent II, both calculated at
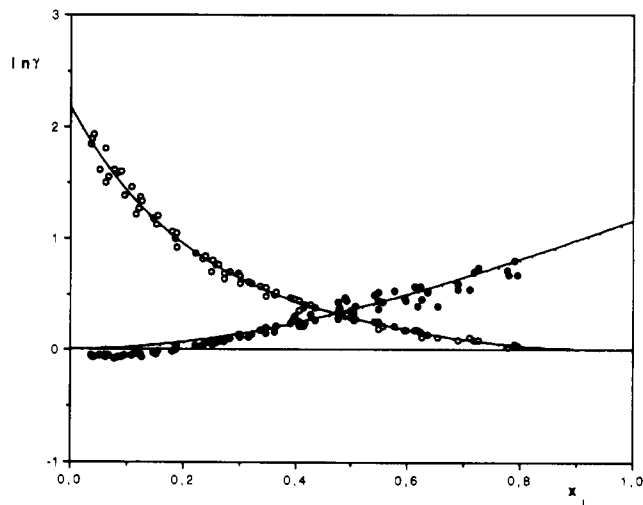
**Figure 1.** Experimental solvent activity coefficients for the system ethanol + water + cobalt(II) chloride at 100.0 kPa: (O) ln $\gamma_I$, (●) ln $\gamma_{II}$.
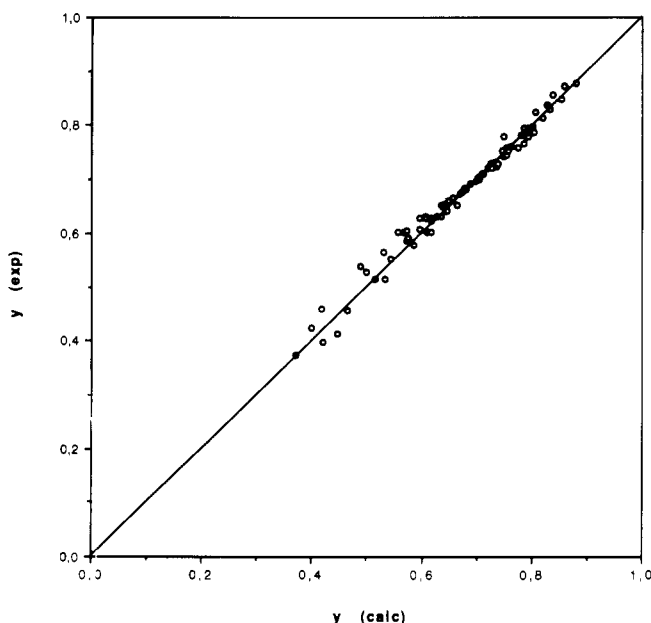


**Figure 2.** Comparison of calculated vapor composition, $y_{calcd}$, with experimental values, $y_{exptl}$.

the equilibrium temperature (kPa). The value of $P_{II}°$ depends on the temperature and on the salt concentration. Jaques and Furter (*16*) propose that this dependency can be expressed as

$$P_{II}° = P_2°(T) \; \epsilon(x_3^*) \qquad (2)$$

where $P_2°$ is the vapor pressure of pure water (kPa) and $\epsilon$ is the vapor pressure correction factor, which only depends on $x_3^*$, the mole fraction of the component salt in the pseudocomponent II ($=x_3/(x_2 + x_3)$).

The vapor pressure correction factor was computed by the method of Jaques and Furter (*16*) from results of the vapor pressure of water with different amounts of salt that we have obtained, given in Table 3, and the vapor pressure of pure water obtained from the Antoine equation with the parameters given in the literature (*17*), both at the same temperature.

The correlation equation obtained from experimental results for the vapor pressure correction factor ($\epsilon$) with the
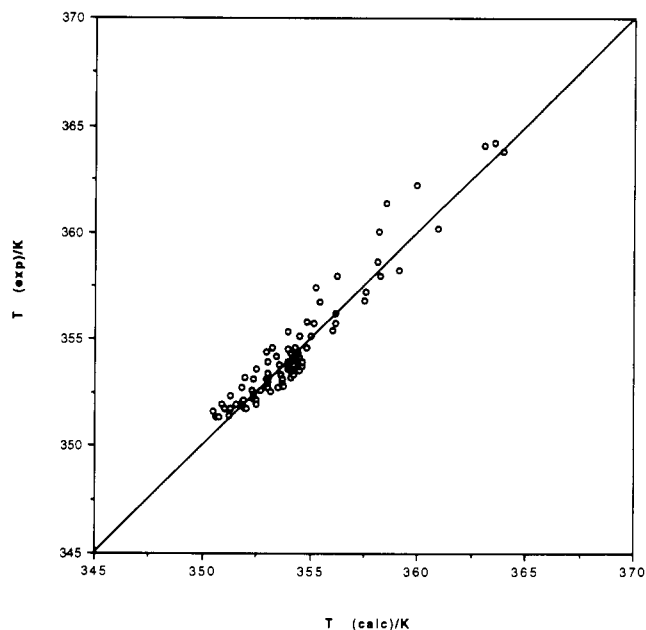


**Figure 3.** Comparison of calculated bubble points with experimental values.

salt mole fraction in pseudocomponent II ($x_3^*$), for the entire range of salt concentrations studied, is

$$\epsilon = 1 - 1.9393x_3^* - 36.6838 \, (x_3^*)^2 + 204.6836 \, (x_3^*)^3 \qquad (3)$$

The fugacity coefficients $\phi_I$ and $\phi_{II}$ were calculated by means of the virial equation of state, and the second virial coefficients were calculated from the Pitzer and Curl equations (*18*) and the Tsonopoulos correlation correction (*19*) for polar compounds.

For each experimental value, the activity coefficients of pseudocomponents I and II in the liquid phase have been calculated following the above procedure. The obtained values of $\gamma_I$ and $\gamma_{II}$ are shown in columns 6 and 7 of Table 1.

In Figure 1, the logarithms of $\gamma_I$ and $\gamma_{II}$ are plotted against $x_I$. In this figure, the logarithms of activity coefficients for both pseudocomponents can be adjusted to one curve whatever the salt concentration may be. This fact implies that the pseudobinary model proposed explains the behavior of the system in the range of compositions established.

The thermodynamic consistency of the results was tested by the integral method described by Herington (*20, 21*) and Redlich and Kister (*22*). The area test parameters, $D$ and $J$, obtained were

$$D = 9.92\%, \quad J = 5.51\%, \quad \text{and} \quad D - J = 4.41\%$$

According to Herington's interpretation of the area test results, the results were probably consistent.

For the purpose of reproducing experimental data, the activity coefficients obtained for every pseudocomponent were adjusted against their composition in the liquid phase, and the equations found were

$$\ln \gamma_I^* = (2.1860 - 5.0650x_I + 8.9881x_I^2 - \\ 5.8914x_I^3)(1 - x_I)^2 \qquad (4)$$

$$\ln \gamma_{II}^* = (1.1558 + 0.56619x_{II})(1 - x_{II})^2 \qquad (5)$$

These equations were used to recalculate the vapor composition and temperature values in equilibrium from the

liquid phase composition. From comparison of experimental and calculated values, we found

$y_{exptl} - y_{calcd}$:  mean, 0.012

standard deviation, 0.015

$T_{exptl} - T_{calcd}$:  mean, 0.67 K

standard deviation, 0.83 K

The experimental values are plotted against the corresponding calculated ones in Figure 2 for the vapor composition and in Figure 3 for the temperature. In these figures, the agreement between both experimental and calculated values can be noted.

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