LOCATING ALL AZEOTROPES IN HOMOGENEOUS AZEOTROPIC SYSTEMS

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Abstract

A global optimization based approach for finding *all* homogeneous azeotropes in multicomponent mixtures is presented. The global optimization approach is based on a branch and bound framework in which upper and lower bounds on the solution are refined by successively partitioning the target region into small disjoint rectangles. The objective of such an approach is to locate all global minima since each global minimum corresponds to an homogeneous azeotrope. The global optimization problem is formulated from the thermodynamic criteria for azeotropy, which involve highly nonlinear and nonconvex expressions. The success of this approach depends upon constructing valid convex lower bounds for each nonconvex function in the constraints. The convex lower bounding procedure is demonstrated with the Wilson activity coefficient equation. The global optimization approach is illustrated in an example problem.

1 Introduction

The ability to predict whether a given mixture will form one or more azeotropes and to calculate the conditions and compositions of each azeotrope is essential if one wants to model separation processes. Similarly, it is necessary to calculate the effects of temperature and pressure on the composition of an azeotrope for process design applications. In order to be most useful, a method for calculating the azeotropes of a mixture must be robust, and must be able to guarantee that *all* azeotropes predicted by the thermodynamic model of the system can be found.

Despite the considerable interest in the area of predicting phase equilibria for chemical mixtures, relatively few methods for prediction of azeotropes have been reported. This is because the task of finding the pressure, temperature, and composition of *all* azeotropes is an especially difficult one, due to the highly nonlinear form of the equations which constitute the thermodynamic models.

Most of the previous work reported in the literature has been limited to calculating homogeneous azeotropes. Aristovich and Stepanova (1970) calculated ternary homogeneous azeotropes using the Wilson model under isothermal conditions. Teja and Rowlinson (1973) calculated homogeneous azeotropes of binary mixtures using an equation of state as the thermodynamic model, as did Wang and Whiting (1986). Fidkowski *et al.* (1993) presented an interesting homotopy continuation method for finding homogeneous azeotropes. Chapman and Goodwin (1993) presented a search method for finding homogeneous and heterogeneous azeotropes which uses a Levenberg-Marquardt algorithm to find all possible homogeneous azeotropes and then checks the stability of each solution with the tangent plane criterion described by Michelsen (1981).

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Finally, an excellent review of nonideal distillation, including a discussion on the computation of azeotropes has recently been provided by Widagdo and Seider (1995).

The purpose of this paper is to propose a new method for determining all homogeneous azeotropes of a non-reacting mixture for several different thermodynamic models. The problem is formulated as a global optimization problem in which each global minimum solution corresponds to an homogeneous azeotrope. This method models the vapor phase as an ideal gas at low pressure, and uses activity coefficient models for the liquid phase. The activity coefficient model examined in this paper is the Wilson equation.

2 Problem Description and Formulation

In order to develop a method for finding all azeotropes of a mixture, it is essential to first determine the thermodynamic conditions for azeotropy. Azeotropes may occur when a mixture at equilibrium forms a vapor phase and at least one liquid phase for some range of temperature and pressure. If the above condition is met, then an homogeneous azeotrope occurs when the equilibrium composition of the vapor phase is identical to the overall composition of the liquid phase.

There are three thermodynamic conditions which a system must meet in order for an azeotrope to exist. These are: 1) equilibrium, 2) azeotropy condition (the composition of vapor phase is identical to the overall composition of the liquid phase(s)), and 3) the system must be physically realizable, that is, the mole fractions in each phase must be positive and sum to unity.

The equilibrium condition requires that the chemical potential of each component must be the same in all phases. Since an homogeneous azeotropic system contains a vapor phase and only one liquid phase, this condition can be written $\left(\frac{y_i}{x_i} = \frac{\gamma_i^L \hat{f}_i^L}{\phi_i^V P} \quad \forall\ i \in N\right)$ when the standard states of all phases are defined to be equal.

At low pressure, the vapor phase can be modeled as an ideal gas, for which $\phi_i^V = 1$, and for the liquid phase we have $\hat{f}_i^L = P_i^{sat}$. Therefore:

$$\frac{y_i}{x_i} = \frac{\gamma_i^L P_i^{sat}}{P} \tag{1}$$

The azeotropy condition requires that the composition of the vapor phase is identical to the overall composition of the liquid phase(s). In the case of an homogeneous azeotrope, this condition simplifies to:

$$y_i = x_i \qquad \forall\ i \in N \tag{2}$$

The third condition requires that the mole fractions in each phase sum to unity and are between 0 and 1.

