

NRTL 모델의 새로운 상수추정 방법

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A new technique of parameter estimation for NRTL model

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1. Introduction

The design of separation processes requires the equilibrium information between vapor and liquid [1-2] or between liquid and liquid [3], which has been experimentally measured and fitted to various thermodynamic equilibrium models. In the practical design of the processes, commercial design software is widely utilized, and the models are essential in the application. The parameter estimation from the experimental data utilizes various optimization techniques to find the best fitted parameters.

In this study the sum of the deviations between the measured and estimated values of VLE data from the NRTL model is examined to design a proper procedure for the parameter estimation of the model. The estimation procedures for various sets of experimental VLE data are presented in detail, and the estimation results for various non-ideal systems are analyzed to examine the performance of the proposed procedure.

2. Property of Parameters

The minimization of the sum of deviations between the experimental data and calculated values using a given set of parameters of the NRTL model leads to the parameters of the best fitted model. The deterministic procedures of the minimization mostly utilize the Newton method, in which the calculated gradient near the solution guides to the direction of the minimum in the next trial until no further reduction of the objective function is made. Fig. 1 shows the sum of absolute deviations between the experimental data and predicted values from the NRTL model with different binary interaction parameters for the given non-randomness factor. Note that the illustrated sum is negative of the actual value to demonstrate the variation of the sum around the minimum better. As shown in the figures the sum does not vary monotonically near the minimum, but instead the distribution is linear and long.

3. Proposed Procedure

3.1 NRTL model

For a multi-component system of n components, the reduced molar excess Gibbs energy is given as the NRTL (non-random two liquid) equation.

$$g = \sum_k x_k \left[\sum_j \frac{g_{kj}}{x_j} - \sum_l \frac{g_{kl}}{x_l} \right] \quad (1)$$

where x_k is the mole fraction of component k , G^E is the molar excess Gibbs energy, R is the gas constant, T is the absolute temperature, and $\overline{\tau G}$ and \overline{G} are mole fraction weighted averages of binary

interaction parameters τ_{ik} and G_{ik} :

$$\frac{g_{12}}{RT} = \frac{z_{12}}{z_1 z_2} \left(\frac{g_{11}}{RT} + \frac{g_{22}}{RT} - \frac{g_{12}}{RT} \right) \quad (2)$$

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and

$$a_{ij} = \frac{g_{ij}}{RT} - \frac{z_{ij}}{z_i z_j} \tau_{ij} \quad (4)$$

In Eq. (4) a_{ij} is the binary interaction parameter, and τ_{ij} is the non-randomness factor. The parameters are found from the regression of the experimental VLE data. The following relations leave three of the parameters to be found from the experimental data with the minimization of sum of estimation errors.

The activity coefficient is found from the partial derivative of the reduced molar excess Gibbs energy with respect to mole fraction.

$$\ln \gamma_i = \frac{1}{RT} \left(\frac{\partial g}{\partial n_i} \right)_{T,P,n_j} \quad (5)$$

$$\ln \gamma_i = \frac{1}{RT} \left(\frac{\partial g}{\partial n_i} \right)_{T,P,n_j} \quad (6)$$

In a closed system involving liquid and vapor phases, the following relation is applied for the computation of vapor compositions.

$$f_i = y_i P \gamma_i \lambda_i \quad (7)$$

where f_i is the component fugacity coefficient, P is the mixture pressure, y_i is the vapor composition of component i , γ_i is the component activity coefficient, P_i^o is the pure-component vapor pressure, and λ_i is the Poynting factor. At low pressure the fugacity coefficient and the Poynting factor are assumed to be 1.

3.2 Preliminary search

For the understanding of the variation of sum of the absolute deviation between measured and estimated compositions in vapor, Fig. 1 demonstrates the sum with different parameters in the system of methanol-*n*-propanol. The figures illustrate the deviation variation with the binary interaction parameters at a given non-randomness factor. Note that the plots are of negative values of the sum of deviation to show the variation around the minimum better. The shape of the surface plots is similar with three different non-randomness factors.

Alternatively in the isobaric measurement, the activity coefficient is computed using Eq. (6), and the temperature at a given liquid composition is iteratively calculated using Eq. (7). Then the mean value of absolute deviation between the measured and calculated temperatures is minimized. When the vapor composition is measured, the deviation of vapor composition between the measured and calculated composition with Eq. (10) is minimized.

4. Results and Discussion

The improved procedure of parameter estimation for the NRTL model is proposed. Though many estimation procedures have been introduced before, no characteristic analysis of the objective function of the parameter estimation was conducted. From the analysis of the function distribution with various sets of parameters an improved procedure is explained here. In the process the derivative of activity coefficient with respect to the parameters was derived for fast and stable computation. The performance of the proposed procedure is compared with the previously reported results.

4.1 Performance evaluation

The systems used for the performance comparison are highly non-ideal systems, which are often encountered in the industrial application of the design software, such as the Aspen Plus and HYSYS. The NRTL model represents better than others for the non-ideal systems, and therefore its parameter estimation using the results of experimental measurement is critical in the industrial implementation of the design programs. The performance of the proposed procedure in the parameter estimation was examined by comparing the resulted minimum deviation of strongly non-ideal systems with the published outcome. Table 1 lists the estimated parameters and mean deviation of 8 systems with 10 sets of experimental data. The selected systems are non-ideal, in which the NRTL model is preferred to use in the practical process design.

