Calculation of Ternary Liquid-Liquid Equilibria

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Interest in the prediction of multicomponent equilibria from binary equilibria has been renewed by the recent paper of Renon and Prausnitz (*1*). They have developed a new activity coefficient equation and have applied it to the prediction of ternary vapor-liquid and liquid-liquid equilibria. We present here some additional observations concerning the prediction of ternary liquid-liquid equilibria. Some conclusions regarding the questionability of using mutual solubility data for parameter evaluation are also offered.

PREDICTION OF TERNARY LIQUID-LIQUID EQUILIBRIA

There have been several previous attempts at predicting ternary liquid-liquid equilibria from binary data employing a rigorous thermodynamic approach. Kenny (*2*) used the Van Laar and Margules equations in an attempt to calculate tie lines for a type I system. (We refer to ternary liquid-liquid systems with only one partially miscible binary as type I systems. Type II systems are designated as those systems with two partially miscible binaries having only one region of immiscibility.) The parameters for the two completely miscible binaries were evaluated from vapor-liquid data, while mutual solubility data were used for the partially miscible binary. Kenny found his calculated results were not in agreement with experimental data. Boberg (*3*) employed the Redlich-Kister equation in an attempt to calculate liquid-liquid equilibria for two type I systems. He also used vapor-liquid data to evaluate the parameters for the completely miscible binaries and mutual solubility data for the parameters for the partially miscible systems. Poor agreement was found between calculated and experimental ternary phase diagrams. Techo (*4*), using the Van Laar and Margules equations, observed reasonably good agreement between calculated and experimental data for several type II systems. His parameters for the partially miscible binaries were evaluated from mutual solubility data and he assumed the completely miscible binaries behaved as ideal solutions. Techo also attempted to predict several type I systems obtaining his parameters in the same manner as Kenny and Boberg. He reported poor agreement between calculated and experimental results.

More recently Renon and Prausnitz (*1*) presented the results of their attempt to predict three ternary liquid-liquid systems using their newly developed activity coefficient equation, the NRTL equation. This equation contains three parameters per binary system and no ternary parameters, however, they have developed rules for assigning a value to one of the NRTL parameters, the nonrandomness parameter, based on a classification of binary systems which allows the equation to be used with only two parameters per binary. Their calculations for these three ternary systems were performed with the NRTL equation by assigning a value to the nonrandomness parameter for each binary in accordance with their rules and then evaluating the two remaining parameters from binary data. Vapor-liquid data were used for completely miscible binaries and mutual solubility data were used for the partially miscible binaries. The comparison of calculated results with experimental data was made on triangular diagrams. As visual observation of their figures 6 through 8 suggests that tie line slopes were not predicted very well, we repeated the calculations for these systems using the NRTL parameters reported by Renon (*5*). In comparing the calculated and experimentally determined selectivity we found reasonably good agreement for the type II system, fair agreement for the acetone-chloroform-water system, and poor agreement for the octane-octene-nitroethane system.

Renon (*5*) has also reported the results of an unsuccessful attempt to apply the NRTL equation to the prediction of two other type I systems. The rules for assignment of the nonrandomness parameter were apparently inapplicable and Renon was able to match the calculated and experimental ternary binodal curves only by adjusting the nonrandomness parameter for the partially miscible binary systems.

Although only a modest number of ternary systems have been studied, when the findings of all investigators are examined collectively two conclusions emerge:

1. Liquid-liquid equilibria for type II ternary systems may be predicted reasonably well from binary data alone when parameters for the two partially miscible binaries are evaluated from mutual solubility data and the completely miscible binary is assumed to behave ideally.
2. Reasonable predictions of liquid-liquid equilibria for type I ternary systems from binary data alone cannot be expected when the ordinary two-parameter activity coefficient equations are used.