$$\begin{gathered} \sum_{i \in N} y_i = \sum_{i \in N} x_i = 1 \\ 0 \leq \mathbf{y}, \mathbf{x} \leq 1 \end{gathered} \tag{3}$$

2.1 Mathematical Formulation

In order to find all azeotropes then, one must find all solutions to the system of nonlinear equations (1), (2), and (3) listed above. This paper uses the approach outlined in Maranas and Floudas (1995), which reformulates the problem of finding all solutions of nonlinear systems of constrained equations into a global optimization problem in which the aim is to obtain all global solutions. For the location of all homogeneous azeotropes, this corresponds to reformulating equations (1), (2), (3) as a global optimization problem. Because $x_i = y_i$ for every i, the system of equations can be simplified by replacing each y_i by x_i. Therefore, the equilibrium constraints become $(x_i(P - P_i^{sat}\gamma_i) = 0 \ \ \forall\ i \in N)$. In order to satisfy these equations, either $x_i = 0$ or $(P - P_i^{sat}\gamma_i) = 0$ for each $i \in N$. If we wish to search only for azeotropes in which all components participate (i.e., an N-ary azeotrope), the condition can be further simplified to $(P - P_i^{sat}\gamma_i) = 0$ for each $i \in N$.

It is convenient to take the natural log of the simplified equilibrium constraint because P_i^{sat} and γ_i are usually given as $\ln P_i^{sat}$ and $\ln \gamma_i$. This results in the following problem:

$$\begin{array}{lrcll}
\min\limits_{\mathbf{x},s} & s & & & \\
\textit{subject to} & \ln P - \ln P_i^{sat} - \ln \gamma_i - s & \leq & 0, & \forall\, i \in N \\
& -\ln P + \ln P_i^{sat} + \ln \gamma_i + s & \leq & 0, & \forall\, i \in N \\
& \sum\limits_{i\in N} x_i & = & 1 & \\
& 0 \leq \mathbf{x} \leq 1 & & & \\
& s \geq 0 & & &
\end{array} \tag{4}$$

Formulation (4) may have several global minima. Each global minimum corresponds to an homogeneous azeotrope since when $s = 0$ the constraints (1), (2), and (3) are satisfied. Note that the first two sets of constraints of (4) correspond to the nonlinear equations (1) of the equilibrium constraint written as two inequalities. The method of Maranas and Floudas (1995) requires that convex underestimators are derived for all constraints in order to guarantee that all ϵ - global minima will be located. Note that the expressions for P_i^{sat} and γ_i are generally not convex, and hence we have to develop valid underestimators for them.

For azeotropes in which less than N of the components participate, the case where $x_i = 0$ for one or more i must be accounted for. This can be done by multiplying the equilibrium constraints used in (4) by x_i. This is referred to as the problem of finding all k-ary azeotropes, where $k \leq N$.

3 Activity Coefficient Models

The problem formulation, (4), contains several nonconvex functions. If a local optimization approach is used to solve these problems, it is likely that some of the multiple global minima will be missed, or even that none will be found. Therefore, in order to guarantee that *all* global minima are located, it is necessary to develop a convex relaxation of the problem. In the proposed approach, a lower bound on the solution of (4) is obtained by replacing each nonconvex constraint with a tight convex underestimator, resulting in a convex lower bounding problem which is solved with MINOS5.4. The upper and lower bounds on the solutions are then refined using a branch and bound approach.

This section analyzes the equations in the azeotropy problem formulation which contain nonconvex terms. For the Wilson equation, the form of the equation is introduced, and the nonconvex terms are identified. For each nonconvex term, a convex lower bounding function must be calculated. While the Wilson equation is the only activity coefficient model examined in this paper, this approach has also been extended for the NRTL and UNIQUAC activity coefficient models. The reader is referred to Harding *et al.* (1996) for the development of the convex lower bounding functions of the NRTL and UNIQUAC equations.

3.1 Saturated Vapor Pressure Equation

In this work, the saturated vapor pressure is calculated using the Antoine equation :

$$\ln P_i^{sat} = a_i - \frac{b_i}{T + c_i} \tag{5}$$

where a_i, b_i, and c_i are constants. The parameters a_i and b_i are always positive, while c_i may be positive or negative but $\mid c_i \mid < T$. In the problem of finding all N-ary azeotropes, denoted as (4), this term appears in the constraints as both $(-lnP_i^{sat})$ and $(+lnP_i^{sat})$. It can be easily shown that the term $(-\frac{b_i}{T+c_i})$ is concave in T. As a result, in the first set of constraints of (4) which have $(-\ln P_i^{sat})$, this term is convex and no underestimation is needed. In the second set of constraints however, this term is concave and hence an underestimator is required. A convex underestimator for this term is simply a line segment between the values of the term at each limit. That is,

$$-\frac{b_i}{T + c_i} \geq -\frac{b_i}{T^L + c_i} + \frac{-\frac{b_i}{T^U+c_i} + \frac{b_i}{T^L+c_i}}{T^U - T^L}(T - T^L) \tag{6}$$

where T^L, T^U are the lower and upper bounds on the temperature in the current region.

