Prediction of Homogeneous Azeotropes with Interval Analysis Techniques Exploiting Topological Considerations

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In this paper, we present an efficient method for the prediction of homogeneous azeotropes. The method is an adaptation of a former method based on interval analysis techniques. An interval Newton with generalized bisection (IN/GB) technique is used to find all the roots of a set of equations representing the azeotropy condition. The novel contribution is to combine this robust technique with the Zharov−Serafimov topological index theory. By checking the topological consistency, it is possible to avoid the numerical verification of the nonexistence and therefore to reduce significantly the total computation time. In addition, a simplified model is selectively used at the first stage of the algorithm for providing good starting points for the second stage, where the full model is used for solution refining. In this way, more computation time is saved without compromising the reliability of the method. As a result, the performance of the method is comparable to the one of the fastest local methods.

Introduction

The prediction of azeotropes based on thermodynamic models of vapor−liquid equilibrium is very important in the synthesis and design of chemical processes. Solvent mixtures used in the reaction and purification steps of these processes normally present a highly nonideal phase behavior and the formation of azeotropes has a strong effect on the operations design.

The problem of finding all the azeotropes of a multicomponent mixture proved to be difficult to solve and has attracted the attention of many researchers. Several solution approaches have been presented, namely, homotopy-continuation methods,[1,2] global optimization techniques,[3,4] and more recently, interval Newton with generalized bisection (IN/GB).[5] Although homotopy-continuation methods have been successfully applied to solve a wide variety of cases, they cannot completely guarantee that all azeotropes have been detected. On the other hand, global optimization and interval analysis provide a mathematical certainty at the expense of a longer computational time, rapidly increasing with the number of components. Additionally, global optimization methods require the development of specific underestimating functions for each thermodynamic model.

In their interval analysis approach, Maier and coworkers[5] present two basic mathematical formulations. In the *simultaneous* formulation, the homogeneous azeotropy condition is written for all components in the mixture, and therefore the IN/GB method is used to find simultaneously all azeotropic compositions and temperatures. The *sequential* formulation decomposes the problem into an unordered sequence of simpler problems of reduced dimension and at each step in the sequence it only obtains the azeotropes whose order corresponds to the dimension of the subsystem under consideration. The authors report a significant reduction in the computation time when using the sequential formulation as compared to the simultaneous approach.

Despite the increase in computational efficiency, in the sequential formulation the algorithm still spends a substantial amount of time in verifying that an azeotrope does not exist in a subsystem.

In this paper, we present an adaptation of the method presented by Maier et al.,[5] which combines the sequential formulation processed in a *given order* with the Zharov−Serafimov topological index theory.[6] By checking the topological consistency of each subsystem, it is possible to avoid the numerical verification of the nonexistence and therefore to reduce significantly the total computation time.

Harding et al.[4] have also explored the use of a simplified model assuming that the temperature dependence of the vapor pressure is much stronger than the temperature dependence of the activity coefficient and therefore a constant reference temperature is used to evaluate the activity coefficient. This simplification leads to a drastic reduction in computation time, but as reported by Maier et al.[5] the obtained azeotropic compositions can be very different or even some azeotropes may be missed depending on the selection of the reference temperature.

In the method we present here, the assumption of the reference temperature is selectively used at the first stage of the algorithm for providing good starting points for the second stage where the full model is used for solution refining. In this way, more computation time is saved without compromising the reliability of the method.

As a result, the very robust algorithm proposed by Maier and co-workers[5] was engineered by the selective use of model assumptions and domain-specific knowledge (the topological constraints) to obtain an improved algorithm to find all the homogeneous azeotropes with a performance that is similar to that of the fastest local methods.

Although the technique can be used for different thermodynamic models, the Wilson equation was selected to represent the nonideal behavior of the liquid phase because this equation enables the systematic modeling of fairly complex nonideal homogeneous mix-

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tures. Ideal behavior of the vapor phase is considered. The extended Antoine equation is used to model the temperature dependence of the vapor pressure of the pure components. Special care must be taken when using models that can predict phase splitting like the NRTL and UNIQUAC models for predicting azeotropy of homogeneous mixtures. Any calculated solution should be then checked for phase stability to guarantee that only one liquid phase is present at the azeotropy condition.

The performance of the novel algorithm will be explained by considering a number of examples in the main body of the paper. However, results for other highly nonideal mixtures are presented in the Appendix together with the values of data and parameters used in the Wilson equation for all the species and mixtures considered in this work. Coefficients used in the extended Antoine equation were taken from HYSYS' coefficients library.[7]

Problem Formulation

The method applied in this work is an interval Newton/generalized bisection (IN/GB) technique based on interval mathematics.[8] The main characteristic of this technique is that enclosures of all solutions of a system of nonlinear equations are guaranteed with mathematical and computational certainty, provided only that initial upper and lower bounds are given for all variables. The existence and uniqueness test offered by the interval Newton method is used to guarantee that all the roots are located.