4.2 Sensitivity analysis

The uniqueness of the distribution of the deviation near the minimum in the NRTL model has been explained in the earlier section. More detailed variation of the deviation around the minimum is demonstrated in Fig. 2 in the system of benzene-acetonitrile. When the binary interaction parameter a_{12} varies, the variation of the mean deviation is shown in Fig. 2(a), in which no monotonic curve is yielded. This is similar to Fig. 2(b) of the binary interaction parameter a_{21} and Fig. 2(c) of the non-randomness factor α_{12} . The variation shown in Fig. 2 explains again the inadequacy of the application of the common optimization procedures. The slopes of the deviation variation with different parameters are listed in Table 2. Two binary interaction parameters have similar values, but the non-randomness factor has much larger slopes than the interaction parameters.

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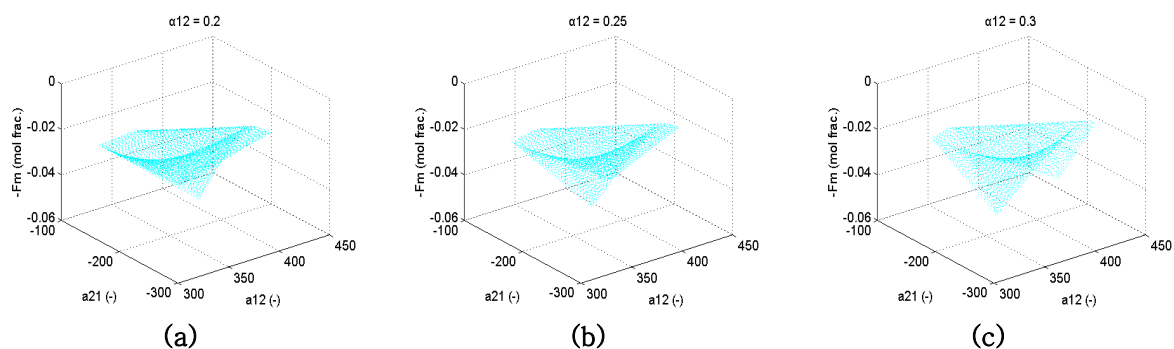


Fig. 1. Surface plots of mean of absolute deviation of measured and calculated vapor composition with different parameters of the NRTL model for the system of methanol-1-propanol: (a) $\alpha_{12}=0.2$, (b) $\alpha_{12}=0.25$, and (c) $\alpha_{12}=0.3$. For better illustration, the deviation is shown in negative values.

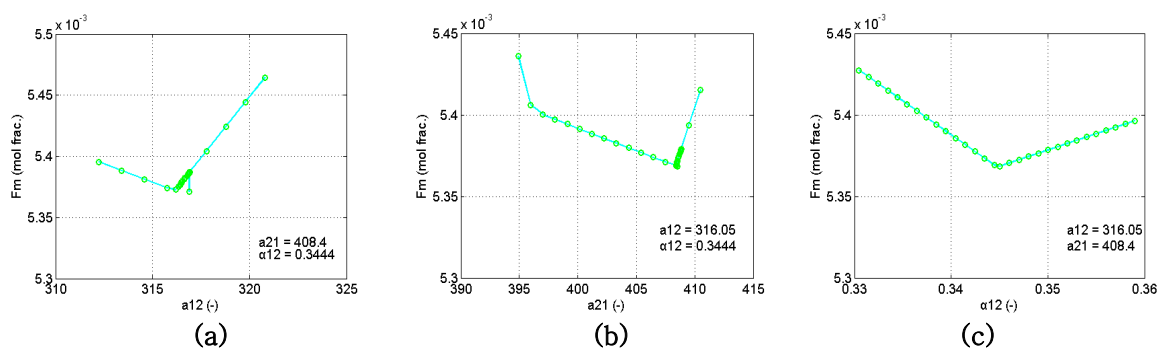


Fig. 2. Variation of the deviation around the minimum with different values of parameters for the system of benzene-acetonitrile: (a) a_{21} and a_{12} fixed, (b) a_{12} and α_{12} fixed, and (c) α_{12} and a_{21} fixed.

Table 1. Results of parameters estimation for various non-ideal binary systems.

System	Isothermal/ isobaric	Objective variable	Calculated parameters			Mean absolute deviation	Reference
			a_{ij}	a_{ji}	α_{ij}		
Ethanol- <i>c</i> -hexane	Isothermal 5 °C	Pressure	809.3	1346.0	0.4244	0.052	0.060
Benzene-acetonitrile	Isobaric 101.3 kPa	Vapor composition	316.1	408.4	0.3444	0.0054	0.0113
Pentane-acetonitrile	Isothermal 90 °C	Pressure	1756.3	791.9	0.3895	8.61	12.67
Pentane-acetonitrile	Isothermal 60 °C	Pressure	1951.4	3321.1	0.3794	12.87	13.52
Pentane-acetonitrile	Isothermal 60 °C	Vapor composition	897.9	829.3	0.2	0.0171	0.0178
Acetone-methanol	Isobaric 101.3 kPa	Temperatur e	-144.9	590.0	0.2	0.16	0.16
Pentane-Propionic aldehyde	Isothermal 60 °C	Vapor composition	516.0	496.9	0.4475	0.0056	0.0058
Triethylamine- 1,4-dioxane	Isothermal 70.05 °C	Vapor composition	169.0	666.6	0.47	0.0127	0.0190
Tetrahydrofuran -hexane	Isobaric 101.3 kPa	Vapor composition	-122.5	473.3	0.2	0.0096	0.0104
Chloroform- tetrahydrofuran	Isothermal 40 °C	Vapor composition	-386.3	-495.6	0.3234	0.0027	0.0035

Table 2. Linear slopes of variation at the minimum deviation in the system of benzene-acetonitrile.

Parameter	Slope 1	Slope 2
a_{12}	-5.18×10^{-6}	2.39×10^{-5}
a_{21}	-3.01×10^{-6}	2.42×10^{-5}
α_{12}	-4.05×10^{-3}	1.98×10^{-3}