In the formulation for finding all k-ary azeotropes, the Antoine equation is multiplied by the liquid mole fraction, x_i. In this case, both the positive and negative terms $(-x_i lnP_i^{sat})$ and

$(+x_i ln P_i^{sat})$ are nonconvex. The convex underestimating functions for these terms are presented in Harding *et al.* (1996).

3.2 Wilson Equation

The Wilson equation is often used to model solutions containing polar and nonpolar components. The Wilson activity coefficient equation is :

$$\ln \gamma_i = 1 - \ln \sum_{j \in N} x_j \Lambda_{ij} - \sum_{j \in N} \frac{x_j \Lambda_{ji}}{\sum\limits_{k \in N} x_k \Lambda_{jk}} \tag{7}$$

where Λ_{ij} is the nonsymmetric binary interaction parameter between components i and j with $\Lambda_{ii} = 1$. When the Wilson equation is used, the problem of finding all N-ary homogeneous azeotropes contains nonconvex terms of two different types. The first nonconvex term is $\ln \sum\limits_{j \in N} x_j \Lambda_{ij}$. This term is concave, so it can be underestimated by the line segment:

$$\ln \sum_{j \in N} x_j \Lambda_{ij} \geq \ln m_i^L + \frac{\ln \frac{m_i^U}{m_i^L}}{(m_i^U - m_i^L)} \left(\sum_{j \in N} (x_j \Lambda_{ij}) - m_i^L \right) \tag{8}$$

where

$$\begin{array}{rcl} m_i^L & = & \min\limits_{i \in N} \sum\limits_{j \in N} x_j \Lambda_{ij} \\ \text{subject to} & & \sum\limits_{j \in N} x_j = 1 \\ & & x_j^L \leq x_j \leq x_j^U \end{array} \tag{9}$$

and m_i^U is the maximum of $\sum\limits_{j \in N}$ subject to the same constraints.

The second type of nonconvex terms in the Wilson equation model include s_j^1, and s_j^2 where:

$$\left(s_j^1 = + \frac{x_j}{\sum\limits_{k \in N} x_k \Lambda_{jk}} \right) \text{ and } \left(s_j^2 = - \frac{x_j}{\sum\limits_{k \in N} x_k \Lambda_{jk}} \right) \tag{10}$$

Convex underestimating functions for these terms can be constructed following the method presented in Maranas and Floudas (1995) for products of univariate functions. The convex underestimators for these terms are:

$$\begin{array}{rcl} s_j^1 & \geq & \max \left\{ \dfrac{x_j^L}{\sum\limits_{k \in N} x_k \Lambda_{jk}} + \dfrac{x_j}{m_j^U} - \dfrac{x_j^L}{m_j^U}, \right. \\ & & \left. \dfrac{x_j^U}{\sum\limits_{k \in N} x_k \Lambda_{jk}} + \dfrac{x_j}{m_j^L} - \dfrac{x_j^U}{m_j^L} \right\} \\ s_j^2 & \geq & \max \left\{ -\dfrac{x_j}{m_j^U} + \dfrac{x_j^U \sum\limits_{k \in N} x_k \Lambda_{jk}}{m_j^L m_j^U} - \dfrac{x_j^U}{m_j^L}, \right. \\ & & \left. -\dfrac{x_j}{m_j^L} + \dfrac{x_j^L \sum\limits_{k \in N} x_k \Lambda_{jk}}{m_j^L m_j^U} - \dfrac{x_j^L}{m_j^U} \right\} \end{array}$$

For the k-ary azeotrope problem the nonconvex terms are:

$$\left(x_i \ln(\sum_{j\in N} x_j\Lambda_{ij})\right), \left(-x_i \ln(\sum_{j\in N} x_j\Lambda_{ij})\right), \left(x_i \sum_{j\in N} s_j^1\Lambda_{ji}\right), \text{and} \left(-x_i \sum_{j\in N} s_j^1\Lambda_{ji}\right) \tag{11}$$

Convex underestimating functions for these terms are developed in Harding *et al.* (1996).