The technique determines verified enclosures of each root. Each of such enclosures is a very narrow interval known to contain a unique root, based on the interval Newton uniqueness test. The technique also performs a point Newton method as a last step that will converge to the unique solution.

Different mathematical formulations can be used to represent the condition of azeotropy as demonstrated by Maier et al.[5] In the simultaneous formulation, the homogeneous azeotropy condition is written for all components in the mixture, and therefore the IN/GB method is used to find all azeotropic compositions and temperatures simultaneously including the trivial roots representing the pure species. The sequential formulation decomposes the problem into an unordered sequence of simpler problems of reduced dimensions and at each step in the sequence it only obtains the azeotropes whose order corresponds to the dimensions of the subsystem under consideration. The authors report a significant reduction in the computation time when using the sequential formulation as compared to the simultaneous approach.

Assuming that there is a set of k components C_{nz} for which $x_i \neq 0$, the azeotropy condition for the sequential formulation can be written as[5]

$$\ln P - \ln P_i^0(T) - \ln \gamma_1(x, T) = 0 \quad \forall \ i \in C_{nz}$$

$$\sum x_i - 1 = 0 \qquad (1)$$

Each root of this $(k + 1) \times (k + 1)$ system is a k-ary azeotrope. To find all the azeotropes of a system with NC components, eq 1 must be solved for each combination of k components, $k = 2, ..., NC$. Each subsystem may have multiple roots or no roots at all. In their solution approach, the aforementioned authors rely on

the IN/GB algorithm for both enclosing all the roots when they exist and for verifying nonexistence.

To improve the computational efficiency of the algorithm, an effort has been made through the development of *interval extensions* tailored to frequently occurring expressions, such as mole fraction weighted averages, which are found in many activity coefficient models. By exploiting the constraint that the summation of the mole fraction is equal to 1, it is possible to implement enclosures for these expressions that are tighter than the natural interval extension.

Further reduction of the computation time can be obtained by introducing a model simplification. This is based on the assumption that the temperature dependence of the vapor pressure of the pure components is stronger than the temperature dependence of the activity coefficients. Hence, the activity coefficients are evaluated at a given reference temperature, T_{ref}, and depend only on the compositions. As shown by the authors, the selection of this reference temperature may be critical for the accuracy of the method.

Besides these efforts, a substantial part of the computation time is still devoted to the verification of nonexistence. This becomes particularly important as the number of components of the mixture does increase. For an original system with NC components, the total number of different subsystems can be computed as $2^{NC} - 1$ (including the unary systems), so the amount of subsystems of an order higher than 1 to be considered is $2^{NC} - 1 - NC$.

We propose a modification of the solution approach of Maier and co-workers[5] that is intended to increase the overall efficiency of the method and is based on two ideas. The first one is to resort to thermodynamic topological considerations to reduce the number of subsystems that must be processed by the IN/GB algorithm. The second one is to apply the simplified model assuming a reference temperature for the computation of the activity coefficient during the first phase of the algorithm where the solutions are enclosed. These solutions are used to initialize the last phase consisting of the point Newton method where the full model is solved to get the final solution.

Performance of the Sequential Formulation

To measure the gained efficiency of the proposed modifications, we implemented the sequential formulation described by eq 1 supported by a Wilson model for the activity coefficients with the choice of full temperature dependence or a constant reference.

The technique requires the point value functions of the logarithms of the vapor pressure and activity coefficients and also their interval extensions. Also, both the point value derivatives of the logarithms of the activity coefficients with respect to all the mole fractions (a matrix) and the derivative of the logarithms of the vapor pressure with respect to the temperature (a vector) together with their interval extensions are needed. The analytical equations of the derivatives for the Wilson equation were taken from Poellmann and Blass.[9]

In addition, the model with full temperature dependence also requires both the point value derivatives of the logarithms of the activity coefficients with respect to the temperature (a vector) and their interval extensions.

Table 1. Performance Comparison between the Full Model and the Model Considering Temperature-Independent Activity Coefficients

			CPU time in seconds	
subsystem	T_{ref} (K)	azeotrope composition	T_{ref} model	temperature-dependent model
1-propanol−water at 1 bar pressure	360.5	[0.4467, 0.5533]	0.2	0.41
benzene−hexafluorobenzene at 0.2 bar pressure	310.0	[0.9546,0.0454] [0.0151,0.9849]	0.26	0.98
acetone−chloroform−methanol at 1 bar pressure	330.5	[0.3314, 0.2290, 0.4396]	0.6	5.25
acetone−chloroform−methanol−benzene at 1 bar pressure	330.4	[0.2406, 0.1661, 0.4713, 0.1220]	10.4	>1200
acetone−chloroform−benzene−toluene at 1 bar pressure	350.0	no quaternary azeotrope	0.7	14.75

As a base line, the performance of the sequential formulation was tested with several examples. Table 1 shows a comparison of the results obtained for five different mixtures by using both the full temperature-dependent model and the model at some reference temperature T_{ref}. For all the examples of Table 1, the search domain was restricted to find azeotropes of the same order to that of the subsystem in question. Thus, ternary azeotropes are sought in ternary systems only and binary azeotropes in binary systems only.

