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Data correlation in homogeneous azeotropic mixtures using NRTL model and stochastic optimization methods

C. Gutiérrez-Antonio [(1)], *A. Bonilla-Petriciolet* [(2)], *J. G. Segovia-Hernández*[(3)], *A. Briones-Ramírez* [(2),(4)]

[(1)] CIATEQ, A.C., Av. del Retablo # 150 Col. Fovissste, 76150, Querétaro, Querétaro, México, Corresponding author: claudia.gutierrez@ciateq.mx

[(2)] Departamento de Ingeniería Química, Instituto Tecnológico de Aguascalientes, Av. Adolfo López Mateos #1801 Ote. Fracc. Bonagens, 20256, Aguascalientes, Aguascalientes, México

[(3)] Universidad de Guanajuato, Campus Guanajuato, División de Ciencias Naturales y Exactas, Departamento de Ingeniería Química, Noria Alta S/N, 36050, Guanajuato, Guanajuato, México.

[(4)] Innovación Integral de Sistemas S.A. de C.V., Calle Número 2 # 125 Interior 13, Parque Industrial Jurica, 76120, Querétaro, Querétaro, México.

Introduction

Azeotropy is a special case of phase equilibrium phenomenon that occurs in many industrial applications, and its presence restricts the separation amount of a multicomponent mixture that can be achieved by distillation. Azeotropes can be classified as homogeneous and heterogeneous, depending on the number of liquid phases involved in the phase equilibrium condition. In the context of process system engineering, the description of homogeneous azeotropy is essential for the selection of strategies in synthesis, design and operation of separation units. Usually, excess Gibbs energy models are used for modeling vapor-liquid equilibrium (VLE) in azeotropic mixtures, due to its simplicity and predictive capabilities. However, proper parameters of these models are necessary for the reliable design of separation systems. Usually, experimental data are used to determine the adjustable parameters of local composition models for vapor-liquid equilibrium modeling.

The parameter estimation problem for vapor-liquid equilibrium modeling in azeotropic mixtures is a challenging numerical task. This problem involves fitting the thermodynamic model to experimental VLE data by minimizing a suitable objective function. However, this objective function may become non-convex due to non-linear form of the thermodynamic equations. Therefore, the parameter estimation requires the solution of a nonlinear and difficult optimization problem even for relatively simple thermodynamic equations such as Wilson, UNIQUAC and NRTL [1, 2].

Recently, some studies have shown that traditional approaches used for parameter estimation in local composition models have several limitations [1-3]. Most of the existing methods for solving optimization problems are local in nature, and, at best, yield only local solutions [4]. It is important to note that local optimal parameters

(i.e. local solutions of the parameter estimation problem) affect the predictive capability of thermodynamic models causing qualitative and quantitative discrepancies of phase behavior [3]. In particular for NRTL model, failures in the data correlation process may result in incorrect predictions of the azeotropic states, and in qualitative discrepancies of the phase behavior such as prediction of spurious phase split and modeling of homogeneous azeotrope as heterogeneous [1,2]. Undoubtedly, these failures imply errors and uncertainties in process design and erroneous conclusions about model performance. Reliable optimization strategies must be used for determining the adjustable parameters of NRTL equation, and other local composition models for VLE modeling in azeotropic mixtures.

In this context, stochastic optimization methods are robust numerical strategies that offer several advantages with respect to conventional optimization methods, and are very attractive for its application in vapor-liquid equilibrium modeling with homogeneous azeotropy. Based on this fact, in this study two stochastic methods are used and compared for parameter estimation in vapor-liquid equilibrium modeling using NRTL equation. Specifically, the performance of Simulated Annealing and Particle Swarm Optimization is tested and compared in this thermodynamic application. In addition, we illustrate the effect of NRTL adjusted parameters by considering the possible qualitatively errors in the prediction of homogeneous azeotropes.

Parameter estimation for VLE modeling

According to classical Thermodynamics, the equilibrium between vapor and liquid phases in a *c* multicomponent system implies that temperature (*T*), pressure (*P*) and the chemical potential of each component *i* must be the same in both phases. At low pressure, the VLE conditions can be simplified because the fugacity coefficient of pure components nearly cancels each other, and Poynting corrections usually are very close to unity. Neglecting these corrections, now yields:

$$\gamma_i x_i P_i^0 = y_i P \text{ for } i = 1,...,c \qquad (1)$$

where γ_i is the activity coefficient of component *i*, P_i^0 is the vapor pressure of pure component *i*, x_i and y_i are the equilibrium mole fraction at liquid and vapor phase, respectively. Using Eq. (1), the non-ideal behavior for non-ideal systems is described solely by liquid-phase activity coefficient. Therefore, the objective function commonly used for VLE data modeling is given as:

$$F_{obj} = \sum_{j=1}^{ndat} \sum_{i=1}^{c} \left(\frac{\gamma_{ij}^{\exp} - \gamma_{ij}^{calc}}{\gamma_{ij}^{\exp}} \right)^2 \qquad (2)$$

where $\gamma_i^{\exp}$ and γ_i^{calc} are the experimental and calculated values for the activity coefficient of component *i* and *ndat* is the number of experimental data used for parameter estimation, respectively.