On first thought it seems paradoxical that better estimations can be obtained for type II systems than for type I systems when the type II system generally represents less ideal solution behavior (as evidenced by a larger region of immiscibility). The paradox can be resolved, however, by an analysis of the sensitivity of the ternary liquid-liquid calculations to errors in estimating activity coefficients. For this purpose we generated ternary phase diagrams for two synthetic systems, a type I and a type II system. These synthetic systems consist of tie

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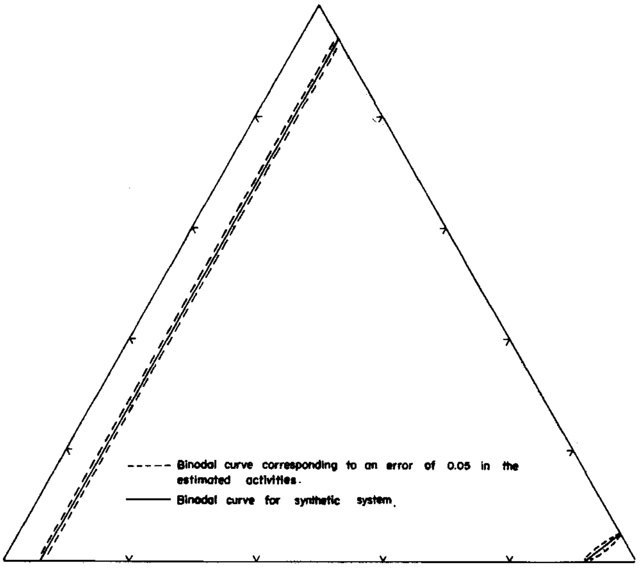

Fig. 1. The effect of an error in the estimated activities on the position of the binodal curve for a synthetic type II system.

lines calculated with a selected set of parameters in the NRTL equation. At each of the tie line compositions the partial derivatives of the activities with respect to the mole fractions

$$\left(\frac{\partial a_i}{\partial x_j}\right) \quad (i \text{ and } j = 1, 2, 3)$$

were also evaluated. The activity coefficients in these synthetic systems are known to be represented by the NRTL equation and therefore these partial derivatives can be used to calculate the displacement of the binodal curve which would result if the activity coefficient equation used to calculate tie lines estimated the activities incorrectly. A detailed account of this calculation procedure has been reported by Joy (*6*). The results of this calculation are shown in Figures 1 and 2 for an error of ± 0.05 in the activity. These figures show that the predictions for type I systems are much more sensitive to activity estimation errors than for type II systems. Essentially, the component in lowest concentration determines the location of the binodal curve and if this component is in very low concentration its activity gradient will be very steep and thus cause the binodal curve to be relatively insensitive to activity estimation errors. This is illustrated for the type I system shown on Figure 2 where the effect of estimation errors on the right-hand part of the binodal curve is so small that it cannot be shown graphically. Thus the binodal curves for ternary systems with low mutual solubility will be insensitive to errors in estimating activity coefficients. For the type II system one has the additional advantage that if the parameters are evaluated from mutual solubility data the binodal curve will be fixed at both ends.

This sensitivity analysis has focused only on the location of the binodal curve. Although no direct method of determining the effect of activity estimation errors on the tie line slopes appeared feasible, the selectivity seems much more sensitive to activity estimation errors. For example, Renon and Prausnitz's Figure 7 shows very good agreement between calculated and experimental binodal curves for the acetone-chloroform-water system suggesting an excellent fit, whereas a comparison based on selectivity indicates only fair agreement.

The sensitivity analysis suggests that the failure of previous prediction attempts for type I systems might be due to the inability of a two-parameter equation to adequately represent activity coefficients. Thus it seems desirable to attempt the prediction of type I systems where sufficient binary data are available to allow the use of a three-parameter activity coefficient equation. This requires some form of vapor-liquid data. Although few such systems are found in the literature, we were able to locate a single type I system for which sufficient equilibrium data were available. Ternary liquid-liquid equilibrium data for the system iso-octane-*n*-octane-nitroethane at 35°C. are reported by Hwa, Techo, and Ziegler (*7*) and isothermal total pressure data for the two binaries involving nitroethane were reported by Edwards (*8*). A Box search technique (*9*) described by Joy (*6*) was used to determine the best value of all three parameters in the NRTL equation from Edwards' data. These parameters represented an excellent fit of the experimental data for both systems. The iso-octane-*n*-octane system was assumed ideal and liquid-liquid equilibrium data were calculated for the ternary system using a procedure described by Joy (*6*). The calculated results, referred to as the *3 parameter NRTL prediction,* are compared with the experimental binodal curve on Figure 3 and the selectivity on Figure 4.

