

A New Approach for Reliable Computation of Homogeneous Azeotropes in Multicomponent Mixtures

Robert W. Maier, Joan F. Brennecke and Mark A. Stadtherr*
Department of Chemical Engineering
University of Notre Dame, Notre Dame, IN 46556

Prepared for presentation at AIChE Annual Meeting, Los Angeles, CA, November 16–21, 1997
Session Number 75: Thermodynamic Properties and Phase Behavior : General II

Copyright ©Robert W. Maier
UNPUBLISHED

October 1997

AIChE shall not be responsible for statements or opinions contained in papers or printed in its publications.

*author to whom all correspondence should be addressed; Fax: (219) 631-8366; E-mail: markst@nd.edu

1 Introduction

The determination of the existence and composition of azeotropes is important both from theoretical and practical standpoints. An important test of the veracity of thermodynamic models is whether or not known azeotropes are predicted, and whether or not they are predicted accurately. Model parameters can be fine tuned by comparing the model predictions with known azeotropic data. In addition, azeotropic predictions can be used as starting points for experimental searches for actual azeotropes. These azeotropes often present limitations in process design which must be known, and their determination strictly from experiment alone can be expensive.

There are two main difficulties in solving the problem. The first is the fact that the equations derived from most thermodynamic models are highly nonlinear, which may make finding any azeotrope a nontrivial exercise. In addition, there is the question of whether or not all of the azeotropes have been found, or of being certain that there are no azeotropes if none have been found. Because of these difficulties there has been much recent interest in the reliable computation of azeotropes, focused primarily on the prediction of homogeneous azeotropes. For example, Fidkowski et al. (1993) have presented a homotopy continuation method for the calculation of homogeneous azeotropes. The primary drawback of this technique is that it can not guarantee that all azeotropes have been found. More recently, Harding et al. (1997) have reported a global optimization procedure based on a branch and bound approach using convex underestimating functions that are continuously refined as the range where azeotropes are possible is narrowed. This technique does provide a guarantee that all azeotropes have been found. Harding et al. (1997) have developed appropriate convex underestimating functions for several specific thermodynamic models.

2 Methodology

We describe here a new approach for reliably finding all homogeneous azeotropes of multicomponent mixtures. The technique is based on interval analysis, in particular the use of an interval Newton/generalized bisection algorithm. The method can determine *with mathematical certainty* all azeotropes for any system. The technique is general-purpose and can be applied in connection with any thermodynamic models. No model-specific convex underestimating functions need be derived. In this presentation, the technique is described and tested and some of the results are discussed.

2.1 Problem Formulation

The equilibrium condition can be rewritten in terms of the equivalence of fugacities,

$$\hat{f}_i^V = \hat{f}_i^L, \forall i \in N \quad (1)$$

where \hat{f}_i refers to the fugacity of component i in solution, and N is the set of all components

in the system. These solution fugacities can in turn be written as

$$y_i \hat{\phi}_i^V P = x_i \gamma_i^L f_i^L, \forall i \in N \quad (2)$$

where $\hat{\phi}_i^V$ is the mixture fugacity coefficient of component i in the vapor phase, γ_i^L is the activity coefficient of component i in the liquid phase, and f_i^L is the pure component fugacity of component i in the liquid phase. The pure component fugacity in the liquid phase can be expressed as

$$f_i^L = \phi_i^{sat} P_i^{sat} (PF)_i, \forall i \in N \quad (3)$$

where ϕ_i^{sat} is the saturated pure component fugacity component for species i , P_i^{sat} is the vapor pressure of component i , and $(PF)_i$ is the Poynting correction factor for species i . Under the assumption of ideal gas behavior of the vapor phase,

$$\hat{\phi}_i^V = \phi_i^{sat} = (PF)_i = 1, \forall i \in N \quad (4)$$

Noting that the mole fraction of each component is the same in both the liquid and vapor phases for homogeneous azeotropes, we arrive at the following equilibrium conditions for homogeneous azeotropy,

$$P = P_i^{sat} \gamma_i^L, \forall i \in N \quad (5)$$

In addition to the equilibrium equations, we also have the constraint that the sum of the mole fractions must equal one.

$$\sum_{i=1}^N x_i - 1 = 0 \quad (6)$$

Since the vapor pressure and activity coefficient relationships are expressed in terms of their logarithms, we express the set of equations (5) as

$$\ln P - \ln P_i^{sat} - \ln \gamma_i^L = 0, \forall i \in N \quad (7)$$

In the terminology of Harding et al. (1997), this is the N -ary formulation, in which each of the N components must have a non-zero mole fraction. In order to find all azeotropes of a system using the N -ary formulation, a series of problems must be run, covering each of the possible component combinations. The k -ary formulation, which allows for zero mole fractions, is derived by multiplying the equilibrium conditions (7) by x_i to obtain

$$x_i (\ln P - \ln P_i^{sat} - \ln \gamma_i^L) = 0, \forall i \in N \quad (8)$$

Using the k -ary formulation, only one problem need be run to find all azeotropes present in a system.