For each one of the examples being considered, the azeotropic composition and temperature were previously known, and hence, the reference temperature was selected to be the azeotropic temperature to compare the performance of both methods. The reference temperature for the system benzene−hexafluorobenzene was set to 310 K because the mixture presents a benzene-rich azeotrope at 308.63 K and a benzene-poor azeotrope at 310.80 K. In all the cases, the compositions were initialized in the range [0,1]. The temperature was constrained to values in the range [300, 400 K]. As stated by Maier and co-workers,[5] Table 1 clearly shows that the model is time-saving when using a reference temperature. The CPU times are given in seconds on a Window NT workstation equipped with an Intel Pentium II 333 MHz Processor.

Later on, we tested a mixed strategy setting the problem formulation so that the simplified model is used only during the first phase of the IN/GB method. This is the phase where the method encloses all possible solutions. The second phase of the method consists of a normal point Newton method, where the solution represented by an interval is reduced to a single value. In this phase, we use the model with full temperature dependence. Table 2 presents the results obtained with this strategy for the quaternary subsystem acetone−chloroform−methanol−benzene at different values of T_{ref}.

Depending on the value of the reference temperature, different enclosures for the azeotropic compositions and temperature are obtained. Moreover, for values of T_{ref} above 380 K the quaternary azeotrope is not found anymore. Again, these results match the results reported in Table 12 of the cited work.[5]

However, in our strategy, every time an enclosure for the root is found in the first phase, the final solution converges to the same temperature and compositions, and these values are solutions of the full model.

Note that while the enclosures for the compositions vary significantly with the reference temperature, temperature is much less sensitive. This is an indication that the simplified model performs better for enclosing

Table 2. Results of the Search on the Acetone−Chloroform−Methanol−Benzene Subsystem at Different Values of T_{ref} (1 bar Pressure)

T_{ref} (K)	azeotrope composition + temperature (calculated)	enclosures for temperature and compositions
310.0	[0.2406, 0.1661, 0.4713, 0.1220], **330.39 K**	**330.2188 330.2189** 0.192236 0.192245 0.147905 0.147910 0.488309 0.488311 0.171542 0.171544
330.4	[0.2406, 0.1661, 0.4713, 0.1220], **330.39 K**	**330.3893 330.3897** 0.240618 0.240651 0.166097 0.166122 0.471257 0.471269 0.121983 0.122002
350.0	[0.2406, 0.1661, 0.4713, 0.1220], **330.39 K**	**330.5280 330.5348** 0.290258 0.291176 0.187970 0.188622 0.451874 0.452242 0.068653 0.069301
370.0	[0.2406, 0.1661, 0.4713, 0.1220], **330.39 K**	**330.6457 330.6462** 0.346220 0.346281 0.216733 0.216768 0.428928 0.428944 0.008052 0.008074
380.0	no quaternary azeotrope	
390.0	no quaternary azeotrope	

the azeotropic temperature than for the azeotropic compositions.

These results suggest that it is possible to partially exploit the benefits that the simplified model offers in terms of computation time, without sacrificing the quality of the final solution. There is still the possibility of missing a solution, depending on the selected reference temperature. Later in this paper, we will come back to this issue and comment on how this simplification can be safely exploited with the help of topology analysis.

A parametric change of T_{ref} was also done for the mixtures acetone−chloroform−methanol and 1-propanol/water, but enclosures were obtained for all of the temperature range [300, 400 K] and these were almost coincident with that calculated using the point Newton method. Tables 3 and 4 present the result for these mixtures.

Table 5 shows the results for all the subsystems of the quaternary mixture acetone−chloroform−methanol−benzene at 1 bar pressure. The system presents four

Table 3. Results of the Search on the Acetone−Chloroform−Methanol Subsystem at Different Values of T_{ref} (1 bar Pressure)

T_{ref} (K)	azeotrope composition + temperature (calculated)	enclosures for temperature and compositions
310	[0.3315, 0.2290, 0.4395], **330.47 K**	**330.3682 330.4406** 0.317032 0.318960 0.234942 0.236220 0.446265 0.446759
330.47	[0.3315, 0.2290, 0.4395], **330.47 K**	**330.4281 330.5226** 0.329936 0.332590 0.228033 0.230168 0.438854 0.440159
350	[0.3315, 0.2290, 0.4395], **330.47 K**	**330.5555 330.5581** 0.342557 0.342635 0.224303 0.224347 0.433070 0.433089
370	[0.3315, 0.2290, 0.4395], **330.47 K**	**330.5217 330.7883** 0.347107 0.357488 0.217129 0.224889 0.424818 0.428526
380	[0.3315, 0.2290, 0.4395], **330.47 K**	**330.6709 330.7167** 0.356026 0.357235 0.219514 0.220261 0.423272 0.423572
390	[0.3315, 0.2290, 0.4395], **330.47 K**	**330.73945 330.73938** 0.3606553 0.3606560 0.2190648 0.2190653 0.4202792 0.4202794