Calculations for this system were also performed using NRTL parameters reported by Renon (*5*). These parameters were obtained by assigning a value to the nonrandomness parameter and thereby determining only two parameters from binary data. Renon used vapor-liquid data to determine the iso-octane-nitroethane parameters and mutual solubility data to determine the n-octane—nitroethane parameters. These calculation results, referred to as the *two-parameter NRTL prediction,* are also shown on Figures 3 and 4.

The data reported by Hwa, et al. were determined by Techo (*4*) who estimated the maximum experimental error in the tie line compositions to be ± 3 wt. %, hence the experimental data points shown on Figure 3 were drawn to reflect this experimental uncertainty. It is un-

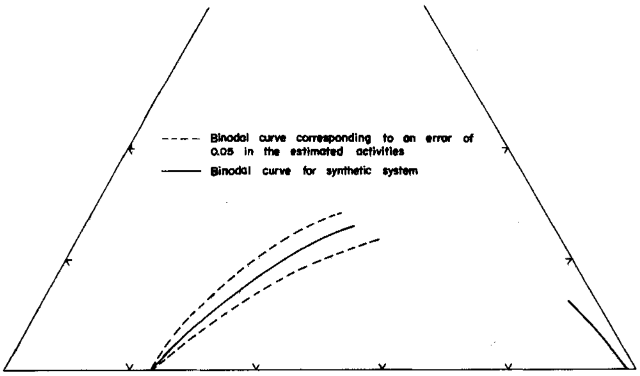

Fig. 2. The effect of an error in the estimated activities on the position of the binodal curve for a synthetic type I system.

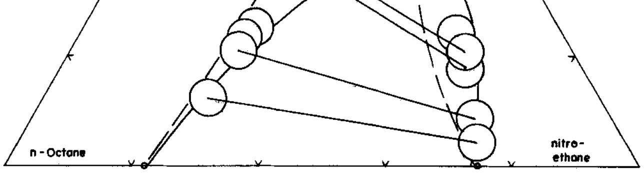

Fig. 3. Comparison of predicted binodal curve with experimental data. System: iso-octane—n-octane—nitroethane at 35°C.

fortunate that this system is subject to such a large experimental error, however, Figures 3 and 4 show that the three-parameter NRTL prediction agrees with the experimental data within the experimental error, whereas the two-parameter NRTL prediction is unsatisfactory. These results are consonant with the previously stated conclusion regarding type I systems and emphasize the necessity of good activity coefficient representation for the prediction of type I systems.

PARAMETERS FROM MUTUAL SOLUBILITY DATA

Because many of the previously cited workers have used binary mutual solubility data for the evaluation of parameters, the deficiencies of this practice should be discussed. There are two major limitations which need to be considered: only two parameters may be evaluated from mutual solubility data, and activity coefficients cannot be directly determined from the mutual solubility data and thus one has no idea of how well the chosen equation actually represents activity coefficients.

The ability to determine only two parameters is a serious limitation because partially miscible systems exhibit extreme deviations from ideal behavior and thus require activity coefficient equations with more flexibility than the common two-parameter variety. The deficiencies of the common two-parameter equations in this regard have been emphasized by Carlson and Colburn (*10*) and by Black (*11*).