In this paper, we use the Antoine equation to determine pure component vapor pressures, and present results for an example in which the Wilson activity coefficient model is used. Problems involving other models, such as NRTL, UNIQUAC and UNIFAC, have also been solved.

2.2 Interval Newton/Generalized Bisection

The solution method used is the interval Newton/generalized bisection technique described by Kearfott (1987a,b), and implemented in INTBIS (Kearfott and Novoa, 1990). The algorithm is also summarized, in the context of chemical process modeling, by Schnepfer and Stadtherr (1996).

For a system of nonlinear equations $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ with $\mathbf{x} \in \mathbf{X}^{(0)}$, the basic iteration step in interval Newton methods is, given an interval $\mathbf{X}^{(k)}$, to solve the linear interval equation system

$$F'(\mathbf{X}^{(k)})(\mathbf{N}^{(k)} - \mathbf{x}^{(k)}) = -\mathbf{f}(\mathbf{x}^{(k)}) \quad (9)$$

for a new interval $\mathbf{N}^{(k)}$, where k is an iteration counter, $F'(\mathbf{X}^{(k)})$ is an interval extension of the real Jacobian $f'(\mathbf{x})$ of $f(\mathbf{x})$ over the current interval $\mathbf{X}^{(k)}$, and $\mathbf{x}^{(k)}$ is a point in the interior of $\mathbf{X}^{(k)}$. It can be shown (Moore, 1966) that any root $\mathbf{x}^* \in \mathbf{X}^{(k)}$ is also contained in the image $\mathbf{N}^{(k)}$, suggesting the iteration scheme $\mathbf{X}^{(k+1)} = \mathbf{X}^{(k)} \cap \mathbf{N}^{(k)}$. While this iteration scheme can be used to tightly enclose a solution, what is also of significance here is the power of equation (9) as an existence and uniqueness test. For several techniques for finding $\mathbf{N}^{(k)}$ from equation (9), it can be proven (e.g., Neumaier, 1990; Kearfott, 1996) that if $\mathbf{N}^{(k)} \subset \mathbf{X}^{(k)}$, then there is a *unique* zero of $\mathbf{f}(\mathbf{x})$ in $\mathbf{X}^{(k)}$, and that Newton's method with real arithmetic can be used to find it, starting from any point in $\mathbf{X}^{(k)}$. This suggests a root inclusion test for $\mathbf{X}^{(k)}$:

1. (Range Test) Compute an interval extension $\mathbf{F}(\mathbf{X}^{(k)})$ containing the range of $\mathbf{f}(\mathbf{x})$ over $\mathbf{X}^{(k)}$ and test to see whether it contains zero. Clearly, if $0 \notin \mathbf{F}(\mathbf{X}^{(k)}) \supseteq \{\mathbf{f}(\mathbf{x}) \mid \mathbf{x} \in \mathbf{X}^{(k)}\}$ then there can be no solution of $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ in $\mathbf{X}^{(k)}$ and this interval need not be further tested.
2. (Interval Newton Test) Compute the image $\mathbf{N}^{(k)}$ by solving equation (9).
 - (a) If $\mathbf{X}^{(k)} \cap \mathbf{N}^{(k)} = \emptyset$, then there is no root in $\mathbf{X}^{(k)}$.
 - (b) If $\mathbf{N}^{(k)} \subset \mathbf{X}^{(k)}$, then there is exactly one root in $\mathbf{X}^{(k)}$.
 - (c) If neither of the above is true, then no further conclusion can be drawn.

In the last case, one could then repeat the root inclusion test on the next interval Newton iterate $\mathbf{X}^{(k+1)}$, assuming it is sufficiently smaller than $\mathbf{X}^{(k)}$, or one could bisect $\mathbf{X}^{(k+1)}$ and repeat the root inclusion test on the resulting intervals. This is the basic idea of interval Newton/generalized bisection methods. If $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ has a finite number of real solutions in the specified initial box, a properly implemented interval Newton/generalized bisection method can find *with mathematical certainty* any and all solutions to a specified tolerance, or can determine *with mathematical certainty* that there are no solutions in the given box (Kearfott and Novoa, 1990; Kearfott, 1990).