Table 4. Results for the Mixture 1-Propanol/Water at Different Values of T_{ref} (1 bar Pressure)

T_{ref} (K)	azeotrope composition + temperature (calculated)	enclosures for temperature and compositions
310	[0.4461, 0.5539], **360.54 K**	**359.0041 359.1272** 0.457303 0.458677 0.541669 0.542441
330	[0.4461, 0.5539], **360.54 K**	**359.5217 359.8010** 0.451349 0.454938 0.546014 0.548181
350	[0.4461, 0.5539], **360.54 K**	**358.8042 361.6784** 0.414831 0.471398 0.526161 0.577818
360.54	[0.4461, 0.5539], **360.54 K**	**358.6660 362.4048** 0.403954 0.486848 0.518628 0.589508
380	[0.4461, 0.5539], **360.54 K**	**360.9312 361.1899** 0.438890 0.444566 0.5561356 0.559882
390	[0.4461, 0.5539], **360.54 K**	**361.3194 361.3286** 0.440345 0.440429 0.559597 0.559631

binaries, one ternary, and one quaternary azeotrope. In this case, T_{ref} was selected as the average of the boiling points of the pure species and the initial box of temperatures was set between $[T_{lower}-50, T_{upper}+50]$. Six binary subsystems, four ternary subsystems, and one quaternary subsystem were solved. The search into the quaternary system took about 76% of the total time.

The results for the mixture acetone−chloroform−methanol−ethanol−benzene are shown in Table 6. In this case, the equation system modeling the azeotropy condition was solved for ten combinations of binary subsystems, ten combinations of ternary systems, five combinations of quaternary mixtures, and one system containing all the components of the initial mixture. For this example, six binary azeotropes, two ternary azeo-

tropes, and one quaternary azeotrope were calculated at T_{ref} of 351.61 K. As in the previous example, the same criterion for the initial box of temperatures was adopted. The total CPU time was 58.12 s and 48.27 s was used for the algorithm to verify the nonexistence of azeotropes in 17 of the subsystems.

This example illustrates a rather typical situation. In multicomponent systems, there will be a significant amount of subsystems having no azeotropes. The verification of such subsystems with the IN/GB method is quite expensive in terms of computation. In the next section, we show how the Zharov−Serafimov topological index theory can be used to do the same verification but with much less computational burden.

Topology Analysis

The vapor−liquid equilibrium can be represented as a vector field **D**, defined over the state space of compositions. Any liquid composition x within this space is associated to a unique vector that points to its vapor composition.

$$\mathbf{D}(x) = y(x) - x \qquad (2)$$

Azeotropes and pure components are the stationary points, that is, the zeroes, of this vector field.

Several authors in the Russian literature have developed a topological relation stating that the summation of the indices of the vector field at the stationary points is a topological invariant. This relation was generalized to multicomponent systems by Zharov and Serafimov.[6] Here, we use the general topological equations given by Poellmann et al.[10]

The index of a stationary point **s** is equal to the sign of the determinant of the Jacobian matrix of the vector field **D**, at the zero. The determinant of a matrix is the product of its eigenvalues. Therefore, the index of a stationary point can be computed as

$$\text{ind}(\mathbf{D},\mathbf{s}) = \text{sgn} \prod_{i=1}^{NC-1} (\lambda_i - 1) \qquad (3)$$

where the eigenvalues λ_i are obtained solving the following eigenvalue problem:

$$\lambda \cdot \mathbf{v} = \begin{pmatrix} \dfrac{\partial y_1}{\partial x_1} - \dfrac{\partial y_1}{\partial x_{NC}} & \cdots & \dfrac{\partial y_1}{\partial x_{NC-1}} - \dfrac{\partial y_1}{\partial x_{NC}} \\ \cdots & & \cdots \\ \dfrac{\partial y_{NC-1}}{\partial x_1} - \dfrac{\partial y_{NC-1}}{\partial x_{NC}} & \cdots & \dfrac{\partial y_{NC-1}}{\partial x_{NC-1}} - \dfrac{\partial y_{NC-1}}{\partial x_{NC}} \end{pmatrix}_s \cdot \mathbf{v} \qquad (4)$$

The subtractions occurring in the elements of the Jacobian matrix arise from the condition that the sum of mole fractions must yield unity and that the partial derivatives with respect to mole fractions are analytically calculated as if all mole fractions were independent.

