

## 무반복 상방정식 계산을 이용한 NRTL 액액평형 상수 추정

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### NRTL Parameter Estimation in LLE Systems Using Non-iterative Phase Equation Computation

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#### 1. Introduction

When process engineers design an extractor, they explore publications in search of a probable solvent and its thermodynamic model parameters, unless these parameters are listed in the process design software. The extraction process design begins with a ternary diagram of a liquid-liquid equilibrium (LLE) system. One of the activity coefficient models, the non-random two-liquid (NRTL) model, is widely used in this design. Although the model parameters, binary interaction parameters, and non-randomness factors are provided by LLE experimentalists, many of them, including those recently published, do not produce the ternary diagram when Aspen Plus and PRO/II, widely used design programs in field applications, are utilized. The Aspen Plus program generates the ternary diagram by examining the thermodynamic stability with the minimum Gibbs free energy. In other words, the parameters are inadequately estimated and do not consider the thermodynamic stability condition [1].

The K-value method for the LLE parameter estimation ensures material balance and isoactivity at the liquid-liquid interface, which does not consider the thermodynamic stability and the minimum Gibbs free energy conditions. The conventional objective functions in the parameter estimation for the NRTL model of the LLE system include deviations between the measured and calculated compositions, while the calculation includes the material balance and isoactivity requirement. The parameters are optimized for minimum deviation, and various optimization procedures have been proposed to ensure efficient estimation. Considering that there is no functional relationship between the parameters and the deviation, owing to the high nonlinearity of the NRTL model, many local minima were found depending on the optimization procedures [2] and the initial trial parameters. In other words, no specific optimization procedure is commonly applied for the parameter estimation.

In this study, we introduce a combined procedure of the NRTL parameter estimation for LLE systems using the K-value method and the minimum Gibbs free energy as an additional constraint to the conventional method. The formulation of the objective function and its solution procedures are explained in detail, and the estimation performances were evaluated using the reported tie-line data and the prediction results of Aspen Plus in the LLE systems.

#### 2. Gibbs Free Energy

The free energy of mixing considering the liquid-liquid systems is obtained, which determines the thermodynamic phase stability, as follows:

$$\frac{\Delta G_{mix}}{RT} = \sum_{k=1}^{N_p} \sum_{i=1}^{N_c} l_i^k (\ln x_i^k + \ln \gamma_i^k) \quad (1)$$

where  $x$  is the mole fraction of a component,  $l$  is the component liquid fraction, and  $R$  and  $T$  are the gas constant and absolute temperature, respectively.  $N_p$  is the number of liquid phases, and is the activity coefficient computed from the NRTL model.

When a mixture has stable multi-phases, its excess Gibbs free energy is minimized, and this can be considered as a constraint in the parameter estimation. This constraint facilitates the parameter estimation because it leads to optimization through a possible solution surface with the thermodynamic stability condition. Additionally, the constraint is used in the parameter estimation with an object function that minimizes the prediction error of the composition and the isoactivity constraint at the liquid-liquid interface, as follows:

$$\gamma_i^I x_i^I = \gamma_i^{II} x_i^{II} \quad (2)$$

where the superscripts denote the separated liquids,  $I$  and  $II$ .

### 3. LLE parameter estimation

For the LLE system of the water/ethanol/hexanol ternary mixture, the variation in the Gibbs free energy of mixing with different water compositions is calculated from Eq. (1). The two minimum compositions are in equilibrium, close to 0.2 and 0.9 of the water mole fraction, and the parameter estimation occurs at these compositions of phase separation while satisfying the material balance and isoactivity conditions.

The K-value method directly computes the compositions of the two liquid phases in equilibrium and satisfies the material balance and isoactivity conditions.

$$x_i^I = z_i / \{1 + (K_i - 1) L^{II}\} \quad (3)$$

where  $z_i$  is the composition of the feed mixture of two separate liquid phases in equilibrium,  $L^{II}$  is the fraction of liquid  $II$ , and  $K_i$  is the equilibrium constant of component  $i$ , derived from the activity coefficients. The feed composition was iteratively computed as using the flash equation in vapor-liquid-equilibrium (VLE) calculations, however, it was obtained from the tie-line data. When  $z_1$  is set to a value considering the liquid compositions measured,  $z_2$  is found from the two liquid compositions in equilibrium and the trigonometric relation. The diagram exhibits for  $z_1$  and  $z_2$  in the same relation. The summation equation results in  $z_3$  using  $z_1$  and  $z_2$ . The fraction of liquid  $II$  is also calculated using the lever rule. The direct computation of the liquid fraction simplifies the conventional K-value method by eliminating the iterative calculation.

Therefore, the objective function in the parameter estimation of an LLE system becomes

$$\text{minimize } f = \sum_{j=1}^{N_d} \sum_{k=1}^{N_p} \sum_{i=1}^{N_c} |x_{exp}^{i,k,j} - x_{pred}^{i,k,j}| \quad (4)$$

subject to

$$\min \frac{\Delta G_{mix}}{RT} = \sum_{k=1}^{N_p} \sum_{i=1}^{N_c} l_i^k (\ln x_i^k + \ln \gamma_i^k) \quad (5)$$

where  $N_d$  is the number of measured data points. Two liquid fractions were distinguished using  $L$  for the total fraction and  $l$  for the component fraction. The liquid  $II$  compositions were updated for the minimization of the Gibbs free energy of mixing, and the component fraction is determined from the total fraction and component composition. The liquid fraction,  $L^{II}$ , was computed directly using the lever rule.