For the case of complete VLE data (i.e., *x–y–P* at constant *T*, or *x–y–T* at constant *P*), excess Gibbs energy equations are widely applied for phase equilibrium

modeling. Given VLE measurements and assuming an ideal vapor phase, the experimental values for the activity coefficients can be calculated from experiments and using Eq. (1). There are several local composition models for the calculation of liquid-phase activity coefficients. Particularly, NRTL equation is a flexible local composition model that can be used for the correlation of γ_i, and for representing complex VLE behaviors in multicomponent systems. For a binary mixture, the activity coefficients using the NRTL model are given by

$$\begin{aligned} \ln \gamma_1 &= x_2^2 \left[\frac{\tau_{21} G_{21}^2}{(x_1 + x_2 G_{21})^2} + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \\ \ln \gamma_2 &= x_1^2 \left[\frac{\tau_{12} G_{12}^2}{(x_2 + x_1 G_{12})^2} + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \end{aligned} \tag{3}$$

being

$$\begin{aligned} \tau_{12} &= \frac{g_{12} - g_{22}}{RT} \\ \tau_{21} &= \frac{g_{21} - g_{11}}{RT} \\ G_{ij} &= \exp(-\alpha_{ij} \tau_{ij}) \end{aligned} \tag{4}$$

where three adjustable parameters are necessary for each binary pair: $\theta_1 = g_{12} - g_{22}$, $\theta_2 = g_{21} - g_{11}$, and the nonrandomness factor $\alpha_{12} = \alpha_{21}$. Parameters of the liquid-phase model are estimated by minimizing Eq. (2). Note that the third parameter α_{12} can be treated as adjustable, but several authors have suggested that better it should be fixed between 0.2 and 0.47. We will show that this choice is very important due to it may cause qualitative errors in the prediction of azeotropic states.

As indicated, several studies have shown that the highly non-linear form of local composition models makes that F_{obj} is non-linear, potentially non-convex with several local minima points within the specified bounds. Previous studies have shown that parameter estimation for VLE data modeling involves the solving of a global optimization problem [1 - 4]. In particular for NRTL model, due to its flexibility, this model can predict more phases that actually exist in the system if the parameter estimation procedure is not performed adequately. This qualitative discrepancy occurs more frequently in the VLE modeling of azeotropic mixtures [4]. Therefore, it is necessary to apply a suitable numerical strategy for reliably solving the parameter estimation in VLE modeling. In this study we have tested the numerical performance of two stochastic optimization methods for VLE data fitting of binary systems using NRTL equation.

Description of optimization strategies: Particle Swarm Optimization and Simulated Annealing

We have used the Simulated Annealing (SA) and Particle Swarm Optimization (PSO) for solving the VLE parameter estimation problem with NRTL model. Both stochastic methods are considered global optimization strategies, and they have

found several applications in science and engineering, including thermodynamic calculations. Specifically, SA simulates the process of slow cooling of metals to achieve the minimum function value in a minimization problem. The cooling phenomenon is modeled by controlling a temperature like parameter introduced with the concept of Boltzmann probability distribution. By a controlled temperature reduction as the algorithm proceeds, the convergence of the algorithm can be controlled. We have used the SA code developed by Goffe et al. [5], which is based on the algorithm developed by Corana et al. [6]. On the other hand, PSO is a novel and promising population based method that belongs to the class of swarm intelligence algorithms. Kennedy and Eberhart [7] introduced this strategy for global optimization, which is inspired by the social behavior of flocking swarms of birds and fish schools. It exploits a population of potential solutions to identify promising areas for optimization. In this context, the population of potential solutions is called the swarm, and each solution is called particle. Particles are conceptual entities, which fly through the multi-dimensional search space. The success histories of the particles influence both their own search patterns and those of their peers. Each particle has two state variables: its current position and its current velocity. In the local version of PSO, which is used in this study, the search is focused on promising regions by biasing each particle's velocity toward both the particle's own remembered best position and the communicated best ever neighborhood location. The relative weights of these two positions are scaled by the social and cognitive parameters. Once the particles are all initialized, the positions and velocities of all the particles are modified. After calculating the velocities and position for the next iteration, the current iteration is completed. The best particle is only updated when a new one is found yielding a decrease in the objective function value. This process is performed until satisfies the stopping criterion.