Thus, each stationary point will have NC−1 associated eigenvalues, which are related to its stability. If all the eigenvalues of a stationary point are <1, then the point is an unstable node. If all the eigenvalues are >1, then the point is a stable node, and if some are >1 and others <1, the point is a saddle. Therefore, and according to eq 3, the index of an unstable node will be −1, if the node is stable, the index will be +1, and for saddles it may be either −1 or +1.

Table 5. Results for the Quaternary Mixture Acetone(A)−Chloroform(C)−Methanol(M)−Benzene(B) (1 bar Pressure)

components	mole fraction	T (K)	time (s), T_{ref} = 338 K	enclosures
AC	[0.3385, 0.6615]	**337.61**	0.2	**337.1704 338.0389** 0.326576 0.353114 0.651448 0.672069
AM	[0.7909, 0.2091]	**328.49**	0.2	**328.4494 328.7076** 0.794121 0.806910 0.195356 0.203856
AB	no azeotrope		0.1	
CM	[0.6552, 0.3448]	**326.96**	0.2	**327.0076 327.0622** 0.651393 0.652019 0.348201 0.348348
CB	no azeotrope		0.1	
MB	[0.6130, 0.3870]	**331.05**	0.2	**331.0310 331.2710** 0.613563 0.617296 0.383518 0.385734
ACM	[0.3314, 0.2290, 0.4396]	**330.48**	0.6	**330.5060 330.5070** 0.335930 0.335954 0.226998 0.227010 0.437050 0.437058
ACB	no azeotrope		0.4	
AMB	no azeotrope		0.9	
CMB	no azeotrope		0.4	
ACMB	[0.2406, 0.1661, 0.4713, 0.1220]	**330.39**	10.4	**330.4461 330.4491** 0.259446 0.259771 0.174025 0.174214 0.464126 0.464220 0.102047 0.102155

Table 6. Results for the Mixture Acetone(A)−Chloroform(C)−Methanol(M)−Ethanol(E)−Benzene(B) (1 bar Pressure)

components	mole fraction	T (K)	CPU time (s), T_{ref} = 351.61 K
EB	[0.4492, 0.5508]	**340.71**	0.06
MB	[0.6130, 0.3870]	**331.05**	0.03
ME	no azeotrope		0.03
CB	no azeotrope		0.03
CE	[0.8590, 0.1410]	**332.76**	0.02
CM	[0.6552, 0.3448]	**326.96**	0.03
AB	no azeotrope		0.02
AE	no azeotrope		0.02
AM	[0.7909, 0.2091]	**328.49**	0.04
AC	[0.3385, 0.6615]	**337.61**	0.03
MEB	no azeotrope		0.30
CEB	no azeotrope		0.33
CMB	no azeotrope		0.37
CME	no azeotrope		0.28
AEB	no azeotrope		0.42
AMB	no azeotrope		0.77
AME	no azeotrope		0.19
ACB	no azeotrope		0.32
ACE	[0.3405, 0.4806, 0.1789]	**336.65**	0.44
ACM	[0.3315, 0.2290, 0.4396]	**330.48**	0.36
CMEB	no azeotrope		3.11
AMEB	no azeotrope		2.36
ACEB	no azeotrope		5.61
ACMB	[0.2407, 0.1661, 0.4713, 0.1220]	**330.39**	8.84
ACME	no azeotrope		2.41
ACMEB	no azeotrope		31.7

The topological relation that every system must satisfy is

$$\sum_{c=1}^{NC} 2^c \times \sum_{s=(s_1,...s_c)} ind(\mathbf{D},\mathbf{s}) = (-1)^{NC-1} + 1 \quad (5)$$

To illustrate how the consistency test can be used in the context of azeotrope prediction, let us consider the ternary subsystem formed by acetone (A), chloroform (C), and methanol (M) and assume that the three binary azeotropes, namely, AC, AM, and CM, have been already identified. Thus, for this ternary system we have six stationary points: [A, C, M, AC, AM, CM]. Solving the eigenvalue problem at each of these points and computing their corresponding indices, we obtain [−1, −1, 1, 1, 1, 1]. Computing the right-hand side of eq 5 gives

$$(-1)^{3-1} + 1 = 2$$

while the left-hand side is

$$2^1(-1 - 1 + 1) + 2^2(1 + 1 + 1) = 10$$

Because the topological constraint is not satisfied, we should conclude that there is a missing stationary point; that is, there is a missing azeotrope and hence a search into the ternary subsystem by means of the IN/GB method must be done. In fact, the system under consideration does have a ternary azeotrope, ACM, whose index is −1. If we add this stationary point to the summation of indices, we obtain

$$2^1(-1 - 1 + 1) + 2^2(1 + 1 + 1) + 2^3(-1) = 2$$

Now, the topological constraint is satisfied and therefore the system is topologically consistent with the identified azeotropes.