4 Procedure for Locating All Azeotropes

The method presented in this paper for locating all homogeneous azeotropes is based on the work of Maranas and Floudas (1995). The problem is formulated by introducing a slack variable to the equilibrium constraint of the initial problem. This transforms the initial problem into a global optimization problem (4) in which each feasible solution corresponding to a zero objective function value denotes the existence of an azeotrope.

The multiple global minima of formulation (4) are localized based on a branch and bound procedure. This procedure creates a convex relaxation of the problem by constructing tight convex lower bounding functions for each nonconvex term in the constraints. Then the global minimum of the convex relaxed problem within some box constraints can be found using any commercially available local optimization algorithm.

If the solution of the relaxed problem is strictly positive inside some rectangular region, then because it is an underestimator, the solution of the original problem must also be strictly positive inside the region. This allows us to fathom (eliminate) parts of the total region which do not contain any solutions. If the solution to the relaxed problem is zero or negative, then the original problem may or may not have a solution in the current region and thus the region cannot be fathomed. Instead, the current region is partitioned into smaller regions and the procedure is repeated until all regions are fathomed, or a feasible solution is found.

As the size of the current region decreases, the maximum separation between the original constraint functions and the convex relaxed functions also decreases. Therefore, any feasible point of the relaxed problem can become at least ϵ-feasible for the original problem by tightening the bounds around the point. In this work, each region which has a non-positive solution of the convex relaxed problem is partitioned into two smaller regions by bisecting the longest side of the initial region. At each iteration in the branch and bound procedure, the lower bound of the original problem is calculated by finding the infimum over all solutions of the relaxed problem in each region which has not been fathomed. Thus, a simple way of improving the lower bound is to halve only the subrectangle responsible for the infimum of the minima of the relaxed problem at each iteration. Convergence is reached when none of the subrectangles inside the total region have a negative lower bound, in which case there are no solutions, or when all of the remaining subrectangles with negative lower bounds have been refined to a prespecified size tolerance. A proof that this procedure is guaranteed to converge is presented in Maranas and Floudas (1995).

5 Illustrative Example

The example presented here shows the results from locating all N-ary azeotropes in the quinary system acetone/chloroform/methanol/ethanol/benzene (A/C/M/E/B) at $P = 1$ atm. The binary interaction parameters used in this work are taken from the DECHEMA Vapor-Liquid Equilibria Data Collection, Gmehling and Onken (1977) and are assumed to be independent of temperature in the narrow range in which the azeotropes are located. Liquid molar volumes for the pure components were calculated by a modified Rackett equation, Yamada and Gunn (1973). The Wilson model using the N-ary formulation was able to locate all six binary azeotropes, two ternary azeotropes, and the quaternary azeotrope reported by Fidkowski *et al.* (1993). The compositions and boiling points of each azeotrope that was located are listed in Table 1.

Computational requirements increased as the number of components participating in the azeotrope increased, and the amount of time needed to compute the quaternary azeotrope was substantially longer than what was needed for the ternary azeotropes. All times reported are the total cpu time in seconds needed to obtain all azeotropes in the system. The algorithm for finding all homogeneous azeotropes in a multicomponent mixture is written in GAMS and was run on a Hewlett Packard 9000/730 machine. The solver MINOS5.4 is used as a subroutine.

6 Conclusions

This work has presented a deterministic global optimization method for computing all homogeneous azeotropes in multicomponent mixtures This method is based on a branch and bound

Solution for Acetone (1) – Chloroform (2) – Methanol (3) – Ethanol (4) – Benzene (5)							
Azeotrope	x_1	x_2	x_3	x_4	x_5	T	CPU
AC	0.3714	0.6286	——	——	——	64.6561	0.78
AM	0.8018	——	0.1982	——	——	55.4567	0.48
CM	——	0.6306	0.3694	——	——	53.0703	0.81
CE	——	0.8415	——	0.1585	——	59.2503	0.95
MB	——	——	0.6235	——	0.3765	58.0149	0.43
EB	——	——	——	0.4544	0.5456	67.7000	0.84
ACM	0.3754	0.1888	0.4358	——	——	57.2184	2.03
ACE	0.3735	0.4380	——	0.1885	——	63.1801	2.11
ACMB	0.2954	0.1475	0.4630	——	0.0941	57.1536	7.58

Table 1: Solutions for Illustrative Example

algorithm to iteratively solve a formulation of the original problem in which the nonconvex constraints are replaced by valid convex underestimating functions. While only one thermodynamic model was presented, this method has also been applied for the NRTL and UNIQUAC equations and can be extended to include the modified Wilson, UNIFAC, and ASOG activity coefficient models. The effectiveness of this method was demonstrated for a system containing five components.

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