3 Results and Discussion

We discuss the results from one of our test problems below. It is a three component system consisting of ethanol, methyl ethyl ketone, and water. The activity coefficient model used is the Wilson equation. This system has also recently been studied by Fidkowski et al. (1993) and Harding et al. (1997) We compare the results between the *N-ary* and *k-ary* formulations for this system for two cases. In the first case, the binary interaction parameters are considered to be constant by assuming a reference temperature as done by Harding et al. (1997), and in the second case, we solve the more difficult problem in which the binary interaction parameters are not assumed to be constant and allowed to vary with temperature. Our results for this problem are shown in Table 1 for the constant reference temperature case and in Table 2 for the temperature dependent case. CPU times are for a Sun Ultra 1/140. Times for each azeotrope are shown for the *N-ary* formulation, and the total times are shown for both formulations. In each case, both formulations give the same results for the compositions and temperatures of the azeotropes found.

The results we obtained for the constant reference temperature case are in good agreement with those published by Harding et al. (1997) for the same test problem, indicating that the method can efficiently and reliably determine all homogeneous azeotropes for multicomponent mixtures. In each case, we obtained faster solution times for the series of *N-ary* problems than for the single *k-ary* problem. The times required for the interval Newton/generalized bisection method are very competitive with those for the branch and bound method of Harding et al. (1997). The computational cost of including temperature dependence is significant, but the CPU times are still reasonable. Including the temperature dependence is useful for systems with no experimental data, because it is difficult to choose a reference temperature, and because for some problems, especially ternary and higher order systems, the calculation of azeotropes is sensitive to the reference temperature.

4 References

- Fidkowski, Z. T., M. F. Malone and M. F. Doherty, Computing azeotropes in multicomponent mixtures. *Comput. Chem. Eng.*, 17, 1141-1155 (1993).
- Harding, S. T., C. D. Maranas, C. M. McDonald and C. A. Floudas, Locating all homogeneous azeotropes in multicomponent mixtures. *Ind. Eng. Chem. Res.*, 36, 160-178 (1997).
- Kearfott, R. B., Abstract generalized bisection and a cost bound. *Math. Comput.*, 49, 187-202 (1987a).
- Kearfott, R. B., Some tests of generalized bisection. *ACM Trans. Math. Softw.*, 13, 197-220 (1987b).

Kearfott, R. B., Interval arithmetic techniques in the computational solution of nonlinear systems of equations: Introduction, examples, and comparisons. *Lectures in Applied Mathematics*, 26, 337-357 (1990).

Kearfott, R. B., *Rigorous Global Search: Continuous Problems*. Kluwer Academic Publishers, Dordrecht (1996).

Kearfott, R. B., and Manuel Novoa III. Algorithm 681: INTBIS, a portable interval-Newton/bisection package. *ACM Transactions on Mathematical Software*, 16(2):152-157, June 1990.

Moore, R. E., *Interval Analysis*. Prentice-Hall, Englewood Cliffs (1966).

Neumaier, A., *Interval Methods for Systems of Equations*. Cambridge University Press, Cambridge, England (1990).

Schnepper, C. A. and M. A. Stadtherr, Robust process simulation using interval methods. *Comput. Chem. Eng.*, 20, 187-199 (1996).

Table 1: Computational results for the system ethanol(1)/methyl ethyl ketone(2)/water(3) at 1.0 atm for the Wilson equation with a reference temperature of 73.65 °C used to determine constant values for the binary interaction parameters. Temperature range for search was 10-100 °C.

x_1	x_2	x_3	T (°C)	CPU (s)
0.485	0.515	0.000	74.099	0.008
0.898	0.000	0.102	78.123	0.008
0.000	0.681	0.319	73.697	0.021
0.232	0.543	0.225	72.776	0.168
Total	N-ary			0.205
Total	k-ary			0.896

Table 2: Computational results for the system ethanol(1)/methyl ethyl ketone(2)/water(3) at 1.0 atm for the Wilson equation with temperature dependent binary interaction parameters. Temperature range for search was 10-100 °C.

x_1	x_2	x_3	T (°C)	CPU (s)
0.485	0.515	0.000	74.104	0.039
0.910	0.000	0.090	78.169	0.038
0.000	0.681	0.319	73.700	0.090
0.231	0.544	0.225	72.747	0.168
Total	N-ary			0.335
Total	k-ary			4.615