Consider now the ternary system formed by acetone (A), chloroform (C), and benzene (B) and assume that one binary azeotrope, namely, AC, has been already identified. We have four stationary points, [A, C, M, AC],

Table 7. Topology Test for Each One of the Subsystems Corresponding to the Mixture Acetone(A)−Chloroform(C)−Methanol(M)−Benzene(B) [A Value of the Matrix Represents the Index of a Node (File) Belonging to a Subsystem (Column); T (True) Means That the Subsystem Is Topologically Consistent]

node	MB	CB	CM	AB	AM	AC	CMB	AMB	ACB	ACM	ACMB
C−M			−1				1			1	−1
A−M					−1			1		1	−1
A				−1	1	−1		−1	1	−1	1
A−C−M−B											1
A−C−M										−1	−1
M−B	−1						−1	−1			−1
C		−1	1			−1	−1		1	−1	1
A−C						1			−1	1	−1
M	1		1		1		1	1		1	1
B	1	1		1			1	1	1		1
test	T	T	T	T	T	T	T	T	T	T	T

whose indices are [1, 1, 1, −1]. The right-hand side of eq 5 is again

$$(-1)^{3-1} + 1 = 2$$

and the left-hand side is

$$2^1(1 + 1 + 1) + 2^2(-1) = 2$$

The topological constraint is hold and therefore we can safely conclude that there are no more azeotropes in this system. The search for ternary azeotropes by means of the IN/GB method can be avoided.

Table 7 shows the results of applying the topology consistency test to each of the 11 subsystems found for the quaternary mixture acetone−chloroform−methanol−benzene. The last row indicates that all subsystems are topologically consistent and hence the computed azeotropes are validated.

The topology analysis described above can also be used to selectively apply the simplified model for activity coefficients at a reference temperature in a safe way. It has already been discussed that depending on the selected temperature of reference, the algorithm may fail in enclosing a solution corresponding to a given subsystem. But the topology analysis is performed just before eventually applying the IN/GB method and it already tells us if a solution has to be found. In case a solution does exist, it is possible to devise a strategy that attempts first to enclose a solution with the simplified model. If it succeeds, then the point Newton method working with the full model will produce the exact solution. If the first phase does not enclose a solution, another reference temperature can be selected until it does, or we can always resort back to the full method to find it.

Outline of the Proposed Algorithm

To combine the IN/GB method of solution with the topological analysis, the solution strategy has to be sequential and this sequence must go from the lower order subsystems to the higher ones. Just with the information of the pure components, all binary subsystems can be tested for consistency, and therefore, those that have to be searched for binary azeotropes can be identified. Having identified all binary azeotropes, now all ternary subsystems can be tested for consistency and so forth.

The proposed algorithm can be summarized through the following steps:

Step 1. Generate All Subsystems

Decompose the original system of NC components into all subsystems of reduced order

$$(NC, NC-1, NC-2...2)$$

For example, a quaternary system is decomposed in one quaternary, four ternaries, and six binaries
The amount of subsystems of reduced order R in a system of NC components is the given by the *combination*

$$\binom{NC}{R} = \frac{NC!}{R! \, (NC - R)!}$$

The total number of different subsystems can be computed as $2^{NC} - 1$ (including the unary systems), so the amount of subsystems of order higher than 1 to be considered is $2^{NC} - 1 - NC$
The sequence of numbers $\{1, 2, ..., 2^{NC}-1\}$ contains in its binary representation a description of the content of each subsystem:
For example, for NC = 4, the total number of subsystems is 15, and the sequence $\{1, 2, ..., 15\}$ in its binary representation is {0001, 0010, 0011, 0100, 0101, 0110, 0111, 1000, 1001, 1010, 1011, 1100, 1101, 1110, 1111}
Interpreting that a "1" in the ith position means the component i belongs to the subsystem, the sequence constitutes a very easy way to obtain a compact representation of the subsystems. Because we are not interested in considering the unary subsystems, they are taken off the list. Unary subsystems are represented by the sequence generated by $\{2^k; k: 0, 1, ..., NC-1\}$
For example, the final list of subsystems to be analyzed is {0011, 0101, 0110, 0111, 1001, 1010, 1011, 1100, 1101, 1110, 1111} containing one quaternary, four ternaries, and six binaries.

Step 2. Initialize

Set Order $O = 2$ (analyze binaries first)
Populate initial list of singular points **PL** (pure components or azeotropes) with the pure species

Step 3. Process Subsystems of Order O

Create a working list **WL** with all subsystems of order O
For each subsystem **S** in **WL** do:
  Create a thermodynamic system with the components of **S**

Select from the current list of singular points **PL**, those belonging to system **S**

For each selected singular points **P**:

Compute the Jacobian of the equilibrium function

Obtain its corresponding eigenvalues by solving the eigenvector problem in eq 4

Compute its topological index, eq 3

Verify the topological consistency constraint, eq 5

If the system is not consistent, then compute azeotropes until consistency, by doing:

Formulate the azeotropy condition for system **S**

Apply the IN/GB method to find the azeotropes

Update the current list of singular points with the azeotropes just found.