For convenience, component 2 is denoted as a solute, and components 1 and 3 are mutually immiscible solvents for a ternary system. Liquid  $I$  contains a smaller amount of the solute (component 2) than that in liquid  $II$ . The predicted liquid composition is computed, where the activity coefficients are estimated using trial parameters. The parameters are updated until the minimum objective function is obtained. A local minimization procedure to solve Eq. (4) provides a thermodynamically stable solution, and the constraint in Eq. (5) results in an easy solution.

Using a newly proposed technique involving an improved optimization procedure the parameters provided less deviation than the previously reported parameters in an LLE system of tetrachloroethene/2-propanol/water. However, the parameters of the former method do not generate a ternary diagram using Aspen Plus or PRO/II, whereas those of the latter method do generate a ternary diagram. Notably, the diagram is the basis of the extraction process design, and it indicates that binary parameters with less deviation are not always useful in process design.

## 4. Results and Discussion

### 4.1. Performance evaluation

The thermodynamic stability of the estimated parameters was examined by drawing a ternary diagram using Aspen Plus. Some of parameters published in the references failed to produce the diagram. Representative systems were selected for the different types of ternary diagrams. The ternary diagrams are classified into three groups: type I, type II, and type 0, based on the number of miscible component pairs. The type I system has one immiscible pair of solvents, to which 75% of LLE systems belong. It includes a common composition in two separate liquid phases, called a plait point. Fig. 1(a) shows a representative of the type-I LLE systems. The ternary diagrams compare the experimental measurements in plus symbols, the NRTL model computed data with the estimated parameters of this study in circles, and Aspen Plus computed values in multiplication signs. The estimated parameters were used in the Aspen Plus computation, which indicates that the proposed parameter estimation procedure is compatible with Aspen Plus. The ternary diagrams of the measured, NRTL estimated, and Aspen Plus computed values were in concord. Therefore, an extraction process can be designed using Aspen Plus with the parameters obtained from the experimental measurements of the targeted ternary system.

The type II system accounts for 20% of LLE systems, and one solvent is partially miscible with others. Fig. 1(b) illustrates a representative system in the group, and no plait point is observed in the systems. A comparison of the measured, estimated, and Aspen Plus computed results shows that the proposed procedure is also suitable for the group. The ternary diagram estimated using Aspen plus, indicated by multiplication symbols, exhibits the thermodynamic stability of the estimated parameters. In comparison

to the reference data, indicated by square symbols, the parameters of this study were predicted to be closer to the experimental data. The RMSD of this study was 0.011, whereas the reference parameters were predicted with an RMSD of 0.058. Further, the reference parameters failed to produce a ternary diagram using Aspen Plus. This indicates that the parameter estimation was not completely accurate for the type-0 system. The proposed parameter estimation procedure worked properly with all groups of LLE systems with less deviation than the previous studies except the parameters of no ternary diagram.

### Conclusions

A new method for estimating the binary parameters of NRTL models in LLE systems is proposed, which involves modifying the conventional K-value method and including the condition of minimum Gibbs free energy of mixing in the optimization of the measured tie-line data and estimated values. The iterative computation of the phase equation is eliminated by directly solving the phase equation to reduce the computation effort and improved convergence during the parameter estimation. Adding the minimum Gibbs free energy of mixing condition ensured the generation of the ternary diagram required for the extraction process design. The mean deviations of this study were less compared to the published results, and the ternary diagrams showed close tie-line data to the Aspen Plus computed values. The representative systems include all three types of LLE ternary diagrams, demonstrating the performance of the proposed procedure.

### References

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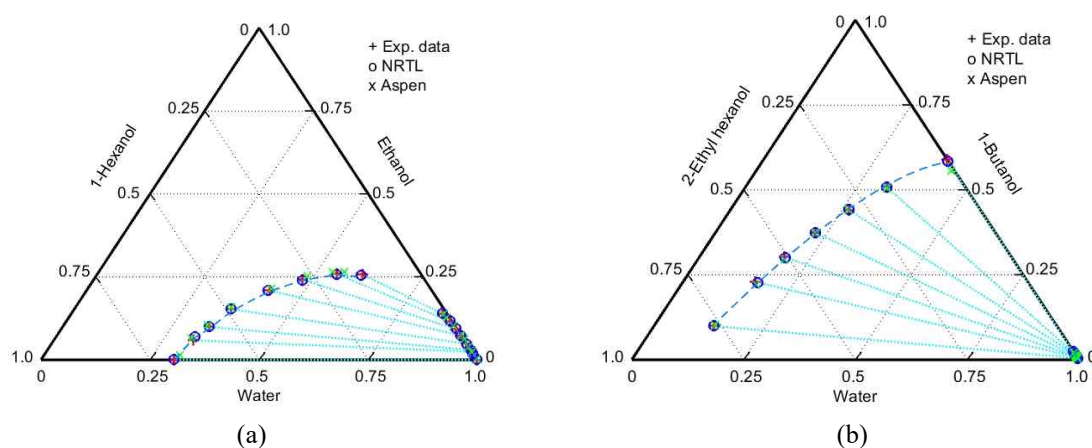


Fig. 1. Comparison of experimental measurements and predicted values using the estimated NRTL parameters in this study and Aspen Plus.