

## 자유에너지 최소화를 이용한 NRTL 기액평형 상수 추정

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### NRTL Parameter Estimation in VLE System Using Minimum Gibbs Free Energy

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#### 1. Introduction

Conventional objective functions in NRTL (non-random two-liquid) binary interaction parameter estimation for VLE (vapor-liquid equilibrium) system include absolute errors between measured and predicted vapor composition, temperature, and activity coefficient, either in one or combination of two. The parameters are optimized for the minimum deviation, and various optimization procedures have been proposed for efficient parameter estimation. Because there is no functional relation between the parameters and deviation due to high nonlinearity of the NRTL model, many local minimums are found depending on the optimization procedure [1]. Therefore, no specific global or local optimization procedure was dominantly applied to the parameter estimation.

When a mixture is stably separated, its excess Gibbs free energy becomes minimum that can be used in the parameter estimation as a constraint. This constraint helps the parameter estimation much easier, because it leads to the optimization through possible solution surface. Its use in LLE (liquid-liquid equilibrium) parameter estimation with an object function minimizing the prediction error of composition and two constraints of isoactivity at two-liquid interface.

$$\gamma_i^I x_i^I = \gamma_i^{II} x_i^{II} \quad (1)$$

where  $\gamma$  and  $x$  are activity coefficient and liquid composition of component  $i$ , and superscripts denote separated liquid  $I$  and  $II$ .

Secondly, the Gibbs tangent plane lying below Gibbs free energy surface [2].

$$\Delta G(T, x^p) + \left. \frac{\partial \Delta G}{\partial x} \right|_{T, x^p} (x - x^p) \leq \Delta G(T, x) \quad (2)$$

where superscript  $p$  indicates a predicted value, and  $T$  is absolute temperature. The searching procedure examines the possible solution of thermodynamically stable ensuring minimum Gibbs free energy, which drastically reduces computation effort. However, the problem is solved with a global optimization technique using a bilevel program.

In this study minimizing the Gibbs free energy of mixing is utilized as an added constraint to the conventional parameter estimation of binary interaction parameters in VLE NRTL model. The

formulation of problems and their solution procedures are explained in detail, and their performances are evaluated with the published parameters for measured data in various ternary systems of VLE model.

## 2. Gibbs Free Energy

When a total of Gibbs free energy of two split phases of a mixture becomes less than that of single phase, phase split occurs spontaneously. The thermodynamic stability condition has been rarely utilized in the estimation of NRTL binary interaction parameters for VLE system. Even widely used commercial program Aspen Plus does not check the minimum Gibbs free energy in its parameter estimation procedure. However, it minimizes the Gibbs free energy, when a ternary diagram of LLE is drawn.

The Gibbs free energy of mixing is given as

$$\Delta g_{mix} = \sum_{k=1}^{N_p} \sum_{i=1}^{N_c} l_i^k (\ln x_i^k + \ln \gamma_i^k) + \sum_{i=1}^{N_c} v_i (\ln y_i + \ln \varphi_i) \quad (3)$$

where  $x$  and  $y$  are mole fraction of a component in liquid and vapor, respectively, and  $\gamma$  and  $\varphi$  are activity and fugacity coefficients. Further  $l$  and  $v$  are molar flow rates of liquid and vapor, and  $N_c$  and  $N_p$  are numbers of components and liquid phases.

## 3. VLE parameter estimation

The NRTL model is an activity coefficient model, and is widely used in process design because its parameters are derived from various ways. Note that the parameters between the same molecules are zero. The following equation gives the activity coefficient of component  $i$  in a liquid phase.

$$\ln \gamma_i = \frac{\sum_{j=1}^N \tau_{ji} G_{ji} x_j}{\sum_{k=1}^N G_{ki} x_k} + \sum_{j=1}^N \frac{x_j G_{ij}}{\sum_{l=1}^N G_{lj} x_l} \left[ \tau_{ij} - \frac{\sum_{m=1}^N \tau_{mj} G_{mj} x_m}{\sum_{k=1}^N G_{kj} x_k} \right] \quad (4)$$

where  $N$  is the component number and  $x_j$  is the liquid composition of component  $j$  in mole fraction. From the binary interaction parameters,  $a_{ji}$ , and non-randomness factors,  $\alpha_{ji}$ , other parameters are given from the estimation.

Though the activity coefficients are applied to liquid, they are related to vapor phase.

$$\gamma_i x_i P_i = \varphi_i y_i P^T \quad (5)$$

where  $P_i$  is pure component pressure, and  $P^T$  is total system pressure.  $\varphi_i$  is fugacity coefficient, and  $y_i$  is vapor composition of component  $i$  in mole fraction.

The prediction accuracy of the thermodynamic models is crucial in process design utilizing modern computer programs, such as Aspen Plus and Pro/II. In the VLE parameter estimation the liquid composition is fixed at the measured composition, where the predicted temperature is matched to the measured by finding a set of parameters, binary interaction parameters in NRTL model. In search of binary interaction parameters the difference of the temperatures is minimized, and the predicted

temperatures are examined only at the minimum Gibbs free energy of mixing. The condition of minimum energy significantly simplifies the parameter estimation. While current estimation techniques examine large range of temperature or vapor composition for the minimum deviation, the proposed scheme searches at limited range by ensuring thermodynamic requirement of phase split.