Step 4. Increment Order

If O < NC then $O = O + 1$ and go to Step 3
else STOP.

Returning to the example comprising the acetone–chloroform–benzene–toluene system at 1 bar pressure, the algorithm decomposes the original system in six binary subsystems, four ternary subsystems, and one quaternary subsystem. At the initialization step, the order of the subsystems to be analyzed is set to 2 and the list of singular points is populated with only the pure species because no azeotrope calculation was performed until this time.

Step 3 performs the topological consistency test for each binary subsystem by calculating the topological index of the corresponding singular points. In the example under consideration only the subsystem made up of acetone and chloroform does not verify the topological consistency test given by eq 5, and hence, the IN/GB method is applied to find the missing azeotrope. Equation 5 is recalculated but now taking the topological index of the calculated azeotrope into account. The list of singular points is updated to include the azeotrope just found before the subsystem order is incremented in Step 4.

When analysis of the four ternary subsystems is performed, the algorithm includes the previously calculated azeotrope A–C in the subsystems A–C–B and A–C–T, and hence, the topological index of the azeotrope is considered in eq 5 for both subsystems. The topological constraint is satisfied for all the ternary mixtures, and hence, no azeotrope calculation is needed at this step.

In a similar way, the binary azeotrope is included by the algorithm in the quaternary subsystem and no azeotrope calculation is performed because eq 5 is satisfied.

On the whole, the IN/GB method was executed only one time (subsystem acetone–chloroform) and the other time-consuming searches were avoided by simply calculating eq 5 for each subsystem.

It is noteworthy that the stability and therefore the topological index of a singular point depends on the subsystem in consideration. For this reason, the eigenvalue problem must be solved for all the singular points belonging to a given subsystem. In this example, the eigenvalue problem was solved 12 times because eq 5 for the subsystem acetone–chloroform was solved twice. The total CPU time consumed in this case to solve all the eigenvalue problems was about 0.02 s while the IN/GB method needs about 0.7 s to verify the nonexistence of a quaternary azeotrope as shown in Table 1. Applying the algorithm to the mixture formed by acetone, chlo-roform, methanol, ethanol, and benzene reduces the time taken by the nonexistence verification from 48.27 to 0.12 s. The results of applying the algorithm to other highly nonideal mixtures are presented in the Appendix.

Conclusions

In this paper, we present an adaptation of the method proposed by Maier et al.[5] that combines the sequential formulation processed in a *given order* with the Zharov–Serafimov topological index theory.[6] By checking the topological consistency of each subsystem, it is possible to avoid the numerical verification of the nonexistence and therefore to reduce significantly the total computation time. It is noteworthy that the topological index theory can be safely applied in combination with the IN/GB technique provided that at most one azeotrope of the same order to that of the subsystem in question is present for each one of the subsystems comprising the multicomponent mixture. Thus, binary subsystems with one binary azeotrope at most, ternary subsystems with one ternary azeotrope at most, and so forth can be appropriately handled for the algorithm. This is a typical situation because *n*-component mixtures having more than one *n*-component azeotrope are very scarce.[11] On the other hand, the topological index theory could theoretically predict nonexistence for subsystems presenting multiplicity. In this case, the topological relation could be only used to check any calculated azeotrope.

In the method we present here, the assumption of the reference temperature is selectively used at the first stage of the algorithm for providing good starting points for the second stage, where the full point Newton model is used for solution refining. Moreover, a method to update the reference temperature can be thought with the aid of the topological consistency test. In fact, if the consistency test indicates the existence of an azeotrope and it was impossible to find a solution at the given reference temperature, the reference temperature must be changed until the consistency test is positive. Alternatively, we can always resort to the full model to find it.

A theoretical disadvantage, however, of using the full model at the last step of the algorithm must be considered. Since the model used to enclose the first solution estimation is different from the one used in the last step, there is no mathematical guarantee that the point Newton method will converge to the solution of the full model. However, in all the cases we explored, the right solution was always found.

With the guidance of the topology consistency test, the mathematical guarantee can be safely sacrificed in exchange for computational performance. And also, we preserve the certainty that when we obtain a solution, it is a solution for the *full* model. Therefore, the obtained azeotrope will be consistent with the thermodynamic model that is more likely to be used in subsequent analysis.

Several problems involving highly nonideal mixtures were tested using the modified algorithm. The performance was similar to the fastest local methods. As an example, only 10.54 s was needed to find the nine azeotropes of the system in Table 6 in comparison with the 58.12 s used by the base algorithm. In addition, the topological consistency of all the systems is calculated.

As a result, the very robust algorithm proposed by Maier and co-workers[5] was engineered by the selective use of model assumptions and domain-specific knowl-

edge (the topological constraints) to obtain an improved algorithm to find all the homogeneous azeotropes with a performance that is similar to that of the fastest local methods.