In order to appreciate the second limitation of using mutual solubility data for parameter evaluation it is helpful to represent the process graphically. Refer to Figure 5 on which curves are drawn representing two activity coefficient equations which have different functional dependence of activity coefficient on composition (exaggerated here for illustrative purposes). The thermodynamic criterion of equilibrium when applied to component 1 can be written

$$\ln \gamma_1' - \ln \gamma_1'' = \ln \frac{x_1''}{x_1'} \qquad (1)$$

where x_1' and x_1'' are the mole fractions of component 1 in the two saturated liquid phases and γ_1' and γ_1'' are the activity coefficients at these compositions. Graphically, Equation (1) requires that the distances a and b, which represent the difference $\ln \gamma_1' - \ln \gamma_1''$ as expressed by equations A and B respectively, be identical and equal to $\ln x_1''/x_1'$. Further application of the same requirement to component 2 allows one to determine two parameters in an activity coefficient equation. One has, however, no assurance that the chosen equation will accurately represent activity coefficients over the range of miscibility or, as seen from Figure 5, even give correct values of the activity coefficients for the saturated phases.

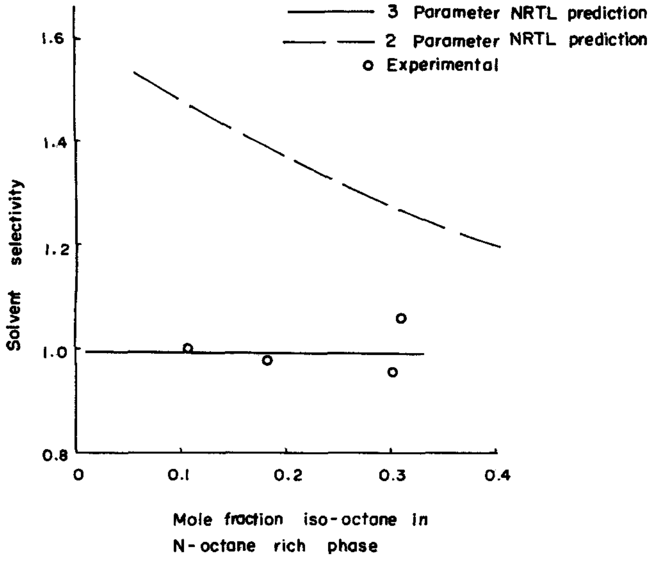

Fig. 4. Comparison of predicted solvent selectivity with experimental data. System: iso-octane—n-octane—nitroethane at 35°C.

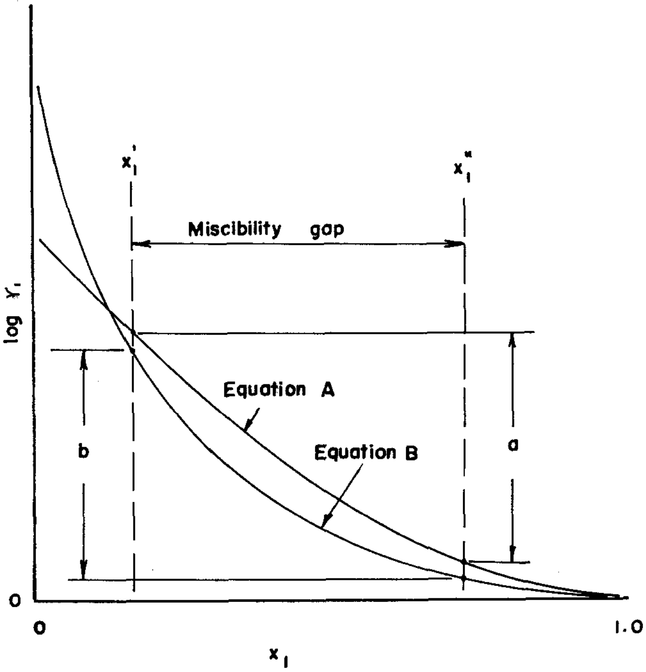

Fig. 5. Plot of log γ_1 vs. x_1 for two different activity coefficient equations.

This analysis conflicts with the claim of Renon and Prausnitz that the NRTL parameters evaluated from mutual solubility data are consistent with parameters obtained from vapor-liquid data. Their claim appears to be based (5) merely on the results of four nitroethane—paraffin hydrocarbon binaries. This is a very small number of systems on which to base such a generalization particularly in view of the fact that all four systems can be expected to exhibit similar solution behavior.

When other types of equilibrium data are lacking, one is often forced by necessity to use mutual solubility data for parameter evaluation, however, he should be aware of the uncertainty involved.

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