An objective function becomes in an isobaric process of VLE here

$$\text{minimize } f = \sum_{j=1}^{N_d} \sum_{k=1}^{N_p} |T_{exp}^{j,k} - T_{pred}^{j,k}| \quad (6)$$

subject to

$$\begin{aligned} \min \Delta G_{mix} &= \sum_{i=1}^{N_c} l_i \ln(\gamma_i x_i) \\ \min \Delta G_{mix} &= \sum_{i=1}^{N_c} v_i \ln(\phi_i y_i) \\ P^T - \sum_{i=1}^{N_c} \gamma_i x_i P_i &= 0 \end{aligned}$$

where  $T$  is temperature,  $N_d$  is number of measured data.  $P^T$  is total system pressure, and  $P_i$  is pure component pressure computed with the Antoine equation, the coefficients of which were taken from the database of Aspen Plus. The summation of vapor compositions becomes unity. Note that the pressure was an atmospheric pressure, and fugacity coefficients are assumed ideal.

#### 4. Results and Discussion

Note that liquid composition was set at the measured value of VLE estimation procedure. Therefore, the mean deviation is computed by

$$dy = \sum_{j=1}^{N_d} \sum_{i=1}^{N_c} |y_{exp}^i - y_{pred}^i| / N_c / N_d \quad (7)$$

In order to validate the predicted temperature, vapor composition, and liquid activity coefficient for a set of NRTL parameters, those of Aspen Plus simulation with the same NRTL parameters were retrieved and compared to the prediction results of this study.

The individual deviations of 17 systems were averaged for better performance evaluation of parameter estimation. While the average deviations of vapor composition in NRTL model prediction of 3 binary systems are between 0.0110 and 0.0219 for 3 estimation procedures, those in ternary systems are 0.0149 and 0.0327. Because the binary parameters were estimated from binary measurement data, the same in 3 procedures, their ternary prediction gives more deviation. The results of the opposite procedure, estimation with ternary data and prediction for binary vapor composition, are explained. The prediction of binary composition and temperature of this study was 16% and 60%, respectively, less than that of the published parameters. In ternary data prediction, 17% and 35% less deviation of vapor

composition and temperature was yielded from the binary parameters of this study compared to the literature parameters.

Figure 1 shows difference in the change of minimum Gibbs free energy between 2 sets of NRTL binary parameters in a system of acetonitrile/*n*-propanol/ethylene glycol. In the reference equilibrium was measured at a temperature of 374.54 K and an acetonitrile mole fraction in liquid of 0.351. As demonstrated in Figure 1a computed with properties found from Aspen Plus using the binary parameters of this study, the temperature and liquid composition are closer to the measurement than Figure 1b, of which the properties are found using the literature binary parameters.

The proposed procedure of this study becomes much easier and faster process. When the condition of minimum Gibbs free energy is satisfied at the compositions in phase split, the NRTL parameter estimation for minimum prediction error becomes much simpler than searching for whole temperature range as one of conventional parameter estimations.

### Conclusions

A new method for estimating the parameters of NRTL models in VLE systems is proposed by considering the basic principle of phase separation and the minimum Gibbs free energy of mixing at the interface. The performance of the newly estimated parameters was evaluated in 17 VLE systems, and it was found that the deviation from the measured vapor composition was 15% less compared with that predicted when using previously reported parameters estimated using the conventional method of minimizing the composition and temperature deviation only. Additionally, extensions to the measured no-vapor-composition VLE data and to the different number of VLE measurement components were investigated to verify the usefulness of the proposed method.

### References

- [1] Marcilla A, Reyes-Labarta JA, Olaya MM. *Fluid Phase Equilib.* 2017, 433, 243-252.
- [2] Bollas GM, Barton PI, Mitsos A. Bilevel optimization formulation for parameter estimation in vapor-liquid(-liquid) phase equilibrium problems. *Chem Eng Sci.* 2009, 64, 1768-1783.

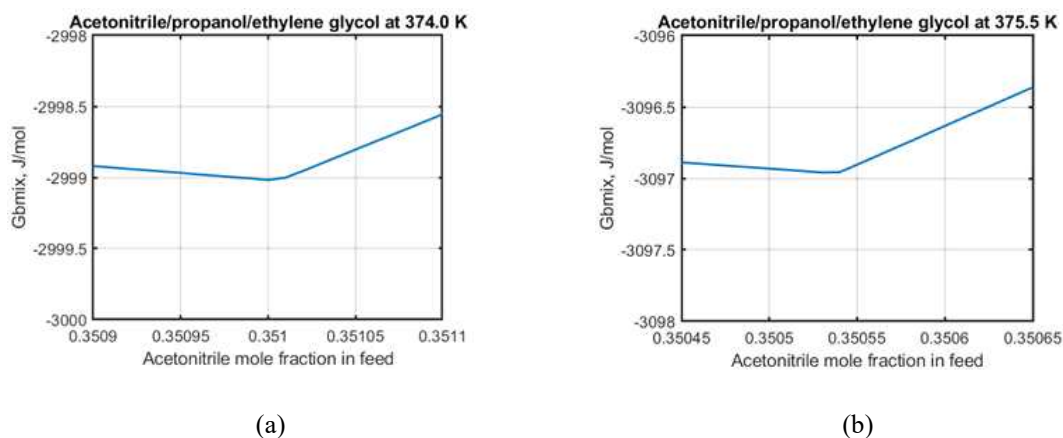


Figure 1. Variation of Gibbs free energy of mixing with varying acetonitrile mole fraction in acetonitrile/*n*-propanol/ethylene glycol VLE system at different temperatures.