Results and discussion

With illustrative purposes, we have tested the performance of SA and PSO for the parameter estimation in binary VLE data of the system water + 1,2 ethanediol at 430 mmHg. This system has no azeotropes but its VLE parameter estimation problem is very challenging [1,2]. Thus, the global optimum of selected example is well identified. Equation (2) is optimized with respect three parameters of NRTL inside following intervals: $\theta_1, \theta_2 \in$(-2000, 5000) and $\alpha_{12} \in$(0.01, 10.0). Experimental data are taken from Dechema collection. We note that the global minimization of objective function can be done as an unconstrained optimization problem using NRTL equation. This VLE problem was solved 100 times using random initial values, via different random number seed for both SA and PSO. Figure 1 shows the plot of success rate (SR) versus the number of iterations for both SA and PSO. Note that SR is defined as the number of runs out of 100 that satisfy the condition $|f_{opt} - f_{calc}| \leq 10^{-04}$; where the known global optimum of the objective function is f_{opt}, and f_{calc} is the value of objective function calculated by stochastic methods. In first instance, to directly compare the performance of algorithms, we keep constant the numerical effort via the number of iterations, and compare the results obtained in terms of SR. Figure 1 shows that the reliability of the stochastic methods highly depends on the maximum number of iterations allowed. It is noticed that as the number of iterations increased, the success rate to find the global optimum of all methods also increased. Based on our numerical practice using PSO and SA, we can

conclude the reliability of SA is better compared to PSO in terms of both success rate and computational time.

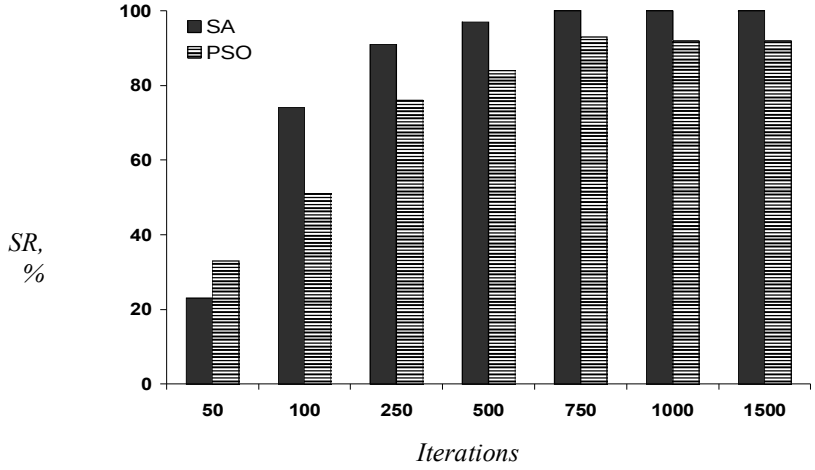

Figure 1. Success rate (SR) versus iterations of Simulated Annealing and Particle Swarm Optimization for parameter estimation in vapor-liquid equilibrium modeling.

To illustrate the qualitative discrepancies that may occur in azeotropic predictions by fixing parameter α_{12} to an unsuitable value, we have considered the parameter estimation for VLE data of the binary mixture 2,3-dimethyl-2-butane + methanol at atmospheric pressure [7]. Experimentally, a homogeneous azeotrope is observed for this mixture. Data correlation was performed using NRTL model and SA method. For parameter estimation, three scenarios were considered: a) VLE data modeling using α_{12} as an adjustable parameter, b) VLE data modeling using α_{12} = 0.2 and c) VLE data modeling using α_{12} = 0.4. Results of parameter estimation are given in Table 1. In this table, we also report the predicted azeotropes (homogeneous and heterogeneous) using adjusted parameters of NRTL model. We can observe that, if α_{12} is fixed to 0.2 or 0.4 inside parameter estimation procedure, NRTL model predicts simultaneously stable heterogeneous azeotropes (i.e., a vapor-liquid-liquid equilibrium), and unstable homogeneous azeotropes. These discrepancies between model and experiment are due to the fact that parameter α_{12} is not used as adjustable parameter, and, under these conditions, NRTL model predicts a liquid-liquid split while experimentally this phase behavior does not occur. However, when three parameters of NRTL are used as optimization variables, this local composition model closely match the experimental data, including the presence of a homogeneous azeotrope. These results highlight the use of a suitable strategy for parameter estimation in VLE modeling in azeotropic systems using NRTL model.

Table 1. Results of VLE data modeling of binary system 2,3-dimethyl-2-butane + methanol at atmospheric pressure using NRTL and Simulated Annealing

NRTL parameters			Prediction of azeotropes	
α_{12}	θ_1	θ_2	Homogeneous	Heterogeneous
0.4447	1454.44	1234.62	Yes	No
0.4	1355.71	1156.13	Yes, Unstable	Yes, Stable
0.2	1026.03	905.01	Yes, Unstable	Yes, Stable

Concluding remarks

Parameter estimation for VLE modeling using local composition models is a difficult global optimization problem, and their characteristics pose a challenge to any optimization technique. Our numerical experience indicates that both PSO and SA are reliable, if properly implemented, for solving this thermodynamic problem. However, it appears that SA is the most suitable method for parameter estimation for VLE modeling. Finally, the improper application of NRTL model for data fitting of azeotropic mixtures may cause severe qualitative and quantitative discrepancies in predicting phase behavior.

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