Acknowledgment

Nomenclature

D = vector field
NC = number of components of a given subsystem
P = pressure, bar
P_i^0 = vapor pressure of component i, bar
s = composition of a stationary state
T = temperature, K
T_{lower} = boiling temperature for the lightest component
T_{upper} = boiling temperature for the heaviest component
x_i, y_i = liquid (vapor) mole fraction of the component i
λ = eigenvalue
γ = activity coefficient

Appendix

Other Examples. Table 8 shows the results for three azeotropic mixtures. The mixture formed by methanol, benzene, 2-propanol. and 1-propanol presents three binary azeotropes at 1 bar pressure. Three binary and one ternary azeotropes were calculated for the ethanol–methyl ethyl ketone–water mixture at 1 bar pressure. The last example comprises the acetone–chloroform–methanol mixture at 15.8 bar pressure. While this system has a ternary azeotrope at normal pressure, no more ternary azeotrope is present at the selected pressure. Because of the pressure change, also a change in the compositions of the three binary azeotropes is predicted.

Table 8. Results for Three Highly Nonideal Mixtures

node ID	mole fraction	temperature (K)	CPU time (s)
Methanol–Benzene–2-Propanol–1-Propanol at 1 bar Pressure			
M–B	[0.6130, 0.3870, 0.0000, 0.0000]	331.05	0.03
B–2P	[0.0000, 0.6287, 0.3713, 0.0000]	344.55	0.04
B–1P	[0.0000, 0.7850, 0.0000, 0.2150]	348.81	0.06
total CPU time			**0.13**
Ethanol–Methyl Ethyl Ketone–Water at 1 bar Pressure			
E–MEK–W	[0.2005, 0.5696, 0.2299]	345.78	0.621
MEK–W	[0.0000, 0.6915, 0.3085]	346.68	0.050
E–MEK	[0.4588, 0.5412, 0.0000]	347.52	0.040
E–W	[0.8975, 0.0000, 0.1205]	351.04	0.030
total CPU time			**0.741**
Acetone–Chloroform–Methanol at 15.8 bar Pressure			
C–M	[0.0000, 0.3545, 0.6455]	424.47	0.04
A–M	[0.2486, 0.0000, 0.7514]	427.60	0.04
A–C	[0.2663, 0.7337, 0.0000]	455.57	0.05
total CPU time			**0.13**

Table 9. Wilson Molar Volume

component	Wilson molar volume	component	Wilson molar volume
acetone	74.477	MEketone	90.166
benzene	89.555	2-propanol	76.916
chloroform	80.731	1-propanol	75.138
ethanol	58.68	water	18.069
hfbenzene	115.8	toluene	106.83
methanol	40.729		

Table 10. Wilson Equation Parameters

component 1	component 2	A_{12} (cal/mol)	A_{21} (cal/mol)
1-propanol	water	1128.1870	1338.7600
benzene	hexafluorobenzene	−414.2492	939.6611
acetone	chloroform	116.1171	−506.8518
acetone	methanol	−124.9328	551.4545
acetone	ethanol	180.4364	252.2864
acetone	benzene	682.4061	−243.9651
chloroform	methanol	−361.7944	1694.0240
chloroform	ethanol	−268.7676	1270.3890
chloroform	benzene	−71.8109	−11.8231
methanol	ethanol	135.8112	−132.0576
methanol	benzene	1621.2340	202.0307
ethanol	benzene	1237.3850	243.6513
methanol	2-propanol	140.1672	−132.7052
methanol	1-propanol	272.4309	−207.7118
benzene	2-propanol	165.0292	1032.6750
benzene	1-propanol	306.4609	1025.6860
2-propanol	1-propanol	818.3291	−481.0590
ethanol	methyl ethyl ketone	939.1442	−348.5653
ethanol	water	276.7557	975.4859
methyl ethyl ketone	water	892.6557	2013.7170
acetone	toluene	809.0955	−345.0733
chloroform	toluene	−365.8309	552.1458
benzene	toluene	323.1221	−310.3073

Vapor Pressure Coefficients. In this work, the vapor pressure of a pure component is calculated by means of an extended Antoine equation of the form

$$\ln P_i^0 = A_i + \frac{B_i}{T + C_i} + D_i \ln T + E_i T^2 \qquad (A1)$$

where *A*, *B*, *C*, *D*, and *E* are fitted coefficients. Data were taken from HYSYS' coefficients library.[7] The temperature is given in K and vapor pressure in kPa.

Wilson Molar Volume. These data were taken from Gmehling et al.[12] and they are listed in Table 9.

Wilson Parameters. These parameters were taken from Gmehling et al.[12] The values for the mixture benzene–hexafluorobenzene were estimated from azeotropic experimental data. Table 10 shows the reported parameters.

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